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*Studies in the chemistry of iodine*

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**How to cite:**

Race, Edward (1936) *Studies in the chemistry of iodine.* Doctoral thesis, Durham University.

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# STUDIES IN THE CHEMISTRY OF IODINE

THESIS

presented in candidature for the degree of

DOCTOR OF PHILOSOPHY

of the University of Durham

by

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An account of the work carried out under the direction of
Professor I. Masson, M.B.E., D.Sc., F.I.C. in the Department
of Science, University of Durham (Durham Division), September
1934 to September 1936.

## NOTE TO READER.

Occasionally in the text there are reported enquiries not undertaken by the author.  These are entered in order that the sequence of reactions might not be unduly broken, and wherever it has been done a note to the effect has been added.

# STUDIES IN THE CHEMISTRY OF IODINE

## SUMMARY

(a) Iodoxybenzene dissolves much more readily in aqueous
alkali than in water. In the first place this is due to a re-
versible salt-formation. These salts, termed _iodoxylates_, have
a transient existence, and by rapid measurements of solubility,
conductivity and freezing point the reaction is shown to be

$$PhIO_2 \; + \; OH' \; \rightleftharpoons \; PhIO_2.OH,$$

the iodoxybenzene behaving as a monobasic acid of dissociation
constant approximately $10^{-11}$.

Phenyliodoxylate changes rapidly and irreversibly in dilute
alkali into stable _diphenyliodyl hydroxide_:

$$2PhIO_2.OH' \longrightarrow Ph_2I.OO' + IO_3 + H_2O$$
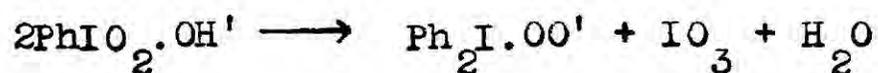
This new compound is a stronger oxidising agent than the parent
substances and yields diphenyliodonium salts on reduction. It
is amphoteric, dissolving in alkalies and behaving as an acid
to phenolphthalein, and forming a moderately stable carbonate
and a stable, crystalline acetate, represented by the structure
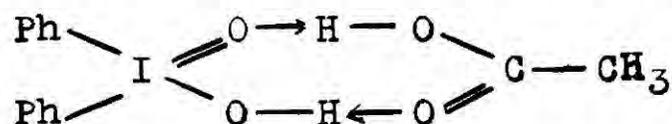


By mixing solutions of phenyliodoxylate and p-acetaminophenyl-

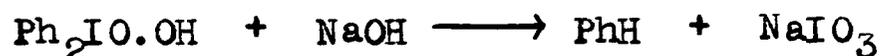iodoxylate there is obtained p-acetaminophenyl-phenyl-iodyl
hydroxide, from the solution of which a carbonate and acetate
can be prepared.

The rapid action of N-alkali at $100^{o}C$ on diphenyliodyl
hydroxide (as on iodoxybenzene) yields benzene and iodate along
with more complex products of a resinous character.

$$Ph_2IO.OH \ + \ NaOH \longrightarrow PhH \ + \ NaIO_3$$

(b) In sulphuric acid of hydration less than $H_2SO_4.H_2O$ iodic
acid reacts with benzene and its derivatives with o-p-directing
substituents with the formation of diaryliodonium salts (e.g.
chlorobenzene yields 80% of the p-iodonium derivative). There
are also formed in small quantity aromatic iodocompounds, carbon
dioxide and a substance in solution readily oxidisable by per-
manganate in acid solution with the formation of carbon dioxide
and a chloride. During permanganate-oxidation, iodonium salt
in solution is totally destroyed with the production of an iodo-
compound.

The action of iodic acid is a secondary one, ensuing upon
a reduction of it to iodine sesquioxide at the expense of org-
anic reagent. By using iodine sesquioxide (as its sulphate,
$I_2O_3.SO_3.\frac{1}{2}H_2O$) the iodonium salt from chlorobenzene is formed
quantitatively and is the sole product.

# STUDIES IN THE CHEMISTRY OF IODINE

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CHAPTER FOUR
A NEW METHOD OF PREPARING DIARYL IODONIUM DERIVATIVES:

# CHAPTER ONE

## HISTORICAL INTRODUCTION.

### 1. Historical Survey.

The study of organic compounds with multivalent iodine opened in the year 1885 with the discovery by C. Willgerodt (J. Pr., 1885, 33, 154) of iodobenzene dichloride $C_6H_5ICl_2$, which he made by chlorinating iodobenzene, using iodine-tri-chloride as halogen-carrier. Seven years later, in the August of 1892, Victor Meyer and Wachter (Ber., 1892, 25, 2632) pre-pared the first iodosocompound, o-iodosobenzoic acid, by the oxidation of o-iodobenzoic acid with fuming nitric acid. Due to this, Willgerodt again turned his attention to his "iodide-chlorides" and in November 1892 he found (Ber., 1892, 25, 3495 that the parent body of Victor Meyer's iodosobenzoic acid, iodosobenzene, could be prepared by treating iodobenzene di-chloride with silver oxide, sodium hydroxide or sodium carbon-ate solutions. He proved that this body is a basic oxide, forming stable, well-crystallised salts with acids. In the light of this knowledge, and because of the colour of his own compound, Willgerodt declared that the o-iodosobenzoic acid was a basic salt, containing no free iodoso-group. To it he gave the formula:
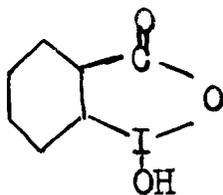
Victor Meyer had therefore prepared the first heterocyclic iodine compound, called by Willgerodt "o-hydroxyiodobenzoate."

Again in 1892 Willgerodt (Ber. 1892, 25, 3500) prepared iodoxybenzene from iodobenzene dichloride and sodium hypochlorite.

By the use of Willgerodt's iodoso- and iodoxycompounds, Victor Meyer and his collaborators, in 1894, discovered a new class of organic bases. Hartmann and Meyer (Ber. 1894, 27, 427) found that by treating iodosobenzene with cold concentrated sulphuric acid the sulphate of phenyliodophenyliodonium hydroxide, $C_6H_5(C_6H_4I)I.OH$, was formed. A little later the same two workers (Ber. 27, 503-509) discovered the general reaction by which iodonium compounds have since been made. By the treatment of an equimolecular mixture of iodoso- and iodoxybenzene with moist silver oxide, diphenyliodonium hydroxide was formed in solution.

Aliphatic-aromatic iodonium compounds were made by Willgerodt (Ber. 1895, 28, 2110) by the interaction of iododichlorides and silver acetylide.

Johannes Thiele and his school (Ber. 1905, 38, 2842; Ann. 1909, 369, 119) showed that aliphatic compounds with multivalent iodine exist at low temperatures.

2. <u>Preparation of Polyvalent Iodine Compounds</u>.

   (a)  <u>Preparation of Iododichlorides</u>.

   "Iododichlorides are probably the most important of the
"compounds of polyvalent iodine when one considers that all
"the others can be prepared from them, either directly or in-
"directly;  for example, iodoso-bases are directly prepared
"from them and it is worthy of note that all attempts to ob-
"tain them by the direct oxidation of iodocompounds have, up
"to the present, been unsuccessful.  On these grounds, and
"because historically they were the first made, it appears
"justifiable, in any description of the preparation of these
"compounds, to begin with the iododichlorides" (Willgerodt,
"Die organischen Verbindungen mit mehrwertigem Jod").  The
best way of preparing iododichlorides is still Willgerodt's
original method (Ber. 1892, <u>25</u>, 3494) by the direct chlorin-
ation of the aryl iodide.  Dry chlorine gas is bubbled through
a wide delivery tube into the cooled solution of the iodocom-
pound, whereby the iododichloride is precipitated.  As solvent
any liquid organic compound which will not reduce the dichlor-
ide can be used.  Chloroform, carbon tetrachloride, carbon di-
sulphide, glacial acetic acid, ligroin or benzene are quite
suitable.  Also in many cases mixtures of these solvents, such
as chloroform and ligroin, give good results.

   Besides using chlorine gas, aromatic iodides can be chlorin-
ated with suitable agents, so easily does the chlorine react.

A. Tohl (Ber. 1893, 26, 2949) used as such sulphuryl chloride.
Finally, iododichlorides are produced when iodoso- or iodoxy-
compounds are treated with aqueous hydrochloric acid, or when
a suspension of either of these in chloroform is reduced with
phosphorus pentachloride; these two last methods, however, are
rarely used.

## (b)  Preparation of Iodosocompounds.

### i)  From the iododichlorides.

Iododichlorides are hydrolysed by water into the corres-
ponding iodosocompounds, and because of this they show an acid
reaction in the presence of water.  The action is, however, re-
versible, and this method, therefore, gives either a poor yield
or none at all.

$$C_6H_5ICl_2 + H_2O \rightleftharpoons C_6H_5IO + 2HCl$$
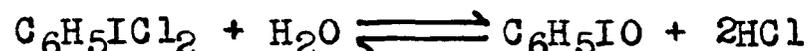
Willgerodt (Ber. 1892, 25, 3455;  1893, 26, 357;  1900, 33,
853)  discovered a method whereby the iododichloride was treated
with a dilute solution of sodium or potassium hydroxide or their
carbonates or bicarbonates, with silver oxide, baryta or calcium
hydroxide solutions, these alkalies preventing a reversal of the
reaction and thus leading to better yields.  Willgerodt's first
method was to grind the iododichloride under water and neutral-
ising the hydrochloric acid produced by adding, drop by drop, a
very dilute solution of caustic soda.  Later he tried the direct
action of dilute alkali or alkali bicarbonate solution as a
means of hydrolysing the dichloride.

In the usual preparation of the iodosobase the iododichloride is ground into a fine sludge with a little dilute alkali; then mechanically shaken with an excess of alkali.  In the course of the reaction the yellow colour of the crystalline dichloride is replaced by the yellow-grey of the amorphous iodoso body.  The filtered product is washed free of alkali with water, but if the last washings show an acid reaction it points to incomplete hydrolysis.  After drying at room temperature, the little parent iodocompound, which is nearly always produced along with the iodosobase, is removed by extracting in the cold with ether, chloroform, benzene or toluene.

Ortoleva (Giornale della Societa di naturale ed Economiche, Vol. 23, 1) obtained a 60% yield of the iodosobase by adding water, with shaking, to a solution of the iododichloride in three parts of pyridine.

### ii.  From the aromatic iodides by direct oxidation.

In a paper by Willgerodt published in 1925 (J. Pr., 111, 353), "On the promotion and hindrance of chemical reactions "connected with the preparation of aromatic compounds of "multivalent iodine," a survey is given of the methods available for the preparation of iodosocompounds by direct oxidation. A brief summary of these methods is given:-

a)  If the oxidation of an o-iodocarboxylic acid is performed with a potassium permanganate solution acidified with

dilute sulphuric acid, the carbonyl group is sufficient to promote the oxidation of the iodine and the following reactions occur:

1. Oxidation of the iodine to the iodosogroup, and
2. Addition of the so-formed iodosogroup to the carbonyl radicle to form a basic hydroxyiodosalt, which is a stable, heterocyclic five-membered ring made up of three carbon atoms, one oxygen and one iodine atom.
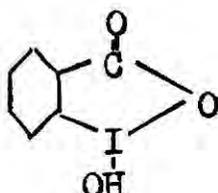


b)  By the use of fuming nitric acid in the oxidation of o-iodobenzoic acid, the nitric acid as well as the carboxylic group aids in the oxidation (J. Pr. 1892 (2), 49, 480).   As early as 1892 Meyer and Wachter (Ber. 25, 2612) used this method in the preparation of "o-iodosobenzoic acid," this latter being proved by the work of both Meyer and Willgerodt (J. Pr. 1894 (2), 49, 468; and Chemie in Einzeldarstell, Vol. 7, pp. 134-5) to be an o-hydroxy iodobenzoate, and given the name by them of o-hydroxyiodophenylformate.   Since that time many workers have used this method in the preparation of iodoso-compounds of carboxylic acids.   Kretzer (Ber. 1897, 30, 1943), by the use both of fuming nitric acid and of acidified potassium permanganate, obtained from monochlor-triiodobenzoic acid "chlorodiiodohydroxyiodobenzoate" $C_6HCl^{(3)}I_2^{(2,4)}CO_2$-I-OH.   It is interesting to note that, due to hindrance, all attempts to

prepare a di-iodosalt failed. Willgerodt and Gartner (Ber. 1908, 41, 2820) similarly oxidised 2-iodo 4-nitro-benzoic acid, and Gumbel (Ber. 1893, 26, 2473) obtained the internal salt of o-iodosonitrobenzoic acid by heating o-iodobenzoic acid with nitric and sulphuric acids for 3 hours at 135° to 140°C. Bode (Heidelburger Dissertation of 1898), Grahl (Ber. 1895, 28, 86), Abbes (Ber. 1893, 26, 2951) and Lutgens (Ber. 1896, 29, 2833) have all studied the effects of oxidising the various iodo-phthalic acids by fuming nitric acid. In only one case, that of tetraiodoterephthalic acid, was a di-iodoso salt formed.

By the oxidation of o-iodophenylacetic acid with fuming nitric acid there is formed a stable, six-membered heterocyclic ring compound of the structure:-
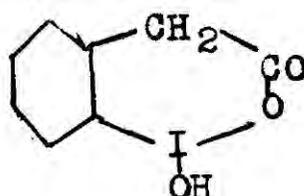


Similar work has been done with success on the oxidation of meta- and para-iodocarboxylic acids.

(See:- Allen, Ber. 1893, 26, 1739.

Meyer and Askenay, Ber. 1893, 26, 1368.

Kloeppel, Ber. 1893, 26, 1733.

Grahl, Ber. 1895, 28, 84.

Bode, Heidelburger Dissertation, 1898.)


(c) Preparation of iodoso salts.

Iodoso salts with organic acids are easily prepared. If

the acid be a liquid, the iodosobase is dissolved in it either
at ordinary temperature or by gently warming, when, on evaporat-
ing the solution, the salt in most cases will crystallise out.
When the organic acid is a solid, it is dissolved in an inact-
ive solvent and the iodosocompound added to the solution. In
the preparation of salts with inorganic acids, the iodoso-base
is ground under an aqueous solution of the acid and allowed to
stand until salt-formation is completed. An alternative method
is to treat a solution of the iodoso acetate in glacial acetic
acid with the inorganic acid. By evaporation of the acetic
acid most of the salt of the inorganic acid separates out.

### (d)  Preparation of Iodoxycompounds.

### i)  From iodosocompounds.

Victor Meyer (Ber. 1893, 26, 1356) and Willgerodt (Ber.
26, 1307) both pointed out that all pure aromatic/bases through
iodoso
time decompose by self-oxidation and reduction into the corres-
ponding iodoxy- and iodo-compounds.

$$e.g. \quad 2RIO = RIO_2 + RI.$$

Because of this self-oxidation of iodoso-bases, one method of
preparing iodoxycompounds is to boil in free steam a suspension
of the iodosocompound in water, when the aryl iodocompound is
steam-distilled off, and in most cases the iodoxycompound left
can be recrystallised from water, glacial acetic acid or formic
acid. This method is naturally undesirable because of the 50%
waste.

A satisfactory way of oxidising the iodosocompounds is, according to Willgerodt (Ber. 1896, 29, 1568), by the use of hypochlorous acid.

## ii) From iododichlorides.

One of the most satisfactory ways of making iodoxycompounds was discovered in 1896 by Willgerodt (Ber. 29, 1572-3) whereby the iododichloride is treated with sodium hypochlorite or bleaching powder.

e.g. $C_6H_5ICl_2 + 2NaOCl = C_6H_5IO_2 + 2NaCl + Cl_2$

The dichloride is ground with a dilute solution of the oxidising material and shaken or stirred until the solid is perfectly white. In most cases the addition of a few drops of glacial acetic acid aids the transformation.

## iii) From the iodide through the iododichloride.

There are several methods available in the preparation of iodoxycompounds from the iodides without actually isolating any intermediate products. If the original material be a liquid (Ber. 1896, 29, 1571), as, for example, iodobenzene, it is covered with water or with chlorine water in a stirring vessel surrounded with ice, and chlorine bubbled into the aqueous liquor with continual stirring. Chlorination is fully completed in a short time, and caustic soda solution is added in drops until the liquor reacts strongly alkaline; this alkalinity is neutralised with chlorine, and finally the iododichloride still remaining is converted into the iodoxy-

compound by stirring. The reaction is completed when the suspended solid is perfectly white. The vigorous evolution of chlorine in the reaction, sufficient to keep the flaky iodoxy-solid as a froth at the surface, led Willgerodt to believe that the reaction proceeds thus:-

$$RICl_2 + 2NaOCl = RIO_2 + 2NaOH + Cl_2$$

Willgerodt (Freiburger Dissertation von W. Eiccholtz, 1914) states that a more satisfactory method, applicable to solids as well as to liquids, is to dissolve the initial material in glacial acetic acid and chlorinate it. The conversion of the iododichloride is performed as above and, providing a small amount of original material has been used, it is possible to dissolve the whole of the yield by boiling the acetic acid; when cooling the solution deposits the iodoxy-compound as fine white needles.

The method of Ortoleva is applicable also to the preparation of iodoxycompounds. The iodide is dissolved in pyridine, water added and chlorine passed through the solution for a long time.

## iv) By the direct oxidation of the iodocompound.

It was in 1896 that Willgerodt (Ber. <u>29</u>, 1572) first oxidised iodobenzene directly to iodoxybenzene. He used for this purpose sodium hypobromite. Bromine water and bromine have no effect on iodobenzene, but when the ice-cold mixture is shaken with sodium hydroxide solution in insufficient quantity completely

to convert the bromine, the iodocompound changes firstly to a semi-solid and later to solid mass, coloured yellow-brown from the bromine still present. By drying in the air, white iodoxy-benzene results. Iodobenzene with bromine yields no iodobenzene-dibromide at ice temperature, and it appears therefore that the iodide is directly oxidised thus:-

$$C_6H_5I + 2NaOBr = C_6H_5IO_2 + 2NaBr$$

Bamberger and Hill (Ber. 1900, 33, 533) used as oxidising agent Caro's acid in the formation of iodoxycompounds directly from the aryl iodides. The oxidising solution, which contained 2.06 grams of active oxygen per 100 c.c. of solution, was prepared from 56 grams of potassium persulphate, 60 grams of concentrated sulphuric acid and 90 grams of ice. Equivalent quantities of iodobenzene and the Caro's acid solution were shaken for $2.^1/_2$ hours and a 97% yield of 98.87% pure iodoxybenzene was obtained.

### (e)  Preparation of Iodonium Compounds.

In 1894 Victor Meyer and Hartmann (Ber. 27, 427) published an account of a new class of aromatic bases containing iodine, called by them iodonium bases. Their first method of prepar-ation was by long boiling and evaporating a solution of iodoso-benzene in dilute sulphuric acid. The oxidising power of the solution disappeared and the sulphate of the inactive base was formed in the solution. The yield, however, was poor, due to the formation of large quantities of iodobenzene, and the method was long. A better method was discovered using concentrated

sulphuric acid, the recipe given by the authors for the preparation of iodoaryl-aryliodonium compounds being as follows:- 5 grams of the iodosocompound are added in small portions to 75 grams of the well cooled concentrated sulphuric acid;  the reaction mixture is further cooled by surrounding it in ice, diluted by the addition of small pieces of ice and allowed to stand for some time.  Finally the acid liquor is drained from the resin which clings to the sides of the vessel, and filtered. This solution contains the sulphate of the iodonium base, and from it the iodide can be precipitated by the addition to it of sodium iodide.  An 82.7% yield was obtained.  The explanation of the reaction, given by Victor Meyer, is shown in the equation:-

$$C_6H_5I(O.SO_3H)_2 + HC_6H_4I(O.SO_3H)_2 + H_2O = (C_6H_5)(C_6H_4I)I.O.$$
$$SO_3H + 3H_2SO_4 + O.$$
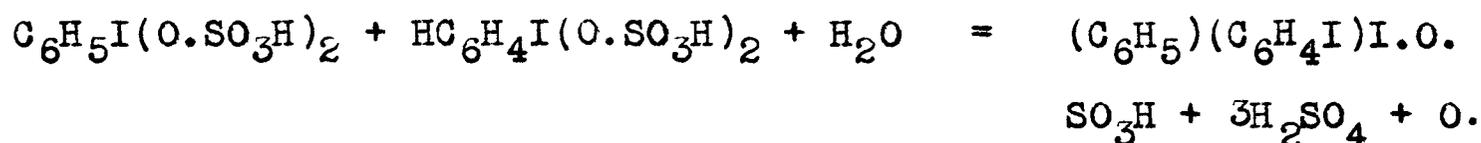
Willgerodt and Sckerl (Ann. 1903, 327, 301) gave an alternative explanation of the preparation, involving the formation of persulphuric acid, but the explanation does not account for the disappearance of oxygen.  No doubt the resins formed from the iodosocompound are the cause of this disappearance.

In the same year Meyer and Hartmann (Ber. 1894, 27, 504) noticed that a several weeks' old sample of iodosobenzene, when ground with moist silver oxide, gave diphenyliodonium salts. They found that freshly made iodosobenzene did not react thus, and concluded that both iodoso- and iodoxybenzene were necessary. From this they derived their general method of preparing iodonium

bases, their method being as follows:- An intimate mixture of the iodoso- and the iodoxy-compound is shaken for three or four hours with freshly precipitated moist silver oxide. The filtered solution contains the free base, which itself cannot be isolated but gives with alkali iodide a heavy precipitate of the iodonium iodide.

$$RIO + RIO_2 + AgOH = R_2I.OH + AgIO_3$$

The method is applicable to the preparation of mixed iodonium bases, by using the iodosocompound of one aryl group and the iodoxycompound of another.

Lead oxide in place of silver oxide was tried by Meyer and Hartmann, but with less success; with caustic soda the same authors (Ber., 1894, 27, 1897-9) obtained smaller yields and found iodobenzene and iodosobenzene present at the end of the experiment. Willgerodt (J. Pr. Chem., 1925, 111, 353) says that the following series of reactions occur:-

(i) The iodosobenzene is partly converted by self-oxidation reduction to iodo- and iodoxybenzene:-

$$2C_6H_5IO = C_6H_5I + C_6H_5IO_2$$

(ii) By the action of sodium hydroxide on iodoxybenzene there is formed, along with hydrogen and phenyl, sodium iodate, and both of the former react with one molecule of iodosobenzene to form diphenyliodonium hydroxide:-

$\alpha$) $\quad C_6H_5IO_2 + NaOH = NaIO_3 + \leftarrow C_6H_5 + \leftarrow H$

$\beta$) $\quad C_6H_5IO + H = C_6H_5\text{-}I\text{-}OH$

$$\gamma) \quad C_6H_5\text{-I-OH} + C_6H_5 = \begin{array}{c} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{array}\text{I-OH}$$
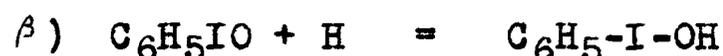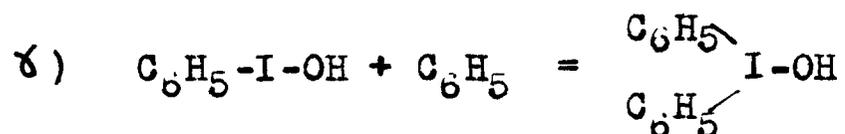
In 1897 and 1898 Willgerodt (Ber., 30, 56;  Ber., 31, 915) indicated an entirely new method of making iodonium compounds. He found that by treating an iododichloride with a metallo-organic mercury compound, the corresponding diaryliodonium chloride was formed. The instructions given for this method of preparation are:- 5 grams of iodobenzene dichloride are ground finely with 5 grams of mercury diphenyl and a little water; the resulting paste is shaken or stirred with more water for twelve hours and, on evaporating the now acid liquors, almost pure diphenyliodonium chloride is deposited as fine needles.

Aromatic-aliphatic and pure aliphatic iodonium compounds were prepared by Willgerodt (Ber., 28, 2110; Ann., 1911, 385, 338) and Thiele (Ann., 1909, 369, 141) by treating iododichlorides with the silver acetylide-silver chloride double compound in the presence of water, when dichlorovinyliodonium compounds were formed:-

$$2\text{R-I-Cl}_2 + \text{HC} \equiv \text{C.Ag.AgCl} = 2\text{AgCl} + \underset{\text{Cl} \ \text{Cl}}{\text{R-I-C}} = \underset{\text{Cl}}{\text{C-H}} + \text{RI}$$
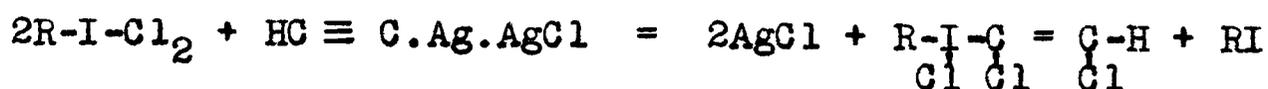
3. Properties of Organic Compounds with Multivalent Iodine.

(a) Iododichlorides.

All iododichlorides are bright-yellow, crystalline solids, their colours varying from a primrose-yellow to a deep orange-yellow, dependent on the substituent groups in the phenyl nucleus.

They are slightly soluble in chloroform, carbon tetrachloride, carbon disulphide, acetone, ether, glacial acetic acid, methyl alcohol and benzene, and from concentrated solutions they crystallise in slender prisms. They do not recrystallise as such from ethyl alcohol, but when a solution of an iododichloride in ethyl alcohol is warmed, chlorine and acetaldehyde are evolved, and addition of water precipitates the corresponding iodocompound from solution.

Iododichlorides have, in general, a pleasant, not severe smell. They decompose on heating (the decomposition point of iodobenzene dichloride is 115-127$^\circ$, varying according to the rate of heating), the products of decomposition being the aryl iodide and chlorine. Under different conditions Keppler (Ber. 1898, 31, 1136) showed that the products of decomposition were different - in a closed vessel iodobenzene dichloride formed hydrochloric acid and p-chloroiodobenzene.

The iododichlorides can be used as chlorinating agents; the following are given as examples:- From metallic iodides they liberate iodine with the formation of the metallic chloride, this being used as a method of estimating the dichloride. Iodine is liberated in the cold by the treatment of iodoparaffin with iododichlorides, this affording an easy method of estimating the iodine in these compounds. A few drops of methyl, ethyl or amyl iodide treated with a crystal of iodobenzene dichloride quickly turns a brownish-yellow colour; if now a glass tube is dipped into the coloured solution and then into

carbon disulphide and water, the carbon disulphide acquires a distinct bright-red colour. This test, which is extremely sensitive, is a characteristic of iodoparaffins. From a dilute aqueous solution of potassium cyanide, iododichlorides liberate cyanogen and form potassium chloride, whilst from a concentrated solution of the cyanide little or no cyanogen is evolved, the solution being rapidly coloured dark-brown. Iododichlorides react vigorously with aniline, forming a chloroaniline dyestuff, and with phenols which they also chlorinate.

Aqueous hydrogen sulphide slowly reduces iododichlorides with the separation of the aryl iodide and free sulphur. With mercaptans they form aryl disulphides, iodides and hydrochloric acid (Otto, Ber. 1893, $\underline{26}$, 305).

e.g. $R'ICl_2 + 2HS.R'' = R'I + (R''S)_2 + 2HCl$
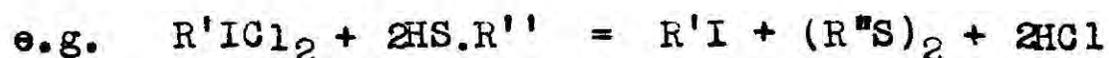
When an aqueous solution of sodium benzene sulphinate is shaken for a short time with iodobenzene dichloride there are formed benzenesulphonechloride, iodobenzene and sodium chloride:

$C_6H_5ICl_2 + C_6H_5SO_2Na = C_6H_5I + NaCl + C_6H_5SO_2Cl$

As indicated earlier, by the treatment of iododichlorides with the silver chloride-silver acetylide double compound aliphatic-aromatic salts are prepared, and with mercury diphenyl aromatic iodonium chlorides are formed.

(b) Iodosocompounds.

Iodosocompounds are amorphous, yellowish-grey-white solids with characteristic "iodoso-smells." The properties of iodosobenzene, the parent of this class, are given as being typical

of all iodosobases.

Iodosobenzene is slightly soluble in water and alkalies. The aqueous solution is completely neutral, but bleaches litmus paper in a short time. Evaporation of the solution still leaves an amorphous solid. Treated with hydrochloric acid, the aqueous solution of the iodosobenzene is reduced to iodobenzenedichloride. In boiling water an appreciable amount of iodosobenzene dissolves and, on cooling, needles of <u>iodoxybenzene</u> deposit, due to the self oxidation-reduction of the iodosocompound, the iodobenzene which is also formed being volatilised in the steam. It is stated that iodosobenzene is soluble to some extent in ethyl alcohol, but on warming or long standing it is reduced to iodobenzene by the alcohol. Almost all other neutral solvents, such as ether, acetone, petroleum ether, benzene and chloroform will not dissolve, or only exceedingly slightly dissolve, iodosobenzene. Iodosobenzene does not melt; on heating, it decomposes into iodo- and iodoxybenzene, detonating violently at $210^{o}$.

On long standing, and more quickly in warmer weather, iodosobenzene changes by self oxidation-reduction into iodo- and iodoxybenzene, even <u>in vacuo</u> and in the dark; because of this it cannot be stored for any length of time. Its acetate is easily made, perfectly stable, and readily reconvertible into the base; therefore iodosobenzene is stabilised as its acetate immediately it is made.

Iodosobenzene is an excellent oxidising agent. It oxidises

boiling formic acid and reacts explosively with aniline.

Tscherniac (Ber. 1903, 36, 218) states that iodosobenzene can be used as reagent in the Hofmann reaction. The conversion of acid-amides into the corresponding amines had, up to that time, been performed only with hypochlorite or hypobromite in alkaline solution, whereas Tscherniac used iodosobenzene as oxidising agent in the following way:-  2.195 grams of pure iodosobenzene were ground with water into a fine paste and added to a solution of 1.47 grams of phthalimide in 15 c.c. 2N potassium hydroxide, the mixture shaken for an hour, when the solution slowly went brown and iodobenzene formed as a heavy oil. By ether extraction, 1.8 grams of iodobenzene were obtained (theoretical 2.14 grams). The residual solution was treated with acetic acid and again ether-extracted;  the ethereal extract yielded 1.136 gram (theoretical 1.37 gram) of a most pure anthranilic acid (m. pt. 142-144$^{o}$).

$$\text{C}_6\text{H}_4(\text{CO})_2\text{NH} + \text{C}_6\text{H}_5\text{IO} + 3\text{KOH} = \text{C}_6\text{H}_4(\text{NH}_2)(\text{COOK}) + \text{C}_6\text{H}_5\text{I} + \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$$
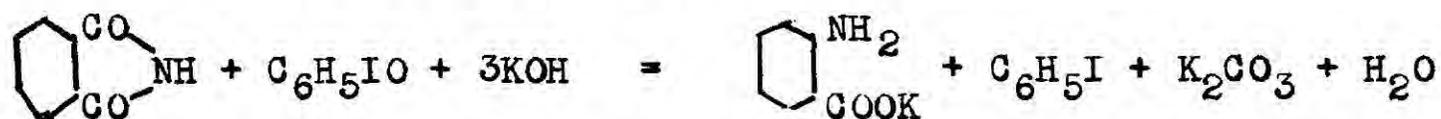
As found by Victor Meyer and his collaborators, and stated earlier (page 12), with concentrated sulphuric acid iodosobenzene forms, along with resinous by-products, p-iodophenyl-phenyl-iodonium sulphate.

### (c) Iodoxycompounds.

The properties of iodoxybenzene are given as being characteristic of all iodoxycompounds:-

Iodoxybenzene is a snow-white solid which, although it can be heated to as much as $230^{\circ}$, neither melts nor vaporises, whilst it is slightly soluble in water, ethyl alcohol, glacial acetic acid and formic acid, from which it crystallises in white needles, it is still less soluble in methyl alcohol and practically insoluble in the chemically inert organic solvents such as benzene, petroleum ether, carbon tetrachloride and chloroform.

Although in his earlier work Willgerodt admitted the possibility of its forming salts with alkalies (called by him "Jodonate"), he afterwards ("Die organischen Verbindungen mit mehrwertigem Jod," p. 35) refuted this statement by saying, "As with all iodoxycompounds, iodoxybenzene is a completely neutral body, forming salts neither with acids nor bases."

From cryoscopic molecular weight measurements of iodoxybenzene in formic acid solution by Mascarelli and Martinelli (Ch. Z. 1907, I, 1322), the authors conclude that it has the simple formula $C_6H_5IO_2$. Their results in all cases, however, are low by more than ten per cent.

| E.g. | Found | Calculated |
|---|---|---|
| $C_6H_5IO_2$ | 207.2 - 217.3 | 236 |
| $o\text{-}C_6H_4(CH_3)IO_2$ | 182.9 - 188.1 | 250 |
| $m\text{-}C_6H_4(CH_3)IO_2$ | 178.4 - 217.4 | 250 |
| $p\text{-}C_6H_4(CH_3)IO_2$ | 219.7 - 220.8 | 250 |

Although the investigators were of the opinion that the

low results are due to dissociation phenomena such as are
shown in the analogous nitrocompounds, probably a better
explanation of these results is that they are due to salt
formation (cf. J.C.S. 1935, 1674). Ebullioscopic determin-
ations with iodoxybenzene in pyridine, acetone and alcohol
have given no satisfactory results.

When an aqueous solution of iodoxybenzene is treated
with hydrochloric acid, chlorine is evolved and iodobenzene-
dichloride deposits; it is in this respect comparable with
manganese dioxide.

$$C_6H_5IO_2 + 4HCl \quad = \quad C_6H_5ICl_2 + Cl_2 + 2H_2O$$
$$MnO_2 + 4HCl \quad = \quad MnCl_2 + Cl_2 + 2H_2O$$
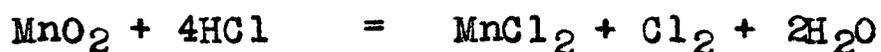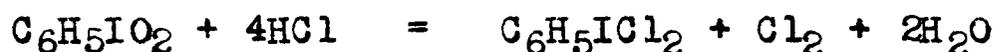
Iodoxybenzene explodes violently when added to phosphorus
pentachloride or to concentrated sulphuric acid. In contrast
to iodosobenzene it reacts quietly with aniline, forming a
blood-red solution. "With fuming nitric acid and iodoxybenz-
"ene there is scarcely a perceptible reaction; if, after the
"mixture has stood for some time, the clear solution is poured
"into water there deposits a yellow-white body with the charac-
"teristic strong smell of p-nitroiodobenzene, and after recrys-
"tallising from chloroform, the needles formed melt at 165°.
"The melting point of pure p-nitroiodobenzene is 171.5°." At-
tempts by Verländer and others to nitrate iodoxybenzene were
equally unsuccessful.

It was discovered by Ciamican and Silber (Ch. Z. 1905, I,
1146; Atti R. Accad. dei Lincei (5), 14, I, 265) that in the

presence of nitrobenzene and under the influence of light benzaldehyde is polymerised. Mascarelli (Ch. Z. 1907, I, 33; Atti R. Accad. dei Lincei (5), 15, II, 375-379) studied the substitution of iodoxybenzene for nitrobenzene in this reaction and found that when 200 grams of benzaldehyde and 50 grams of iodoxybenzene were left in a glass vessel in the light from 31st July, 1905 until 21st May, 1906, part of the product was not extractable with ether, but recrystallised from glacial acetic acid in white prisms and proved to be tribenzaldehyde of melting point $250^{\circ}$.

Mascarelli (Ch. Z. 1905, II, 893; Atti R. Accad. dei Lincei Roma (5), 14, II, 199-205) gives three methods for the preparation of double compounds of iodoxybenzene with mercuric chloride and bromide:- (a) By the addition of mercuric chloride or bromide to a suspension of iodoxybenzene in water; (b) by the treatment of iodobenzene dichloride with mercuric chloride and chlorine; and (c) by passing chlorine gas through a solution of iodobenzene in glacial acetic acid in the presence of mercuric chloride. These double compounds form in white, needle-shaped crystals and are more stable to heat than iodoxycompounds. Double salts can also be formed with gold chloride and platinum chloride.

Iodoxybenzene reduces potassium iodide in acid medium, yielding free iodine. The purity of the iodoxycompound is estimated by this reaction. Willgerodt (Ber. 1896, 29, 2008)

found that by boiling iodoxybenzene with aqueous potassium
iodide the solution developed a strongly alkaline reaction,
contained free iodine and formed exceptionally pure diphenyl-
iodonium periodide, $(C_6H_5)_2I.I_3$.    Longer boiling decomposed
the polyiodide, giving the iodonium iodide and free iodine.
He formulated the reaction as taking place in the following
sequence:-

$$PhIO_2 + 2KI + H_2O = PhIO + KOH + I_2$$

$$PhIO + PhIO_2 + KOH = Ph_2I.OH + KIO_3$$

$$Ph_2I.OH + KI = Ph_2I.I + KOH$$

$$Ph_2I.I + I_2 = Ph_2I.I_3$$

$$Ph_2I.I_3 \xrightarrow{\text{boiling water}} Ph_2I.I + I_2$$
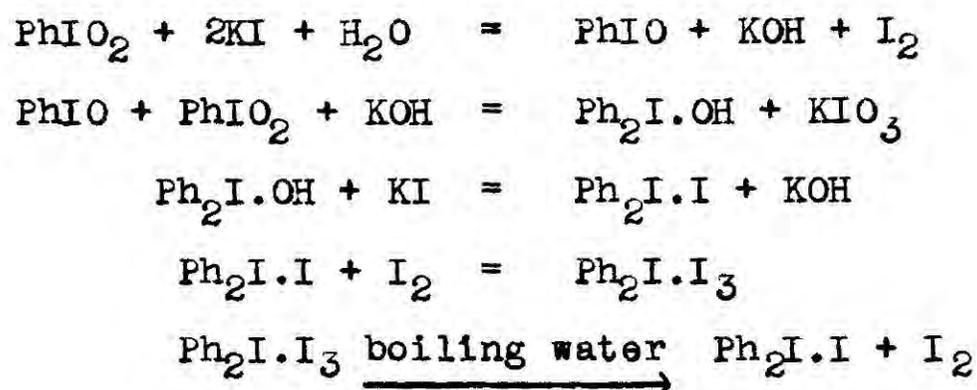
For the action of alkali on iodoxybenzene see Chapter
Three on "Iodoxybenzene and Alkalies."

(d)  Diaryliodonium Compounds.

The iodide of Hartmann and Meyer's "new non-nitrogenous
base containing iodine" was found by them to decompose on heat
ing into p-diiodobenzene and iodobenzene, and was therefore
given the structure:-

$$C_6H_5-\underset{I}{I}-C_6H_4I$$
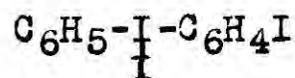
and this class of compound was termed "iodonium compounds,"
although Willgerodt, by comparing and contrasting them with
sulphinium and ammonium bases, expresses the opinion that a
more suitable name is iodinium compounds.

In chemical properties the diphenyliodonium radicle
resembles lead, silver and, more particularly, thallium, even
in physiological action.

E.g.    Sulphate ...    Easily soluble in water;   decomposition
                        point 153-4$^\circ$.

        Nitrate ....    Less soluble in water;   decomposition
                        point 153-4$^\circ$.

        Iodide .....    White solid, sparingly soluble in water.
                        Recrystallises from alcohol in yellowish
                        needles, decomposing at 180$^\circ$.   Turns yellow
                        in the light.

        Bromide ....    White solid, recrystallising from hot water
                        in large needles;   more soluble than iodide,
                        Decomposition point 230$^\circ$.

        Chloride ...    More soluble than bromide and iodide.
                        Recrystallises from hot water in white
                        needles.   Decomposes at 230$^\circ$.

        Chromate ...    Orange-coloured solid, recrystallising
                        from water in leaflets and decomposing
                        on slow heating at 157$^\circ$.

        Carbonate ..    Slightly soluble in water;   by evaporat-
                        ing the solution a varnish is formed which
                        solidifies on long standing.

        Acetate ....    Small white crystals;   decomposition point
                        120$^\circ$.

The free base is known only in its aqueous, strongly alkaline
solution.   From measurements of conductivity and saponification-
coefficient using methyl alcohol Sullivan (Ch. Z. 1899, I, 1078;
and Z. Phys. Ch., 28, 528) concludes that as a base it is com-
parable with caustic soda.   Evaporation of the aqueous solu-
tion results in the formation of a strongly alkaline syrup.

A cold aqueous solution of diphenyliodonium hydroxide is
reduced by 5% sodium amalgam, forming benzene and diphenyl-

iodonium iodide, thus:-

$$(C_6H_5)_2I.OH + 4H = 2C_6H_5 + H_2O + HI$$

$$(C_6H_5)_2I.OH + HI = (C_6H_5)_2I.I + H_2O$$

Diphenyliodonium iodide is capable of forming perhalides. The periodide, $(C_6H_5)_2I.I.I_2$, is formed when the iodonium iodide is treated with alcohol or methyl alcohol containing the calculated amount of iodine, and the solution boiled. It crystallises in dark red, almost black, lustrous needles of melting point $138^O$. Diphenyliodonium iodide-dichloride, $(C_6H_5)_2I.I.Cl_2$, and diphenyliodonium trichloride, both decomposing at $138^O$, are formed when the alkaline mother liquors in the preparation of iodosobenzene are acidified with hydrochloric acid. These two perhalides are also preparable by suspending diphenyliodonium iodide in chloroform and chlorinating this. The suspended solid is first coloured dark brown by liberated iodine, but it soon dissolves to form a yellow solution; by further chlorination there deposits a yellow crystalline mixture of diphenyliodonium iodide-dichloride and diphenyliodonium trichloride, these being separated by fractional crystallisation from alcohol. Both these products are identical with the perhalides obtained from the iodoso-alkaline liquor. Diphenyliodonium iodide-dibromide and diphenyliodonium tribromide can be made by a similar method, using bromine water; they decompose at about $140^O$, the former crystallising in brown leaflets and the latter in brown needles. Forster and Schaeppi (Ch. Z. 1912, I, 1702; J.C.S., 101, 382)

have prepared a number of iodonium polyhalides with higher
halogen content, e.g. diphenyliodonium iodide-tetrachloride,
$[(C_6H_5)_2I.ICl_4 \rightleftharpoons (C_6H_5)_2I.Cl.ICl_3]$, melting point 118-120$^O$,
diphenyliodonium iodide-iodochloride, $[(C_6H_5)_2I.I.ICl)]$, melt-
ing point 134-135$^O$.

# CHAPTER TWO.

## PREPARATION OF STARTING MATERIALS.

1. **General**.

In all the preparations and analyses which follow, stoppers and exposed joints were made of glass and only sintered glass filters were used because of the strong oxidising agents encountered. Except where reduction was actually intended, the use of reducing solvents, such as alcohol and acetone, had to be avoided, and generally this added to the difficulty of drying products.

2. **Iodobenzene Dichloride**.

Willgerodt's original method (Ber. 1892, 25, 3494) was employed in the preparation of iodobenzene dichloride, the solvent being carbon tetrachloride. In order to regulate the amount of chlorine introduced, a wash-bottle with glass taps at both inlet and outlet tubes was partially filled with carbon tetrachloride, weighed, and chlorine passed into the solvent until it contained the required amount of chlorine. The pressure of gas in the apparatus was sufficient to force the chlorinated carbon tetrachloride into the iodobenzene liquor, the latter being contained in a flask with a ground glass delivery connection.

Before use the iodobenzene was freed from aniline with dilute hydrochloric acid and redistilled under reduced pressure. In the first preparation, 35 grams (0.16 gram-molecule) of iodobenzene were dissolved in 19 c.c. of pure dried carbon tetrachloride, and 16 grams (0.23 gram-molecule) of chlorine (generated from hydrochloric acid and potassium permanganate, washed and dried through calcium chloride) in 31 c.c. of carbon tetrachloride introduced. The 90% yield obtained was dried <u>in vacuo</u>. In a second preparation of the dichloride, 97 grams (0.48 gm.-mol.) of pure iodobenzene in 30 c.c. of carbon tetrachloride were used, and chlorinated with 51 grams (0.71 gm.-mol.) chlorine in 90 c.c. of carbon tetrachloride. The iodobenzene dichloride was allowed to form overnight, and the dried product weighed 119 grams (92% yield).

### 3. <u>Iodosobenzene.</u>

The iodobenzene dichloride, stored in vacuum dessicator, was found after a few days to be decomposing, and on one occasion had to be suspended in carbon tetrachloride and re-chlorinated. It was therefore converted at the earliest convenience into iodosobenzene acetate.

The hydrolysis of the dichloride was preformed with a 5% sodium hydroxide solution, using a slight excess of that shown in the equation:-

$$PhICl_2 + 2NaOH = PhIO + 2NaCl + H_2O$$

In the first attempt 38 grams of the dichloride were ground in portions of about 4 grams each with the 5% caustic

soda, each grinding continuing over 15 minutes. The mixture was shaken on a machine for $16.\frac{1}{2}$ hours, after which the yield of iodosobenzene, washed sparingly but efficiently with water until alkali-free, and dried <u>in vacuo</u> in the dark, was only 42.4%. An iodometric titration of the product showed it to be 94.6% pure. In the course of a day the filtrate and first washings deposited white, flaky crystals of diphenyl-iodonium chloride, and neutralisation of the alkaline solution with dilute hydrochloric acid yielded more of this by-product. The filtered, washed and dried chloride weighed 1.3 grams. After reduction of the iodosobenzene in the residual liquor with sulphur dioxide, the diphenyliodonium salt still in solution was precipitated as iodide with normal aqueous sodium iodide. The dried precipitate weighed 1.3 grams.

In a second preparation of iodosobenzene the mixture of dichloride and sodium hydroxide solution was shaken for only 3 hours and resulted in an 87% yield of 97.1% purity.

Attempts to prepare iodosobenzene by substituting magnesium hydroxide and disodium hydrogen phosphate for sodium hydroxide proved less successful. In the first case the excess magnesium hydroxide was removed with 5N acetic acid and a 68% yield of only 60.5% pure iodosobenzene was obtained. Using sodium phosphate there was a 56% yield of base containing only 72% iodosobenzene.

4. <u>Iodosobenzene Acetate.</u>

The conversion of iodosobenzene into its acetate was

effected simply by grinding the base with 2.1 molecular proportions of glacial acetic acid. The mass turned white and practically dry. After standing 24 hours the acetate was recrystallised from benzene. It was beautifully crystalline, perfectly white and was free from detectable impurities, giving iodometric titrations showing it to be 100.0% pure.

5. Iodoxybenzene and Iodoxytoluene.

Because of the poor yields obtainable in the preparation of iodoxybenzene by the oxidation of iodosobenzene with sodium hypochlorite (the method which had been used hithertofore in this laboratory by Professor Masson and Dr. Pounder), it was decided to make some preliminary tests of the method described by Bamberger and Hill (Ber. 1900, 33, 533; see also page 11 of this book) whereby the iodobenzene was directly oxidised by Caro's acid (monopersulphuric acid) to the iodoxybody.

The stock of potassium persulphate used in the making of the Caro's acid was analysed by titrating it against standard ferrous sulphate and potassium permanganate solutions (Treadwell and Hall, "Analytical Chemistry", Vol. 2, pp. 534-5) and found to be 98.2% pure. In the first attempt of the preparation of the Caro's acid the recipe given by Bamberger and Hill was followed: 60 grams of concentrated sulphuric acid were added slowly to 56 grams of potassium persulphate immersed in an ice bath. There was a slight escape of ozonised oxygen, and after 45 minutes the mass had caked solid. Addition of 90 grams of ice in small portions did not dissolve all of this solid. When,

using the same weight of ingredients, the order of addition
was reversed, the ice being added first to the persulphate
and then the concentrated sulphuric acid added, the solid
still remained out of solution. The active oxygen in the
sludge formed was determined by shaking 10 c.c. of it with
100 c.c. 0.3505N ferrous sulphate, the excess of the latter
being determined with $\frac{N}{10}$ permanganate. The sludge contained
12.1 grams of active oxygen per litre. 84.36 c.c. of this
Caro's acid "solution" were shaken with 6.55 grams of iodo-
benzene (requiring 1.02 grams of active oxygen) for 15 hours.
The solid formed was perfectly and microcrystalline, but on
examination it proved to be potassium persulphate.

The method for preparing Caro's acid described by Houben
("Methoden", 1923, Vol. 2, p. 58) also proved unsuccessful:
56 grams of potassium persulphate were stirred with 61.5 grams
of concentrated sulphuric acid for 10 minutes, and to the re-
sulting paste 168 grams of powdered potassium sulphate were
added, and the mixture ground for 40 minutes, when a perfectly
dry powder was formed. The Caro's acid was made as required
by dissolving this powder in three times its weight of concen-
trated sulphuric acid. Such a solution, however, contained
only 1.42 grams of active oxygen per litre.

An attempt was made to prepare Caro's acid using hydrogen
peroxide. The stock 100 volume hydrogen peroxide was found by
titration to contain 32.2% peroxide. To 450 grams of concen-
trated sulphuric acid, cooled to $-14^{\circ}$, 100 grams of this hydro-
gen

peroxide were added, and into this solution 100 c.c. of water slowly poured. The resulting solution was pale yellow and contained 18.1 grams of active oxygen per litre. When an equivalent amount (58.6 c.c.) of it was used to oxidise 7 grams of iodobenzene, the frothing was too great for any effective shaking to be performed and the preparation had to be abandoned.

Attention was again directed to the original recipe of Bamberger and Hill; it was thought that the former failures might be due to the sulphuric acid used being of a higher concentration than that employed by the authors, and it was therefore deemed advisable to use an acid of approximate composition $H_2SO_4.H_2O$. 64 grams of an acid of this strength, cooled to $-24^\circ$, were added with stirring to 56 grams of potassium persulphate and, after standing 50 minutes, the sludge formed was diluted by grinding with 90 grams of ice. The suspension was filtered, this having been omitted on previous occasions, and the clear filtrate was found by titration to contain 13.6 grams of active oxygen per litre. 7 grams of iodobenzene were shaken with 82 c.c. of the Caro's acid solution for $2.^1/_2$ hours, after which the iodoxybenzene formed was filtered off and washed acid-free with water. Iodosobenzene was detected in the filtrate both by its smell and by its oxidising action on sodium iodide solution in saturated sodium bicarbonate medium. The solution was shaken, therefore, for a further 4 hours, thereby yielding a second amount of iodoxybenzene. The final dried yield was

80.1% of the theoretical, and by iodometric titration in acid
medium was 93.2% pure. This result, it was thought, warranted
a preparation on a larger scale. In the first large-scale
preparation of iodoxybenzene, 0.96 kilogram of potassium per-
sulphate was treated with 1.2 kilograms of sulphuric acid of
the composition $H_2SO_4.H_2O$ and the mixture diluted with 1.5
kilograms of ice. $1.^1/_4$ litres of the filtered solution
(which contained 13.1 grams of active oxygen per litre) were
used to oxidise 103 grams of iodobenzene. Owing to excessive
frothing some part of the mixture was lost during the shaking
on a machine, the final yield being 89 grams of iodoxybenzene,
which, after 40 minutes boiling with 150 c.c. of water, to
convert any iodosobenzene into the iodoxybody, and warming it
with 100 c.c. of benzene to rid it of unchanged or re-formed
iodide, gave iodometric titrations showing it to be 100.0% pure.

In all of the foregoing attempts to oxidise iodobenzene
directly to iodoxybenzene, it was noticed that the iodosocom-
pound was an intermediate product; hence in the ultimate
method, which was employed on four occasions, an excess of the
Caro's acid was used. Also, because of the unavoidable froth-
ing during the vigorous shaking necessary, and because mechan-
ical stirring was insufficient to mix effectively the heavy
iodobenzene oil with the aqueous Caro's acid, it was found
advisable to perform all shaking by hand. The final method
adopted for the preparation of the iodoxycompound is as fol-
lows: 1.6 kilograms of concentrated sulphuric acid are diluted

with 214 grams of water and the cooled acid mixed with 1.5 kilograms of potassium persulphate with thorough grinding for 45 minutes, and stood with occasional grinding for an hour. 2.5 kilograms of ice are added in about 20 portions, the sludge well ground and filtered. Such a solution contains about 2.2 equivalents of active oxygen per litre, and for 100 grams of iodobenzene 1.5 litres of the Caro's acid is used. The mixture is shaken vigorously by hand in a long-necked 5-litre round-bottomed flask. After about $2.^1/_2$ hours the iodoxybenzene begins to form, and at the end of 5 hours the solid is filtered, ground well, remixed with its mother-liquor and allowed to stand a further 12 to 14 hours. The filtered iodoxybenzene is washed with 150 c.c. of water, but in general this is insufficient to rid it completely of an acid reaction. The solid is suspended in 300-400 c.c. of water and boiled for an hour with free steam, which converts traces of iodosobenzene into iodoxy- and iodobenzene and expels the latter, as well as taking out the slight trace of sulphuric acid still remaining. The iodoxybenzene dissolved in the water is recovered by evaporation, and the final yield, dried in vacuo, represents 94-96% of the theoretical, and is free from detectable impurities, giving iodometric titrations in acid medium showing it to be 100.0% pure, and yielding no iodine from iodide solution in saturated borax medium. The iodoxybenzene which remains dissolved in the main liquors is recoverable as iodobenzene by treating them with 10 c.c. of perhydrol.

This method was also found applicable to the preparation of iodoxytoluene, and again it was noticed that the iodosocompound was formed as an intermediate product. Apparently, however, a longer time of shaking is necessary, since it was found that the iodoxytoluene formed contained an appreciable amount of iodotoluene, from which it had to be separated by benzene extraction. The final product was 97.3% pure.

# CHAPTER THREE

## IODOXYBENZENE AND ALKALIES.

1. **Historical**.

The decomposition of iodoxybenzene by alkalies (sodium hydroxide and baryta solutions) had been observed by Victor Meyer and Hartmann and independently by Willgerodt, but no examination had been made by these workers of the mechanism and the quantitative nature of the apparently complex reactions involved, a knowledge of which is necessary for an understanding of Meyer and Hartmann's process of preparing iodonium compounds with silver oxide, iodoso- and iodoxybenzene. Such an examination, in any case, would help in an understanding of the nature of the iodoxygroup itself.

It had been noted that iodoxybenzene and alkali react to give some small amount (or, at any rate, no great amount) of diphenyliodonium radicle. Meyer and Hartmann (Ber. 1892, 27, 1592) noted that this was a cause of the faulty efficiency of their process if caustic soda be substituted for silver oxide, the iodoxybenzene being consumed by the alkali to some extent instead of being available for reaction with the iodosocompound. Willgerodt (Ber. 1894, 29, 2009) observed it when he used baryta solutions, and noted that barium iodate deposited from the

liquid; he also stated that the filtrate would not yield a precipitate of iodonium iodide with potassium iodide until some time had elapsed. He noticed also a smell as of diphenyl. On this basis Willgerodt formulated the reactions between alkali and iodoxybenzene as follows:-

(a)         $PhIO_2 + Ba(OH)_2 = BaO.O_2IPh + H_2O$
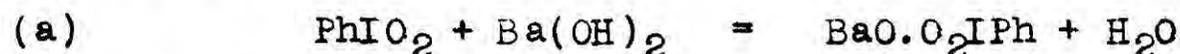
(This salt formation - called by Willgerodt "Jodonate" - was afterwards ("Die organischen Verbindungen mit mehrwertigem Jod") refuted by him.)

(b)     $3(BaO.O_2IPh) = PhIO + Ph.Ph + Ba(IO_3)_2 + 2BaO$

(c)     $Ba(OH)_2 + 2PhIO + 2PhIO_2 = 2Ph_2I.OH + Ba(IO_3)_2$
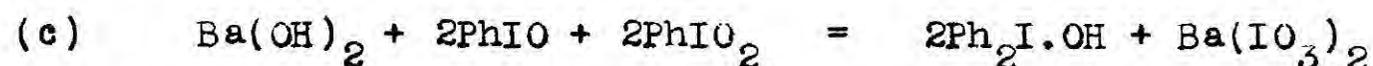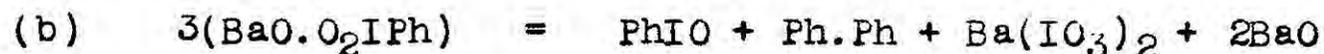
Clearly this series of reactions involves guesswork even if it, or some of it, be true.

The study of the action of alkalies on iodoxybenzene was begun in this laboratory by Professor Masson and Dr. Pounder. It seemed not unlikely that, just as one can express the reaction of Meyer and Hartmann as

$$PhIO_2 + PhIO \xrightarrow{OH'} Ph_2I + IO_3,$$
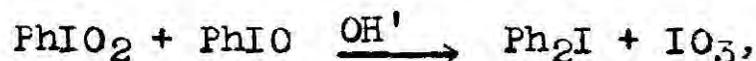
so also there might be the reaction

$$PhIO_2 + PhIO_2 \xrightarrow{OH'} Ph_2I + IO_4 \qquad \ldots\ldots\ldots(i)$$
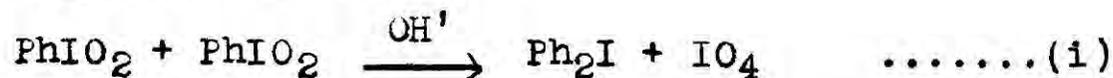
that is, a bimolecular decomposition of iodoxybenzene under the influence of the alkali yielding the molecule of diphenyl-iodonium periodate. The presence of this periodate did not seem to have been tested for or thought of by former workers. Such a reaction proceeding to completion would mean that in

the solution there would be no change in the total alkalinity or in its oxidising power, periodate should be detectable and half the iodine originally present would finally be present in an "ionic" form.

Besides the appearance of iodate and iodonium radicle in the alkali-iodoxybenzene mixtures, there quickly develops an oily turbidity, to account for which the most probable compounds are:- Iodobenzene, phenol, benzene and diphenyl; the two former substances are decomposition products of diphenyl-iodonium hydroxide:-

$$Ph_2I.OH \longrightarrow PhI + PhOH \qquad \ldots\ldots\ldots (ii)$$
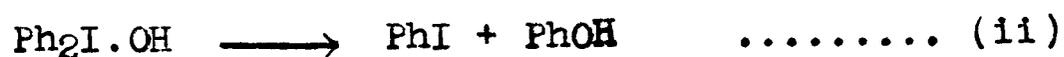
Benzene might conceivably be produced along with iodate, thus:-

$$PhIO_2 + NaOH \longrightarrow PhH + NaIO_3 \qquad \ldots\ldots (iii)$$
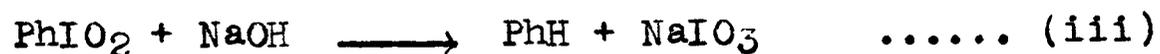
and Willgerodt's hypothesis might account for the presence of diphenyl in the products.

The formation of phenol would have an effect on iodometric titrations in certain media, and the occurrence of the reaction (ii) would be indicated by a loss of one molecule of alkali per one of iodoxybenzene using methyl orange as indicator and two molecules of alkali using as indicator phenolphthalein. The formation of benzene and iodate according to (ii) would also imply a loss in alkalinity and cause an increase in the total oxidising power from four to six.

Because of the possibility, therefore, of complex mixtures resulting from the reaction of the alkali and iodoxybenzene, it

was found necessary to perform many experiments on the modes of analysis and detection of the various substances involved.

Potassium periodate and diphenyliodonium hydroxide (the latter prepared by grinding and shaking the iodide with moist silver oxide) were found to be stable in alkali solutions. Tests on the liberation of iodine from potassium periodate by iodide in the presence of phenol were made, and it was found that in acid solution the full amount of iodine (8 atoms per molecule) was liberated without any absorption of the iodine by the phenol, whilst in bicarbonate medium no free iodine was formed, the phenol taking up to 6 atoms of iodine per molecule of phenol. It was found that in mixtures of iodoxy- and iodosobenzene, the latter could be estimated quantitatively by liberation of iodine from iodide solutions in bicarbonate solutions, in which iodoxybenzene is inactive. Mixtures of iodosobenzene and potassium periodate in saturated borax maintained undiminished their oxidising power, proving that no oxidation of iodoso- to iodoxybenzene occurs in such circumstances.

That iodoxybenzene is not diphenyliodonium periodate (which would have the empirical composition and aqueous molecular weight of $C_6H_5IO_2$), was proved by preparing the salt by mixing equivalent aqueous solutions of its free base and its free acid, the former made from the iodide and silver oxide, the latter from dilute sulphuric acid and barium periodate, which in turn was made by igniting barium iodate (Rammelsburg,

Ber. 1869, 2, 1869). The compound formed large, tabular cryst-
als, nearly colourless, m. pt. 129° (decomposition); its molar
solubility was several times that of iodoxybenzene, and analysis
showed it to have the composition and quantitative reactions of
$(C_6H_5)_2I.IO_4$ 91.3 mols., with possibly an orthoperiodate $R_5IO_6$
3.6 mols., and iodate, $(C_6H_5)_2I.IO_4$, 5.0 mols. Its liberation
of iodine from an added iodide in saturated aqueous borax was
alone sufficient to differentiate it from iodoxybenzene.  Di-
phenyliodonium periodate was found to dissolve quietly in con-
centrated sulphuric acid, in which iodoxybenzene explodes, and
it was found to be stable in dilute alkali solutions.

Systematic experiments on iodoxybenzene in water from 14°
to 100°, in $\frac{N}{100}$, $\frac{N}{50}$, $\frac{N}{25}$, $\frac{N}{10}$, $\frac{N}{5}$ and N aqueous sodium hydroxide
at 25°, and in N NaOH at 100° were made. In water, iodoxybenz-
ene dissolves as such to a small extent (11.6 millimols. per
litre at 14° and 49.7 millimols. per litre at 99°). Its solu-
tion has no electrical conductivity of its own and is neutral.
On being kept at 98-100°, the solution gradually develops a
slight but increasing conduction, but still remains neutral;
this conduction remains on cooling the solution.

The action of boiling N sodium hydroxide on iodoxybenzene
was found to yield benzene, identified by its boiling point and
by the melting point of its dinitro-derivative both alone and
mixed with m-dinitrobenzene;  there was also a smell resembling
that of diphenyl in some of the distillate. The oxidising power
of the material simultaneously increased;  hence it appeared

that one reaction, at least at higher temperatures and with normal alkali, is

$$PhIO_2 + NaOH \longrightarrow PhH + NaIO_3 \qquad \dots\dots\dots (iv)$$
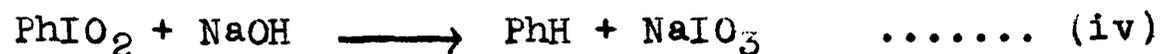
In boiling alkali, diphenyliodonium hydroxide would be unstable (equation (ii)), but it is worthy of note that in the foregoing experiment traces of phenol, but only traces, were detected when looked for; iodobenzene was present along with benzene in quantity enough to make a mixture denser than water. Measurements were made in the residual liquors of alkalinity, iodate and (?)periodate(?), and these agreed almost exactly with the simultaneous occurrence of (iv) with (i) and (ii). The fact that diphenyliodonium periodate is stable in alkaline solution, shown by analysis for iodonium radicle, alkalinity and periodate of a several days' old solution, when none of these had significantly changed, seemed to indicate that at room temperature reaction (ii) (the decomposition of diphenyliodonium hydroxide) is so slow as to be almost negligible.

As to the series of dilute alkali solutions of iodoxybenzene, each was analysed several times (except $\frac{N}{5}$) during several days' keeping at $25^O$. The analyses determined:-

(a) Alkalinity to methyl orange,

(b) Oxidising power to added potassium iodide in acid solution,

(c) Oxidising power to added potassium iodide in saturated borax solution (in which iodate and iodoxybenzene do not react),

(d) The diphenyliodonium radicle by precipitating and weighing its iodide,

(e) The oxidised-iodine anions ($IO_3'$, $IO_4'$) by reduction with sulphur dioxide, precipitation and weighing of silver iodide.

The electrical conductivities were measured at the same time.

Some of the main facts brought out in this series were:-
More iodoxybenzene dissolves in alkali than in water. The dissolution is not rapid and most, if not all, of it seems to be due to chemical action. This action is really a train of reactions. In the most dilute alkali ($\frac{N}{100}$) it appears that in the early stages some of the dissolved iodoxybenzene still exists undecomposed in the liquid; but if this is so, it is combined with the alkali, for the conductivity has decreased, although the alkalinity to methyl orange has not. Later on (and in middle strengths of alkali, sooner) no appreciable iodoxybenzene remains undecomposed; it is represented as to its iodine by iodonium radicle and by oxidised-iodine anions, and as to its oxidising power by these anions (which may be named conjointly as $IO_x$). But of the original phenyl groups a small proportion is not accounted for by the analysed components. In all the liquids there is a slight oily scum and a little tawny amorphous suspended matter. The deficiency of phenyl radicle is most noticeable in the higher concentrations of alkali and in their later stages; and in these also the decrease of alkalinity per molecule of iodoxybenzene initially taken is greatest. This decrease of alkalinity is progressive with them all, but the conductivity does not fall off after its first

drop. The indications are that in the later stages, especially with the less dilute alkali solutions, the diphenyliodonium and the oxidising power in borax medium both fall off from a maximum value; the oxidised iodine-anion, however, does not appear to do so; and the oxidising power in acid media, at first a little low in the higher concentrations of alkali, in these tends, if anything, towards regaining its initial value. These observations accord with the following chain of reactions:-

(i)          $PhIO_2 + OH \longrightarrow (PhIO_2.OH)$  ............. Possibly

(ii)        $2PhIO_2 \xrightarrow{(OH)'} (Ph_2I)^\cdot + (IO_4)'$

(iii)       $(PhIO_2.OH) \longrightarrow PhH + (IO_3)'$  ... Proved definitely

(iv)       $(Ph_2I) + OH' \longrightarrow PhOH + PhI$  ... Proved in certain circumstances but not marked except in concentrated solution and in later stages of it.
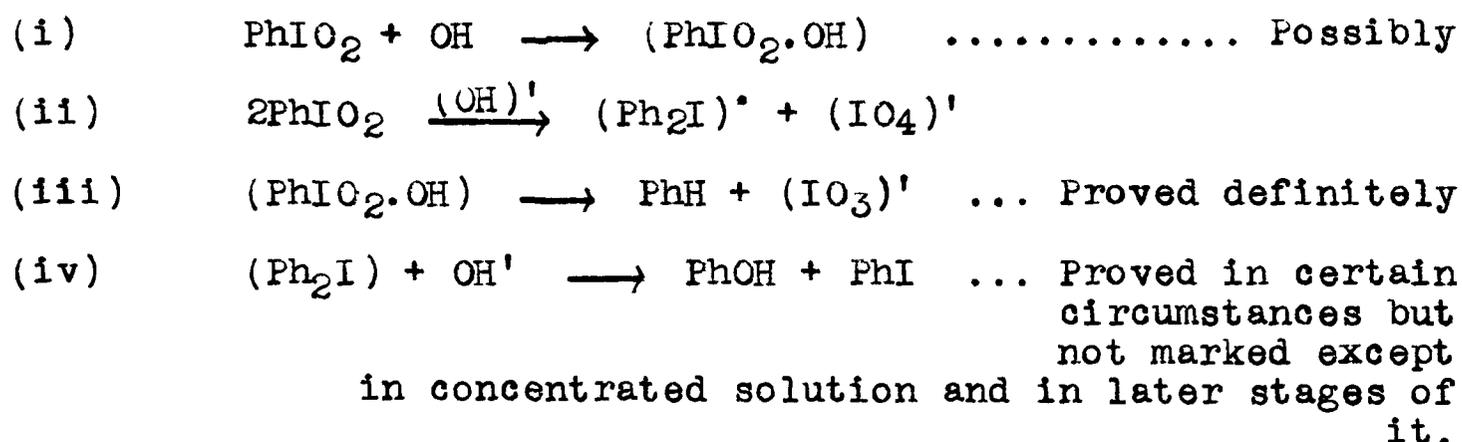
Lack of time prevented sufficient evidence being brought to light to assert definitely that these are true or otherwise. Notably, periodate was not proved to be present, for the reaction used to detect and measure it (borax-medium oxidation of potassium iodide) turned out to be qualitatively applicable to iodosobenzene. Further, the presence of the diphenyliodonium radicle complicated the iodide reaction and titration, both in borax and in acid media, by forming a polyiodide precipitate which was very slow to give up its excess of iodine to arsenite or thiosulphate in the titration. This slowness made for bad end-points.

Before any firm conclusions could be made, therefore, other control experiments were deemed necessary; the following preliminary investigations were carried out:-

2. __Preliminary Investigations.__

(a) __Titration of potassium periodate against arsenite in__
__saturated borax.__

In saturated borax, with sodium iodide added, potassium periodate is reduced to iodate:-

$$IO'_4 + 2HI \longrightarrow IO'_3 + 2I + H_2O$$

and the iodine had been titrated with arsenite. Experiments were performed to see if the arsenite could be used directly as reducing agent, determining the excess with standard iodine. The titration was done several times and, although it appeared as if the reaction were, if not solely, then mainly a reduction of the periodate to iodate, in each case the end-point was found to be unreliable owing to a further liberation of iodine on adding the slightest excess of the standard iodine solution.

Because of this, the existing method was tried as a back titration. That is, to the potassium periodate in saturated borax sodium iodide and a known excess of standard arsenite were added and the residual arsenite titrated against standard iodine. The results in this case were favourable:-

| KIO$_4$ taken (millimols.) | As$_2$O$_3$ added (milliequivs.) | Iodine for excess As$_2$O$_3$ | As$_2$O$_3$ per molecule KIO$_4$ |
|---|---|---|---|
| 0.5879 | 2.443 | 1.270 | 1.994 |
| 1.091 | 2.470 | 0.291 | 1.998 |

The complication arising from the relative stability of the diphenyliodonium polyiodide could therefore be overcome in the active-oxygen titrations in borax medium by this procedure. The method is also applicable to the determination of the acid-active oxygen in a solution, since, after liberating the iodine in the acid medium, the solution can be neutralised and saturated with bicarbonate and shaken with excess arsenite solution.

### (b) The extent of reduction of iodoxy- and iodosobenzene in saturated sodium bicarbonate and in borax media.

This series of reactions was performed with a view to finding which medium is the more suitable for the estimation of iodosobenzene in the presence of the iodoxycompound, as well as to determine the minimum time for complete reduction in each case. Because of the sparing solubilities of the compounds the reactions were best carried out by clipping by rubber bands tubes of 100 c.c. capacity to the spokes of a bicycle wheel bracketed to a wall and turned over 20 to 40 times a minute. In each case the tube contained about 0.2 gram of either iodosobenzene acetate or iodoxybenzene, 25 c.c. saturated sodium

bicarbonate or borax, solid powdered bicarbonate or borax and 10 c.c. N sodium iodide.    The liberated iodine was titrated against standard arsenite.

## Iodosobenzene acetate

| In saturated bicarbonate | | In saturated borax | |
|---|---|---|---|
| Time on wheel (minutes) | Percentage reduced. | Time on wheel (minutes) | Percentage reduced |
| 35 | 76.58 | | |
| | | 69 | 94.48 |
| 60 | 96.31 | | |
| 120 | 97.57 | 114 | 95.41 |
| 155 | 100.1 | | |
| | | 200 | 99.86 |
| 1180 | 100.0 | | |

## Iodoxybenzene

| In saturated bicarbonate | | In saturated borax | |
|---|---|---|---|
| Time on wheel (minutes) | Percentage reduced | Time on wheel (minutes) | Percentage reduced |
| 76 | 12.06 | 284 | 0.406 |
| 138 | 20.46 | 1328 | 1.79 |
| 188 | 27.86 | | |
| 1087 | 67.66 | | |

In later preparations of iodoxybenzene there was no liberation of iodine from iodide in saturated borax after 48 hours wheeling.

Since iodoxybenzene is partially reduced by iodide in bicarbonate, whilst it is not in borax, any determinations of

iodoso- in the presence of iodoxybenzene must be done in the borax medium.

(c) The determination of iodine by Stepanow's method.

In trial experiments using iodotoluene and iodobenzene, the total iodine was found to be determinable accurately. With benzene present, however, which is probable when extractions of organic material from aqueous solution or suspension have to be made, it was found advisable to use 70 to 80 c.c. of alcohol and 7 or 8 grams of sodium per milliatom of iodine determined. With these modifications the method was equally accurate.

(d) Reaction of iodine and phenol in sodium bicarbonate solution.

Four reaction tubes were made up containing 10 c.c. 0.02667M phenol, 25 c.c. saturated sodium bicarbonate and 25 c.c. 0.1057N iodine, and wheeled for various lengths of time, after which the excess iodine was titrated against 0.1298N arsenite. The results given were:-

| Time in minutes | Extent of reaction<br>$PhOH + 6I = C_6H_5I_3 + 3HI$ |
|:---:|:---:|
| 50 | 0.9720 |
| 64 | 0.9884 |
| 100 | 0.9884 |
| 1035 | 0.9884 |

Assuming the phenol to be slightly impure, the reaction seems to complete itself quantitatively after an hour.

A similar series of experiments performed with phenol dissolved in benzene, showed that not less than 20 hours shaking on the wheel were required to complete the reaction.

### (e)   Effect of potassium periodate on acid-alkali titrations

The presence of potassium periodate in an alkaline solution was found to have no effect in a titration against standard sulphuric acid when methyl orange was used as indicator.

### (f)   The precipitation of iodates and periodates with barium salts.

Iodometric titrations of the stock sodium iodate showed it to have the composition $Na_2H_2I_2O_7$ (i.e. $2NaIO_3.H_2O$, molecular weight 414) rather than $NaIO_3$ (molecular weight 198).

The object of this series of experiments was to determine whether or not barium iodate and periodate are quantitatively precipitated from solution, the type of these precipitates and the most suitable medium to use.   In the first attempt, 7 to 8 millimols. of sodium iodate and periodate were treated separately with 40 c.c. $\frac{N}{5}$ sodium hydroxide, neutralised. made just acid with acetic acid and shaken on the wheel with 30 millimols. of barium acetate for 24 hours.   The precipitates formed were almost colloidal, too fine to be filtered through a grade 3, sintered-glass filter and blocking the pores of a grade 4 filter. They centrifuged only with difficulty and settled extremely

slowly. It was observed, however, that in dilute alkali the precipitates coagulated more satisfactorily, and therefore the precipitation was tried in this medium. 2.611 millimols. of potassium periodate were shaken with 150 c.c. $\frac{N}{5}$ alkali and 25 c.c. $\frac{M}{2}$ barium acetate added drop by drop. The vessel was wheeled for 20 hours, after which the fine, bulky precipitate settled quite rapidly. It was filtered and washed by a decantation-syphon arrangement, but as the alkali weakened the settling became poorer, and finally it had to be washed by centrifuging. The washings were kept separate from the filtrate, in both the excess barium being precipitated with sulphuric acid at $40^{o}$. Once again filtering and washing were difficult. The barium precipitate was decomposed by shaking with sulphuric acid for 28 hours, and all solutions were made to standard volumes.

Sodium iodate (1.3170 grams, equivalent to 37.921 milliequivalents of active oxygen) was treated similarly. The barium iodate precipitate was much coarser grained and settled more rapidly than did the periodate precipitate. As before, the barium iodate was decomposed by wheeling for 24 hours with sulphuric acid; in the filtrate solution and in the washings excess barium was precipitated with sulphuric acid; and all solutions were made to standard volumes.

The filters and syphon-tubes used in each case were washed with acidified sodium iodide solution and any iodine liberated thereby titrated against standard thiosulphate.

The various solutions were aliquoted for determinations of active oxygen in acid and in saturated borax media (called respectively A and B titrations) by liberation of iodine from sodium iodide.   Results were as follows:-

### PERIODATE.

#### Decomposed precipitate

| Analysis | Active oxygen (equivs.) per initial 2.611 mols. $KIO_4$. | Active oxygen (equivs.) per one mol. $KIO_4$ |
|---|---|---|
| A | 19.87 | 7.606 |
| A | 19.76 | 7.568 |
| A | 19.96 | 7.644 |

#### Filtrate

| Analysis | Active oxygen |
|---|---|
| A | Nil |
| B | Nil |

#### Washings

| Analysis | Active O per initial 2.611 mols.$KIO_4$ | Active O per one mol. $KIO_4$. |
|---|---|---|
| A | 0.290 | 0.11 |
| B | 0.035 | 0.013 |

#### Decomposed precipitate (cont.)

| Analysis | Active O per initial 2.611 mols.$KIO_4$ | Active O per one mol. $KIO_4$. |
|---|---|---|
| B | 4.663 | 1.786 |
| B | 4.663 | 1.786 |
| B | 4.646 | 1.778 |

### Filters and syphon-tubes

| Analysis | Active O per initial 2.611 mols. $KIO_4$ | Active O per one mol. $KIO_4$ |
|:---:|:---:|:---:|
| A | 0.206 | 0.005 |

### Totals.

Per 1.00 mols. (230 gms.) $KIO_4$ initially

| Analysis | Active oxygen originally | Active oxygen recovered |
|:---:|:---:|:---:|
| A | 8.00 | 7.72 |
| B | 2.00 | 1.80 |

## IODATE.

### Decomposed precipitate

| Analysis | Active O (equivs.) per initial 37.93 equivs. | Active O per 6 equivs. |
|---|---|---|
| A | 35.63 | 5.637 |
| B | Nil | Nil |

### Filtrate

| Analysis | Active O per initial 37.93 equivs. | Active O per 6 equivs. |
|---|---|---|
| A | 0.13 | 0.003 |
| B | Nil | Nil |

### Washings.

| Analysis | Active O (equivs.) per initial 37.93 equivs. | Active O per 6 equivs. |
|---|---|---|
| A | 1.25 | 0.033 |
| B | Nil | Nil |

### Filters and syphon-tubes

| Analysis | Active O per initial 37.93 equivs. | Active O per 6 equivs. |
|---|---|---|
| A | 0.69 | 0.02 |
| B | Not done | |

### Totals.

Per $\frac{1}{2}$ mol. $Na_2H_2I_2O_7$ (207 gms.) initially

| Analysis | Active oxygen originally | Active oxygen recovered |
|---|---|---|
| A | 6.00 | 5.69 |
| B | Nil | Nil |

The small amount of oxidising power found in the filtrates and in the washings (more especially in the latter because as the alkali strength becomes weaker the washing of the precipitates became more difficult) was probably due to traces of precipitate passing into them as much as to the solubilities of the barium iodate and periodate.

It was evident from these tests that iodate and periodate together in solution can be detected and estimated by precipitation of their barium salts.

### (g)   Reaction between phenol and periodate in various media.

To four reaction tubes containing respectively 0.4783, 0.6635, 0.7561 and 0.5961 millimols. of potassium periodate were added:-

i.    25 c.c. 0.05005N sodium hydroxide + 6.29 c.c. 0.07609M phenol.

ii.   25 c.c. 0.2003N sodium hydroxide + 8.72 c.c. 0.07609M phenol.

iii.  25 c.c. saturated and solid sodium bicarbonate + 9.94 c.c. phenol.

iv.   25 c.c. 0.2113N sulphuric acid + 7.83 c.c. 0.07609M phenol.

All the tubes were wheeled for 19 to 20 hours. Tubes i and ii assumed a pale yellow colour, tube iii was considerably darker and tube iv was a deep brown. Each solution was made 0.2N $H_2SO_4$, 10 c.c. N sodium iodide added and the iodine liberated titrated against 0.09983N thiosulphate. The iodine liberated from the four tubes was as follows:-

Tube i ...3.791 (= 8 x 0.4738) milliequivalents.

" ii ..5.291 (= 8 x 0.6614)          "

" iii..6.047 (= 8 x 0.7558)          "

" iv ..4.625 (= 8 x 0.5781)          "

That is, after 19 to 20 hours at room temperature, in $\frac{N}{5}$ sulphuric acid, 3% of the oxidising power of the periodate has been destroyed; in $\frac{N}{20}$ alkali, 0.94%; in $\frac{N}{5}$ alkali, 0.32%; and in saturated sodium bicarbonate there has been no change in oxidising power of the periodate.

Therefore, except that solutions containing them should not be kept acid for any length of time, periodate is not appreciably attacked by phenol.

### (h) Effect of prolonged shaking in acid and in alkali on A and B titrations of potassium periodate.

The tubes employed for these tests contained about 2.5 millimols. of potassium periodate, accurately weighed, in each. Both acid and alkali used were normal, 30 c.c. being added at a time, and the tubes wheeled for several hours. A summary of the results is given on the next page.

From these analyses, 230 grams of the solid contain $\frac{1.94}{2}$ mols. of potassium periodate and $\frac{8.023 - 4 \times 1.940}{6}$ mols. of potassium iodate, = 0.970 + 0.027 = 0.997 mols. That is, the $IO_x$ content of the solid is practically the theoretical of that for $KIO_4$, and prolonged shaking of it with alkali and with acid has no effect on its composition.

Equivalents of active oxygen per gm. mol. (230 gms.) potassium periodate.

| Medium | Time on Wheel | A Analysis | B Analysis | Ratio $\frac{A}{B}$ | Ratio A/B of barium ppt. |
|--------|--------------|-----------|-----------|---------|---------|
| Neutral | Nil | 7.989 | - | | |
| Neutral | Nil | 8.043 | - | | |
| Neutral | Nil | - | 1.941 | 4.130 | |
| Alkali | 22 hours | 8.034 | 1.929 | 4.164 | 4.255 |
| Alkali | 46 hours | 7.995 | 1.941 | 4.119 | |
| Acid | 22 hours | 8.044 | 1.941 | 4.144 | |
| Acid | 46 hours | 8.035 | 1.946 | 4.129 | |
| | | Mean 8.023 | Mean 1.940 | Mean ratio of means 4.135 | |
| | | | | $\frac{Max.A}{Min.B}$ 4.170 | $\frac{Min.A}{Max.B}$ 4.105 |

## (i) Reaction between phenol and iodosobenzene in various strengths of acid and in borax.

The iodosobenzene used in this series of experiments had been made four months previously and by iodometric titrations in acid and saturated borax media analysed to the composition:-

By weight ... Iodosobenzene ... 44.66%

Iodoxybenzene ... 31.37%

Iodobenzene .... 23.97%

Tests of the reaction between iodosobenzene and phenol were performed in N, $\frac{N}{5}$ and $\frac{N}{20}$ sulphuric acid and in saturated borax solution, after a short time and after prolonged wheeling; in each case the residual active oxygen was measured by titration of the iodine liberated from sodium iodide solution. See page 56.

In the acid media in all cases the solution turned brown and a resinous material was formed from which, in the iodometric titrations, dissolved iodine had to be removed by addition of a few c.c. of carbon tetrachloride. In the saturated borax the whole mass turned a dirty grey and liberated no iodine from aqueous sodium iodide. An excess of iodine was added and the reaction tube shaken a further two hours, after which the iodine remaining was titrated against standard arsenite. 0.736 milliequivalents of iodine were absorbed by the residual phenol, indicating that there remained after the iodosobenzene-phenol reaction in borax 0.123 millimol. phenol.

It was apparent from these tests that iodosobenzene oxidises phenol in acid medium as well as not being determinable in the presence of phenol in borax solutions.

56.

| Medium | Weight stock PhIO | A Ox. equivs. | Actual PhIO grams | PhIO mols. | PhOH mols. | Time on wheel. | A Ox. left equiv. | A Ox. used equiv. | O:PhIO | O:PhOH |
|---|---|---|---|---|---|---|---|---|---|---|
| $NH_2SO_4$ | .4648 | 4.358 | .2075 | .9434 | 1.233 | 20 mins. | 1.478 | 2.880 | 3.053 | 2.536 |
| $NH_2SO_4$ | .4015 | 3.764 | .1793 | .8149 | 0.906 | 15 hrs. | 0.947 | 2.817 | 3.457 | 3.111 |
| $\frac{N}{5}H_2SO_4$ | .4052 | 3.800 | .1809 | .8226 | 1.101 | 15 hrs. | 0.879 | 2.921 | 3.551 | 2.592 |
| $\frac{N}{5}H_2SO_4$ | .2169 | 2.034 | .0969 | .4403 | 0.493 | 20 mins. | 1.126 | 0.908 | 2.062 | 1.642 |
| $\frac{N}{20}H_2SO_4$ | .4972 | 4.663 | .2221 | 1.009 | 1.299 | 45 hrs. | 1.288 | 3.375 | 3.346 | 2.597 |
| Sat. $Na_2B_4O_7$ | .2284 | 2.142 | .1020 | .4636 | 0.519 | 4 hrs. | Nil | 2.142 | See below | 1.170 |

## (j) The precipitation of diphenyliodonium iodide from solutions of the sulphate.

17 grams of pure silver nitrate were dissolved in 28 c.c. of water, 100 c.c. 1.22N sodium hydroxide added slowly with shaking and the mixture shaken for an hour. The silver oxide settled well; the supernatant liquor was sucked off and the precipitate shaken with successive lots of 60 c.c. of water until acid-free, each washing being sucked off by a decantation-syphon and titrated against 0.07N sulphuric acid. The final washing, the twelfth, showed the liquor to be 0.0001N.

Diphenyliodonium iodide (10 grams, free from iodobenzene and phenol) were added to the silver oxide sludge and the mixture wheeled for 24 hours. The diphenyliodonium hydroxide solution was filtered, the filtrate being a clear yellow, and the remaining precipitate washed with 2 x 10 c.c. of water. Titrated against 0.1989N sulphuric acid, the solution was 0.3397N. 35 c.c. of this diphenyliodonium hydroxide were neutralised with 11.96 c.c. of 0.9944N sulphuric acid, the solution, made up to 50 c.c., being therefore 0.2378N. To 10 c.c. of the sulphate solution were added 10 c.c. N sodium iodide and, after standing, the iodonium iodide was filtered through a tared glass filter, washed with 4 x 5 c.c. of water and 2 x 2 c.c. each of acetone and ether, dried to constant weight on an oil pump and weighed. The weight of iodide (0.9789 gm.) indicated that the original iodonium sulphate solution was 0.2399N. To a second 10 c.c. of the diphenyl-

iodonium sulphate 0.6 gram of sodium iodate dissolved in 25 c.c. of water was added and the clear solution formed reduced with 20 c.c. N sulphur dioxide. The solution was neutralised with N sodium hydroxide solution and, after standing, the iodide was filtered, washed and weighed as before. The weight of iodide was 0.9732 gram, meaning that by this method the diphenyliodonium sulphate was 0.2385N.

Within experimental error, therefore, a diphenyliodonium salt in solution can be estimated by precipitating and weighing its iodide.

### (k) Diphenyliodonium silicotungstate.

This compound was prepared in an attempt to find a non-reducing quantitative precipitant for the diphenyliodonium radicle. To a solution of 10 mgms. of diphenyliodonium chloride in 4 c.c. of water were added 4 c.c. of a solution of silicotungstic acid of similar strength. The almost gelatinous, copious white precipitate filtered only with difficulty through a double layer of toughened filter paper. The practically clear filtrate gave no precipitate with sodium iodide solution, indicating that diphenyliodonium silicotungstate is as insoluble as the iodide. When, from a solution of the iodonium chloride, the iodide was precipitated with sodium iodide, the filtrate gave no precipitate of silicotungstate with silicotungstic acid. Apparently, therefore, the silicotungstate is not less soluble than the iodide. In $\frac{N}{5}$ sodium hydroxide solution

the iodonium silicotungstate precipitate was just as colloidal,
and warming dissolved it irreversibly. Similarly, tests done
in dilute acetic acid showed the precipitate to be equally un-
desirable for quantitative work, the solid being, if anything,
even more colloidal and less easily filtered than in neutral
or alkaline solution.

(A similar experiment on diphenyliodonium picrate showed
it to be a beautifully crystalline solid of melting point $132^{\circ}$,
but it was more soluble in water than either the iodide or the
silicotungstate, as was shown by washing the picrate on a filter,
when the washings gave a precipitate of iodonium iodide with
sodium iodide solution.)

Iodide seems, therefore, to be the only suitable quantit-
ative precipitant for the determination of diphenyliodonium in
solution; this is unfortunate in that, as stated before, iodo-
metric titrations first produce free iodine and then, in the
presence of the iodonium, form a polyiodide which is convert-
ible into the ordinary iodide only with difficulty, especially
in acid medium. Moreover, as recorded later, diphenyliodonium
thiosulphate readily decomposes into aryl sulphides and other
products, thus preventing thiosulphate from being used with
any accuracy in titrations when diphenyliodonium salts are
present.

### (1)  Diphenyliodonium sulphate and sodium hydroxide solutions.

Two solutions were made up:-

    (i)    0.2378N diphenyliodonium sulphate ... 10.0 c.c.

           0.1987N sodium hydroxide ........... 47.86 c.c.

           Water ............................... 133.58 c.c.

in which $(Ph_2I)_2.SO_4$ : NaOH = 1 : 4, and the sodium hydroxide is 0.04969N.

    (ii)   0.2378N diphenyliodonium sulphate ... 15.0 c.c,

           0.9936N sodium hydroxide ............ 19.14 c.c.

           Water ............................... 61.58 c.c.

in which $(Ph_2I)_2.SO_4$ : NaOH = 1 : 2.67, and the sodium hydroxide is 0.1987N.

The two vessels were kept in running water and at intervals the alkali-content was found by titration against 0.07228N sulphuric acid.

| | Time | Volume drawn. | $H_2SO_4$ required | $OH'$ equivalents |
|---|---|---|---|---|
| (i) | 30 mins. | 10 c.c. | 6.87 c.c. | 0.4966 |
| | 7 days | 10 c.c. | 6.85 c.c. | 0.4951 |
| | 14 days | 10 c.c. | 6.85 c.c. | 0.4951 |
| (ii) | 30 mins. | 10 c.c. | 0.1989N $\overline{10.00}$ c.c. | 1.989 |
| | 14 days | 10 c.c. | 9.96 c.c. | 1.981 |

It appears, therefore, that in the strengths of alkali employed, diphenyliodonium sulphate, if it decomposes at all, is very slow to do so.

(m) The solubility of iodosobenzene in water, $\frac{N}{10}$ alkali

and $\frac{N}{10}$ acid.

In water. Iodosobenzene acetate (2.157 millimols., by
iodometric titration 100% pure) was ground with 4.13 c.c. 0.1045N
sodium hydroxide until completely converted into the free base,
and shaken with 200 c.c. of water at 15.7$^{\circ}$ for 2.$^{1}/_{2}$ hours.
After filtering through dry apparatus, 100 c.c. of the pale
greenish-yellow filtrate were wheeled with 15 c.c. 2N sulph-
uric acid and 10 c.c. N sodium iodide, and the free iodine
titrated against $\frac{N}{10}$ thiosulphate. A similar titration was
done in saturated borax solution.

In $\frac{N}{10}$ sodium hydroxide. 2.341 millimols. of iodosobenzene
acetate were converted into the free base by grinding with
4.48 c.c. 1.045N sodium hydroxide and wheeled for 2 hours with
182 c.c. 0.1045N sodium hydroxide. No apparent reaction was
observed, and the filtrate, which had the same colour as that
of the aqueous solution, was treated for A and B titrations as
above.

In $\frac{N}{10}$ sulphuric acid. 6.586 millimols. of the acetate
were converted into iodosobenzene and shaken for 2 hours with
78 c.c. 0.1128N sulphuric acid, the actual strength of the
sulphuric acid in the reaction vessel being 0.09711N. The
filtrate, in this case colourless, was titrated for A and B
oxygen as before.

| Medium | Temperature | Milliequivs. A oxygen per 100 c.c. | Milliequivs. B oxygen per 100 c.c. | From B, solubility of PhIO (millimols per litre) |
|--------|-------------|------------------------------------|------------------------------------|--------------------------------------------------|
| Water | 15.7° | 0.816 | 0.744 | 3.72 |
| 0.1273N NaOH | 15.8° | 1.069 | 0.974 | 4.87 |
| .09711N $H_2SO_4$ | 15.8° | 6.884 | 6.520 | 32.60 |

(It is interesting to compare the solubilities of iodoso- and iodoxybenzene in water. The following is a table (Masson, Race and Pounder, J.C.S., 1935, 1673), not done by the author, of the solubilities of iodoxybenzene in water:-

| Temperature ........ | 0° | 14° | 40° | 61° | 83° | 99° |
|----------------------|-----|------|------|------|------|------|
| Millimols./litre ... | 10.1 | 11.6 | 18.3 | 27.8 | 40.0 | 49.7 |

(The last two values have been corrected by about a unit for a slight gradual decomposition at high temperature, detectable by the conductivity and assumed to be of the kind which occurs in alkali.)  No change in solid phase was observed throughout the temperature range, and the curve is smooth.

The solubility of iodoxybenzene in quite dilute alkali differs little from that in water at the same temperature.)

(n)  Methods of performing A and B titrations in iodoxy-benzene-alkali solutions.

To 5.079 millimols. of finely-sieved iodoxybenzene were added 101.38 c.c. of 0.0501N sodium hydroxide (5.079 milli-

equivalents) and the mixture shaken on the wheel for 16 hours. The solution had assumed a slight turbidity whibh remained on neutralising with 19.74 c.c. 0.2041N sulphuric acid. After dilution to 250 c.c. it was aliquoted for A and B titrations, 25 c.c. being used for each A determination and 75 c.c. for each B. For the former, to each of three lots of 25 c.c. were added 25 c.c. 0.2N sulphuric acid and 10 c.c. N sodium iodide; the first was kept at $60^{o}$ for 15 minutes, the second shaken in the cold for 2 hours, and the third, after shaking for $3.^{1}/_{2}$ hours, was neutralised and saturated with sodium bicarbonate. Those two kept acid were titrated against $\frac{N}{10}$ thiosulphate, and to the bicarbonated solution excess standard sodium arsenite was added and, after the colour of the polyiodide had been discharged, the excess arsenite was determined with standard iodine. In each case the time necessary for the destruction of the polyiodide colour was noted.

To each of the 75 c.c. aliquoted for the B determinations 25 c.c. saturated aqueous borax and 10 grams of solid powdered borax were added. One was treated with 10 c.c. N sodium iodide and wheeled for an hour, a known excess of arsenite added, shaken until the iodine had been released from the polyiodide and the excess arsenite back titrated with standard iodine. To the other were added 10 c.c. sodium iodide and immediately a known excess of standard arsenite run in from a burette; after $1.^{1}/_{2}$ hours' shaking the excess arsenite was determined with iodine.

The results obtained were as follows:-

| Titration | Method | Ox. equivs. per 10 mols. $PhIO_2$ init. | Time for release of iodine from $Ph_2I.I_3$ |
|---|---|---|---|
| A | 15 mins. at $60^\circ$ | 28.79 | Still peculiarly grey after an hour (see below). |
| A | 2 hours shaking in cold. | 38.08 | 2 minutes. |
| A | 3 hours shaking in cold, neutralised and sat. with $NaHCO_3$, then $As_2O_3$. | 37.96 | 5-10 minutes. |
| B | 1 hour shaking in cold. | 5.81 | 30 minutes. |
| B | Excess $As_2O_3$ before any $I_2$ liberation, 1½ hours' shaking. | 7.10 | Nil |

The thiosulphate in the first A determination, in contact with the solution for an hour, developed a smell as of aryl sulphur products, due presumably to the decomposition of diphenyliodonium thiosulphate; this method, therefore, was of no value. The other two methods for A titrations gave, within experimental error, identical results, but because of the possibility of aryl sulphide formation, the arsenite method was deemed the safer.

For the B determinations, an hour's shaking was definitely insufficient, and the second method, in which no time was allowed for the polyiodide to form, was a much cleaner titration. Not sufficient data, however, was known about either determination,

and another series of titrations of the iodoxybenzene-alkali solutions for borax-active oxygen was performed,

11.26 millimols. of iodoxybenzene were shaken for 16 hours with 224.75 c.c. 0.0501N sodium hydroxide, and the slightly turbid solution neutralised with 11.15 c.c. 1.0N sulphuric acid. The solution was made up to 500 c.c. and for each titration 60 c.c. of this were taken.

($\alpha$) To each of four of the aliquoted parts were added 20 c.c. of saturated borax, 10 grams of powdered borax and 10 c.c. N sodium iodide. The tubes were wheeled for varying lengths of time and the liberated iodine determined with standard arsenite solution.

($\beta$) Three other tubes of 60 c.c. each were treated similarly, and immediately on addition of the aqueous iodide to each 20.0 c.c. 0.1250N sodium arsenite were added, and the tubes wheeled.

## Method ($\alpha$)

### Per 10.0 mols. of PhIO$_2$ initially.

| Time wheeled (hours) | Time shaken for Ph$_2$I.I$_3$ decomp. after As$_2$O$_3$ (mins.). | B oxygen (equivs.) |
|:---:|:---:|:---:|
| 1 | 15 | 6.06 |
| 2 | 25 | 5.53 |
| 4 | 15 | 5.71 |
| 48 | 8 | 5.59 |

### Method ($\beta$)

| Time wheeled (hours) ... | 1 | 2 | 48 |
|---|---|---|---|
| B Oxygen (equivs.) ..... | 6.98 | 6.86 | 7.28 |

The former method apparently cannot detect the full amount of borax-active oxygen, and even in the second method 48 hours are required for complete reduction.

### (o)  Reaction between iodoxybenzene and arsenite in borax.

To weighed amounts of iodoxybenzene were added 20.0 c.c. $\frac{N}{10}$ arsenite. After wheeling for an hour no arsenite had been consumed, and even after shaking for a day, only 0.008 milli-equivalents of arsenite were used.

### (p)  Iodoxybenzene and iodine in borax.

There was no reaction between iodoxybenzene and iodine in saturated borax after three hours' shaking on the wheel.

### 3.  Theoretical Considerations.

Iodoxybenzene is much more soluble in dilute alkali than in water. Eventually this is connected with irreversible changes, but in the first place it is due to a reversible salt-formation. Dilute sodium hydroxide solution quickly dissolves about one molecule of iodoxybenzene per two equivalents of alkali. This means, for $\frac{N}{10}$ sodium hydroxide, a solubility five times that in water, whilst N alkali dissolves 50 times the amount soluble in water. The twofold proportion of dilute alkali is ordinarily needed to prevent reversal, iodoxybenzene

therefore reacting as if it were a monobasic acid of dissociation constant apparently $10^{-11}$. (Measurements of conductivity of a saturated aqueous solution of iodoxybenzene, done by a student in his laboratory course, indicate that iodoxybenzene has an apparent dissociation constant of $10^{-10.4}$.)

The salts of iodoxybenzene with alkalies have not been isolated; their existence is transient, and to establish their formation and formulae it was necessary to perform a series of rapid measurements of solubilities, conductivities and freezing points. The solutions of the salts are colourless and have a very slight turbidity and, like iodoxybenzene itself, reduction of the solution with sulphur dioxide or acidified sodium iodide solution yields iodobenzene. No radicles (such as iodonium or iodate) can be detected in the solutions, and neutralisation by carbon dioxide causes a slow but quantitative deposition of pure iodoxybenzene. That there is no hydration of these crystals when wet is seen by the fact that from their first precipitation until their final drying there is microscopically no change in the crystals.

It is improbable that this acidity of iodoxybenzene is due to tautomerism in the hydrogen atoms of the benzene nucleus, and therefore the experiments prove that the first reaction between iodoxybenzene and alkali is:-

$$PhIO_2 + OH' \rightleftharpoons PhIO_2.OH'$$

These salts have been called "phenyliodoxylates". The statement made by Willgerodt in 1896 (Ber. <u>29</u>, 2008) as to the

possible formation of salts of iodoxybenzene with alkalies
(see page 36) is now justified, although Willgerodt himself
contradicted it in his monograph of 1914 by the observation
on the complete neutrality of iodoxybenzene.  The formation,
easy reversibility and subsequent behaviour of iodoxylates
can be explained by a local electrovalency joining the large,
positive donor iodine of the I—O dipole and the small hydroxyl
anion, whilst, as indicated by freezing point measurement, the
sodium is ionically free:-

$$
\text{Ph——}\overset{\displaystyle O}{\underset{\displaystyle O^-}{\overset{\|}{\underset{\downarrow}{I^+}}}}\text{.....(OH)'}
$$
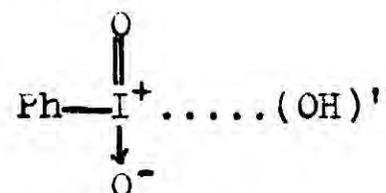
In the corresponding aromatic sulphur compounds, the diaryl
sulphones, the donor atom, sulphur, being small, is too well
covered by surrounding groups to allow the anion access;
similarly, in an aromatic nitrocompound the nitrogen atom is
too small to permit the anionic access.  It seems unlikely
that in the iodoxylates the electrovalent link can ever become
covalent:-

$$
\left(\text{Ph——}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{|}{I}}}}\text{——O——H}\right)'
$$
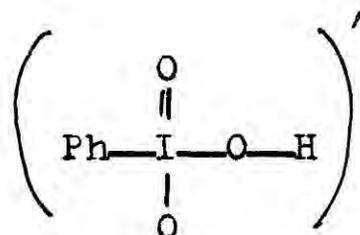
This iodoxylate formation, coupled with the fact that iodoxy-
benzene is capable of forming salts also with acids, points
to the simultaneous accessibility of both ends of the I-O di-
pole, and from this view it is possible to explain a number

of remarkable reactions of iodoxy- and iodosobenzene, such as
Meyer and Hartmann's method of preparing iodonium compounds
(see J.C.S., 1935, 1670).

In aqueous alkalies of concentrations from 0.05N upwards
iodoxylates change rapidly and irreversibly, iodoxybenzene is
no longer detectable, the solution contains iodate and addition
of aqueous sodium iodide precipitates diphenyliodonium iodide
and liberates iodine, both in acid and in saturated borax media.
This change, due to the formation of a new class of compound,
is quantitatively represented by the equation:-

$$2PhIO_3H \Longrightarrow Ph_2IO.OH + IO_3' + OH'$$
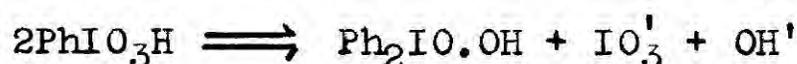
Again in this reaction, the simultaneous accessibility of the
iodyl (I--O) dipole can explain the change. To the donor iodine
of the iodyl dipole of one iodoxybenzene molecule is added the
phenyl radicle of a second, and simultaneously to the negative
oxygen of the dipole is added the $IO_2$ of the second iodoxybenz-
ene molecule, thus:-
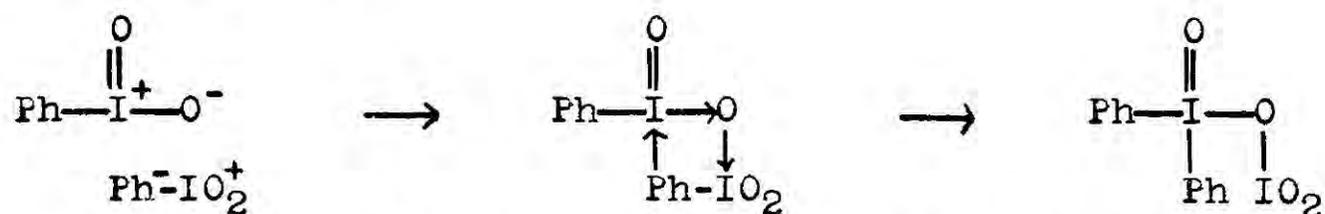


Coupling these two equations together, the total change
undergone by the iodoxybenzene in cold dilute alkali is:-

$$2PhIO_2 + OH' = Ph_2IO.OH + IO_3'$$
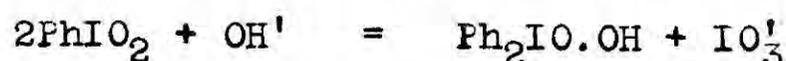
The new compound, termed diphenyliodyl hydroxide, is a
stronger oxidising agent than the parent iodoxybenzene or
iodoxylates, oxidising iodine in saturated borax as well as in

acid medium, and being readily reduced by sulphur dioxide, hydrogen peroxide or dilute hydrochloric acid to diphenyliodonium salts:-

e.g.

$$Ph_2IO.OH + 3HI = Ph_2I.I + I_2 + 2H_2O$$

$$Ph_2IO.OH + SO_2 = Ph_2I.HSO_4$$

$$Ph_2IO.OH + H_2O_2 = Ph_2I.OH + H_2O + O_2$$

$$Ph_2IO.OH + 3HCl = Ph_2I.Cl + 2H_2O + Cl_2$$
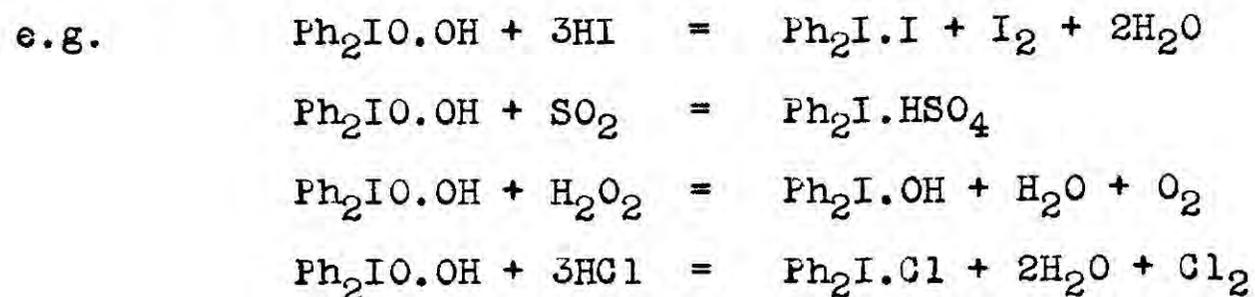
The iodyl compound is therefore the source of the iodonium salts obtained by Willgerodt in the action of barium hydroxide on iodoxybenzene and also in the action of the boiling aqueous potassium iodide on iodoxybenzene. In using the latter reagent, the alkali is formed by the action of the potassium iodide on the initial iodoxybenzene, and this is followed by the reactions described:-

$$PhIO_2 + 2KI + H_2O = PhI + I_2 + 2KOH$$

$$4PhIO_2 + 2KOH = 2Ph_2IO.OH + 2KIO_3$$

The phosphorus and arsenic compounds analogous to the iodyl body are the phosphinic and arsinic acids $(R_2.PO.OH, R_2.AsO.OH)$, and, like these, diphenyliodyl hydroxide is amphoteric. It dissolves readily in alkalies, forming iodylates which have not been isolated as solids and it is acid to phenolphthalein but neutral to methyl orange. Diphenyliodyl hydroxide has been isolated as a yellowish, not very stable, amorphous solid. On neutralising a solution of the hydroxide in alkali with carbon dioxide, diphenyliodyl carbonate is formed as a fairly stable, cream-coloured, amorphous solid; treatment of this with glacial

acetic acid forms the acetate as a well crystallised, stable compound. Its salts with the stronger acids, such as sulphuric, are not so stable as the acetate; this is noticed when the carbonate is treated with the acids; with cold N acetic acid there is a brisk effervescence of carbon dioxide, whereas with cold 5N sulphuric acid the action is extremely slow. This apparently anomalous fact is readily explained when one considers that the "salts" which the iodyl compound forms with carbonic and acetic acids are not the normal ionised salts, but are co-ordinated ring compounds (cf. Sidgewick, Annual Reports, 1933, 144, where it is pointed out that various carboxylic compounds are co-ordinated ring substances). Acetic acid, not being strongly anionic, readily undergoes chelation to form the ring compound, whereas the powerful inorganic acids are too markedly anionic to form stable rings, and the salts are therefore more readily hydrolysed to the free acid and the unstable base, the latter subsequently decomposing. The stability of the acetate is also noticed in the liberation of iodine from added aqueous iodide. Solutions of the diphenyliodyl hydroxide readily release the quantitative amount of iodine in a B titration, whereas this reaction is extremely slow in the case of the acetate. Analysis of the acetate shows it to have the composition $(C_6H_5)_2I(OH)_2O.CO.CH_3$; it is sparingly soluble in water, almost insoluble in ether, rather more so in benzene and carbon tetrachloride and fairly soluble in chloroform; at boiling temperatures it is readily soluble in these liquids,

but prolonged warming of the solution in any solvent tends to decompose the salt. The acetate is extremely soluble in glacial acetic acid, whilst in alcohol and acetone it dissolves with decomposition. Its mildly alkaline reaction to moist litmus paper is due to its oxidation of the litmus, whereby the alkalinity of diphenyliodonium hydroxide is registered. Refluxing of diphenyliodyl acetate with an excess of N sodium hydroxide yields benzene and sodium iodate, along with more complex products almost resinous in character. These properties, and others recorded later, are well represented by the structure:-

$$\text{Ph} \underset{\text{Ph}}{\overset{}{\diagdown}} \text{I} \underset{\text{O}-\text{H}\leftarrow\text{O}}{\overset{\text{O}\rightarrow\text{H}-\text{O}}{\diagup}} \text{C}-\text{CH}_3$$

in which a perfect symmetry lends itself to ready tautomerism, a fact in agreement with the relatively great stability of the acetate. Another structure which cannot, on evidence obtained up to the present, be dismissed, but which has neither the symmetrical configuration nor the tautomeric possibilities of the above formula, is:-

$$\text{Ph} \underset{\text{Ph}}{\overset{}{\diagdown}} \overset{}{\underset{\overset{|}{\text{O}}{\phantom{x}}}{\text{I}}} \underset{\text{O}-\text{H}}{\overset{\text{O}-\text{C}\overset{\text{CH}_3}{\underset{\text{O}}{\diagup}}}{\diagup}}$$

By the mixing of solutions of phenyliodoxylate and p-acetaminophenyliodoxylate in N sodium hydroxide, p-acetamino-phenylphenyliodyl hydroxide was formed in solution, presumably along with diphenyliodyl and di-p-acetaminophenyliodyl hydroxides;

from this solution, by way of the carbonate, there was obtained

p-acetaminophenylphenyliodyl acetate, of the structure:-

$$CH_3.OCNHC_6H_4 \diagdown \underset{C_6H_5 \diagup}{I} \diagup \overset{O \rightarrow H-O}{\underset{O-H \leftarrow O}{}} \diagdown C-CH_3$$

or

$$CH_3.OCNHC_6H_4 \diagdown \underset{C_6H_5 \diagup}{I} \underset{\overset{|}{O} \atop H}{} \overset{O-C \diagup CH_3}{\underset{O-H}{}} \diagdown O$$
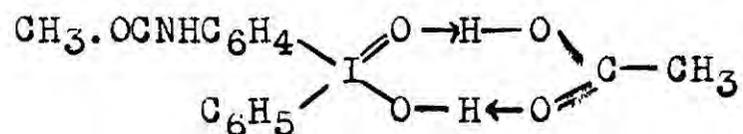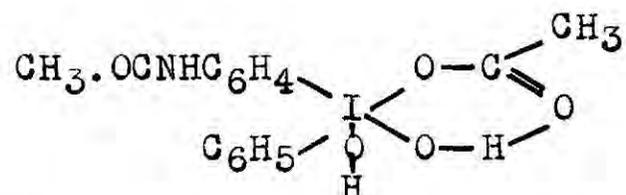
Although the properties of this compound have not been pursued

further, there is the possibility that, by the choice of a suit-

able non-reducing, optically-active acid, it can be used as the

forerunner of iodine compounds possessing optically-active

properties.

Finally, the prolonged action of cold dilute alkali upon

iodoxybenzene or the refluxing of iodoxybenzene for an hour

with an excess of N sodium hydroxide produces iodate and benz-

ene. As stated above, diphenyliodyl acetate also shows a

similar hydrolysis, so that in all probability the action

occurs via the iodyl compound, thus:-

$$Ph_2IO.OH + OH' \longrightarrow PhH + IO_3'$$

The ultimate reaction, however, can be expressed:-

$$C_6H_5IO_2 + NaOH = NaIO_3 + C_6H_5$$

Hartmann and Victor Meyer (Ber. 1893, 26, 1727) showed that the

alkaline hydrolysis of o-iodoxybenzoic acid yields iodate and

benzoic acid, and in 1925 Vorländer and Büchner (Ber. 58, 1291)

found a similar hydrolysis of p-iodoxynitrobenzene, whilst

Thiele and Haakh (Ann. 1909, $\underline{369}$, 132) showed that their aliphatic iodoxy-compound, iodoxychloroethylene, behaved in the same way. It might be argued that in these cases the proximity of other substituents has the effect of making the iodoxy-group labile; in the case of simple iodoxybenzene, however, no such groups are present and therefore the iodoxy-group alone is labile in alkali.

4. <u>Experimental</u>.

(a) <u>Initial reaction between iodoxybenzene and alkali</u>.

i. <u>Reversibility of dissolution of iodoxybenzene</u>.

To 4.591 millimols. iodoxybenzene were added 46.21 c.c. 0.1987N sodium hydroxide (i.e. a ratio $NaOH:PhIO_2 = 2:1$); 10 minutes' vigorous shaking were required to dissolve the solid, and addition of 2.0 c.c. 4.591N sulphuric acid gave no immediate precipitate. On standing for 19 hours there deposited from the liquor white needle crystals which had the qualitative reactions of iodoxybenzene, e.g. they liberated iodine but not diphenyl- - iodonium iodide from aqueous iodide in acid but not in borax; on reduction with sulphur dioxide an oily suspension, which totally cleared on shaking with carbon tetrachloride, was formed, addition of silver nitrate to the reduced solution gave no iodide precipitate; barium chloride on a solution of the crystals in water gave no precipitate.

Later, this was repeated more quantitatively by Professor Masson. 0.503 gram iodoxybenzene was dissolved in 9 minutes

in 50 c.c. 0.0997N sodium hydroxide, and immediately carbon
dioxide passed through the solution. After $\frac{3}{4}$ hour crystals
of iodoxybenzene deposited which, when washed with 20 c.c.
water and dried, weighed 0.12 gram. An iodometric titration
of these crystals gave an equivalent of 59.6 (theoretical for
iodoxybenzene 59.0). The initial dissolution of iodoxybenzene
in alkali is therefore reversible. The neutral filtrate would
have in solution about 0.5 millimol. = 0.12 gram of iodoxy-
benzene and the wash-water, which had had a chance of satur-
ation; 0.05 gram or nearly half is still there/after neutral-
isation. The remaining iodoxybenzene had changed irreversibly,
as was seen on examining the filtrate from the reprecipitation,
to the next stage at which it gives β oxygen, iodate and di-
phenyliodonium.

Tests on alkalies stronger than $\frac{N}{10}$ showed that the primary
reversible dissolution of the iodoxybenzene is too transient
for any recovery of the initial material on neutralisation.
This meant that in the measurements which follow readings had
to be taken rapidly.

ii. Conductivity measurements of iodoxybenzene in
dilute alkalies.

In the measurements of electrical conductivity which follow,
the cell used was of 25 c.c. capacity, had smooth platinum
electrodes and was of the following shape:-

For the present purposes a "Megger" instrument, which produced an alternating current at the cell of frequency, 60, and had a negligible heating effect if readings were taken rapidly, was found sufficiently accurate, besides enabling the rapid changes occurring in the solutions to be readily followed. The instrument read directly in ohms.　The strengths of the alkalies used were 0.02484, 0.04969, 0.06954 and 0.09944N, and in all cases the conductivity of the pure alkali solutions was first measured over a period of one to two hours, 10 c.c. of the solution being in the cell which was kept in running water in the sink.　For the dissolution of the iodoxybenzene a double proportion of alkali was used, 100 to 200 c.c. of the iodoxylate being made at a time, kept at the temperature of the running water and 10 c.c. samples drawn for each reading.

Measurements obtained were as follows:-

(1)  Alkali strength ... 0.02484N

Shunt in parallel with instrument ... 500 ohms.

Alkali alone.

| Time from first reading (mins.) | Temperature ($^{o}C$) | Reading of instrument (ohms) | Conductivity x $10^5$ of alkali |
|---|---|---|---|
| 0 | 10.2 | 236 | 224 |
| 15 | 10.2 | 237 | 222 |
| 30 | 9.9 | 237 | 222 |
| 45 | 9.3 | 238 | 220 |
| 60 | 9.4 | 237 | 222 |

Iodoxybenzene-alkali solution.

Time necessary for dissolution of iodoxybenzene .... 30 mins.

| Time from first mixing (mins.) | Temperature ($^{o}C$) | Reading of instrument (ohms) | Conductivity x $10^5$ of alkali |
|---|---|---|---|
| 30 | 10.0 | 262 | 182 |
| 95 | 10.1 | 257 | 189 |
| 155 | 10.4 | 263 | 180 |
| 215 | 10.3 | 262 | 182 |
| 275 | 10.0 | 262 | 182 |
| 310 | 10.1 | 263 | 180 |
| 22 hrs. | 11.2 | 259 | 186 |
| 29 hrs. | 11.3 | 258 | 187 |

(2)                  Alkali strength ... 0.04969N

Alkali alone.

| Time from first reading (mins.) | Temperature ($^o$C) | Reading of instrument (ohms) | Conductivity x $10^5$ of alkali |
|---|---|---|---|
| 0 | 11.6 | 224 | 446 |
| 15 | 11.4 | 224 | 446 |
| 30 | 11.4 | 224 | 446 |
| 45 | 11.5 | 224 | 446 |

Iodoxybenzene-alkali solution.

Time necessary for dissolution of iodoxybenzene ..... 25 mins.

Shunt in parallel with instrument ..... 200 ohms.

| Time from first mixing (mins.) | Temperature ($^o$C) | Reading of instrument (ohms) | Conductivity x $10^5$ of alkaline solution |
|---|---|---|---|
| 25 | 11.3 | 120 | 333 |
| 60 | 11.3 | 120 | 333 |
| 120 | 11.3 | 120 | 333 |
| 210 | 11.3 | 119 | 340 |
| 270 | 11.3 | 119 | 340 |
| 330 | 11.3 | 119 | 340 |

(3)                Alkali strength ... 0.06954N

Alkali alone.

| Time from first reading (mins.) | Temperature ($^{o}$C) | Reading of instrument (ohms) | Conductivity x $10^5$ of alkali |
|---|---|---|---|
| 0 | 11.0 | 157 | 637 |
| 30 | 11.0 | 156 | 641 |
| 60 | 11.0 | 157 | 637 |
| 75 | 11.0 | 156 | 641 |
| 90 | 10.8 | 158 | 632 |

Iodoxybenzene-alkali solution.

Time necessary for dissolution of iodoxybenzene .... 17 mins.

| Time from first mixing (mins.) | Temperature ($^{o}$C) | Reading of instrument (ohms) | Conductivity x $10^5$ of alkaline solution |
|---|---|---|---|
| 20 | 11.0 | 204 | 490 |
| 60 | 11.0 | 205 | 488 |
| | | With 200 w shunt | |
| 120 | 11.0 | 106 | 443 |
| 180 | 11.0 | 105 | 452 |
| 240 | 11.0 | 105 | 452 |
| 530 | 11.1 | 104 | 462 |
| 22 hrs. | 11.2 | 105 | 452 |

(4)                    Alkali strength ... 0.09974N

Alkali alone.

| Time from first reading (mins.) | Temperature ($^{\circ}$C) | Reading of instrument (ohms) | Conductivity x $10^5$ of alkali |
|---|---|---|---|
| 0 | 11.0 | 116 | 862 |
| 10 | 11.0 | 116 | 862 |
| 25 | 11.0 | 116 | 862 |

Iodoxybenzene-alkali solution.

Time necessary for dissolution of iodoxybenzene .... 20 mins.

Shunt in parallel with instrument ..... 200 ohms.

| Time from first mixing (mins.) | Temperature ($^{\circ}$C) | Reading of instrument (ohms) | Conductivity x $10^5$ of alkaline solution |
|---|---|---|---|
| 20 | 11.0 | 90 | 611 |
| 65 | 10.8 | 92 | 587 |
| 95 | 11.0 | 90 | 611 |
| 180 | 11.0 | 88 | 636 |
| 210 | 11.0 | 88 | 636 |
| 240 | 11.0 | 87 | 649 |
| 300 | 11.0 | 87 | 649 |
| 360 | 11.0 | 87 | 649 |
| 24 hrs. | 11.0 | 87 | 649 |

Assuming that throughout the readings the only cation present is the sodium ion, and knowing the transport number of sodium hydroxide (0.81), the following summary can be made:-

| Alkali strength | Conductances x $10^5$ at $11^0$ | | Contribution by Na = 0.19 x KNaOH | Contribution by anions | |
|---|---|---|---|---|---|
| | NaOH alone. | Solution at steady value. | | Initial (OH') | Later |
| 0.02484 | 222 | 187(?) | 42 | 180 | 145 |
| 0.04969 | 446 | 340 | 85 | 361 | 265 |
| 0.06954 | 637 | 460 | 121 | 516 | 339 |
| 0.09974 | 862 | 649 | 164 | 698 | 485 |

The following are values given by Kohl and Holb for the mobilities of the hydroxyl at $18^0$C:-

| Alkali N ......... | 0.1 | 0.07 | 0.05 | 0.025 |
|---|---|---|---|---|
| Mobility OH' ..... | 157 | 159 | 161 | 163 |

and from these and the last column of the above table it is possible to calculate by simple proportion the mobilities of the anions in the iodoxybenzene-alkali solutions. The values of the mobilities of the anions at $18^0$ work out as follows:-

| NaOH N .... | 0.09944 | 0.06954 | 0.04969 | 0.02484 |
|---|---|---|---|---|
| Mobility .. | 101 | 100.5 | 102 | 131 |

It seems likely that the weakest alkali has not yet finished reacting with the iodoxybenzene because of the wide discrepancy

between this and the other three results;  and with this excep-
tion the mobility of the anions is in all cases approximately
100, a value which would be given at $18^{\circ}$ by a 1:1 mixture of
the hydroxyl ion (mobility 157 to 163 units) and an ion of
mobility 37 to 43 units.  The mobilities of any other poss-
ible anions are 30 to 40 units (e.g. $IO_3$, 40 units);  hence
it follows that about one-half, and not less, of the original
hydroxyl ions are still present as such.  Therefore, since
practically all the iodoxybenzene owes its dissolution to the
alkali, one OH', and only one, unites with each formula-weight
of iodoxybenzene to form the new anion.  The double proportion
of alkali required for the quick dissolution of the iodoxybenz-
ene must therefore be necessary to suppress a reversal of the
action.

(These conductivity measurements, whilst establishing the
ratio $OH:PhIO_2$ in the new anion, are not sufficient to decide
whether the ion is simple and univalent or polymerised and
multivalent.  This question, which is important from a struct-
ural point of view, was settled by measurement of freezing
point done by Professor Masson.  It was found, with the poss-
ible reservation as to a small fraction, that each newly-formed
anion takes the place of one hydroxyl ion, which means that
this former is an unpolymerised, univalent ion.)

The initial reaction is thus proved to be:-

$$PhIO_2 + OH' \rightleftharpoons (PhIO_2.OH)'$$

### iii.  Ionisation constant of phenyliodoxylic acid.

Turning again to the tables of conductivity measurements (pp. 77-80), from them a similar summary table to that of page 81 can be drawn up, with the minimum value in each case of the conductivity of the solutions.

| Alkali strength | Minimum conductances x $10^5$ at $11^0$ | Contribution by anions | | Mobilities at $18^0$. | |
|---|---|---|---|---|---|
| | | Initial OH | At minimum | of OH | of anions at minimum. |
| 0.02484 | 180 | 180 | 138 | 163 | 125 |
| 0.04969 | 333 | 361 | 248 | 161 | 101 |
| 0.06954 | 443 | 516 | 322 | 159 | 99 |
| 0.09944 | 587 | 698 | 423 | 157 | 95 |

These figures imply an increasing reverse decomposition of the phenyliodoxylate ion, and by adopting probable values for the mobilities of this ion, a calculation based on the simple principles of mass action indicates that the figures correspond with the salt of an acid of ionisation constant approximately $K = 10^{-11}$.

(That no more strongly acidic aci-form of hydrated iodoxybenzene (e.g. a Ph—I(OH)(OH)=O form) exists as a transient product of neutralisation was proved by Professor Masson by determining the conductivity, before any iodoxybenzene had time to reprecipitate, of a solution of it in $\frac{N}{10}$ alkali neutralised with
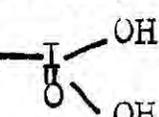
carbon dioxide. The conductance of the neutralised solution was not distinguishable from that of the sodium bicarbonate formed.)

### (b) Systematic analyses of the products of the iodoxy-benzene-alkali reactions.

#### i. Methods and summarised tables.

Three series of analyses were made in which iodoxybenzene and alkali of different strengths in a 1:1 ratio were mixed and fixed on to a rotator set in a thermostat at $25^{\circ}$. The reaction-tubes were of large test-tube shape and were sealed off after the substances were mixed. The analyses were performed not earlier than the first dissolution of the iodoxybenzene, that is, 24 hours at the earliest. The strengths of alkali employed were 0.05N, 0.20N and 1.0N, and the methods of analyses were as follows:-

#### Analysis 1.    Hydroxyl ion.

This was done by titration against standard sulphuric acid and methyl orange, using a water-methyl orange control and per-forming the titrations in daylight.

#### Analysis 2.    The diphenyliodonium radicle.

The solution was reduced with sulphur dioxide (using only a slight excess) which produced iodide from the iodate formed, thereby precipitating diphenyliodonium iodide, but, owing to the acidity, this precipitation was not complete;  the acidity was carefully neutralised with sodium hydroxide, the liquors stood with shaking for some hours to allow for the rather slow

precipitation of the iodide, filtered on a weighed grade 4 tube-filter, washed with minimal doses of water (about 4 x 5 c.c. generally, with thorough stirring), twice with acetone and twice with ether. The tube was dried by fixing it in a drying tower of silica gels, both ends being attached to an oil-pump. The dried precipitate was weighed. The filtrate and water washings were used for:-

Analysis 3.    Remaining ionic iodine.

After reacidifying slightly with dilute nitric acid (free from nitrous acid), the remaining ionic iodine was precipitated hot by the addition of dilute silver nitrate solution. The precipitate, which may have adsorbed silver sulphate, was washed well with boiling water acidulated with nitric acid, oven-dried on a glass Gooch crucible at $100^\circ$ to $110^\circ$ and weighed.

Analysis 4.    Active oxygen in acid medium.

Using the result of Analysis 1, a sample of the solution was approximately neutralised with dilute sulphuric acid, then made about 0.2N with sulphuric acid. After wheeling with excess sodium iodide in a stoppered bulb-tube for from $3.^1/_2$ to 4 hours (determined by control analyses), the solution was neutralised and saturated with sodium bicarbonate, a known excess of standard sodium arsenite added, and the tube re-spun on the wheel until the polyiodide was decolorised. The excess arsenite was determined with standard iodine.

Analysis 5.    Active oxygen in borax medium.

After neutralising the solution it was saturated with well

powdered borax, a suitable excess of sodium iodide and a known excess of standard arsenite added. The tube was wheeled, an indication of the completion of the reduction being when the strong yellow tint invariably accompanying such titrations had disappeared. As before, the excess arsenite was determined with standard iodine.

Analysis 6.    Free iodobenzene.  (Not performed on liquors of dilutest alkali.)

A sample of the liquors was acidified with sulphuric acid and extracted with minimal doses of benzene in successive amounts, the acidified solution layering better than would an alkaline liquor.  A Stepanow determination was performed immed- iately on the extract, using 70 to 80 c.c. absolute alcohol and 6 to 8 grams of sodium.  After the addition of 100 c.c. of water and the distilling-off of the alcohol, the liquor was acidified with pure 2N nitric acid and the iodide in it determined by Volhard's method.

Analysis 7.    Oxidised ionic iodine.

This was performed by precipitation with N barium acetate or nitrate of the liquors, weakly acidified with acetic acid. After overnight spinning of the mixture on the wheel, so as to allow the complete formation of the barium precipitate, the filtrate and minimal washes were aliquoted for Analyses 4 and 5.  The barium precipitate was decomposed by wheeling with dilute sulphuric acid and on the filtrate from this Analyses 4 and 5 performed.

Analysis 8.    Phenol. (Not performed on liquors of
dilutest alkali.)

The determination was done on a benzene extract of the
iodoxybenzene-alkali liquor. Solid sodium bicarbonate and a
known excess of standard iodine were added to the extract which
was then wheeled for at least an hour. The residual iodine
was estimated with standard arsenite solution.

Analysis 9.    Unchanged iodoxybenzene. (Not performed on
solutions of the stronger alkalies or on the
later samples.)

The alkaline solution was reduced with sulphur dioxide and
extracted with small successive amounts of benzene. A Stepanow
estimation was performed on the benzene extract.

For each alkali-strength and given time of reaction, one
tube was used for Analyses 1, 2 and 3, which were performed con-
secutively on the whole solution;  one tube for Analyses 4 and
5, done on aliquot halves of the liquor;  one tube for Analyses
6 and 9, by extracting before and after reduction with sulphur
dioxide;  and one tube each for Analyses 7 and 8. When one tube
was drawn for analysis, all belonging to that time of reaction
and that alkali strength were also drawn, and as soon as Analy-
sis 1 had been done, each tube of the set was neutralised with
the appropriate acid, after which it was deemed safe, as well
as necessary, to leave it until it was convenient for the part-
icular analysis to be performed.

A summarised table of the results is given:-

Per 10.0 gram-mols. of $PhIO_2$ initially.

| Alkali (N) | Time | Analysis 1 Equivs. OH left | Equivs. OH used | Analysis 2 $Ph_2I$ gm.-ions | Analysis 3 1 not ppted. as $Ph_2I.I$ |
|---|---|---|---|---|---|
| 0.04969 | 50 mins. | 8.78 | 1.22 | 0.319 | 0.737 |
| 0.04969 | 24 hrs. | 8.40 | 1.60 | 3.61 | 0.809 |
| 0.04969 | 70 hrs. | 8.18 | 1.82 | 3.92 | 0.922 |
| 0.2002 | 24 hrs. | 6.41 | 3.59 | 3.79 | 2.23 |
| 1.001 | 17 days | 1.66 | 8.34 | 0.374 | 6.62 |

| Alkali (N) | Time | Analysis 4 Active $O_2$ equivs. in acid. | Analysis 5 Active $O_2$ equivs. in borax. | Analysis 6 $PhI$ Gm.-mols. |
|---|---|---|---|---|
| 0.04969 | 50 mins. | 35.94 | 2.79 | Not done |
| 0.04969 | 24 hrs. | 38.57 | 7.56 | Not done |
| 0.04969 | 70 hrs. | 38.36 | 7.74 | 0.027 |
| 0.2002 | 24 hrs. | 39.16 | 3.62 | 0.158 |
| 1.001 | 17 days | 39.80 | Nil | 2.043 |

| Alkali (N) | Time | Analysis 7. A Oxygen equivs. in Ba" ppt. | B Oxygen equivs. in Ba" ppt. | A oxygen equivs. in filtrate | B oxygen equivs. in filtrate |
|---|---|---|---|---|---|
| 0.2002 | 24 hrs. | 32.03 | NIL | 6.87 | 4.04 |

Not performed in any other alkali strength or reaction time.

| Alkali (N) | Time | Analysis 8 Phenol gm.-mols. | Analysis 9 Unchanged iodoxy-benzene gm.-mols. |
|---|---|---|---|
| 0.04969 | 50 mins. | - | 5.95 |
| 0.04969 | 24 hrs. | - | 0.75 |
| 0.04969 | 70 hrs. | Nil | 0.68 |
| 0.2002 | 24 hrs. | Nil | - |
| 1.001 | 17 days | 0.015 | - |

For each alkali-strength and time-interval a "balance sheet" was made for the atoms and radicles known to be present. This is given on page 90.

Along with this "balance sheet" was drawn up a table (see page 91) in which those positive and negative ions known to be present were compared.

From these figures it is seen that the maximum yield of diphenyliodonium salt is obtained in 0.05N sodium hydroxide after 70 hours; at this alkali-strength and time-interval the amount of iodate formed is approximately equivalent to the diphenyliodonium yield, whilst the number of atoms of the newly-formed borax-active oxygen is almost exactly the same as the number of ions of diphenyliodonium radicle. In the same strength of alkali, but in shorter times, the iodonium, iodate and borax-active oxygen are still growing, whilst in the 0.2N alkali the amount of iodate is in excess of both iodonium and

# B A L A N C E   S H E E T

Per 10.0 mols. PhIO$_2$, 20.0 equivalents NaOH initially.

(The figures after each radicle or atom refer to the individual analyses from which the aggregate has been obtained.)

| | 0.04969N alkali | | | 0.02N alkali | N alkali |
|---|---|---|---|---|---|
| | 50 mins. | 24 hrs. | 70 hrs. | 24 hrs. | 17 days. |
| Phenyl groups 2 2-6-8-9 .... | 6.59 | 7.97 | 8.55 | 7.74 | 2.81 |
| Deficit ...... | 3.41 | 2.03 | 1.45 | 2.26 | 7.19 |
| Iodine atoms 2 2-3-8-9 ..... | 7.33 | 8.78 | 9.47 | 9.81 | 7.39 |
| Deficit ...... | 2.67 | 1.22 | 0.53 | 0.19 | 2.61 |
| A Oxygen atoms 4 | 17.97 | 19.29 | 19.18 | 19.58 | 19.90 |
| Deficit ...... | 2.03 | 0.71 | 0.82 | 0.42 | 0.10 |
| OH Groups 1-8 | 18.78 | 18.40 | 18.18 | 12.82 | 3.34 |
| Deficit ...... | 1.22 | 1.60 | 1.82 | 7.18 | 16.66 |

Ion Count

0.04969N alkali.

**50 minutes**

| Na˙ | Ph$_2$I˙ | OH˙ | IO$_3'$ |
|---|---|---|---|
| 20.0 | 0.52 | 18.78 | 1.06 |
| 20.32 | | 19.84 | |

Missing  −0.48

**24 hours**

| Na˙ | Ph$_2$I˙ | OH' | IO$_3'$ |
|---|---|---|---|
| 20.0 | 3.61 | 18.40 | 4.41 |
| 23.61 | | 22.81 | |

Missing  −0.80

**70 hours**

| Na˙ | Ph$_2$I˙ | OH' | IO$_3'$ |
|---|---|---|---|
| 20.0 | 3.92 | 18.18 | 4.84 |
| 23.92 | | 23.02 | |

Missing  −0.90

0.2002N alkali

**24 hours**

| Na˙ | Ph$_2$I˙ | OH' | IO$_3'$ |
|---|---|---|---|
| 20.0 | 3.79 | 12.82 | 6.02 |
| 23.79 | | 18.84 | |

Missing  −4.95

**17 days**

| Na˙ | Ph$_2$I˙ | OH' | IO$_3'$ |
|---|---|---|---|
| 20.0 | 0.57 | 3.52 | 6.99 |
| 20.57 | | 10.51 | |

Missing  −10.06

1.001N alkali

borax-active oxygen, the two latter again being equal on amount.
In the normal alkali the β oxygen has entirely disappeared,
and the quantity of iodonium ion is extremely small after 17
days;   the iodate, on the other hand, has increased to almost
double the amount present in the 0.2 and 0.05N alkalies.  These
results would indicate that after a certain time, or, presumably
to a less extent, all the time, the diphenyliodonium salt (or
that radicle which gives this in analysis) is decomposing and
in doing so gives rise to more iodate together with iodobenz-
ene.  That some other substance not accounted for in the
analyses in this series is formed along with iodobenzene and
iodate in this tertiary reaction is apparent because of the
large deficit in hydroxyl ions and phenyl groups in the 17
days' sample of the N-alkali-iodoxybenzene solution.

Apart from subsidiary reactions, however, the above
studies can be summarised into the following statement:  After
several hours in dilute alkali of two molecules of initial
iodoxybenzene, about 90% is represented analytically by one
molecule of diphenyliodonium iodate and one atom of oxygen
capable of setting free iodine from aqueous iodide in borax
medium.   This might be expressed thus:-

$$2PhIO_2 \longrightarrow PhI.IO_3 + O^*$$
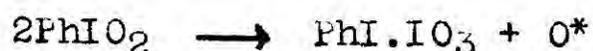
However, this equation does not explain the excess of sodium
and diphenyliodonium ions over hydroxyl (to methyl orange) and
iodate ions;   and it is extremely significant that this excess
increases with time and with alkali-strength, until in normal

alkali after several days the positive ions are double the negative ions discoverable by the analyses employed. Nor does the equation explain that which follows:-

### ii. Titrations of iodoxybenzene-alkali mixtures after various time-intervals using methyl orange and phenolphthalein.

The solutions used for this series of titrations were those employed in the conductivity measurements (pp. 75 to 82), in which the alkali-strengths were 0.02484, 0.04969, 0.06954 and 0.09944N, a double proportion of alkali being used for the dissolution of the iodoxybenzene in each case. The stock liquors were kept in a sink of running water, where the temperature varied little from 11.0$^{\circ}$, and at intervals two samples of the solutions were withdrawn and titrated against standard sulphuric acid, using, for one, methyl orange and, for the other, phenolphthalein as indicator. The results showed that in each case there was a decided decrease in alkalinity to phenolphthalein, whilst that to methyl orange altered only slightly. It seemed as though, in the secondary reaction following that of iodoxylate-formation, a weak acid was being formed which, although neutral to methyl-orange, was sufficiently strong to register acid to the phenolphthalein.

Alkali-strength ... 0.02484N.

Initially, 10.0 c.c. of this required:-

    Using methyl orange ..... 10.08 c.c. 0.02486N $H_2SO_4$
    Using phenolphthalein ...  9.87 c.c. 0.02486N $H_2SO_4$

| Time from initial mixing (mins.) | 0.02486N $H_2SO_4$ required for 10.0 c.c. (methyl orange) | 0.02486N $H_2SO_4$ required for 10.0 c.c. (phenolphthalein) |
|---|---|---|
| 30 | 9.97 | 9.43 |
| 95 | 10.30 | 9.31 |
| 155 | 10.01 | 9.18 |
| 215 | 10.00 | 9.15 |
| 275 | 9.98 | 9.02 |
| 310 | 9.98 | 8.90 |
| 22 hrs. | 9.95 | 8.34 |

Alkali-strength ... 0.04969N.

Initially, 10.0 c.c. of this required:-

    Using methyl orange ..... 10.01 c.c. 0.04972N $H_2SO_4$

| Time from initial mixing (mins.) | 0.04972N $H_2SO_4$ required for 10.0 c.c. (methyl orange) | 0.04972N $H_2SO_4$ required for 10.0 c.c. (phenolphthalein) |
|---|---|---|
| 25 | 9.94 | 9.56 |
| 60 | 9.93 | 9.37 |
| 120 | 9.94 | 8.99 |
| 210 | 9.95 | 8.87 |
| 270 | - | 8.68 |
| 330 | - | 8.51 |

<u>Alkali-strength ... 0.06954N.</u>

Initially, 10.0 c.c. of this required:-
    Using methyl orange ..... 14.00 c.c. 0.04972N $H_2SO_4$
    Using phenolphthalein ... 13.89 c.c. 0.04972N $H_2SO_4$

| Time from initial mixing (mins.) | 0.04972N $H_2SO_4$ required for 10.0 c.c. (methyl orange) | 0.04972N $H_2SO_4$ required for 10.0 c.c. (phenolphthalein) |
|---|---|---|
| 20 | 13.94 | 13.28 |
| 60 | 13.83 | 12.77 |
| 120 | 13.78 | 12.26 |
| 180 | 13.81 | 11.79 |
| 240 | 13.76 | 11.61 |
| 290 | 13.76 | 11.59 |
| 22 hrs. | 13.62 | 11.02 |

<u>Alkali-strength ... 0.09974N.</u>

Initially, 10.0 c.c. of this required:-
    Using methyl orange ..... 10.03 c.c. 0.09944N $H_2SO_4$
    Using phenolphthalein ... 10.03 c.c. 0.09944N $H_2SO_4$

| Time from initial mixing (mins.) | 0.09944N $H_2SO_4$ required for 10.0 c.c. (methyl orange) | 0.09944N $H_2SO_4$ required for 10.0 c.c. (phenolphthalein) |
|---|---|---|
| 20 | 9.91 | 9.31 |
| 65 | 9.90 | 8.86 |
| 95 | 9.89 | 8.63 |
| 180 | 9.83 | 8.19 |
| 210 | 9.84 | 8.07 |
| 240 | 9.91 | 8.00 |
| 300 | 9.87 | 7.96 |
| 360 | 9.85 | 7.80 |

The development of this fall in alkalinity to phenol-phthalein, indicating the presence of a weak acid, appeared to be undoubtedly connected with the excess of anions over kations found in the velocity experiments on the iodoxybenzene-alkali solutions, and it seemed not unlikely that both facts were associated with the appearance of the borax-active oxygen, the source of which was as yet unknown, but which must of necessity have formed part of some molecule or radicle. Therefore independent experiments were performed to find the source of this borax active oxygen.

### (c) Source of B-oxygen in the iodoxybenzene-alkali secondary reaction.

Apart from any hypothesis requiring the formation of new types of iodine compounds, those substances which possibly could be present and which fulfilled the condition of being strong enough oxidising agents to liberate iodine from aqueous iodide in saturated borax medium are:- Periodates, iodites (if they exist), hypoiodites, iodosobenzene (a possible intermediate product in the production of the diphenyliodonium salt), ozone (which is known to be a decomposition product of periodates), peroxide or a compound of a "peroxyiodate" type. These were proved in turn, by direct experiment, to be absent, as follows:-

### i) Iodites and Hypoiodites.

Acidifying of the iodoxybenzene-alkali liquors which had developed borax-active oxygen did not yield free iodine; had

iodites or hypoiodites been present, iodine would have been liberated immediately on acidifying the solution. That iodine liberated thus would not be absorbed by any phenolic body was ascertained by proving that iodine and phenol do not react in the slightest degree in acidic media. Also, as well as the negative results obtained in the direct search for phenols in the velocity experiments (pp. 87 and 90) the presence of phenols in the liquors would have made iodometric determinations of B-oxygen impossible as control tests proved (see page 47). The balance sheets in the velocity reactions left no room for iodophenols.

### ii. Periodate.

The control experiments of pp. 47 to 53 proved conclusively that normal periodate is discoverable in the presence of iodate by barium precipitation. That no periodate was formed in the iodoxybenzene-alkali reaction was eminent from a barium precipitation of a sample of the liquors in the velocity tests in 0.2N alkali (page 88), when the barium precipitate was wholly devoid of borax-active oxygen and was therefore solely barium iodate, whereas the whole of the B oxygen was found in the filtrate from the barium precipitation.

To confirm this result a separate barium precipitation was done. 11.92 millimols. of iodoxybenzene were dissolved in 15 minutes in 23.84 milliequivalents of 0.09936N sodium hydroxide. The solution was shaken on the wheel for 22 hours. The resulting turbid liquor was extracted with benzene, which

did not remove the turbidity, and the organic extract used for a Stepanow determination of iodobenzene. The aqueous solution, made up to 250 c.c., was aliquoted for the following determinations:-

A Titration. 10 c.c. of the solution was wheeled in 0.2N sulphuric acid with sodium iodide for 24 hours, and the liberated iodine titrated against standard thiosulphate.

B Titration, by neutralising 25 c.c. of the alkaline liquor with sulphuric acid, saturating with borax, wheeling with sodium iodide and excess standard arsenite for 23 hours and titrating the excess arsenite with iodine. A duplicate, except that the solution was shaken for 4 hours only, gave a smaller titration.

Barium precipitation, performed by neutralising a sample (175 c.c.) of the liquor with N acetic acid and wheeling overnight with 50 c.c. of N barium acetate. After filtering and washing by means of a decantation syphon, the precipitate was decomposed and analysed for A and B oxygen as in previous barium determinations. The filtrate and washings were aliquoted for estimations of A and B oxygen and of diphenyliodonium radicle by precipitation and weighing of the iodide.

## Summary of Results.

Per 10.0 mols. of $PhIO_2$ (40.0 equivalents of A oxygen) and 20.0
equivalents of NaOH initially.

A Oxygen ...... 40.06

B Oxygen ...... 7.91

Iodobenzene ... 0.08

## Barium precipitation.

Filtrate: A Oxygen ...... 7.96

B Oxygen ...... 8.27

$Ph_2I$ ......... 3.83

Total A ... 39.94

Total B ... 8.27

Precipitate: A Oxygen ...... 31.97

B Oxygen ...... Nil

In the filtrate from the barium precipitation the borax-active
oxygen approximately equals the acid-active oxygen; this ex-
cludes the possibility of there being present a barium periodate
of a soluble form, since the latter would liberate 4 times the
amount of iodine in acid as in borax. Once again it was noted
that the atoms of B oxygen were almost equal to the diphenyl-
iodonium ion.

A further barium precipitation, done in a similar way, was
performed on an iodoxybenzene-0.05N alkali mixture after 18
hours reaction. The results were:-

Per 10.0 mols. $PhIO_2$ initially:

A Oxygen ... 34.00

B Oxygen ... 5.84

Barium precipitation.

Filtrate: A Oxygen ... 8.84

B Oxygen ... 7.58

Precipitate: A Oxygen ... 28.23

B Oxygen ... Nil

Total A ... 37.07

Total B ... 7.58

In the course of later work it was found necessary, on several occasions, to perform barium precipitations on the iodoxybenzene-alkali liquors, and on only one occasion had the barium precipitate any B oxygen. The presence of this, which was not due to periodate, is explained later.

### iii. Peroxides or "Peroxy-iodate".

A solution was made by digesting about $\frac{1}{4}$ gram of titanium dioxide in 8 c.c. concentrated sulphuric acid; the clear liquid was diluted to 50 c.c. Of this, 1 c.c. very easily showed yellow in a column of water of volume 10 c.c., containing, by appropriate aliquoting, 0.002 c.c. of a 40-volume hydrogen peroxide solution. That is, the titanium solution can readily detect 0.0001 gram of hydrogen peroxide in a volume of 10 c.c.

At no stage of reaction and at no alkali-strength of the iodoxybenzene-alkali liquors was there obtained, after acidifying the solution, the slightest colour with the titanium test

liquor. A barium precipitate, obtained by precipitation of the products of a 0.2N alkali reaction-solution and decomposed with sulphuric acid, also gave no sign of colouration with the titanium solution.

Up to that time, in determinations of the oxidised-iodine anions, barium acetate had been used as precipitant. It was conceivable that, had the borax-active oxygen been present as a "peroxy-iodate" (that is, $IO_3'-O$), the acetate ion might suffer oxidation to a peracetate, resulting in the filtrate from the barium precipitation showing a negative titanium test. It seemed necessary, therefore, to perform two barium precipitations of the 0.05N alkali liquors, one using barium acetate and the other barium hydroxide as precipitant.

To eliminate local changes, the solutions for all the determinations were drawn from the same tube of iodoxybenzene-alkali mixture, after a $5.^1/_2$ hours' reaction. Because of the necessarily large volumes encountered all aliquoting was done by weighing, and both barium precipitations were performed on the neutralised liquors. At the same time direct A and B oxygen determinations were carried out.

A summary of the results is given:-

Per 10.0 mols. of iodoxybenzene initially:

A Oxygen ... 33.42

B Oxygen ... 4.41

Barium precipitation:

(a) By Ba(OH)$_2$.

Filtrate: A Oxygen ... 13.30

B Oxygen ... 6.93

Precipitate: A Oxygen ... 21.86     Total A ... 35.16

B Oxygen ... Nil             Total B ...  6.93

(b) By Ba($\overline{Ac}$)$_2$.

Filtrate: A Oxygen ... 20.19

B Oxygen ... 4.75

Precipitate: A Oxygen ... 16.65     Total A ... 36.84

B Oxygen ... Nil             Total B ...  4.75

(The greater borax-active oxygen and iodate in that precipit-
ation using baryta was undoubtedly due to the longer exposure
to alkali of this liquor, the alkali being barium hydroxide.)

The decomposed barium iodate precipitate obtained by
baryta gave no tint whatever with the titanium solution in acid
solution; nor was there any colour produced by addition of the
titanium solution to the filtrate from this barium iodate.
Similarly, no colour was observed on treating with the titanium
sulphate the decomposed precipitate and filtrate in the barium
acetate precipitation. Therefore peroxide and anything giving
hydrogen peroxide in acid are absent from the products of the
iodoxybenzene-alkali reaction.

## iv. Iodosobenzene.

That the borax-active oxygen was not that of iodosobenzene was proved by benzene-extraction of the iodoxybenzene-alkali liquor after reduction of it with aqueous sodium iodide and removal of the liberated iodine with arsenite, followed by a Stepanow determination of the benzene extract, when no iodine whatever was detectable.

1.148 millimols. of iodoxybenzene were shaken for 22 hours with 22.94 c.c. of 0.05005N sodium hydroxide. The slightly turbid solution was extracted with 10 10 c.c. benzene and, after neutralising with sulphuric acid and saturating with borax, shaken with aqueous sodium iodide. The iodine liberated required 0.875 milliequivalents of arsenite. Excess arsenite was added to the liquor which was then extracted with 60 c.c. of benzene in four successive lots; the iodonium iodide formed in the iodide reduction of the liquor proved troublesome and necessitated the filtering of the benzene extract, the apparatus used being washed with a fifth extract. Because of this precipitate of iodide, a straight separation of benzene and aqueous solution was prevented, and therefore the extract was washed with water. A Stepanow analysis, using 100 c.c. absolute alcohol and 9.3 grams of sodium, gave the following titration:-

Silver nitrate added ... 1.139 milliequivalents, giving no trace of silver iodide precipitate.

Potassium thiocyanate required for silver nitrate ................ 1.140 milliequivalents.

(A Stepanow analysis of the benzene extract, before iodide-reduction, showed that no iodobenzene had been formed by alkali action on the iodoxybenzene.)

A duplicate experiment gave similar results.

A control determination on iodosobenzene was necessary; iodosobenzene acetate (0.752 millimols.) was reduced with aqueous sodium iodide in saturated borax and, after 2 hours' shaking, the liberated iodine required 1.473 milliequivalents of arsenite, indicating the purity of the acetate to be 97.9%. 3 c.c. excess of sodium arsenite were added and the liquor extracted with 100 c.c. of benzene in five lots. A determination for iodine was made, using 120 c.c. of absolute alcohol and 10.3 grams of sodium metal. 1.551 milliequivalents of silver nitrate solution were added, giving a copious silver iodide precipitate; the excess silver salt required 0.896 milliequivalents of thiocyanate. That is, of 0.736 millimols. of iodosobenzene initially used, 0.655 milliatoms (89% of the total) of iodine have been discovered.

### v.  Ozone.

There was never detectable in the iodoxybenzene-alkali liquors a smell resembling that of ozone, a characteristic in itself sufficient for the detection of minute quantities of the gas. Supplementary tests confirming the absence of ozone in the reaction-mixtures were performed as follows:-

a)  1.5252 grams (6.463 millimols.) of iodoxybenzene were weighed into a bubbling tube of 120 c.c. capacity, and an

equivalent amount (64.50 c.c.) of 0.1002N sodium hydroxide added from pipettes. Air, purified from carbon dioxide by bubbling through 30% caustic soda and washed through N potassium iodide solution, was passed through the reaction tube and then through potassium iodide in a Geissler bulb for 17 hours. There was not the slightest liberation of iodine from the aqueous iodide in the Geissler bulb.

After this time, by iodometric titration of 25 c.c. of the iodoxybenzene-alkali liquor, it was found that the solution contained 4.10 milliequivalents of borax-active oxygen.

b) The remaining 40 c.c. in the reaction vessel were acidified with 19 c.c. N sulphuric acid and pure air again aspirated through the apparatus. There was no liberation of iodine in the Geissler bulb after $7.^1/_2$ hours.

c) The same solution was precipitated with saturated baryta solution and, after allowing 30 minutes for the barium iodate to deposit, filtered, the filtrate being tested for ozone in the bubbling apparatus, but with negative result; whilst a qualitative test showed that it still contained borax-active oxygen.

d) Ozonised oxygen was passed through $\frac{N}{3}$ sodium hydroxide for 30 minutes, after which time the solution had developed only an extremely slight smell of ozone. A 25 c.c. sample of the alkali, treated thus, on acidifying and shaking with aqueous iodide, yielded no iodine in 30 minutes. A second 25 c.c. was neutralised, saturated with borax and shaken with sodium

iodide and standard arsenite; no arsenite was consumed in $\frac{1}{2}$ hour.

Therefore, had ozone been produced in the iodoxybenzene-alkali reaction, the sodium hydroxide present would not have prevented its being carried off in the air-stream.

e) Into 120 c.c. of a solution in $\frac{N}{10}$ alkali of 2 grams of sodium iodate ($2NaIO_3.H_2O$) ozonised oxygen was passed for 15 minutes. A B titration gave a slight iodine liberation requiring 0.025 milliequivalents of arsenite. A similar solution, treated with ozonised oxygen for 45 minutes, absorbed sufficient ozone to give a B titration of 0.4 milliequivalents of active oxygen per 120 c.c., although a sample of the liquor in the bubbling apparatus produced no liberation of iodine in the Geissler bulb. A repetition of this test, in which the solution was cooled to $0^\circ$ during the passage of the ozone, showed that, although the liquor contained 3.0 milliequivalents of B oxygen, no ozone was carried off in the air-stream when the solution was transferred to the bubbling apparatus. Apparently, therefore, ozone was not present as such in the ozonised alkaline iodate liquor; it seemed most probable that the borax-active oxygen was due to periodate. This was proved in the succeeding test.

f) 1.9984 grams $2NaIO_3.H_2O$ (representing 57.84 milliequivalents of active oxygen) were dissolved by prolonged shaking in 100 c.c. N/10 sodium hydroxide. Through the solution,

cooled to $0^\circ$, ozonised oxygen was passed for 7 hours.   The
pale-yellow liquor produced was diluted to 250 c.c. and ali-
quoted for A and B titrations and a barium precipitation, the
results obtained being as follows:-

Per 1.9984 grams $2NaIO_3.H_2O$

Initially:        A Oxygen .. 57.84 m.equivs.

                  B Oxygen .. Nil

After $O_2$-$O_3$:   A Oxygen .. 60.07 m.equivs.

                  B Oxygen ..  1.74 m. equivs.

Ba" precipitation:

   Filtrate: A Oxygen .. Nil

             B Oxygen .. Nil

   Precipitate: A Oxygen .. 57.25 m.equivs.

                B Oxygen ..  1.63 m.equivs.

Thus, the traces of borax-active oxygen found in the iodate
solutions after ozone treatment is due to the formation of
ordinary periodate, precipitable and determinable by barium
analysis.

### (d)  Diphenyliodyl hydroxide and its derivatives.

All the known possibilities of substances containing borax-
active oxygen had, by this series of experiments, been elimin-
ated;  only one explanation remained, namely, that the active

oxygen atom was associated with a new type of compound. In the velocity analyses of the iodoxybenzene-alkali liquors, all of the iodine atoms and at least 90% of the phenyl groups had been accounted for; it was apparent, therefore, that the oxygen atom was originally part of one of the radicles produced, not as a product of reaction, but in analysis, since there was no room for a third product of reaction other than those previously proved absent. Therefore, it wa associated either with the iodate or with the diphenyliodonium ion; of these, the former had been excluded by the above experiments, and thus it was concluded that the new compound was one which yielded the diphenyliodonium radicle when reduced by the aqueous sodium iodide used to precipitate diphenyliodonium iodide from the solutions, the active oxygen at the same time liberating iodine from the added iodide. This would mean that the iodonium radicle, as such, was not present in the liquors, but was produced in analysis from the new substance, which would be of the form $Ph_2IO.OH$ or as the hydrate $Ph_2I(OH)_3$.

A suggestion of the possibility of such a compound existing was provided in a barium precipitation performed after the borax-active oxygen search. Of a 23 hours' old sample of a solution of 11.92 millimols. of iodoxybenzene in 240 c.c. 0.09936N sodium hydroxide, made up to 250 c.c., 175 c.c. were neutralised with 1.17N acetic acid and precipitated by wheeling overnight with 50 c.c. N barium acetate. On allowing the contents of the tube to settle, comparatively large and not

perfectly white crystals floated on the surface of the liquor, whereas the pure white barium iodate precipitate settled in the bottom of the vessel. After washing the precipitate, by decantation, five times with 40 c.c. of water, a final wash- ing still gave iodine and diphenyliodonium iodide in a B titr- ation, seemingly due to the slight solubility of some precipit- ate other than barium iodate. The solid decomposed at $50^{\circ}$ with 2N sulphuric acid with which it was shaken overnight, con- tained both A and B oxygen, and liberated diphenyliodonium iod- ide as well as iodine in both titrations; per 10.0 molecules of iodoxybenzene originally, of a total of 8.27 equivalents of B oxygen produced, 3.0 of these were in the precipitate. Ap- parently the less dense, larger crystals mixed with the barium iodate were either the compound responsible for the B oxygen or a derivative of it.

Because of this, an iodoxybenzene-alkali solution was treated solely in an attempt to isolate this product. A solu- tion of 7.77 millimols. of iodoxybenzene in 156.4 c.c. 0.0994N alkali, after wheeling for 24 hours, was neutralised with 1.4N acetic acid and allowed to stand. After two days a sediment of light-brown solid of negligible weight had formed. The solid after filtering was found to be acetone-soluble and to contain no B oxygen. The liquor was therefore acidified with 25 c.c. of 1.4N acetic acid and allowed to stand for 24 hours; there was no sign of crystal-formation. After neutralising with N alkali, 46 c.c. of N barium acetate were added to the solution,

which was again left standing overnight. As well as barium iodate in the bottom of the vessel there were needle-shaped crystals floating on the surface of the liquor and clinging to the sides. A partial separation of the two types of deposit was afforded by rapid filtering and washing through bolting silk of 120 holes per inch, after which it was possible to pick out individual crystals for microscope tests. These indicated that the solid, which was in the form of elongated rhombic crystals, was not appreciably soluble in water, N acetic acid, aqueous sodium acetate, acetone, ether or chloroform, and possibly slightly soluble in 2N sulphuric acid and in carbon tetrachloride; it dissolved slowly in ethyl alcohol, giving a brown solution, presumably due to decomposition. The solid was readily soluble in all strengths of sodium hydroxide, from which it reprecipitated on acidifying with dilute sulphuric acid; from sodium iodide it liberated iodine and formed hair-like needles which in time absorbed the iodine, apparently with the formation of brown iodonium polyiodide. Sulphur dioxide, dissolved in aqueous sodium iodide, reduced the solid with the formation of new and much finer colourless needles, thought to be diphenyliodonium iodide. Unlike diphenyliodonium salts, the crystals did not form an insoluble picrate. Quantitative analyses of the new body prepared thus gave misleading results, due to the imperfect separation of it from the barium iodate precipitated at the same time.

This method of preparing the oxy-iodonium compound was finally abandoned as impracticable owing to the difficulty encountered in freeing the solid from sodium iodate. A more satisfactory way suggested itself during the series of tests on the reversibility of the iodoxylate formation. When N caustic soda was used the iodoxybenzene dissolved in 2 minutes, and a minute or so later there deposited yellowish needles which coagulated, due to the simultaneous slight resin formation; after 8 minutes the liquor was filtered and neutralised with 4.6N sulphuric acid, which caused the immediate precipitation of a voluminous white amorphous solid. Washing the precipitate on a filter with water seemed partially to dissolve it, that remaining being dried _in vacuo_. This white solid was not iodoxybenzene; it gave a B titration, indicating an equivalent of approximately 180, and along with iodine in this titration diphenyliodonium iodide was formed. Qualitative tests on the new solid pointed to its being either the same compound as, or of a similar type to, that formed in the barium precipitations, but quantitative estimations of A and B oxygen and of diphenyliodonium radicle, many of which were performed under varying conditions, indicated that the solid was impure and probably not perfectly stable.

Because of the solubility of the iodyl compound in water, it was deemed advisable to neutralise the liquors with carbon dioxide; also, since unchanged iodoxybenzene was detectable in the filtrate from the above test, it seemed that a longer

time was necessary for the complete irreversible decomposition of the iodoxybenzene. 25.8 millimols. of iodoxybenzene were dissolved with shaking in 51.8 c.c. of ice-cold 0.0997N sodium hydroxide, then stood in ice, with frequent shaking, for an hour; a cream-coloured, needle-crystalline solid was slowly formed. The liquor was filtered through ice-cold apparatus, and during an hour a brisk stream of carbon dioxide passed through the filtrate, from which there deposited slowly a white, amorphous solid. This was also filtered through cooled apparatus and washed sparingly with water, in which the compound was visibly soluble. A further yield of this solid was formed from the filtrate by saturating it with carbon dioxide. Both yields were dried overnight in vacuo. Although not as ready to decompose as the iodyl solid obtained by sulphuric acid neutralisation of the iodoxybenzene-alkali liquors, this body darkened from white to cream-yellow in 10 hours.

Those needles which deposited from the still alkaline liquor proved, by iodometric titration and ignition, to be slightly impure sodium iodate.

Qualitative tests on the precipitate formed from the solution by carbon dioxide neutralisation showed it to have similar properties to those exhibited by the solid obtained from the sulphuric acid-neutralised solution; that is, it contained B oxygen and, along with iodine, liberated diphenyl-iodonium iodide on treatment with aqueous sodium iodide, did

not contain iodate, and gave no precipitate by sulphur dioxide reduction. One remarkable physical property of this solid was that when dry it seemed to be highly electrified, clinging to the sides of any vessel in which it was stored, and being difficult to handle, due to its flyingabout when stirred, a property noticed to a less marked degree in iodoxybenzene and in the iodyl compound formed by neutralising the solutions with sulphuric acid.

Quantitative analysis of this iodyl body proved to be difficult. Apart from its tendency to decompose on keeping, the solid could not be titrated for A oxygen using thiosulphate, since the iodonium polyiodide formed was not decolorised before the thiosulphate started to decompose into free sulphur and evil-smelling aryl sulphur compounds, presumably owing to the formation and subsequent decomposition of diphenyliodonium thiosulphate. Standard sodium sulphite was tried as reducing agent, using an iodine back-titration, and controlling all wheelings of sulphite solutions in case of air oxidation. Although many attempts were made, reproducible results could not be obtained; the sulphite reduction gave an oil, which, when extracted with benzene, was found by a Stepanow estimation to contain no iodine. The borax-active oxygen was also difficult to estimate owing to the slowness in reduction of the iodyl compound, overnight wheeling with an excess of standard arsenite being necessary to complete the reduction. Due to the

slight solubility of diphenyliodonium iodide in water, the quantitative estimation of iodonium radicle (by suspending the solid in a little water, reducing with sulphur dioxide followed by aqueous sodium iodide) was not above criticism. The results, which were in fairly good agreement, were as follows:-

B Oxygen, 1 gram-atom per ....... 206 grams.

Iodonium, 1 gram-radicle per .... 376.5 grams.

Total iodine, 1 gram-atom per ... 378 grams.

However, due to the possibility of the solid decomposing whilst, or immediately after, drying, it seemed necessary to prepare a fresh sample of the compound, analyse it before drying to obtain the ratios of the various atoms and radicles, and repeat the analyses on the dried product. For this purpose 29 millimols. of iodoxybenzene were dissolved in a double molecular proportion of ice-cold N sodium hydroxide and shaken, enclosed with ice, for 70 minutes. The solid sodium iodate formed was filtered and the filtrate, cooled to $0^o$, saturated with carbon dioxide. The iodyl solid was filtered, sucked as dry as possible and analysed whilst still damp. An A oxygen titration which appeared to be successful was performed by overnight shaking of the solid in $\frac{N}{5}$ sulphuric acid with sodium iodide, neutralising and saturating with sodium bicarbonate, wheeling with excess arsenite and back-titrating the arsenite with iodine. The analyses of the damp solid gave:

A Oxygen:    1 gram-atom per ....... 866 grams

B Oxygen:    1 gram-atom per ....... 892 grams

Iodonium:    1 gram-radicle per .... 872 grams

The remainder of the solid was dried in a vacuum, which caused
it to darken slightly and, when crushed, it possessed the same
highly "electrified" character as shown by previously prepared
samples of the compound.  Analyses were performed as with the
damp solid, the results being as follows:-

A Oxygen:    1 gram-atom per ........ 440 grams

B Oxygen:    1 gram-atom per ........ 428 grams

Iodonium:    1 gram-radicle per ..... 396 grams

Total iodine:  1 gram-atom per .... 383 grams

Although the purity of the solid was doubtful, it appeared that
both
/before and after drying there is one active-oxygen atom per one
diphenyliodonium radicle.  That this oxygen atom was directly
attached to the diphenyliodonium radicle was proved by the
preparation and qualitative examination of its picrate.  A few
c.c. of a 3% sodium picrate solution were added to a saturated
aqueous solution of the iodyl material;  a yellow crystalline
precipitate deposited but dissolved in excess of the picrate
solution, due to the alkalinity of the latter.  One drop of
5N acetic acid reprecipitated the iodyl picrate, which was
filtered and efficiently washed.  The filtrate contained B
oxygen and iodonium ion.  The precipitate dissolved but
slightly in water, and when saturated with borax yielded

iodine and diphenyliodonium iodide on addition of sodium iodide. To ensure complete freedom from impurities, which might have given rise to the B oxygen and iodonium compound, the solid was rewashed six times with water and again tested with sodium iodide with the same result as before.

From these tests it appeared that the solid iodyl compound was of the form $Ph_2IO.X$, and up to that time nothing was known of the radicle X. Because of this, it seemed necessary to perform a complete analysis of all the products, both solid and those in solution, of a neutralised iodoxybenzene N-alkali liquor, after which a balance sheet would show any marked deficiency of atoms or radicles not evident in the balance sheets of the iodoxybenzene-alkali velocity reactions. For this purpose 35.07 millimols. of iodoxybenzene were shaken at $0^\circ$ for 2 hours with 70.22 c.c. 0.9988N sodium hydroxide. The sodium iodate formed was filtered from the liquor through ice-cooled apparatus and the solid washed from the filter into a 2-litre bottle; 500 c.c. of water were insufficient to dissolve the iodate. Therefore, after ascertaining, by testing a sample of the suspension, that it contained no B oxygen or iodonium compound, the whole was acidified with 150 c.c. 2N sulphuric acid, and 10 grams of sodium iodide added. After shaking overnight, the resulting iodine solution was diluted to a litre and an aliquot part titrated against standard thiosulphate. Meanwhile the alkaline liquor and washings from which the sodium

iodate had been filtered were subject to a brisk stream of carbon dioxide for 2.$^1/_2$ hours. The perfectly white material formed was filtered and washed with ice-water, the filtrate and washings being aliquoted for A and B oxygen, iodonium and iodobenzene estimations as described earlier. Due to the removal of the greater part of the iodate as solid, there was an excess of iodonium over iodate present in the filtrate, the latter ion therefore being estimated by weighing the diphenyl-iodonium iodide precipitated from the liquor by sulphur dioxide reduction alone, whilst the iodonium ion was determined by sulphur dioxide reduction followed by the addition of excess aqueous sodium iodide.

The washed and dried solid iodyl compound, which weighed 0.807 grams, was also analysed and gave the following equivalents:-

i)   A Oxygen:  One oxygen atom per 397.2 grams.

ii)  B Oxygen:  One oxygen atom per 412.0 grams.

iii) Iodonium:  One iodonium  ion per 401.6 grams.

iv)  Total iodine:  One iodine atom per 401.1 grams.

v)   Alkalinity:  One hydroxyl ion per 391.4 grams.

vi)  Inorganic content:  There was no involatile matter in
                                              the solid.

In analysis v) methyl orange was used as indicator, but the usage of sulphuric acid was too slow for the titration to be done directly; because of this, an excess of acid was added to the liquor, which was then wheeled for 3 hours and back-titrated.

The sixth determination was done by suspending 28 milligrams of the solid in 2 c.c. of water, reducing it with sulphur dioxide and, after addition of concentrated sulphuric acid, evaporating the resulting liquor to dryness. There was an increase in weight of 0.1 milligrams.

A summary and balance sheet of the total analysis is given:-

### Initially.

Iodoxybenzene: 10.0 gram-mols.$\equiv$ 40.0 equivalents A Oxygen.
Sodium hydroxide: 20.0 equivalents.

### Finally.

|  | | Phenyl Groups | Iodine Atoms. | A Oxygen Atoms. | B Oxygen Atoms. |
|---|---|---|---|---|---|
| i) **Sodium Iodate.** | | | | | |
| A Oxygen ... | 16.0 | - | 2.6 | 8.0 | - |
| B Oxygen ... | Nil | - | - | - | - |
| ii) **Iodyl Solid.** | | | | | |
| A Oxygen ... | 1.16 | - | - | 0.58 | - |
| B Oxygen ... | 1.12 | - | - | - | 0.56 |
| $Ph_2I$ ........ | 0.57 | 1.15 | 0.57 | - | - |
| Total I .... | 0.57 | - | - | - | - |
| iii) **Neutralised Filtrate.** | | | | | |
| A Oxygen ... | 22.1 | - | - | 11.1 | - |
| B Oxygen ... | 7.39 | - | - | - | 3.70 |
| $Ph_2I$ ........ | 3.74 | 7.47 | 3.74 | - | - |
| Iodate ..... | 2.40 | - | 2.40 | - | - |
| PhI ........ | 0.95 | 0.95 | 0.95 | - | - |
| TOTALS ............ | | 9.59 | 10.25 | 19.7 | 4.25 |
| Missing .......... | | 0.41 | -0.25 | 0.3 | - |

Apart from the great turbidity of the solution, the main part of which was not extractable by benzene, there was a resinous residue weighing 0.09 gram which was not taken into account in the balance sheet. When it was considered that, without allowing for these, the deficiency in phenyl groups was only 4.1%, it was apparent that there was no room for more than two whole phenyl groups in the iodyl compound. On the other hand, the iodyl solid, by all five analyses done on it seemed to have a molecular weight of approximately 390; if this solid were of the form $Ph_2IO.OH.X$, then the weight of the unknown residue X would be approximately 80 units. There was no sodium in the compound, which meant three possibilities presented themselves as explanations of the nature of this part of the molecule:-

i) The remote one of its being composed of five or more hydroxyl groups,

ii) That it was composed of break-down products of the benzene rings not accounted for,

iii) That the compound in solution, being basic, had combined with the neutralising agent, that is, that it was a carbonate.

It was of interest to note that both in the analysis of the neutralised filtrate and in that of the solid iodyl compound the $\beta$ oxygen and the iodonium were equal in amount, which meant that, per 10.0 mols. of iodoxybenzene originally, 4.29 mols. of the iodyl body had been formed. This value, coupled with the fact that a large amount (0.95 mols.) of iodobenzene was produced in the reaction, indicated that the two hours allowed for the formation of the new oxidising agent was too long a time.

As well as the influence of time of reaction on the yield of the iodyl compound, nothing was known of the optimum strength of alkali required to give a maximum yield, or whether or not other alkalies than sodium hydroxide could be used to better advantage in reaction with the iodoxybenzene. In order to test these points, into each of four centrifuge tubes was weighed 0.60 gram of iodoxybenzene and the various samples of solid treated ice-cold with the following amounts of alkali:-

i)   2.54 c.c. 2.00N sodium hydroxide,

ii)  2.46 c.c. 2.07N potassium hydroxide,

iii) 5.09 c.c. 1.00N sodium hydroxide,

iv)  5.46 c.c. 0.93N potassium hydroxide.

In the cases of the stronger alkalies the iodoxybenzene dissolved with the immediate formation of solid iodate; the tubes were shaken for half an hour, centrifuged at 3000 r.p.m. for four minutes, and the heights of solid iodate formed measured with a travelling microscope. The turbid liquor was decanted off and carbon dioxide passed through each solution for an hour, after which the tubes were centrifuged again and the heights of the iodyl compound measured. The normal alkali solutions were treated similarly, except that the reaction was allowed to proceed for $1.^{1}/_{2}$ hours, much clearer solutions resulting than those produced in half an hour of 2N alkali. In both strengths of alkali more sodium than potassium iodate deposited, and neutralising yielded more solid in the sodium

hydroxide liquors due, no doubt, to the greater solubility of potassium bicarbonate. Almost twice the amount of solid was obtained with the N as with the 2N solutions; this, coupled with the great milkiness of the stronger alkali liquors, seemed to point to the rapid decomposition of the iodyl solid in this strength of alkali. Weaker solutions than normal gave much poorer yields or none at all; therefore, for the preparation of the iodyl compound, the optimum strength of alkali is normal and the better alkali is sodium hydroxide.

Light was thrown on the nature of the part X of the iodyl molecule when it was noticed that with glacial acetic acid the solid gave a brisk effervescence. More dilute acid was tried and it was found that with as weak acid as normal, carbon dioxide was evolved from the solid; however, when sulphuric acid was used it was not until a strength of 5N acid had been reached that there was any marked evolution of gas from the iodyl compound.

Apparatus was therefore fitted up in an attempt to determine the carbonate content of the substance by weighing the carbon dioxide liberated from it. In the first and second attempts 5N and 2.5N sulphuric acid respectively was used and the carbon dioxide trapped by potash. However, the liberation of gas from the material was so slow that it was found, after dismantling the apparatus, that the reaction was incomplete. In a second estimation this method was modified; glacial

acetic acid was used as reactant and baryta as absorbent for
the carbon dioxide.  The apparatus appeared thus:-



a    b     c       d     e     f   g    h     i         j       k    l    m
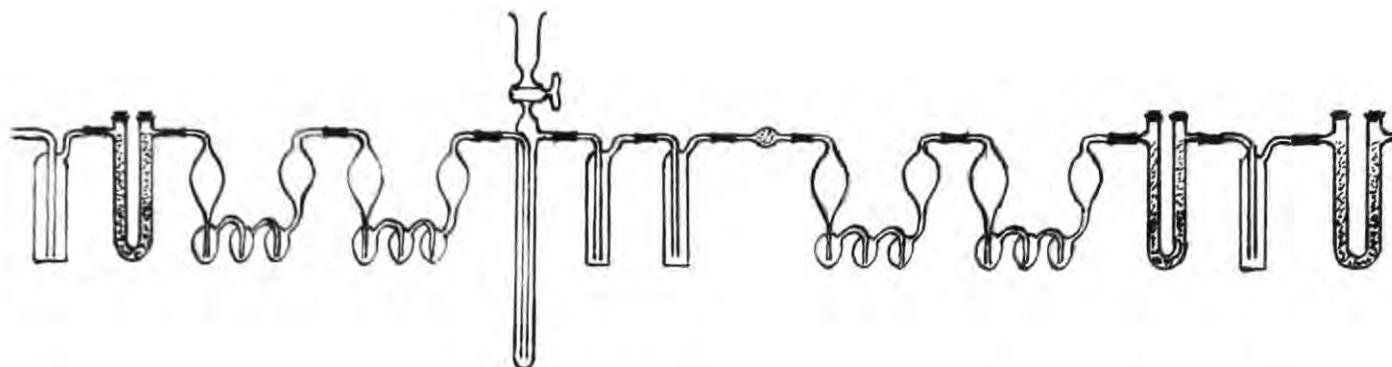
The various bubblers and tubes were as follows:-

a.    Concentrated sulphuric acid,

b.    Solid caustic potash and calcium chloride,

c.    40% potash solution,

d.    Saturated barium hydroxide,

e.    Reaction tube,

f.    Water,

g.    Concentrated sulphuric acid,

h.    Calcium chloride,

i.    Saturated barium hydroxide,

j.    40% potash solution,

k.    Solid caustic potash and calcium chloride,

l.    40% potash solution,

m.    Calcium chloride.

The tubes which were weighed before and after the reaction were
h, i, j and k.  The solid (0.9315 gram) was weighed directly
into the oven-dried reaction tube, nitrogen passed through the

apparatus at one bubble per second and four c.c. glacial acetic acid added from the dropping funnel of the reaction vessel. After 4 hours the tubes recorded an increase in weight of 0.0507 gram, and remained unaltered after a further 3 hours' bubbling of nitrogen through the apparatus. This means that there is one equivalent of carbon dioxide per 404.3 grams of the solid iodyl compound.

The white precipitate formed in the baryta trap, i, was tested and proved to be barium carbonate.

Although the analyses performed on this iodyl carbonate all gave equivalents within one per cent of 400, the compound could not have been a normal carbonate of the base $Ph_2I.O.OH$. It seemed likely that the solid analysed was either a basic carbonate or a mixture of base and carbonate. This view was enhanced by a micro-combustion performed on a sample of the iodyl carbonate by Dr. G. Weiler. The results found were:-

$$C, 40.26\%; \quad H, 3.05\%; \quad I, 35.48\%;$$

values which do not conform with a simple carbonate of $Ph_2I.O.OH$.

Because of these results, further work on the carbonate of the new base was postponed and attempts were made to prepare purer and, if possible, more stable derivatives of the substance. Because of the readiness with which acetic acid attacked the iodyl carbonate, the preparation of an acetate of the new base presented itself as a possibility. Microscope tests on this showed that the brown oil formed from the carbonate and acetic acid yielded, on careful dilution, large, colour-
less,

well defined rhombic crystals; too great dilution produced a dirty, amorphous solid, presumably the free base. A preparation of the acetate on a 0.2 gram scale produced, without any dilution of the acetic acid solution, large rhombic crystals. These, after cleaning with ether, in which they did not dissolve, yielded iodine and diphenyliodonium iodide when treated with aqueous sodium iodide. The crystals were not appreciably soluble in water or ether, slightly soluble in cold chloroform, carbon tetrachloride and benzene, and readily soluble in these at higher temperatures, although prolonged warming of the solutions tended to decompose the substance; acetic acid dissolved the acetate most readily, whilst alcohol and acetone were oxidised by it. Recrystallising from benzene gave almost colourless, elongated orthorhombic prisms, giving the same qualitative tests as the uncrystallised material. A second preparation of the acetate, using 9.5 grams of iodoxybenzene, gave similar results. Both before and after recrystallising from benzene the solid decomposed at 114°, although in later preparations of the acetate this decomposition point was found to be sensitive both to very slight impurities and to the rate of heating. Under crossed nicols the prisms showed a straight extinction and high polarisation colours.

Before dealing with the methods of analysis of this acetate, the final method evolved for its preparation on a larger scale is given:-

50 grams of iodoxybenzene, finely sieved from lumps, were dissolved with shaking in 424 c.c. of ice-cold N sodium hydroxide (a double molecular proportion); the solution was kept cold for $1.^1/_2$ hours, after which the deposit of sodium iodate was filtered off through a sintered glass filter surrounded in ice. For this purpose a small inverted bell-jar was found suitable. The slightly white turbid filtrate, still kept at $0^o$, was transferred to a well-chilled soda-water bottle and 18 grams of carbon dioxide squirted from two bombs into the liquor. After vigorous shaking the bottle was stood in ice for $2.^1/_2$ hours, the diphenyliodyl carbonate filtered through the ice-cold apparatus and washed sparingly but efficiently with ice-cold carbonic acid (which was found to dissolve the solid much less than did water alone). The weight of the dried product was 25 grams, but since drying in vacuo tended slightly to decompose the carbonate, it was found advisable to dry it as well as possible on a porous plate and treat this still damp material with a minimum (about 30 c.c.) of glacial acetic acid, which gave a pale-brown, viscous solution. The liquor was diluted with 20 c.c. of water and, after rubbing, stood in ice for several hours. The crystals of diphenyliodyl acetate which deposited were filtered, washed with small quantities of 5N acetic acid and dried in a vacuum. Distillation under reduced pressure of the mother liquor gave a further yield of large white acetate crystals. The total yield, which

was 99.5 to 100.0% pure without recrystallising from benzene, was 18 to 19 grams.

## (e)  Analyses of diphenyliodyl acetate.

### i.  Acid-active oxygen.

The analytical reduction of diphenyliodyl acetate was found difficult to make quantitatively complete owing to the chelation of the active oxygen atom, as explained on page 71. Many attempts were made, but reproducible results were not obtainable by the methods employed.  By suspending the well-ground solid in 0.2N sulphuric acid and performing on it a straightforward A titration, by wheeling from 10 to 24 hours with aqueous sodium iodide, neutralising and saturating the liquor with sodium bicarbonate, wheeling with excess standard arsenite and back-titrating the arsenite with iodine, an equivalent of 240 was obtained on a number of occasions.  Repetition of this method, with acetic substituted for sulphuric acid, gave an equivalent of 224, whilst under similar conditions, using hydrochloric acid, an equivalent of 230 was given. Grinding with a few c.c. of saturated borax solution before acidifying with sulphuric acid gave, on various occasions, equivalents varying from 197 to 200, the time allowed for reaction being from 16 to 24 hours;  sodium bicarbonate instead of borax at the beginning of the titration reduced the equivalent to 196.  Finally, it was found that reproducible results which were in agreement with the other analyses of the acetate

were obtainable by grinding the sample under a slight excess of 0.05N sodium hydroxide solution; the solid dissolved in about 30 seconds, giving a colourless, slightly turbid solution which, after making 0.57N with sulphuric acid and titrated by the usual method, gave the following values for the equivalent of the acetate per A oxygen:-

189.9, 186.7, 187.9.

## ii. Borax-active oxygen.

The quantitative reduction of the iodyl acetate in saturated borax medium was found to be even more difficult than that in acid. Analyses performed by grinding the solid with saturated borax solution and wheeling with excess aqueous iodide and standard arsenite for times ranging from 4 to 24 hours gave values for the equivalent of the acetate varying between 230 and 243. Warming of the solution of acetate, iodide and arsenite in aqueous borax caused the production of side-reactions and resulted in an equivalent of 261. As in the A titrations, grinding with bicarbonate reduced the B equivalent of the solid to 205 to 210, and again more constant results were obtainable by effecting the initial dissolution of the material in 0.05N caustic soda; values of 192.5 and 198.0 were found by this treatment.

## iii. Iodonium radicle.

The main difficulties encountered in the determination of the iodonium content of the diphenyliodyl acetate were:-

a)  Reduction by sulphur dioxide of a fine suspension of the solid in water produced the unstable sulphate which quickly decomposed with the formation of an oil, thereby registering too low a weight of diphenyliodonium iodide on treating the product with aqueous sodium iodide.

b)  By adding sodium iodide first, wheeling and then reducing with either arsenite or sulphur dioxide, the iodonium iodide formed was yellow rather than white, and washing with organic solvents did not effectively remove this colour.

c)  Diphenyliodonium iodide was found to be slightly soluble in water, sufficient to give unreliable results;  also in washing the iodide precipitate with water, the mixing of filtrate and washings precipitated iodonium iodide due, as was shown in independent tests, to the common iodide ion effect.  This was overcome by washing the iodonium iodide with sodium iodide solution, but then the acetone used for freeing the precipitate of the sodium iodide also dissolved the iodonium salt to a slight extent.

d)  The iodonium iodide produced by reduction of the acetate with aqueous hydriodic acid (made from iodine and sulphurous acid) was clean, but it was found extremely difficult to free completely from sulphuric acid by ether-washing.

Iodonium determinations in aqueous media, using sulphur dioxide and sodium iodide followed by water, acetone and ether washing of the iodide, gave values of one $Ph_2I^{\cdot}$ per 407.7 and 411.9 grams of iodyl acetate.  The wheeling of a sample with

sodium iodide before sulphur dioxide reduction gave a result of 413.6; and using hydriodic acid as reducing agent (d above), 390.0 and 365.8.

Methyl alcohol was tried as medium; a sample of the iodyl acetate, dissolved in methyl alcohol, was reduced with sulphur dioxide and 10 c.c. of methyl alcoholic sodium iodide added. The white, coarsely crystalline diphenyliodonium iodide formed slowly and, after allowing a day in which to deposit, the precipitate was filtered; the methyl alcohol used for washing the solid, when mixed with the main filtrate, yielded more iodonium iodide, proving that the latter was not completely insoluble in the alcohol. By evaporating the solutions used to a volume of 10 c.c., refiltering and washing the precipitate sparingly with methyl alcohol until free from sodium iodide, followed by ether washing, a result of one $Ph_2I^{\cdot}$ per 377.6 grams of iodyl acetate was obtained. Clearly this method, as well as being tedious, was liable to give erroneous results.

The final method evolved was by far the simplest; a sample of the well ground solid (0.3 to 0.5 gram) was weighed directly into a grade 4 tubular, sintered-glass filter and treated in situ with an ethereal solution of hydriodic acid. This latter was made by passing sulphur dioxide through a water-saturated ethereal solution of iodine. The resulting iodonium iodide, which was a more pure white than that produced by the former methods of reduction, was washed acid-free

with ether and vacuum-dried.

Values obtained by this method were:-
One $Ph_2I^\cdot$ per 373.7, 378.3, 370.8 grams of diphenyliodyl acetate.

### (iv) Total iodine by the Stepanow method.

The Stepanow analyses of the iodyl acetate proved to be the most reliable; the solid (0.6 to 0.8 gram) was dissolved in 70 c.c. absolute alcohol, which was boiled under reflux and treated with 8 to 10 grams of clean sodium in small pieces during an hour. After cooling to $50^\circ$, the solution was diluted with 10 c.c. of water and the alcohol distilled off; by ridding the liquor of all its alcohol it was found that a cleaner precipitate of silver iodide was obtained on acidifying with 2N nitric acid and adding silver nitrate solution. The silver was determined both volumetrically by Volhard's method and gravimetrically. Results were:- One gram-atom of iodine per 374.0, 373.2, 373.6 grams of diphenyliodyl acetate.

### (v) Acetyl groups.

Because of the strongly oxidising power of diphenyliodyl acetate, no alcoholic reagent was permissible in the estimation of the acetyl groups in the substance.

An approximate determination of the acetyl-content of the iodyl acetate was afforded by hydrolysing 0.4024 gram of the salt with 4.6 c.c. N sodium hydroxide and, after thorough

grinding, reacidifying the solution with 6 c.c. 2N sulphuric acid and distilling the resulting liquor from all-glass apparatus; the residue (about 1/8th of the total volume) was diluted with 30 c.c. of water and redistilled. Finally, 10 c.c. of a concentrated solution of sodium phosphate and 3 c.c. 0.4N ferrous sulphate were added to the distilling flask and the distillation continued. The distillate required 10.44 c.c. 0.1045N sodium hydroxide, indicating an equivalent of the iodyl acetate per acetyl group of 369 grams. Qualitative tests on the neutralised distillate indicated definitely that the solution contained acetate and had in it no phosphate or iodide.

This method, which appeared too crude and subject to error, was supplemented by a determination of the acetyl-content of the iodyl substance by Wenzel's method (Monats., 1897, 18, 659) in which the special features were: (a) Distillation from phosphoric acid, (b) A flask of glass beads between the distilling flask and the condenser, and (c) Distillation in vacuo. The modifications of the method given by the author were: (a) Initial saponification of the acetate by N sodium hydroxide, (b) Two potassium hydroxide traps instead of one were used for collecting the acetic acid; these traps were connected by a 100 c.c. pipette in order to prevent potassium hydroxide from the second trap sucking back into the first; and (c) Standard acetic rather than sulphuric acid was used in determining the excess of alkali in the traps. Control

experiments using acetic acid proved the method to be effect-
ive.  Results showed:-

One acetyl group per 354.0, 343.8 grams of diphenyliodyl
acetate.

Although the estimation was less accurate than the other
analyses, it was sufficient to decide that in the molecule of
diphenyliodyl acetate there was one, and only one, acetyl group.
This was further demonstrated qualitatively as follows:    10
milligrams of the acetate were treated with 0.5 c.c. 15% hydro-
gen peroxide and stirred until dissolved;  the excess peroxide
was decomposed with platinum black and the resulting solution
was, if anything, slightly alkaline to litmus, and a fraction
of a drop of 0.02N sodium hydroxide was sufficient to make it
register strongly alkaline to phenolphthalein.  Had the acet-
ate been a diacetyl derivative, reaction with hydrogen peroxide
would have formed diphenyliodonium acetate and free acetic
acid;  since the latter was absent, the presence of a mono-
acetyl derivative was indicated.

(vi)  Micro-analyses.

A series of micro-analyses of diphenyliodyl acetate was
performed by Dr. G. Weiler, with the following results:-

$$
\begin{array}{lll}
& \% & \\
C \ldots\ldots\ldots & 45.2, & 44.7 \\
H \ldots\ldots\ldots & 4.66, & 4.36 \\
I \ldots\ldots\ldots & 33.0, & 33.6 \\
CH_3.CO \ldots & 11.45, & 12.25 \\
\end{array}
$$

These analyses, together with those of (i), (ii), (iii), (iv) and (v) give to the acetate the composition $(C_6H_5)_2I(OH)_2O.COCH_3$. This is shown in the following summary:-

### (vii) Summary of analyses of diphenyliodyl acetate, per cent.

|  | Found | | | | Calculated |
|  | Lab. Analyses | | Micro-Analyses | | |
| --- | --- | --- | --- | --- | --- |
| Active Oxygen | 4.21 | 4.28 | | | 4.28 |
| Iodonium ($Ph_2I$) | 75.2 | 74.3 | | | 75.1 |
| Acetyl ($CH_3.CO$) | 12.5 | 12.15 | 11.45 | 12.25 | 11.50 |
| Carbon | | | 45.2 | 44.7 | 44.92 |
| Hydrogen | | | 4.66 | 4.36 | 4.04 |
| Iodine | 34.0 | 34.25 | 33.0 | 33.6 | 33.93 |

### (viii) Molecular weight of diphenyliodyl acetate.

Two of the greatest difficulties encountered in the attempts to determine the molecular weight of the iodyl acetate were (a) its sparing solubility in the cold in all solvents except acetic acid, which was scarcely suitable for freezing point measurements, and alcohol, in which the compound decomposed, and (b) although quite readily soluble in boiling benzene or chloroform, the acetate tended to decompose when the solutions were kept at the boiling temperatures for long periods. It was hoped, however, that an attempted determination of the molecular weight of the compound would be of sufficient accuracy to decide the extent of association of the molecules of

the acetate.

The Menzies-Wright apparatus was used and the solvent employed benzene (B.D.H. "Analytical Reagent", distilled from phosphorus pentoxide, middle runnings, thiophene free). The apparatus was fitted up in a draught-free, glass cupboard and the instructions given in the literature by Menzies and Wright (J. Am. C. S., Nov. 1921, 43, No. 11) carefully followed. The introduction of samples of the solid into the apparatus proved difficult since they could not be made into pastilles as the authors suggested; when dropped in tubes of platinum closed at one end, it was found, on dismantling the apparatus, that a portion of the solid had remained undissolved. A better method of adding the substance was to pack it tightly into thin-walled, glass tubes of about 1" long and 1/8th-inch cross section. Trial estimations were performed on 5-bromovanillin, each glass tube containing 0.12 to 0.20 gram of the substance and the working volume of the benzene being 29 to 30 c.c. The molecular weight found for the successive additions of the bromovanillin were:-

227.4, '223.5, 226.8, 232.5; average, 227.6. Calculated
230.98.

when diphenyliodyl acetate was used in the estimation the values given for its molecular weight showed a progressive decrease, thus:-

447.8, 439.5, 398.4, 320.5.

and after 80 minutes' boiling (the time found necessary for a

complete series of readings) there deposited from the solution
an amorphous brown solid which, when tested under the micro-
scope, appeared to be diphenyliodyl hydroxide. It seemed that
a lower-boiling solvent was necessary and, if possible, read-
ings taken in more rapid succession. Chloroform, purified from
alcohol by shaking with concentrated sulphuric acid and with
water and dried over calcium chloride, was tried as solvent and,
as before, the molecular weight of 5-bromovanillin determined
first. Results were:-

224.0,   233.8,   232.1,   233.5;   average, 233.1.   Calculated
230.98.

With the iodyl acetate, values found for the molecular weight
were:-

415,   418,   409,   420;   average, 415.   Calculated, 374.

It seemed that, with a possible reservation of about 10%, the
diphenyliodyl acetate molecules were unpolymerised in chloro-
form solution.

### (f)  Further properties of diphenyliodyl acetate.

### (i)  Alkaline hydrolysis of the iodyl acetate.

The final products in the iodoxybenzene-alkali reaction
were found to be sodium iodate and benzene (page 39), and with
the discovery of diphenyliodyl hydroxide it was thought poss-
ible that this base was an intermediate product in the form-
ation of iodate and benzene. That this was at least qualitat-
ively true was proved by the following experiments:-

A series of preliminary quantitative tests was made, but the amounts of acetate employed were too small for any definite conclusions to be asserted. 0.671 millimols. of diphenyliodyl acetate, representing 1.342 milliequivalents of active oxygen, was dissolved at room temperature in 2.67 c.c. 0.5053N sodium hydroxide; dissolution was rapid, the resulting solution, after half an hour, being quite turbid. This liquor was diluted to 0.05N and boiled for 15 minutes, which caused a great increase in the turbidity, accompanied by the formation of a floating oil. An iodometric titration of the aqueous product showed that it contained 1.334 milliequivalents of active oxygen, practically the same as that of the iodyl compound initially. A similar sample (0.706 millimol.) of the acetate was treated in the same way and, after extraction with benzene, which did not remove the turbidity, and with chloroform, which completely cleared the aqueous solution, the latter was treated with 20 c.c. saturated baryta solution. There was no precipitate formed; however, a control test done with a comparable amount of sodium iodate in a similar volume of alkali showed that, under these conditions, baryta treatment did not yield a barium iodate precipitate. The third sample of iodyl acetate (0.657 millimol.) was refluxed for 15 minutes with 2.36 c.c. 0.5N sodium hydroxide and the product distilled. A heavy brown oil, smelling strongly of iodobenzene, steam-distilled over; the aqueous residue contained only 0.049 milliequivalents of borax-active oxygen; therefore 1.265 milliequivalents

of B oxygen had been destroyed by the hydrolysis. Also, in the titration no visible iodonium iodide or polyiodide was formed, apparently this also having been destroyed. The next test done, as in the third, by refluxing for 45 minutes 0.598 millimol. of iodyl acetate with 2.4 c.c. 0.5N alkali, contradicted the result of the first.in which the liquor had been boiled only after dilution to 0.05N. In this latest test the A oxygen in the solution increased from 1.196 milliequivalents to 1.572 milliequivalents, that is, by 31.4%. This experiment was repeated on 0.792 millimol. of the iodyl compound, which was kept with the $\frac{N}{2}$ alkali at $100^{\circ}$ for $1.^{1}/_{2}$ hours. The A oxygen content of the solution increased from 1.584 to 2.026 milliequivalents. Again in the iodometric titration no iodonium iodide was formed.

It was evident from these initial tests that a further analysis of the hydrolysis products on a larger scale was needed. 10.06 millimols. of diphenyliodyl acetate were boiled under reflux with 20 c.c. N sodium hydroxide in a bath of saturated salt solution. The vapour had a temperature varying from $74^{\circ}$ to $79^{\circ}$ during the whole of the hydrolysis, and during this time the condensate seemed more oily than aqueous. After 80 minutes the apparatus was reversed and the liquor distilled to half of its original volume. The distillate contained a colourless, floating oil with an unmistakable smell of benzene; from the cooled aqueous residue there deposited clusters of colourless

needle crystals which gave microscope tests identifying them
as sodium iodate. The liquor, drained from these crystals, was
saturated with carbon dioxide, thereby depositing a pale-brown,
amorphous solid of weight 0.0189 gram; this solid contained B
oxygen and no sodium bicarbonate. The carbonated filtrate,
made up to 50 c.c., was aliquoted for A and B titrations and
for a barium precipitation; in this latter analyses were per-
formed on the slight precipitate and on the filtrate, a sample
of the filtrate also extracted with benzene, evaporation of
which yielded a residue of a few milligrams with a phenolic
smell and an ability to take up iodine in saturated bicarbonate.
The colourless, needle-shaped crystals from which the main
liquor had been decanted were washed with 6×5 c.c. 5N sodium
hydroxide followed by ethyl-alcohol until alkali-free.  The
solid, dried to constant weight, weighed 0.5655 gram; a sample
(0.0292 gram) of this was ignited with sulphuric acid with am-
monium sulphate and carbonate addition, the ignited residue
weighing 0.0101 gram.  (Required for $NaIO_3$ 0.0104 gram and for
$2NaIO_3.H_2O$ 0.0100 gram.  Most probably the crystals were the
latter.)  On the remainder of the crystals were performed A
and B titrations.  The A titration gave an equivalent for the
solid of 35.8.  (Required for $2NaIO_3.H_2O$ 34.5.)  There was no
B oxygen in the solid.  The sodium hydroxide washings of the
crystals, made up to 50 c.c., were analysed for A and B oxygen
and a barium precipitation done on an aliquot  part.  In the

distillation flask there remained an oily residue intermixed with more sodium iodate crystals; these latter were removed by hot water washing and the aqueous liquor, after chloroform extraction aliquoted for A and B titrations.

Results were as follows:-

Initially: 10.06 millimols. diphenyliodyl acetate
≡ 20.12 milliequivalents active oxygen.

Aqueous residue of distilling flask:-

Main liquor: A Oxygen equivalents ... 3.62

B Oxygen equivalents ... Nil

Barium precipitation:-

Precipitate: A Oxygen equivalents ... 3.06

B Oxygen equivalents ... Nil

Filtrate: A Oxygen equivalents ... 0.48

Total

B Oxygen equivalents ... Nil    A 3.45

Crystals (NaIO$_3$) 0.3655 grams:-

A Oxygen equivalents ... 10.21

B Oxygen equivalents ... Nil

Sodium hydroxide washings of crystals:-

A Oxygen equivalents ... 5.63

B Oxygen equivalents ... Nil

Barium precipitation:-

Precipitate: A Oxygen equivalents ... 4.44

Total

B Oxygen equivalents ... Nil    A 5.62

Filtrate: A Oxygen equivalents ... 1.18

B Oxygen equivalents ... Nil

<u>Aqueous washings of residual oil</u>:-

A Oxygen equivalents ... 8.71

Total A Oxygen equivalents ... 28.17

<u>Total Iodate A Oxygen Atoms, 12.67.   Other A Oxygen Atoms, 1.52.</u>

Since there was no borax-active oxygen discoverable throughout the whole of the analysis, if it were assumed that that acid-active oxygen not precipitable by barium were unchanged iodyl hydroxide (a justifiable assumption when it was considered that a solid containing B oxygen was deposited from the carbonated liquor), then it had also to be assumed that a substance, probably of a phenolic character, capable of absorbing iodine in bicarbonate medium was a simultaneous product; this latter supposition was partly justified because of such a compound being extractable by benzene from the filtrate of the barium precipitation performed on the main liquor.  This supposition that the active oxygen not present as iodate belonged to unchanged iodyl compound meant that 8.54 millimols. of the acetate had been fully converted, yielding 12.67 atoms of active oxygen as iodate.  Now 8.54 x 1.5 = 12.81, which indicates a 99% molecular conversion of the iodyl acetate into iodate.

The determination of the organic products in the distillate proved to be more difficult and less successful than the water soluble products, because of the small quantities obtained. The distillate contained three distinct layers which centrifuging at 1000 r.p.m. did not affect;  the middle layer (water)

was removed by a suction syphon and the remainder micro-distilled, at first at atmospheric pressure and later in a vacuum. The first fraction, coming over up to 88° and boiling sharply at 79°, was unmistakably benzene, although an insufficient amount to characterise it by derivative-preparation was obtained; the second fraction was a mixture of benzene and water and the third, distilling at 75° and 9 mm. boiled at 189° and had the smell of iodobenzene. From 75° to 150° and 7 to 8 mm. there distilled an oil which had a tendency to solidify and which had a boiling point of 244°. This fraction, which was proved by a micro-Stepanow determination to contain no iodine, had a smell reminiscent of that of diphenyl. The residue was now a resin; an attempted distillation of this by sealing the distillation tube directly to a mercury vapour pump, which was backed by a new oil pump, gave no further distillate after three-quarters of an hour at 200° to 209° and a pressure too low to be measured with an ordinary gauge.

Therefore, although the change in oxidising power by alkaline hydrolysis of the iodyl acetate is 1.5 times its initial value, a change due to quantitative conversion to iodate, it appears that the formation of benzene and iodate is accompanied by less simple reactions producing, among other substances, iodobenzene and, possibly, diphenyl.

### (ii)  Refractive indices of diphenyliodyl acetate.

For both the ordinary and the extraordinary rays the refractive index was determined approximately by the Becker line

test, and then more accurately by choosing a liquid in which the crystal was totally invisible; the refractive indices of the corresponding liquids were determined by the use of an Abbé refractometer.

Refractive index of ordinary ray .......... 1.679

Refractive index of extraordinary ray .... 1.685

Birefringence .... 0.006

Optical sign .... Positive

The examination of other optical properties of the iodyl acetate was not practicable owing to the impossibility of growing large enough crystals.

5.    p-Acetaminophenyl-phenyliodyl Acetate.

(a)  Preparation of p-Iodoxyacetanilide.

The preparation of p-iodoxyacetanilide proved to be much less straightforward than that of iodoxybenzene. Caro's acid did not oxidise p-iodoacetanilide even after shaking the mixture for 24 hours; therefore, the method via the iododichloride had to be resorted to. The iododichloride was made by the method given by werner (J.C.S., 1906, 89, 1633); a saturated solution (about 1%) of one gram of p-iodoacetanilide was made in chloroform and chlorine passed into the liquor for 15 minutes. The canary-yellow crystalline deposit of dichloride, after filtering and drying, was treated with 75 c.c. sodium hypochlorite made by bubbling chlorine through 2N sodium hydroxide for 2 hours, neutralising and saturating with sodium bicarbonate. However,

the dichloride proved to be so stable that after $2.^1/_2$ hours
at $45^o$ it was found, on filtering, that clotted pieces of the
solid contained unchanged yellow dichloride.  Grinding and re-
heating the solid to $50^o$ for 2 hours with a fresh lot of sodium
hypochlorite effected the change completely.  The washed and
dried solid, which had a hypochlorite smell not removed by
further washing, gave an A titration of 54.9 instead of 73.3.
This equivalent corresponded to that of p-iodoxy N-chlor acet-
anilide (theoretical A-equivalent 54.8) and treatment overnight
with N/10 hydrochloric acid only partially converted the chlor-
amine to 4-iodoxy 2-chloracetanilide, the new equivalent being
72.9 (theoretical for 4-iodoxy 2-chloracetanilide 82.1) and
the product of iodide reduction had a melting point from $122^o$
to $160^o$.

Repetition of the preparation on a 10-gram scale gave a
69% yield of p-iodoxy N-chloracetanilide with an A equivalent
of 54.9 and a B equivalent of 156.3 (theoretical 54.8 and 164.2
respectively).  Samples of this were treated with various re-
agents without effective conversion of the compound into either
p-iodoxyacetanilide or 4-iodoxy 2-chloracetanilide.  Those re-
agents tried in the conversion were:  N/10 hydrochloric acid,
N/10 sulphuric acid, glacial acetic acid, a mixture of glacial
acetic and hydrochloric acids, 20% aqueous acetic acid, a mix-
ture of 20% acetic acid and hydrochloric acid, benzene with
ultra violet irradiations from a mercury vapour lamp, all of

which had little or no effect on the chloramine, and boiling ethyl alcohol which wholly reduced the iodoxycompound to 4-iodo 2-chloracetanilide. An attempt was made to convert the dichloride into the iodosocompound by mechanically shaking it with 101 c.c. 0.4N sodium hydroxide at $0^O$, but after 6.$^1/_2$ hours the change was far from complete, and wheeling of the mixture overnight caused a decomposition of any iodosocompound formed.

Oxidation of the iododichloride in pyridine was attempted as follows:- 5 millimols. of the dichloride were dissolved in 10 c.c. of pyridine and 10 c.c. of water. 0.8 gram of dichloramine T was added as a source of the hypochlorous acid, but after several hours' wheeling no iodoxycompound was produced.

The effect of ammonia on the p-iodoxy N-chloracetanilide seemed more satisfactory; after shaking a weighed sample of the solid with 10 c.c. 2N ammonia for 2 hours its equivalent was increased to 76.0, the B oxygen was totally destroyed and the product of iodide reduction melted sharply at $184^O$. (Melting point of p-iodoacetanilide $184.5^O$.) 3.33 grams of the iodoxychloramine were treated similarly, but the resulting product contained 20% iodoacetanilide and needed four extractions with boiling benzene to raise the purity of the iodoxy-compound to 95%. The final product exploded at $162^O$ (Willgerodt, "Die organischen Verbindungen mit mehrwertigem Jod", gives as the decomposition point of p-iodoxyacetanilide $163^O$), and the iodide reduction product, both alone and mixed with stock

p-iodoacetanilide, melted at 183.5°. 11.5 grams of p-iodoxy-acetanilide (representing an 80% yield of the theoretical amount) were prepared from the iodocompound by this method.

### (b)  p-Iodoxyacetanilide and sodium hydroxide.

Before any attempt at the preparation of a "mixed" iodyl compound could be made it was necessary to discover something of the nature of the reaction between p-iodoxyacetanilide and sodium hydroxide, whether in fact the initial dissolution of the iodoxycompound was reversible, that is, whether or not the substance formed an iodoxylate analogous with the simpler benz-ene derivative, and whether this body, if formed, suffered the further irreversible change into the iodylcompound.

### (i)  Initial dissolution of the p-iodoxyacetanilide.

0.5054 millimol. of well ground p-iodoxyacetanilide was shaken with 20.0 c.c. 0.0504N sodium hydroxide for $1.^1/_4$ hours without any apparent dissolution of the solid;  after a further 15 hours' shaking there was formed a solution turbid with a small amount too fine to be filtered.  Saturation of the liquor with carbon dioxide increased this turbidity but little, and long standing of the neutralised solution gave 10 milligrams only of a rather dirty-looking solid which, with acidified aqueous iodide, gave 0.093 milliequivalents of iodine and poss-ibly iodonium iodide.  The filtrate contained 1.77 milliequival-ents of A oxygen, 0.256 milliequivalents of B oxygen and reduc-tion with sulphur dioxide followed by sodium iodide gave an

iodonium iodide precipitate. The weakness of the alkali used in this test had necessitated an overnight wheeling of the p-acetanilide-alkali mixture (due to the less rapid initial reaction than in the case of iodoxybenzene itself), and during this period the iodoxylate, if formed at all, had had ample time to decompose further. In order to reduce this time of dissolution 0.2N instead of 0.05N alkali was used. A mixture of 0.524 millimol. of the iodoxycompound and 5.53 c.c. 0.1997N sodium hydroxide was shaken for 53 minutes, and the remaining solid filtered off. This solid, which weighed 0.0538 gram when dried, proved, on iodometric titration, to be unchanged iodoxyacetanilide. Neutralising and saturating the filtrate with carbon dioxide gave no deposit; therefore the liquor was made to standard volume and aliquoted for A and B titrations and a barium precipitation. The A oxygen in solution was 1.35 milliequivalents and this, added to that of the residual solid iodoxycompound, gave a total of 2.04 milliequivalents; originally there were 2.09 milliequivalents of A oxygen. The total borax-active oxygen in the solution was only 0.40 milliequivalents, whilst in the barium precipitation, for which half of the filtrate was used, only a faint turbidity resulted on long standing.

Although it was evident from these tests, which were done on very small amounts of material, that the p-iodoxyacetanilide produced an iodyl compound on alkali treatment, there was no

evidence of a reversible iodoxylate formation having occurred.

### 11. Di-p-Acetaminophenyl-phenyl-iodyl hydroxide.

Following the method employed in the preparation of di-phenyl-iodyl compounds, 3.079 millimols. of p-iodoxyacetanilide were shaken with 6.36 c.c. of ice-cold 0.9687N alkali; after 35 minutes the whole mass went extremely stiff and very slightly coloured. During 5 hours the mixture was shaken continually and frequently ground, but even dilution to 10 c.c. did not appreciably dissolve the solid which had formed; had this latter been sodium iodate, it would have dissolved with ease in this volume of alkali. The resulting products were filtered and the cream-coloured solid on the filter washed alkali-free with water, without visible dissolution of the precipitate. This solid, when analysed, gave the following results:-

    a)     One A oxygen equivalent per ... 248 grams,

    b)     One B oxygen equivalent per ... 267 grams,

    c)     One iodonium radicle per ...... 422 grams,

    d)     One iodine atom per .......... 429 grams.

The iodonium iodide from c) contained, by a silver precipitation, one ionic iodine per 540 grams.

The substance therefore appeared to be rather impure di-p-acetaminophenyliodyl hydroxide, $(CH_3COHNC_6H_4)_2I.O.OH$ (molecular weight 428).

In an attempt to prepare the acetate of this iodyl base, 0.0433 gram was treated with 0.013 gram of glacial acetic acid;

dilution with water of the viscous liquid formed gave no deposit, whereas treatment with ether gave a white solid which, after washing acid-free with ether and vacuum-drying, weighed 0.0484 gram; for the formation of the acetate a weight of 0.0493 gram should have been recorded. An insufficient quantity of the solid was made for any analyses to be done on it.

The alkaline filtrate was also aliquoted for analyses, giving the following results:-

### Per 10.0 gram-molecules $RIO_2$ initially:-

Alkalinity decrease ..... 2.13 equivalents (phenol-phthalein)

Iodonium radicle ........ 0.55 gram-ion.

A oxygen ................. 30.92 equivalents.

B oxygen ................. 1.59 equivalents.

### Barium precipitation:-

Precipitate:

A oxygen ................. 25.8 equivalents.

B oxygen ................. Nil.

Total A, 27.4

Filtrate:

Total B, 1.59

A oxygen ................. 1.61 equivalents.

B oxygen ................. 1.59 equivalents.

That this iodyl base is very sparingly soluble in dilute alkali is shown by the relatively small proportion of total iodonium that is precipitable from the filtrate.

(c)  p-Acetaminophenyl-phenyl-iodyl hydroxide.

Having ascertained that p-iodoxyacetanilide formed relatively stable iodyl derivatives, attempts were made to prepare p-acetaminophenyl-phenyl-iodyl acetate, a "mixed" iodyl compound.  An equimolecular mixture of finely-ground iodoxybenzene and p-iodoxyacetanilide (3.33 millimols. of each) was shaken at $0^{o}C$ with 14.1 c.c. 0.97N sodium hydroxide for two hours.  Sodium iodate deposited in long needles from the pale-brown liquor and, after filtering, the latter was neutralised and saturated with carbon dioxide which caused an appreciable precipitation of an almost white, amorphous solid;  this solid was filtered, washed well with water, in which it was very sparingly soluble, and dried in vacuo.  When dry the material, weighing 0.80 gram, was cream coloured and had the peculiar flying and clinging properties of the previous iodyl carbonate even to a more pronounced degree.  Titrations for acid-active oxygen were performed on the solid carbonate, the carbonated filtrate from it, the washings of the solid and the deposited sodium iodate.  The following is a summary of these titrations:-

Initially: A oxygen ..... 26.64 milliequivalents.

Finally:  A oxygen from

    a) Deposited sodium iodate .... 11.24 milliequivs

    b) Main carbonated filtrate ... 10.79

    c) Solid iodyl carbonate ...... 3.25

    d) Washings of c) ............. 1.44

Total 26.72 milliequivs

The iodonium salt in the main filtrate was precipitated as iodide after sulphur dioxide reduction; it formed as a yellow, crystalline solid and, after washing and drying, was used for an estimation of its ionic iodine content by addition of and long wheeling with silver nitrate solution, a value of one gramion of iodine per 463 grams of iodonium iodide being obtained. p-Acetaminophenyl-phenyl-iodonium iodide would require a value of one gramion of iodine per 465 grams of iodide, which meant the formation of either (a) a "mixed" iodyl base, $(CH_3COHNC_6H_4)(C_6H_5)I.O.OH$, or (b) an equimolecular mixture of di-p-acetaminophenyl iodyl hydroxide, $(CH_3COHN.C_6H_4)_2I.O.OH$ and diphenyliodyl hydroxide, $(C_6H_5)_2I.O.OH$; the latter would imply the equal solubilities in water of the respective carbonates of these bases, and this seemed unlikely in view of the greatly differing properties expected in the two substances due to the presence in one of them of the acetamino group. Another point worthy of note and favouring (a) above is that, although both diphenyliodonium iodide and di-p-acetaminophenyl iodonium iodide are perfectly white solids, the iodide precipitated from the liquors of the mixed iodoxy-compounds was a definite yellow, whilst the literature describes p-acetaminophenyl-phenyl iodonium iodide as bright yellow.

A further preparation of the "mixed" iodyl carbonate was attempted on a larger scale, and in this case the carbonate, which was almost white and, when dry, weighed 2.1 grams, was treated with the least amount of glacial acetic acid necessary

to dissolve it. The pale-brown solution formed deposited no solid either on evaporation or dilution, and therefore was ground with successive amounts of ether until the whole mass had turned solid and no longer contained acetic acid. After drying, the acetate weighed 1.66 grams, decomposed at $104.5^{\circ}C$, and gave the following results on analysis:-

    a)  One A oxygen atom per ........ 438 grams

    b)  One iodonium radicle per ..... 427 grams

    c)  One iodine atom per ......... 432 grams.

In each case the theoretical value for

$$(CH_3CONH.C_6H_4)(C_6H_5)I.O.OHCH_3COOH$$
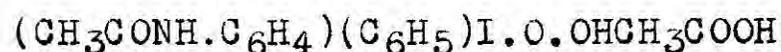
is 431. Also a silver precipitation of the iodonium iodide formed from this solid gave a value of one ionic iodine atom per 478 grams of the salt. (Theoretical 465.)

Here again, as in the case of the iodonium iodide, there is no definite proof of the formation of a "mixed" iodyl compound and not of an equimolecular mixture of the two separate acetates. The latter would imply not only the equal solubilities of the carbonates in both saturated sodium carbonate solution and water, but also that their acetates were equally soluble in the ether-glacial acetic acid mixture used in the preparation, as well as in ether alone. From the different chemical nature of the two compounds, these properties would not be expected. Also, the solution in glacial acetic acid of the "mixed" iodyl acetate gave no sign of crystal formation on dilution or evaporation; were the substance a mixture of acetates,

some appearance of the rhombic crystals so often obtained in the diphenyl iodyl acetate preparations might have been expected. It was also found that the "mixed" iodyl acetate was instantaneously and completely hydrolysed by water with the immediate formation of a yellow oil; diphenyliodyl acetate does not behave thus, although there was no evidence of unchanged solid in the hydrolysed product. Although not proving definitely the formation of the acetate of p-acetamino-phenyl-phenyl iodyl hydroxide, the above results seem definitely in favour of its existence.

CHAPTER  FOUR

A  NEW  METHOD  OF  PREPARING  DIARYL  IODONIUM  DERIVATIVES.

(Note:  The experimental work described in the introd-
uction to this chapter was not undertaken by the
Author.)

1.  Introduction.

The foregoing enquiries arose in the first place in an
attempt to discover to what extent the analogy between iodic
acid and nitric acid was maintained, particularly in their
action on benzene and its derivatives.  It was because actions
encountered early in the investigations showed that many funda-
mental properties of aromatic compounds of multivalent iodine
had remained obscure that the previous studies were carried
out.

When small quantities of benzene were shaken with well-
powdered iodine pentoxide suspended in concentrated sulphuric
acid there was an immediate reaction resulting in a dark solu-
tion which, when drowned with water, gave a flocky, buff-
coloured precipitate, accompanied by the smell of aromatic
iodocompounds.  The precipitate formed dissolved readily in
acetone and, on ignition, evolved iodine, whilst the filtrate
from it (a) contained no free iodine;  (b) did not give iod-
ine on addition of sodium iodide solution, but formed a slight

white precipitate; (c) with aqueous bromine gave a slow precipitation of a white micro-crystalline solid of greater bulk than that of (b); (d) suffered no change on neutralisation with aqueous sodium hydroxide; and (e) gave only a slight, slow-forming precipitate on addition of silver nitrate solution. In place of benzene, derivatives of it were used in the reaction, when it was found that chloro- and bromobenzene reacted more smoothly but also more slowly than did benzene itself, whereas nitrobenzene did not react, and with anisole the reaction was too vigorous to be controlled under normal conditions.

Tests showed that cleaner products were possible by using sulphuric acid more dilute than concentrated, and therefore an experiment on a larger scale was attempted by adding a solution of 25 milligrammols. of iodine pentoxide in 7 c.c. of water to 27.8 c.c. concentrated sulphuric acid, shaking the suspension thus formed with 0.1 grammol. of chlorobenzene and adding at intervals 50.2 c.c. concentrated sulphuric acid, the latter addition being so regulated that the temperature was kept below 26°C. After dilution with ice, the mixture was allowed to stand for 24 hours, after which time large buff-coloured crystals and a heavy red oil had deposited. The product was filtered and excess iodic acid washed from the solid with 8 to 10N sulphuric acid. It was found possible to remove the oil by washing the filtered mixture alternately with ether and chloroform, although, later, objection was found to the use of the latter solvent.

Qualitative tests on the crystals, which had a dry weight of 9.5 grams, showed (a) water readily attacked the solid, disintegrating, then dissolving it and finally leaving drops of a colourless oil; the solution formed was strongly acid to litmus; (b) the crystals dissolved rapidly in alcohol and redeposited in ferns, the same oil being visible when the alcohol evaporated; (c) aqueous sodium iodide precipitated from a solution of the crystals in water a thick white solid, but there was no trace of iodine liberated; (d) a solution of the crystals gave with potassium chromate a thick yellow precipitate; and (e) with barium chloride or nitrate solution precipitated barium sulphate. From these tests it was suggested that the crystals had the composition $(C_6H_4Cl)_2.I.X.HSO_4$ or $\left[(C_6H_4Cl)_2IX\right]_2SO_4$, where X represented the oil liberated by the action of water. Other products formed in the reaction were p-chloriodobenzene and a small amount of a phenolic body which was not characterised.

Several problems presented themselves as a result of this preliminary work. Primarily, the yield of iodonium acid-sulphate, even if the crystals deposited were solely this compound, was only 40% of the theoretical, and therefore the method used in its preparation needed modifying if possible to increase the yield; this solid, which qualitatively gave the reactions of iodonium acid-sulphate, needed thoroughly analysing and its apparent decomposition by water as well as other properties investigating; thirdly, the secondary products needed characterising

and the amounts of them formed determined and, if possible.
reduced; fourthly, in the former "iodylations" there was a
great deficiency in iodine and chlorine atoms and in phenyl
groups. It seemed most probable that the missing groups were
in the filtrate from the main solid product and therefore this
filtrate required examination; and, fifthly, according to the
equation:

$$HIO_3 + 2RH + H_2SO_4 \longrightarrow R_2I.HSO_4 + 2H_2O + O$$

there was one atom of oxygen not accounted for in the actual
product of the reaction, unless this oxygen were used in the
production of by-products, in which case some of these latter
still remained to be identified, since those already found
were insufficient to account for the usage of one atom of oxy-
gen per one molecule of iodic acid initially.

2.    Attempts to Increase the yield of Iodonium Acid-Sulphate
                and Modifications in the Method.

(a)  First iodylation.

8.35 grams (22.7 milligrammols.) of powdered iodine pent-
oxide (90.7% pure by iodometric titration) were dissolved in 5.0
c.c. of water and the solution added to 20 c.c. concentrated
sulphuric acid, whereby a fine suspension of the acid was ob-
tained. The suspension was cooled in ice, mixed well with 10.0
c.c. (97.0 millimols.) of chlorobenzene, and the mixture shaken
for 20 minutes, a careful watch being kept on the temperature,
which was not allowed to rise above 20°C. Concentrated sulph-
uric acid in quantities of about 2 c.c. at a time was run into

the mixture at intervals during 7 hours, with continual shak-
ing and, since there was the possibility of sudden and compar-
itively large increases in temperature, with frequent cooling
of the reaction vessel in ice. The slight pink colour which
first developed changed during the first hour to a light-brown,
the colour gradually darkening as more sulphuric acid was added,
until the final product had a deeper colour than that of bromine.
Altogether 48.5 c.c. of sulphuric acid (0.874 grammol.) were
used and the temperature range was $15^O$ to $28^OC$. However, even
at the end of this time some small amount of solid iodine pent-
oxide remained. 150 grams of clean ice were added slowly to
the mixture, the temperature being kept below $8^O$ during the ad-
dition, and thereby were produced a heavy red oil and a turbid,
pale-orange solution which, after remaining overnight surrounded
with ice, deposited a yield of buff-coloured needle crystals.
After filtering, the crystals were washed free from iodic acid
with 8N sulphuric acid at $0^O$, followed by ether which had been
purified by distillation from and drying over sodium. This
latter washing lightened the crystals to a pale-brown colour,
and the washings themselves were red. The ether washing was
followed by one of chloroform from which ethyl alcohol had
been removed by shaking several times with concentrated sulph-
uric acid and water, the latter being removed by drying over
calcium chloride. Addition of chloroform caused an immediate
darkening of the solid with the simultaneous extraction of a
dark-red product. A second ether washing again cleaned the

crystals and, by washing alternately with chloroform and ether, it was seen that the former caused a darkening of the solid and that this was removed each time by the ether; it was thought at this stage that the chloroform was loosening some product which the ether afterwards dissolved, although later it was found that the chloroform used actually decomposed the product and in subsequent iodylations the use of this solvent was avoided. The washing was continued until the solid was free from sulphuric acid, and the now pale-brown crystals were dried in vacuo, the dried product weighing 10.0 grams.

As well as this main product addition of ethereal hydriodic acid (made by reduction with sulphur dioxide of a solution of iodine in ether) to the filtrate and sulphuric acid washings of the crystals yielded an almost white precipitate, the dry weight of which was 2.22 grams, and which had both the qualitative and quantitative properties of di-chlorophenyl iodonium iodide. (For the quantitative analyses of this and other products of the reaction see section 3 of this chapter.) Also the ether and chloroform washes of the main product yielded respectively 0.72 and 0.23 gram of p-iodochlorobenzene, whilst extraction of the oily filtrate furnished a further 0.34 gram of the same compound together with about 0.1 gram of a brown phenolic body with a penetrating smell. By iodometric titration it was estimated that the filtrate and acid washings contained iodic acid equivalent to 23.0 milliequivalents of active oxygen.

## Summary of Yields of First Iodylation.

Charge:-

Iodine pentoxide (90.7%) ..... 8.35 grams ... 22.7 millimols.

Chlorobenzene ................. 10.0 c.c.  .... 97.0 millimols.

Concentrated sulphuric acid ,, 48.5 c.c.  ... 874.0 millimols.

Recovered:-

Di-chlorophenyl iodonium acid sulphate ....... 9.99 grams.

Di-chlorophenyl iodonium ion, weighed as iodide 2.22 grams.

p-Iodochlorobenzene ........................... 1.29 grams.

Acid-active oxygen ............................ 23.0 milliequivs.

Yields:-

Chlorophenyl groups:  from

Iodonium acid-sulphate ....... 44.7

Iodonium in solution ......... 9.4

Iodochlorobenzene ............ 5.4

Total ................... 59.5

Missing ................. 37.5

Percentage recovered .... 60.3

Iodine atoms:  from

Iodonium acid-sulphate ....... 22.4

Iodonium in solution ......... 4.7

Iodochlorobenzene ............ 5.4

Unchanged iodic acid ......... 3.8

Total ................... 36.3

Missing ................. 9.1

Percentage recovered .... 78.0

<u>Oxygen atoms</u>: through formation of

Iodonium hydroxide ........... 27.1

Iodochlorobenzene ............ 2.7

Total .................... 29.8

Missing .................. 74.2

Percentage recovered .... 28.6

## (b)  Second iodylation.

It was thought possible that part of the great deficiencies encountered in the first iodylation was due to insufficient care being observed in the protection from loss of volatile products; therefore in the second preparation greater attention was paid to products extractable by organic solvents.

Except that the iodine pentoxide used was of purity 99.4%, the recipe and method employed were similar to those of the previous iodylation;  the temperature range during reaction was 17° to 30°C and the total concentrated sulphuric acid used was 0.919 grammol.  After dilution with ice and standing over-night, the crystals formed were filtered and shaken as dry as possible, and, as before, care was taken that by the use of calcium chloride traps only dry air passed through the crystals. The solid was now washed with 200 c.c. benzene, 20 c.c. at a time, and these washings together with a further 300 c.c. were used for extracting the filtrate from the crystals; the benzene extracts were red.  Following this, the solid on the filter was washed alternately with pure dry ether and purified chloroform, about 200 c.c. of each being used, and the now fawn-coloured

precipitate was dried _in vacuo_.   Its dry weight was 14.27 grams.

The benzene extract, after drying over calcium chloride, was vacuum distilled at $26^{o}C$, when it was found to contain free iodine.  Iodometric titration of an aliquot portion showed that 1.61 milliequivalents of iodine were present in this extract. The actual weight of residue from the benzene was 3.58 grams, but since 0.18 gram of this had been shown to be iodine, the weight of product other than the latter present was 3.40 grams. This solid was washed free from iodine with aqueous sodium iodide, but this washing removed, as well as iodine, yellow needle crystals which redeposited from the aqueous solution on cooling it overnight in ice;  these crystals, weighing 0.70 gram, proved to be iodochlorobenzene, whilst the filtrate from them, after addition of excess thiosulphate and extraction with benzene, yielded 0.10 gram of a dark-brown oil which tests showed to be a non-phenolic mixture.  On adding excess sodium hydroxide to the liquor and re-extracting with benzene, evaporation of the extract left 0.10 gram of a light-brown lachrymatory oil with a pungent smell.  The nature of neither of these by-products could be ascertained.  The crystalline solid left after sodium iodide extraction weighed 1.63 grams and was quite pure p-iodochlorobenzene.

The ether washings of the main product contained 0.42 milliequivalents of free iodine, and distillation _in vacuo_ yielded 0.74 gram of a dark-brown, oily solid, the purification

of which was attempted under a high vacuum, but even after being kept at 65$^{o}$C for 7 hours there was only a trace of a yellow, pungent-smelling sublimate consisting of a mixture of an amorphous solid and micro-crystalline plates in too small quantities to be characterised.

There was no free iodine in the chloroform washings of the main yield, and distillation of it <u>in vacuo</u> left only 0.14 gram of a crystalline solid which was mainly p-iodochlorobenzene.

From an aliquot portion of the acid filtrate and washings of the reaction, which, in this iodylation, contained no iodic acid, the iodonium in solution was precipitated with aqueous hydriodic acid; the precipitate was white and, after washing acid-free with water, followed by ether and drying in a vacuum, weighed 1.92 gram (calculated on the total volume of liquor). The remainder of the liquor, after standing for five days, deposited a cluster of brown fern-crystals of not more than 0.1 gram weight and which proved to be p-iodochlorobenzene, together with 0.11 gram of a lustrous, micro-crystalline black product, probably iodonium polyiodide.

## Summary of Second Iodylation.

Charge:-

Iodine pentoxide (99.4) ........ 8.35 grams .... 24.9 millimols.

Chlorobenzene ................. 10.0 c.c. ..... 97.0 millimols.

Concentrated sulphuric acid ... 50.0 c.c. .... 919 millimols.

Recovered:-

Di-chlorophenyl iodonium acid-sulphate ......... 14.27 grams.

Di-chlorophenyl iodonium ion, weighed as iodide  1.92 grams.

p-Iodochlorobenzene ............................. 2.57 grams.

Free iodine ..................................... 2.03 milliequivs

Non-phenolic volatile solid mixture, not
                              characterised  0.94 gram.

Yields:-

Chlorophenyl groups:  from

Iodonium acid-sulphate ........ 63.85

Iodonium in solution .......... 8.15

Iodochlorobenzene ............. 10.8

     Total ................... 82.8

     Missing ................. 14.2

     Percentage recovered ..... 85.4

Iodine atoms:  from

Iodonium acid-sulphate ........ 31.9

Iodonium in solution .......... 4.1

Iodochlorobenzene ............. 10.8

Free iodine ................... 2.0

     Total ................... 48.8

     Missing ................. 1.0

Percentage recovered ..... 98.0

Oxygen atoms: through formation of

Iodonium hydroxide ............ 36.0

Iodochlorobenzene ............. 5.4

Total .................... 41.4

Missing .................. 83.1

Percentage recovered ..... 33.2

## (c)  Third iodylation.

It seemed conceivable that the reaction proceeded via the production of iodine trioxide or dioxide, formed thus:-

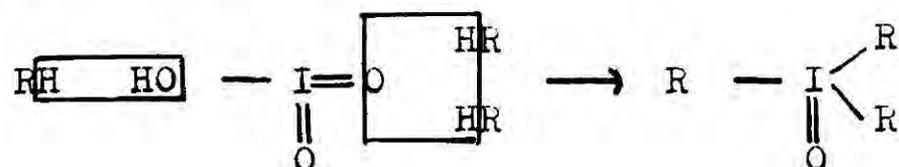$$3I_2O_5 + 2I_2 = 5I_2O_3; \quad 4I_2O_5 + I_2 = 5I_2O_4,$$

the iodine required being produced by the destruction of the organic material by some of the iodine pentoxide. Were this so, then addition of iodine to the reaction mixture would tend to prevent the formation of by-products due to oxidation. An iodylation was therefore attempted in which elementary iodine was added to the initial materials.

Iodine (0.635 gram) was dissolved in 10.3 c.c. (0.10 mol.) chlorobenzene and this solution mixed with a solution of 6.68 grams (20 millimols.) iodine pentoxide in 5.0 c.c. water. 20 c.c. concentrated sulphuric acid were added with vigorous shaking during 55 minutes. The iodine colour disappeared very slowly and after 30 minutes' shaking sulphuric acid was added in 2 c.c. lots, all evidence of free iodine having disappeared after the addition of 10 c.c. The total time of shaking of the

reaction mixture was five hours, in all 45 c.c. sulphuric acid being used, and the temperature range throughout was $24^O$ to $30^O C$. Treatment of the final mixture was as in previous iodylations, and the resulting products were of a similar appearance and nature to those of the first and second preparations. However, the yield of iodonium acid-sulphate crystals was only 9.26 grams, less than had been previously obtained from 25 millimols. of iodine pentoxide; it therefore seemed that the theory advanced was incorrect, although later proof was afforded that the reaction did proceed smoother and with greater yields by the use of iodine trioxide in place of iodic acid (see section 6 of this chapter).

### (d) Fourth iodylation.

A possible explanation of the iodylation process, which would account for the disappearance of oxygen without production of an oxidising agent, was that in reaction triphenyliodine oxide was formed, thus:-



of which the acid-sulphate would be
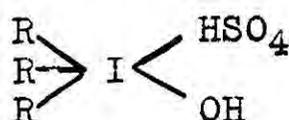


Actually, according to this scheme, four such reactions are possible:-

(i)     $RH + HIO_3 \rightarrow H_2O + RIO_2$, forming an iodoxycompound,

(ii)    $2RH + HIO_3 \rightarrow H_2O + R_2I.O.OH$, forming diaryl iodyl
hydroxide,

(iii)   $3RH + HIO_3 \rightarrow 2H_2O + R_3IO$, forming a triaryl iodine
oxide,

(iv)    $4RH + HIO_3 \rightarrow 2H_2O + R_4I.OH$, forming a tetra aryl
iodonium base;

of which (i) and (ii) had definitely been proved not to take place. However, if the reaction were that of forming a triaryl iodine oxide or a tetra-aryl iodonium salt, or went via this formation, an insufficient amount of chlorobenzene had been used in the previous preparations. In this fourth iodylation, therefore, a twofold excess of the organic reagent was used.

0.05 grammol. (16.70 grams) iodine pentoxide was dissolved in 10 c.c. water, and the solution poured with stirring into 50 c.c. concentrated sulphuric acid; to the resulting suspension 40.9 c.c. (0.40 grammol.) chlorobenzene were added. After half an hour's shaking, during which a slight darkening of the reaction mixture occurred, addition of sulphuric acid was begun. The shaking was continued over $5.^1/_2$ hours, a total of 122 c.c. sulphuric acid being used. The mixture, which was very dark in colour and appeared to contain unused oil, was diluted with 300 c.c. ice, forming thereby a dark-brown oil and a yellow solution. Rubbing for $1.^1/_2$ hours caused most of the oil to solidify, and to complete this the solid was ground with successive parts of the liquor for 20 minutes. The product was left at $0^o$ for 12 hours, filtered through a tared, sintered-glass filter

and washed, first with 8N sulphuric acid, then with pure ether until acid-free. The dried crystals weighed 32.9 grams.

In the mixed filtrate and acid-washings, which contained no iodic acid, there was iodonium salt equivalent to 3.33 grams of the iodide. There was an amount of unused chlorobenzene in the filtrate, and because of this the determination of organic products was not effected.

### Summary of ~~Second~~ **Fourth** Iodylation.

Charge:-

Iodine pentoxide (99.4%) ........ 16.70 grams ... 49.8 millimols.

Chlorobenzene .................... 40.9 c.c. .... 0.40 grammols.

Concentrated sulphuric acid ....122.0 c.c. .... 2.25 grammols.

Recovered:-

Di-chlorophenyl iodonium acid-sulphate .......... 32.9 grams.

Di-chlorophenyl iodonium ion, weighed as iodide 3.33 grams.

Yields:-

Chlorophenyl groups: from

Iodonium acid-sulphate ....... 147.2

Iodonium in solution .......... 14.1

Total ..................... 161.3

Not recovered as iodonium .... 238.7

Percentage converted into iod-
onium 40.3

Iodine atoms: from

Iodonium acid-sulphate ........ 73.6

Iodonium in solution .......... 7.1

Total ................... 80.7

Not recovered as iodonium .... 18.9

Percentage converted into iod-
                          onium 81.0

<u>Oxygen atoms</u>: through formation of

Iodonium hydroxide ............ 80.7

Missing ................. 168.3

Percentage recovered .... 32.4

From these figures it is seen that on the iodine count there was an increase in yield, but 60% of the chlorobenzene used was not converted into iodonium salt. There was no evidence from the preparation, therefore, that the diaryl iodonium acid-sulphate had been produced via the formation of a tri- or tetra-aryl iodine compound.

Other iodylations of chlorobenzene were performed, but as each was undertaken for some specific analysis, the yields from them were not determined. In these later preparations it was found advisable to cool the reaction mixture to $-20^{\circ}C$ before dilution with ice also cooled to this temperature, thereby preventing the sudden and comparatively large increase in temperature which previously had accompanied the dilution. However, it was not until experiments were attempted using iodine sesquioxide, instead of iodic acid, that yields approximating to the theoretical were obtainable. (For these experiments see section 6 of this chapter.)

(e)  Benzene iodylation.

A trial test showed that for the iodylation of benzene an acid of composition stronger than $H_2SO_4.H_2O$ caused the reaction to proceed too violently and produced mainly an intractable tar. The actual iodylation of benzene, therefore, was performed by starting with an acid of composition $H_2SO_4.2H_2O$ and running in- to the mixture an acid of composition $H_2SO_4.H_2O$. Also it seemed advisable to work at lower temperatures than had been employed in the chlorobenzene iodylations.

8.35 grams iodine pentoxide were dissolved in 11.4 c.c. water and 20.0 c.c. concentrated sulphuric acid added (making $H_2SO_4.2H_2O$);  the suspension was cooled in ice and 8.77 c.c. (0.10 grammol.) purified benzene run in.  The reaction mixture was shaken surrounded in ice for half an hour, when the temper- ature remained constant at $0.8^{\circ}C$, but during this time there was no apparent change.  Therefore, sulphuric acid of composi- tion $H_2SO_4.H_2O$ was added in portions of 2 c.c., the temperature being kept at about $5^{\circ}C$;  after the addition of 10 c.c. of this acid the reaction began and continued slowly during the addition of a further 75 c.c.  The total sulphuric acid used, therefore, was 1.14 grammol. and the time of reaction $7.^{1}/_{4}$ hours.  Dilu- tion was carried out with 175 grams of clean ice, the resulting liquor then being 8.8N sulphuric acid.  After standing over- night the product appeared to be as clean as that obtained in the iodylation of chlorobenzene.  A viscous red oil which had formed along with the crystalline precipitate did not solidify

on rubbing. The crystals were filtered, washed firstly with 40 c.c. 8N sulphuric acid and then with pure ether, the washings from which were orange-red. Continued extraction of the solid with ether seemed to convert it to a semi-solid mass which dissolved in the extractant leaving only a trace of a dark-brown, amorphous solid.

Precipitation of the filtrate and acid-washings with an aqueous hydriodic acid-sulphur dioxide solution yielded 5.30 grams of diphenyl iodonium iodide. The actual yield, therefore, of iodonium salt from the reaction was 26% of the theoretical.

### (f) Summary of method.

It was apparent from the above iodylations with iodic acid that the main factors determining the yield of product were:-

(i) The strength of sulphuric acid employed; an acid was required stronger than that in which the reaction did not proceed at all and weaker than that in which the reaction tended to become violent and producing thereby a greater quantity of by-product or tar. In the case of chlorobenzene the final sulphuric acid in the reaction-mixture needed to be of composition about $2H_2SO_4.H_2O$, and at no time during the reaction could it become stronger than this without increasing the possibility of the production of more by-product. With benzene the final sulphuric acid had to be of composition

$H_2SO_4.1.25H_2O$ and never weaker than $H_2SO_4.2H_2O$.

(ii) The temperature-range of the reaction. Here again a suitable mean had to be struck between the temperature at which the reaction did not proceed and that at which secondary reactions became too pronounced. From the foregoing experiments it appeared that below $16^{\circ}C$ the iodylation of chlorobenzene was very slow, whereas above $24^{\circ}-28^{\circ}C$ the yield of iodonium salt diminished. In the case of benzene, however, the maximum temperature allowable appeared to be considerably below $10^{\circ}C$.

(iii) The benzene derivative used. Apparently, under those conditions employed, only certain derivatives of benzene could be iodylated. Of these, monohalogen aromatic compounds, that is, those containing an o-p-directing substituent, were iodylated with greater ease and larger yields than was benzene itself; there was, however, a limit to this type of derivative since the methoxy group, for example, appeared to be too highly activating, and with anisole the reaction was too vigorous to be controlled so as to yield an iodonium compound. On the other hand, tests suggested that nitrobenzene, containing an m-directing substituent, was not iodylated under similar conditions to those used for chlorobenzene.

3.    Analyses of the Products of Iodylation.

(a)  Di-p-chlorophenyl iodonium acid-sulphate.

(i)  Titration of free acid liberated in water.

A sample of the acid-sulphate crystals (0.4551 gram) was shaken with 25 c.c. of water;  the solid only partially dissolved, giving a pale-brown solution and a darkening of the undissolved particles.  Using methyl orange as indicator, the solution required 1.031 milliequivalents of N/10 sodium hydroxide, that is, one equivalent of alkali per 441.4 grams of the acid-sulphate.  The liquor now contained the normal iodonium sulphate and was treated with excess N/10 sodium hydroxide, boiled for half an hour to decompose the sulphate, cooled, and the excess alkali titrated against hydrochloric acid.    1.026 milliequivalents sodium hydroxide were used in the decomposition, or one equivalent per 443.5 grams of original solid. (Molecular weight of $(C_6H_4Cl)_2I.HSO_4$, 446.9.)

(ii)  Sulphate content.

To 0.6128 gram of the product was added 100 c.c. of a boiling solution of 2 grams of barium chloride in N/10 hydrochloric acid.  The mixture was boiled for 2 hours, the volume of liquor being kept constant and filtered hot.  After washing the white precipitate 12 times with boiling water it was oven-dried and ignited in a platinum crucible.  The weight of the precipitate was 0.3236 gram, which meant one sulphate equivalent per 441.9 grams of initial substance.

## (iii) Chlorine and iodine by Stepanow's method.

The method employed for formation of the alkali halogen
solution was similar to that used in Chapter Three. However,
because of the presence of both chlorine and iodine, the estim-
ation of halogens in this solution needed modification. Total
halogen was determined by neutralising an aliquot portion of
the alkaline halide solution with nitric acid, adding a known
excess of standard silver nitrate solution and weighing the
silver halide precipitated; by determining the amount of ex-
cess silver nitrate in the filtrate, the quantities of each
halogen present could be estimated. As a check on this result,
iodide in the solution was estimated separately by the use of
the fact that in sulphuric acid medium of suitable strength
acetone and iodine react to give iodoacetone (Dawson and Leslie, J.CS.
1909, 95, 1860)
An aliquot part of the halide solution was neutralised
with 7N sulphuric acid and excess acid added until the liquor
was about 5N; 30 c.c. acetone and 2 c.c. starch were added
and the solution titrated against N/10 sodium iodate. Near
the end-point the blue starch-iodide colour persisted and when
this disappeared the end-point was reached. Control determin-
ations showed that the method was very accurate and that a
sensitive end-point was obtainable. Results were as follows:-

Gravimetrically:

 1 gram-atom of halogen per 149.7 grams of solid;

 1 gram-atom of iodine per 450.0 grams of solid;

 1 gram-atom of chlorine per 223.9 grams of solid;

Iodate titration:

 1 gram-atom of iodine per 449.0 grams of solid.

### (iv) Iodonium content by precipitation of the iodide.

The method was similar to that used in the determination of the iodonium content of iodyl compounds in Chapter Three. The sample (about 0.5 gram) was weighed directly on to the sintered-glass filter, treated in situ with successive amounts of the ethereal hydriodic acid solution, washed acid-free with ether and dried to constant weight in vacuo. Assuming that the molecular weight of the iodide produced was 477, the results showed one gram-ion of iodonium per 443.7 grams of initial acid-sulphate.

### Summary of analyses of acid-sulphate.

|  | Per cent. | Required for $(C_6H_5Cl)_2IHSO_4$ |
|---|---|---|
| Sulphate $(SO_4)$ .......... | 21.48 | 21.73 |
| Iodine $(I)$ .............. | 28.39 | 28.27 |
| Chlorine $(Cl)$ ........... | 15.86 | 15.84 |
| Iodonium $(C_6H_4Cl)_2I$ ..... | 78.28 | 78.86 |

(b) Di-p-chlorophenyl iodonium iodide.

(i) Iodide ion by silver precipitation.

A weighed sample of the iodonium iodide was treated with 2 c.c. 2N nitric acid and 10 c.c. 0.15N silver nitrate solution; after warming on a water-bath for a few minutes the mixture was shaken for 24 hours and the silver iodide filtered, washed with water, methyl alcohol, acetone and ether, the latter solvents being used to rid the precipitate of iodonium nitrate which was found to be more soluble in methyl alcohol than in water. The silver iodide was dried firstly in vacuo and then in the oven at 105° to 110°C. Results showed one ionic iodine per 474.5 grams of iodonium iodide. (Molecular weight of $(C_6H_4Cl)_2I.I$, 476.8.)

(ii) Chlorine and iodine content.

The method was similar to that employed in the determination of halogens in iodonium acid-sulphate. The results obtained were as follows:-

1 gram-atom of halogen  per 120.4 grams of iodide;

1 gram-atom of chlorine per 240.8 grams of iodide;

1 gram-atom of iodine   per 235.0 grams of iodide.

(iii) Decomposition of iodonium iodide by dry heat.

0.72 gram of the iodide was weighed into a dry, stout-walled tube, 9 cm. long, the tube sealed and heated for 20 minutes in a sulphuric acid bath at 125°C. The iodide decomposed into a dark-brown oil which solidified to a mushy solid on cooling,

with a slight evolution of free iodine, sufficient to necessitate a recrystallisation of the decomposition product; this was done from ethyl alcohol, the solution being drowned with water and the colourless flakes filtered, washed with water and dried. The melting point of the crystals was $52.9^{\circ}C$, whilst mixed with p-iodochlorobenzene (of melting point $52.1^{\circ}C$) the mixture melted at $52.3^{\circ}C$.

A Stepanow determination of this decomposition product gave the following results:-

    1 gram-atom of halogen  per 119.6 grams of solid;

    1 gram-atom of iodine   per 240.2 grams of solid;

    1 gram-atom of chlorine per 238.2 grams of solid.

These values are in agreement with those required by p-iodochlorobenzene (molecular weight 238.4), and since m- and o-iodochlorobenzenes are both liquids, any mixture of the p-isomeride with these would be an oil. Apart, therefore, from a slight amount of elementary iodine, the sole decomposition product of the iodonium iodide was p-iodochlorobenzene.

### (c)  p-Iodochlorobenzene.

That solid which deposited from organic extracts of the main product and which had the appearance and smell of p-iodochlorobenzene, melted at $51.2^{\circ}C$, and when mixed with synthetic p-iodochlorobenzene had a melting point of $50.7^{\circ}C$.

4.   Some Properties of the Iodonium Acid-Sulphate in relation
to the Iodylation Process.

(a)  Iodonium acid-sulphate and sulphuric acid.

There was the possibility that the low yields of iodonium
compound in the iodylation reaction was due to the subsequent
decomposition of the acid-sulphate by the strong sulphuric
acid employed.  To test this, three samples of about one gram
of the acid-sulphate were dissolved in 5 c.c. of sulphuric
acid of the same strength as that finally obtained in the iodyl-
ation mixture, and the solutions treated in the following ways:-

(i)  Immediately diluted with water to a strength of 4N
and precipitated with aqueous N hydriodic acid.

(ii)  Wheeled for 24 hours in a sealed tube, stood for
3 days, diluted to the same extent as (i) and precipitated
with hydriodic acid.

(iii)  Warmed in a sealed tube at $60^{\circ}C$ for $4.^{1}/_{2}$ hours,
cooled and treated as before.

In all cases the solid dissolved to give a brown, clear
liquid and developed a smell of iodochlorobenzene not present
originally, this smell being strongest in tube (iii).   The
iodonium iodide in each case was filtered, washed acid-free
with ether, dried in vacuo and weighed.  Because of the solub-
ility of the iodonium iodide in water, a control precipitation
was needed of the acid-sulphate dissolved in 4N sulphuric acid.
The results were as follows:-

| Treatment: | i | ii | iii |
|---|---|---|---|
| Percentage iodonium recovered: | 98.50 | 96.87 | 96.97 |

There had been little destruction of the acid-sulphate by any of the treatments, and in two of these experiments the treatment was much more severe than in the actual iodylation process. It would appear, therefore, that the small yields obtained in the latter were not due to decomposition of the acid-sulphate by sulphuric acid.

### (b) Iodonium acid-sulphate, sulphuric acid and iodine pentoxide.

Since strong sulphuric acid alone was not responsible for the decomposition of iodonium acid-sulphate, the effect of sulphuric acid and iodine pentoxide together was examined. To two weighed samples of approximately one gram of the acid-sulphate were added 5.0 c.c. of the iodylating acid and 0.600 gram iodine pentoxide (this amount being the weight required in iodylation for the production of one gram of the iodonium salt). The treatment was similar to (ii) and (iii) above; in that mixture, shaken for 24 hours, there was no apparent usage of iodine pentoxide and no smell of iodochlorobenzene produced. After dilution to 4N, iodonium iodide was precipitated from the solution by reduction with sulphur dioxide and the precipitate filtered, washed acid-free with ether and weighed, 98.12% of the initial iodonium salt being recovered as iodide. After warming the second mixture in a sealed tube for 6 hours at 60°C, on opening the tube there was a violent blow-out of gas; therefore the test was repeated in an open tube leading to a saturated solution of baryta. There was a slow evolution of carbon

dioxide throughout the warming, together with the disappearance of some of the iodine pentoxide and the simultaneous formation of a slight amount of a cream-coloured solid which had the appearance of iodonium iodide and which did not dissolve on diluting the liquor to 4N. The iodonium iodide precipitated from the diluted liquor represented a recovery of 92.57%.

Here again the amount of acid-sulphate decomposed did not support any supposition that the cause of the low yields in iodylation was destruction of the products by the reagents used.

### (c) Solubility of the iodonium acid-sulphate in 6N sulphuric acid.

There had been no proof afforded that the substance in solution in the iodylation filtrate which, on addition of hydriodic acid, yielded iodonium iodide, was present as the acid-sulphate of the same iodonium base in this solution, and it was thought that light could be thrown on this matter by an estimation of the solubility of the acid-sulphate in an acid of similar strength to that from which the iodide was precipitated in a normal iodylation.

In a certain iodylation, which yielded 36.0 grams of iodonium acid-sulphate, the amount of sulphuric acid used was 3.78 grammols., and since the dilution was to 500 c.c., this means a final acid-strength in the filtrate of 6.0N. One gram of the crystals was shaken in 90 c.c. 6.0N sulphuric acid for 5 hours, the resulting suspension filtered through a dry glass

filter and 50 c.c. of the clear, pale-yellow filtrate treated with 10 c.c. N hydriodic acid. The iodide precipitated weighed 0.1948 gram, which meant a solubility of the iodonium acid-sulphate of 8.17 milligrammols. per litre of 6N sulphuric acid. The iodonium iodide precipitated from the iodylation filtrate was equivalent to 13.97 milligrammols. per litre.

There seemed to be evidence here of the iodonium in solution in the iodylation filtrate being of a different form from that deposited as acid-sulphate crystals; the possibility of this found further support when permanganate titrations of the filtrate were performed. (See section 5 of this chapter.)

### (d) Action of water on the iodonium acid-sulphate.

### (i) Change in iodonium content.

It had been observed from the beginning of these investigations that water in some manner decomposed the acid-sulphate crystals, resulting in a darkening of the solid. To each of three weighed samples of approximately 1.0 gram were added 30 c.c. water and the suspensions treated in the following ways:-

i.     Immediately ground with 10.0 c.c. N hydriodic acid and shaken for 42 hours to complete precipitation. The iodide was filtered, washed three times with minimal amounts of water, five times with ether, dried in vacuo and weighed.

ii.    Shaken for 24 hours with 30 c.c. water, which caused the development of a slight smell, possibly of iodochlorobenzene. Treatment of the product was similar to i.

iii.   Kept at 60°C for 6 hours and treated as before.

From the weights of the iodonium iodide precipitated, the following percentages of iodonium recoverable as such were calculated:-

| Treatment: | i | ii | iii |
|---|---|---|---|
| Percentage iodonium recovered: | (100) | 100.0 | 98.6 |

Thus, shaking with water for 24 hours has had no effect on the iodonium content of the acid-sulphate, whilst even warming the aqueous suspension to 60°C for 6 hours has not greatly reduced it.

### (ii)   Examination of the product of water-treatment.

It was found that grinding the acid-sulphate crystals with acetone cleaned them to a pale-cream colour without affecting the results of analysis of the solid.   The acetone-purified acid-sulphate was used in the following test.

9.55 grams of the solid were ground in a glass mortar with 100 c.c. water, causing an immediate change to a pale cocoa colour, but without the formation of any oil.   By the use of a further 80 c.c. water the contents of the mortar were removed to a flask and warmed for 15 minutes at 65°C.   After filtering, the solid was re-treated with water (150 c.c.) at 40°C for 5 minutes.   The filtrates were allowed to cool and deposited large, white, needle clusters, whilst vacuum distillation gave a further yield.   Because of the possibility of the acid-strength becoming too great, this distillation was not carried too far,

the iodonium salt still remaining in solution being precipit-
ated and weighed as iodide. The yields of solid, which were
thoroughly ground with acetone, were practically pure white
and weighed 8.08 grams.

The product of water-treatment of the acid-sulphate was
analysed as follows:-

### i. Sulphate content.

A barium precipitation of a solution of 1.1775 gram of
the solid gave 0.3449 gram (2.948 milliequivs.) of barium
sulphate; that is, there was one sulphate equivalent per
399.4 grams of initial solid.

### ii. Halogens by the Stepanow method.

The method was similar to that used in the analysis of
the acid-sulphate crystals, and gave the following results:-
Gravimetrically:

  1 gram-atom of halogen per 133.9 grams of solid;

  1 gram-atom of iodine  per 398.9 grams of solid;

  1 gram-atom of chlorine per 201.5 grams of solid;

Iodate titration:

  1 gram-atom of iodine  per 397.4 grams of solid.

### iii. Iodonium content.

By precipitation of a weighed sample of the solid with
ethereal hydriodic acid-sulphur dioxide solution, it was found
that 447 grams (the molecular weight of $(C_6H_4Cl)_2I.I$) of iodide
were obtained from 396 grams of the substance. On subsequent
grinding of this iodide with ether, however, it lost weight

slightly as though soluble to some extent; therefore a quant-
itative precipitation of the chloride was attempted by grind-
ing a weighed sample with successive amounts of a saturated
ethereal solution of hydrogen chloride until constant in weight.
Assuming that the chloride thus produced was $(C_6H_4Cl)_2I.Cl$,
the result showed one iodonium radicle per 397.8 grams of in-
itial material.

### Summary of Analyses of Water-Treated Acid-Sulphate.

|  | Per cent. | Required for $[(C_6H_4Cl)_2I]_2SO_4$ |
|---|---|---|
| Sulphate ($SO_4$) ......... | 12.02 | 12.06 |
| Iodine (I) ............ | 30.92 | 30.92 |
| Chlorine (Cl) ......... | 17.62 | 17.84 |
| Iodonium $[(C_6H_4Cl)_2I]$ ... | 87.71 | 87.69 |

Water, therefore, had decomposed the iodonium acid-sulphate
with the formation of the normal sulphate and free sulphuric
acid, thus:-

$$2R_2I.HSO_4 \longrightarrow (R_2I)_2SO_4 + H_2SO_4$$
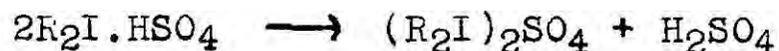
5.   Search for other products of the iodylation reaction.

Although it seemed possible to account for as much as 98%
of the initial iodide and 83% of the chlorophenyl groups in the
products of the iodylation, the yield of oxygen atoms was at a
maximum only one-third of the original.  It was necessary,
therefore, that systematic searches be made for products other
than those identified.

(a) <u>Barium precipitation of iodylation filtrate.</u>

After removing the iodonium salt in solution in an iodyl-ation filtrate with aqueous hydriodic acid, the liquor was ex-tracted with ether, neutralised with solid barium carbonate and filtered. In order to extract any barium sulphonate which might have been mixed with the precipitate, the latter was ex-tracted by boiling for $1.^{1}/_{2}$ hours with water and filtered hot; the filtrate from this, evaporated to dryness, left only a minute deposit of a mixture of barium carbonate and iodide. The main filtrate was clear, contained a small amount of barium and, on distillation <u>in vacuo</u>, left a residue of 0.5 gram of white needle crystals. These contained neither sulphur nor halogen, effervesced with hydrochloric acid, gave a barium sulphate precipitate with sulphuric acid and would not form a sulphon-chloride with phosphorus pentachloride; ignition of a weighed amount of the deposit with sulphuric acid proved it to be barium carbonate.

Thus this test suggested that none of the missing chloro-phenyl radicles was present as sulphonate.

(b) <u>Permanganate titrations.</u>

Because of the possibility of the formation in solution of oxidisable material, the action of permanganate on the prod-ucts of iodylation was studied. It was found in preliminary tests that a one-tenth aliquot of the second iodylation filtrate decolorised 2.6 milliequivalents of potassium permanganate,

both at 70°C and at room temperature. Most of the permanganate was used up very rapidly, although the reaction became slower and no definite end-point was obtainable owing to the slow usage of the oxidising solution. The liquor, which developed a smell of iodochlorobenzene during the titration, at first turned turbid and later deposited a white solid which melted at 45° to 53°C and which smelled of p-iodochlorobenzene. A control test done on a solution of 80 milligrams of iodonium acid-sulphate in 50 c.c. 2N sulphuric acid showed that such a solution used up only two drops of permanganate rapidly, although a further 4.7 c.c. were decolorised slowly.

Apparently there was some product present other than the iodonium salt in the iodylation filtrate, but because of the difficulty of obtaining a definite end-point, due to the slow usage of the permanganate, a series of titrations were done in which were recorded the times required for the decolorising of half c.cs. of the permanganate. Those solutions used in the series of titrations were:- (i) The iodylation filtrate, before and after benzene extraction; (ii) The iodylation filtrate after making just alkaline, benzene-extracting and reacidifying; (iii) Di-chlorophenyl iodonium sulphate of the same strength as (i) and (ii), made by shaking iodonium iodide (precipitated from the iodylation liquors) with silver sulphate; (iv) A similar strength of diphenyl iodonium sulphate prepared from the iodide and silver sulphate. The results, shown graphically, were as follows:-

Time (secs) for decolourising successive 0·5 c.c.
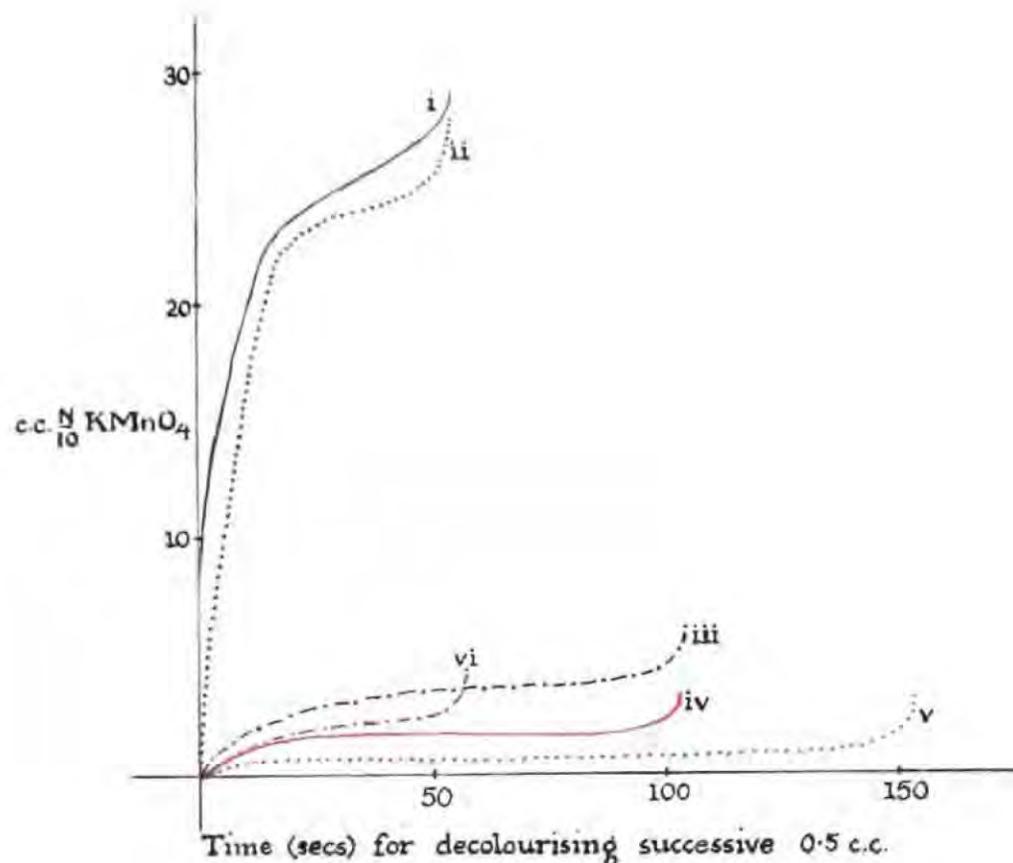
i.    10 c.c. iodylation filtrate + 10 c.c. 5N sulphuric acid.

ii.   10 c.c. iodylation filtrate, extracted twice with benzene,
      + 10 c.c. 5N sulphuric acid.

iii.  10 c.c. iodylation filtrate, made just alkaline, extracted
      twice with benzene, then made 5N sulphuric acid.

iv.   10 c.c. di-chlorophenyl iodonium sulphate of the same
      strength as i + 10 c.c. 10N sulphuric acid.

v.    10 c.c. diphenyl iodonium sulphate of the same strength
      as i + 10 c.c. 10N sulphuric acid.

vi.   Solution in 10N sulphuric acid of diphenyl iodonium
      sulphate equivalent to the total yield of iodonium salt
      in iodylation.

It was apparent from this series that there was present in

the iodylation filtrate some relatively strong reducing agent,

since the iodonium salt itself appeared to be only very slowly

destroyed by the permanganate. (Later, however, it was found that after further purification of the iodonium acid-sulphate by thorough grinding with acetone, a solution of it in 6N sulphuric acid was coloured a permanent pink with one drop of N/10 permanganate. A similar solution of pure normal iodonium sulphate, made by water-treatment of the acid-salt, also had no reducing power whatever.) An interesting fact was that after making mildly alkaline and benzene-extracting the iodylation filtrate, the residual liquor, on permanganate titration, gave results similar to those obtained for the iodonium solutions alone, due, apparently, to the removal of the oxidisable material. Neutralisation of the liquor had caused the formation of a dark-brown, tarry mass, probably decomposition products of the iodonium hydroxide, and washing of this with 5N sulphuric acid, with subsequent permanganate titration, showed that the reducing material was not extractable from this solid with acid; a suspension of the solid in sulphuric acid did not decolorise permanganate. The benzene extract of the alkaline liquor had no oxidisable substance in it. Apparently, making the iodylation liquor alkaline had totally destroyed the reducing agent.

A permanganate titration of a larger proportion of an iodylation filtrate showed that the iodonium acid-sulphate present was totally destroyed during the rapid decolorising of the permanganate. In contrast to this, wheeling overnight a solution of iodonium acid-sulphate in 5N sulphuric acid with excess permanganate did not decolorise the latter and, after reduction

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with sulphur dioxide, gave a copious precipitate of iodonium
iodide with aqueous sodium iodide.

100 c.c. of a saturated solution of iodonium acid-sulphate
in 9N sulphuric acid was added to 100 c.c. of iodylation filt-
rate (which alone would require 10.0 milliequivalents perman-
ganate) and half of the resulting solution titrated against
N/10 permanganate. 8.8 milliequivalents of the oxidising agent
were rapidly decolorised, and after extraction with ether, the
oxidised liquor had no trace of iodonium salt discoverable with
aqueous iodide. To a further 40 c.c. of the saturated acid-
sulphate solution was added excess permanganate; reduction
of a few c.c. of this with sulphur dioxide and addition of
sodium iodide gave a copious iodonium iodide precipitate.
Addition of 2 c.c. of the iodylation filtrate to the perman-
ganated acid-sulphate solution did not cause decolorising
even after two days. A solution was made containing one-
fiftieth of the total iodylation filtrate and one fiftieth
of the total yield of iodonium acid-sulphate from all sources.
This liquor, which was of the same acid strength as had been
used in the previous titrations, after shaking with excess
permanganate for $2.\frac{1}{2}$ hours still contained a large amount
of unchanged iodonium salt.

These tests indicate:- (i) As well as destroying that
iodonium acid-sulphate already present, permanganate destroyed
acid sulphate added to the iodylation filtrate; (ii) There
was a limit to the amount of iodonium salt destroyed by per-
manganate and this amount was less than the total yield of acid-

sulphate from all sources. It would appear, therefore,

i)   That the reaction was not an ordinary catalytic destruction, unless the catalyst in this case was one which was itself oxidised by permanganate;

ii)  That if the oxidation reaction was not a catalysis, then that material which was responsible for the disappearance of the iodonium salt from the liquor during permanganate treatment was not present in an equivalent amount to the total iodonium formed;

iii) That the destruction of iodonium in the iodylation filtrate was not necessarily due to its being, say, a 2-chlorophenyl, 4-chlorophenyl iodonium acid-sulphate, since the salt added and destroyed was proved to be the di-p-chlorophenyl iodonium compound.  Coupled with the study of the amount of iodonium in the iodylation filtrate, compared with the solubility of iodonium acid-sulphate in 6N sulphuric acid (section 4 (c) of this chapter), this test meant that the possibility of the  iodonium in the iodylation liquors being in a different form from that deposited as crystals could not be dismissed.

The low-melting solid which deposited during permanganate oxidation of the iodylation liquor, after recrystallisation from methyl alcohol, formed large, colourless plates which melted at $52.1^{\circ}C$, and a mixture of it with synthetic p-iodochlorobenzene had a melting point of $52.0^{\circ}C$.  One product of oxidation of the liquor was therefore p-iodochlorobenzene.

Permanganate titrations were attempted on the iodylation

liquor from which the iodonium salt in solution was removed; this latter was effected by precipitation with a slight excess of aqueous sodium iodide, the excess of which was in turn removed by shaking with solid silver sulphate. When this iodonium-free solution was used for titration against permanganate, it was found that oxidation was rapid and a definite, sharp end-point was obtainable, whilst the quantity of permanganate required was of a similar amount to that used for liquors in which the iodonium salt was present; for example, the liquors from an iodylation which had been performed with 25 millimols. iodine pentoxide and 100 millimols. chlorobenzene required, after the removal of the iodonium in solution, 25 milliequivalents of permanganate. 1.36 millimols. silver chloride was precipitated during this oxidation (silver sulphate having been added to the solution). Chloride was apparently, therefore, one of the oxidation products.

In the permanganate titrations from which the iodonium was removed, there was no sign of the formation of iodochlorobenzene, this product being formed, apparently, by decomposition of the iodonium salt in those titrations in which this was still present.

It was found that carbon dioxide was also a product of oxidation of the iodylation liquor. The amount of carbon dioxide evolved was estimated by the use of an apparatus similar to that described on page 122, except that the reaction tube was replaced by a flask holding a burette from which the permanganate was added.

Without removal of the iodonium in solution, it was found that the liquor (from 25 millimols. iodic acid and 48.5 millimols. chlorobenzene) decolorised rapidly 25.6 milliequivalents of permanganate with liberation of 7.88 millimols. carbon dioxide, and used up more slowly a further 5.5 milliequivalents of permanganate, which caused the evolution of 2.82 millimols. carbon dioxide. In a titration liquor from which the iodonium in solution had been removed a similar iodylation filtrate to the above required 25.5 milliequivalents of permanganate and evolved 10.12 millimols. of carbon dioxide. It would appear from these titrations that the carbon dioxide evolved did not come from the iodonium salt but from that substance responsible for the rapid decolorising of the permanganate.

Finally, a series of tests was done on small amounts of iodylation filtrate from which the iodonium salt had been removed by precipitation in turn with aqueous iodide, silver sulphate and sodium chloride. By permanganate titration it was ascertained that theoxidisable material i) was not extractable with benzene from acid or alkaline solution, ii) was not destroyed by boiling and did not steam-distil, iii) was precipitable with barium carbonate, the precipitate being insoluble in hot and cold water but soluble in hot 12N sulphuric acid.

Lack of time prevented further investigations of this reaction being made, and the data collected was insufficient to indicate the nature of the reducing material present in the

iodylation filtrate. It seemed not impossible that the sub-
stance causing the usage of permanganate was a chloro-derivative
of an unsaturated aliphatic acid (e.g. fumaric), formed by the
rupture of an aromatic nucleus. This would account for a large
proportion of the missing oxygen atoms.

### c) Carbon dioxide.

During the estimation of the carbon dioxide liberated in
permanganate oxidation of the iodylation liquors, it was dis-
covered that carbon dioxide was evolved during the iodylation
process itself. This carbon dioxide was determined in a similar
manner to that described in (b), an iodylation using 25.0 milli-
mols. iodic acid and 48.5 millimols. chlorobenzene yielding 4.00
millimols. carbon dioxide. The formation of this small amount,
therefore, must have been due to a very minor secondary reaction,
although the formation of carbon dioxide and p-chloroiodobenzene
in both the iodylation process and the permanganate titration
seemed to indicate that the secondary reaction in iodylation
and the permanganate oxidation were of a similar nature and
that possibly the latter reagent was finishing a process begun
by the iodic acid.

### (d)  Solvent-extractable material in iodylation liquors.

100 c.c. of an iodylation filtrate from a preparation in
which 0.10 mol. iodic acid had been used, was subject to an
exhaustive search for organic products soluble in benzene or
ether. The following scheme gives a summary of the tests:-

### 100 c.c. IODYLATION FILTRATE

Washed with 5 x 50 c.c. benzene

**Aqueous Liquor**
**Red-brown.**

**Benzene extract**
**vacuum distilled.**
**Negligible residue.**

50 c.c. for permanganate
titration

50 c.c. + HI.SO$_2$

Used 5 m.e. rapidly,
6.4 m.e. altogether.
Formed oily-solid

R$_2$I.I ground
with ether.

Filtrate
extracted
with
3 x 50 c.c.
ether

Oily solid 0.12 to
0.14 gram, was p-
iodochlorobenzene.

Aqueous soln.
+ HI gave no
sign of ppt.

Extracted with 2 x 50 c.c. benzene

Extract colourless,
distilled in vacuo,
no residue.

Aqueous liquor
colourless.
Extracted with
2 x 60 c.c. ether.

Extract colourless,
distilled in vacuo,
no residue.

Aqueous liquor
extracted with
2 x 60 c.c. CHCl$_3$.

Chloroform extract
distilled in vacuo,
no residue.

Extract yellow,
distilled in vacuo.
Few mgms. hair-
crystals, m.p. 47.5°.

Aqueous residue
extracted with
2 x 50 c.c.
benzene.

Extract yellow,
distilled in
vacuo. Very
slight residue
of brown matter
and fine hair-
needles.

Aqueous liquor
pale brown,
neutralised with
NaOH and made
just alkaline,
Still clear, ex-
tracted with 2 x
50 c.c. ether.

Extract colour-
less, distilled
in vacuo. No
residue.

Aqueous liquor still
brown. Extracted
with 2 x 50 c.c. benzene.

Extract colourless,
distilled in vacuo.
No residue.

(continued)

```
                    |
           _____/ _____
          /                   \
Aqueous solution        Extract colourless,
neutralised + sat.      distilled in vacuo.
NaHCO3 + standard          No residue.
iodine, no usage
    of latter.
```

Apart from the extraction of a little p-iodochlorobenzene, therefore, there is no organic product of iodylation extractable by the solvents used. In the permanganate titration also, the only organic oxidation product found was p-iodochlorobenzene, a decomposition product of the iodonium salt in solution.

### (e)  Analysis of undried iodonium acid-sulphate crystals.

Because of the possibility of vacuum-drying decomposing the initially formed buff-coloured crystals with the formation of iodonium acid-sulphate and some volatile product, a sample of the yield in an iodylation was analysed without drying, and the ratio of the percentages of iodine and chlorine compared with that from the analysis of the dried product. By this means it could be ascertained whether or not the initial substance formed was a tri- or tetra-aryl iodine compound, in which case the ratio of iodine to chlorine would be smaller than that in iodonium acid-sulphate. The results obtained were:-

One halogen  gram-atom per 189.8 grams of undried crystals.

One iodine   gram-atom per 570.8 grams of undried crystals.

One chlorine gram-atom per 286.6 grams of undried crystals.

Such a result means two chlorine atoms per one iodine in the undried product, the ratio required for the diaryl iodonium salt.

Also, a solution of the undried salt in 9N sulphuric acid

behaved towards permanganate as did the dried product.

6.   Iodylations with Iodine Sesquioxide.

Despite the 83% yield of iodonium derivative obtainable in the iodylation of chlorobenzene with iodic acid, it was found that this reaction was a secondary one, the iodic acid being reduced first at the expense of some of the chlorobenzene with the formation of iodine sesquioxide, this latter being the reagent responsible for the production of the iodonium salt.
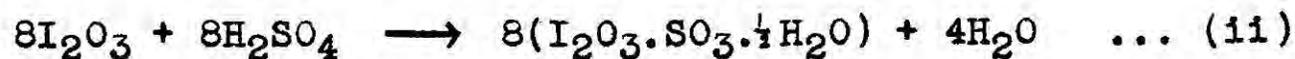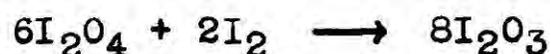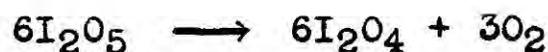
The preparation of iodine sesquioxide proved troublesome. Chrétien (C.r., 1896, 123, 814-816), following some work by Millon (Ann. Chim. Phys., XII, 336) found that sulphuric acid dissolves at $200^{o}C$ one-fifth of its weight of iodic acid and that heating such a solution to $250^{o}$ to $260^{o}C$ causes the evolution of abundant oxygen, whilst prolonged heating results in the production of iodine vapour and a darkening of the solution almost to black. After some days the cooled solution deposits yellow crystals which form slowly during several months; at the same time the mother liquor loses its colour. By analysis Chrétien found that the crystals could be represented by $SO_3.\frac{1}{2}H_2O.I_2O_3$. A less tedious method of obtaining these crystals is to acd an excess of iodine to a hot solution of iodic acid in sulphuric acid; the iodine dissolves with the formation of a dark solution from which the yellow sesquioxide sulphate deposits. Because of the slow formation of the yellow crystals, Chrétien (Ann. Chim. Phys. [VII] , 15, (1898) 358-432) suggested

that they are produced by slow reaction in the cold.
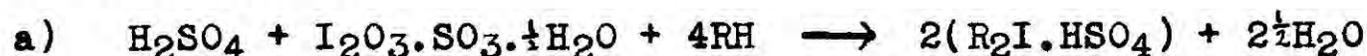
The ideal reaction can be expressed thus:-

$$6I_2O_5 + 4I_2 + 10H_2SO_4 \longrightarrow 10(I_2O_3.SO_3.\tfrac{1}{2}H_2O) + 5H_2O \quad \dots \text{(i)}$$
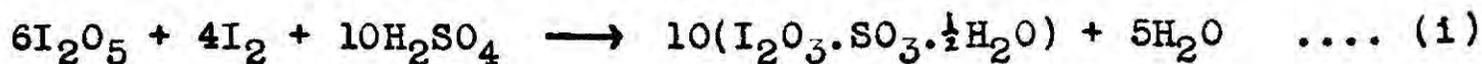
but here the unjustifiable assumption is made that no free oxygen is evolved. Possibly the reaction proceeds via the formation of $I_2O_4$, thus:-
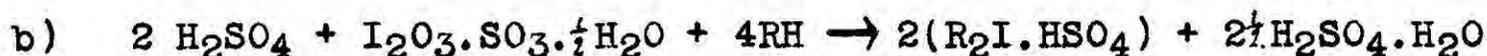
$$6I_2O_5 \longrightarrow 6I_2O_4 + 3O_2$$

$$6I_2O_4 + 2I_2 \longrightarrow 8I_2O_3$$

$$6I_2O_5 + 2I_2 \longrightarrow 8I_2O_3 + 3O_2$$

$$8I_2O_3 + 8H_2SO_4 \longrightarrow 8(I_2O_3.SO_3.\tfrac{1}{2}H_2O) + 4H_2O \quad \dots \text{(ii)}$$

The reaction between the iodine sesquioxide and the organic derivative being

$$I_2O_3 + 4RH \longrightarrow 2(R_2I.OH) + H_2O,$$

the complete equation for the production of the iodonium derivative is either

a) $\quad H_2SO_4 + I_2O_3.SO_3.\tfrac{1}{2}H_2O + 4RH \longrightarrow 2(R_2I.HSO_4) + 2\tfrac{1}{2}H_2O$

or

b) $\quad 2 H_2SO_4 + I_2O_3.SO_3.\tfrac{1}{2}H_2O + 4RH \longrightarrow 2(R_2I.HSO_4) + 2\tfrac{1}{2}H_2SO_4.H_2O$

the latter equation assuming that an acid of strength $H_2SO_4.H_2O$ is too weak to take part in the reaction.

The most effective method appeared to be to add the chlorobenzene to the cooled solution without separation of the iodine sulphate. Thus, if (i) worked wholly, the theoretical charge giving 10 grammols. of iodonium acid-sulphate would be:-

> 95% sulphuric acid ... 2000 c.c.
>
> Iodine pentoxide ..... 1002 grams.
>
> Iodine ............... 508 grams.
>
> Chlorobenzene ........ 2250 grams.

If the reaction proceed as in (ii), however, the charge required would be:-

> 95% sulphuric acid ... 1600 c.c.
>
> Iodine pentoxide ..... 1002 grams.
>
> Iodine ............... 254 grams.
>
> Chlorobenzene ........ 1800 grams.

with a theoretical yield of 8 grammols. of iodonium derivative.

Because preliminary tests showed that oxygen was evolved in the preparation, the second recipe was favoured, and attempts were made to prepare iodine sesquioxide by this method. 54.5 grams 95% sulphuric acid and 12.52 grams iodine pentoxide were heated together to $252^{\circ}$ to $255^{\circ}$C. Dissolution took 25 minutes, the liquor darkening from a pale yellow to a rich brown and oxygen being evolved throughout the heating. After 75 minutes' warming the evolution of iodine, which previously had been very slight, became heavy. The solution was cooled to $200^{\circ}$C, 3.18 grams of iodine added and reheated to $230^{\circ}$ for 5 minutes, after which the vessel was allowed to cool during 24 hours in a concentrated sulphuric acid dessicator. To 2 c.c. of the liquor was added 100 c.c. water; there was an immediate deposition of iodine crystals which were extracted with carbon tetrachloride and estimated against standard thiosulphate solution. The

aqueous residue was treated with sodium iodide solution and the iodine liberated thereby determined. The ratio  Iodine liberated from aqueous layer by iodide treatment : Iodine extracted by carbon tetrachloride was 12.1 : 1, whereas according to the equation

$$5I_2O_3 \longrightarrow 3I_2O_5 + 2I_2$$
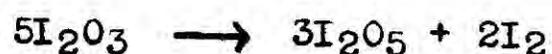
the theoretical value of this ratio is 9 : 1.  Apparently unused iodic acid (or iodine tetroxide) was present in the liquor. Other attempts were no more successful, whilst a preparation made from the charge required by equation (i) gave a ratio 14.2 : 1.

However, an iodylation, using the first sesquioxide preparation and 50 millimols. chlorobenzene showed that the reaction proceeded more quickly and more cleanly at $0^{\circ}C$ than did the iodic acid iodylations.  The acid-sulphate formed was cleaner than had been obtained in previous preparations using iodine pentoxide, and the amount of chloroiodobenzene produced was less than before.  A Stepanow analysis of the dried iodonium product showed it to be pure acid-sulphate.  It was interesting to note that, although the liquors from this iodylation decolorised permanganate slowly, the iodonium salt in solution was not destroyed thereby.  The yield in this iodylation, however, was only 64% of the theoretical.  The poor yield and the evidences of secondary reaction still remaining in the process were attributed to the presence of unchanged iodic acid in the initial reagent.

Finally, the yellow crystals of iodine sesquioxide sulphate which had deposited from all the attempts at its preparation were collected, washed with sulphuric acid and dissolved at 200°C in 140 c.c. concentrated sulphuric acid. Successive amounts of iodine were added to the solution until the ratio

$$\frac{\text{Iodine liberated in water}}{\text{Iodine liberated from iodic acid formed}} \quad \text{was} \quad \frac{1}{9.77}$$

Such a solution was used for an iodylation. A 94% yield of pure iodonium acid-sulphate was obtained, without the formation of chloroiodobenzene, and the acid liquors of the iodylation had no appreciable reducing properties when titrated against permanganate.

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