Chemical effects of nuclear recoil

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"CHEMICAL EFFECTS OF NUCLEAR RECOIL"

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being an account of work carried out at the Londonderry Laboratory for Radiochemistry, University of Durham, during the period October 1956 — July 1959 under the supervision of Mr. G.R. Martin, B.Sc., A.R.C.S., F.R.I.C., Reader in Radiochemistry.

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ABSTRACT

The investigations recorded in this thesis relate to a radiochemical study of the fates of iodine atoms recoiling after undergoing radiative neutron capture. Particular attention has been focussed upon mixtures of alkyl iodides, using the 'quasi-stable' fission product ^{129}I (1.72 x 10^7 y) to fix unequivocally the origin of the recoil iodine found in the products.

Techniques have been developed for the synthesis of methyl and propyl iodides labelled with ^{129}I on a micro-scale, and mixtures of these with unlabelled alkyl iodides have been irradiated in the Harwell reactor "BEPO". Other irradiations have been made with 14 MeV neutrons from the D+T reaction; with a Ra-α-Be neutron source; and with a 100 curie ^{60}Co source. Separation (by gas/liquid chromatography) and measurement techniques have also been perfected.

From a study of the distribution of the active iodine between methyl and propyl iodides it seems that the recoiling atom is more likely to appear as methyl than as propyl iodide. In the case of ^{130}I recoils this ratio is about 3:1, for ^{128}I it is about 1.8:1 and for ^{126}I (produced by n,2n reaction) it is about 2.2:1. The results can only be explained if it is also assumed that about 10% of the neutron captures (in ^{129}I) either do not result in bond

rupture or lead to an immediate recombination with the residue of the parent molecule.

The effect of γ-radiation (unavoidably present in neutron irradiations) on the exchange of iodine between methyl and propyl iodides, has been studied with the aid of ^{131}I, using a 100 curie ^{60}Co source.

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CHAPTER I

Introduction

When a nucleus captures a neutron, the compound nucleus formed becomes excited. In order to attain relative stability the compound nucleus either ejects a nuclear particle or dissipates the excess energy by the emission of γ radiation as one or more γ photons. This latter reaction occurs predominently with atoms of atomic weight greater than about 30, as the potential barriers tend to prevent the passage of charged particles. This reaction, whereby the nucleus captures a neutron and emits γ photons, is termed radiative neutron capture. The energies of the more energetic radiative neutron capture γ rays for a large number of elements range up to ≈ 7 Mev.

According to the principle of conservation of momentum a γ ray departing from a nucleus must impart to that nucleus a momentum equal to that of the photon. For γ ray energies of the magnitude observed, the recoil energies imparted to the nuclei are often many times those required to break chemical bonds. In order that an atom undergoing neutron capture be ejected from a molecule by γ recoil, the recoil kinetic energy of the atom must be greater than the bond energy of the chemical bond holding the atom in the molecule. The recoil energy will tend to propel the active nucleus in the opposite direction to the emitted γ quanta, and in doing so will exert a strain on its bonds.

Calculation of recoil energy

If thermal neutrons are used for the (n,γ) reaction, the momentum of the incident neutron is negligible and therefore the momentum of the γ quantum is balanced energetically by the momentum of recoil.

According to the quantum theory of radiation the energy of a γ quantum E_γ is equal to $h\nu$ where 'ν' is the frequency of the γ radiation and 'h' the Planck's Constant.

Since $h\nu = m'c^2$ where m' is the mass equivalent of the given photon, the momentum

$$P_\gamma = m'c = \frac{h\nu}{c} = \frac{E_\gamma}{c}$$

Assuming that the momentum P_γ of the γ photon is entirely balanced by the momentum P_M of the recoiling atom, the kinetic energy E_M of recoil of the nucleus

$$= \frac{1}{2} Mv^2 = \frac{P_M^2}{2M}$$ where M is the mass of the nucleus.

Since $P_M = P_\gamma = \frac{h\nu}{c}$,

$$E_M = \frac{(h\nu/c)^2}{2M} = \frac{(E_\gamma/c)^2}{2M} = \frac{E_\gamma^2}{2Mc^2}$$

By representing the energy of the γ quantum and the value of c^2 in electron volts,

~~$E_M = 5.36 \times 10^{-10} \frac{E_\gamma^2}{M}$ e.V.~~

$= \frac{536\ E_\gamma^2}{M}$ Mev. where M is represented in atomic mass unit.

The derivation shown above is made on the assumption that the entire energy is emitted as one γ photon only. If more than one γ photon is ejected in cascade or if two γ photons are ejected simultaneously in different directions, the recoil energy will not be as large as calculated above.

Since the energy of the γ quantum was found to vary between 1-10 Mev for various elements it was calculated that for an element such as Iodine the recoil energy E_M would be of the order of 5-300 ev and as the bond energies of carbon-halogen bonds in alkyl halides is of the order of 2 to 4 ev, bond rupture is expected in a large majority of cases.

However Suess (1) has indicated that only a part of this recoil energy would be available for bond rupture as some would be lost as kinetic energy transferred to the remainder of the molecule to which the active atom was attached.

According to this approach, the recoil energy will tend to propel the active nucleus in the opposite direction to the γ quanta, and in doing so will exert a strain on its bond. According to the direction of the exerted strain, the force on this bond will vary and the recoil energy will be transferred through this bond to the remainder of the molecule and converted into excitation or translational energy of the whole molecule. If the bond is strong and a sufficient quantity of the recoil energy can be transferred to the molecule so that the velocity of the recoil atom equals the velocity of the whole molecule, then the active nucleus will not break away. In such a situation the internal energy E_1, available for bond rupture is only the difference between the recoil energy of the free atom and that of the molecule

$$E_1 = E_M - E_{M-M'} = 536\ E\gamma^2 \left(\frac{1}{M} - \frac{1}{M + M'} \right)$$

$$= E_M \left(\frac{M'}{M + M'} \right)$$

where E_M is the energy of the recoiling atom.

Thus bond rupture might be relatively improbable when the active atom is attached to a very light atom (mass M') or group of atoms.

Chemical effects of nuclear recoil in alkyl halides

The chemical properties of recoil halogen atoms arising from (n,γ) reaction on halogens in organic halides have been extensively studied over the past twenty years. Because of the relatively simple chemical properties of the alkyl halides and because of the favourable nuclear properties of the halogens, investigations of the chemical reactions initiated by neutron capture in these compounds have proved to be particularly fruitful.

From the data on the strength of the C-Halogen bonds in alkyl halides, it seems that complete rupture of the C-Halogen bonds may be expected when alkyl halides are bombarded with thermal neutrons.

In 1934, Szilard and Chalmers (2) found that a fraction of the total number of radioactive iodine atoms produced by neutron capture in Ethyl Iodide could be extracted with water containing a little of Iodine as carrier. Since then it has been found that nearly 50% of the total activity could be extracted from the organic halide by various aqueous solutions. The remaining radioactive atoms are found organically combined and hence non-extractable.

Amaldi et al (3) as early as 1935 came to the conclusion that the ejection of a γ photon would cause a recoil which was sufficient to overcome the chemical binding forces and release the active isotope. Provided that the molecule was not reformed or that exchange did not take place with an inactive atom already bound, it was expected that the active atoms could be extracted.

Because energetic considerations indicate that nearly all the radioactive atoms formed should break the bond, several investigations have been carried out to determine the reasons for the observed activity in the organic phase.

Glueckauf and Fay in 1936 (4) showed that when Iodine in Methyl Iodide underwent the reaction $^{127}I(n,\gamma)^{128}I$, 44% of the radioactive iodine appeared in Methyl Iodide. They suggested that the ejection of the atom from the molecule, after recoil due to γ emission, occurred with such energy that it was capable of entering another molecule and becoming bound in such a way that repeated extraction failed to remove the atom and therefore it was permanently retained. Further, the appearance of nearly 11% of the active ^{128}I as CH_2I_2 when Methyl Iodide undergoes radiative neutron capture confirmed the view that the active Iodine recoiling out of the Methyl Iodide molecule was capable of breaking C-H bonds. It was later demonstrated that higher halides were formed not only from Methyl Iodide but also from many other aliphatic alkyl halides.

The effect of free halogen in the organic halide has a marked effect upon the fraction of total radio-halogen extractable into an aqueous phase. Several experiments using Iodine in organic iodides, and bromine in organic bromides have shown that there is an increase in the amount of inorganic activity extractable into the aqueous phase after irradiation. Halogens added for this purpose have been termed "Scavengers".

When gaseous alkyl halides undergo radiative neutron capture, it has been found that most of the radioactive halogen could be extracted out leaving only a fraction of the total activity in the organic halides. This seems to indicate that the efficiency of bond rupture following the nuclear process is high. Consequently it has been suggested that the retention of 30% or more normally observed in liquid phase reactions of the organic halides, result from re-entry of the recoil atom into organic combination.

Hence all the explanations so far put forward to explain the retention of activity in the organic phase after the (n, γ) reaction in liquid alkyl halides, have been concerned with the modes of re-entry of the highly energetic recoiling atom into the organic phase.

Libby's billiard ball hypothesis (5) assumes that the atom emerging from the molecule after recoil has a kinetic energy of the order of thousands of kilocalories/mole. The re-entry process consists of an essentially head on collision of the recoiling atom with a bound halogen atom. The radioactive halogen transferring its momentum nearly completely to the inactive atom and being itself left with a relatively small energy in the immediate vicinity of the free radical formed by the removal of the non-radioactive atom, both the free radical and the radioactive atom being contained in the same "solvent cage" and being free, recombine with a dissipation of their excess energy to the solvent through the "cage".

Substitution for hydrogen atoms in an organic halide, forming dihalides as experimentally observed, has been explained as occurring near the end of the range of the recoiling halogen atom where the energy is still somewhat larger than the chemical bond energy but not a great deal larger.

In this region, but not in the high energy region, the halogen atom may transfer energy to molecules as a whole in inelasticcollisions, with subsequent rupture of one of the bonds of the molecule resulting from vibrational excitation. If a hydrogen bond was broken in such a process, the halogen atom would be in the cage with the radical formed thus would have an opportunity to substitute for the hydrogen in reforming a stable molecule. Reactions of this type have been termed "epithermal" reactions in contrast to those occurring at higher energies.

In addition to these processes in the hot or high energy range and in the epithermal range, we may have reactions proceeding in the thermal range between the solution and those halogen atoms which do manage to enter the thermal range without chemical combination.

The "Random Fragmentation" hypothesis (6) postulates that the recoiling atom in a liquid or solid medium collides with molecules which are packed relatively tightly together and backed by a thick wall of other molecules. The result is that the energy is dissipated by breaking bonds in a rather indiscriminate fashion in the immediate vicinity of the energetic atom. When the energy of the atom has been reduced below bond breaking energies it will find itself in or adjacent to, a pocket of high local concentration of organic radicals and inorganic atoms. It may combine with one of these after it has been moderated to an energy where combination is possible but before it has had opportunity to diffuse in the system as a thermal atom. Alternatively after losing its energy, the active atom, together with some of the free radicals produced, diffuses into the surrounding liquid. After many collisions with solvent molecules these radicals might combine among themselves, or with the active atom, until the system becomes so dispersed by diffusion that the probability of such reactions is negligible.

If the atom enters stable combination immediately after its energy has been reduced below bond energies and before it has diffused in thermal equilibrium with the solvent, the process has been called a "high energy process" to distinguish it from the thermal processes which involve those atoms which reach thermal equilibrium before entering combination.

The "high energy processes" may be distinguished experimentally because they are temperature independent, are relatively insensitive to added reagents like free halogens which would inhibit analogous thermal radical reactions and, in the gas phase, are inhibited by the presence of inert gases which can thermalise the hot particle before it encounters a reactant molecule.

By contrast halogens greatly reduce the probability of thermalised radioactive atoms combining with radicals to form stable organic products. It does so by fixing the atom in inorganic combination and also by removing the radicals as explained below:

$$Br^{*} + Br_2 \longrightarrow BrBr^{*} + Br$$

$$R' + Br_2 \longrightarrow RBr + Br.$$

Halogens added for this purpose are called "thermal scavengers".

It has been demonstrated (7) that about 0.1 mole % of elemental Iodine present in ethyl iodide during neutron irradiation reduces the organic yield by about 15% of its value for the pure liquid but that a further eightfold increase in the halogen concentration reduces the yield relatively little. The basic notion is that the presence of a fraction of a mole % of free halogen can hardly affect the course of the hot and epithermal reactions and yet be quite sufficient to insure a short lifetime for radioactive halogen atoms as such in solution by exchanging the radioactive atoms into more abundant and non radioactive species. In addition, the use of molecular halogen will tend to reduce the concentration of free radicals produced by radiation decomposition by reacting with them so that the danger of radiation chemical effects should be considerably reduced. Of course, if large quantities of the free halogen are used in the system, the course of the hot and epithermal reactions themselves may be affected by reaction of the excited product molecules containing radiohalogen with the additive.

Levey and Willard (8) have studied in detail the effect of scavenger iodine in alkyl iodide systems during neutron irradiation. All the iodides tested showed a rapid decrease in organic yield at low iodine concentrations as the concentration of iodine present during neutron irradiation was increased. The process most sensitive to added Iodine and responsible for the sharp fall in the organic yield is essentially eliminated at a mole fraction of 0.01 or less. The ratio of iodine molecules to alkyl iodide molecules at this concentration is so low that the chance of a recoiling ^{128}I atom encountering an iodine molecule before becoming thermalised is nearly negligible. They conclude that the effect of Iodine in the low concentration region must be to reduce the organic yield by competing with processes in which ^{128}I atoms normally enter organic combination after they have been thermalised and undergone many collisions with molecules of the medium.

Levey and Willard (9) have also shown that (i) although the organic yield is reduced by nearly 15% by the presence of minute amounts of molecular halogen during neutron irradiation, a significant fraction of the tagged atoms which enter inorganic combination as well as those which enter organic combination does so by "high energy processes" and (ii) low concentrations of free halogen present in Methyl Iodide during neutron irradiation preferentially decrease the organic yield of the parent molecule relative to more complex products.

Reid (10) has observed that Iodine activated by (n,γ) process while in Pentane solutions can react to enter organic combination. Similar results have been found for bromine in Pentane (11) for Iodine in Hexane, Heptane and Octane, and for halogen originating from ethyl bromide and ethyl Iodide in Hexane (12) and in several other media.

In order to determine whether recoil Iodine can rupture C-H bonds, solutions of Iodine in liquid methane were irradiated with neutrons (13). Both Methyl Iodide and Ethyl Iodide were detected among the products of this irradiation.

According to Willard (14) this type of reaction is significant because it establishes the fact that an energetic heavy atom can cause the rupture of bonds in a molecule containing only light weight atoms. Such rupture must result from the inelastic transfer of energy to molecules rather than from a billiard ball type of transfer between atoms of approximately equal weight.

When a mixture of Iodine and gaseous methane was irradiated with thermal neutrons, nearly 45% of the activity was detected as Methyl Iodide (15). Willard concludes that the ^{128}I produced by the (n,γ) reaction in gaseous methane has the ability to undergo a reaction of the type $CH_4 + I \text{ —— } CH_3I + H$. This unique reactivity must be due to either the high kinetic energy of recoil of the ^{128}I or the positivecharge acquired as a result of internal conversion.

It has been suggested that a certain % of the γ rays ejected during the (n,γ) process in Iodine are internally converted thus giving the atom a positive charge. So far there has been no conclusive evidence to prove this and hence the effect, if any, of electrical charge of the atom on the surrounding molecules is not clearly understood.

Most methods of providing thermal neutrons for irradiations also generate γ rays and in some cases fast neutrons are present too. These radiations may produce ions, free radicals and, excited molecules in the medium.

In many studies of the radiative neutron capture type, it is essential to know with certainty whether the fate of any of the atoms activated by nuclear transformation is altered by these radiation-produced species. In alkyl iodides for example, the organic yield following (n,γ) reaction might be changed if such radicals reacted with either the activated atoms or with their stable products.

Various workers have made the observation that with Ra-Be neutron sources or with pile bombardments of moderate duration wide variations in γ intensity cause very little alteration in organic yields. However the effect of γ radiation on alkyl iodide systems can be put to test using a radioactive tracer like ^{131}I.

A striking demonstration that initial energy of the recoil particle does not influence its final chemical combination has been given by Schuler (16) who showed that ^{128}I and ^{126}I atoms produced in Methyl and Ethyl Iodides with kinetic energies in excess of 100,000 e.v by the $^{127}I\ (d,p)\ ^{128}I$, $^{127}I\ (n,2n)^{126}I$ and $^{127}I(\gamma,n)^{126}I$ processes give organic yields indistinguishable from those which have been observed for the same compounds with Iodine atoms of very much lower energy produced by (n,γ) process.

Measurements of partial γ ray spectra from radiative neutron capture have been made for several elements. Their energies could be measured by any of the following methods.

i. Measurement of the length of proton recoil tracks from the D(γ,n)H reaction in photographic plates soaked in Heavy water.

ii. Scintillation spectrometer, and

iii. Coincidence pair spectrometer.

In a majority of cases the spectrum has been found to be complex. The average number of γ rays emitted as a result of the (n,γ) process in the elements from $_{11}$Na to $_{72}$Hf varied from about two to six and was independent of neutron energy in the low energy region (17).

The Present Work

So far the general methods of approach to the problems of recoil studies of halogens in alkyl halides have been enumerated. The complexity of the chemical effects following neutron capture makes it difficult to understand the important steps in the recoil mechanism in the alkyl halides.

As has already been pointed out, Suess has shown by theoretical calculations that only a part of the total recoil energy would be available for bond rupture as some would be lost as kinetic energy transferred to the remainder of the molecule to which the active atom was attached.

The energy of recoil resulting from the emission of the γ quantum could be dissipated partially in the form of translational energy imparted to the whole molecule through the bond and partially as the recoil energy of the active atom provided bond rupture occurs. The extent to which either of these mechanisms predominates over the other depends on the strength of the bond, and also on the relative masses of the active atom and the remainder of the molecule.

Starke (18) calculated not only the recoil energy but also the proportion of this energy available for chemical dissociation for aliphatic organic halides. Thus in the case of Methyl Iodide with a γ ray energy of about 4 x 10^6 e.v. he found that the energy available for recoil was about 8 e.v. He argued that since the C-Halogen bond in Methyl Iodide is only about 2 e.v., rupture would occur in every case.

There were no methods of testing this reasoning experimentally and hence it has been assumed that bond rupture always occurs in Methyl Iodide when the Iodine undergoes radiative neutron capture.

The experiments detailed in the following pages were conducted to test this hypothesis.

If by some means we could identify those CH_3I molecules whose Iodine atoms undergo the (n, γ) process and show that the CH_3-I bond in them is not broken, our problem would be solved.

Consider Methyl Iodide labelled with a different isotope of Iodine than the normal ^{127}I. Mix it with a large excess of another Iodide, say Propyl Iodide, containing only the ordinary Iodine. If the new isotope of Iodine in Methyl Iodide is capable of underoing the (n, γ) reaction like the normal ^{127}I, then irradiate the mixture with slow neutrons, separate the two alkyl iodides and identify the new isotopic iodine and its distribution in them. By this means we would be able to get some idea as to what happens when iodine undergoes recoil due to γ emission.

An Isotope ideally suited for this purpose is ^{129}I which could be obtained from nuclear fission of natural Uranium (19). It is radioactive with an estimated half life of about 10^7 years. It can readily undergo radiative neutron capture giving ^{130}I which is also radioactive with a half life of 12.6 hrs.

Therefore if we take a mixture of Methyl Iodide and Propyl Iodide where Methyl Iodide alone is labelled with ^{129}I and PrI is in large excess, irradiate them with slow neutrons, separate the mixture and look for the 12.6 hr activity of ^{130}I in the two fractions of Methyl Iodide and Propyl Iodide, we would get usefulinformation.

Assume, for the sake of argument, that no bond rupture takes place when Iodine in Methyl Iodide undergoes radiative neutron capture. Therefore every ^{129}I in Methyl Iodide which undergoes the (n, γ) process producing the 12.6 hr ^{130}I, must be associated only with methyl groups. In other words all the 12.6 hr ^{130}I in the experiment above must be present only as Methyl Iodide and no such activity should be identifiable in the Propyl Iodide. On the other hand if the ^{130}I activity appears in the Propyl Iodide as well, it shows that bond rupture has taken place and the distribution of the ^{130}I activity would give information as to the extent of bond rupture in Methyl Iodide.

The pages which follow this will show how the ^{129}I was incorporated into the Methyl Iodide, how the mixture of Iodides was irradiated and separated and what the results of the experiments were.

CHAPTER II

Preliminary Experiments

Part I

The ^{129}I used in these experiments was obtained in this laboratory by extraction from the products of fission of natural Uranium (20). The total quantity of ^{129}I available was roughly estimated to be about 500 micrograms.

The solution of $^{129}I^-$ in about 50 c.c. was first oxidised using Sodium nitrite and dilute Sulphuric acid, and the molecular iodine extracted into carbon tetrachloride. This was reduced back to iodide using about 2 c.c. of sodium sulphite solution. When ^{129}I was required in the reduced form this stock solution was used. When molecular ^{129}I was required, it was obtained by heating precipitated Palladium Iodide (21). The procedure consisted in adding a dilute solution of Palladous chloride to the Iodide solution kept at about 70°C. when a thick black precipitate was formed. The precipitate was allowed to remain in contact with excess Palladous chloride for 48 hours before the precipitate was filtered. After washing the precipitate several times with warm distilled water it was dried under vacuum. The Iodine released by heating the Palladium Iodide under vacuum was trapped out using a liquid air bath.

Part II

Exchange of the Iodide radical between Methyl and Propyl iodides

For the success of the experiment with ^{129}I it is absolutely essential that the ^{129}I labelled in Methyl Iodide does not exchange with the Propyl iodide added to it. If it does exchange then the ^{129}I would appear in the Propyl iodide before neutron irradiation thus obscuring the purpose and results of the experiment.

In particular the Methyl iodide labelled with ^{129}I must be prepared without any ionising impurity present as otherwise, the ^{129}I would readily exchange with the Propyl iodide when added to it before irradiation.

Methods of labelling Methyl Iodide

The more common methods used for preparing Methyl Iodide can be adopted to prepare labelled Methyl Iodide.

(a) When Methyl alcohol reacts with red phosphorus and Iodine, Methyl Iodide is formed. Preliminary experiments suggested, however, that on a small scale (necessitated by the limited amount of ^{129}I available) it was difficult to separate the Methyl Iodide formed from the excess of reactants which were inevitably present in the mixture.

(b) Methyl Iodide could be obtained by the action of Iodine on methyl magnesium iodide.

$$CH_3MgI + I_2 \text{ —— } CH_3I + MgI_2.$$

Because of the side reactions associated with this process it was not pursued further.

(c) When Aluminium Iodide is treated with Methyl bromide, Methyl Iodide is formed by a substitution reaction.

$$AlI_3 + 3CH_3Br \rightleftharpoons AlBr_3 + 3CH_3I.$$

Because of the obvious advantage that this method did not involve any ionising impurity other than Aluminium iodide, it was decided to investigate this method in detail.

Aluminium iodide was first prepared by heating aluminium filings with Iodine obtained by heating precipitated Palladium Iodide. This was mixed in vacuo with Methyl bromide and kept overnight for completion of the reaction. Unfortunately it was found that the Methyl Iodide formed an addition complex with the excess aluminium halide present. The method was therefore abandoned.

(d) The problem was solved by simple exchange of Methyl Iodide with I^- in an ionising medium e.g. alcohol. In these experiments ^{131}I was used as the radioactive tracer because of its favourable nuclear properties and ready availability. The rate of exchange between Methyl Iodide and I^- is high in an alcoholic medium and takes no more than 30 minutes to reach equilibrium (22).

The alcohol and the associated impurities had to be removed before Methyl Iodide could be mixed with Propyl Iodide.

It is known that anhydrous Calcium chloride is as good an absorbent of water as of alcohol. Therefore it was decided to pass the Methyl Iodide-alcohol mixture through a column packed with fairly granular anhydrous calcium chloride. Since the quantities involved in these experiments were only about 0.2 c.c. it was obviously not possible to pour it down a column of Calcium chloride. Since both Methyl Iodide and alcohol were appreciably volatile at or above room temperature, it was decided to pass the mixture through in a stream of hydrogen.

A column of "anhydrone" was also attached to the system to remove any water vapour escaping capture in the Calcium chloride. A third column of activated alumina was incorporated at the end of the system to remove any other polar impurities finding their way in the hydrogen stream.

The apparatus used is illustrated in Figure (i):

About 0.2 gm. of purified Methyl Iodide was mixed with the calculated quantity of $^{131}I^-$ obtained as a carrier free solution from the Radiochemical Centre, Amersham. A few drops of alcohol were also added and the whole mixture was kept in a B.10 test tube for two hours to attain exchange equilibrium.

The tube was now connected to A in Figure I whilst D was cooled in liquid nitrogen in order to collect the

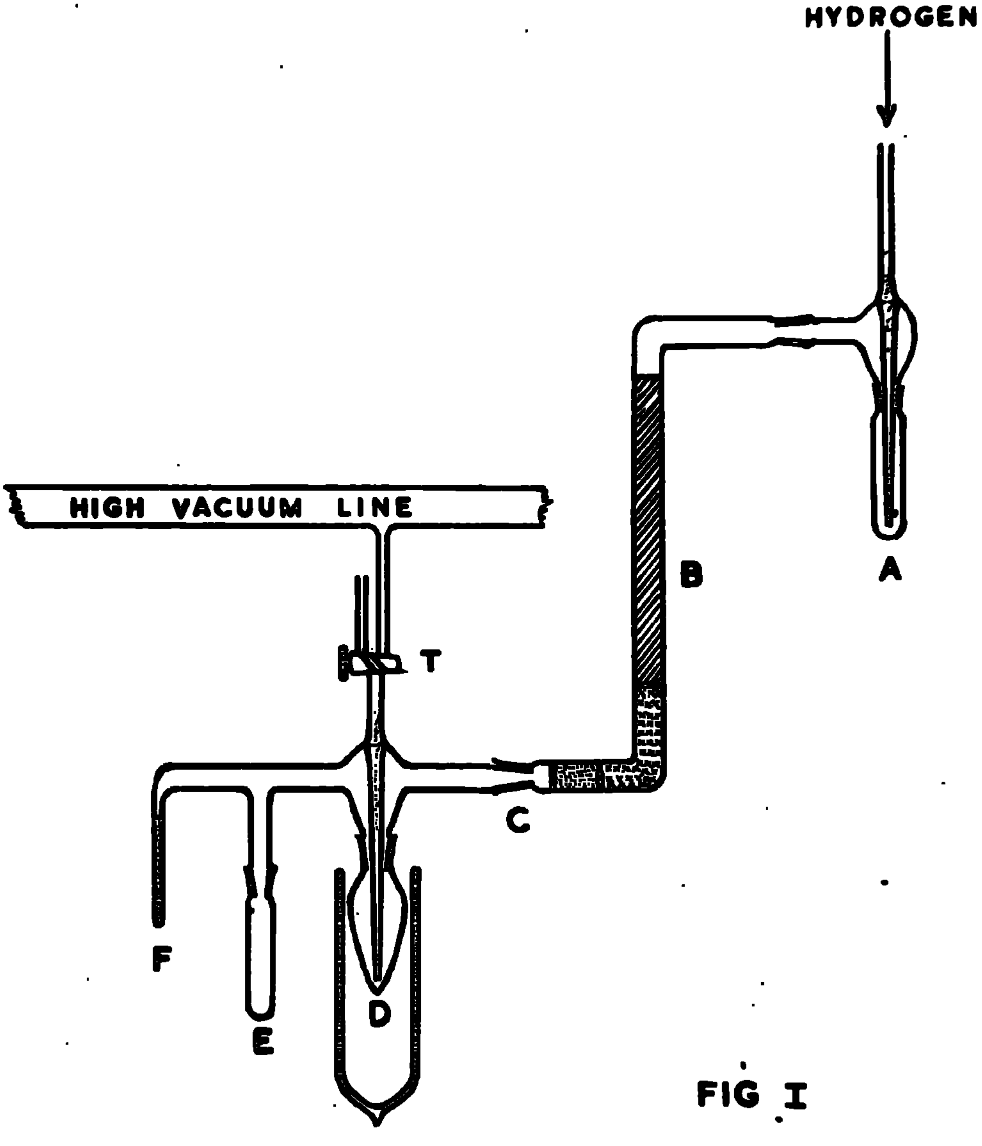

FIG I

Methyl Iodide. As the hydrogen bubbled through the solution it carried with it both Methyl Iodide and alcohol. The alcohol was absorbed by the Calcium Chloride while other polar impurities were removed by the Alumina.

To test whether the Methyl Iodide carried with it any ionising impurities, the column containing the absorbents was disconnected at C. A known amount of Ethyl Iodide was taken in the B.10 test tube E and connected to the system. Keeping both D and E in liquid nitrogen, the system was evacuated by connecting to the high vacuum line through tap T. Under vacuum, and with tap T closed, the Methyl Iodide in D was transferred to E by removing the liquid nitrogen trap in D. The Methyl Iodide-Ethyl Iodide mixture thus obtained was kept for six hours to make sure of any possible exchange in the presence of ionising impurities.

The mixture was now put through a gas chromatographic column and separated. The details of separation and the apparatus used are given in the next chapter. The Methyl Iodide and Ethyl Iodide fractions were collected in alcohol and the activity of ^{131}I in both fractions was measured using a thin walled liquid Geiger-Muller Counter. The amounts of Iodide present in each of the two solutions were estimated using a spectrophotometer. Chapter IV gives details.

If the Methyl Iodide contained any ionising impurity, it was assumed that the Ethyl Iodide would have also been active, due to exchange. The results of two independent experiments are in the table shown below:

Table I

Iodides used	App. Ratio of MeI: EtI by wt. of Iodine in the mixture before separat^{n}.		Activities as Counts/ Minute		Concentration in milligrams of Iodine as the Iodides		Activity/ mgm of Iodine as Iodide	
	Exp. I	Exp. II	Exp. I	Exp. II	Exp. I	Exp. II	Exp. I	Exp. II
MeI	1:1	1:2	12380	8404	22	13	563	646.4
EtI			108	51.1	19	11.4	5.6	4.4

It is quite evident from the lack of any appreciable activity in the Ethyl Iodide that the $CaCl_2.Mg(ClO_4)_2.Al_2O_3$ column completely holds back the ionising impurities.

Possible Exchange of Iodine between Methyl Iodide and Propyl Iodide in the absence of any ionising impurities.

MeI labelled with ^{131}I was prepared as above and was mixed with a known amount of purified Propyl Iodide and left in the dark for a week. If there was any appreciable exchange of ^{131}I between Methyl Iodide and Propyl Iodide, it was assumed, that it would appear in the Propyl Iodide which did not originally contain any ^{131}I. The Iodides were now separated using the gas chromatographic technique and their activities due to ^{131}I were determined. The quantities involved were also estimated using the spectrophotometer.

Table II

Iodides used	App. Ratio of MeI to PrI by wt. in the original mixture		Activities as counts/ minute		Concentration in milligrams of Iodine as Iodide		Activity/ Milligram of Iodine as Iodide	
	Exp. I	Exp. II	Exp. I	Exp. II	Exp. I	Exp. II	Exp. I	Exp. II
MeI	1:1	1:2	5417	3401	6.5	11.4	833	296
PrI			57.3	31.8	6.1	14.5	9.4	2.2

It was concluded that the effect of exchange in the dark was negligible.

Part III

Effect of γ radiation on exchange of Iodine between Methyl Iodide and Propyl Iodide in a mixture of the two Iodides

It is known that γ-radiation may induce and accelerate exchange reactions. Since the ultimate purpose of this study is to irradiate $CH_3{}^{129}I$ and C_3H_7I with neutrons in a pile it is pertinent to enquire whether the γ-radiation has any effect on the exchange of Iodine between the two iodides.

Methyl Iodide labelled with ^{131}I was prepared by the method mentioned before and the quantity was accurately estimated by transferring it under vacuum into a narrow side arm which was calibrated previously (F in Fig. I). The known amount of $Me^{131}I$ was mixed with a measured quantity of Propyl Iodide in the tube E in Fig. I.

The mixture was now sealed into six narrow silica tubes. The method of introducing the liquids into the silica tubes and sealing is given in detail in a later chapter. Of the six tubes filled, three were kept aside in the dark for the purpose of comparing results of the irradiated and unirradiated samples. The three tubes for irradiation were wrapped up in thin Aluminium foil and put into a standard Aluminium can used for irradiation by the Atomic Energy Research Establishment at Harwell. The Aluminium can was packed with cotton wool to keep the tubes from breaking.

The Iodides were irradiated in the thermal column of the pile BEPO for twenty four hours. The pile factor used was 0.5 [illegible] (i.e. 5 x 10^{10} n/cm^2/sec). The purpose of irradiation for such a long time was that when ^{129}I was to be used it would need about two half lives of irradiation to get enough activity of ^{130}I (12.6 hrs.).

On a rough estimate one can assume that the number of γ rays present in the thermal column of a pile like BEPO would be the same as the number of neutrons. Hence in the case cited here it would be about 10^{10} γ photons per second per square centimetre. Because of the distance between Durham and Harwell, it was about twelve hours before the irradiated iodides were available for separation, counting, and estimation.

Table III

Iodides used	Ratio of MeI to PrI by wt.	Without Irradiation			After Irradiation		
		Act. c.p.m.	Concentration in mgms.	Activity/ mgm	Act. c.p.m.	Concentration in mgms.	Activity/ mgm
MeI	1:9	2300	3.81	604	1733	2.02	854
PrI		38	117.5	0.3	61.5	59.6	1.04

The results were reassuring in that the effect of irradiation induced exchange was not appreciable.

Part IV

Purification of the Alkyl Iodides

It has been shown that impurities present in alkyl halides profoundly influence the organic yield in radiative neutron capture reactions (23). Since most alkyl Iodides are susceptible to both thermal and photolytic decompositions it is important that these iodides are thoroughly purified before using them for any irradiations. The common impurities in the commercially available Iodides are unsaturated hydrocarbons and their derivatives. The method given below was used to purify both Methyl and propyl Iodides.

The Methyl Iodide was first shaken with sulphur dioxide solution to remove any free halogen or hydrogen Iodide present. The Methyl Iodide layer was repeatedly washed with water and dried over magnesium sulphate. It was then distilled and the distillate coming over between 42° and 43°C. was collected. It was decided to purify this further. Keeping the Methyl Iodide cooled in an ice bath, dry ozonised oxygen produced from an ozoniser, was bubbled through for a sufficiently long time to ensure that all the unsaturated impurities had been ozonised. The Methyl Iodide was now vacuum distilled from a bath of freezing mixture at -10°C. when all the more volatile ozonides distilled off leaving behind most of the Methyl Iodide. It was now shaken in a separating funnel with Sulphur dioxide water to remove all the Iodine and any hydrogen Iodide still present. The Methyl Iodide layer was repeatedly washed with distilled water and dried over anhydrous magnesium sulphate. An 18" Vigreoux column was used to distil the Methyl Iodide and a 40% middle cut boiling not beyond 0.05°C. of the boiling point of Methyl Iodide (42.4°C.) was collected. As a further precaution the Methyl Iodide was poured down a column of activated alumina to remove any polar impurities. As a final check on the purity, the refractive index of the Methyl Iodide was determined using an Abbe' refractometer. The value was in excellent agreement with the values given in standard tables.

Because Methyl Iodide was sensitive to light, being decomposed readily, it was always stored in dark bottles and kept in a dark cupboard. Although the purified Methyl Iodide would remain pure for a long time, as a precaution it was always purified again if kept for more than four weeks.

In the case of Propyl Iodide, ozonisation followed by vacuum distillation and drying were all carried out as for Methyl Iodide. Because propyl Iodide had a fairly high boiling point (102°C.) and decomposed slightly near its boiling point, it had to be distilled under reduced pressure. It was usually distilled at a pressure of about 40 cms. and a 40% middle cut boiling steadily was collected. It was passed through a column of alumina and its refractive index checked. The result was satisfactory. Like Methyl Iodide, Propyl Iodide was always stored in dark bottles in dark cupboards and purified again if kept after four weeks.

CHAPTER III

Separation of the Alkyl Iodides

The volumes of mixtures of Methyl Iodide and Propyl Iodide used in the experiments recorded here were of the order of a fraction of a cubic centimeter. Good separation of the two iodides from such a small volume of the mixture by ordinary fractional distillation is extremely difficult and can be carried out effectively only by diluting the mixture with more of inactive alkyl iodides. This raises doubts about possible exchange during distillation and, more important still, reduces the specific activities of the irradiated iodides. Further, it is known that when alkyl iodides undergo radiative neutron capture reactions, new iodides are produced which would necessarily introduce difficulties in separation if the difference in boiling points of the iodides were not very different from each other. Thus, although there are several references in the literature where large volumes of irradiated iodides have been separated by fractional distillation, on a small scale the method may not be equally effective.

An ideal method for identifying and separating small concentrations of volatile compounds is the gas-liquid partition chromatographic technique. It was by this method that the alkyl iodides were successfully separated in this laboratory.

Gas-liquid partition Chromatography

The gas chromatographic technique depends on repeated distribution of the substances to be separated between the moving gas and the fixed phase packed into a column. In the case of gas-liquid partition chromatography, the fixed phase is a liquid held in an inert supporting material. The substances which are being separated move through the chromatographic column in the gas stream and are detected at the outlet by means of a vapour detector.

In the chromatographic apparatus used in this laboratory, oxygen-free nitrogen from a cylinder was used as the mobile phase. The flow rate of nitrogen at the inlet of the column was controlled by a flow meter and a constant pressure drop using a rotary vacuum pump at the outlet. The detection device used was a thermal conductivity cell.

Flow Control

Since the identification of the components in the gas stream is usually effected by measurement of their retention times, it is important to control the flow rate of gas through the column. This control may be obtained by maintaining a constant pressure drop across the column. In the apparatus described here, the inlet pressure of nitrogen was maintained at about the atmospheric pressure and controlled by a conventional capillary flow-meter illustrated

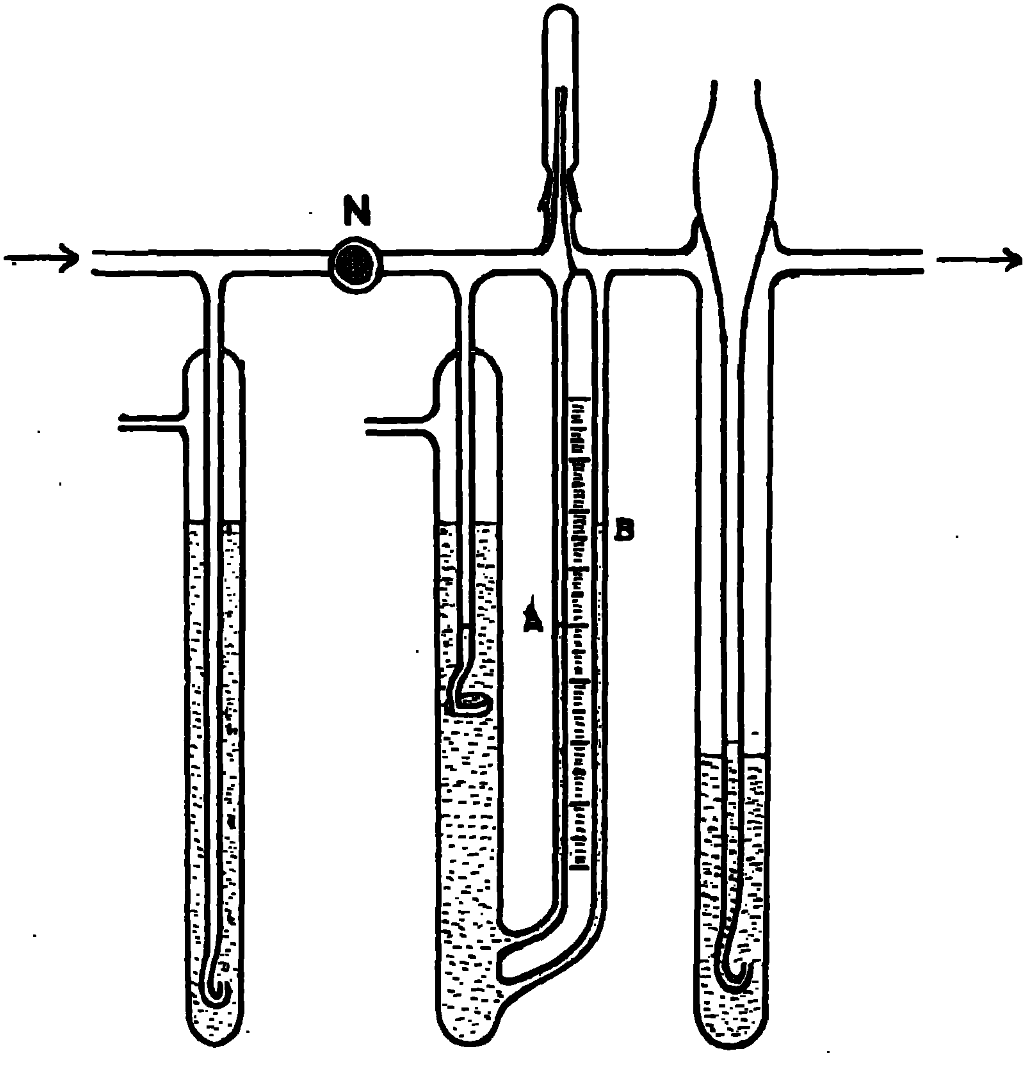

FIG II

in Fig. II. The gas was dried by passage through a column of silica gel before it entered the flowmeter. By adjusting the Needle valve 'N' the pressure difference in the arms 'A' and 'B' was kept steady. Obviously the pressure indicated by arm 'B' was the pressure at which the nitrogen was entering the column. This could be altered by turning the needle valve N.

The Fixed Phase

Among the fixed phases tried were Silicone Oil and dinonyl phthalate. A column carrying Silicone Oil was found to give quicker separation than one carrying dinonyl phthalate. However when the concentrations of the lower iodides like Methyl Iodide were appreciable, slight overlapping of separation peaks was observed whereas dinonyl phthalate gave a fairly rapid but clear separation of the iodides. Hence dinonyl phthalate was used in the column.

Celite 545 was used as the inert supporting material for the dinonyl phthalate. The Commercial Celite was size graded by suspension in water. The resultant material was heated in a muffle oven for about three hours at 300°C. and then washed with concentrated Hydrochloric acid to remove Iron and basic impurities. The Celite was now washed several times with distilled water to remove all the acid and dried again in an oven at 150°C.

The dried Celite was now mixed with dinonyl phthalate in the ratio, by weight, of 10:3. To ensure uniform distribution of the liquid phase over the inert support, a slurry was formed by adding excess ether and the whole was thoroughly stirred. All the ether had to be removed before packing the column. For this the porcelain dish containing the slurry was first kept stirring over a boiling water bath to remove most of the ether and later kept in an oven at 100°C. for 3 hours to make absolutely sure that all the ether had been removed from the mixture.

The Celite supporting the ester was now packed fairly tightly into a 5-foot U-shaped column. The diameter of the tube used was about 0.7 cms. To facilitate uniform and fairly tight packing, the column was agitated against the spindle of an electric motor. Since it was important that the column be packed uniformly every care was taken to see that no gaps were left in the column packing.

Since retention times are very dependent upon the column temperature, it was necessary to control this as precisely as possible. For this the column was mounted horizontally in an electrically heated jacket lagged ~~the~~ outside with asbestos sheathing. The heating was regulated through a "Simmerstat" control utilising a bimetallic strip.

The column was connected to the gas flow-meter at the inlet and the thermal conductivity cell at the outlet through hemispherical joints.

The detection system

Gas chromatographic separations are normally followed and recorded by means of some form of vapour detector, which is placed in the effluent gas stream from the column. The thermal conductivity cell which has been successfully used as a vapour detector consists of a hot wire held in the centre of a tube through which passes the gas from the column. The wire is heated by an electric current so that its temperature rises until a balance is reached between the input of electrical energy and the loss of heat energy. The hot wire acts as a resistance thermometer. It is incorporated in some form of Wheatstone bridge circuit, the battery providing the current for the bridge and for the heating of the wire. The off-balance of the bridge is thus a measure of the rate of loss of heat from the wire. Heat is principally lost by conduction by the gas to the walls of the tube.

At normal temperatures large molecules tend to have lower thermal conductivities than small molecules so that a gas vapour mixture has a lower thermal conductivity than has the gas alone. The relation between vapour concentration and heat loss (and hence off-balance of bridge) is effectively linear at moderate concentrations. Since the

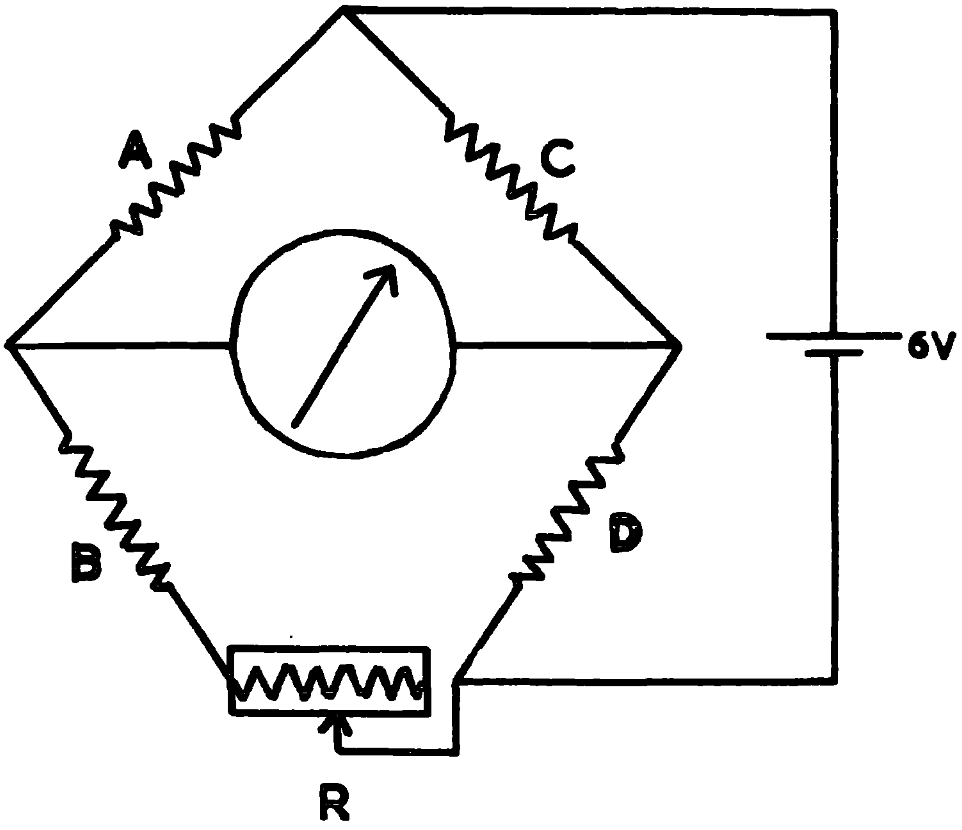

FIG III

rate of heat loss depends on the temperature of the tube walls, this must be kept as constant as possible. In order to overcome the effect of drift due to variation of temperature, 2 or 4 cells are usually fitted closely together in the same block and arranged in opposition in the Wheatstone Bridge circuit. The effluent gas from the flow-meter is first passed through the compensating cell or cells before it enters the column.

The Thermal Conductivity Cell made in this laboratory consisted of a solid copper cylindrical block into which 4 parallel holes were drilled. Into each of the chambers a Nickel wire of about 0.001 inches diameter was stretched and the two leads from each wire were connected through glass seals to the Wheatstone bridge, as illustrated in Fig. III. The gas inlets and outlets to the two sets of cells were through horizontally drilled holes. All the four cells were kept vacuum tight by sealing them with wax. Cells 'A' and 'B' were connected to the gas stream from the flow-meter while cells 'C' and 'D' received the gas stream from the column.

Gas Regulator at the outlet

Since a pressure drop across the column was kept by using a rotary pump at the outlet, a regulator was necessary to maintain this at a steady level. The device used is illustrated in Fig. IV. The gas stream from the

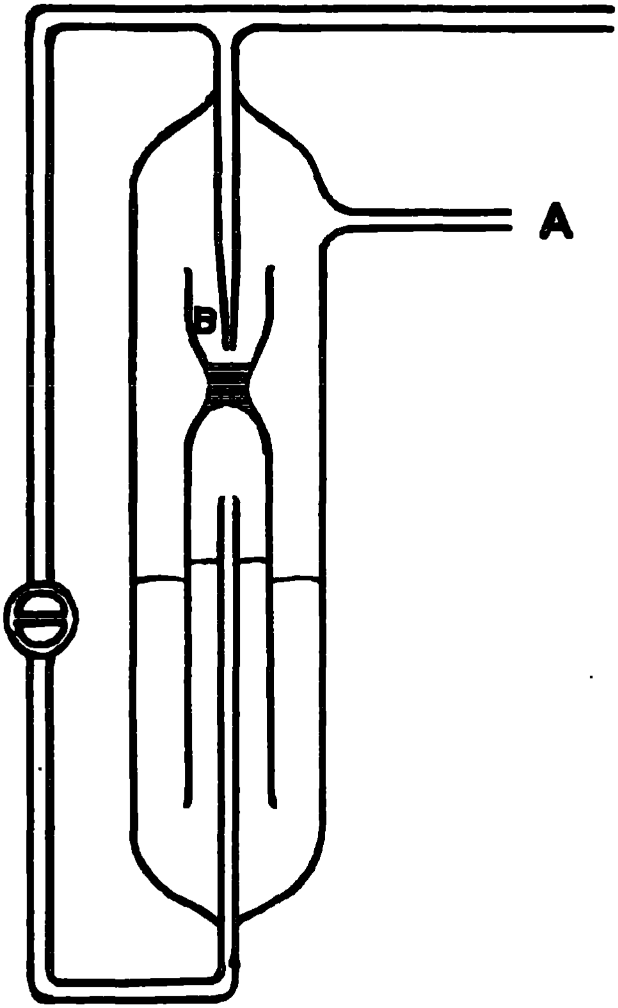

FIG IV

column, after passage through the thermal conductivity cell, enters the regulator at 'A' and escapes through the capillary 'B' to the pump.

With the stopcock open, the system is evacuated to very nearly the desired pressure as indicated on a Mercury manometer and the stopcock is closed. Thus the gas trapped inside the regulator is used to control the flow of gas through the capillary. As evacuation continues, the pressure in the inner chamber increases relative to the pressure in the outer chamber and raises the floating bell until the disc (a rubber bung) closes the exhaust port to stop further reduction of the pressure in the system. When the pressure increases in the outer chamber, mercury rises into the floating bell thus providing extra space for the gas to expand until the pressure becomes the same as the trapped gas. Thus by the rising and falling of the floating bell the pressure is maintained at a steady level. In fact the float takes up a steady position with just the right flow through.

Method of Collecting the separated fractions

Fig. V illustrates the arrangement used for collecting the separated fractions.

Since the separated iodides are being carried in a stream of nitrogen, if the out going gas stream from the detector is cooled sufficiently one would expect to freeze

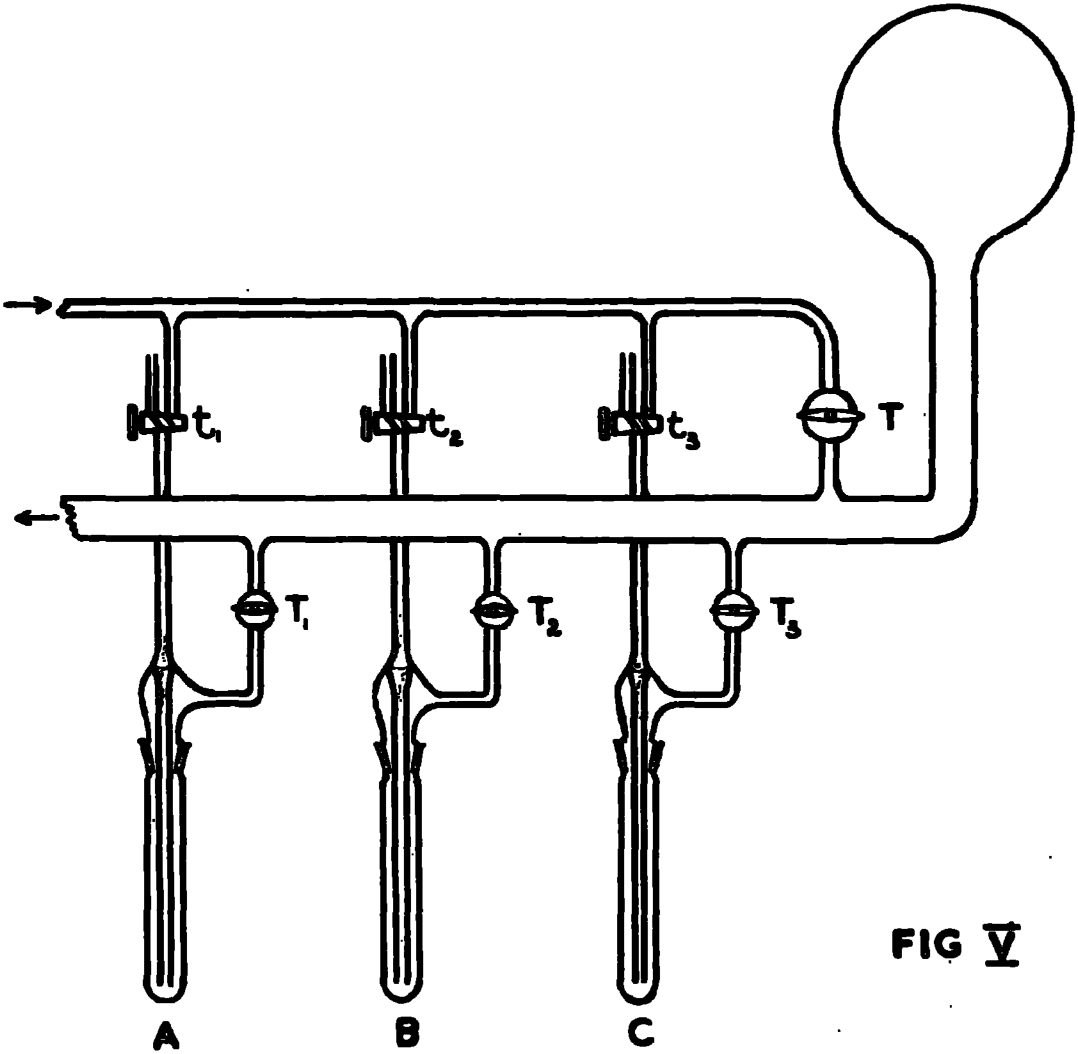

FIG V

out the iodides. However it was found that, unless a large surface was provided, much of the small concentration of the separated compound in the effluent gas escaped condensation and passed on. To avoid this the gas was bubbled through a solvent in which the iodides were soluble. Alcohol was chosen as the solvent to collect the iodides and since it had an appreciable vapour pressure at room temperature, and at the low pressure used it had to be cooled in a bath of solid CO_2.

In a typical experiment, B-14 test tubes containing about 8 c.c. each of pure alcohol were attached at 'A', 'B', 'C' etc. and they were externally cooled in a bath of acetone or alcohol kept at about -60°C. by the addition of solid CO_2. Keeping the tubes cooled, taps T_1, T_2, T_3 etc. were opened to the system to unify the pressure in the tubes with that in the system. When an iodide was due for collection, as indicated by the deflection on the galvo, taps 't_1' and 'T_1' were opened to the system and the main tap 'T' closed. Since the gas must bubble through the alcohol in the B-14 tube, any iodide carried in the stream of nitrogen was dissolved in the alcohol.

The sample introduction system

An ideal injection device for gas chromatography should possess the following characteristics:-

i. The entire sample should be delivered to the inlet of the column as a vapour over a short time interval.

ii. The introduction of sample should not necessitate stopping or changing the flow-rate of carrier gas, and

iii. The quantity of air introduced with the sample should be minimal. The normal injection method of a sample into a column is to use a microsyringe and a syrum cap to inject through.

As has already been pointed out, the quantities of sample used for separation in the experiments recorded here, were of the order of a few milligrams. It was noticed that there was a lot of waste due to wetting the sides of the syringe. Hence a new method of introducing the liquids into the stream of nitrogen was devised. The iodides to be separated were transferred under vacuum to an injection cell of design shown in Fig. VI. Now nitrogen (from the same source as the effluent gas) was let into the system at about atmospheric pressure and the cell was sealed off. Now it contained the material to be used in the column and nitrogen at slightly higher pressure than at the inlet of the column.

The cell was now attached to the inlet of the column as shown in Fig. VII. When the system had been stabilised as shown by the steadiness of the spot of the galvanometer, the handle 'H' was turned when the fragile tip of the cell

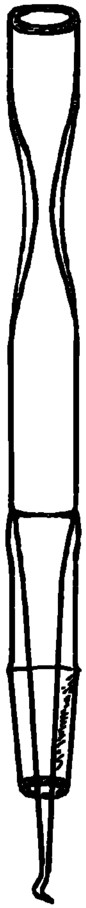

FIG VI

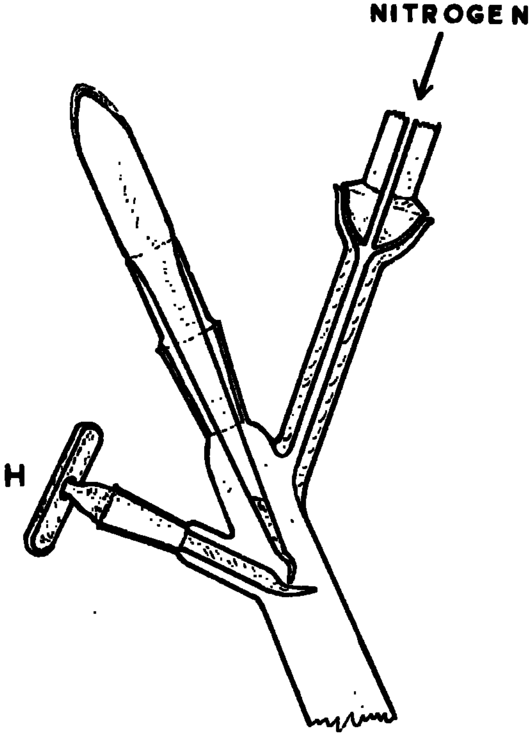

FIG VII

was broken and the iodides were pushed into the system by the pressure of the nitrogen in the cell. This method was found to be the most satisfactory of all methods tried.

Details of a typical experiment

The inlet pressure of nitrogen of the column was kept at atmospheric pressure. The temperature of the column was maintained at 105°C. and the pressure at the outlet was 16 cms. Hg. The current to the thermal conductivity cell was switched on at least one hour before the actual experiment to avoid any drift. By adjusting the variable resistance the spot of the galvo was moved to a fixed point which was taken as the zero point when no vapour was in the system.

The injection cell containing the iodide was put into position and the system allowed to settle down for ten minutes to ensure that all air had been carried away. This was indicated by the return of the spot of the galvo to the zero point. Since the identification of the material depends on the retention time, it is identified by the time taken for it to deflect the galvo spot. Therefore, simultaneously with the tip of the cell being broken by turning the handle, a stop watch was started.

A mixture containing Methyl Iodide, Vinyl iodide, Ethyl Iodide, Isopropyl Iodide, normal propyl iodide and methylene iodide gave the chromatogram shown in Fig. VIII.

CHAPTER IV

Removal of Inorganic Iodine before separation of the Alkyl Iodides

Since it was known that at higher temperatures, the exchange of iodine in alkyl iodides was appreciable, it was desirable to remove the inorganic iodine formed by the Szilard Chalmers' Process in alkyl iodides before the iodides were put through the hot gas chromatographic column for separation. By this means any possible exchange of the molecular iodine between the iodides in the 100°C. gas chromatographic column would be avoided.

Preliminary experiments indicated that the often used removal of the inorganic iodine with sulphur dioxide was inconvenient when small volumes of the iodides were involved. Chromatographic alumina was found to be an ideal adsorbent for iodine (24). As in the purification of labelled Methyl Iodide, the irradiated iodides were passed in a stream of hydrogen over chromatographic alumina. The apparatus used is illustrated in figure IX.

The silica tubes containing the irradiated iodides were introduced at 'A' after cutting their tips off. Cooling 'A' in liquid air, the system was evacuated through tap T_1. Keeping the tap T_1 closed, the iodides were transferred to 'B' by cooling 'B' in liquid air instead of 'A'. After removing the liquid air trap, the tap T_1

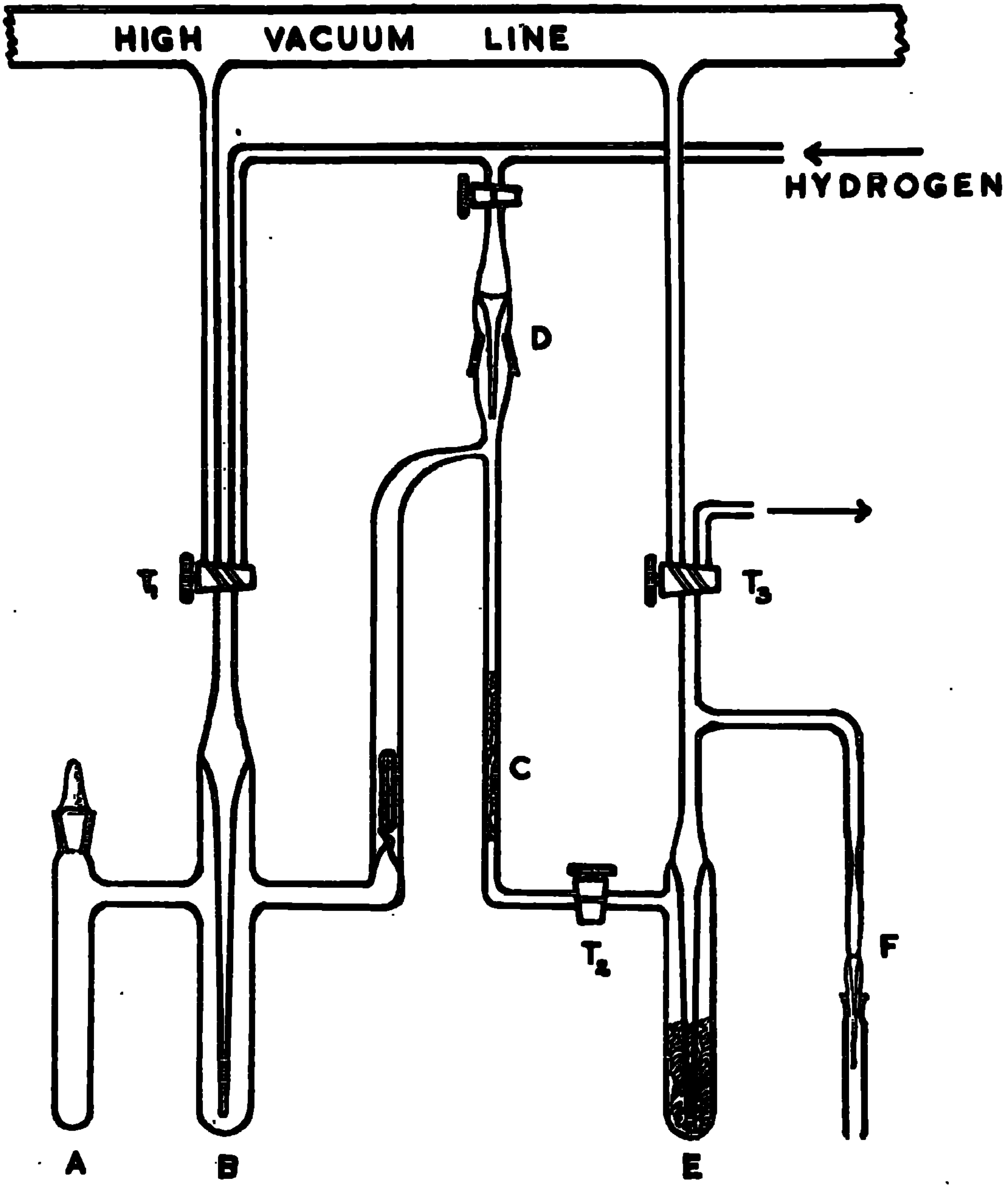

FIG IX

was turned appropriately to connect it to the supply of pure dry hydrogen. The break-off seal was now broken by dropping the iron rod (encased in glass) with the aid of a magnet. And the hydrogen stream was allowed to pass through the alumina in the narrow tube at 'C'. The condenser 'E' containing Fenske helices was cooled in liquid air to enable the iodides to condense in it. The stream of hydrogen after passing through tap T_2 and the condenser escaped finally through the tap T_3.

When all the iodides had been swept away by the hydrogen the tap T_2 was closed and keeping the condenser 'E' in liquid air, the system was evacuated through the tap T_3. Keeping T_3 closed the injection cell 'F' used for separation by gas chromatography was cooled in liquid air instead of the condenser when all the iodides were transferred into the cell. Nitrogen used as carrier gas in the gas chromatography column, wasxadmitted to the system through tap T_3 and the cell was sealed off.

In figure IX a secondary hydrogen entry system is shown at 'D'. The purpose of this was to remove any water adsorbed on the alumina before the iodides were passed over it. Without opening the break-off seal, hydrogen was allowed to pass through the alumina for at least one hour and when the condenser 'E' was kept cooled in liquid air, all the water escaping from the alumina was condensed in it.

This was later removed by evacuating the system through tap T_3.

Quantitative estimation of the Alkyl Iodides

In order to determine the specific activity of any material, its activity as well as its concentration must be known. Therefore in the study of the chemical effects of recoiling iodine atoms in alkyl iodides, it is necessary to determine the concentration of the iodides present. It has already been indicated that the quantities of alkyl iodides involved in the experiments recorded here, were of the order of a fraction of a cubic centimeter. An accurate method of estimating such small concentrations of an iodide in a suitable solvent is that using absorption spectrometry. An ultra violet spectrophotometer was successfully used to estimate the concentrations of the alkyl iodides.

The Unicam Sp 500 Spectrophotometer consisted of a light source, (a hydrogen lamp in this case) a quartz monochromator, a sample holder and phototubes and an amplifier to measure the intensity of radiation (25). The wavelength at which the absorption was maximum for the lower alkyl iodides in alcohol was found to be 256 $m\mu$. Values of optical density for various concentrations were plotted for Methyl Iodide and Propyl Iodide in alcohol and a straight line graph as shown in figure X was obtained. By referring to the graph the concentration of the iodide in a solution of alcohol could be determined.

Measuring the radioactivity

In order to measure the radioactivity associated with the irradiated alkyl iodides, an alcohol-quenched Geiger-Müller liquid counter was used. A measured volume of the solution to be 'counted' was transferred to the counter and it was lowered into the lead castle. The associated equipment necessary for measuring the activity, consisted of a probe unit type 110A with a paralysis time of 500µ secs, a potentiometer unit type 1007 and, a scaling unit type 1221C.

In practice the alkyl iodide whose activity was to be measured was diluted to 10 c.c. in a standard volumetric flask by the addition of alcohol. From this flask 9 c.c. were transferred to the counter. To attain a reasonable statistical accuracy — i.e. low standard deviation — the counting was continued wherever possible until the total was in the region of about 10,000. Appropriate corrections were also applied for loss due to decay during the period of counting. When several activities were counted, all the values were corrected for comparison at a standard time. When the rate of counting was high correction for dead time of the counter (500µ secs) was also applied.

When solutions of varying densities were used for measuring the radioactivity, a correction had to be applied for the effect of the differences in density of the medium (26). The correction factor is not a smooth function of the density of the liquid when widely differing media are involved. But it is a smooth function of the electron density of the medium. In order to determine the correction for differing electron densities of media, the following experiment was conducted.

Radioactive CH_3I^{128} was prepared by refluxing for ten minutes, 10 c.c. of CH_3I with alcohol and $^{128}I_2$ obtained by the Szilard-Chalmers reaction in about 200 c.c. of Methyl Iodide. By adding water to the mixture the Methyl Iodide was separated and it was washed and dried with magnesium sulphate. From this stock volume of active Methyl Iodide, known volumes were mixed with n-pentane, chloroform, alcohol and Methyl Iodide. Four solutions of each solvent having a range of known density differences were made and each one of them was counted. After correcting for decay and dead time a graph was plotted between counting yield (as c.p.m.) and electron density for each solution. A straight line graph as shown in figure XI was obtained using which the correction for density difference in any solution was applied.

CHAPTER V

CHAPTER V

Recoil Studies with Iodine-129

$Me^{129}I$ + PrI Experiment

Methyl Iodide labelled with iodine-129 was prepared by the method mentioned in Chapter II and the quantity was accurately estimated by using the calibrated narrow side arm in fig. I. The known amount of Methyl Iodide-129 was mixed with a measured excess of Propyl Iodide in the tube E in figure I. In order to seal this mixture in silica capillary tubes for irradiation, the tubes were put into the tube E with their open ends dipping in the mixture. After freezing the mixture in a liquid air bath, the system was thoroughly evacuated and the tap closed. The liquid air bath was removed and the frozen mixture allowed to thaw. When dry air was let into the system through the tap, the mixture rushed into the silica capillaries filling them. By keeping the contents frozen each silica tube was sealed. The tubes were wrapped in aluminium foil and placed in a standard aluminium can.

The Iodides were irradiated in the thermal column of the pile BEPO for 22 hours at a pile factor of 0.3 (i.e. 3 x 10^{10} n/cm^2/sec). By the time the iodides were available for analysis, all the ^{128}I activity had decayed completely. One of the irradiated tubes was used to determine the total activity. The inorganic iodine from the irradiated mixture was removed before separation by passing the mixture over alumina, as detailed in Chapter IV. The Methyl Iodide and Propyl Iodide fractions were collected by gas chromatographic separation and their activities measured. The concentration involved was determined, as already indicated by spectrophotometry. In order to ascertain the mode of decay and hence to confirm the isotope present, the decay of the iodides were followed at constant intervals.

Several independent experiments were conducted by varying the proportion of Methyl Iodide to Propyl Iodide. The following table gives the results of these experiments:-

Table IV

Expt. No.	Ratio of MeI to PrI in the Mixture in terms of Iodine content.	Activity of the untreated mixture as c.p.m. per mgm. of Iodine content.	Activity of MeI as c.p.m. per mgm. of Iodine content.	Activity of PrI as c.p.m. per mgm. of Iodine content.	Organic yield.	% of MeI Activity	% of PrI Activity	Ratio of $\frac{\text{MeI}}{\text{PrI}}$ Activity	Ratio of $\frac{\text{MeI}}{\text{PrI}}$ Specific Activity	Remarks
i	1:8	381.7	832.0	165.3	62.7	24.23	38.47	0.6297	5.033	In presence of air.
ii	1:12.8	91.2	287.1	36.67	63.2	26.40	36.8	0.7150	7.82	In presence of air.
iii	1:5.82	453.0	1347.0	266.1	76.2	35.46	40.74	0.8703	5.065	In the absence of air

(a) The concentration of the untreated mixture was determined by first removing the inorganic iodine with silver powder and then estimating its concentration by the spectrometer, knowing the ratio of Methyl Iodide to Propyl Iodide it was possible to calculate the concentration of the mixture in terms of iodine content.

(b) Organic yield here is meant as the total % activity of MeI and PrI alone - ignoring the fractions of activities of other products of recoil reaction.

Conclusions from these experiments:-

In the first place it was confirmed that there was extensive bond breakage as a result of recoil as shown by the presence of activity in the Propyl Iodide fraction.

Assuming that complete bond breakage occurs, the disproportionate distribution of activity between the two iodides is puzzling. If the two theories put forward for the explanation of recoil are considered it is at once clear that in a mixture of the two iodides, the distribution of the activity must be dependent on the concentrations of the iodides. The marked difference in the distribution of activity may be due to several factors.

i. A certain % of recoil fails to break the bond.

ii. On the re-entry of the recoil iodine into organic combination, there is a marked preference for Methyl Iodide over Propyl Iodide. This could happen both in the hot and epithermal regions and also in the thermal region.

iii. The inorganic iodine released in the reaction exchanges faster with the Methyl Iodide than with the Propyl Iodide after irradiation.

In order to find which of the above explanations is responsible for the greater activity of the MeI it was decided to investigate them one after the other.

$C_3H_7{}^{129}I + CH_3I$ experiment:-

Consider the case where Methyl Iodide is in large excess and propyl iodide is in small concentration and is labelled with ^{129}I. If the mixture is irradiated and the activities of the two iodides determined, one should be able to distinguish between the effect of real non-breakage of bond, and the effect of distribution of the recoil Iodine between the two iodides. If the distribution of the activity is similar to the previous experiment where the Methyl Iodide was labelled instead of the Propyl Iodide, the effect may not be due to non-breakage of bond.

Before labelling the Propyl Iodide with Iodine-129, it was desirable to find whether there would be any exchange of iodine between labelled propyl iodide and excess methyl iodide. The same method as used for the preparation of labelled methyl iodide, was used to prepare Propyl Iodide labelled with ^{131}I. Since the exchange was slower than in the case of Methyl Iodide, the Propyl Iodide-^{131}I-Alcohol mixture was kept in a 35°C. thermostat for 12 hours to attain exchange equilibrium. The alcohol and other impurities were removed by using the calcium chloride column shown in figure I. The $Pr^{131}I$ was mixed with excess of Methyl Iodide and kept for two days in the dark. The mixture was separated in the gas chromatographic column. The results of two independent experiments are given below:-

Table V

Alkyl Iodides used	Ratio of PrI to MeI by wt. in the original mixture.		Activities as c.p.m.		Concentration in milligrams of Iodine as Iodide		Activity/ mgm of Iodine as Iodide.	
	Experiments		Experiments		Experiments		Experiments	
	I	II	I	II	I	II	I	II
PrI	1.3:20	1.3:2	3774	2180	4.8	11.4	783.3	191.2
MeI			70.5	12.5	67.07	14.5	1.05	0.86

Since the exchange was not appreciable the Propyl Iodide was similarly labelled with Iodine-129. After purifying the Propyl Iodide using the calcium chloride column in figure I and measuring its volume, it was mixed with a known excess of Methyl Iodide and irradiated for the same length of time and at the same pile factor as for the Methyl Iodide experiment. The analytical procedures were exactly similar to that used for the $Me^{129}I$ experiment:

Table VI

Expt. No.	Ratio of PrI to MeI in the mixture in terms of Iodine content.	Activity of the untreated mixture as c.p.m./mgm. of Iodine content.	Activity of PrI as c.p.m./mgm. of Iodine content.	Activity of MeI as c.p.m./mgm. of Iodine content.	Organic yield	% of PrI Activity	% of MeI Activity	Ratio of PrI/MeI Activity	Ratio of PrI/MeI Specific Activity	Remarks
i	1:5.68	407.3	292.2	263.0	65.6	10.7	54.9	0.1948	1.107	All in presence of air
ii	1:19.95	35.72	31.62	23.25	66.1	4.15	61.97	0.06696	1.336	
iii	1:23.43	82.1	71.3	52.2	64.51	3.51	61.0	0.05754	1.366	

Conclusions from these experiments:-

i. It is clear that some sort of preferential attachment of the recoil ^{130}I to MeI is involved in the reaction.

ii. It is also evident that the Propyl Iodide activity is higher than it ought to be if one assumes complete bond breakage in every case of recoil.

One method of finding out the nature of this disproportionate distribution of the recoiling iodine atoms, is to irradiate a mixture of Methyl Iodide and Propyl Iodide of known ratio with molecular $^{129}I_2$.

CHAPTER VI

CHAPTER VI

The method of preparing molecular iodine by heating palladous iodide was found to be suitable only when the quantity of iodine was in excess of about 200μ gms. Below this value it was difficult to obtain complete precipitation of all iodide as palladous iodide. Further, to filter such minute amounts of the precipitate and later purify and dry it was also equally difficult. By using known concentrations of potassium iodide solutions containing ^{131}I as tracer it was found that as much as 50% of the iodine was lost during the process of precipitation, filtration, washing of the precipitate, drying and final heating. If $^{129}I_2$ was to be used, such a great loss was not permissible because of the small amount of ^{129}I available. Several methods were tried specifically to prepare molecular iodine in a pure form and in amounts not exceeding 100μ gms.

i. It is known that precipitated silver in the form of powder combines with iodine very efficiently to give silver iodide. It was decided to decompose the silver iodide by heating under vacuum and collect the iodine in a liquid air trap. Since silver iodide decomposes only at about 550°C. it was found necessary to use silica tubes for heating in the vacuum line instead of pyrex glass as otherwise the glass softened and collapsed before the silver iodide could be decomposed. Silver iodide labelled with iodine-131 was prepared by shaking a carbon-tetra-chloride solution of $^{131}I_2$ with precipitated silver powder. The silver powder containing the $Ag^{131}I$ was now washed with ether to remove most of the carbon-tetra-chloride and connected to the vacuum line for complete drying. A side arm in the system was cooled in liquid air to collect the iodine liberated. When the silica tube containing the $Ag^{131}I$ was heated it was found that under vacuum the AgI itself began volatalising and the yellow colour due to the silver iodide began to spread into the cooler sides of the silica tube. Even by chasing the silver iodide with a flame it was found that although there was some decomposition, the majority of the iodide escaped decomposition. This was particularly apparent when the concentration of iodine was below 100 μ gms. As the quantity of iodine present as silver iodide increased more of the silver iodide decomposed up to a ceiling value of 80%. But for quantities of the order of 100 μ gms, only about 15% of the $^{131}I_2$ originally used to prepare the silver iodide was trapped in the arm cooled in liquid air. If the silver iodide was heated in a closed system, as soon as the silver iodide decomposed the products recombined.

ii. Electrodeposition on a palladium foil was tried by electrolysing an alkaline solution of the iodide with Nickel cathodes. Using $^{131}I^-$ as tracer it was found that only about 10% of the iodine put in was recoverable on the palladium foil. Varying the pH or electrodes gave little improvement.

iii. A palladium foil was activated by heating to 300° in a stream of hydrogen. It was now dipped in a solution of molecular iodine in carbon-tetra-chloride and kept for a while. The palladium foil after washing and drying was heated under vacuum to decompose any palladium iodide formed. Using $^{131}I_2$ as tracer it was found that very little of palladium iodide was formed since only 20% of the activity was recoverable.

iv. The problem was solved by using freshly prepared palladium powder to pick up iodine. It was found that 95% of iodine can be removed by freshly prepared palladium powder from a carbon-tetra-chloride solution of the iodine. Palladium powder necessary for this cannot be obtained by simply powdering metallic palladium. This was found to be inefficient as only about 10% of the iodine was picked up. The palladium powder was obtained by heating palladium iodide under vacuum when the iodine liberated was removed in a liquid air trap, leaving behind palladium in a finely divided form. If the palladium iodide were to be heated in air palladous oxide was formed instead of palladium and this was found to be ineffective.

The detailed procedure consisted in precipitating in bulk palladium iodide by adding excess palladium chloride to about 100 milligrams of potassium iodide solution. The precipitate after being kept at about 35° for 46 hours was centrifuged off, washed several times with warm water, and introduced wet into the vacuum system. Residual water was pumped off, and when a very high vacuum was attained the palladium iodide was heated and the liberated iodine trapped out using a liquid air bath. When all the iodine had been removed - i.e. no more palladium iodide was present - the palladium left behind was allowed to cool to room temperature before air was let into the system. Otherwise the hot palladium would easily form the oxide above 100°C. The palladium powder obtained this way was used to prepare molecular iodine of any amount up to 200 μ gms.

A solution of molecular iodine in carbon-tetra-chloride was first prepared and the concentration of iodine present was estimated using the spectrophotometer. The wavelength used was 520 mμ. Into this solution the freshly prepared palladium powder was dropped. Since the palladium picked up the iodine only slowly, the solution was kept aside overnight. It was found that within about 4 hours most of the violet colour of iodine in the carbon-tetra-chloride solution vanished. When all the iodine had been picked up by the palladium powder as shown by the colourless solution, the carbon-tetra-chloride was removed and the palladium powder was kept under vacuum to remove all the carbon-tetra-chloride. When it was heated, the iodine readily came out and could be trapped out using liquid air. Experiments with ^{131}I showed that 85% of the iodine was invariably recoverable. The palladium powder if left open to air for a few days was found to be less efficient in picking up iodine than when it was fresh.

The molecular Iodine-129 experiment:-

It was decided to find the distribution of the recoil iodine in the two alkyl iodides at varying concentrations of the iodides. The method used was as follows:-

The Iodine-129 in the reduced form was first oxidised by acidified sodium nitrite and the molecular iodine collected in carbon-tetra-chloride. This was shaken up several times with water to remove the last traces of any acidic impurity and the solution was dried over silica gel. The concentration of iodine per c.c. of this solution was estimated using the spectrophotometer and a known volume was shaken up with freshly prepared palladium powder. When all the iodine had been picked up by the palladium, the carbon-tetra-chloride was rejected and the tube containing the palladium powder sealed to a vacuum line and evacuated thoroughly to remove all the carbon-tetra-chloride. A mixture of equimolecular proportions of Methyl Iodide and Propyl Iodide was prepared and a known weight of this mixture was taken in a B-7 test tube and attached to the vacuum line. Keeping the iodides cooled in liquid air, the palladium powder was heated and the released iodine allowed to condense in the mixture of iodides. From this stock solution of the mixture known amounts were transferred to 3 different silica tubes. To one of the tubes a known excess of an equimolecular mixture of the two iodides was added and the tube sealed under vacuum. Particular care was taken to drive away any dissolved air in the tube before sealing by repeated evacuation, thawing and freezing. To the second tube containing the $^{129}I_2$ and the equimolecular mixture of the iodides was added a known excess of Propyl Iodide alone and it also was sealed under vacuum. To the third tube was added a known excess of Methyl Iodide and it was also similarly sealed under vacuum.

In order to determine the extent of any exchange from molecular iodine to the two iodides, molecular iodine containing ^{131}I as tracer was prepared by the palladium powder method and dissolved in an equimolecular mixture of the two iodides. The mixture was sealed into two tubes under vacuum. One tube was left in the dark to determine the extent of exchange without any irradiation while the other tube was wrapped in aluminium foil along with the three tubes containing $^{129}I_2$. The 4 tubes were irradiated in the pile BEPO for 22 hours at a pile factor of 0.3.

Table VII

Expt. No.	Ratio of MeI to PrI in the mixture in terms of Iodine content.	Activity of the untreated mixture as c.p.m./mgm of ~~Iodine~~ Iodine content.	Activity of MeI as c.p.m./mgm of Iodine content.	Activity of PrI as c.p.m./mgm of Iodine content.	% of MeI Activity	% of PrI Activity	Ratio of MeI/PrI Activity	Ratio of MeI/PrI Specific Activity
Molecular Iodine-129 Experiment:- (0.05 mole %)								
(i)	1:1	165.9	198.9	69.06	59.97	20.73	2.892	2.892
(ii)	0.176:1	204.3	296.5	75.66	21.72	31.48	0.6899	3.920
(iii)	8. 93:1	139.4	96.72	29.15	62.40	2.10	29.70	3.320
Molecular Iodine-131 Experiment:-								
(iv)	1:1	183.7	157.0	34.3	42.70	9.29	4.586	4.586
(v)	1:1 ↑	183.7 ↑	99.8	15.7	27.17	4.27	6.356	6.356
	(Without any irradiation).							

The results show clearly that whatever be the ratio of Methyl Iodide to Propyl Iodide in the irradiated mixture, the Methyl Iodide had nearly three times more activity than the Propyl Iodide. The slight difference in the three values may be attributable to experimental errors.

Let us consider the recoil of iodine-130 from molecular iodine. One can assume that in the great majority of events only one iodine in the molecule captures a neutron and since the recoil energy is sufficient to break the bond, the iodine atoms break loose and move away. According to both the billiard ball hypothesis and the random fragmentation theory, irrespective of whether the recoil iodine originates from an organic molecule or from molecular iodine, the re-entry must be governed by the energy associated with the recoil fragment and the nature of the medium. If one assumes that there is almost an equal chance for the iodine to enter the Methyl Iodide or Propyl Iodide in an equimolecular mixture of these iodides, it is puzzling to find that the Methyl Iodide seems to be three times more efficient than propyl Iodide in picking up the recoiling iodine atom. Whether the reaction takes place in the hot and epithermal regions or thermal region the distribution of the activity of ^{130}I must be very nearly proportional to the concentrations of the two iodides in the mixture. It is significant here to remember that when pure Methyl Iodide undergoes radiative neutron capture reactions the percentage of activity present in the parent molecule is about 42 and 27 in the presence of scavenger iodine (27). Although no similar result has been reported for the Propyl Iodide undergoing radiative neutron capture, Schuler et al (28) have reported that for the (n,2n) reaction the percentage of activity present in the parent molecule of Propyl Iodide is about 33 and in the presence of scavenger iodine it is about 25. Even if one uses these values here, it becomes clear that in a mixture of the two the ratio is very different from that one would expect. This preferential attachment to Methyl Iodide may be the reason why in the experiments in Chapter V where Methyl Iodide or Propyl Iodide was labelled with iodine-129, one invariably found greater activity in the Methyl Iodide.

However the results are not clear enough because if one looks at the $^{131}I_2$ experiments it seems to indicate that γ radiation in the pile has a lot to do with this effect. The presence of ^{131}I in Methyl Iodide to a greater degree than in Propyl Iodide as is shown in table VII, confuses the results obtained with ^{129}I. In a later chapter, the exclusive effect of γ radiation on exchange in the two iodides is dealt in greater detail.

The inconclusive proof from these experiments for the mode of re-entry brings us back to our original problem of finding the distribution of activity when the iodine-129 is labelled in one of the iodides. The previous experiments where Methyl Iodide or Propyl Iodide was labelled with ^{129}I, were handicapped by the fact that within practical limits, it was not possible to widen the ratios of the amounts of the two iodides in the mixture without undue dilution. We would get a sharper perspective if the ratio of the concentration of the two iodides in the irradiation mixture were of the order of say about 1:200 instead of being 1:10.

The next chapter deals with the method of preparing Methyl Iodide labelled with ^{129}I in very small amounts without sacrificing the specific concentration of ^{129}I present. This would enable wider ratios of Methyl Iodide to Propyl Iodide to be chosen.

CHAPTER VII

CHAPTER VII

Part I

Preparation of labelled Methyl Iodide by photolysis

The photolysis of Methyl Iodide with added radioiodine is accompanied by isotopic exchange (29). The primary process involves separation into an iodine atom and a "hot" alkyl radical. A fraction of the radicals then undergo secondary chemical reactions before they have been reduced to thermal energies. Methyl Iodide begins absorbing continuously from about 3600Å and approaches the maximum between 2600 and 2500, while molecular iodine starts dissociating from 4989Å downwards. But near the maximum hot radical reactions predominate, necessarily introducing undesirable decomposition products such as Methylene Iodide. However, if the radiation beyond 3000Å is cut off, most of these impurities can be minimised while the radical exchange between Methyl Iodide and Iodine proceeds fairly rapidly. This can be achieved by using Pyrex photolytic cells instead of cells made of Silica, since Pyrex is virtually opaque to radiation beyond 3000Å.

To determine the extent of exchange, a few milligrams of Methyl Iodide were mixed with a known quantity of molecular $^{131}I_2$ prepared by the Pd powder method, and the mixture introduced into the Pyrex cell. Since during photolysis oxygen would be an undesirable competitor to Iodine for the

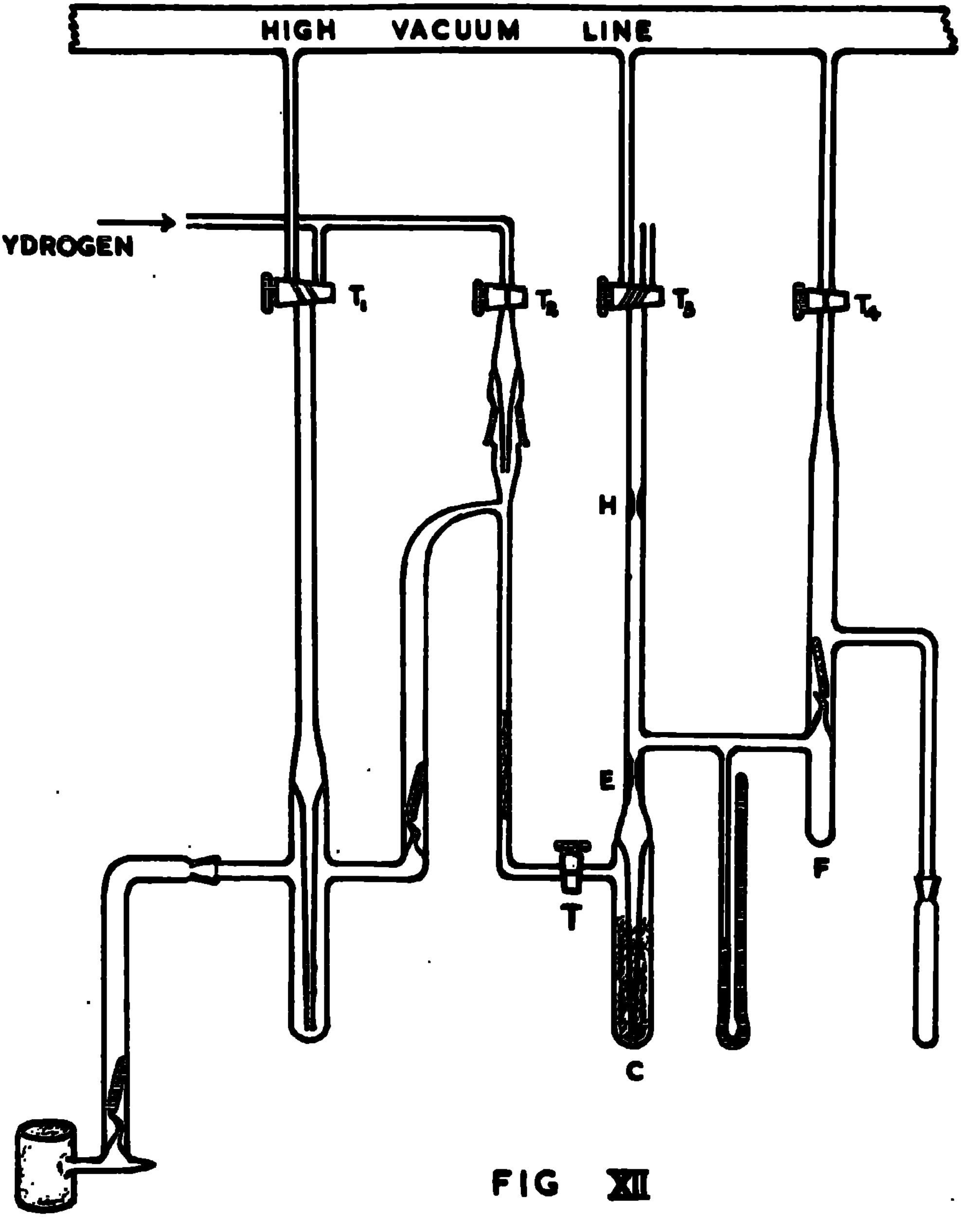

FIG XII

reaction with the radicals produced, the Pyrex cell was sealed under high vacuum. The cell was exposed for three hours to a low pressure Hg discharge lamp without filters. The radiations from this source range from 4000Å to about 2200Å. A small centrifugal blower was used to circulate air over the sample cell in order to keep it at a reasonable temperature.

After the photolysis the MeI + I_2 mixture was passed in a stream of dry hydrogen over dry Alumina to remove all the molecular Iodine. Figure XII shows the apparatus used. The Methyl Iodide was collected in the condenser 'C' along with traces of Methane, Ethane etc. which were products of photolysis. To remove the impurities, the condenser was kept cooled at -70° and the system evacuated when any Methane or Ethane present were removed. The Methyl Iodide was now transferred to the arm 'F' by cooling it in liquid air while the condenser was kept at -40°. Any Methylene Iodide present was left behind in the condenser. The system was now isolated by sealing off at 'E' and 'H'. Since the volume of the enclosed system was known fairly accurately, the amount of Methyl Iodide present was estimated by the pressure on the Hg manometer.

It was found from the estimation of the activity on the Methyl Iodide that nearly complete exchange equilibrium was achieved. Since it was possible to recover the molecular

Iodine adsorbed on the Alumina, there was no wastage of the active Iodine. However, it was desirable to ascertain whether the photolysed Methyl Iodide had any other active impurity. The Methyl Iodide present in the system was taken out under vacuum through the magnetically operated breaker, and mixed with a known excess of ordinary Methyl Iodide, the total volume being divided into two halves under vacuum. One half was counted for its activity and the concentration determined using the Spectrophotometer. The other half was put through a gas chromatographic column and the Methyl Iodide fraction was collected and counted, and the concentration estimated. The results are given below:-

TABLE VIII

Without Separation				After Separation		
Expt. No.	Activity as c.p.m.	Concentration in milligrams.	Activity /mgm of Iodide.	Activity as c.p.m.	Concentration in milligrams.	Activity /mgm of Iodide
1	332	32	10.37	225	22.5	10.00
2	712	12.4	57.4	557.6	9.8	56.92

Taking into account the possible errors in the experimental procedure and counting, it was concluded that after passage throug activated alumina and preferential evacuation all the active impurities were removed from the photolysed methyl iodide.

In order to ascertain whether the active Methyl Iodide prepared thus, had any ionising impurities, it was mixed with a known quantity of inactive Propyl Iodide and after keeping for 4 hours was separated and the activities and concentrations estimated. The results showed just under 0.5% of the total activity on the Propyl Iodide. It was concluded that the effect, if any, of such ionising impurities was not significant.

Part II

Recoil Study with $Me^{129}I$

Because of the encouraging results obtained from the above mentioned experiments, Methyl Iodide was prepared similarly labelled with ^{129}I. In the experiment recorded here, 1.2 mgm of Methyl Iodide was obtained which was now mixed with a known excess of Propyl Iodide. The mole ratio of the mixture in terms of Iodine content was 1:170. The mixture was sealed under vacuum and irradiated as before for 22 hours at a pile factor of 0.3 in the reactor BEPO. As soon as the irradiated mixture was available for analysis it was mixed with a known excess of pure Methyl Iodide and the mixture separated into two halves under vacuum. One half was used to measure the total activity while the other half was used to determine the individual activities of the two iodides. The result is given below:-

TABLE IX

Mole Ratio of MeI to PrI in the irradiated mixture.	Activity /mgm of Iodine as MeI.	Activity /mgm of Iodine as PrI.	Activity /mgm of Iodine as untreated mixture.	% of MeI Activity.	% of PrI Activity.	Ratio of MeI to PrI Specific Activity
1:170	186	6.55	16.78	6.24	39.41	28.4

If we assume that there is three times more preferential attachment of the recoil iodine to Methyl Iodide than to Propyl Iodide the distribution of the percentage activities should read 0.9 for MeI and 39.41 for PrI. The extra activity of 5.4% in the Methyl Iodide may be considered for the present as being due to non-random processes. Before analysing the results any further, it was desirable to find the extent of activity in Methyl Iodide when Propyl Iodide was labelled instead of Methyl Iodide and if identical ratios of concentrations and duration of irradiation were maintained, direct comparison would be more accurate.

Part III

Labelling Propyl Iodide with Radio Iodine by photolysis:-

To prepare Propyl Iodide labelled with ^{129}I in small concentrations so that such a wide ratio as 1:170 could be chosen, the method of photolytic exchange was tried. It has been reported that both Methyl and Ethyl Iodides are photolytic products of Propyl Iodide (30). To confirm this and also to determine the extent of Methyl Iodide formation, Propyl Iodide was exchanged with molecular Radioiodine-131 by photolysing in a Pyrex photolytic cell and, after removing the Iodine by passing over Alumina, the Propyl Iodide was mixed with known amounts of Methyl Iodide and Propyl Iodide and divided into two halves. One half was immediately put through the gas chromatographic column and the two iodides were counted and the quantities involved estimated. The other half was kept for a day and then separated. The purpose of this was to find out whether any activity on the Methyl Iodide was due to being a product of photolysis or due to exchange with the $Pr^{131}I$ in presence of ionising impurities. The results of two independent experiments are shown below:-

TABLE X.

Expt. No.	Ratio of MeI to PrI in the mixture.	After immediate separation.		After keeping for 24 hours.	
		Activity per milligram of MeI	Activity per milligram of PrI	Activity per milligram of MeI	Activity per milligram of PrI.
1	1:1	5.05	12.77	5.044	11.93
2	1:1	15.4	39.4	15.45	38.8

Since the previous experiments indicated that Methyl Iodide was a product of photolysis of Propyl Iodide, it was decided to isolate the active Propyl Iodide from the photolysed Propyl Iodide by separation on the gas chromatographic column. To avoid losing any Propyl Iodide during such a separation, the Propyl Iodide was collected as soon as it left the column (i.e. before it passed through the conductivity cell) in a U-tube containing Fenske Helices cooled in liquid air. Since the time at which the Propyl Iodide fraction was expected to come through under known conditions of temperature and pressure was known, the U-tube could be cooled in liquid air at the right time. The Propyl Iodide collected was estimated by means of an Hg manometer. Two independent experiments revealed, however, that the overall efficiency of the procedure was no more than 42%.

CHAPTER VIII

CHAPTER VIII

Part I

Preparation of labelled Propyl Iodide from Tetra-propyl-Tin.

When tetra-normal propyl tin reacts with molecular Iodine, Propyl Iodide is formed.

$$(C_3H_7)_4Sn + I_2 \longrightarrow (C_3H_7)_3SnI + C_3H_7I.$$

Tetra propyl tin was prepared (31) by the following method:

n-Propyl Magnesium bromide was first prepared by treating Magnesium with n-Propyl bromide in an ethereal solution. The Grignard reagent was now treated with stannic bromide when tetrapropyl-tin was formed.

$$4PrMgBr + SnBr_4 \longrightarrow Pr_4Sn + 4MgBr_2.$$

The experimental procedure is given below:-

A 500 ml. three necked flask fitted with a wide reflux condenser a stirrer and a dropping funnel was suspended in a steam cone which could also be used as a cooling bath. In the flask were placed freshly prepared Magnesium turnings. Of a solution of 85 gms. of Propyl Bromide in 150 ml of anhydrous ether, 5 ml. were mixed with three drops of bromine and added to the Magnesium. The Grignard reaction began at once and was maintained by gradually adding the remainder of the Propyl bromide solution. When the spontaneous reaction subsided the mixture was gently boiled, with stirring, for half an hour. After cooling the flask in ice, about 40 gms. of stannic bromide in ether was added in the course of about 20 minutes, the mixture being stirred vigorously meanwhile. The mixture was then refluxed for one hour after which the condenser was set for distillation. During an hour and half the ether was distilled off using an ample supply of steam in order to raise the reaction temperature. After cooling the flask again in ice and returning the collected ether to the reaction mixture the latter was decomposed by slowly adding first 25 ml. of iced water and finally 8 ml. of 20% KOH, and shaking for 10 minutes. The contents were transferred to a separating funnel. A stream of dry ammonia was passed through the filtered ethereal solution. Any impurities still present were precipitated as ammonia complexes. The filtrate was dried over Sodium-Sulphate and evaporated. The residue was distilled at 12 mm. pressure and the fraction coming over between 108-109° was collected. The yield was about 18 gms. of halogen free tetra-propyl-tin.

In order to study the formation of Propyl Iodide from tetra-propyl-tin, about 100 μ gms. of molecular Iodine containing ^{131}I as tracer was prepared by the Pd powder method and mixed with excess of Pr_4Sn. A preliminary experiment indicated that for the complete removal of Iodine

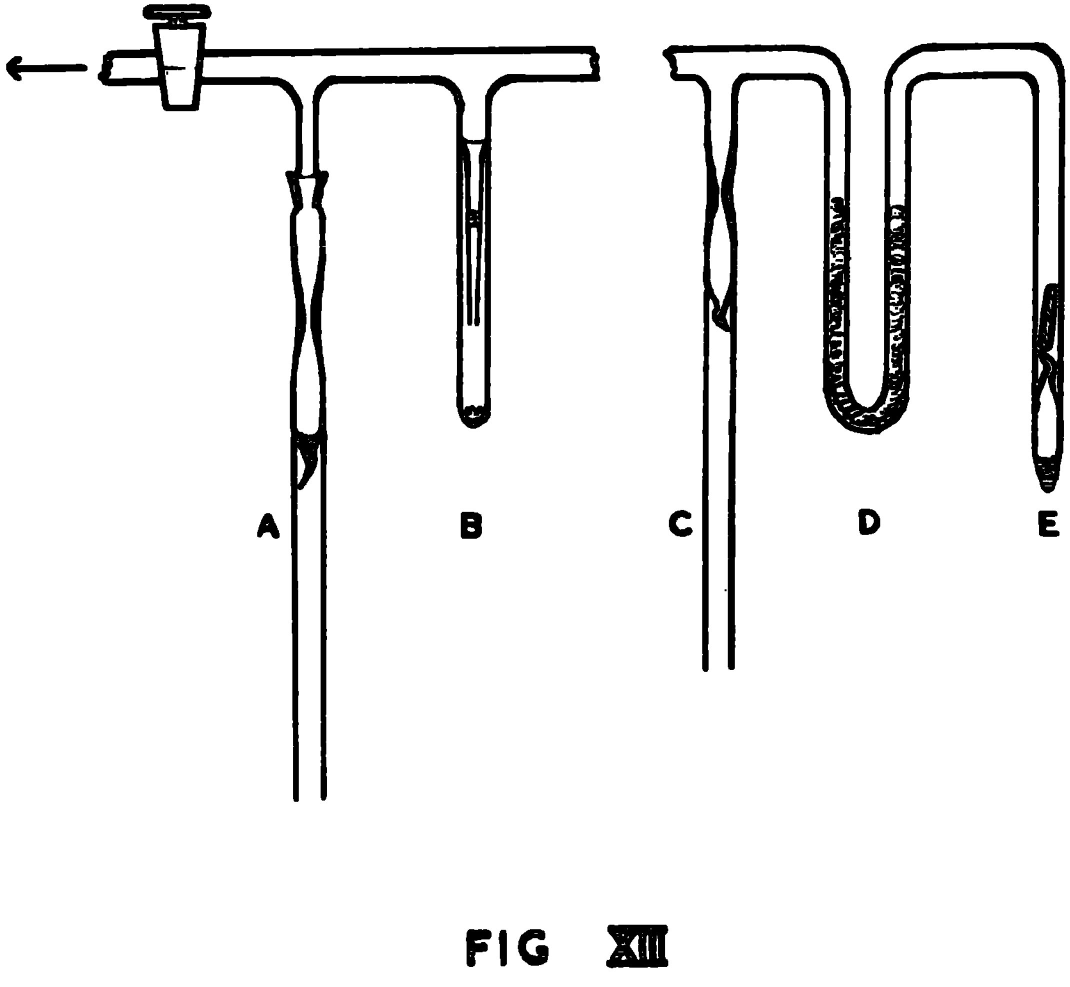

FIG XII

as Propyl Iodide, the amount of Pr_4Sn must be higher than indicated by the stoichiometric data. It was found that the weight of Pr_4Sn needed was approximately double the weight of Iodine taken. Since both tetra-propyl-tin and the product tripropyl-tin iodide, had very high boiling points, they had a negligible vapour pressure at room temperature. Therefore the Propyl Iodide could be pumped out of the reaction vessel under vacuum. The experimental arrangement is shown in Figure XIII. The tube containing the Pd powder used for preparing the molecular Iodine was sealed onto the system at 'B' while 'A' contained the Pr_4Sn. After evacuating the system, the Pd powder was heated to release the I_2 and the Iodine was transferred to 'A' by cooling this in liquid air. The tube was sealed off and when the Iodine had completely reacted with the Pr_4Sn, as shown by the absence of any colour, the tube was inverted and connected at 'E' in the same figure. The system was thoroughly evacuated and after isolating the system from the vacuum line, the arm 'C' was cooled in liquid air to collect the Propyl Iodide released from 'E', and 'D' containing Fenske Helices was kept at -60°C. to prevent any trace of the tin compounds entering the arm 'C'. The overall efficiency of the method was 90%. Only one half of the Iodine put in was transformed into Propyl Iodide the other half forming tri-propyl-tin iodide. The Iodine present in this compound could be recovered by hydrolysing it in ether with Potassium hydroxide solution.

Part II.

To find any possible exchange of Iodine with Methyl Iodide, the Propyl Iodide prepared by the tetra-propyl-tin method was divided into two parts. One part was mixed with more of Propyl Iodide and excess Methyl Iodide and kept for 48 hours before separation. The other half of $Pr^{131}I$ was mixed with a large excess of MeI and kept for 48 hours. Excess PrI was added just before separation. The results are given below:-

TABLE XI

Expt. No.	Conc.^{n} of $Pr^{131}I$ (app.)	Conc.^{n} of PrI added immediately after the prep.^{n} of $Pr^{131}I$	Conc.^{n} of PrI added just before separation	Conc.^{n} of MeI added immediately after the prep.^{n} of $Pr^{131}I$	Activity of MeI as c.p.m./ mgm.	Activity of PrI as c.p.m./ mgm.	Ratio of MeI: PrI Specific activity
1	40µgms.	40mgms.	-	60mgms.	3.08	98.4	0.031
2	50µgms.	-	45mgms.	54mgms.	5.999	39850	0.0001

The marked difference in the ratios of the specific activities indicates that the presence of activity in the MeI fraction may not be due to exchange and since the activity itself in the MeI was only a fraction of the activity in the PrI, for practical purposes one could consider it as almost negligible.

Part III

Propyl Iodide-129 experiment

$Pr^{129}I$ was prepared by the tetra-propyl-tin method and mixed with MeI in three different concentrations to give the ratios by weight of Iodine of approximately 1:170, 1:200 and 1:270 respectively. After irradiation for 22 hours at a pile factor of 0.3, the contents of each tube were mixed with a known excess of PrI before separation. For the purpose of finding out the γ-radiation effect in these experiments, a mixture of $Pr^{131}I$ + MeI was also irradiated and the result is given in experiment (4) in the following table. All experiments were conducted in the complete absence of air.

TABLE XII

Expt. No.	Ratio of PrI to MeI in terms of Iodine content.	Total Activity of PrI as c.p.m.	Total Activity of MeI as c.p.m.	% Activity of PrI	% Activity of MeI	Ratio of MeI: PrI Specific Activity.
1	1:178	127.5	672.4	8.5	45.1	5.3
2	1:200	57.54	600.73	3.61	37.7	10.44
3	1:267	460.1	2838.0	7.67	47.3	6.16
4	1:302	1959.3	52.05	96.36	2.54	0.0265

Part IV.

Effect of Scavenger Iodine

To determine the effect of scavenger Iodine on the recoil reaction and, in particular, the distribution of the activity between the two iodides, $Pr^{129}I$ was mixed with a known excess of MeI and about 0.1 mole % of molecular Iodine was added to the mixture. The small concentration of Iodine (about 10 μ gms.) necessary for this experiment was obtained by the Pd powder method. For comparison purposes a similar experiment where PrI was labelled with ^{131}I was also conducted. All mixtures were irradiated under vacuum.

TABLE XIII

Expt. No.	Ratio of PrI to MeI in terms of Iodine content.	Total activity of the mixture as c.p.m.	Activity of the PrI as c.p.m.	Activity of the MeI as c.p.m.	% of inorganic activity	% of PrI activity	% of MeI activity	Ratio of MeI to PrI Specific activity
1	1:140.5	1564	49.6	448.7	68.2	3.17	28.6	9.02
2	1:225	6114	245	1996	63.4	4.01	32.59	8.14
3	1:293 (^{131}I expt.)	1023	446.8	230.0	34.0	43.7	22.4	0.514

Part V.

There is a definite possibility that part of the activity found in the MeI may be due to the formation of MeI as a product of PrI recoil reaction. In order to find the extent of such activity in the MeI, PrI labelled with Iodine-129 was mixed under vacuum with a known excess of ordinary PrI. After irradiation it was mixed with a known amount of MeI for the sake of separation.

TABLE XIV

Expt. No.	Ratio of $Pr^{129}I$: prI in the mixture in terms of Iodine content.	Total PrI activity	Total MeI activity	% of PrI activity	% of MeI activity	Ratio of MeI to PrI activity
1	1:287	1938	84	47.4	2.05	0.0433

Part VI.

Recoil reactions in the gas phase

It has been shown experimentally that recoil reactions in the alkyl iodides in the gaseous state provide a very high percentage of Inorganic activity and this has been interpreted as proving that a large majority of recoil events result in bond breakage. To confirm this as well as to determine the nature of the recoiling atoms and their possible re-entry into organic combination in the gaseous phase, a mixture of PrI and MeI where PrI was labelled with ^{129}I and MeI was in large excess was irradiated in the gas phase.

A silica cell of volume approximately 6 c.c. was filled with $Pr^{129}I$ (prepared by the Pr_4Sn method), and excess MeI and sealed under vacuum. The pressure in the cell was calculated to be about 240 mm. of Hg. After irradiation in the pile the mixture was mixed with a known amount of PrI and the analytical procedures followed as before. In a second experiment the mixture of $Pr^{129}I$ and MeI was mixed with roughly 0.1 mole % of molecular Iodine to deal with thermalised reactions in the gas phase. The results are given below:-

TABLE XV

Ratio of $Pr^{129}I$ to MeI in terms of Iodine content	Approximate pressure of the mixture in the irradiation cell	Total activity of untreated mixture as c.p.m.	Total PrI activity as c.p.m.	Total MeI activity as c.p.m.	% of PrI activity	% of MeI activity	% of inorganic activity
$Pr^{129}I$ + MeI							
1:200	238 mm.	1772	100.7	1582.5	5.6	89.3	5.1
$Pr^{129}I$ + MeI + I_2							
1:166	130 mm.	662.5	11.47	561.6	1.73	84.78	13.5

The general conclusions arrived at from the results recorded in this chapter are given in a later chapter.

CHAPTER IX

CHAPTER IX

Effect of gamma radiation on the exchange of iodine between alkyl iodides

In the study of reactions activated by nuclear processes other than radioactive decay, neutrons or other bombarding particles are used. Most methods of providing such particles also generate γ rays, and in some cases fast neutrons are present. These radiations may produce ions, free radicals and excited molecules in the medium. In many studies of the type discussed here it is essential to know with certainty whether the fate of any of the atoms activated by nuclear transformation is altered by these radiation-produced species. It has been shown (32) that the probability of the reaction with atoms is negligible because the steady state concentration of radicals maintained in a typical experiment with, for example, a radiation level of 5000 r/hr is of the order of 10^{-11} mole fraction whereas each thermalised recoil atom is present in a volume element of solution containing radicals which it itself has produced at a mole fraction of 10^{-3}.

The irradiations conducted in the pile for the ^{129}I (n, γ) ^{130}I reaction with slow neutrons were accompanied by a γ ray flux equivalent to 5000 r/hr. In order to find to what extent the ^{129}I experimental results have been affected by the γ flux, several experiments were conducted using ^{131}I as a radioactive tracer. A 100 curie ^{60}Co source was used to provide the γ flux required and it was estimated by means of a ferrous iron dosimetric study that at a distance of 15 cms. from the source the γ-ray dose rate was 5000 r/hr. In order to simulate the conditions under which the ^{129}I experiments were conducted, the irradiations were carried out for 22 hours and the iodides were kept aside for 12 hours before they were analysed.

Since experiments with irradiated mixtures of $Pr^{131}I$ and excess MeI has shown that the activity on the MeI fraction was only 2.4% it was decided not to pursue this particular experiment further. Instead, the effect of γ rays on a mixture $Pr^{131}I + I_2 + MeI$ where PrI was in very small concentration, was examined for varying molecular iodine concentrations.

The detailed procedure consisted in preparing PrI labelled with ^{131}I by the tétra-propyl-tin method. Since in the ^{129}I experiments only very small amounts of PrI were used in the irradiations, similar amounts were used in the ^{131}I experiments too. Since all experiments were to be conducted at very low iodine concentrations, usually about 0.1% or less, such small amounts of iodine could not be weighed out accurately. To overcome this difficulty, a known weighable amount of PdI_2 was prepared and the iodine released by heating was dissolved in a known large volume of MeI. From this known mixture of MeI and I_2, appropriate amounts were weighed in sealed capillary tubes and later mixed with different known excesses of MeI to give a range of iodine concentrations.

The ratio of $Pr^{131}I$ to MeI was always kept constant by mixing 300 μ gms. of $Pr^{131}I$ with 60 mgms of MeI containing molecular iodine. This gave a ratio of 1:243 by weight of Iodine content. All preparations and mixing were conducted under vacuum and as far as possible the system was shielded from direct light. This mixture of MeI, I_2, and $Pr^{131}I$ was now divided into 3 parts and sealed under vacuum into three Pyrex capillary tubes. Two tubes were used for irradiation while the third was kept in the dark for comparison purposes. The method of dividing a mixture such as this into 3 parts without affecting the relative concentration ratios of the 3 constituents was a difficult problem. The method finally adopted was to freeze the mixture into an absolute minimum volume of a capillary tube and sealing the tube off from the main vacuum line. This tube had sealed onto it three capillary tubes of roughly equal diameter and length. When the iodides had thawed, the mixture was well shaken up and tilted into the three tubes. By cooling the three tubes in water, the mixture easily ran into them and later by freezing simultaneously in liquid air the tubes were sealed off.

TABLE XVI

Exchange of ^{131}I between propyl and methyl iodides in the presence of molecular iodine, with and without gamma irradiation.

Each sample contained approximately 20 mgm. of MeI, with the addition of ^{131}I-labelled PrI at a concentration of 66µmoles/c.c., and iodine at the concentration indicated in column 2.

Expt. No.	Conc.^{n} of Iodine in µmoles/c.c.	% of Organic activity		% of MeI activity		% of PrI activity		Ratio of MeI/PrI activity	
		non-irradiated	irradiated	non-irradiated	irradiated	non-irradiated	irradiated	non-irradiated	irradiated
1	12.68	61.2	64.8 64.3	31.8	37.60 34.90	29.3	27.2 29.4	1.086	1.386 1.187
2	9.946	53.1	54.2 51.2	21.86	22.70 23.10	31.2	31.5 28.1	0.6995	0.722 0.822
3*	4.432	46.6	49.4	38.84	40.64	7.8	8.7	4.97	4.63
4	0.8622	77.3	78.8 89.2	2.67	2.18 1.87	74.6	76.6 87.3	0.035	0.0285 0.0193
5	0.3448	100.5	85.2	2.50	5.12	98.0	80.1	0.025	0.063
6	0.2099	101.6	78.5	8.5	9.5	93.1	68.9	0.091	0.138

* The results of Expt. 3 are less reliable than those of the other experiments on account of instrumental defects in the spectrophotometer.

By the usual analytical procedures the iodides were separated and their activities and concentrations determined.

It is quite clear from the results given in Table XVI that there is extensive exchange taking place between Propyl iodide and methyl iodide in the presence of molecular iodine. The effect of γ radiation seen to be negligible in accelerating the exchange, quite probably because, the radiation-produced radicals are removed from the sphere of action by the molecular iodine present. This is particularly evident in the experiments where higher molecular iodine concentrations were used.

The fact that even in the absence of any γ radiation or direct light, there is appreciable exchange as shown by the considerable proportion of activity in the MeI, indicates that the exchange may not be due to a mechanism involving radicals. Similar conclusions have been arrived at by Schmid and Fink (33) in the course of their study of the exchange of labelled iodine with MeI.

It is difficult to predict the steps involved in the exchange process. If we accept a bimolecular exchange mechanism, the two steps possible are

$$Ax^* + Bx \xrightleftharpoons{K_1} Bx^* + Ax \qquad \text{and,}$$

$$Bx^* + Cx \xrightleftharpoons{K_2} Cx^* + Bx$$

and if we denote the concentrations,

$$\begin{array}{llll}
[Ax] = a, & [Ax^*] = a'; & a + a' & = A \\
[Bx] = b, & [Bx^*] = b'; & b + b' & = B \\
[Cx] = c; & [Cx^*] = c'; & c + c' & = C \\
\sum[x] = x; & \sum[x^*] = x'; & x + x' & = X
\end{array}$$

and at $t = o$, $a' = a'_o$

$$b' = o$$

$$c' = o$$

$$x' = a'_o$$

it can be shown that,

$$\frac{d^2c'}{dt^2} + \left[K_1(X-C) + K_2(X-A)\right]\frac{dc'}{dt} + K_1K_2AC\,(x'-c')$$

$$+ K_1K_2(X-C)\,(X-A)\,c' - K_2C\left[K_1(X-C)\right]x' = o.$$

Under our conditions of experiment, A, B $\ll$ C, and it is reasonable to assume that K_1A, K_1B, and $K_2B \ll K_2C$. The solution of this equation then reduces to

$$c' = \frac{cx'}{X}\left[1 + \left\{\frac{K_1B}{K_2C}\right\}e^{-(K_1A + K_2B + K_2C)t} - \left\{1 + \frac{K_1B}{K_2C}\right\}e^{-K_1Bt}\right]$$

This can be further simplified (since the second term will be negligible compared to the third), to give

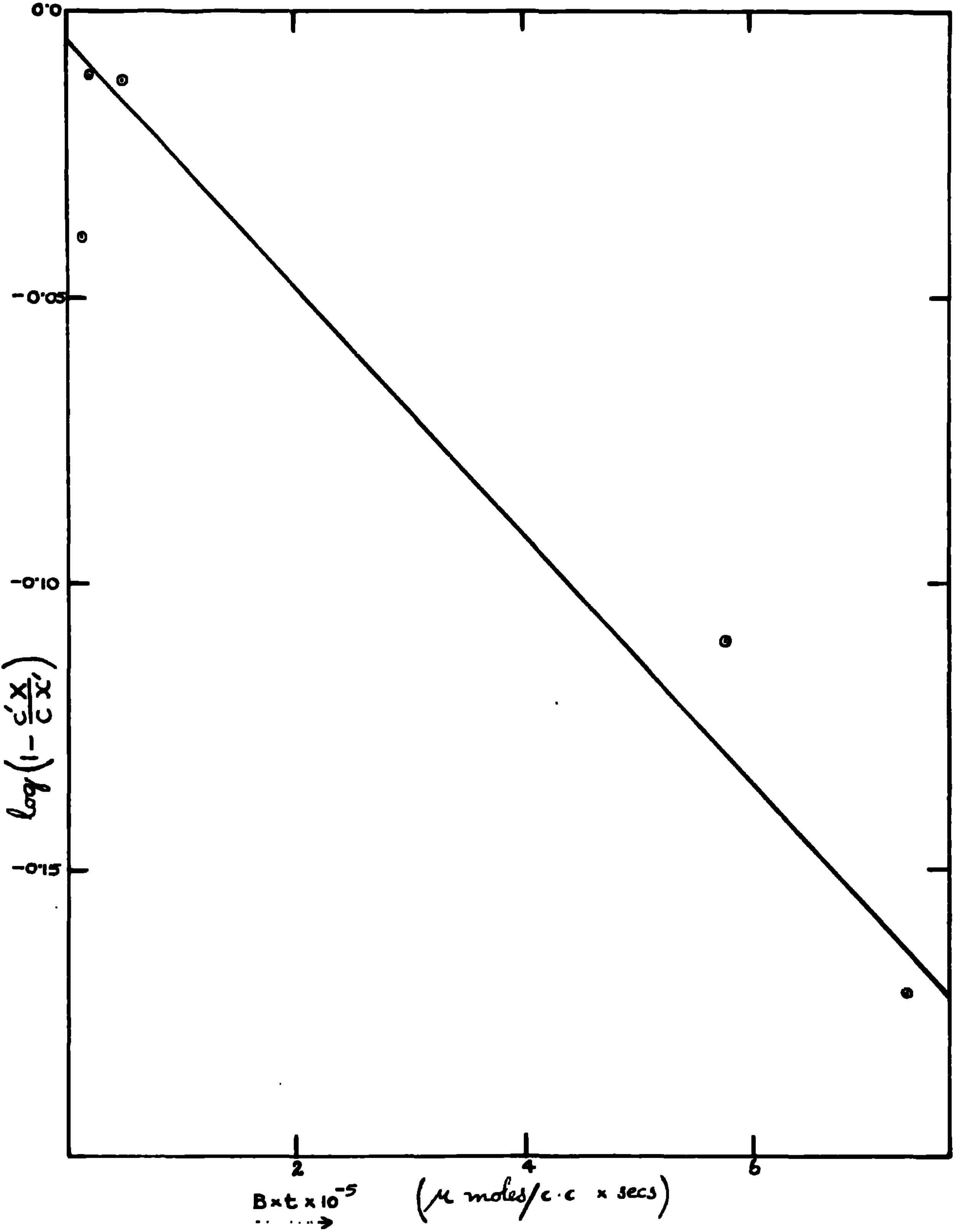
0·0
-0·05
-0·10
-0·15
$\log\left(1-\frac{c'x}{cx'}\right)$
2
4
6
$B \times t \times 10^{-5}$ (μ moles/c·c × secs)

FIG XIV

$$c' = \frac{cx'}{X} (1 - e^{-K_1Bt})$$

i.e. $\log_e (1 - \frac{c'X}{cx'}) = - K_1Bt.$

Thus, if we make a semi-logarithmic plot of $(1 - \frac{c'X}{cx'})$ against Bt a straight line graph should be obtained, the slope of which should give the value of K_1. The graph shown in figure XIV was obtained from the known values of c', X, c, x' and Bt.

It will be seen that the relationship between $\log (1 - \frac{c'X}{cx'})$ and Bt is linear, giving a value of K_1 of about 0.5 $\sec^{-1}$ moles^{-1} c.c. The point at the lowest concentration examined deviates markedly from the straight line; this may arise from several causes of which the most likely seems to be the possible decomposition of the reactants, which will be relatively much more serious at this low concentration of iodine.

CHAPTER X

CHAPTER X

Discussion of the results

Let us consider here the specific case of the possible reaction paths available to an energetic recoil iodine atom as it loses energy and comes to rest in an alkyl iodide medium. The recoil atom at first loses energy principally by collision with individual atoms of the alkyl iodide molecules. Apart from the small amount of energy required to break the bond or bonds holding the struck atom in the molecule, these collisions are essentially elastic. The target atoms so expelled may often have sufficient energy to disrupt nearby molecules and this cascade effect will leave a widening cylinder of molecular fragments in the wake of the original recoil. Complete momentum transfer is possible only in collisions with iodine atoms and then only under unusually favourable circumstances. However, as the recoil approaches thermal energies the momentum transfer requirement is less and it becomes more probable than the recoil atom will undergo collisions which result in the substitution of the active atom for inactive atoms of the parent species. As the energy of the activated atom approaches thermal energies, the collisions become more inelastic in character and result in epithermal reactions which form a variety of products.

The iodine atom, immediately after it has been fully thermalised, will begin diffusing through a medium in which there is initially an extremely high concentration of radicals which it iteelf has produced. It will have a high probability of reacting with these radicals to form both organic and inorganic activity. Finally after the unreacted iodine atoms have been thermalised and have diffused out of the zone of high radical concentration, they will be fixed as inorganic activity.

Summarised below are some of the conclusions arrived at from the experiments recorded in the previous chapters:-

i. It is confirmed that there is extensive bond breakage resulting from nuclear recoil in alkyl iodides.

ii. There is disproportionate distribution of the recoil atom between the two iodides studied here. Methyl iodide always had nearly three times more activity than the propyl iodide whether the ^{129}I was labelled in MeI or PrI.

iii. While there is confirmation for extensive bond breakage in both MeI and PrI, the extent of the activities in both MeI and PrI is such that it indicates that a definite, though small, proportion of recoil fails to break the bond in the alkyl iodides.

The results shown in table XII in Chapter VIII can be analysed as follows:-

Since the PrI was labelled with ^{129}I, one can safely assume that any activity found in the large excess of MeI must have been produced by entry of the recoiling atom. And if we assume as is shown by the $^{129}I_2$ experiments in Chapter VI that the recoiling atom enters MeI in preference to PrI to the extent of 3:1, we can divide the % of MeI activity by three times the MeI/PrI ratio in the mixture to get the activity that should be expected in PrI due to normal (random) re-entry processes. But in fact this value is found, as shown in the following table, to be small compared with the experimentally determined activity. The difference can be considered as due to non-random processes and can be represented as a ratio of total organic retention.

TABLE XVII

Pr^{129}I + MeI (in large excess)

Expt. No.	Ratio of PrI to MeI	% of MeI activity	% of PrI activity	% of activity in PrI due to non-random processes.	Activity due to non-random processes as % of the organic retention.
1	1:178	45.1	8.5	8.41	15.5
2	1:200	37.7	3.61	3.54	8.6
3	1:267	47.3	7.67	7.6	13.8

Similar analysis of the experiments where scavenger iodine was used to remove the thermal radical ~~reactions~~ gives the following results.

TABLE XVIII

$Pr^{129}I$ + MeI (in large excess) + I_2 (0.1%)

Expt. No.	Ratio of PrI to MeI	% of MeI activity	% of PrI activity	% of activity in PrI due to non-random processes.	Activity due to non-random processes as % of the organic retention.
1	1:140.5	28.6	3.17	3.10	10.0
2	1:225	32.59	4.01	3.96	10.8

Although MeI is a product of recoil in PrI, as is shown by the result in table XIV Chapter VIII, the MeI fraction was only 2.05%. Hence this would not appreciably alter the results given above.

Similar arguments in the analysis of the results from Chapter VII where MeI was labelled with ^{129}I and PrI was in large excess, gives 12.1% as the activity in MeI due to non-random processes.

Comparison of the two series of results leads one to believe that about 10% of the activity appearing in the originally labelled alkyl iodide cannot be explained away by the normal re-entry processes. Either this activity is due to genuine non-breakage of bonds or in some way related to post irradiation exchange with the inorganic iodine. The γ radiation in the pile does not play any appreciable part in the exchange as shown by the ^{131}I experiments.

Gordon and Willard (34) have reported that comparison of the activity of ^{128}I produced by neutron capture from the iodine atom in ethyl iodide in hydrocarbon media with those activities originating from molecular iodine in hydrocarbon media, shows that the ratio of $C_2H_5{}^{128}I$ to $CH_3{}^{128}I$ was always higher when C_2H_5I was the parent compound. Although part of the increase was removed when scavenger iodine was present (compare with our results), in no case, was all of the $C_2H_5{}^{128}I$ eliminated by the scavenger. They suggest that this may be an indication of failure of the C-I bond to rupture.

A look at the two gas phase reactions reported in Chapter VIII shows rather startling results. Most of the activity was in the MeI which could only be explained by some sort of displacement reaction during or after recoil. This is proved by the fact that even in the presence of scavenger iodine, which would remove any radicals present, the proportion of MeI activity did not fall appreciably.

In gas phase reactions initiated by nuclear processes, in the presence of scavengers for radicals, the recoil atom or ion must enter combination by a bimolecular displacement of an atom or radical of one of the gaseous molecules. If such reactions can occur in the gas phase it is to be assumed that they also occur in condensed phases, where it is impossible to distinguish them experimentally from reactions of a recoil atom with a radical it has formed and with which it combines before escaping from the immediate region where the radical was produced.

It is pertinent to note that it has been reported (35) that in gas phase recoil reactions of I_2 in CH_4, about 50% of the activity was found as CH_3I while under similar conditions $I_2 + C_2H_6$ showed only 2% of activity in the organic fraction. A very similar result has been obtained with I_2, C_3H_8 mixture. That γ radiation is not responsible for the 50% of activity found as $Me^{128}I$ when I_2, CH_4 in gaseous state undergo radiative neutron capture, is shown by the work of Levey and Willard (36).

Therefore it is not very strange to find nearly 80% of the activity in the MeI fraction when MeI + $Pr^{129}I$ mixture undergoes recoil reactions in the gas phase. The explanation for many of these types of reactions has been ascribed to ion-molecule reactions.

Comparison of the non-random processes in the gas and liquid phases of the alkyl iodides:- We could consider the 10% of non-random processes in liquid phase in both MeI and PrI as due to non breakage of bonds. The non-random activity in PrI in the gas phase reaction could be considered as starting at 10% due to non-breakage of bonds, and later, due to exchange in gas phase in presence of scavenger iodine, being reduced to 1.5. This is supported by the following:-

The 10% non-random activity in liquid phase cannot be due to exchange since MeI has a preference over PrI of up to 3:1. Therefore one would expect the PrI activity not to be increased from 1.5 (if this is the true % of non-breakage of bonds) to 10 without similar increase in MeI.

The fact that the % of non-random processes in both MeI and PrI is about 10 when they undergo the $^{129}I(n,\gamma)^{130}I$ recoil reaction, perhaps indicates that the recoil energy is not sufficient to break 10% of the bonds even in PrI where the bond strength is smaller. This further confirms the conclusion that in the ^{130}I recoil, 10% of the recoil events do not break the bond in alkyl iodides.

APPENDIX

Studies of the activity distributions in alkyl iodides undergoing (n,γ) and (n,2n) recoil reactions

It has been shown in the preceding chapters that when a mixture of methyl iodide and propyl iodide undergoes the radiative neutron capture reaction, the newly formed nuclide tends to enter methyl iodide in preference to propyl iodide. This particular re-entry has been noted for the (n,γ) reaction involving ^{129}I. In order to find out whether this preferential attachment to methyl iodide is exclusive to the ^{129}I (n,γ) ^{130}I reaction, several experiments were conducted.

In the first place the (n,γ) reaction of ^{127}I in the organic mixture was studied. In brief the method consisted in irradiating an equimolecular mixture of the two iodides with thermal neutrons from a Ra-Be source. The mixture was now separated and the individual activities of the two fractions determined. Because of the short half life (25 minutes) of the resulting nuclide (^{128}I) the method of separation had to be rapid. With the Ra-Be source available in the laboratory (500 mcs) the specific activity of the mixture due to ^{128}I was not very high. Therefore, unless a large volume of the irradiated mixture was separated quickly, the individual activities of the iodides were very poor. This meant that the gas chromatographic technique of separation was unsatisfactory because of the small size of the column. Even the use of a column of about 3 cms diameter was found to effect little improvement. Hence fractional distillation using an 18" Vigreux column was used to separate the mixture. The methyl iodide fraction was stripped off at atmospheric pressure and propyl iodide was distilled over under reduced pressure. Since Pyrex glass reduced the neutron flux from the Ra-Be source, a Soda glass cell was used for the irradiation.

After irradiating for one hour, a part of the mixture was used for measuring the total activity while the rest was shaken up with SO_2-water to remove inorganic iodine and after washing with distilled water, the mixture was dried quickly with anhydrous $MgSO_4$ and fractionally distilled. The whole analytical procedure normally took about 40 minutes to complete.

TABLE XIX

Expt. No.	Total activity as c.p.m.	Total MeI activity	Total PrI activity	Organic retention %	MeI activity %	Ratio of $\frac{\text{MeI}}{\text{PrI}}$ activity.
A. Irradiation in presence of air.						
1	1134	323.2	174.8	43.9	28.5	1.86
2	1019	272.0	161.0	42.5	26.7	1.69

TABLE XIX (continued)

Expt. No.	Total activity as c.p.m.	Total MeI activity	Total PrI activity	Organic retention %	MeI activity %	Ratio of $\frac{\text{MeI}}{\text{PrI}}$ activity.
B. Irradiation in the absence of air.						
1	1039.4	315.8	177.6	47.5	30.4	1.793
2	1040.5	325.6	181.7	48.75	31.3	1.799
C. Irradiation in presence of about 0.1% mole of molecular iodine but under vacuum.						
1	1058.0	203.1	147.2	33.11	19.2	1.385
2	1097.4	220.5	164.4	35.08	20.1	1.35

It is quite evident from the results shown above that the extent of re-entry of the recoil iodine into methyl iodide is different from that involving ^{130}I. Even if the results are not conclusive enough, there is a strong indication that the process of re-entry of the recoil iodine into organic combination is not identical in all radiative neutron capture reactions involving iodine. Whereas in the case of the ^{129}I experiments it was shown that the activity ratio MeI/PrI was about 3:1, for the (n, γ) reaction involving ^{127}I it was found to be much less. However, it must be pointed out that direct comparison between the two series of experiments may not be very dependable because, (i) the γ ray flux in the ^{129}I experiments was much higher and this might have had the effect of increasing the methyl iodide activity.

(ii) in the case of the ^{129}I experiments the 12 hours that usually elapsed before the mixture was analysed might have tended to increase the methyl iodide activity due to differences in the rate of exchange of the two iodides with the inorganic iodine.

In order to find the extent of active methyl iodide formation due to recoil reaction, propyl iodide was irradiated alone and later mixed with a known volume of methyl iodide and, as before, fractionally separated. The results would give the extent of methyl iodide formation due to recoil and also any exchange happening during the process of fractional distillation.

TABLE XX

Irradiation in presence of air

Expt. No.	Total activity of mixture c.p.m.	Total MeI activity	Total PrI activity	Organic retention %	MeI activity %	PrI activity %
1	548.8	34.1	183.2	41.4	6.22	33.4
2	590.3	42.5	188.3	40.8	7.02	31.9

In order to confirm that the activity ratio MeI/PrI of about 1.8, for the (n, γ) reaction involving ^{127}I, was dependent on the concentration of the iodides, a mixture made up in the ratio of one mole of MeI to 1.8 moles of PrI was irradiated. It was expected that the ratio of MeI/PrI activity in this new mixture would be about one.

TABLE XXI

Irradiation in presence of air

Expt. No.	Total activity of mixture c.p.m.	Total MeI activity	Total PrI activity	Organic retention %	% of MeI activity	Ratio of MeI/PrI activity
1	810.4	164.5	171.5	41.47	20.3	0.965
2	842.2	168.4	172.9	40.52	19.99	0.974

To find whether the degree of preference for the lower alkyl iodide, in the re-entry process of recoil iodine, gradually changes as the alkyl iodide is varied, an equimolecular mixture of methyl iodide and ethyl iodide was irradiated similarly, separated, and their individual activities determined:

TABLE XXII

Expt. No.	Total activity of mixture c.p.m.	Total MeI activity	Total EtI activity	% of Organic retention	% of MeI activity	Ratio of MeI/EtI activity
A. Irradiation in presence of air						
1	1028.2	241.8	225.9	45.5	23.52	1.07
2	1054.0	247.3	240.3	44.3	22.48	1.03
B. Irradiation in presence of 0.1% mole of molecular iodine but under vacuum.						
1	1018.9	183.8	201.8	38.6	18.84	0.9535
2	1034.4	184.4	194.2	37.7	17.94	0.9494

It is evident that there is practically no preferential attachment to methyl iodide in the recoil reaction involving methyl iodide and ethyl iodide.

To find whether the energy of recoil contributes to the preferential attachment of the recoil atom to the methyl iodide, an equimolecular mixture of methyl iodide and propyl iodide was irradiated, for the ^{127}I (n,2n) ^{126}I reaction, with 14.6 MeV neutrons obtained by the (D,T) reaction in a linear accelerator. The iodide fractions were kept aside before counting for a sufficiently long time to allow the 25 minute ^{128}I activity to decay.

TABLE XXIII

Expt. No.	Total activity of mixture c.p.m.	Total MeI activity	Total PrI activity	Organic retention %	MeI activity %	Ratio of MeI/PrI activity
A. Irradiation in the absence of air.						
1	740.2	269.3	117.7	52.3	36.4	2.28
2	540.3	197.3	82.52	51.8	36.52	2.39
B. Irradiation in presence of about 0.1% mole of molecular iodine but under vacuum.						
1	804.1	156.9	110.5	33.24	19.51	1.42
2	1028.0	208.0	142.5	34.10	20.24	1.46
C. Irradiation of PrI alone.						
1	604.2	29.65	190.9	42.3	4.909	
2	494.2	20.95	161.1	39.9	4.240	

The results again clearly show that the recoil iodine enters MeI in preference to PrI. The values of the activity ratios of PrI to MeI for the reactions ^{127}I (n,γ) ^{128}I and ^{127}I(n,2n) ^{126}I are 1:1.35 and 1:1.4 respectively in the presence of scavenger iodine; in the absence of scavenger these values become 1:1.8 and 1:2.3 respectively. A possible explanation of this difference in the degree of preferential attachment of recoil iodine to MeI could be that in the thermal energy region the re-entry processes differ in the two nuclear reactions.

REFERENCES

1. H. Suess. Z. Physik. Chem. B45, 297, 312, (1940).
2. Szilard & Chalmers. Nature 134, (1934).
3. Amaldi, Fermi et al. Proc. Roy. Soc. A149, 522, (1935).
4. Glueckauf & Fay. J. Chem. Soc. 390, (1936).
5. W.F. Libby. J. Am. Chem. Soc. 69, 2523, (1947).

   Friedman & Libby. J. Chem. Phys. 17, 647, (1949).
6. J.E. Willard. Ann. Rev. nucl. Sci. 198, (1953).
7. Goldhaber & Willard. J. Am. Chem. Soc. 74, 318, (1952).
8. Levey & Willard. J. Am. Chem. Soc. 74, 6161, (1952).
9. Levey & Willard. J. Am. Chem. Soc. 74, 6163, (1952).
10. Reid. Phys. Rev. 69, 530, (1946).
11. Friedman & Libby. J. Chem. Phys. 17, 647, (1949).
12. Goldhaber, Chiang & Willard. J. Am. Chem. Soc. 73, 2271, (1951).
13. Hornig, Levey & Willard. J. Chem. Phys. 20, 1556, (1952)
14. Hornig, Levey & Willard. J. Chem. Phys. 20, 1556, (1952)
15. Hornig, Levey & Willard. J. Chem. Phys. 20, 1557, (1952)
16. Schuler. J. Chem. Phys. 20, 2026, (1954)
17. Muehlhause. Phys. Rev. 79, 277, (1950).
18. Starke. Physik. Z. 42, 184, (1941).
19. S. Katcoff. Phys. Rev. 71. 826, (1947).

20. Purkayastha & Martin. Can. J. Chem. 293, (1956).

21. P. Sue & Beydon. Bull. Soc. Chim. 55, 11, (1944).

22. H.A.C. McKay. Nature, 139, 283, (1937).

23. Willard. Ann. Rev. nucl. Sci. 202, (1953).

24. Apers & Capron. J. Inorg. Nucl. Chem. 219, (1956).

25. Gilfillan et al. Analytical Chemistry Vol. II.

26. R.S.H. Chiang & Willard. Science, 112, 81, (1950).

27. Levey & Willard. J. Am. Chem. Soc. 74, 6161 (1952).

28. McCauley et al. J. Am. Chem. Soc. 78, 3246, (1956).

29. Hamill & Schuler. J. Am. Chem. Soc. 3466, (1951).

30. McCauley, Williams & Hamill. J. Am. Chem. Soc. 76, 6263 (1954).

31. Luijten et al. Investigations in the field of Organotin Chemistry. Tin research institute (1955).

32. Levey & Willard. J. Am. Chem. Soc. 74, 6161 (1952).

33. H. Schmied & R. Fink. J. Chem. Phys. 27, 1034, (1957).

34. Gordus & Willard. J. Am. Chem. Soc. 79, 4609, (1957).

35. Hornig, Levey & Willard. J. Chem. Phys. 20, 1556, (1952).