Tracer studies of reaction mechanisms photolysis of the acetone – iodine system using (^{1}91)Iastracer

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THESIS

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by

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TRACER STUDIES OF REACTION MECHANISMS

PHOTOLYSIS OF THE ACETONE - IODINE SYSTEM USING ^{131}I AS TRACER.

An investigation of the primary process of reaction of the radicals formed.

C O N T E N T S.

FIGURE TO FACE PAGE.

TABLE TO FACE PAGE

1. INTRODUCTION

Numerous investigations have been carried out on the photolysis of acetone, largely due to its use as a convenient source of methyl radicals. At temperatures above 100°C, when irradiated with Ultra violet light, the photodecomposition yields one radical pair (methyl + acetyl) for each quantum of irradiation absorbed, [1] and there it is possible to have a controlled production of methyl radicals, attention being paid to the intensity of the incident ultra violet light and the acetone pressure.

It has been demonstrated in earlier investigations [2] [3] that the addition of other reactants to the system changes its basic characteristics, and in the presence of iodine the quantum yield of acetone decomposition, Φd, falls far short of unity at 100°C.

It has also been shown that carbon monoxide and nitrogen have a similar but less drastic effect, whereas reagents like biacetyl have a similarly pronounced effect upon the quantum yield.

It would be desirable for workers in this field to be in a position which enabled them to predict the quantum yields of acetone decomposition and product formation, under any conditions and with any added reagents. This present investigation is aimed at extending the work already done in these laboratories on the system, with the hope that the new data will help resolve some of the doubts concerning the exact nature of the primary process, and help the above general aim.

2. THE PRIMARY PROCESS.

Before dealing with the acetone - iodine system under investigation here, it would be worthwhile giving a brief resumé of the primary processes involved in the photolysis of acetone alone.

It has been reasonably proved [4] [5] that the primary process following the absorption of a quantum of ultra violet radiation, involves the rupture of a carbon - carbon bond to produce a methyl and an acetyl radical.

$$CH_3\ CO\ CH_3 \xrightarrow{h\nu} CH_3\ CO\ CH_3^* \quad \ldots\ldots\ldots \quad (1)$$

$$CH_3\ CO\ CH_3^* \longrightarrow CH_3^{\cdot} + CH_3\ CO^{\cdot} \quad \ldots\ldots\ldots \quad (2)$$

The non radical split once suggested (reaction 3) has been dismissed as being of no importance. For example the photolysis of a

$$CH_3\ CO\ CH_3^* \longrightarrow C_2H_6 + CO \quad \ldots\ldots\ldots \quad (3)$$

1 : 1 mixture of acetone and fully deuterated acetone ($CD_3\ CO\ CD_3$) gave an ethane product that on mass spectrometric analysis agreed to 2% of the predicted value assuming a 100% radical split. [6]

Any difference in the products formed under varying conditions of temperature, acetone pressure and ultra violet wavelength, are explained by secondary reactions of the radicals. At the wavelengths 3130 A^o (used exclusively in this present work) and 2157 A^o the reactions 1 and 2 are certainly the primary process involved.

Other products found on analysis of the photolysed system (carbon monoxide, biacetyl, ethane, methane,) have been explained by the following secondary reactions.

$$CH_3CO^{\cdot} \longrightarrow CH_3^{\cdot} + CO^{\cdot} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$2CH_3^{\cdot} \longrightarrow C_2H_6 \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

$$CH_3^{\cdot} + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2^{\cdot} \quad \ldots\ldots\ldots \quad (6)$$

$$2CH_3CO^{\cdot} \longrightarrow (CH_3CO)_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

There is evidence that for photolysis at high temperatures (>250°C) the products of secondary reactions also include ethylene and ketene. Variations of temperature, pressure and wavelength upon the relative yields of products is discussed below.

TEMPERATURE

The apparent quantum yield of dissociation of acetone, Φd, has a value of around 0.3 at room temperature when irradiated with light of wavelength 3130 A°, but this rises to a value of almost unity at 100°C.[7] This value is maintained over a large temperature range.[8]

At lower temperatures ethane is a major product, but increasing temperature produces a falling value of $\Phi_{C_2H_6}$ in favour of an increase in methane production. This is explained by the activation energy required by reactions 5 and 6, the latter remaining relatively constant in comparison to that required for reaction 5, (with a rise in temperature) which increases rapidly. The production of biacetyl at higher temperature is negligable, due to the thermal decomposition of acetyl radicals, by reaction 4, before recombination can take place. This latter fact is illustrated by the rapid rise in the quantum yield of carbon monoxide with increase in temperature. ($\Phi_{CO} = 1$ at 120°C)

PRESSURE

Increases in acetone pressure at a fixed temperature cause a reduction in the observed values of ϕd, this reduction being initially sharp, but as the pressure increases further the values of ϕd level out. At all temperatures the value of ϕd tends to unity as acetone pressure tends to zero.

All the above remarks apply to a system irradiated with ultra violet light of 3130 A° wavelength. At shorter wavelengths (in the region of about 2000 A°) other primary processes become important. Little work has been done at the short wavelengths, but evidence for a primary split producing hydrogen has been put forward.(9)

$$CH_3\,CO\,CH_3^* \longrightarrow CH_3\,CO\,CH_2^{\cdot} + H^{\cdot} \quad \ldots\ldots\ldots\ldots\ldots (8)$$

However since all the present work was carried out at 3130 A° the effects of shorter wavelengths will not be further discussed.

Acetone – Iodine System.

The earliest work conducted on this system was by Gorin [10][11], but the whole work is open to much doubt due to inconsistancy and improbably high quantum yields for methyl iodide when viewed in the light of later work.

The first investigations to yield important information was that of Forbes and Benson [12], which noted the absence of ethane and biacetyl in the products. Their attempts to isolate acetyl iodide from the products were not successful. This was due to the extremely unstable nature of the substance, which decomposes when in contact with mercury vapour, in light, and is extremely susceptible to hydrolysis by traces of water. Later work with blank runs using acetyl iodide gave very low recovery yields. [13] Yields of carbon monoxide obtained by Forbes and Benson have not been confirmed and seem to be high.

Work by Sutton and Martin [2] in this laboratory was carried out with superior techniques and the results obtained were in good agreement (where comparison was possible) with that done at the same time by Pitts and Blacet [14] using different methods. Sutton and Martin also had difficulty in seperating acetyl iodide.

A brief summary of their findings is given;

1) Products isolated were mainly methyl iodide, acetyl iodide and carbon monoxide.

2) Yields of carbon monoxide were low ($\phi_{CO} < 0.01$). This yield increased with temperature and decreased with acetone or iodine pressure increases.

3) Acetyl iodide results were unsatisfactory for reasons mentioned above. In the absence of much carbon monoxide and biacetyl, acetyl iodide yields should be of the same magnitude as methyl iodide yields.

4) Methyl iodide quantum yields varied with iodine pressure, dropping in value with an increase in iodine concentration until a constant value was obtained. Increases in acetone pressure also decreased the methyl iodide yield.

Mechanism.

Martin and Sutton put forward the first theoretical scheme to fit the accumulated evidence. This postulated that on absorbing a quantum of radiation the acetone molecule is converted into an electronically excited state A'.

$$A + h\nu \longrightarrow A' \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1A)$$

This state they argued, was susceptible to two forms of removal, forming either products (methyl and acetyl radicals) or a partial - deactivation by iodine molecules to a second excited state A".

$$A' \longrightarrow CH_3^{\cdot} + CH_3CO^{\cdot} \ldots\ldots\ldots\ldots \quad (2A)$$

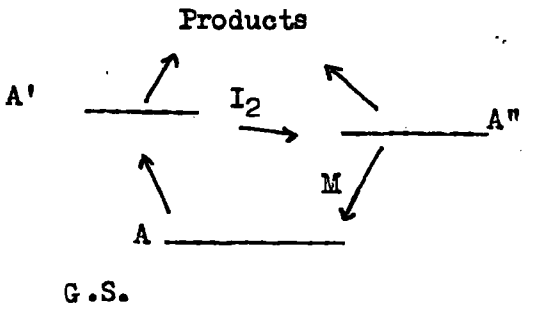
$$A' \xrightarrow{I_2} A'' \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

This second state still has enough energy to decompose to products in competition with a further deactivation by collision with acetone or iodine molecules to the ground state of acetone.

$$A'' \longrightarrow CH_3^{\cdot} + CH_3CO^{\cdot} \ldots\ldots\ldots\ldots \quad (2B)$$

$$A'' + M \longrightarrow A + M \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

This scheme can be represented graphically.



The formation of the observed products was explained by the following secondary reactions.

$$CH_3^{\bullet} + I^{\bullet} \longrightarrow CH_3 I \quad \text{.....(11)}$$

$$CH_3^{\bullet} + I_2 \longrightarrow CH_3 I + I^{\bullet} \quad \text{.....(11A)}$$

$$CH_3 CO^{\bullet} + I^{\bullet} \longrightarrow CH_3 CO I \quad \text{.....(12)}$$

$$CH_3 CO^{\bullet} + I_2 \longrightarrow CH_3 CO I + I^{\bullet} \quad \text{.....(12A)}$$

$$I^{\bullet} + I^{\bullet} \longrightarrow I_2 \quad \text{.....(13)}$$

The small amount of carbon monoxide isolated was explained by including reaction 4 ($CH_3 CO^{\bullet} \longrightarrow CO + CH_3^{\bullet}$) competing unfavourably with reaction 12, as a mode of removal of acetyl radicals. Iodine reacting with the radicals produced, suppresses any recombination of the radicals explaining the absence of ethane and biacetyl in the products.

Applying the steady state treatment to this scheme the following kinetic equation was obtained.

$$\Phi_{CH_3 I} - \Phi_{co} = 1 - \left[1 + \frac{K_{2A}}{K_9[I_2]}\right]^{-1}\left[1 + \frac{K_{2B}}{K_{10}[M]}\right]^{-1} \quad \ldots\ldots(14)$$

(APPENDIX I)

Making the assumption that acetone and iodine are equally likely to deactivate A", (M) can be put equal to the total pressure in the system. Using 'best fit' values of $\frac{K_{2A}}{K_9}$ and $\frac{K_{2B}}{K_{10}}$ the above equation shows good agreement over the range of $(\Phi_{CH_3 I} - \Phi_{co})$ values obtained experimentally.

Subsequent work by Brown [15] in this laboratory led to a revision of the Martin and Sutton mechanism with regard to the mode of deactivation of the A' and A" species.

In the revised mechanism Brown suggested that A' is deactivated to the A" species by acetone molecules, and that A" is itself deactivated by the iodine present. Both species are still assumed to also decompose to yield products.

$$A' + M \longrightarrow A'' + M \quad \ldots\ldots\ldots\ldots (15)$$

$$A'' + I_2 \longrightarrow A + I_2 \quad \ldots\ldots\ldots\ldots (16)$$

This revision also permits acetone molecules to deactivate A" but competing unfavourably with reaction 16. Also the revision has the effect of postulating that both A' and A" species would be present in the photolysis of pure acetone (i.e. with no added iodine.) Applying the steady state theory to the new system a similar kinetic equation is produced, which still shows good agreement with the experimental results.

$$\Phi_{CH_3I} - \Phi_{CO} = 1 - \left[1 + \frac{K_{2A}}{K_{15}[M]}\right]^{-1} \left[1 + \frac{K_{2B}}{K_{16}[I_2]}\right]^{-1} \quad \ldots\ldots(17)$$

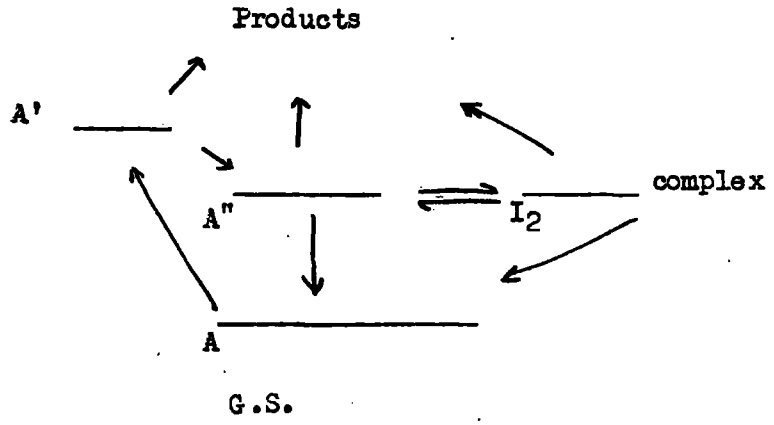
Later work by Mitchell [13] on the fluorescence of acetone in the pressence of iodine strengthened Browns revised mechanism. In the pure acetone system there are two electronically excited states A* and A** of which A** is the longer lived, and responsible for the greater intensity of fluorescence. Martin and Sutton by assuming reasonable collision diameters for the A' deactivation, and assuming each collision promoted a deactivation, obtained a half life for A' of 4×10^{-7} sec. which was close enough to that of A* to enable its identification with this species.[2.]

Rise of temperature quenches the fluorescence efficiency of A** much more than that of A*, such that the relative contributions at 5°C are 3:1 whilst at 85°C the ratio is 2:1. [13] However at all temperatures within the range of experimental results under consideration here, A** contributes the major intensity to the final fluorescence. Whereas in the Martin and Sutton scheme, iodine quenches the A' species, in the revision of Brown it would be A", thus the addition of iodine to the system would cause little difference or a sharp decrease in fluorescence, depending upon which theory is applicable. Mitchell's work resulted in a decrease in intensity with added iodine, and this was more pronounced at lower temperatures. This was a good indication that Browns mechanism was acceptable and also that A" could now be positively identified with A**. It also enabled the suggestion that A" was itself an acetone - iodine complex to be overruled.

A further possibility is that the deactivation of A" leads to a

complex of acetone and iodine which itself is capable of decomposition to produce or to return acetone to its ground state.

$$A'' + I_2 \longrightarrow \text{Complex} \quad \ldots\ldots\ldots\ldots (18)$$



$$\text{Complex} \longrightarrow \text{Products} \quad \ldots\ldots\ldots\ldots\ldots (19)$$

$$\text{Complex} \longrightarrow A + I_2 \quad \ldots\ldots\ldots\ldots\ldots (20)$$

Such a system has one drawback. The presence of oxygen, biacetyl and iodine in the photolysis of acetone each have the same effect and reduce the value of Φ d to a similar value. This would suggest that the values of K_{19} and K_{20} were similar for each reagent, and this fact, whilst not impossible does seem rather unlikely.

This mechanism could be improved in the above respect by assuming that the complex does not decompose to yield products, but only to reduce the acetone to its ground state, thus eliminating reaction 19.

Applying the steady state theory to this system the following equation is obtained (Appendix 3)

$$(\Phi_d - \Phi_\infty)^{-1} = \left(1 + \frac{K_{2A}}{K_{15}[A]}\right)\left(\frac{J_{18}(I_a)}{h_{2b}[A]}\left(1 + \frac{K_{-18}}{K_{20}}\right)^{+1}\right) \quad \ldots\ldots(21)$$

From the appendix it may be seen that this mechanism would explain the similar limiting values of Φ_d, regardless of the quenching reagent introduced into the system. If this mechanism is tenable a graph of $\left[(\Phi_d - \Phi_\infty)^{-1}\left(1 + \frac{K_{2a}}{K_{15}[A]}\right) + 1\right]$ against iodine should be a straight line. A value of $\frac{K_{2a}}{K_{15}[A]}$ can be obtained from the limiting value of Φ_d (i.e. Φ_∞) as explained in the appendix. Work carried out recently in this laboratory by Clough when interpreted in the above manner gave a plot which was tolerably a straight line, but with a fair degree of scatter, which became more pronounced at the higher iodine concentrations. The agreement was however enough to warrant, perhaps the partial acceptance of this mechanism as contributing towards the overall mode of reaction, and certainly to a further investigation of the problem.

2A APPENDIX I Martin & Sutton theory.

$$A + h\nu \longrightarrow A' \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1A)$$

$$A' \longrightarrow CH_3^{\bullet} + CH_3\,CO^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2A)$$

$$A' + I_2 \longrightarrow A'' + I_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

$$A'' \longrightarrow CH_3^{\bullet} + CH_3\,CO^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2B)$$

$$A'' + M \longrightarrow A + M \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

$$CH_3\,CO \longrightarrow CH_3 + CO \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

The reaction products are formed from the radicals by the reactions:-

$$CH_3^{\bullet} + I^{\bullet} \longrightarrow CH_3\,I \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

$$CH_3^{\bullet} + I_2 \longrightarrow CH_3\,I + I^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11A)$$

$$CH_3\,CO^{\bullet} + I^{\bullet} \longrightarrow CH_3\,CO\,I \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

$$CH_3\,CO^{\bullet} + I_2 \longrightarrow CH_3\,CO\,I + I^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12A)$$

Now by the steady state theory

$$\frac{d(CH_3)}{dt} = 0 = K_{2A}(A') + K_{2B}(A'') + K_4(CH_3\,CO) - K_{11}(CH_3)(I) - K11_A(CH_3)(I_2).$$

Now $$\frac{d(CH_3\,I)}{dt} = K_{11}(CH_3)(I) + K11_A(CH_3)(I_2)$$

and $\frac{d(CO)}{dt} = K_4 (CH_3 CO)$

therefore $\frac{d.(CH_3 I)}{dt} - \frac{d(CO)}{dt} = K_{2A} (A') + K_{2B}(A")$.....(a)

now $(A') = \frac{I_a}{K_{2A} + K_9 (I_2)}$

and $A" = \frac{I_a K_9 [I_2]}{(K_{2B} + K_{10} [M])(K_{2A} + K_9 [I_2])}$

Therefore, since

$$\Phi CH_3 I - \Phi CO = \frac{\frac{d(CH_3 I)}{dt} - \frac{d(CO)}{dt}}{I_a}$$

and substituting values of A' and A" in equation (a)

$$\Phi CH_3 I - \Phi CO = \frac{K_{2A}}{K_{2A} + K_9 [I_2]} + \frac{K_{2B} K_9 [I_2]}{(K_{2B} + K_{10} [M])(K_{2A} + K_9 [I_2])}$$

$$= \frac{K_{2A}K_{2B} + K_{2A} K_{10}[M] + K_{2B} K_9 [I_2]}{(K_{2B} + K_{10}[M])(K_{2A} + K_9 [I_2])}$$

$$= \frac{(K_{2A} + K_9 [I_2])(K_{2B} + K_{10}[M]) - K_9 K_{10} [I_2][M]}{(K_{2B} + K_{10} [M])(K_{2A} + K_9 [I_2])}$$

$$= 1 - \frac{K_9 K_{10} [I_2][M]}{(K_{2B} + K_{10}[M])(K_{2A} + K_9 [I_2])}$$

$$= 1 - \left(1 + \frac{1}{\frac{K_{2B}}{K_{10}[M]}}\right)\left(1 + \frac{1}{\frac{K_{2A}}{K_9 [I_2]}}\right)$$

$$\Phi CH_3I - \Phi CO = 1 - \left(1 + \frac{K_{2A}}{K_9 [I_2]}\right)^{-1} \left(1 + \frac{K_{2B}}{K_{10}[M]}\right)^{-1} \quad \text{——(14)}$$

APPENDIX II Brown Revision.

This is essentially the same except that reactions 15 and 16 replace 9 and 10 .

$$A' + I_2 \longrightarrow A'' \quad \text{.....(9)}$$

replaced by $A' + M \longrightarrow A'' + M$ .....(15)

and $A'' + M \longrightarrow A + M$ .....(10)

by $A'' + I_2 \longrightarrow A + I_2$ .....(16)

Similar calculations as before yield the new kinetic equation

$$\Phi_{CH_3 I} - \Phi_{CO} = 1 - \left(1 + \frac{K_{2A}}{K_{15}[M]}\right)^{-1} \left(1 + \frac{K_{2B}}{K_{16}[I_2]}\right)^{-1} \quad \text{....(17)}$$

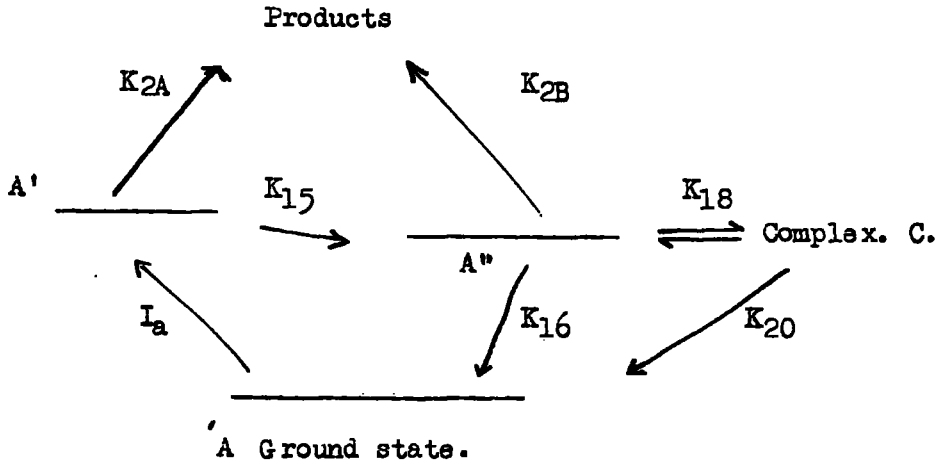
Assuming that methyl iodide can arise from acetyl radicals only as a result of prior decomposition of the radical via reaction 4, then:

$$\Phi_d = \Phi_{CH_3 I} - \Phi_{CO}$$

Φ_{CO} is less than 1% of the corresponding $\Phi_{CH_3 I}$ value, thus within the limits of experimental error

$$\Phi_d = \Phi_{CH_3 I}$$

APPENDIX III



Applying steady state theory:-

$$A' = \frac{I_a}{K_{2A} + K_{15}} \qquad A'' = \frac{K_{15}\,A' + K_{-18}\,C}{K_{16} + K_{18} + K_{2B}}$$

$$C = \frac{K_{18}\,A''}{K_{-18} + K_{20}}$$

Thus

$$A'' = \frac{\dfrac{K_{15}\,I_a}{K_{2A} + K_{15}} + \dfrac{K_{-18}\,K_{18}\,A''}{K_{-18} + K_{20}}}{K_{16} + K_{18} + K_{2B}}$$

$$= \frac{\dfrac{K_{15}\,I_a}{K_{2A} + K_{15}}}{K_{16} + K_{18} + K_{2B} - \dfrac{K_{18}\,K_{18}}{K_{-18} + K_{20}}}$$

$$A'' = \frac{K_{15} I_a}{(K_{2A} + K_{15})\left(K_{16} + K_{2B} + \frac{K_{18} K_{20}}{K_{20} + K_{-18}}\right)}$$

Decomposition to products

$$I_a \Phi_d = K_{2A} A' + K_{2B} A''$$

$$I_a \Phi_d = \frac{K_{2A} I_a}{K2A + K15} + \frac{K_{2B} K_{15} I_a}{(K_{2A} + K_{15})(K_{16} + K_{2B} + \frac{K_{18} K_{20}}{K_{20} + K_{-18}})}$$

$$\Phi_d = \frac{K_{2A}}{K_{2A} + K_{15}} + \frac{K_{2B} K_{15}}{(K_{2A} + K_{15})(K_{16} + K_{2B} + \frac{K_{18} K_{20}}{K_{20} + K_{-18}})}$$

Now at infinite iodine concentration $K_{18} \longrightarrow \infty$

Thus the second term $\longrightarrow 0$

$$\text{thus } \Phi_\infty = \frac{K_{2A}}{K_{2A} + K_{15}} = \frac{1}{1 + \frac{K_{15}}{K_{2A}}}$$

Now assume that $K_{15} = h_{15}$ [A]

$$\Phi_\infty = \frac{1}{1 + \frac{K_{15}\text{ [A]}}{K_{2A}}}$$

As the acetone pressure is constant in the series of runs, a value of $\frac{h_{15}[A]}{h_{2A}}$ can be obtained from the limiting value of Φ_d. (i.e. Φ_∞)

This now would account for the similar limiting values of obtained by using different quenching agents.

For fixed [A], from above :

$$\Phi_d - \Phi_\infty = \frac{K_{2B}\, K_{15}}{(K_{2A} + K_{15})\left(K_{16} + K_{2B} + \frac{K_{18}\, K_{20}}{K_{20} + K_{-18}}\right)}$$

$$\Phi_d - \Phi_\infty = \left(\frac{1}{1 + \frac{K_{2A}}{K_{15}}}\right)\left(\frac{1}{\frac{K_{16}}{K_{2B}} + 1 + \frac{K_{18}\, K_{20}}{K_{2B}(K_{20} + K_{-18})}}\right)$$

In the absence of quenching agent $\Phi_d \longrightarrow 1$, thus the ratio $\frac{K_{16}}{K_{2B}}$ must be very small, thus:

$$\Phi_d - \Phi_\infty = \left(\frac{1}{1 + \frac{K_{2A}}{K_{15}}}\right)\left(\frac{1}{1 + \frac{K_{18}\, K_{20}}{K_{2B}\,(K_{20} + K_{-18})}}\right)$$

Thus putting $K_{18} = J_{18}[I_2]$ and $K_{2B} = h_{2B}[A]$

$$\Phi_d - \Phi_\infty = \left(\frac{1}{1 + \frac{K_{2A}}{K_{15}}}\right)\left(1 + \frac{1}{\frac{J_{18}[I_2]}{K_{2B}}\left\{1 + \frac{K_{-18}}{K_{20}}\right\}}\right)^{-1}$$

$$\frac{1}{\Phi d - \Phi_\infty} = \left(1 + \frac{K_{2A}}{h_{15}[A]}\right)\left(\frac{J_{18}[I_2]}{h_{2B}[A]\left(1 + \frac{K_{-18}}{K_{20}}\right)} + 1\right)$$

Therefore a plot of $\left[\left(\frac{1}{\Phi d - \Phi_\infty}\right)\left(\frac{1}{1 + \frac{K_{2A}}{h_{15}[A]}}\right) - 1\right]$ against iodine concentration should be a straight line.

3. Experimental Techniques.

Preparation of samples.

Iodine ..... The method of preparing iodine samples was that used by Sutton.[2] The 8 day isotope I_{131} was used, being the most practical from both counting and half life considerations. It was obtained carrier free from the Radiochemical centre at Amersham. Enough iodine was prepared for about two - three weeks work at a time.

The active iodine (supplied as potassium iodide) was diluted by addition of a known weight of potassium iodide. The iodine in this solution was then precipitated in the form of palladous iodide, Pd. I_2, by treatment with a slightly acidic (HCl) solution of palladous chloride. After completing the precipitation and coagulation by heating upon a hot plate, the precipitate was washed several times with distilled water and finally transfered to the container A in figure 1. It was found convenient that the preliminary steps mentioned above should be carried out in A, thus reducing the possibility of loss in the final transfer. After attaching A to the rest of the apparatus, the system was evacuated until a sticking vacuum was obtained. Slight warming of A was helpful to completely remove water from the precipitate.

When the vacuum had been obtained the palladous iodide was heated to about 400°C, at which temperature it decomposed to yield iodine and palladium. The U tube U, was cooled by immersion in liquid nitrogen, and thus the iodine liberated was collected in this portion of the apparatus.

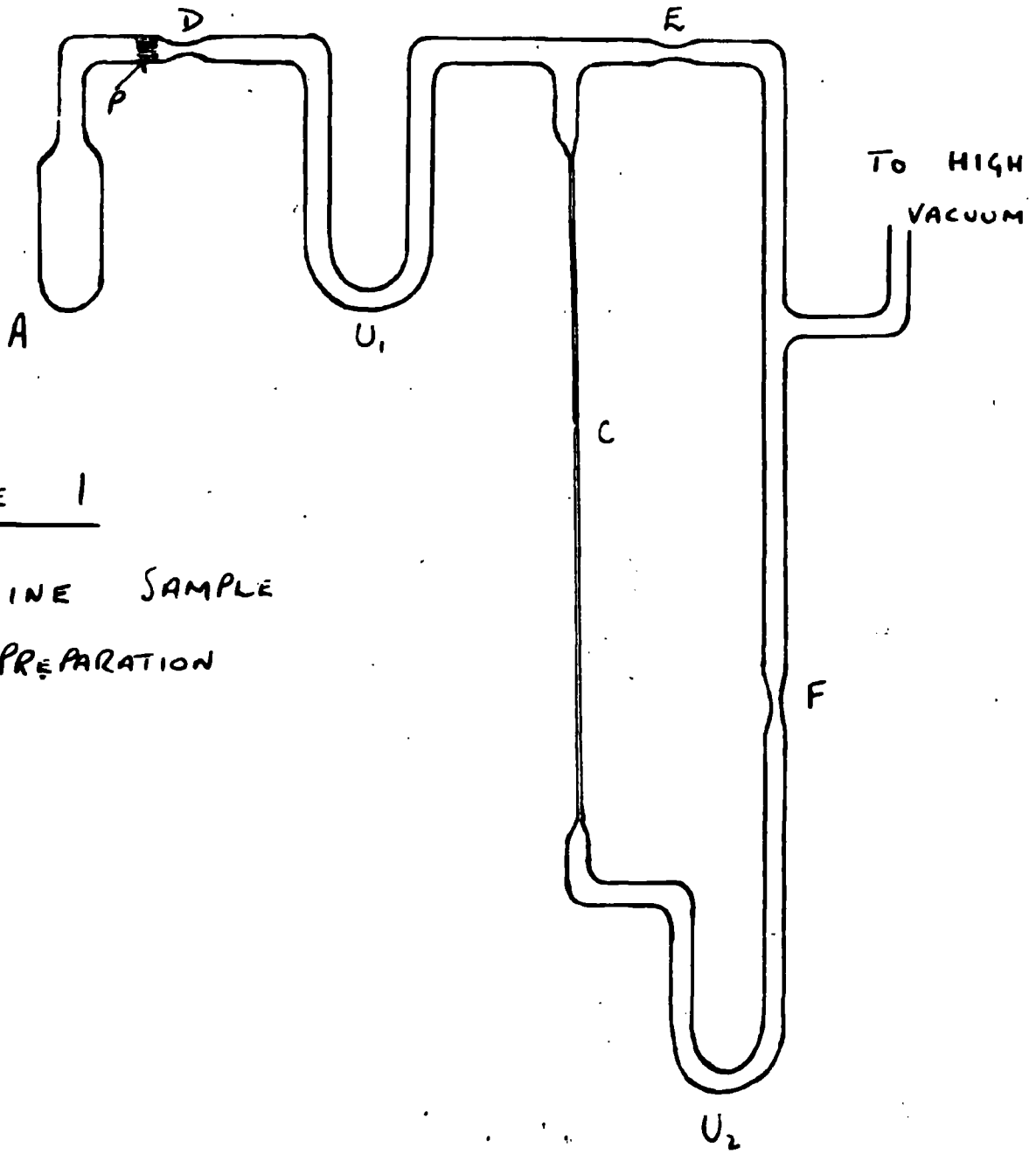


FIGURE 1

IODINE SAMPLE PREPARATION

The glass wool plug P prevented any flakes of palladium being carried over with the iodine. When all the iodine had been sublimed into the U tube the constrictions D and E were sealed.

The U tube U_2 was then cooled in liquid nitrogen and U_1 allowed to warm up. The iodine was sublimed into the capilliary tubing C. This was a delicate process and great care was needed especially if the capilliary was very thin. (The thickness of the tube is of great importance. If it is too thin, then it is liable to be broken during the filling process. If on the other hand it is too robust, difficulty would be encountered later on when it had to be broken to release the iodine into the reaction vessel.) The system was kept open to the pumps during this final sublimation to help the distribution of iodine along the whole length of the capilliary. When all the iodine was in the tube the two ends were sealed as was constriction F. The single length of tubing was then subdivided in smaller units containing amounts of iodine, this being estimated by their γ activities relative to one chosen capilliary which was later broken under a potassium iodide solution and titrated with sodium thiosulphate solution. In determining the γ activities it was found desirable to sublime the iodine to one end of each small tube, to ensure a uniform positioning of the sample in the well crystal of the scintillator. The activities of the separate samples immediately after preparation varied between 15,000 to 100,000 c.p.m, this upper limit being within the range of the counting equipment. (The usual corrections for resolving time (50 μsec) were made.)

The yield of iodine produced in this manner was very high. The losses were from two sources. However much it was attempted to keep mercury vapour out of the system it was never achieved, and yellow/red traces of mercury iodide were always found. The second loss was due to the iodine passing through the capilliary into U_2. This iodine however could be used as a check upon the calibration titration mentioned above. The amount was generally very small.

Other workers in this laboratory have used the fact that the thermal decomposition of palladous iodide is virtually 100%, to introduce the iodine directly into the reaction vessel during the filling process, by heating a weighed amount of iodide. This method has one distinct advantage that it is easy to produce a desired iodine concentration, simply by weighing out the necessary iodide, a possibility that is obviously not permissable with the technique used in this investigation, where only approximations can be made. This method had the disadvantages that the decomposition may not be complete, giving incorrect iodine concentrations, and that the palladous iodide may not be pure, which would lead to the same error as the weight of the iodide would be incorrect. A third but minor drawback is the possibility of flakes of palladium entering the reaction vessel.

ACETONE ..... Previous workers have used Analar grade acetone which they redistilled and fractionated, using the middle third. However Trotman-Dickenson[16] found no difference between this and normal dried Analar grade acetone in a series of photolyses carried out. Thus in

the present work analar grade was dried thoroughly with preheated magnesium sulphate and then distilled in vacuo into the resevoir R of figure 2. Finally it was vigorously degassed by pumping on the sample which was held fast by an acetone -ethanol- dry ice mixture at - 78° C,. This process removed any permanent gases to an amount below detectable limits.

Filling of the Reaction Vessel.

Before each irradiation the reaction vessel itself was cleansed thoroughly, internally, by steeping it in a sulphuric - chromic acid mixture. Naturally any trace of this cleansing solution had to be removed, and this necessitated washing the vessel many times with distilled water. Special attention was paid to cleansing the side arm into which the acetone was to be frozen.

The section C_4, C_3, B, and C_2 in figure 2 was constructed for each run and attached to the reaction vessel. The capilliary of iodine was placed in portion B which contained a soft iron plunger. The gas and water in the system were pumped until a sticking vacuum was obtained, and then the whole system was isolated from the vacuum line by means of the tap T_1. Initially this tap was also cut off from the filling system by means of a mercury cut off valve, thus preventing the acetone coming into contact with tap grease. However, in the work reported here the apparatus was attached to a line with many taps so this refinement was not necessary. The amount of acetone absorbed by the grease would be negligable, especially since it was only in contact with the grease for a very brief time period.

By lowering the mercury float valve V acetone was allowed to evaporate into the closed system. From a prior knowledge of the volumes of the respective parts of the system, the pressure required at room temperature in the total volume to give the required concentration under photolysis conditions was obtained. The acetone was then condensed into the side arm S and the valve V_1, which had previously been held

open by a magnet, was now allowed to fall into position. When the acetone was frozen the U tube containing gold foil was immersed in liquid nitrogen, this preventing the passage of mercury vapour into the reaction vessel. The constriction C_2 was then sealed. In calibration runs, C_3 was sealed and the reaction vessel taken away, cleaned and placed in the irradiation oven.

In runs with iodine, the capilliary was next broken by the soft iron plunger which was enclosed in glass, thus preventing the iodine coming into contact with the iron. The base of the reaction vessel was cooled in liquid nitrogen whilst the iodine was heated slightly to aid the sublimation process. When complete the constriction C.3 was sealed and the iodine allowed to warm up until the reaction vessel (apart from the side arm) was at room temperature. The liquid nitrogen was then removed from the side arm and the acetone allowed to thaw and evaporate through the valve into the rest of the reaction vessel. Such a method of warming up the frozen reactants ensures that neither one is condensed onto the other, thus causing premature reaction products.

Finally the reaction vessel was washed with a teepol solution and then distilled water. This removes any grease from the vessel which in ultra-violet light fluoresces. After drying and polishing, the reaction vessel was placed in the oven.

3B Irradiation system and procedure.

System.

This system is illustrated in figure 3. The source of the ultra violet light was a mercury lamp operated from a stabilized D.C. supply which produced a steady emission. Any slight variations of output were negligible.

The filter system was based upon the system used by Kasha.[17] The aim of this was to produce a monochromatic beam of radiation of wavelength 3130 A^{o}. The nickel sulphate solution (50gm/l) which filled the quartz flask was positioned, in respect to the lamp, such that a parallel beam was produced. This position was found by trial and error. A movable shutter was placed between this flask and the remainder of the system which consisted of;

A) A disc shaped quartz cell (of 1cm width between the two faces) containing a solution of potassium chromate (.48gm/l) and sodium hydroxide. (.4gm/l) The latter was added to prevent the formation of dichromate.

B) A 2mm thick plate filter of type OX 7. (Chance Bros. Ltd.)

C) A second cell, as above, between an OX7 plate on the leading side, and a 2mm quartz optical flat on the other, containing a solution of potassium biphthalete (5gm/l). The thickness of this cell was 6mms.

Figure 4 shows the absorption spectrum of each component used in the system. The emissions of importance from the mercury lamp consist

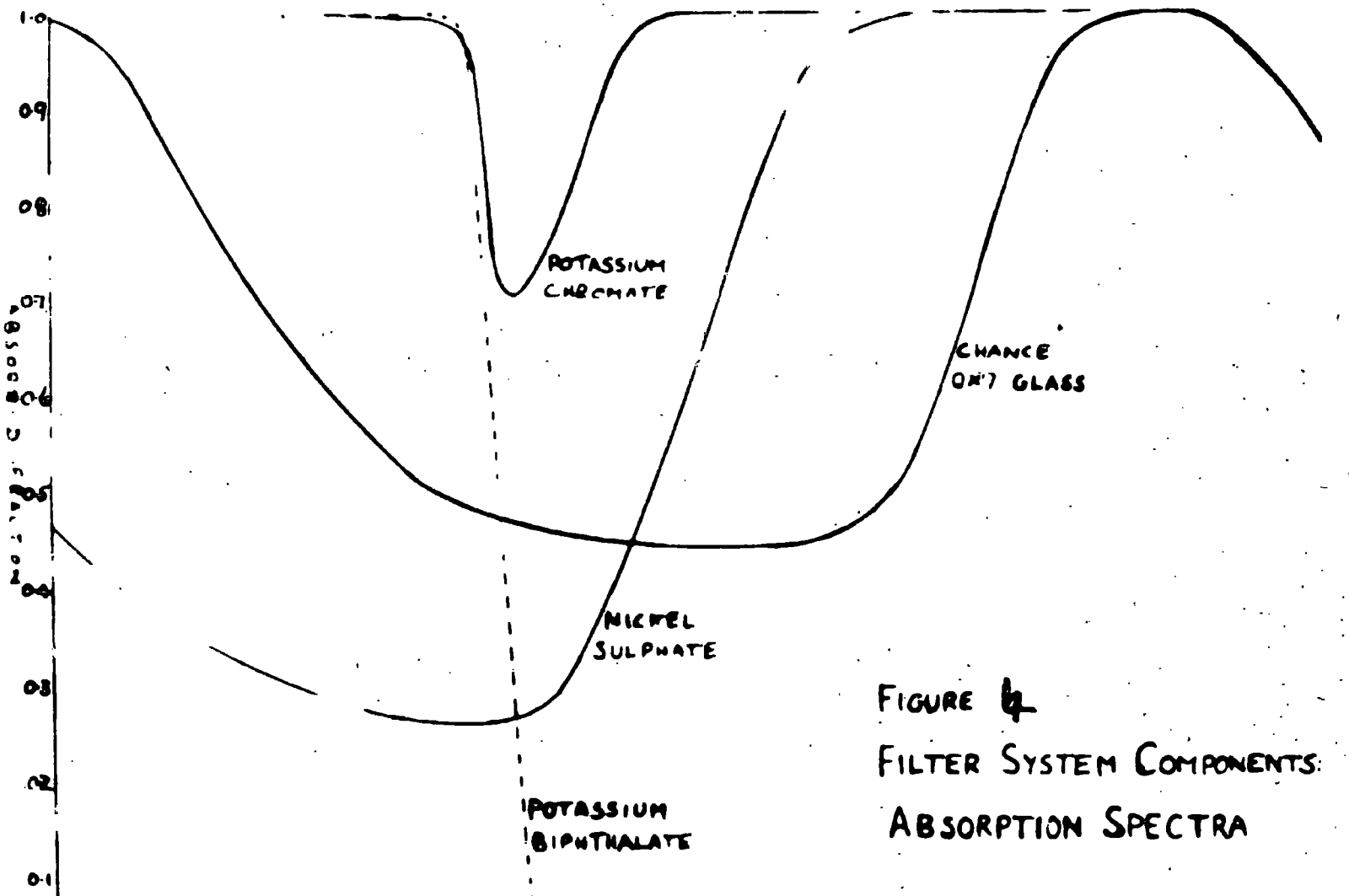


FIGURE 4

FILTER SYSTEM COMPONENTS:
ABSORPTION SPECTRA

of a group at 3130 A^{o}, another at 3022 A^{o} and a line at 3342 A^{o}. The output is such that the group at 3130 A^{o} about 2 - 3 times as intense as each of the other emissions. The absorption system above removes 99.9% and 99.8% of the 3022 and 3342 A^{o} emissions respectively, but only 92% of that at 3130 A^{o}. Thus virtually a monochromatic beam of 3130 A^{o} was produced. It is seen however that this purity has been obtained only at the expense of intensity of which more than 90% has been removed.

The oven in which the reaction vessel was to be placed is a cylinder 40 cms long, with an internal diameter of 16 cms. It was heavily lagged with cotton wool etc. to avoid heat losses. The heating was obtained from a nichrome element which was wound round the inside on an insulated shell. The element was supplied by a Sunvic energy regulator. This system was capable of giving an oven temperature up to about 250°C. The temperature inside the oven varied from the floor to the ceiling, the overall fluctuation between the top and bottom of the reaction vessel when in position was found to be about 8°C. The floor temperature was maintained at 120°C ($\pm \frac{1}{2}$) which gave a mean temperature for the reactants in the vessel of 124° ($\pm$ 1).

Both ends of the furnace were closed by asbestos sheeting into which had been set optical quartz flats to allow passage of the ultra violet light. The rear end consisted of two pieces of asbestos, such that the lower piece, containing the quartz flat, could be easily removed to allow the reaction vessel to be inserted, and then replaced

equally rapidly.

The reaction vessel was constructed of pure fused quartz and was cylindrical in shape. (24 cms length 6 cms diameter.) Attached to it by means of a graded seal, G.S, was a side arm containing the cold finger , C.F, which was used for freezing the contents of the flask during calibration runs, thus obtaining a value for the incident intensity of the ultra violet light, and also during the filling process.

The reaction vessel lay upon two glass covered steel bars which acted as runners and located the axis of the reaction vessel along that of the ultra violet beam. The two optical flats in the asbestos sheeting were of slightly smaller size than the reaction vessel, thus ensuring utilization of all the radiation entering the furnace.

The transmitted beam was absorbed by a selenium layer type photocell, which was placed close up to the rear end of the furnace such that all the transmitted light was incident upon the sensitive surface. This type of cell used no direct voltage and it was connected up in series to a unipivot microammeter and the current produced noted. Brown,[15] in his earlier work in this laboratory, demonstrated that the current recorded on the ammeter varied proportionately with the amount of energy incident upon the cell, thus an arbitary value for the transmitted intensity is available.

All the items mentioned above, lamp, filters, photocell etc. were each supported upon identical chairs which in turn were free to travel linearly along the optical bench or track mentioned before. This

system permits an accuracy of mounting which is easily reproducible.

Irradiation procedure.

Before each run it was necessary to check upon the solution in the filter system. Over a period of time the nickel sulphate solution was found to overflow, due to its proximity to the mercury lamp, and this left a coating of sulphate on the quartz flask. This coating drastically reduced the amount of ultra violet light transmitted, and so any signs of the coat was removed. The chromate solution needed very little attention although once a mould was found to have grown on it. Also slight evaporation may take place as it is close to the furnace. The potassium biphthalate solution deteriorated rapidly and also evaporated at a much faster rate than the other solutions as it is the nearest to the furnace. The sample of biphthalate was replaced every week or after 40 minutes irradiation time.

The lamp source, unlike that of Mitchell and Brown, was stabilized and thus it was not necessary to allow a long 'warm up' period, while the lamp settled down to a steady emission, and in general it was switched on about 10 - 15 minutes before use. The irradiation commenced about 75 minutes after the reaction vessel had been placed in the furnace, this period of time being sufficient for the reactants to be uniformly heated to the required furnace temperature. Once all the preliminary precautions had been taken (solution purity etc.) the overall fluctuation in the emissions from the lamp was small, $< 3\%$, and the average intensity during irradiation was calculated by frequent readings of the photocell

current.

In runs containing acetone - iodine mixtures, immediately after irradiation (5 or 10 mins) the lamp was switched off and the reaction vessel removed and allowed to cool. In calibration runs, containing acetone alone, after lowering the shutter at the finish of the irradiation, the reaction vessel was removed and its contents frozen by immersing the cold finger in liquid nitrogen. The reaction vessel was then replaced in the furnace, the shutter pulled up and the new photocell reading noted, this being an arbitary value for I_o the incident intensity. This whole process should be completed rapidly (2 - 3 minutes) to ensure,

a) The beam intensity has not changed.

b) No acetone evaporates.

Then from a value of both I_T and I_o a value for the absorbed intensity is available ($I_o - I_T$). This can be related directly to the amount of carbon monoxide produced, which in turn, (assuming Φ_{CO} is unity) gives the number of quanta of radiation absorbed.

3C. Analysis of the products from photolysis.

At the beginning of this work the procedure adopted was essentially that used by Clough, but later this was modified with respect to the removal of the iodine, for reasons stated below.

On removal of the vessel from the the furnace it was allowed to cool and then attached to the apparatus shown in figure 5. Instead of attachment being made through a ground glass joint, it was constructed for each run. This reduced any possibility of product removal by the grease which would have to be used.

The system was evacuated until a 'sticking vacuum' was obtained. The traps A and B were then immersed in liquid nitrogen and pumping continued for about a further 5 minutes, and then the taps T_1 and T_2 were closed, and the break seal broken by means of a ball bearing. The condensible products and unused acetone were frozen in the two traps so that any permanent gases could now be isolated. The alumina column, D, served to remove any iodine and acetyl iodide present which it was not desired to collect in the traps. Two traps were needed to ensure no product is carried through to the pumps.

Calibration runs

Extraction of permanent gas

This was necessary only in calibration runs to find out the yield of carbon monoxide produced by the photolysis. As seen above it is known that quantum yield for carbon monoxide under these conditions is unity, thus by comparing the actual yield of carbon monoxide with

the yield of products a value for the quantum yield of the product may be obtained. The gas volatile at - 196°C is a mixture of carbon monoxide and methane. This mixture was transferred from the reaction vessel to the gas burette G. The tap T_2 was opened as was the mercury cut-off valve V_1, whilst V_2 was kept shut, and by means of the toepler pump T_1 the gas transferred. Each stroke pushes some gas into G past the valve V_3, and when the pressure in T_1 is removed and the mercury falls, the ball bearing in V_3 is seated by a small magnet trapping about 2 cms of mercury, this acting as a non return valve. About 30 - 40 strokes were needed to complete this transfer process, a situation reached when the pressure of a given volume (marked on burette) remained unaltered after several successive strokes. Thus the temperature, pressure and volume of the mixture was known.

The measurement of the carbon monoxide was effected by removing it completely, whence the gas remaining would be mainly methane, which was measured in the same manner as above.

For this removal of carbon monoxide, iodine pentoxide was used. This reagent at a temperature of 150°C and in the conditions encountered here, is specific in its oxidation of carbon monoxide to yield carbon dioxide.

$$I_2O_5 + 5CO \rightarrow 5\ CO_2 + I_2 \quad \ldots\ldots\ldots\ldots (22)$$

The iodine produced was absorbed onto silver impregnated glass wool plugs, and the carbon dioxide frozen out in the U tube immersed in liquid nitrogen.

After its initial measurement in the gas burette the mixture was pumped into the portion of the apparatus containing the iodine pentoxide by means of the second toepler pump T_2. Seven strokes were adequate for complete transfer. The gas was left in contact with the iodine pentoxide for a short period, and then after immersing the U tube in liquid nitrogen, closing the mercury valve V_1 and opening V_2, the gas was measured in the gas burette. This cycling process was repeated until a constant value was obtained for the amount of gas remaining. From this value and that of the initial mixture, the amount of gas removed (i.e. carbon monoxide) was calculated.

The efficiency with which the iodine pentoxide oxidizes the carbon monoxide depends upon the immediate history of the reagent. The manufacturers suggest heating before use, and it was also found[13] that on contact with air the iodine pentoxide becomes a very sluggish oxidizer. To overcome this drawback, before its use the reagent was heated to 190° C and pumped upon for about 12 hours by which time a sticking vacuum had been obtained. After such treatment the carbon monoxide produced ($<10^{-6}$ moles) was oxidized in no more than two hours. In several runs the gas was further exposed to the pentoxide for considerably longer periods (i.e. 24 hours) to see if any oxidation of methane took place. In all such cases the final amount of residual gas was unaltered by this additional and prolonged exposure to the iodine pentoxide. If at any time the pentoxide came into contact with air, even only momentarily, the pumping process was repeated.

Analysis of runs containing iodine.

In these runs only methyl iodide yields were required. After obtaining a sticking vacuum in the analytical apparatus the break seal was broken in the same manner described above, with both taps T_2 and T_1, closed. The reactants and products were allowed to condense into the traps, except for any iodine and acetyl iodide which were kept from the traps by the alumina column D . After about 30 minutes the taps T_2 and T_1 were opened to the pumps so that any gas 'trapped' in the alumina column was drawn into the traps, and to ensure that the reaction vessel was completely evacuated. In some runs air was admitted into the system between the column D and the reaction vessel, and then swept away through the traps to carry with it any iodide not previously condensed into the traps. However no apparent difference in the final methyl iodide yield was noticed when this procedure was employed, when compared to runs in which it was absent.

The tap T_2 was now closed and the traps allowed to warm up whilst container C was cooled with liquid nitrogen. This container was constructed so that it just fitted into the well crystal of the scintillator used for counting the γ s' from the iodine. After a further thirty minutes the tap T_3 was closed, it had previously been open, and a fixed amount of acetone admitted to dissolve the iodide for counting purposes. The sample was allowed to warm up prior to placement in the counter. The amount of acetone added must be identical for each run, to ensure that the counting rates are related to one another. If

too much acetone is added the level in the container will be above the top of the well crystal and the recorded counting rate will be lower than the true value. Various tests were carried out to find the maximum possible volume of acetone permitted without reducing the counting rate, and in all the runs just under ½" depth of acetone was used.

In the second series of photolyses a different method of iodine removal was employed for reasons stated later. The new method was that used by Sutton and the portion which replaces the alumina column is shown in figure 6. The piece of apparatus was constructed for each run, and not until the last moment was the potassium hydroxide (6 pellets) introduced through X which was then sealed. The potassium hydroxide removed any hydrogen iodide and acetyl iodide present, together with some of the iodine, as was noted by the colour changes. The remainder of the iodine was absorbed by the silver glass wool barrier S. In runs with very large iodine concentration much iodine remained upon the walls of the reaction vessel, and even when these were gently warmed, it was found to recondense.

Table 1

Calibrations

No.	DT mins.	Acetone pressure* mm of Hg	I_T Arbitary units	I_o	$\frac{I_o - I_T}{I_o}$	Yield of CO moles x10^{-7}	'Q' factor yie of $\frac{CO}{I_T DT}$ x 10^{-9}
A_1**	5	30.8	14.3	17.8	.196	4.04	5.65
A_2**	5	30.8	14.0	17.1	.181	3.977	5.64
B_1	5	30.8	12.1	15.2	.204	1.614	2.470
B_2	5	30.8	9.5	12.2	.221	1.389	2.92
C_1	10	30.8	3.5	4.5	.222	1.090	3.11
C_2	11	30.8	3.9	4.8	.187	1.282	2.988
D_1	5	30.8	8.25	10.4	.206	1.315	3.188
D_2	5	30.8	8.45	10.5	.195	1.365	3.230

*Acetone pressure with an accuracy of 2%

**Timing errors

4 Photolysis of Acetone - Iodine mixtures.

A Calibrations - Photolysis of Acetone.

As stated earlier it has been shown that the quantum yield of formation of carbon monoxide under the prevailing conditions is unity. These calibration runs were carried out to enable the quantum yield of products to be determined, from a knowledge of the carbon monoxide produced.

The absorption of ultra violet light by acetone follows the relationship $I_T = I_o e^{\epsilon lp}$.

p = acetone pressure l = path length ϵ = absorption coefficient

$$\text{thus } I_A = I_o - I_T$$

$$I_A = K I_T$$

This applies to runs in which the acetone pressure is constant, as in the present series. Thus an arbitary value of I_a can be obtained by noting I_T.

In the work carried out all factors (position of cell, pressure of acetone, lens system etc.) which could effect the product yield from run to run were kept constant. Thus the yield of any product was proportional to the time of irradiation and the absorbed intensity of the ultra violet light.

The results obtained are set out in table 1. The lettering relates the calibrations to the actual photolyses which are recorded later.

The Q factor is a measure of the reproducibility of the results and is the following expression

$$= \frac{\text{Yield of carbon monoxide}}{I_T \text{ (Time of irradiation)}}.$$

It is then, the amount of carbon monoxide produced per arbitary unit of incident ultra violet light, per minute. From the last column it can be seen that the values obtained are reasonably constant for the C and D series, which were the only ones whose results have been used.

As the acetone concentration was constant (within 2%) for each photolysis, the ratio of the absorbed intensity to incident intensity should be constant (i.e. $\frac{I_o - I_T}{I_o}$) for all runs. As is seen from column six there is a large degree of variation, up to 20%. However the readings of the I_T and I_o values are subject to errors in reading due to their small value. Consider calibration C_2. Assuming an accuracy of reading ± o.1, which is in fact the least which is realistic, I_T and I_o could be 3.8 and 4.9 respectively

$$\text{therefore,} \quad \frac{I_o - I_T}{I_o} = \frac{1.1}{4.9} = .224 \text{ (c.f. .187)}$$

$$\text{and calibration D,} \quad \frac{I_o - I_T}{I_o} \longrightarrow .217 \quad \text{(c.f. .195)}$$

It is therefore reasonable to say that the figures presented in column 6 are to a great extent constant when the errors in reading are accounted for.

The volume of the carbon monoxide and methane under various pressures and temperatures during analysis was .1172 mls. In calibration D2;

Pressure of gas mixture ($CO + CH_4$+) = 32.5 mms.

Pressure after recycling through L_{gs} = 11·2 mms.

Pressure of carbon monoxide = 21.3 mms.

Volume of gas burette = .1172 mls.

Temperature = 293°C.

Volume of carbon monoxide at N.T.P. = $\frac{273(.1172)21.3}{293.760}$

thus the amount of CO = $\frac{273(.1172)21.3}{293.760.\ 22414}$

= 1.365×10^{-7} moles CO

Table 2

First Series: Results

No.	T mins	I_T	Acetone pressure mm of Hg	I mgms	I molecules /cc x 10^{15}	Me I moles x 10^{-8}	ΦCH_3I
A1	5	14.2	30.8	7.661	29.45	4.150	0.103
A2	5	14.3	30.8	5.142	19.79	4.597	0.114
B1	5	12.1	30.8	1.297	4.991	2.186	0.134
B2	5	11.5	30.8	.5859	2.255	3.504	0.226
B3	5	11.5	30.8	.4341	1.670	4.011	0.258
B4	5	10.9	30.8	.9393	3.614	2.717	0.185
B5	5	11.45	30.8	.4007	1.566	4.300	0.278
B6	4.0	10.0	30.8	2.234	8.596	1.35	0.125
B7	5	10.0	30.8	.7607	2.927	3.238	0.240
B8	5	10.0	30.8	1.686	6.488	1.873	0.139

FIGURE 7

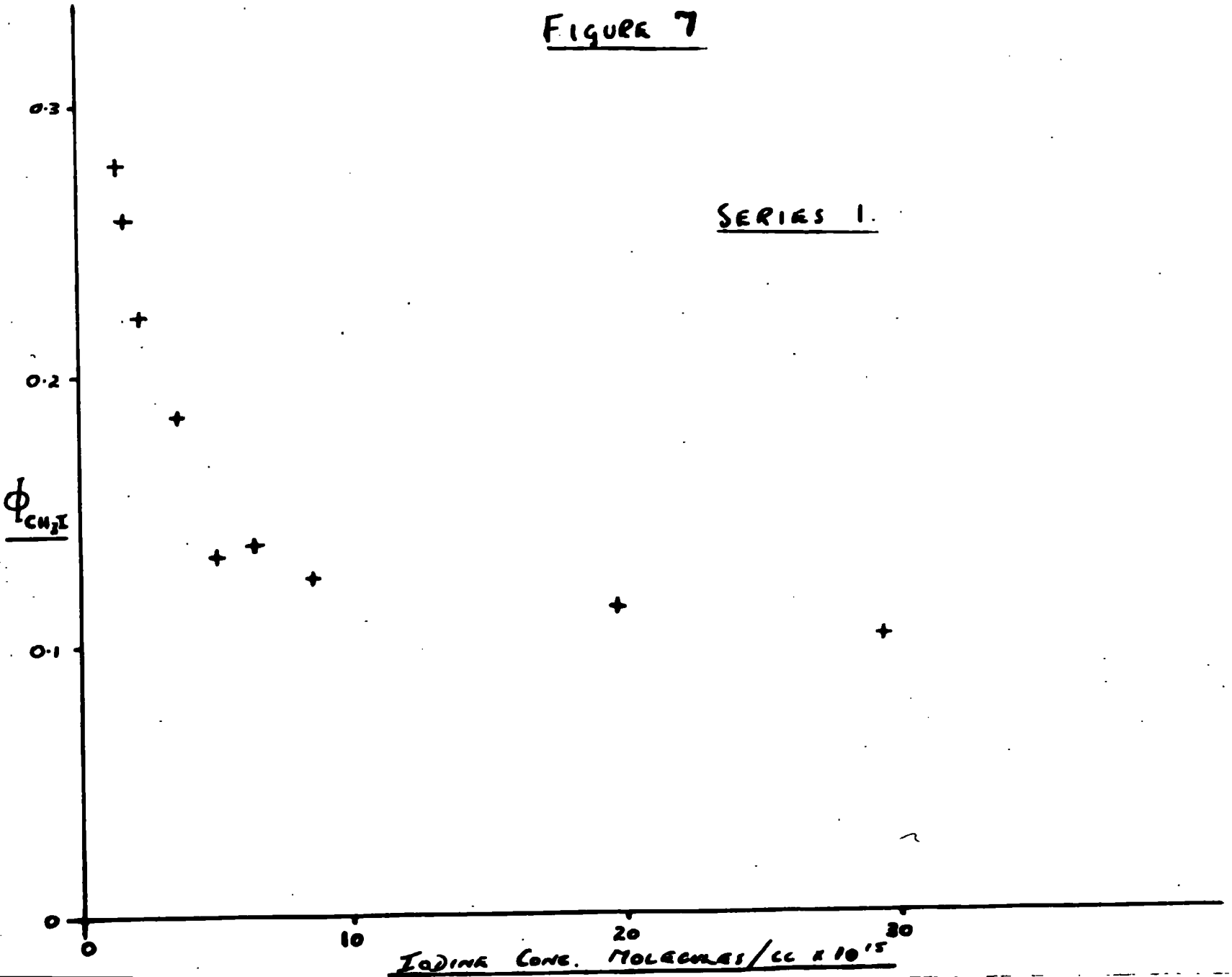

SERIES 1.
0·3
0·2
0·1
0
Φ_{CH_2I}
0
10
20
30
IODINE CONC. MOLECULES/CC x 10^15

Table 3

Second Series: Results

No.	DT	I_T	Acetone Pressure	I mgms	I molecules /cc x 10^{15}	Me I moles x 10^{-8}	ΦCH_3I
D1	5	7.95	30.8	.3171	1.22	10.08	.790
D2	5	8.6	30.8	1.214	4.298	8.754	.634
D3	5	8.35	30.8	1.206	4.268	8.097	.604
D4	5.25	7.9	30.8	2.253	7.97	7.158	.562
D5	5	7.8	30.8	.6183	2.193	8.337	.666
D6	5	7.95	30.8	3.486	12.26	6.864	.538
D7	10	8.6	30.8	4.092	14.72	13.75	.4981
D8	10	10.0	30.8	3.2727	11.5	17.59	.548
D9	10	6.5	30.8	28.46	99.9	8.189	.393
D10	10	6.5	30.8	17.70	62.26	7.814	.3747

FIGURE 8

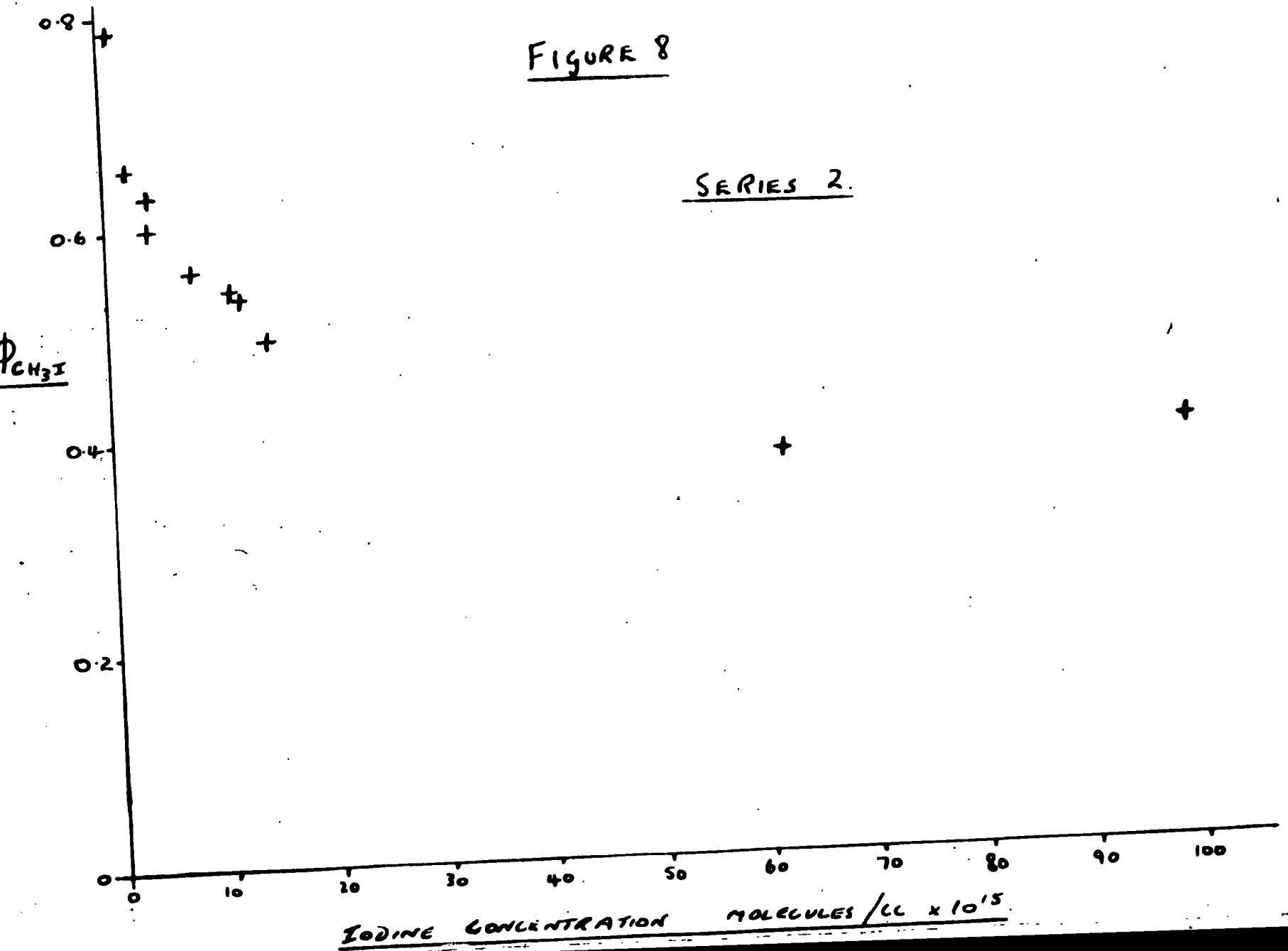
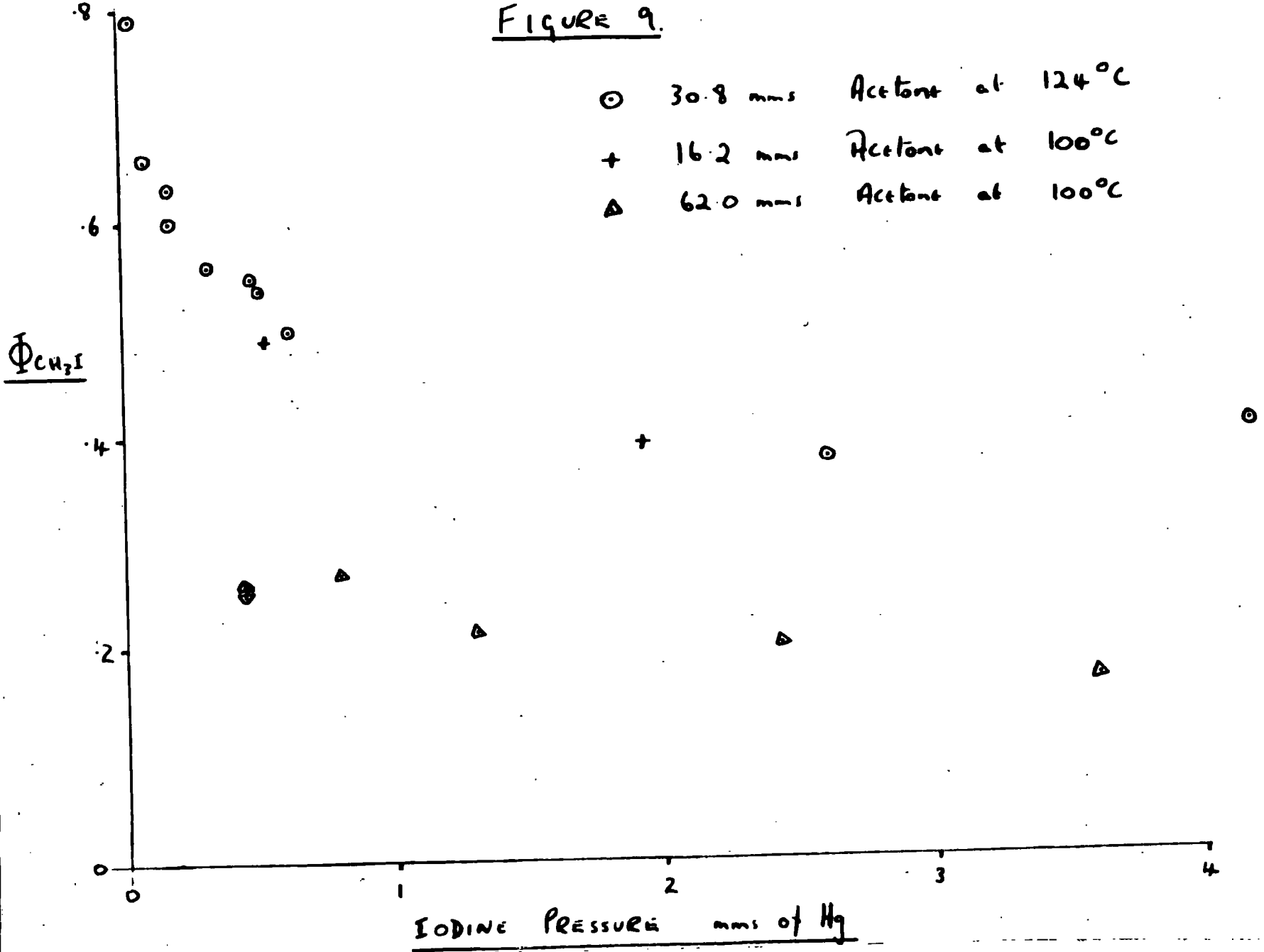

SERIES 2.
Φ_{CH_3I}
0·8
0·6
0·4
0·2
0
0
10
20
30
40
50
60
70
80
90
100
IODINE CONCENTRATION MOLECULES/cc x 10^{15}

FIGURE 9.


⊙ 30·8 mms Acetone at 124°C
+ 16·2 mms Acetone at 100°C
△ 62·0 mms Acetone at 100°C
·8
·6
·4
·2
0
Φ_{CH_3I}
0
1
2
3
4
IODINE PRESSURE mms of Hg

4B Photolysis of acetone - iodine mixture.

In all runs the acetone pressure was maintained at 30.8 mms of Hg under photolysis conditions. The temperature was maintained at $124^{\circ} \pm 1^{\circ}C$. (ref. page 131)

In these runs only the methyl iodide was seperated for determination. The work may be divided into two parts depending upon the method used for removal of iodine in the analytical process. Table 2 gives the details of the results obtained using the alumina column, and figure 7 represents them graphically as a plot of the quantum yield of methyl iodide against iodine concentration. The reduction in the value of $\Phi_{CH_3 I} - \Phi_{\infty}$ with increase in iodine concentration is as would be expected in the light of previous work. However the actual values are much lower than all previous results would suggest. Not only are they low in value, but the runs were at low acetone pressure, and previous evidence[2] indicates this would produce higher quantum yields:

It was then decided to repeat the work using the Sutton method for removal of the iodine, and the results are tabulated in table 3, with the graphical relationship in figure 8. It may be seen from figure 9 that these new results are much more likely when compared with earlier work. The reasons why the first series are so low is not at all clear especially in view of the well defined curve of figure 7. A discussion of this is left until the next chapter.

As suggested in chapter 2 a plot of $\left[(\Phi_d - \Phi_{\infty})^{-1} \left(1 + \frac{K_{2a}}{k_{15}[A]}\right)^{-1} - 1\right]$

Table 4

No.	Φ d	$\Phi d - \Phi_\infty$	$(\Phi d - \Phi_\infty)^{-1}$	'X'	'X'-1	I molecules /cc x 10^{-15}
D1	.790	.420	2.38	1.499	.499	1.22
D2	.634	.264	3.781	2.382	1.382	4.298
D3	.604	.234	4.270	2.689	1.689	4.268
D4	.562	.192	5.208	3.381	2.281	7.97
D5	.666	.296	3.378	2.128	1.128	2.193
D6	.538	.168	5.952	3.749	2.749	12.26
D7	.498	.128	7.795	4.91	3.91	14.72
D8	.548	.178	5.618	3.539	2.539	11.5

From figure 8 the limiting value of ΦCH_3I used = 0.37

This yields a value of 0.63 for $\left(1 + \frac{k2a}{his[A]}\right)^{-1}$

$$'X' = (\Phi d - \Phi_\infty)^{-1}\left(1 + \frac{k2a}{his[A]}\right)$$

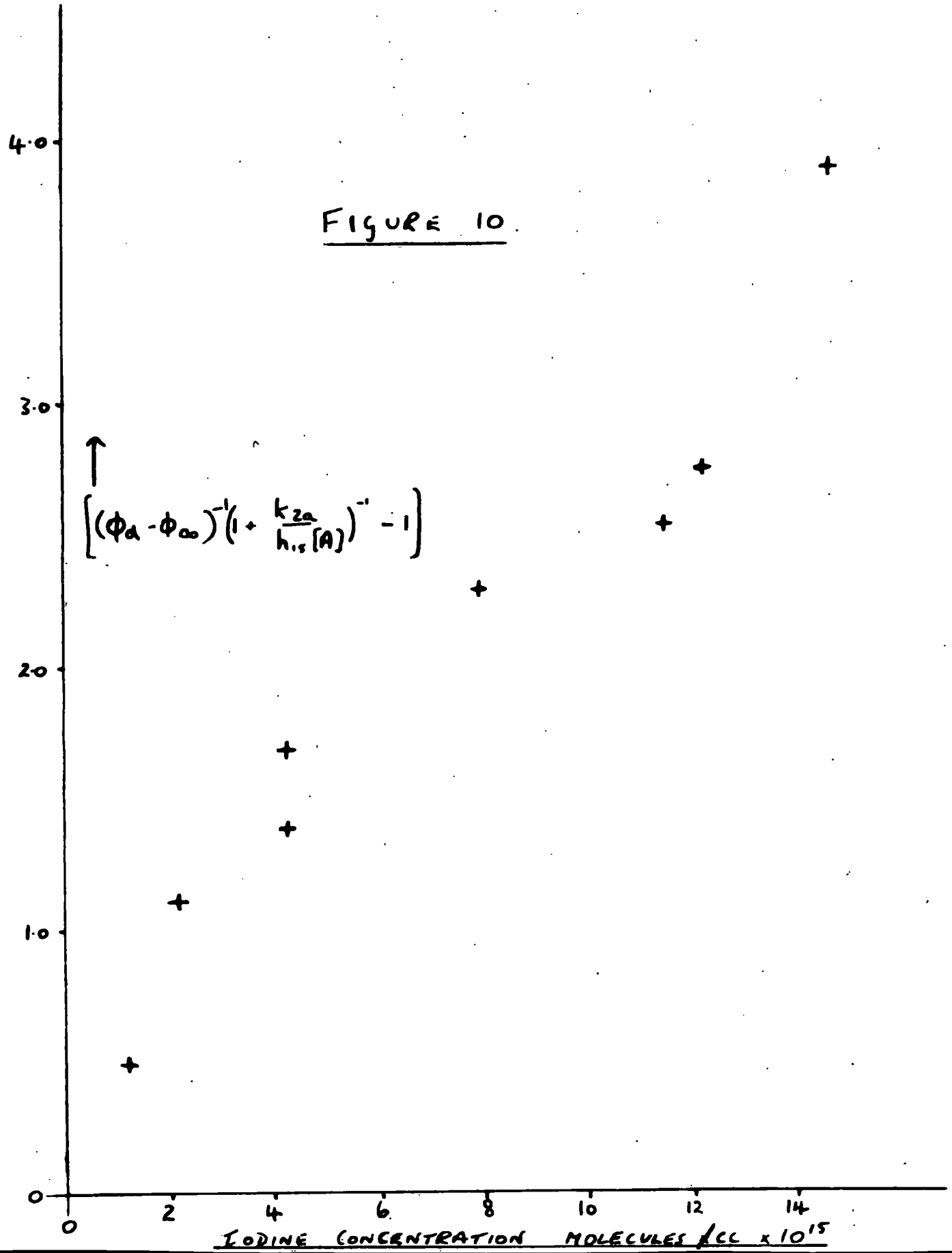


FIGURE 10
$\left[(\phi_a - \phi_\infty)^{-1}\left(1 + \frac{k_{2a}}{k_{1s}[A]}\right)^{-1} - 1\right]$
4·0
3·0
2·0
1·0
0
0
2
4
6
8
10
12
14
IODINE CONCENTRATION MOLECULES/CC x 10^{15}

against iodine concentration should be a straight line, if the proposed mechanism involving an acetone - iodine complex is tenable. Table 4 sets out the values of the above function, and figure 10 shows the graphical relationship. A discussion is left until the next chapter.

APPENDIX IV. TYPICAL CALCULATION.

Calculation of run D.8.

Value of incident intensity = 10 ± 0.1

Time of irradiation = 10 minutes.

Methyl iodide yield = $17.59\ (\pm .34) \times 10^{-8}$

'Q' value from calibrations D_1 and D_2 = $3.209\ (\pm 0.9) \times 10^{-9}$

Expected carbon monoxide yield at 10.0 units of intensity

$$= 3.209 \times 10^{-9} \times 10 \times 10 = 3.209 \times 10^{-7}\ (\pm 0.12)$$

$$\text{Thus } \Phi_{CH_3 I} = \frac{17.59 \times 10^{-8}\ (.34)}{3.209 \times 10^{-7}\ (0.9)}$$

$$= \underline{0.548\ (\pm .032)}$$

From figure 8 a value for Φ_∞ = .37

Thus for D8 :- $\Phi_d - \Phi_\infty$ = .178(± .032)

$$(\Phi_d - \Phi_\infty)^{-1} = 5.618\ (\pm 1.04)$$

Now from appendix III $\left(1 + \frac{h_{15}\ [A]}{K_{2a}}\right)^{-1} = 2.703$

$$\frac{h_{15}\ [A]}{K_{2a}} = 1.703$$

thus $$\frac{K_{2a}}{h_{15}[A]} = .5872$$

thus $$\left(1 + \frac{K_{2a}}{h_{15}[A]}\right)^{-1} = (1.5872)^{-1} = .630$$

thus $$\left[(\Phi d - \Phi\infty)^{-1}\left(1 + \frac{K_{2a}}{h_{15}[A]}\right)^{-1} - 1\right]$$

$$= 5.618\ (\pm 1.04) \times .630 - 1$$

$$= 3539\ (\pm .75) - 1$$

$$= \underline{2.539\ (\pm 0.65)}$$

The error is fairly considerable for this function, being caused by the various measurements needed in quantum yield detirmination. The other factors involved depend upon the value used for Φ_∞, and although this maybe any value from about 0.36 to 0.4, the error would not affect the relative positions of the points on figure 10. when the previous errors are allowed for. Avariation in the value of Φ_∞ will however change the slope of graph.

APPENDIX V.

To see how the results obtained in this work fit in with the Brown - Mitchell mechanism, equation 17 is expanded:

$$\Phi CH_3 I - \Phi CO = \left[1 - \left(1 + \frac{K_{2a}}{K_{15}[M]}\right)^{-1}\left(1 + \frac{K_{2b}}{K_{16}[I]}\right)^{-1}\right] \quad \ldots\ldots (17)$$

The yields of carbon monoxide as mentioned before are very small, thus:

$$\Phi CH_3 I = 1 - \left(1 + \frac{K_{2a}}{K_{15}[M]}\right)^{-1}\left(1 + \frac{K_{2b}}{K_{16}[I_2]}\right)^{-1} \quad \ldots\ldots\ldots\ldots\ldots (18)$$

Now at infinite iodine concentration a limiting value of $\Phi CH_3 I$ is obtained experimentally, therefore

$$\Phi_\infty = 1 - \left(1 + \frac{K_{2a}}{K_{15}[M]}\right)^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (19)$$

It was stated before, that M could be either acetone or iodine, and in this case the limiting value of the quantum yield from the above equation would be zero. This is plainly contrary to the accumulated evidence, thus the use of equation (19) is reasonably justifiable. Thus

$$\Phi_\infty = 1 - \left(1 + \frac{K_{2a}}{K_{15}[M]}\right)^{-1} = 1 - \frac{K_{15}[M]}{K_{15}[M] + K_{2a}}$$

$$= \frac{K_{15}[M] + K_{2a} - K_{15}[M]}{K_{15}[M] + K_{2a}} = \frac{K_{2a}}{K_{2a} + K_{15}[M]}$$

$$= \frac{1}{1 + \frac{K_{15}[M]}{K_{2a}}}$$

Substituting in reaction 18*

$$\Phi_{CH_3I} = 1 - \left(\frac{K_{15}[M]}{K_{2a}}\Phi_\infty\right)\left(1 + \frac{K_{2b}}{K_{16}[I_2]}\right)^{-1}$$

$$1 - \Phi_{CH_3I} = \Phi_\infty \frac{K_{15}[M]}{K_{2a}}\left(1 + \frac{K_{2b}}{K_{16}[I_2]}\right)^{-1}$$

$$\left(\frac{1 - \Phi_{CH_3I}}{\Phi_\infty}\right)\frac{K_{2a}}{K_{15}[M]} = \left(1 + \frac{K_{2b}}{K_{16}[I_2]}\right)^{-1}$$

$$\frac{1}{\left(\frac{1 - \Phi_{CH_3I}}{\Phi_\infty}\right)\left(\frac{K_{2a}}{K_{15}[M]}\right)}^{+1} - 1 = \frac{K_{2b}}{K_{16}[I_2]}$$

$$\left[\left(\frac{\Phi_\infty}{1 - \Phi_{CH_3I}}\right)\left(\frac{K_{15}[M]}{K_{2a}}\right) - 1\right]^{-1} = [I_2]\frac{K_{16}}{K_{2b}}$$

Thus a plot of $\left[\left(\frac{\Phi_\infty}{1 - \Phi_{CH_3I}}\right)\left(\frac{K_{15}[M]}{K_{2a}}\right) - 1\right]^{-1}$ verses

Iodine concentration should be a straight line, a value for $\frac{K_{15}[M]}{K_{2a}}$

being obtained from the limiting value of the quantum yield of methyl

iodide.

Table 5 sets out the values for this function and it is clearly seen that the values obtained are identical with those for the function,

$$\left[(\Phi_d - \Phi_\infty)^{-1} \left(1 + \frac{K_{2a}}{h_{15}[A]} \right)^{-1} - 1 \right]$$ (table 4) derived

from the previous mechanism. Hence it is not possible to differentiate between the two mechanisms in this manner.

6. Discussion of Results.

The cause of the large discrepency between the two series of results is not at all clear. One possibility lies in the type of alumina used for iodine removal in the analytical process. This fact was not realised until the middle of the work and accounts for the fact that no precautions had been taken to pretreat the sample used. Also no details were available that revealed the type of alumina used by previous workers. That used in series 1 was obtained from B.D.H, and as it is in part intended for gas chromatography it was possibly washed in either acid or alkali, during its preparation. The other sample of alumina available (Wölm) could have been treated in a different manner.

One or two quick tests were carried out, but lack of time prevented any thorough investigation of the problem. A sample from series 2 was recirculated through an alumina column and 99% of the product recovered. However this sample of methyl iodide was accompanied by the small amount of acetone added before counting, and this may have facilitated its passage through the column. Another run was performed with the original analytical set up. After completing the normal process and collecting the iodide in C , tap T_3 was closed. A quantity of acetone, the same as normally added to C, was then introduced to the system in between the alumina column and the reaction vessel. After obtaining a sticking vacuum in the system the acetone was allowed to evaporate through the column and finally condensed into C. This was removed, allowed to

warm up, and counted. Absolutely no difference was found between this and the expected values for a series one photolysis. In view of the previous test this makes the disappearance of the product even more incomprehensible. One final point on this subject. It was noticed that after each photolysis on allowing the reaction vessel to cool, a brown film formed upon the walls of the vessel, presumably iodine. In series one, to a large extent, this film remained, even after prolonged pumping through the traps A and B. On adopting the second procedure with the potassium hydroxide present, this coating rapidly disappeared. It may be that this film traps methyl iodide, thus preventing its collecting, but it is difficult to see why the presence of potassium hydroxide should ease its release. In the first series of results it was attempted to remove the film by gently heating the walls of the reaction vessel, but this proved to be less successful than would be expected.

One thing remains clear, that the use of alumina may not be as predictable as was supposed. The reasons however, especially in the light of the fact that the results obtained were so regular, are not apparent. However in the second series, tests were carried out using alumina (Wolm variety) in conjunction with the silver glass wool, and it was shown that no apparent decrease in quantum yield was observed. This fact tends to support the idea that somehow the residual brown film is responsible for the low quantum yields obtained, and that the presence of potassium hydroxide removes this source of error in an unknown manner.

It has been demonstrated that there is no kinetic treatment which can differentiate between the various proposed mechanisms.

If a mechanism is to be satisfactory, then any ratio of rate constants should be similar for both photolysis and fluorescence studies, and hence in this manner a comparison may be made. From his work on the fluorescence of the acetone iodine systems Clough [18] obtained values for the ratio $\frac{J_{18}}{h_{2b}[A]}\left\{1 + \frac{K_{-18}}{K_{20}}\right\}^{-1}$ but not under the same conditions of temperature and acetone pressure, used in this study. From a comparison with the behaviour of more comprehensive results on the acetone - oxygen system, allowances for the different temperature and acetone pressure can be made, and a value for the above ratio of 4.8×10^{-16} is obtained. It is seen from appendix 3 that the slope of the graph in figure 10 will give a value for the same ratio. The value ob tained in this manner is 3.0×10^{-16}. Although this is not as close as would be hoped for acceptance of the proposed mechanism, it must be noted that an exact comparison was not permitted as no data with identical acetone pressure and temperature values is available. Also because of the size of the errors in plotting figure 10, the value for the above ratio could concievably be higher, (error due to Φ_∞ value $\pm 0.7 \times 10^{-16}$)

From the limiting value of ΦCH_3I a value for the ratio of $\frac{h_{15}}{K_{2a}}$ was obtained, 2.27×10^{-18} (±0.3) This is less than the value obtained by Clough, 3. $\times 10^{-18}$, working at a lower temperature (100° C), and this decrease signifies that the value of K_{2a} increases more than

h_{15} with rise in temperature. This is to be expected as the decomposition of the A' species has an activation energy, whereas its deactivation to the triplet state A'' obviously has none, and this rate h_{15} is less affected by temperature change.

It is clear that the results are not conclusive on support of the complex-containing mechanism but they are encouraging enough to warrant further investigation along this line. More results are required at other temperatures, and acetone pressures, in order that more direct comparisons can be made.

7. Summary

A study has been made of the photolysis of acetone in the presence of iodine, in the hope that the fresh data will help to resolve some of the problems of the primary process. All the photochemcial work was carried out at a temperature of 124° C, using radiation of wavelength 3130 A° throughout. ^{131}I was used as tracer for the detirmination of the quantum yields of methyl iodide. The various experimental techniques were based on a combination of those used by Sutton and Martin [2] and Clough [18].

From the results of this investigation it has been shown that under certain conditions, the use of alumina alone to remove iodine from the products, is not satisfactory, but the reasons for this are not clear. It has not been possible to favour positively any particular mechanism, but comparison of ratios for particular rates of reaction, with similar rates obtained from work on the fluorescence of acetone iodine mixtures are encouraging, as far as the mechanism involving an acetone - iodine complex are concerned.

The available data on this system is still not sufficient, and more is needed especially that at comparable temperatures and acetone pressures to the results from the fluorescence studies, so that a direct comparison can be made.

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Reaction Key.

(1) $CH_3\,CO\,CH_3 + h\nu \longrightarrow CH_3\,CO\,CH_3^*$

(1a) $A + h\nu \longrightarrow A'$

(2) $CH_3\,CO\,CH_3^* \longrightarrow CH_3^\cdot + CH_3\,CO^\cdot$

(2a) $A' \longrightarrow CH_3^\cdot + CH_3\,CO^\cdot$

(2B) $A'' \longrightarrow CH_3^\cdot + CH_3\,CO^\cdot$

(3) $CH_3\,CO\,CH_3^* \longrightarrow C_2H_6 + CO$

(4) $CH_3\,CO^\cdot \longrightarrow CH_3^\cdot + CO$

(5) $CH_3^\cdot + CH_3^\cdot \longrightarrow C_2H_6$

(6) $CH_3^\cdot + CH_3\,CO\,CH_3 \longrightarrow CH_4 + CH_3\,CO\,CH_2^\cdot$

(7) $CH_3\,CO^\cdot + CH_3\,CO^\cdot \longrightarrow (CH_3\,CO)_2$

(8) $CH_3CO\,CH_3^* \longrightarrow H^\cdot + CH_3\,CO\,CH_2^\cdot$

(9) $A' + I_2 \longrightarrow A'' + I_2$

(10) $A'' + M \longrightarrow A + M$

(11) $CH_3^\cdot + I \longrightarrow CH_3\,I$

(11a) $CH_3 + I_2 \longrightarrow CH_3\,I + I^\cdot$

(12) $CH_3\,CO + I^\cdot \longrightarrow CH_3\,CO\,I$

(12a) $CH_3\,CO + I_2 \longrightarrow CH_3\,CO\,I + I^\cdot$

(13) $I^\cdot + I^\cdot \longrightarrow I_2$

(14) $\Phi_{CH_3I} - \Phi_{CO} = 1 - \left(1 + \frac{K_{2a}}{K_9[I_2]}\right)^{-1}\left(1 + \frac{K_{2b}}{K_{10}[M]}\right)^{-1}$

(15) $A' + M \longrightarrow A'' + M$

(16) $A'' + I_2 \longrightarrow A + I_2$

(17) $\Phi CH_3I - \Phi CO = 1 - \left(1 + \frac{K_{2b}}{K_{16}[I_2]}\right)^{-1}\left(1 + \frac{K_{2a}}{K_{15}[M]}\right)$

(18) $A'' + I_2 \longrightarrow \text{Complex}$

(19) $\text{Complex} \longrightarrow CH_3^{\cdot} + CH_3CO^{\cdot} + I_2$

(20) $\text{Complex} \longrightarrow A + I_2$

(21) $\left(\Phi d - \Phi_\infty\right)^{-1} = \left(1 + \frac{K_{2a}}{h_{15}[A]}\right)\left(\frac{J_{18}[I_2]}{h_{2b}[A]\left(1 + \frac{K_{18}}{K_{20}}\right)} + 1\right)$

(22) $I_2O_5 + 5\ CO \longrightarrow 5\ CO_2 + I_2$

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