

THE DECOMPOSITION OF LUMINESCENT COMPOUNDS
BY HIGH ENERGY RADIATION

II. The Radiolysis of Dilute Solutions
of Anthracene in n-Hexane

by

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Abstract

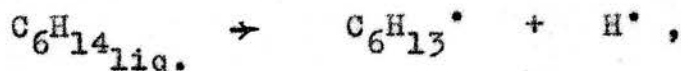
The radiolysis in vacuum of pure, liquid n-hexane by ^{60}Co γ -rays yields mainly the products H_2 , CH_4 , C_2H_6 and an unsaturated liquid hydrocarbon. The yields, G , in terms of molecules of products per 100 ev of γ -ray energy absorbed by the hexane, are:

$$\begin{array}{ll} G_{\text{H}_2} = 4.89 \pm 0.2 & G_{\text{C}=\text{C}} = 4 \pm 2 \\ G_{\text{CH}_4} = 0.41 \pm 0.1 & G_{\text{C}_2\text{H}_6} = 0.69 \pm 0.1 \end{array}$$

The radiolysis in vacuum of dilute solutions of anthracene in n-hexane shows that anthracene in concentrations up to 10^{-3} Mpl has no effect upon G_{H_2} , G_{CH_4} or $G_{\text{C}_2\text{H}_6}$, but causes a diminution of $G_{\text{C}=\text{C}}$.

In these solutions the anthracene is transformed upon radiolysis into compounds resembling dianthracene.

These and other effects are adequately explained by a theory based on the central assumption that the primary radiation chemical process in liquid hexane is



in which $\text{C}_6\text{H}_{13}^{\bullet}$ and H^{\bullet} are a hexyl free radical and a hydrogen atom resulting from the rupture of a C-H bond in the molecule. It is estimated that in some ruptures the free radical may be formed with ca 5 ev of excitation energy.

The fluorescence of anthracene in hexane solutions absorbing γ -rays is explained as the result of a transfer of excitation energy from the excited radicals to the anthracene by a type of resonance interaction (Förster mechanism).

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Note concerning references:

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Footnotes are indicated *

NOTE: ERRATUM

Attention is drawn to the erratum described in
footnote to Table 1., p. 14.

Introduction

1. Energy Transfer in Liquid Scintillators:

In a series of papers beginning in 1950, Kallmann and Furst (58,59-61) have described the properties of a large number of luminescent solutions which have since come to be known as liquid scintillators, or solution scintillators. These solutions usually consist of a fluorescent organic compound, most often a polycyclic aryl hydrocarbon, dissolved in a liquid which is transparent to the fluorescence. The light emitted by such solutions upon exposure to ionizing radiation is the characteristic solute fluorescence (60,51). The intensity of the emission is, in most cases, far too great to be attributed to solute molecules directly excited by the radiation (59,56). This may be illustrated by an example taken from the second paper of the series above (59).

Emission fr. 5.5 gm anth. crystal	=	1
Conc'n anth. in sol'n scintillator	=	1 Gpl
Volume of solution compared	=	~10 ml
Mass of anth. in 10 ml	=	0.01 gm
Intensity of directly excited fl. rel. to 5.5 gm crystal	=	0.002
Intensity observed from 10 ml of		
1 Gpl anthracene in hexane	=	0.016
1 Gpl anthracene in benzene	=	0.066

Kallmann and Furst concluded from evidence of this kind

that the greater part of the emission must come from solute molecules excited by energy originally absorbed by the solvent, i.e. that energy transfer between solvent and solute must occur (59,60).

2. Proposed Mechanisms of Energy Transfer:

The mechanism of energy transfer in liquid scintillators has been a matter for much speculation. Birks (B2,12) has suggested that since the relatively efficient scintillators are those in which the solvent is itself capable of fluorescence (e.g. benzene, toluene, xylene) the mechanism of energy transfer may involve solvent fluorescence followed by solute absorption and secondary solute fluorescence. This mechanism, which forms the basis of a general theory of fluorescence in organic compounds due to Birks (12), will be referred to as the Birks mechanism, or photon transfer.

A second theory has been attributed to F. N. Hayes (R1), but has never been published in a completely stated form. The theory proposes that the solute molecules are positively ionized by charge transfer with the primary solvent ions. The solute ions then capture an electron and emit fluorescence in returning to the neutral ground state.

Furst and Kallmann (44) consider a mechanism involving charge transfer to be unlikely, chiefly because energy transfer may be observed in systems excited by non-ionizing radiation, i.e. U. V. light which is absorbed by the solvent but not by the solute (32). They propose, on the basis of experiments

with mixed solutes excited by light at 3130 \AA , that the mechanism of energy transfer may be by collisions between excited and unexcited molecules (44). Their experimental evidence does not support this hypothesis unequivocally, however, and the critical test of a collisional mechanism - a determination of the effect of temperature upon the transfer efficiency - was not made.

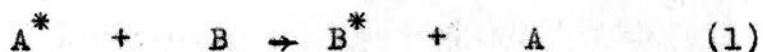
A mechanism proposed by Förster (40,B6) on the basis of theoretical considerations, and later demonstrated experimentally by Bowen and Livingston (19) may account for the results both of U. V. excitation and of excitation by ionizing radiation. This involves energy transfer between coupled electronic levels of excited and unexcited molecules. It will be referred to as the Förster mechanism, or resonance transfer. It implies an overlap between the electronic energy levels of the molecules taking part in the transfer, a condition which is in fact implicit in any exchange of electronic energy.

Moody and Reid (85,86) have recently studied energy transfer between fluorescent compounds in solid solutions at $90 \text{ }^\circ\text{K}$, and have concluded that efficient transfer takes place only between compounds forming a type of coördination complex. No evidence was found for transfer of the Förster type, either in liquid or in solid solutions, between compounds for which the possibility of complex formation could be ruled out. The transfer within such a complex may resemble intra-molecular energy migration, many examples of which have been recently

fairly well established (5,128).

3. Radiolysis and Energy Transfer:

The magnitude of the energy transfer effect has suggested to Maddock (77) that a measurable reduction in the radiolysis of a pure liquid, such as benzene, might be observed upon addition of a solute capable of extracting excitation energy from the liquid. The liquid might, in this sense, be " protected " by the solute (47). This possibility has been investigated by Burton and Patrick (23) who measured - in terms of hydrogen evolution - the fast electron radiolysis of benzene with and without solutes such as anthracene, m- or p-terphenyl. Of these only m-terphenyl reduced significantly the decomposition of the solvent, i.e. the evolution of hydrogen, and only at concentrations high enough that an appreciable fraction of the incident electrons was absorbed by the solute. Reid (100) has offered an interpretation of these results in the following terms: for a transfer of the type



to occur, the two states must be degenerate, i.e. the available (*) emission from A must find an absorption process in B requiring the same energy. When highly excited states of benzene are involved, energy transfer may occur with equal facility between benzene molecules and between benzene and anthracene, for instance. The solute does not provide

a particularly efficient trap, since the solute molecule may pass on the energy of excitation to the benzene (the reverse of reaction (1)). The situation is altered, however, when we consider the lowest excited level of benzene. The emission from this level is not appreciably absorbed by benzene itself, and the solute therefore becomes an efficient trap for energy transferred by reaction (1). The energy of this level is too low to effect chemical decomposition, and hence the solute has little effect upon the course of the radiolysis.

4. Pulse Rise Times in Liquid Scintillators:

Any successful theory of energy transfer in liquid scintillators must take into consideration the extremely short time required for transfer to be effected. This is shown by measurements of the scintillation decay times in liquid scintillators. Liebson (70) and Harrison (50) have found decay times for light pulses from solutions of terphenyl in toluene excited by γ -rays to be $2.2 - 2.5 \times 10^{-9}$ seconds. An even shorter time was found for the decay of the fluorescence of anthracene in benzene (2.0×10^{-9} seconds) when the solution was excited by u.v. light from a pulsed source. These times are considerably shorter than the natural decay time of the fluorescence (ca 10^{-8} seconds) but as Bowen has indicated (16), the measurements were made under conditions in which a greater part of the fluorescence was quenched. The natural decay time is obtained by dividing the observed

decay time by the fluorescence efficiency. Bowen estimates a value of 0.145 for the fluorescence efficiency of anthracene in benzene at the concentration used in the measurement above. The corrected decay time is then 1.4×10^{-8} sec, in close agreement with the natural decay time determined by an independent method (16).

The extremely short decay times above imply an even shorter time required for energy transfer from the solvent. Post has attempted to measure the rise time of scintillation pulses in solutions of terphenyl in toluene (136). These were found to be approximately 10^{-9} sec, but were undoubtedly shorter than this, the observed times being fixed by the limitations of the apparatus (101). A statistical analysis by Post and Schiff (136a) indicates that pulse rise times are probably of the order of 10^{-10} sec. Reynolds (101) considers that the extremely short transfer times eliminate the possibility of energy transfer by collisions with excited solvent molecules. This conclusion is by no means secure, as will be demonstrated by a calculation in Chapter III of this Thesis, and the possibility of energy transfer by collisions cannot be excluded.

5. Relative Efficiencies of Different Scintillators:

A distinction must be drawn between the practical efficiency of a scintillator and the efficiency of energy transfer. The former quantity is measured in terms of the photocurrent or the mean pulse height at the output of a photomultiplier

when the photocathode is exposed to the luminescence of the scintillator under standard conditions of excitation. The transfer efficiency refers to the proportion of solute molecules excited by energy transfer from the solvent under the same conditions of excitation. The difference is illustrated by a consideration of the numerical example already given on p. 1.

On the basis of the direct comparison made by Kallmann and Furst (59) a solution of anthracene in benzene has roughly four times the efficiency of a solution of anthracene in hexane. The measurements were made in solutions saturated with atmospheric oxygen, and part of the fluorescence was undoubtedly quenched by oxygen (21,31,98). To compare the transfer efficiencies in the two solvents a correction must be made for oxygen quenching. This can be done using the quenching constants measured by Bowen and Norton (21). The fluorescence efficiency, F , in the presence of quenchers is given by

$$F = \frac{1}{1 + k Q} F_0 \quad (2)$$

where F_0 is the fluorescence efficiency in the absence of the quencher, Q the concentration of the quencher and k a constant. The correction is made below.

Solvent	Benzene	Hexane
Anth. Conc'n.	5.6 X 10 ⁻³	Mpl
Rel. Pract. Eff'cy.	0.066	0.016
k_{O_2}	113 Mpl ⁻¹	154 Mpl ⁻¹
Q	7.2 X 10 ⁻³ Mpl	15.6 X 10 ⁻³ Mpl
Coeff. of F_0	0.55	0.29

The relative efficiencies corrected for oxygen quenching are therefore:

Solvent	Benzene	Hexane
Corr. Rel. Eff'cy.	0.12	0.049

At concentrations of the magnitude found in liquid scintillators a considerable fraction of the fluorescence is self-quenched (16,17,21). The self-quenching constants of anthracene in the two solvents above have also been measured by Bowen and Norton (21) who found that the reduction of the fluorescence efficiency, F_0 , by self-quenching was also described by Expression (2) above. The relative efficiencies, corrected for self-quenching, are calculated as follows:

$k_{\text{Anth.}}$	26 Mpl ⁻¹	90 Mpl ⁻¹
$Q_{\text{Anth.}}$	5.6×10^{-3} Mpl	5.6×10^{-3} Mpl
Coeff. of F_0	0.87	0.67
Corr. Rel. Eff'cy	0.138	0.082

The corrected relative efficiencies are thus considerably different from the practical relative efficiencies measured by Kallmann and Furst. When allowance is made for oxygen quenching and self-quenching, the solution in hexane has roughly two thirds the efficiency of the solution in benzene.

6. The Magnitude of Energy Transfer:

The efficiencies just considered were expressed in terms of light emission relative to the emission of an approximately

equal mass of solid anthracene. To appreciate the magnitude of energy transfer in the solutions, an account must be taken of the difference between the absolute fluorescence efficiency of anthracene in the solid state and in solution. Bowen (21) estimates the absolute fluorescence efficiency of solid anthracene to be 0.9 at room temperature, i.e. of 10 molecules excited, 9 fluoresce. The limiting absolute fluorescence efficiency in solutions in benzene and hexane (i.e. the efficiency without quenching) is only 0.23 at room temperature (21) owing, presumably, to deactivating collisions with solvent molecules (18,104). The efficiency in solution relative to that in the solid is therefore 0.26 . The relative efficiencies considered above must be divided by this figure to appreciate the magnitude of the energy transfer. We obtain:

Solvent	Benzene	Hexane
Anthracene molecules excited per molecule excited in the pure solid.....	0.53	0.32
Mass of anthracene in solution relative to mass in solid....	0.002	0.002

7. Errors Caused by Self-absorption:

No account has been taken in the discussion above of errors in the comparison of the relative efficiencies which might be caused by self-absorption, an effect arising from the proximity of the 0-0 fluorescence and absorption

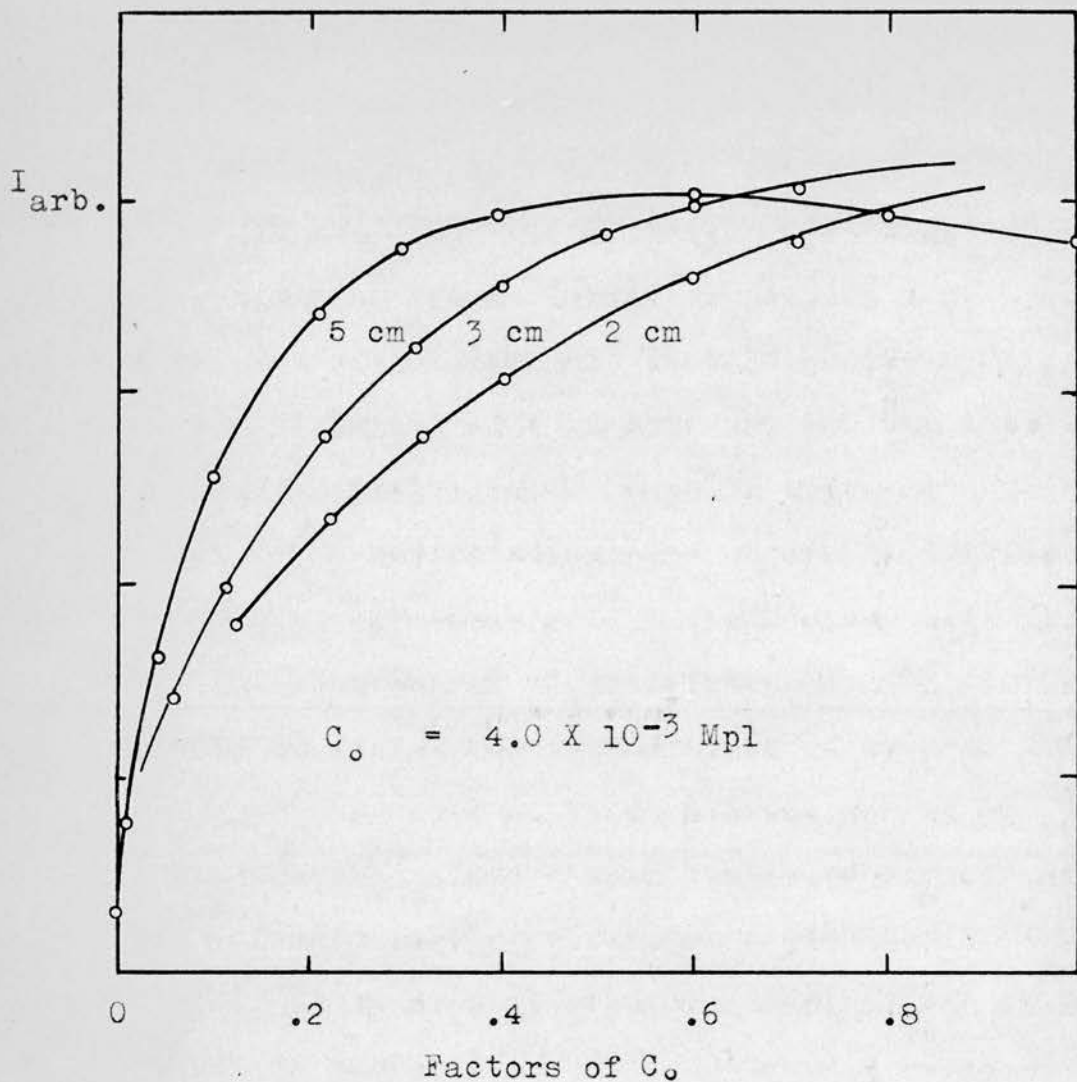


Fig. 1. The intensity of fluorescence (in arbitrary units) emitted by airfree solutions of anthracene in hexane excited by ^{60}Co γ -rays plotted as a function of the anthracene concentration for three different depths of solution: 5 cm, 3 cm and 2 cm. The curves are normalized at the maximum intensity.

bands of anthracene in solution (See Bowen (15) for a discussion of this effect in relation to solution scintillators). In anthracene vapour the two bands are almost superimposed (65) and the 0-0 emission corresponds to anthracene "resonance" radiation. In solutions the bands are separated to a greater or lesser extent depending, presumably, upon solvation effects (65,104). Some overlap remains, however, and the emission in this region of the spectrum is usually strongly absorbed. The effect is greater in hexane solutions than in benzene solutions (104), the former being more "gas-like" in this respect.

The effect of self-absorption on measurements of the fluorescence emitted by solutions of anthracene in hexane is illustrated by the results shown in Fig. 1. The fluorescence was excited by γ -rays from a small ^{60}Co source. The curves of fluorescence intensity vs concentration are normalized at the maximum intensity in each case. They should be compared with similar curves obtained by Kallmann and Furst (59,60). Details of the present measurements are discussed in Chapters I and II of this Thesis.

While the overlap between absorption and fluorescence bands of solid anthracene is not extensive, self-absorption is nevertheless important owing to the relatively high concentration of anthracene molecules in the solid. For this reason the comparative measurements discussed above must be considered only approximate. The discussion

has served, however, to show that the magnitude of the energy transfer effect is larger than is probably generally appreciated. Furthermore, the relative practical efficiencies of the solution scintillators have been shown not to be a reliable index of the efficiencies of energy transfer in the different solvents. When errors due to overlap are taken into account, energy transfer in hexane, for instance, may be almost as efficient as energy transfer in benzene, if not equally efficient; a conclusion which puts in a different light some of the theories discussed in the paragraphs above.

8. Aims of the present work:

This work was undertaken with a view to establishing, if possible, the mechanism of energy transfer in solutions of anthracene in hexane excited by γ -rays. The phenomenon of energy transfer has been studied together with the effects of γ -rays upon pure hexane and solutions of anthracene in hexane to determine the relation of energy transfer to the radiation chemical processes also occurring. In this connection, attention has been fixed upon the initial stages of the radiolysis of pure hexane and of the solutions, since it is only in the initial stages that energy transfer might be expected to play an important part.

Chapter I: Experimental Details

1. The ^{60}Co Sources:

Several small ^{60}Co sources, ranging in strength from 100 to 300 μc , were used in these experiments to excite fluorescence; and two large sources, approximately 0.6 and 1.5 curies, were used for the chemical studies. ^{60}Co decays with a half-life of 5.3 years, emitting in the process a β -particle ($E_{\text{max}} = .31 \text{ Mev}$) followed by two γ -rays (1.1, 1.3 Mev) in cascade (133). The large sources were sheathed in sufficient aluminium and brass that the β -particles emitted by the cobalt were absorbed completely. The small sources were simply short lengths of Ni-Co wire, approximately 1 mm in diameter. The experimental arrangement in which they were used (Fig. 7) interposed sufficient aluminium between the source and the irradiated solution to insure that all the β -particles were absorbed. It will be assumed that only the γ -rays were effective in producing the experimental results to be described, though it is possible (Chapter III, Sec.2) that this consideration is of relatively minor importance.

The manner in which the large sources were used is described as follows: each source in the irradiation position rested in a hole drilled along the axis of a cylindrical block of teak. Around this hole, and parallel to it, a series of other holes were drilled to take the

samples for irradiation, their centres evenly spaced on a circle concentric with the central hole. The block for the 1.5 c source had two such rings of holes, that for the 0.6 c source, one. Three different intensities of γ -radiation were thus available. The corresponding intensities of energy absorption in the different sample positions were determined with the ferrous sulfate actinometer developed by Miller (36,83,84), Hochanadel (54,135) and others (See ref.36 for a bibliography). The effect of ^{60}Co γ -rays on dilute solutions of ferrous sulfate in 0.8 N sulfuric acid saturated with atmospheric oxygen can be represented (as far as the actinometric measurement is concerned) by the reaction:



The yield, G , in terms of Fe^{3+} ions formed per 100 ev of γ -ray energy absorbed by the solution, has been shown by recent work to lie in the range between 15.2 and 16.0 $\text{Fe}^{3+}/100$ ev. The calculations below have been made assuming a value of $G_{\text{Fe}^{3+}}$ of $15.6 \pm .3$ (36).

The ferrous sulfate oxidation rates were determined in 5 ml samples of the ferrous sulfate solution in Pyrex test-tubes which fitted snugly into the holes in the irradiation block. The hexane was subsequently irradiated in the same holes in irradiation cells (Figs. 3 and 9) made from Pyrex tubing having the same diameter and wall thickness as the test-tubes above. The 5 ml volume was rigidly adhered

to in the subsequent irradiations, since the distributions of γ -ray intensity in the cell positions were highly asymmetric, and the measured oxidation rate was sensitive to small changes in the volume of the ferrous sulfate.

The oxidation rates listed in Table I below were the mean of several determinations at each intensity. In both irradiation blocks oxidation rates were measured to $\pm 3\%$. The usual precautions were taken to reduce contamination of the ferrous sulfate solutions by organic impurities which might cause spuriously high oxidation rates (132a). No change in the oxidation rate was observed when the solutions were made 10^{-2} molar in chloride ion, a test which often reveals the presence of organic impurities (36).

Table 1.

Determinations of the Intensity, I,
of Energy Absorption:

I_{γ}	$\mu\text{M Fe}^{3+}/\text{L/hr}$	ev/5ml/hr * (0.8 N sulf)	ev/5ml/hr ** (hexane)	Date
1.	$5.5 \pm .2$	$1.07 \pm .05 \cdot 10^{17}$	$0.70 \pm .04 \cdot 10^{17}$	April 15 - 18 1954
2.	$10.8 \pm .3$	$2.10 \pm .11$	$1.34 \pm .07$	
3.	$24.5 \pm .7$	$4.75 \pm .24$	$3.12 \pm .16$	

* i.e. $1 \mu\text{M}/\text{L}/\text{hr} = 1.94 \times 10^{16}$ ev/5ml/hr.

** based on the ratio of electron densities,
R = 0.658

ADDED NOTE: The experimental results of Chapter II have been computed using a ratio of densities = 0.690 which, though incorrect, has no effect except to lower the absolute yields by ca 5%. Corrected values of the yields are summarized in Chapter II, Sec. 7. and are inserted wherever the error is significant.

2: Preparation of the Materials:

The preparation of samples of pure n-hexane and of solutions of anthracene in hexane which were free from dissolved air and hydrocarbon gases presented the most formidable difficulty encountered in this work. In the section which follows a description is given of the techniques which were developed for this purpose.

B.D.H. n-hexane (special for spectroscopy) was used as a starting material. The U.V. transmission of the pure hexane measured with respect to air in a 1 cm spectrophotometer cell was 7-10 % at 200 μ and rose to 75 % at 225 μ . Batches of used hexane were reworked using a method of purification devised by Pirlot (88). The material to be purified was distilled through a fractionating column filled with granules of silica gel. The column thus combined fractionation with selective adsorption of the polarisable impurities, the refluxing hexane acting as an eluant which washed the adsorbed impurities back into the distillation flask. The column used was 1.5 cm i.d. by 50 cm long, and was lagged to reduce the loss of heat by radiation and conduction. A single distillation with this column yielded hexane with transparency in the U.V. comparable to that of the B.D.H. 'spectroscopic' material, even when the original

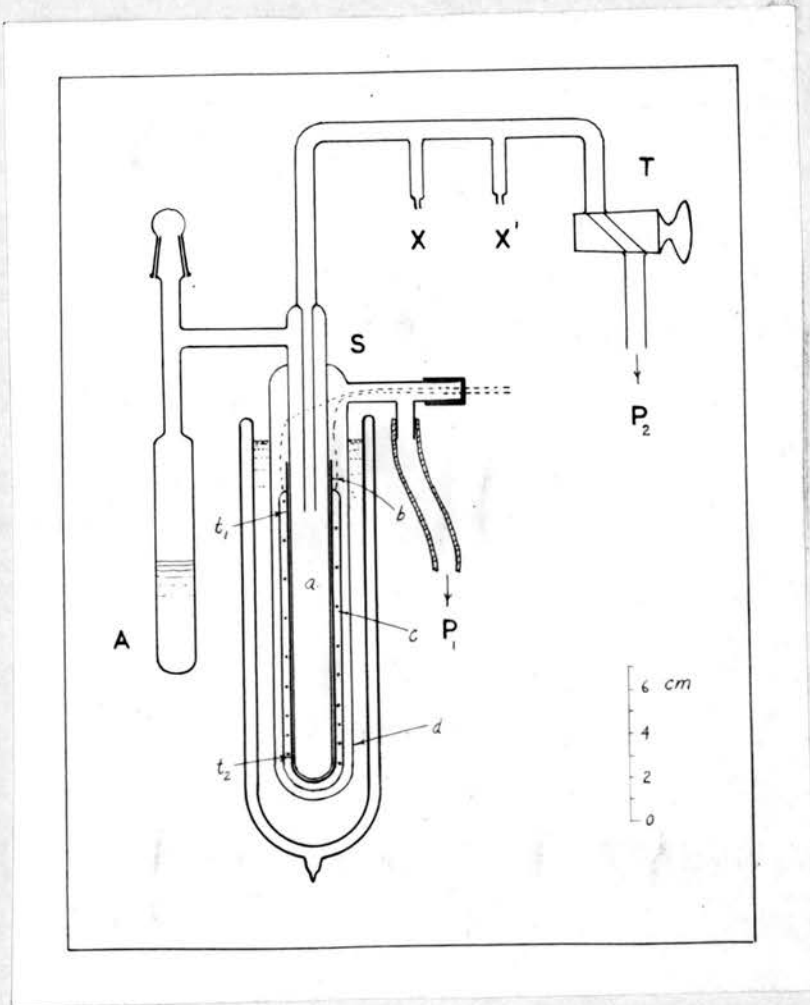


Fig. 2. The Vacuum Still.

hexane was opaque at ca 220 μ . All the hexane used was completely transparent at wavelengths longer than 250 μ .

n-Hexane (m.p. -94.3°C ; b.p. 69.3°C) is a liquid at -80°C with a vapour pressure of 0.1 mm. It can therefore be refluxed under vacuum with very little loss to the pumps, using an efficient reflux condenser cooled with a mixture of solid CO_2 and acetone. This technique was used to prepare the first samples of hexane for irradiation. It was found that dissolved air was completely removed by this treatment (traces of air had a pronounced effect on the results of irradiation) but that the hydrocarbon gases (methane, ethane, acetylene, etc.) were left in amounts up to 5 mm^3 per ml of hexane. Since amounts of the hydrocarbon gases of this order were formed in hexane under irradiation, it was necessary to lower the residual hydrocarbon content still further. To do this the apparatus shown in Fig. 2 was devised.

The sample of hexane to be deaerated and purified of residual hydrocarbon gases was poured through a column of activated silica gel into the reservoir A. The stopper, very sparingly greased with Apiezon L vacuum grease, was put in place. The hexane in A was then cooled with liquid nitrogen and the tap, T, connecting the apparatus to the pumping system was opened. A double trap

immersed in liquid nitrogen connected T to the pumps, and effectively prevented hexane vapour from diffusing into the pumps. The trap also prevented the back-diffusion of mercury and oil vapours into the apparatus. The partial pressure of vapours other than hexane was between 10^{-5} and 10^{-6} mm of mercury.

If the hexane in A was partially frozen, the removal of most of the dissolved air proceeded very smoothly, the solid phase apparently acting as a centre for the nucleation of air bubbles. When most of the air had been removed, T was closed, and the hexane in A was allowed to distil slowly into S, a low temperature still of the type described by Lossing (75) and Leroy(68). The body of the still, a, was tightly wrapped with several layers of aluminium foil, b, over which was wound a layer of asbestos paper supporting an electrical heater, c. The whole was mounted in an evacuated jacket, d. Leads to the heater and to the copper-constantan thermocouples (t_1 , t_2) imbedded in the aluminium foil were brought out through a side-arm on the jacket. The side-arm was also connected to the fore-pump, so that the jacket could be evacuated to a pressure of 0.1 - 1 mm of mercury when the still was operated. The outside of the jacket was cooled with liquid nitrogen. With this arrangement the temperature in the still could be varied between -194 °c and -60 °C by varying the current in

the heater. A temperature within this range could be maintained within 1 - 2 °C for several hours.

When the hexane in A had been transferred to S, the temperature of the still was slowly raised to a value just below the melting point of hexane, i.e., ca - 96° C, and held at this value for 50 - 60 minutes with the pumps full on. The tap, T, was then closed, and the hexane was distilled back into the reservoir, A, which was cooled with a mixture of solid CO₂ and acetone, the still being allowed to come gradually to room temperature in the process. The hexane was then ready for distillation into irradiation cells (described below) sealed to the apparatus at X and X'. The irradiation cell receiving the hexane was cooled with the CO₂ - acetone mixture. The reservoir, A, was allowed to come to a temperature between - 20 ° and - 40 °C, fixed by the rate of heat transfer through the walls of the reservoir from the surrounding atmosphere. When 5 ml of hexane had been collected in the irradiation cell, the distillation was stopped by freezing the hexane in A with liquid nitrogen. The hexane in the irradiation cell was similarly frozen, and the tap, T, was opened. The glass at the constriction joining the irradiation cell to the still was then gradually warmed with the hand-torch to the softening point, and the cell finally sealed off under vacuum.

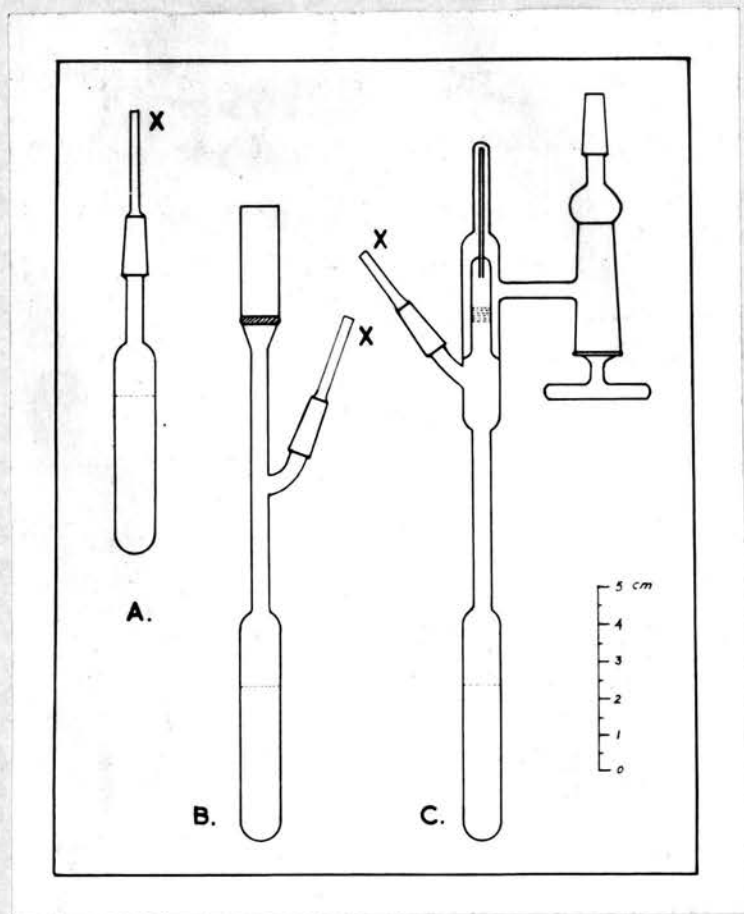


Fig. 3. Three irradiation cells.

The procedure just described was dictated by the following consideration. It was found that quite appreciable amounts of methane, ethane, ethylene, etc., were formed by thermal "cracking" of hexane vapour on the hot glass of the constriction in the process of sealing off the irradiation cell. This necessitated freezing the hexane in liquid nitrogen during the sealing-off process. Furthermore, all the hexane in the apparatus had to be either in A or in the irradiation cell, since hexane in parts of the apparatus not cooled with liquid nitrogen gave rise to a dynamic pressure of hexane sufficient to cause appreciable thermal cracking at the seal. For this reason the still, S, was kept at room temperature during the distillation. It was not convenient to distil hexane directly from the still into the irradiation cells because of the time-lag involved in changing the temperature of the hexane in the still.

An analysis of the hexane prepared in this way is given in the next section under Analytical Methods. The irradiation cells will be given a brief description before proceeding to the preparation of solutions of anthracene in hexane.

Three of the four types of irradiation cells used are illustrated in Fig. 3. The fourth will be described in a later section. In Fig. 3 cell A. was used for

samples on which a single determination was to be made. The body of the cell was made from selected Pyrex tubing, 1.40 cm O.D., which fitted snugly into the cell-holder designed for irradiations with the Co^{60} source. Above the inscribed 5 ml mark the cell was joined to a B-10 cone joint, which was joined in turn to a short length of 4 mm capillary tubing. The cell was sealed to the still at X. The walls of the capillary were sufficiently thick that the cell could be sealed off at the capillary without danger of "sucking through" the hot glass. After an irradiation the cell was opened under vacuum for gas analysis by snapping off the capillary with a device made for this purpose (see below) when the cell was attached to the gas analysis line by the B-10 cone.

Cell B. of Fig. 3 was used to follow changes in the concentration of anthracene in solutions irradiated in the dark. Above the side-arm with the B-10 cone the cell was flanged to match a standard spectrophotometer cell (1 cm light path) fitting the cell-holder of the Unicam spectrophotometer. The flange and open end of the cell were ground flat with fine emery dust, finally lapped together, carefully cleaned and sealed together with silver chloride. It was found that a permanently vacuum-tight seal could be made if, after the molten silver chloride had cooled and set, the cell was put under vacuum and the silver chloride again heated just to melting and at

once allowed to cool. A vacuum-tight seal could also be made by coating a defective silver chloride seal with Picein or Araldite, but it was found that such seals usually gave rise to spurious results probably owing to contamination of the hexane with Picein or Araldite. Later a cell was made in which the spectrophotometer cell was attached through a quartz-to-Pyrex graded seal. The results obtained with this cell were in complete agreement with those obtained with cell B. of Fig. 3 .

Cell C. of Fig. 3 was designed so that a measurement of the hydrogen evolved from a sample of irradiated hexane could be made without breaking open the cell. The upper part of this cell is attached to a palladium thimble, Pd, gold-soldered to a platinum tube sealed in lead glass at the end of a graded lead-to-Pyrex glass seal. The Pyrex envelope enclosing the thimble was attached through the vacuum stopcock, T, to a second B-10 cone. To measure the hydrogen evolved from the sample the cell was attached by this cone to the gas analysis line and the envelope near the tip of the thimble was heated with the hand-torch until the temperature of the palladium was such (200 - 250 °C) that the metal became permeable to hydrogen. Reproducible results were obtained by adhering to the procedure described below.

While the cell was attached at X to the still the palladium thimble was outgassed (still open to the pumps)

by heating the envelope with the hand-torch. When the cell was sealed off at X with the sample under vacuum, it was attached to the gas analysis line by the B-10 cone on T and the envelope then evacuated. The sample was frozen in liquid nitrogen throughout the remainder of the operations. The envelope was heated to bring the palladium to 200 - 250 °C, and pure hydrogen was added from the gas analysis line until the surface of the thimble was completely reduced (surface goes from blue to silver) and it was ascertained that hydrogen was actually passing through the thimble into the cell. The thimble was then allowed to cool, and the excess hydrogen on the line side of the thimble pumped off. The hydrogen in the cell was then measured. This was done by heating the thimble to the required temperature and measuring the rise in pressure caused by the outflow of hydrogen. If there was no hydrogen in the cell (i.e., inner surface of palladium not reduced) the above procedure was repeated. When the palladium had been completely reduced, the envelope was pumped down hard with the thimble at the maximum safe temperature. T was then closed and the cell removed from the gas analysis line. After this treatment the thimble was always kept under vacuum.

In measuring the hydrogen evolved under irradiation the liquid was equilibrated with the gas phase

by shaking the cell for 1 - 2 minutes before immersing it in liquid nitrogen. The measurement then proceeded as above, except that the hydrogen passed by the thimble was collected and analysed. Very little was retained by the liquid phase. The method tended to compensate for incomplete abstraction of hydrogen from the sample, since if one measurement was low, the following one was usually high.

The relatively large gas phase over the sample in the Type C. cell did not introduce an ambiguity when the measurements were concerned only with the initial stages of hexane decomposition. This was apparent from the agreement between results obtained with Type A. and Type C. cells.

The preparation of solutions of anthracene in hexane suitable for irradiation was also governed by the necessity to keep the hexane pressure very low during the sealing-off process. This was achieved by the procedure described below.

Anthracene of very high purity was obtained from Messrs. Nash and Thompson, Ltd., and was used without further purification. A standard solution of anthracene in hexane was made up containing 10^{-3} M p L of anthracene. To prepare a 5 ml sample containing 10^{-4} M p L of anthracene 0.5 ml of the above solution was pipetted

through a capillary funnel into the irradiation cell. The cell was then attached by the B-10 cone joint to a trap, the other side of which was connected to the pumping system. A rough vacuum was produced, and the hexane in the cell was distilled into the trap. The anthracene was deposited as a thin layer at the bottom of the cell. When the hexane was removed, the cell was detached from the trap and sealed to the still at X. This could not, of course, have been done with hexane in the cell. The anthracene was sufficiently non-volatile that the cell could be thoroughly evacuated for several hours without appreciable loss of anthracene. When a good vacuum had been obtained, and it had been ascertained that system was vacuum-tight, hexane was added to the reservoir, A, and following the procedure given above, the cell was filled to the 5 ml mark with hexane and sealed at the capillary. Using Cell B. of Fig. 3 it was found that solutions prepared in this way contained within 1 - 2 % of the calculated concentration of anthracene.

Each sample had to be prepared individually by the above procedure, and since it was advisable to keep the amount of hexane in the still to somewhat less than 25 ml in each run (to avoid plugging the still) only four samples were prepared in each run. However, no other method of preparation was found to be satisfactory.

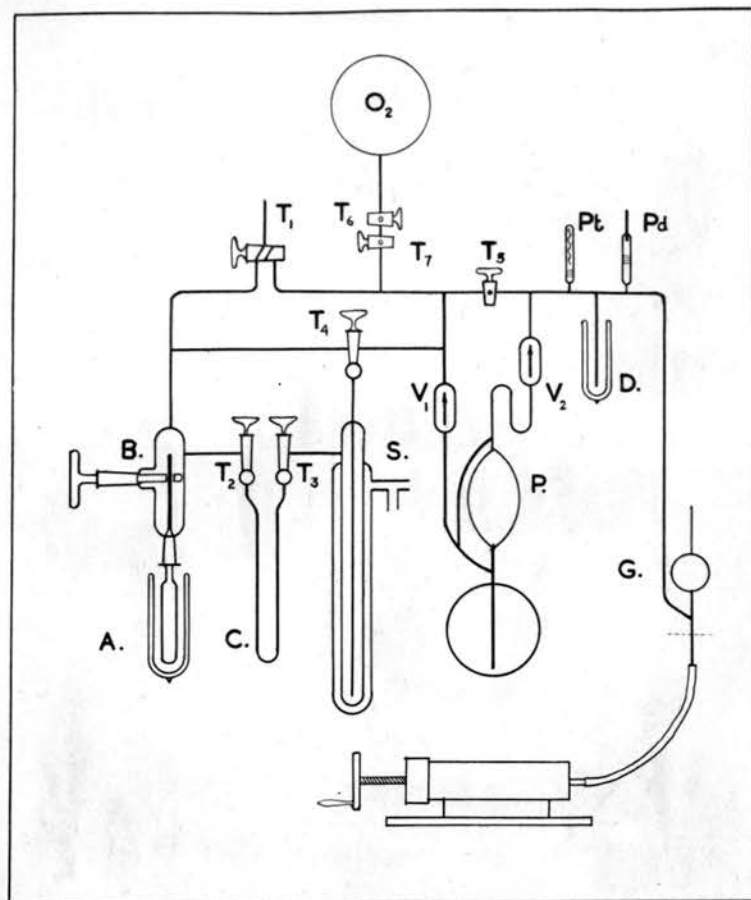


Fig. 4. The Gas Analysis Apparatus

3: Analytical Methods:

Fig. 4 illustrates schematically the apparatus used to analyse the gases formed by the decomposition of hexane and solutions of anthracene in hexane under the action of ^{60}Co γ -rays.

The irradiated sample contained in one of the irradiation cells described in the last section (Cell A. is shown in Fig. 4) was attached by the B-10 cone to the apparatus at A . The capillary tip then protruded into the sample breaker, B , and passed through a hole in the shaft of the breaker. The shaft was turned by a handle outside the envelope of the breaker, and if a file scratch was made on the capillary near the part which passed through the shaft, the capillary was usually broken off neatly at the scratch when the shaft was turned.

The tap, T₁ , connected the apparatus to a pumping system which produced a vacuum of 10^{-6} mm of Hg. The sample breaker was thoroughly evacuated before the sample was opened, and the sample was cooled with a mixture of solid CO_2 and acetone to lower the vapour pressure of the hexane to ca 0.1 mm.

The U-trap, C , connected the sample breaker to S, a low temperature still constructed on the pattern of the still shown in Fig. 2 , but with a greater length

and much extended region of fractionation. Both C and S were cooled with liquid nitrogen at the start of an analysis. The entire apparatus was, of course, very thoroughly evacuated in preparation for an analysis.

When the irradiation cell had been successfully opened, T_2 , T_3 and T_4 were turned so as to connect the sample breaker with the Töpler pump, P. The first fraction, that volatile at -196°C , was then transferred into the calibrated volume defined by T_5 , the vent, V_2 , and the mercury level (broken line) in the McLeod gauge, G. The gauge was supplied with mercury from a steel cylinder and piston rather than the conventional glass reservoir. The mercury level in the gauge was therefore raised and lowered mechanically, by cranking the piston in and out, rather than pneumatically, as in the conventional device, and this feature greatly increased the speed with which the gauge could be operated and the ease with which the mercury level could be brought to a mark on the gauge. The speed of operation was an important advantage, particularly during the combustion analyses (see below). The design owes its origin to a manometric gas analysis apparatus described by Pitts, de Ford and Recktenwald (90).

When the first fraction had been transferred quantitatively into the calibrated volume (i.e., the

pressure over the sample had been reduced to 1 / 100 th of the starting pressure) T_4 was closed, but T_3 and T_2 left open, so that hexane continued to distil from A into C and S . The distillation was allowed to proceed for 30 - 45 minutes, or at least until the analysis of the first fraction was complete, it being the view that the steady diffusion of hexane vapour into C would carry residual lighter gases into the trap and still. At the same time vertical convection currents set up in the liquid sample would continually bring fresh hexane to the surface where evaporation was occurring.

The first fraction contained the gases from the decomposition of hexane which were volatile at -196°C , namely, H_2 , CH_4 , possibly CO and, if the sample had been pumped down to ca $1\ \mu$ pressure, possibly some C_2H_4 from the second fraction. Traces of air in the sample during irradiation appeared as N_2 in the first fraction. Traces of air introduced in error during the transfer of the first fraction gave rise to both N_2 and O_2 in their proportion in air.

It was soon established that H_2 was the principal gaseous decomposition product from the irradiation of liquid hexane. The first fraction always contained H_2 in amounts ten fold greater than the amounts of other gases. The first step in the analysis was therefore to combust any O_2 introduced accidentally with the great

excess of H_2 present in the first fraction. This was done by heating the small spiral of platinum foil, Pt, contained in a quartz tube connected to the apparatus through a quartz-to-Pyrex graded seal. An electrical heater, consisting of a few turns of nichrome wire wound directly on the quartz tube, brought the platinum up to combustion temperature in 20 - 30 seconds. The combustion of O_2 in an excess of H_2 was completed with this apparatus in 30 - 40 seconds. Very few analyses (less than 1%) showed O_2 in the first fraction.

When the step above had been completed, the H_2 in the first fraction was separated from the other components of the gas mixture by effusion through the heated palladium thimble, Pd, attached to the apparatus by the conventional lead-to-Pyrex graded glass seal. A small furnace which fitted over the thimble was carefully adjusted to bring the tip of the thimble to a temperature (ca 200 °C) at which the palladium just became permeable to H_2 . The H_2 diffusing through the metal to the outer surface was immediately oxidised catalytically by oxygen from the atmosphere. Thus a pressure gradient of H_2 was maintained which removed H_2 quantitatively from the apparatus even down to residual pressures of 10^{-5} mm of Hg. The removal was complete in 3 - 4 minutes.

A more rapid removal of H_2 was achieved by raising

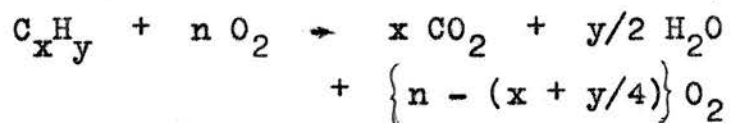
the temperature of the thimble. At the higher temperatures there was some danger that CH_4 and C_2H_4 might be decomposed on the hot palladium to C and H_2 . Fliieger (39) has cautioned against the use of a heated palladium membrane to separate H_2 from hydrocarbon gases for this reason. He was, however, analysing large quantities of gas at atmospheric pressure. Marshal and Constabaris (80) claim that at the low pressures used for micro-analysis CH_4 is not decomposed by hot palladium.

In the present system the total gas pressure during an analysis was seldom greater than 200μ , and the partial pressure of hydrocarbon gases was at least an order of magnitude lower than this. Several of the larger samples were divided, and duplicate analyses were made on the first fraction, one in which the H_2 was determined by combustion in excess O_2 (see below) and one in which the H_2 was determined using the palladium thimble at ca 200°C . Good checks were obtained when there was no ethylene present, but in the presence of this gas there was evidence for the decomposition to C and H_2 on the hot palladium. This difficulty could be avoided, however, by freezing the C_2H_4 in the cold trap, D, with liquid nitrogen when the palladium was heated.

After the H_2 had been removed, a measured quantity of O_2 was added to the remaining gases (Pd cold !)

and the quantities of CH_4 and C_2H_4 were determined by fractional combustion. Of the many techniques which have been developed employing combustion over a catalyst to determine small quantities of hydrocarbon gases (see Bayer, B 1 , for a review) none have, to the writer's knowledge, the simplicity and speed of the present method, nor do they allow a determination of both the carbon number and the hydrogen number from a single combustion. A brief description of the present method will therefore be given, together with an illustration of its potentialities.

Pure O_2 , generated from KMnO_4 , was admitted to the low pressure side of P through the metering taps, T_6 and T_7 , and transferred by the pump into the calibrated volume. The quantity of O_2 added was determined by measurements of the pressure before and after the addition. D was cooled with a mixture of solid CO_2 and acetone. The temperature of the platinum spiral was then raised to ca 350°C at which combustion of the hydrocarbon gases other than CH_4 proceeded rapidly and quantitatively. CH_4 combustion proceeded relatively slowly with the highest temperature attainable, ca 450°C . The combustion reaction may be written in the general form:



It will be seen that the combustion was accompanied by a fall in pressure as H_2O was frozen in the trap at $-80\text{ }^\circ\text{C}$. Measurements of pressure as a function of the time of combustion showed that the pressure fell to a steady value in 2 - 3 minutes. The general equation shows that the quantity of H in the original hydrocarbon - measured in the same pressure units- was four times the pressure drop.

The CO_2 - acetone bath was then replaced by liquid nitrogen. A second drop in pressure occurred as the CO_2 formed in the combustion was frozen in the trap. The "pressure" of C was exactly equivalent to the fall in pressure, if a correction was made for a small change in pressure due to thermal transpiration when the temperature of the trap was lowered from -80 ° to $-196\text{ }^\circ\text{C}$. In practice all the relevant pressures were corrected for thermal transpiration measured with respect to the pressure with the trap, \underline{D} , at room temperature. This correction amounted to less than 1% when the trap was at $-80\text{ }^\circ\text{C}$, but was 6.5% when the trap was at $-196\text{ }^\circ\text{C}$.

The carbon and hydrogen numbers, x and y, were determined directly from the ratios of $p\text{C} / p\text{C}_x\text{H}_y$ and $p\text{H} / p\text{C}_x\text{H}_y$. The accuracy and sensitivity of the method are illustrated by the results of the analysis of standard samples of C_2H_4 in the table below.

Table 2.

Analyses of standard samples of C_2H_4 by the combustion method described.

Sample	Volume at S. T. P.	Carbon No.	Hydrogen No.
1	0.68 mm ³	2.05	3.77
2	0.98	2.09	4.04
3	0.56	2.03	3.80

Table 2. shows that the method is applicable to extremely small amounts of gas, and though the precision of the determination of carbon and hydrogen numbers is not great, it provides a reliable guide to the composition of the gas.

It was found that the determination of the hydrogen number was particularly sensitive to the condition of the platinum foil. Analyses of the quality of those in Table 2. were obtained only if the foil had been 'conditioned' by being heated in pure O_2 for several minutes prior to the analysis. Once this had been done, the foil gave good results for a large number of consecutive analyses; but on standing in disuse for several days, it again required to be 'conditioned'. Determinations of the carbon number were much less affected.

It is easy to show that a determination of the carbon and hydrogen numbers of a mixture of two hydrocarbons (say, C_2H_4 and C_2H_6) permits a calculation

of the amount of each present in the mixture. The precision is inherently low if one component is present in great excess over the other, and is not great even when the two gases are present in equal amounts. Fortunately, this situation was not often encountered.

In the first fraction CO was oxidised with the C_2H_4 . The determination of the hydrogen number permitted these two gases to be distinguished. CO was found in less than 1% of the samples irradiated. CH_4 was barely oxidised in the time required for the complete combustion of C_2H_4 . CH_4 was therefore determined after C_2H_4 , and the temperature of the platinum was raised to ca 450 °C to hasten the oxidation. Even at this temperature CH_4 was oxidised relatively slowly, 30 - 40 minutes being required for the oxidation of a small sample (0.5 mm³). The carbon and hydrogen numbers were determined as described just above.

When the combustion analysis of the first fraction had been completed, the trap, D, was at -196 °C, this being required for the last determination of the analysis. Any gas then remaining was N_2 and the O_2 remaining from the combustion. The N_2 was estimated by calculating the amount of O_2 which should be left from the combustion and subtracting this from the final pressure; or, if there was some doubt, the O_2 was removed by combustion with excess H_2 , and the remaining H_2 removed by ef-

fusion through Pd , leaving only the N_2 . This could be distinguished from CH_4 by the Tesla discharge in the tip of the McLeod gauge, G . N_2 gave the characteristic purple discharge with very little pressure change, whereas CH_4 gave a pink discharge characteristic of H_2 (due to the very rapid decomposition into H_2 and hydrocarbons of higher molecular weight) accompanied by a rapid diminution in pressure. As the work proceeded it was found that samples containing N_2 always contained either O_2 or CO , and if neither of these gases were found, it became customary to assume that any gas remaining after the low temperature combustion was CH_4 , and the Tesla discharge test was made in preference to the time-consuming combustion. Most of the methane determinations reported under Results: were made in this way. Those actually determined by combustion are reported marked with an asterisk.

When the analysis of the first fraction was completed, attention was turned to fractions trapped at $-196^\circ C$ in the U-trap, C . These contained all the lower boiling hydrocarbons together with part of the C_2H_4 . The trap also contained about 1 ml of solid hexane. T_2 was closed, and the liquid N_2 surrounding the trap was lowered until the bottom of the trap was above the surface of the N_2 , but several inches of the trap were surrounded by the cold walls of the dewar flask. The trap

was thus warmed very gradually, and some fractionation was effected as the hydrocarbons in C distilled very slowly into the still, S. It was found that the U-trap was absolutely essential to the successful separation of the various fractions with the still. Without the trap, the separation was poor, and all the fractions from the still were heavily contaminated with hexane. With the procedure just described, the various fractions were laid down evenly in the different temperature zones of the still, the fractions as far as C_4H_{10} being completely free from contamination with hexane.

During the above distillation, the temperature of the still was adjusted so that the end of the central outlet tube was in a zone at $-180\text{ }^\circ\text{C}$. C_2H_4 and C_2H_6 are volatile at this temperature (vap. press. $10 - 15\ \mu$) but C_2H_2 and the ' C_3 ' hydrocarbons are not. The first two could then be separated from the lower boiling fractions, and this was done as the next step, while the gradual distillation from C to S was in progress, the $C_2H_4 + C_2H_6$ fraction was transferred into the calibrated volume with the Töpler pump, P, and was the second fraction of the volatile decomposition products to be analysed.

The analysis was performed in the same way as the first step, though omitting the O_2 determination and the separation of H_2 . It was found that C_2H_6 constituted

the major part of the 'C₂' fraction. In samples in which there was evidence of thermal "cracking" of hexane, much larger amounts of C₂H₄ were found. The other fractions were also relatively rich in unsaturated compounds. It appeared that the small amounts of C₂H₄ found in the normal samples might be due to residual impurity of the hexane.

The third fraction was transferred with the lowest zone of the still at - 155 °C. At this temperature C₂H₂, C₃H₆, C₃H₈ and CO₂, if this was present, were separated from the higher boiling fractions. Cyclopropane, which might have prevented the clean separation of the 'C₃' from the 'C₄' fractions, was never found. CO₂ was found in many of the earlier samples which contained abnormally high amounts of residual O₂. In samples prepared by the technique described in the preceding section and illustrated in Fig. 2, there was no CO₂ within the limits of detection. The principal component of the 'C₃' fraction in a normal analysis was C₃H₈, the unsaturated compounds being found in abundance only when there was thermal "cracking" of hexane. The accuracy of the analysis was not great, however, since the quantities of 'C₃' involved in a normal analysis were near the limit of detection.

The fourth, or 'C₄' fraction was transferred with the lowest zone of the still at - 135 °C. In a nor-

mal analysis the amounts of 'C₄' were also near the limit of detection.

The fifth, or 'C₅', fraction was never obtained free from contamination by hexane, and it was uncertain whether the 'C₅' s were transferred quantitatively. The results of the 'C₅' analyses were never reproducible. They are reported under Results: in parentheses, and probably indicate that the amounts of 'C₅' hydrocarbons found were residual amounts left after the purification.

With the analysis of the fifth fraction the gas analysis was complete. The sample at A was replaced with an empty tube, terminating in a B-10 cone joint, and the hexane in C and S was distilled into the tube. The tube was then removed, and its contents poured into a bottle kept for hexane residues. It was important to ensure that no appreciable hexane was left in the various traps when they came to room temperature, since the hexane dissolved in the Apiezon L vacuum grease with which the taps and cone joints were lubricated. If a small reservoir of liquid hexane was left in the apparatus, this process continued until the grease liquified and ran into various inaccessible parts of the apparatus. When this happened the background pressure of hexane vapour in the apparatus became so high that the apparatus had to be taken down, cleaned

and re-assembled before further analyses could be made. The apparatus would have been decidedly improved if the various taps had been replaced with mercury cut-offs or mercury operated glass ventils. However, no difficulty was experienced so long as precautions were taken to ensure that the pressure of hexane in the apparatus never rose above ca 0.1 mm .

Some relevant constants of the apparatus are listed in the table below.

Table 2a.

Some constants of the gas analysis apparatus.

Volume bounded by T ₅ , V ₂ and Hg cut-off	113.9 cc
Sensitivity of McLeod Gauge:		
1st Range:	1 scale mm =	8.76 X 10 ⁻⁵ mm or 5.86 X 10 ⁻¹⁰ M
2nd Range:	.. =	2.89 X 10 ⁻⁴ mm · 1.94 X 10 ⁻⁹ M
3rd Range:	.. =	8.52 X 10 ⁻⁴ mm 5.71 X 10 ⁻⁹ M

It follows from the above constants of the apparatus that the useful limit of detection of a gas was in the region of 5 X 10⁻⁹ M. Greater sensitivity could have been obtained with a larger and more sensitive gauge, but at the cost of speed of operation. Greater sensitivity did not seem worthwhile, since the background of light hydrocarbons was not reduced below the limit of detection.

Since refluxing under vacuum failed to remove the last traces of the light hydrocarbons from hexane, some doubt existed whether the technique of gas transfer just described actually removed all the light hydrocarbons from the irradiated sample. The samples were too large to be transferred into the still in toto, but amounts up to 2 ml could be transferred without plugging the still.

It was found that the pressure of light hydrocarbons in the still rose by about 15 % during the distillation of the first ml, but approached a steady value during the distillation of the second. In actual practice between 1 and 2 ml were distilled from the sample at A into the U-trap, C, and this amount distilled very gradually from C into the still. It seemed reasonable to assume that all the light fractions had been transferred. The quantity of liquid hexane involved was only a tenth of that refluxed under vacuum, and whereas under reflux an appreciable quantity of liquid hexane was flowing back into the reservoir, in the gas transfer experiment there was a steady diffusion of hexane vapour from the sample into the U-trap, and no reflux of the liquid occurred. The measurements also seemed to be very sensitive to small amounts of unsaturated light hydrocarbons in the samples when these were formed by the accidental thermal decomposition of hexane vapour in the process of sealing off the irradiation cell.

3a: Analysis of the Starting Materials: Hexane:

The analysis of a typical sample of hexane by the method just described is given below:

H ₂	1 X 10 ⁻⁹ M in 5 ml.
'C ₁ ' (CH ₄ , CO)	1 X 10 ⁻⁸ ..
'C ₂ ' (C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆)	1 X 10 ⁻⁸ ..
'C ₃ ' (C ₃ H ₆ , C ₃ H ₈)	2 X 10 ⁻⁸ ..
'C ₄ ' (C ₄ H ₈ , etc.)	1.5 X 10 ⁻⁸ ..
'C ₅ ' (C ₅ H ₁₀ , C ₆ H ₁₂ ?)	(1 X 10 ⁻⁷ M)..
CO ₂	---
N ₂	5 X 10 ⁻⁹ M ..
O ₂	---

In the event of confusion between the meaning of the term 'C₁' as used above and as used in Sec. 3, where it referred to the first fraction of the analysis, that containing some C₂H₄ as well as the 'C₁' compounds, the meaning implied above will be adhered to henceforth. Similarly the term 'C₂' will refer henceforth to compounds with two carbon atoms, etc.

The results above show that the residual amounts of light hydrocarbons in the hexane were well within the limits of detection. The fifth fraction was particularly large compared to the others. A considerable error was introduced by

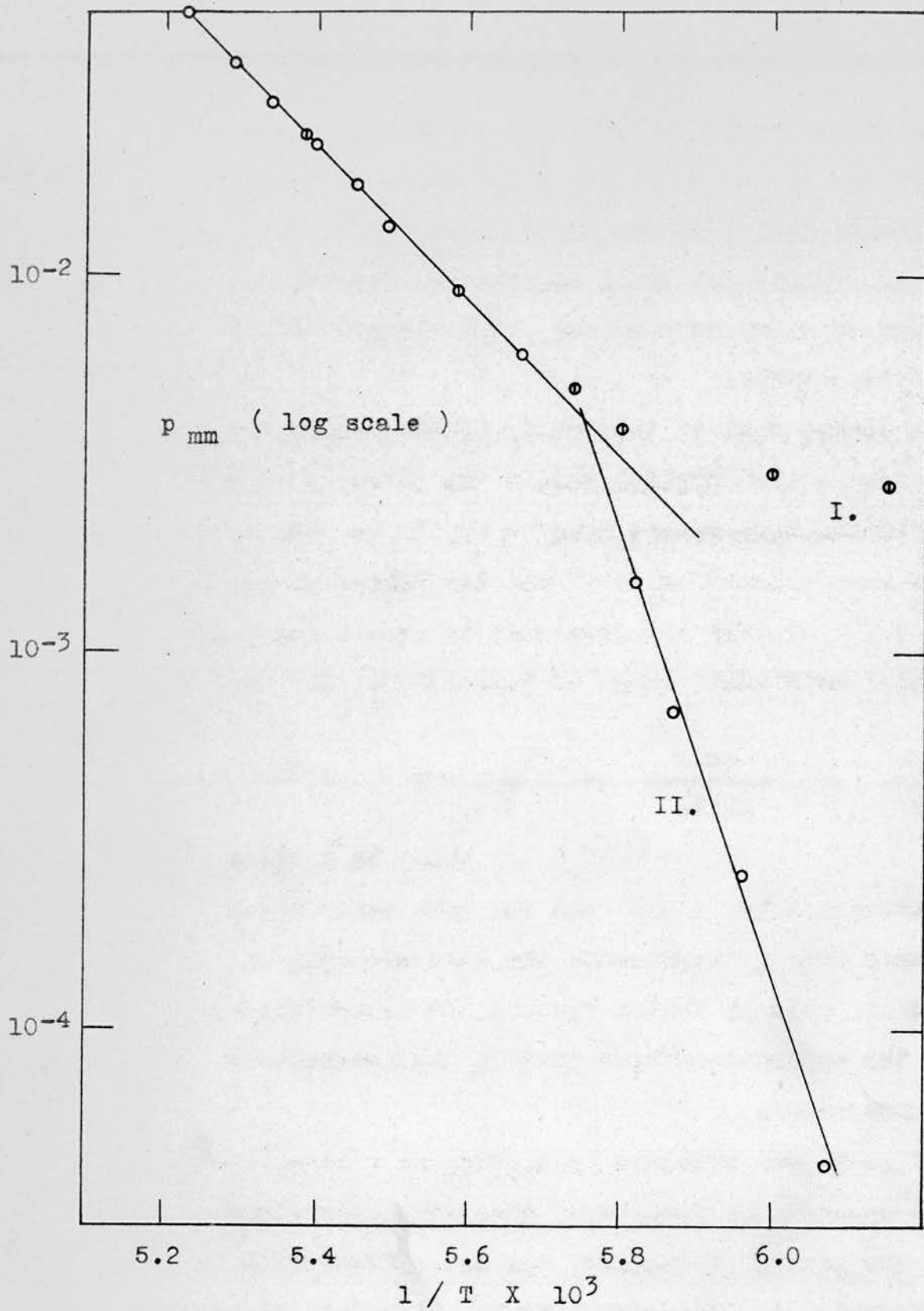


Fig. 5. A plot of pressure (log scale) against the reciprocal absolute temperature with pure hexane in the still.
 I. Direct from sample. II. Same material after pumping 10 minutes at -110°C .

contamination of this fraction with hexane, since the separation was poor. This concentration of pentane, etc., probably had no effect on the decomposition of the hexane. It was obviously impossible, however, to look for small amounts of the 'C₅' hydrocarbons in irradiated hexane.

As a second test of the purity of the hexane, the vapour pressure of a typical sample was measured as a function of the temperature from -116 °C to -80 °C using the low-temperature still and the McLeod gauge, G, Fig. 4. At very low pressures of hexane measured over a relatively small range of temperature, the expression

$$\frac{\ln p}{(1/T)} = - Q / R$$

holds to a close approximation. Here p , T and R have their usual significance and Q represents the heat absorbed in producing 1 mole of hexane vapour. It is assumed in deriving the expression above that Q is independent of the temperature.

In Fig. 5 the pressure is plotted on a logarithmic scale against the reciprocal absolute temperature for I.) the hexane produced by the method described in Section 2: and II.) the same material after ten minutes pumping at -110 °C while in the still.

Both sets of data give a straight line above the apparent melting point of hexane, $-99\text{ }^{\circ}\text{C}$. The slope of this line leads to a value of Q_v , the latent heat of vapourisation of hexane, equal to 9.6 Kcal / mole , which is in reasonable agreement with published values. ($\sim 10\text{ Kc}$) Curve I. approaches a constant pressure at the lower temperatures arising chiefly from the contamination by ' C_5 ' hydrocarbons. Curve II. shows that in the absence of contaminants the pressure falls with decreasing temperature to yield a plot which is an approximately straight line down to pressures of $5 \times 10^{-5}\text{ mm}$ of Hg. The slope of this line leads to a value of Q_s , the latent heat of sublimation, equal to 26 Kcal / mole , a value rather higher than the published values. (16 Kc) It is possible that the pressures measured over solid hexane were not true equilibrium pressures at the temperatures concerned. The apparent melting point, $-99\text{ }^{\circ}\text{C}$, is about 5 ° lower than the published values (-94.3) a fact which is understandable if the slope of the lower curve was too great for the reason just given. The thermocouples attached to the still were not calibrated, since the approximate temperature was sufficient for the operation of the still.

Fig. 5 shows that the hexane did not contain lower- or higher-boiling isomers in any appreciable amounts.

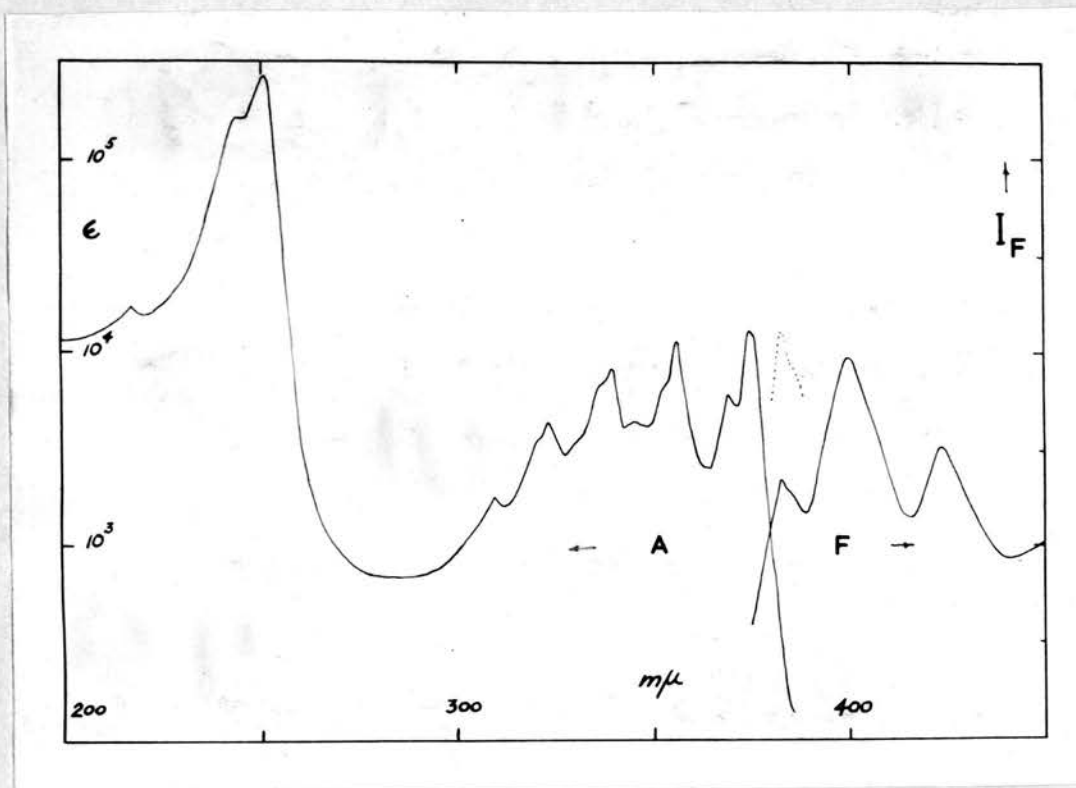


Fig. 6. The absorption and fluorescence spectra of anthracene in n-hexane.

3b: Analysis of the Starting Materials: Anthracene.

The concentration of anthracene in hexane solutions was measured spectrophotometrically using a quartz absorption cell with a 1 cm light path. The measurements were made with a Unicam SP 500 spectrophotometer. The absorption spectrum* of anthracene in pure, air-free hexane is shown in Fig. 6. The spectrum was obtained with the solution sealed under vacuum in Cell B of Fig. 3. In Table 3. below are listed the wavelengths, wave numbers and decadic molar extinction coefficients, ϵ_{10} , of the principal bands. The last quantities were computed from the optical densities measured for six concentrations of anthracene from 10^{-5} to 3×10^{-4} M. Beer's Law was obeyed to $\pm 0.5\%$ over this range.

Table 3.

The principal A-bands of anthracene in hexane.

λ in μ	ω in cm^{-1}	ϵ_{10}
375.0 \pm 0.5	26 670	11 600 \pm 0.5%
355.5	28 130	11 800
339.0	29 500	7 940
323.0	30 960	4 190
309.5	32 300	1 840
252.0	39 680	\sim 300 000
218.0	45 870	---

* Hereafter abbreviated to A-spectrum.
Fluorescence spectrum will be F-spectrum, etc.

Fig. 6. shows the F-bands of anthracene in hexane solution, also measured with the spectrophotometer. The solution was placed so that the fluorescence emitted by the anthracene fell on the entrance slit of the spectrophotometer. A photomultiplier was mounted at the exit slit. The F-bands were excited by light mainly in the region of 3650 \AA which fell on the solution at an angle of 45° to the direction of observation. The intensities of the different bands (measured in arbitrary units in Fig. 6.) were measured in terms of the d.c. current at the output of the photomultiplier. No correction was made for the response of the photomultiplier or for the dispersion of the monochromator at the different wavelengths, since the measurements were made merely to locate approximately the position of the F-bands.

The bands were situated at 381, 398, 421 and 449 μ approximately.

The spectrum shown in Fig. 6. was emitted by a solution which was approximately 10^{-4} molar in anthracene. The relative intensities of the 381 and 398 bands were strongly dependent upon the concentration of anthracene, a variation of 15 - 20 % in the relative intensities of the two bands being found for concentrations varying between 10^{-5} and 10^{-4} M p L of anthracene. This effect is due to the overlap between the A- and F-bands.

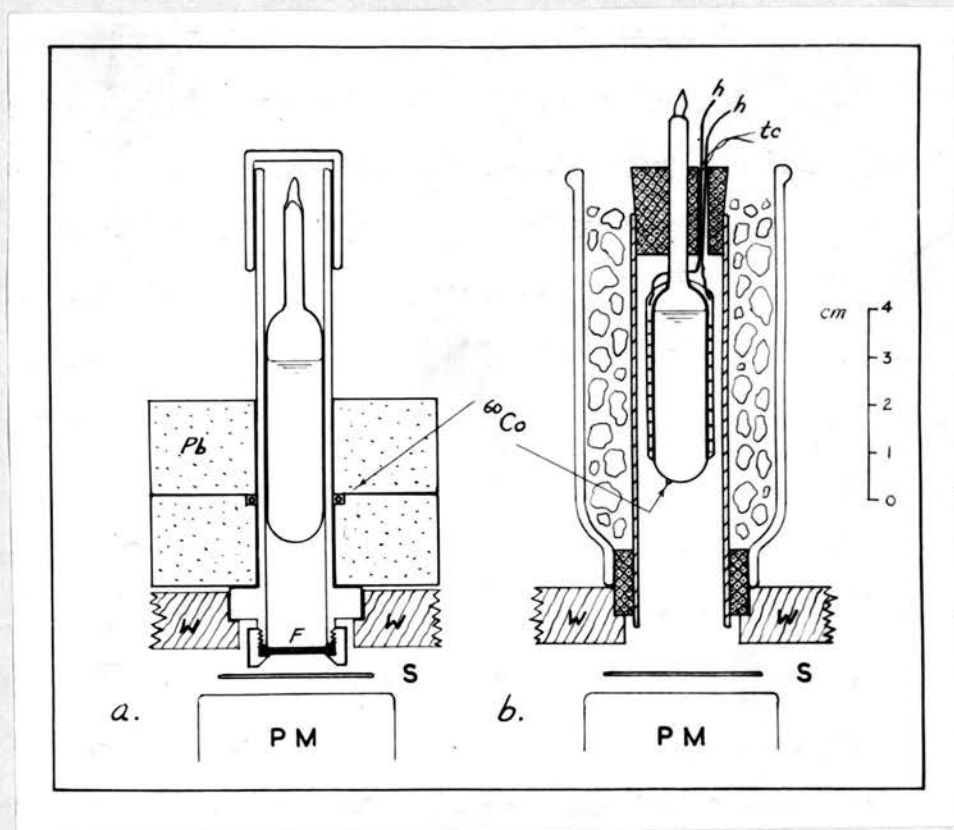


Fig. 7. Two arrangements of sample, source and photomultiplier used for fluorescence measurements.

4. Measurements with the Photomultiplier:

Fig. 7 shows two arrangements of sample, source and photomultiplier used to measure the fluorescence excited by the γ -rays in solutions of anthracene.

The photomultiplier (hereafter called the P M) was an E. M. I. type 6260 instrument mounted vertically in a cylindrical, light-tight housing, the top of which is shown as W - W in Fig. 7. Cartridges of silica gel mounted in the housing kept the atmosphere about the photomultiplier dry. An aperture in W - W directly opposite the photocathode opened on to the irradiation chamber. A shutter, S , covered the aperture when measurements of the background current were made.

High tension was supplied by an E. K. Cole type 1140 A power supply. The output current from the photomultiplier was fed through a Cambridge galvanometer to earth, the photocathode being connected to high tension negative with respect to earth. A set of gain curves for different intensities of photocathode illumination were measured, and it was the practice to hold the sensitivity of the galvanometer constant and to vary the gain when measuring experimental intensities. This method has the drawback that the voltage settings of the power supply are subject to errors caused by contact resistance in the H. T. switch. The measurements may be unreliable unless frequent test measurements are made with a light source of standard intensity. This was

done, using a standard sample of anthracene in hexane, but the measurements would have been improved by fixing the H. T. at a constant value (for maximum gain) and varying the sensitivity of the galvanometer with an Ayrton shunt.

In Fig. 7 arrangement a. was used when it was desired to measure the intensity of light emitted by different samples for a fixed intensity of γ -radiation, or to measure the intensity as a function of the anthracene concentration (See Fig. 8 and text below). The ^{60}Co source was disposed in a ring about the aluminium tube forming the irradiation chamber, and was surrounded by $1\frac{1}{2}$ inches of lead. The end of the aluminium tube fitted closely into the aperture in the P.M housing, and a filter - or combination of filters - could be attached to the end nearest the P M . The open end of the tube could be closed with the cap shown in the figure, or the upper part of the apparatus could be covered with a dark cloth.

Arrangement b. in Fig. 7 was used to measure the temperature coefficient of the fluorescence excited by the γ -rays. The sample was mounted in a brass tube within a cooling jacket filled with crushed 'cardice' (solid CO_2). The open end of the tube passed through a rubber ring, which in turn fitted snugly into the aperture in the P M housing. Surrounding the tube containing the sample was a close-fitting sleeve made of several layers of aluminium foil. Upon this, and insulated from it by a sheet of asbestos, was

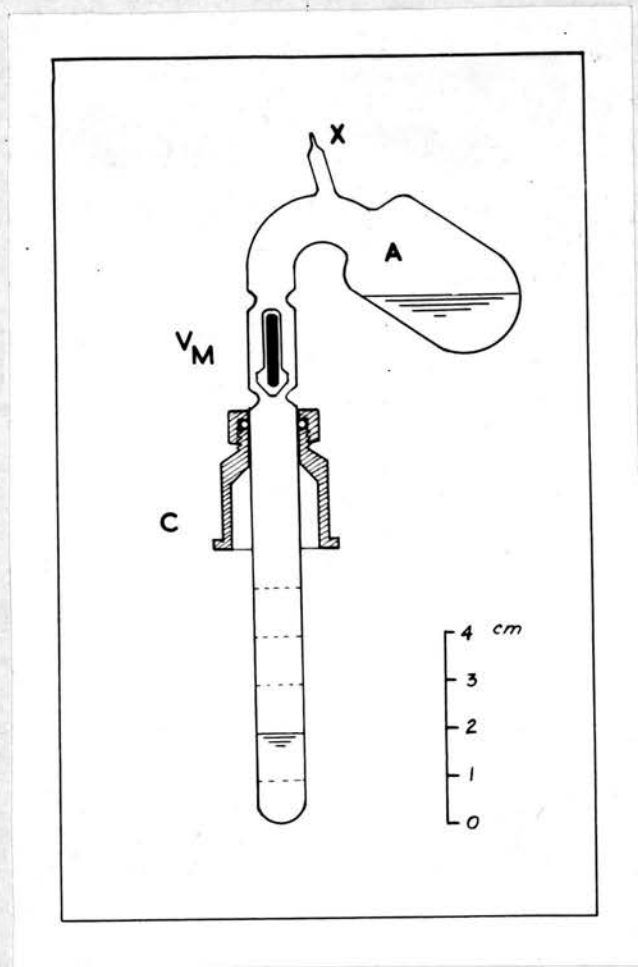


Fig. 8. The C_0 , or variable concentration cell.

wound a small electrical heater, h, h. A thermocouple, tc, was embedded in the aluminium foil, its junction nearest the end opposite the photocathode. In the apparatus shown, the jacket holding the 'cardice' was made from a piece of Pyrex tubing. In a later modification this was exchanged for a much larger jacket made of tin and wood. During a run the 'cardice' was heaped over the upper end of the tube containing the sample. The lowest temperature then attainable at the thermocouple was $- 50^{\circ}\text{C}$. The temperature was varied between this value and $+ 60^{\circ}\text{C}$ by varying the current in the heater. In practice, only part of this range was feasible, that between $- 30^{\circ}$ and $+ 60^{\circ}\text{C}$. At temperatures below $- 30^{\circ}$ a lack of reproducibility was found in the measurements of intensity, caused evidently by the precipitation of anthracene out of the solutions.

It should be stated that the intensity of $\sqrt{\text{v}}$ -rays used to excite fluorescence was so low that the chemical effects of the $\sqrt{\text{v}}$ -rays could be ignored, even during the longest exposures. The aggregate strength of the sources used could not have been greater than 200 - 300 μc (Comp. Tab. 1, p 14).

Fig. 8 shows a cell which was constructed so that the concentration could be varied continuously in a single sample sealed off under vacuum. An anthracene solution of concentration C was made up in the reservoir, A, using the techniques described in Sec. 2. The cell was then sealed off under vacuum at X in Fig. 8. The required amount of

solution was poured past the magnetically operated valve, V_M , which was held open by a small magnet outside the cell, into the graduated irradiation tube. The solution in the tube was then diluted with pure hexane by distilling hexane from the reservoir into the graduated tube. This was best accomplished by holding the cell so that the irradiation tube was at an angle of 45° from the vertical. The reservoir was then immersed in a beaker of hot water while the irradiation tube was cooled under the cold water tap. The final concentration was calculated from the measured volumes before and after dilution and the initial concentration, C_0 . Successive dilutions could be performed by pouring back part of the solution in the irradiation tube into the reservoir, and distilling more hexane into the irradiation tube.

The valve, V_M , was built into the cell to prevent further changes in the concentration once the solution in the irradiation tube had been made up.

The collar, C , which was clamped to the irradiation tube by an O-ring gland, fitted snugly over the aluminium tube in Fig. 7.a, and returned the irradiation tube each time to the same position with respect to the ^{60}Co source. This position could be varied by loosening the O-ring gland and moving the collar to a different place on the irradiation tube.

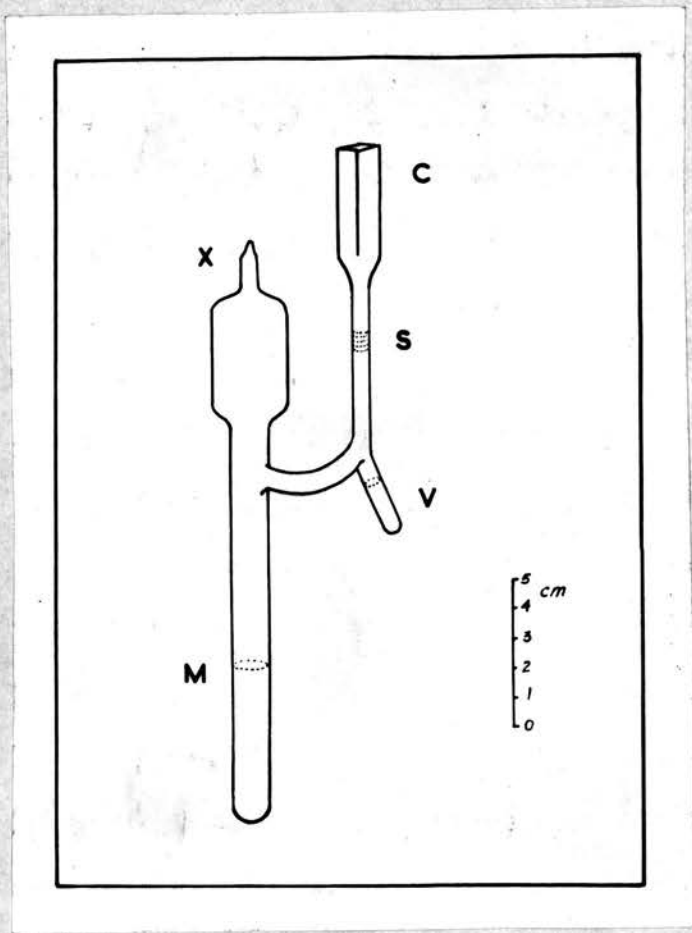


Fig. 9. Type D cell.

5. Type D Irradiation Cell:

Fig. 9 shows the Type D irradiation cell, which was designed so that the volatile part of the irradiated sample could be distilled into the silica absorption cell, C, attached to the apparatus by the silica-to-pyrex graded seal, S. The apparatus is shown in the position for irradiation. After an irradiation, the apparatus could be inverted in such a way that the liquid collected in the bulb terminating in the seal-off, X, without entering the side-arm leading to the absorption cell. The volatile components were then distilled into the absorption cell. This was accomplished by cooling the absorption cell in a bath of ice and water and, if necessary, heating the contents of the bulb in a bath of warm water.

A small, calibrated volume, V, was also attached to the arm carrying the absorption cell. This was for use in analyzing concentrated solutions of anthracene, which had to be diluted to bring the optical densities within a measurable range. The volume, V, was filled to the mark with the concentrated solution, and the apparatus was then inverted so that the measured quantity collected in the absorption cell, while the rest collected in the bulb. The solution in the absorption cell was then diluted with hexane distilled from the solution in the bulb. A ten-fold dilution could be made in this way.

Chapter II ; Experimental Results

1. Measurement of Anthracene Fluorescence:

The measurement of the fluorescence emitted by solutions of anthracene in hexane under γ -ray excitation poses several interesting problems which arise principally because of:

1) quenching of the fluorescence by dissolved atmospheric oxygen (16,21,31,37,77,98), 2) anthracene self-quenching in solution (16,17,21) and 3) absorption of part of the anthracene fluorescence by the anthracene in solution, i.e. anthracene self-absorption (15,134).

Dissolved oxygen plays an important part in determining the extent to which the fluorescence of anthracene is quenched in most solvents. This effect was first reported by Maddock (77) in relation to solution scintillators, but has since been discovered independently by Pringle et al (98). Bowen and Norton (21) have studied oxygen quenching of the fluorescence of anthracene in several solvents, and find that in general the fluorescence efficiency is accurately described in terms of the oxygen concentration by the expression:

$$F = \frac{k_1}{1 + k_2 C}$$

i.e., by the Stern - Volmer quenching law (137)

where F is the fluorescence efficiency of anthracene in solution and C is the concentration of oxygen. Bowen and Norton list values of k_1 and k_2 for several solvents, including hexane. The normal procedure in measurements of the fluorescence efficiency of anthracene in air-saturated solutions is to correct the measured fluorescence intensity for oxygen quenching, using the above expression. While this method is applicable to the fluorescence excited by radiation absorbed only by the anthracene, it obviously cannot be used for measurements in which ν -rays are used to excite the fluorescence since oxygen can enter into radiation chemical reactions with both anthracene and hexane. It was therefore necessary to irradiate the anthracene solutions in the absence of air. The method used to de-aerate the solutions is described in Chapter I, Section 2.

The second effect enumerated on the preceding page, that of anthracene self-quenching, has been the subject of extensive study by Bowen and his school (17,21, B3) and by several others (40,B4). Like oxygen quenching, anthracene self-quenching is incompletely understood, although an empirical expression like that just given above, but relating to the effect of the anthracene concentration on the efficiency, has been applied successfully by Bowen and Norton (21). In hexane the anthracene self-quenching constant, k_2 , is

$$k_2 = 90 \text{ Mpl}^{-1}$$

Self-quenching therefore becomes a determining factor only



at concentrations greater than 10^{-4} Mpl.

The third effect enumerated above, that of anthracene self-absorption, is caused by the overlap between the fluorescence and absorption spectrum of anthracene in solution (see Fig. 6, also pp. 10 and 44). The molar extinction coefficient, ϵ , is of the order of 10^2 in the spectral region of the 0-0 fluorescence band at 381 m μ . ϵ can be measured over the entire range of the anthracene fluorescence spectrum, and it is possible - at least in principle - to compute the relative intensities of the various fluorescence bands emitted from the surface of solutions as functions of the geometry of the solution and the distribution of excited anthracene molecules. Such a calculation is obviously difficult, and in practice the measurements are usually made in such a way that the effects of self-absorption are minimized. This is not easy to do when γ -rays are used to excite fluorescence, as will become apparent below.

It can be shown that self-absorption must be appreciable with the experimental arrangement usually employed for scintillation counting. The molar extinction coefficient of anthracene in the spectral region of the principal fluorescence bands may be taken as $10 - 15 \text{ Mpl}^{-1} \text{ cm}^{-1}$. The fluorescence intensity is therefore reduced by 15 - 20 % in passing through 4 - 5 cm of solution when the concentration is of the order of 5×10^{-3} Mpl, i.e. 1 Gpl.

This effect appears to have been overlooked by Kallmann and Furst (59,60) and by Reynolds (101) in their measurements of practical fluorescence output as a function of fluorescor concentration, and probably accounts for discrepancies between the work of the two schools (see Ref. 101 for a discussion). Valid comparisons between measurements at a given concentration cannot be made unless the same geometry (i.e., same thickness of solution) was used. This is particularly true for anthracene, which has a broad region of overlap in most solvents, but appears to be true as well for terphenyl, for which the region of overlap is relatively slight (ref. 101, Fig. 6).

Calculations by Kallmann and Furst (59), Reynolds (101) and others (56) of k_2 , the self-quenching constant, from scintillation data for anthracene in xylene (59) appear to give a result which is several times too large when compared with values of k_2 found by Bowen and Norton (21) for anthracene in benzene and toluene. This is to be expected if no corrections were made to the data to account for self-absorption.

The difference found by Kallmann and Furst (61) between the 'transfer' and 'quenching' constants of scintillating solutions excited by γ -rays and by α -particles can undoubtedly be explained, at least in part, by the difference in the geometry between the α -particle and γ -ray measurements. Fig. 1 (opp. p. 10) should be compared with their results.

The measurements reported below were made with the apparatus illustrated in Figs. 7a and 8 of Chapter I. ^{60}Co γ -rays were used to excite fluorescence. Since γ -rays of this energy (ca 1 Mev) are but weakly absorbed in hexane, a compromise had to be reached between a volume of solution large enough to absorb sufficient γ -ray energy to excite an easily measurable intensity of fluorescence and a volume small enough to introduce negligible errors due to self-absorption. This problem must always exist in measurements of the fluorescence excited by γ -rays, and no complete solution seems possible. Thin layers of solution might be studied if a strongly absorbed radiation such as α -particle radiation were employed. A new variable is then introduced by the extremely rapid decomposition of the solvent, though this effect might be minimised by making the necessary measurements in a sufficiently short time after the commencement of irradiation. In the present case it seemed inadvisable to excite fluorescence with a radiation differing strongly from the ^{60}Co radiation used to study the radiation chemistry of the solutions.

Using the variable concentration cell of Fig. 8 both the depth of solution and the position relative to the source could be varied. It was found that the optimum results were obtained with about 4 cm depth of solution when

the source was about 1 cm away from the end of the irradiation tube nearest the P M (Fig. 7a). To minimize self-quenching and self-absorption, the upper concentration limit was set at about 5×10^{-4} Mpl. It was found by making measurements with different filter combinations that, even at concentrations of this order and lower, there was an appreciable change in the F-spectrum with concentration owing to self-absorption. The precise shape of the fluorescence vs concentration curve depended upon the particular filter combination used as well as upon the depth of the solution (Fig. 1). This was due to the breadth of the spectral region which could be isolated with the available filters. This difficulty was overcome by using a combination which gave the P M a peak response midway between the 0-0 and 0-1 F-bands, and about equal response to either band. The measured intensity was then directly proportional to the intensity of the fluorescence falling on the photocathode, and independent of the spectral distribution of the fluorescence.

It was necessary to restrict the response of the P M to that region of the spectrum containing the principal F-bands of anthracene because of the rather high background of general luminescence excited by the γ -rays. The precise nature of this luminescence is not known, but part of it was undoubtedly emitted by the pyrex tube. Before proceeding
to a description

scription of the results of the fluorescence measurements an account will be given of some observations on the luminescence of pyrex under γ -ray bombardment.

la. Luminescence of Pyrex:

It is well known that both vitreous and crystalline silica luminesce on exposure to ionising radiation (B8,103). Fewer studies have been made with pyrex (109). The green luminescence exhibited by pyrex vacuum vessels under the Tesla discharge is familiar to most workers using vacuum techniques. The pyrex envelope of E.M.I. photomultipliers will scintillate when exposed directly to α -particles.

To determine the nature of the background luminescence found in these experiments a brief study was made of the luminescence excited in pyrex by γ -radiation. Eight samples were selected at random from the supply of pyrex tubing used for constructing apparatus. They were cleaned with chromic acid, rinsed several times with distilled water and finally heated nearly to melting in a stream of filtered tank oxygen for several minutes. The luminescence excited by γ -rays was then measured with the experimental arrangement shown in Fig.7a, Chapter I. The emission spectrum was determined very approximately with a series of Ilford spectrum filters, and it was found, rather unexpectedly, that the maximum intensity occurred between 350 and 400 $m\mu$.

It was next found that the intensity of luminescence

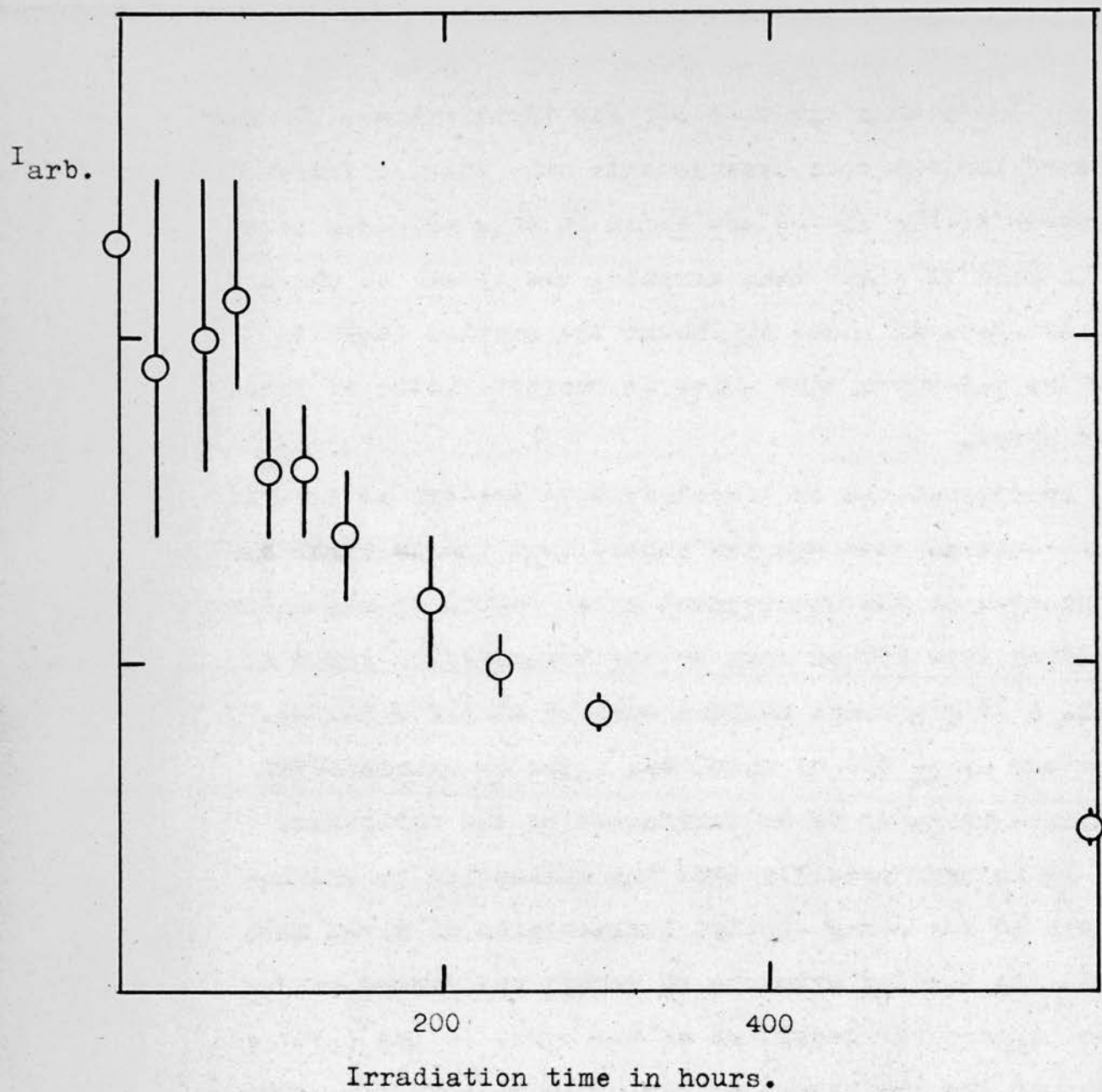


Fig. 10 Effect of irradiation with the 1.5 curie ^{60}Co on the γ -ray excited luminescence of pyrex. The characteristic red-brown tint became noticeable after 200 hours.

diminished with increasing exposure to γ -rays. The 1.5 curie ^{60}Co source was used for the irradiations. The results of luminescence measurements made after different exposures to the source are shown in Fig. 10. Each point is the mean of eight measurements, the spread of which is indicated. At about 200 hours the samples began to show the red-brown tint which is characteristic of irradiated pyrex.

Determinations of the absorption spectra of irradiated and unirradiated samples showed that the colouration was related to the development of a region of absorption extending from 650 μ down to the transmission limit of pyrex. A single broad maximum occurred at 310 - 320 μ . A maximum at ca 500 μ which was shown by unirradiated specimens appeared to be unaffected by the radiation.

It is thus possible that the diminution in the intensity of the γ -ray excited luminescence of pyrex with increasing time of exposure to γ -rays was caused merely by the increased absorption of the pyrex in the spectral region of the luminescence. The diminution in the spread of the measurements which is to be seen in Fig. 10 after about 200 hours irradiation suggests that the preparatory cleaning treatment did not leave all the samples in the same condition, but that differences between samples became smaller as the irradiation proceeded. A possible effect of this kind might have been the gradual oxidation

under the influence of the γ -rays of material left on the surface of the glass by the cleaning process. A very small amount of contamination would be required to cause a measurable change in the observed luminescence, which was of very low intensity. The well known green luminescence under the Tesla discharge may also be an effect of surface contamination, since the luminescence of the pyrex in bulk (i.e. excited by γ -rays) appears to be predominantly in the violet and near U. V. The wave lengths of luminescence may, of course, be profoundly affected by traces of metallic elements in the pyrex.

The brown tint exhibited by the irradiated pyrex can - as is well known - be "annealed out" by holding the specimen at 400 - 500 °C for a few seconds. When this was done with the present samples, the strong absorption band disappeared, and the samples were found to luminesce with approximately their original intensity.

To the writers' knowledge no adequate theory of the effects of ionizing radiation on glasses has been published, probably because of the tentative state of present knowledge regarding the structure of glasses. A theoretical description of the above results will not be attempted, though it seems probable that the effects relate to the formation of colour-centres in the pyrex (109).

The results seemed to indicate the importance of using a single, freshly annealed pyrex cell for comparative measurements, and led to the design of the cell in Fig. 8.

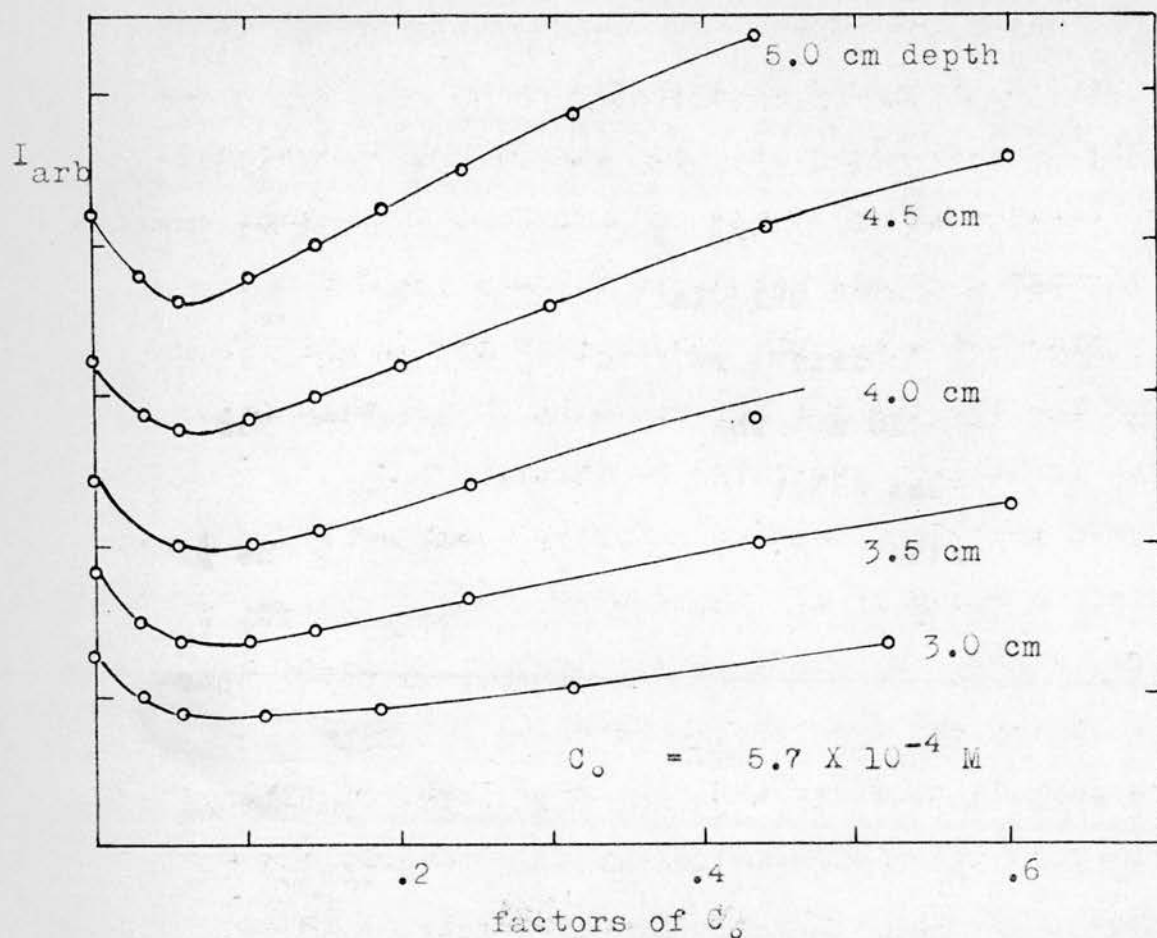


Fig. 11. The fluorescence observed through a Chance OV1 glass filter plotted as a function of the anthracene concentration for five different depths of solution. The P M - filter combination had a maximum response at 380 mu and 50% of maximum response at 360 and 410 mu. The fluorescence was excited with a 200 uc source of ^{60}Co γ -rays.

1b. Fluorescence of the Solutions:

Fig. 11 shows the results of fluorescence measurements made with the experimental arrangement shown in Fig. 7a and the variable concentration cell in Fig. 8. The fluorescence emitted by de-aerated solutions of anthracene in hexane was observed through a Chance OV1 glass filter. The P M - filter combination had a maximum response at 380 $m\mu$ and 50 % response at 360 and 410 $m\mu$. The solution in the cell was prepared by techniques described in Chapter I, 2.

The most important feature of these results is the pronounced minimum shown by all the curves of $I_{arb.}$ vs xC_0 . A second feature is the shift of the minimum to lower concentrations as the depth of the solution is increased.

These effects together indicate that light is emitted by the system at very low concentrations of anthracene at wave lengths which are absorbed by anthracene. It is impossible to say whether the light seen by the photocathode as $xC_0 \rightarrow 0$ was emitted by the pure hexane. The measured emission may have been the luminescence of the glass excited by primary hexane fluorescence. The primary emission may have been merely that part of the Čerenkov radiation to which the hexane was transparent. This view is favoured by later considerations. Whatever the source of the primary emission, the results shown in Fig. 11 indicate that the initial decrease in the light intensity with increasing anthracene concentration is the result of an inner absorp-

tion (compare Krenz (134)). The experimental curves are therefore the resultant of a) the decrease in the intensity of a primary component which is absorbed by anthracene and b) the increase in intensity of a second component with increasing anthracene concentration. It has been demonstrated spectrographically (51,60) and with filters (L02) that the second component is the characteristic anthracene fluorescence.

Measurements similar to those above, but using the Chance OB10 filter which transmits only the anthracene component of the fluorescence, gave curves which when normalised with those of Fig. 11 at C_0 , coincided with them down to a concentration of $0.2C_0$, thus showing that the u.v. component of the emission was completely absorbed at concentrations of the order of 10^{-4} M p l. Reference to Fig. 1 in the Introduction will show that the maximum fluorescence intensity is reached at a concentration of ca 10^{-3} M p l of anthracene. The intensity is then roughly ten times the intensity at 10^{-4} M p l. Thus while photon transfer does play a part in producing indirectly excited anthracene (B2) the proportion of excited molecules arising from photon transfer is roughly a tenth of the total number at concentrations of anthracene of the order used in solution scintillators. Later considerations will show the intensity of the primary emission is of the correct magnitude for Čerenkov radiation. Hence in hexane even the proportion of in-

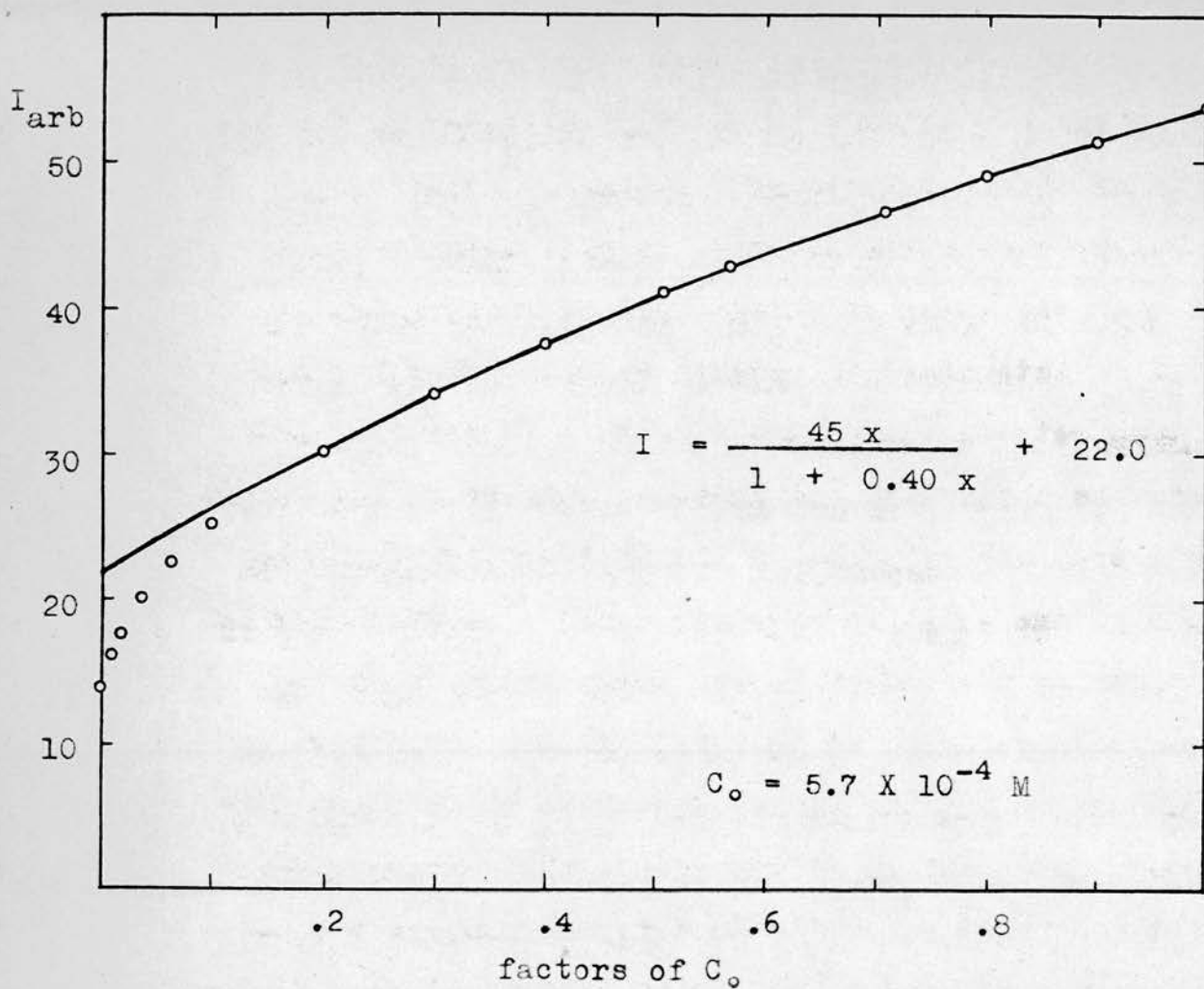


Fig. 12. Fluorescence observed through Chance OV1+OB2 filters plotted as a function of the anthracene concentration. The curve through the points is given by the empirical expression for I above in which x is the coefficient of C_0 .

direct excitation that does occur 'optically' probably does not occur precisely in the way suggested by the proponents of the photon transfer mechanism (B2,7).

Before proceeding further, it will again be emphasised that the shape of curves such as those shown in Fig. 11 is determined in general by rather complex relationships between the volume (depth) of solution observed, the absorption and emission spectra of the solute and the spectral response of the photomultiplier. When changes in the emission spectrum occur - particularly if they occur in a spectral region where the spectral response characteristic is changing rapidly - inflections or even maxima and minima may appear in the plot of fluorescence intensity vs solute concentration. These bear very little relation to the fundamental processes of indirect excitation and fluorescence quenching which occur in solution.

Fig. 12 shows the results of measurements with 5 cm depth of solution using a filter combination (OV1 + OB2) chosen to give a maximum response at wave lengths about midway between the 0-0 and 0-1 fluorescence bands of anthracene in hexane (See Fig. 6). The P M - filter combination had approximately equal response to either band, and was therefore insensitive to variations in the relative intensities of the two bands. While this combination greatly improved the ratio of anthracene emission

to background emission, it did not cut out the latter entirely, and some light was transmitted by the filters even when the anthracene concentration became vanishingly small. The anthracene fluorescence was measured above this background.

The experimental points in Fig. 12 show that with increasing anthracene concentration the intensity of the anthracene fluorescence increases in a way which suggests that two distinct modes of excitation were operative, one causing a rapid rise of intensity with concentration in the range between 0 and $.2C_0$, and a second causing a more gradual rise of intensity with concentration over the entire range studied. The first mode can almost certainly be identified with optical excitation, which was discussed in relation to the results of Fig. 11. The second mode accounts for the major part of the experimental curve, and is the chief process of interest in this study.

The experimental points between $.2C_0$ and C_0 lie on a curve which is accurately described by the empirical expression

$$I = \frac{45 x}{1 + .40 x} + 22.0 \quad (I.)$$

in which x is the coefficient of C_0 . Both the background luminescence and the contribution of optical excitation to the anthracene fluorescence are included in the second term on the right hand side of expression I. No

attempt has been made to fit the empirical expression to the relatively unimportant part of the experimental curve below $.2C_0$.

Expression I. is similar to expressions derived by Kallmann and Furst (59) Reynolds (101) and Buck and Swank (122) and was, in fact, suggested by this earlier work. The fit to the experimental points between $.2C_0$ and C_0 is sensitive to a 5% variation in the coefficient of x in the denominator, and somewhat less sensitive to the coefficient in the numerator. In the next section the former quantity will be related to k' , the coefficient of energy transfer in liquid hexane.

2. k' , the Coefficient of Energy Transfer:

The considerations leading to the definition of k' below are largely derived from the theoretical section of a paper by Kallmann and Furst (59). For the sake of clarity the development is given in greater detail here.

If we consider a quantity of liquid hexane absorbing energy from $\sqrt{\text{-}}$ rays at an average rate of R ev/cc/sec, then electronically excited molecules of hexane are formed at a rate

$$N_H = R / E \quad \text{molecules/cc/sec}$$

where E is the average energy (in ev) expended for each hexane molecule excited. The probable magnitude of E will be considered later in this study. No distinction is made

for the present between molecules which are ionised (one or more electrons removed to ∞) and those which are electronically excited (one or more electrons raised to higher energy levels). The ions are transformed into excited molecules upon electron capture and charge neutralisation, a process occurring within ca 10^{-13} sec (132a).

In solutions of anthracene some excited hexane may transfer energy to anthracene. The singlet excited anthracene molecules so produced emit, in returning to the singlet ground state, the characteristic fluorescence which is observed. Owing to the low concentration of anthracene present even in a saturated solution (ca 5×10^{-3} Mpl) the proportion of the anthracene molecules directly excited by the radiation is negligible. The probability that an excited hexane molecule transfers energy to a molecule of anthracene depends on the concentration of anthracene in solution. As an approximation, we assume that the dependence is first order, i.e. that the probability of a transfer to anthracene, p_t , is given by

$$p_t = k C$$

where C is the concentration of anthracene, and k is the probability of transfer at unit concentration. The fraction, f , of excitation energy transferred to anthracene is

$$f = \frac{p_t}{\sum_j p_j} = \frac{k C}{\sum_j p_j}$$

where $\sum_j p_j$ is the sum of probabilities for each mode

of energy dissipation by which the excited hexane molecule may lose energy, including that of transfer to anthracene. \underline{f} can also be written

$$f = \frac{k C}{\sum_i p_i + k C} = \frac{k' C}{1 + k' C}$$

where \underline{k}' is the ratio of \underline{k} to $\sum_i p_i$. The constant, \underline{k}' , thus defined is the coefficient of energy transfer, and is the ratio of the probability of transfer at unit concentration to the probability that the energy of the excited hexane is dissipated in some other way. The actual mechanism of transfer is, of course, not specified. The mechanism will be considered later under Discussion.

To relate \underline{k}' to the data of Fig. 12 in the preceding section we must consider that the number, \underline{N}_A , of excited anthracene molecules formed per cc per second is

$$\underline{N}_A = \underline{N}_H \frac{k' C}{1 + k' C} = R/E \frac{k' C}{1 + k' C}$$

The number, \underline{N}_F , actually fluorescent is determined by the fluorescence efficiency of anthracene in hexane. In oxygen-free solutions this is given by

$$F = \frac{k_1}{1 + k_2 C} \quad \text{Ref(21).}$$

\underline{F} is the fluorescence efficiency. \underline{k}_1 and \underline{k}_2 are constants. In hexane $k_1 = 0.23$; $k_2 = 90 \text{ Mpl}^{-1}$.

The number of anthracene molecules actually fluorescing is thus

$$N_F = R/E \frac{0.23 k'C}{(1+k'C)(1+90C)} \text{ molecules/cc/sec.}$$

In a well designed experiment the measured intensity of fluorescence is proportional to N_F over a range of C . For the reasons discussed in section 1. this proportionality is usually only approximate. In the measurements in Fig. 12 the proportionality probably holds to within $\pm 5\%$. Although the filter combination used made the measurements independent of the relative intensities of the 0-0 and 0-1 fluorescence bands, no account was taken of the intensity lost due to self-absorption (pp 55 and 61). It was estimated that the loss might amount to 5% at the highest concentration. Within $\pm 5\%$ the measured intensity of fluorescence, $I_{arb.}$, may be equated to αN_F , where α is a constant of proportionality determined by the experimental arrangement.

$$\begin{aligned} I_{arb} &= \alpha R/E \frac{0.23 k'C}{(1+k'C)(1+90C)} \\ &= \frac{B C}{1 + (k'+90)C + 90k'C^2} \quad (R \text{ const.}) \end{aligned}$$

Neglecting terms in C^2 in comparison with terms in C , and adding a constant, B , for background, etc.,

$$I_{arb} = \frac{B C}{1 + (k'+90) C} + B \quad \text{II.}$$

A comparison between expression II. above and expression I. in the preceding section shows that

$$(k'+90) C = 0.40 x ;$$

or since $C = x C_0$, and $C_0 = 5.7 \times 10^{-4}$ Mpl,

$$\underline{k'} = \underline{610 \pm 60} \text{ (Mpl)}^{-1}$$

The error of $\pm 10\%$ is the sum of the uncertainty involved in the fit of expression I. to the experimental points ($\pm 5\%$) and the probable error in equating I_{arb} to αN_F . Since a small part of the curvature in Fig. 12 was caused by loss of intensity through self-absorption, $\underline{k'}$ is probably slightly too high rather than too low.

$\underline{k'}$ for a solution of anthracene in xylene can similarly be calculated from the published data of Kallmann and Furst (59). The calculation is very approximate, for only the data at low concentrations can be used, and here the determinations are neither numerous nor accurate, particularly as no effort was made to separate the anthracene fluorescence from the luminescence of the solvent. The value of $\underline{k'}$ thus found for xylene is

$$k' \sim 700 \text{ (Mpl)}^{-1}$$

Using the same set of data Reynolds (101) has calculated both $\underline{k'}$ and \underline{k}_2 , the self-quenching constant, for anthracene in xylene. He finds that

$$k' = k_2 = 0.77 \text{ (gpl)}^{-1} \text{ or } 138 \text{ (Mpl)}^{-1}$$

The values of $\underline{k'}$ and \underline{k} are interdependent in this calcu-

lation, and it appears that in order to fit the experimental data at the higher concentrations (where the data are undoubtedly invalidated by self-absorption) a value of \underline{k}_2 was chosen which must be several times too large. It is unlikely that \underline{k}_2 in xylene is greatly different from \underline{k}_2 in benzene, which was found by Bowen and Norton (21) to be 25 (Mpl)^{-1} . Thus \underline{k}' should be roughly five times as large as the quantity calculated by Reynolds, i.e. ca 700 (Mpl)^{-1} , a value which is in agreement with those given above.

The discrepancy between \underline{k}' for anthracene in xylene and \underline{k}' for anthracene in hexane is hardly significant in view of some of the very approximate calculations involved. It is interesting, however, that similar calculations using Kallmann and Furst's data for terphenyl (p-diphenylbenzene) in xylene lead to a much larger value of \underline{k}' for this system, $k' = 10^3$. Here the error due to self-absorption cannot be very large, even at concentrations in the neighborhood of 1 Gpl, since there is very little overlap between the absorption and fluorescence spectra of terphenyl (14). Hence the result is probably significant, and indicates that the solute rather than the solvent determines the magnitude of \underline{k}' , i.e. the efficiency with which energy is transferred in solution. This point will be considered again in a later section.

3. G_t , the Absolute Efficiency of Energy Transfer:

The estimate of G_t , the absolute transfer efficiency, requires a knowledge of ϕ , the absolute scintillation efficiency of the solution for γ -rays, and of F , the absolute fluorescence efficiency of anthracene in hexane. F has been calculated from the data of Bowen and Norton (21) in an earlier section (p. 7, et seq.). In this section we shall estimate the magnitude of G_t from published data relating to scintillation efficiencies. While the precision obtained will not be great (i.e. $\pm 25\%$), it will suffice for the present purpose.

No measurement of the absolute scintillation efficiency of a solution scintillator has been reported in the literature. It has been the general practice to measure the luminescence of the solutions with reference to a standard, usually a single crystal of anthracene, placed in the same flux of ionizing radiation. Thus Kallmann and Furst (59) report that the luminescence of a solution containing 1 Gpl of anthracene in hexane is 0.016 relative to that of an anthracene crystal of equal mass, exposed to the same flux of γ -radiation (Chap. I, Sec 1). The absolute scintillation efficiency of the solution can therefore be estimated in relation to the absolute scintillation efficiency of anthracene. Several estimates of this latter quantity are to be found in the literature. Table 4. lists those for which some of the details of the measurements are given.

Table 4.

The absolute scintillation efficiency, ϕ ,
of crystalline anthracene:

Radiation	ϕ , photons/100ev	Authors
e's 15-25 Kev	1.7	Ramler and Friedmann (99)
" 5.3 Mev	1.4	Birks and Szendrei (14)
γ 's 1.2 Mev (ave)	3	Furst, Kallmann and Kramer (46)

A brief consideration of the values compared above may illustrate the difficulties involved in the measurements of the absolute scintillation efficiency. Ramler and Friedmann have made an accurate measurement of the energy absorbed by a crystal of anthracene exposed to a known flux of monokinetic electrons, but their value of ϕ above relies upon an assumed value of light collection and photocathode efficiency. Birks and Szendrei have made an accurate measurement of the absolute scintillation efficiency of anthracene for 5.3 Mev α -particles, but the value for 5.3 Mev electrons depends upon a determination by Hopkins (133a) of the relative efficiencies of 5.3 Mev electrons and α -particles. This latter determination is in some doubt because of the different distribution of light emitting centres in the crystal for the different types of excitation. Furst et al have used an ingenious method to determine the response of their photomultiplier to a light-source of known intensity emitting in approximately the same

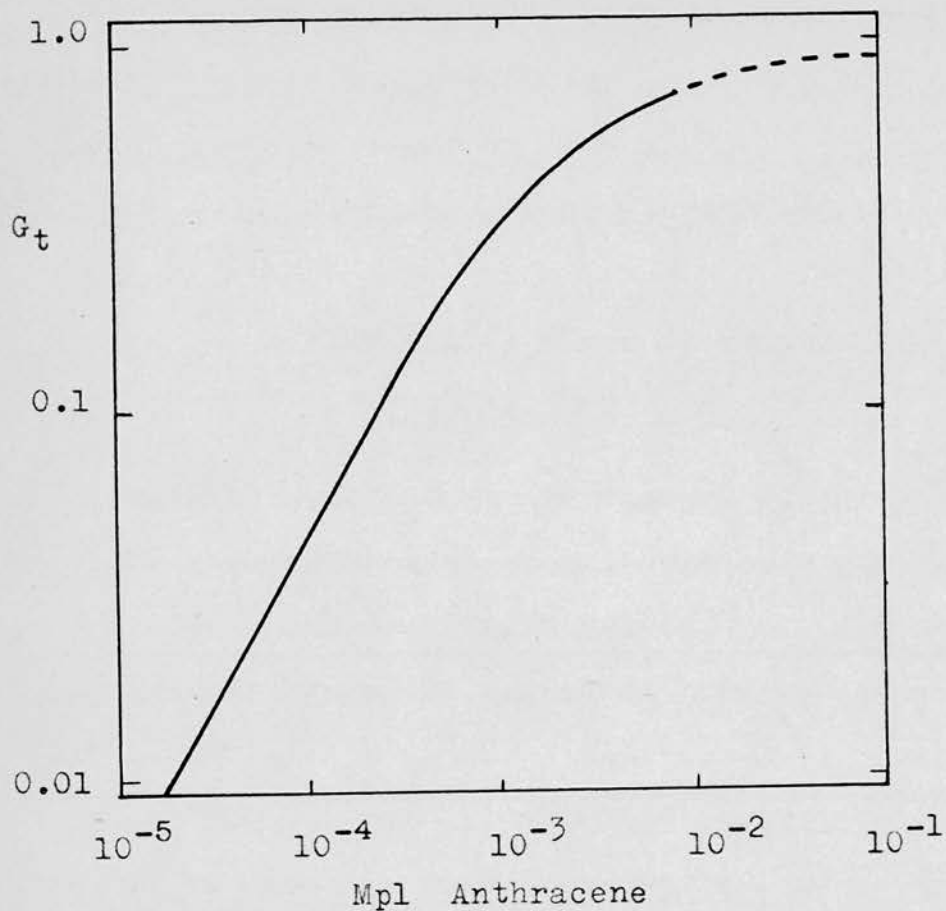


Fig. 13. A plot of G_t vs the anthracene concentration in hexane solutions. $k' = 610$ for this system. Saturation with respect to dissolved anthracene occurs at ca 6×10^{-3} Mpl.

spectral region as the anthracene fluorescence, but considerable uncertainty must be attached to their estimate of the γ -ray energy absorbed by the anthracene crystal used for the measurement of ϕ . In view of these uncertainties, the values of ϕ compared above are probably in fairly good agreement.

In this calculation we shall assume that

$$\phi = 2 \text{ phot./100ev .}$$

This value is probably correct to $\pm .5$, i.e. $\pm 25\%$. Recalling that the absolute fluorescence efficiency of crystalline anthracene is 0.9 and that there are 0.32 anthracene molecules excited in hexane for every anthracene molecule excited in the crystal (See p. 9) in the comparison made by Kallmann and Furst (59), then the number of anthracene molecules excited per 100 ev of γ -ray energy absorbed in a solution of the above concentration is:

$$G_t = \frac{2}{0.9} \times 0.32 = 0.71$$

G_t for any concentration of anthracene can be calculated from the value just found for 1 Gpl (5.6×10^{-3} Mpl) and f , the fraction of the available energy transferred to anthracene (See p. 65). Fig. 13 shows G_t plotted as a function of the anthracene concentration.

It is of considerable interest that G_t reaches a limit of 0.92 at a concentration of ca 10^{-1} Mpl. This situation

is purely hypothetical, since the solution becomes saturated with anthracene at a concentration of ca 6×10^{-3} Mpl, but it is of interest because it represents the concentration at which the energy transfer process would become "saturated". At 10^{-1} Mpl the mean separation between anthracene molecules in solution is approximately 25 Å. The energy transfer process therefore has a range of approximately 12 Å, or two molecular diameters.*

3a. The Nature of the Background Luminescence:

With G_t established absolutely, we may reconsider the nature of the background luminescence which became evident in very dilute solutions of anthracene in hexane. In what follows we shall refer to the intensity of the anthracene fluorescence which was 'optically' excited by this background radiation rather than intensity of background radiation measured by the P M, since the spectral distribution of the background radiation - and hence the response of the P M - was not known.

It has been noted above (p. 60) that the contribution of 'optically' excited molecules to the fluorescence at ca 10^{-3} Mpl was less than 10%. At this concentration G_t is 0.35 and F is 0.153 (p. 65). G for photon emission is therefore

$$G_{\text{emission}} = 0.35 \times 0.153 = 0.054 .$$

The mean energy of the fluorescence photons is about 3 ev.

* The molecular diameter of hexane is 6.7 Å, calculated for spherical close-packing of the liquid. That of anthracene is 3.3 Å (16).

The energy emitted as fluorescence is therefore roughly

$$\left(\frac{0.054}{100} \times 3 = 0.0016 \quad \text{or} \quad 0.16 \% \right)$$

0.16% of the total energy absorbed by the solution. That emitted by 'optically' excited anthracene is rather less than a tenth of this, i.e. $\sim 0.01\%$. At the concentration of anthracene at which all the background radiation was absorbed (ca 10^{-4} Mpl, p. 61) the fluorescence efficiency of anthracene is 0.23 (21); and hence the background emission must have corresponded to roughly 0.05% of the energy absorbed by the hexane. This is of the correct order for Čerenkov emission. Belcher (7) has calculated that in water approximately 0.02% of the energy of a 1 Mev electron totally absorbed is emitted as Čerenkov radiation between 3000 and 7000 Å. While this figure depends to some extent upon the index of refraction of the absorbing medium, it depends very markedly on the spectral limits defined, since the intensity of the Čerenkov emission varies inversely as the wavelength. It is estimated that in hexane ($n = 1.37 - 1.38$) between the limits of 1700 and 4000 Å the efficiency of Čerenkov emission is 0.1% of the energy of the 1 Mev electron. Since the mean energy of the Compton electrons traversing the solutions under consideration was less than 1 Mev, and since part of the background emission undoubtedly came from the Pyrex walls, a closer estimate and comparison cannot be made. It is concluded, however, that Čerenkov emission would account for the background.

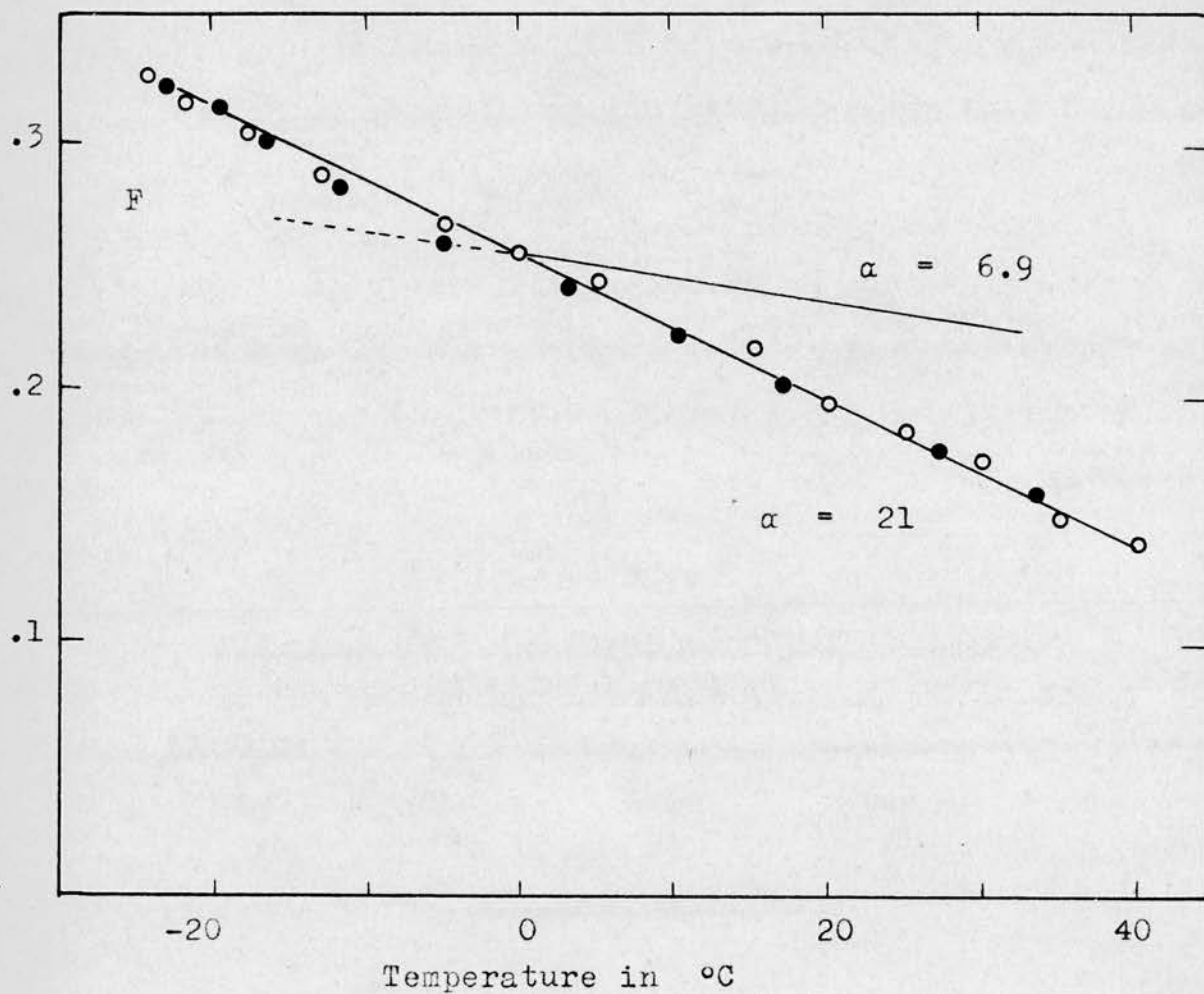


Fig. 14. Measurements of the intensity of γ -ray excited fluorescence in a 5×10^{-4} Mpl solution of anthracene in hexane as a function of the temperature. The straight lines are given by the expression (see opp.)

$$F = F_0 - 10^{-4} \alpha t.$$

The data are normalized for $F_0 = 0.26$ at $t = 0$ °C.

Filled circles represent measurements with a 'brown' cell, open circles measurements with a clear cell. See p.75.

4. The Temperature Coefficient of the Fluorescence:

Bowen and Cook (18) have measured the temperature coefficient of fluorescence of anthracene in several solvents, and find that their results fit the general equation:

$$F = F_0 - \alpha t \times 10^{-4}$$

in which F is the fluorescence efficiency at t °C, F_0 the fluorescence efficiency at 0 °C, and α is a constant, characteristic of the solvent. Several values of α are listed in the table below.

Table 5.

Values of α found by Bowen and Cook (18) for
A: Anthracene; B: 9,10-dichloroanthracene in

		Kerosene	CHCl ₃	C ₆ H ₆	CH ₃ COCH ₃
A:	$\alpha =$	6.9	-3.9	-3.1	2.45
B:	$\alpha =$	58	36	46	56

Some values of α for 9,10-dichloroanthracene are included above for comparison. Metcalfe* has shown that α for anthracene in hexane is approximately equal to α for anthracene in kerosene.

Fig. 14 shows some results of measurements of the ν -ray excited fluorescence of anthracene in hexane between -30 °C and +50 °C. The measurements were made on solutions containing $5 - 6 \times 10^{-4}$ Mpl anthracene, deaerated and sealed under vacuum by the techniques described in Chap. I, Sec. 2.

* Dr. E. J. Bowen, private communication. An error in the published form of the general equation (18) was also communicated.

The measurements were made with a modified version of the apparatus shown in Fig. 7b. A greatly enlarged cooling jacket was used, consisting of a cylindrical tin 4" in diameter by 8" high, mounted on a wooden base which fitted snugly into the aperture in the P M housing (W-W in Fig.7b). The measurements were made without a filter, since it was important to know to what extent a temperature dependent background luminescence (e.g. from the Pyrex) might affect the results. A slight negative temperature coefficient of background luminescence was in fact found, and the uncertainty which this introduced lead to an experiment with an irradiation cell which had been "browned" by a prolonged exposure to an intense source of γ -rays. This treatment greatly reduced the luminescence of the glass (Chap. II, Sec. 1a) and also rendered it completely opaque to the anthracene fluorescence. A transparent window was therefore made in the end of the cell nearest the P M by carefully annealing the glass in a small flame confined to this end of the cell. The solution was then made up in this cell in the usual way, the only other part which was annealed being a relatively small portion of glass at the end sealed-off from the still.

The results obtained with a "browned" cell are compared in Fig. 14 with results obtained with an annealed cell. The background luminescence of the glass has been subtracted from the latter measurements. Both sets of data can evidently be described by the general equation on p. 74, using

a value of 21 for α . The scatter of experimental points is considerably greater than in measurements at a single temperature. A possible explanation of this is that the temperatures recorded by the thermocouple were not uniform through the sample, and that a lack of reproducibility was caused by this. A more uniform temperature could probably have been obtained in a smaller sample, but at the cost of fluorescence intensity.

No correction has been applied to the results in Fig. 14 for the 3-4% change in the density of the solution over the temperature range studied. Likewise, no correction was made for the small contribution (< 5%) made to the results by self-quenching (p. 65). The combined effect of these corrections would be to diminish α by 10-15%. The value above should probably be reduced to ca 19, but in view of the rather large experimental errors the correction is of doubtful significance. A value of α two to three times as great as that found by Metcalfe (p. 74) for anthracene in hexane appears to be definitely established, however, and this difference in magnitude is possibly significant. In the measurements made by Metcalfe and by Bowen and Cook the anthracene fluorescence was excited by light absorbed only by the anthracene. The temperature coefficient therefore measures the effect of temperature on processes subsequent to excitation. In the present work both these processes and those occurring prior to excitation may be affected by the temperature, i.e. part of the temperature coefficient may relate to energy transfer.

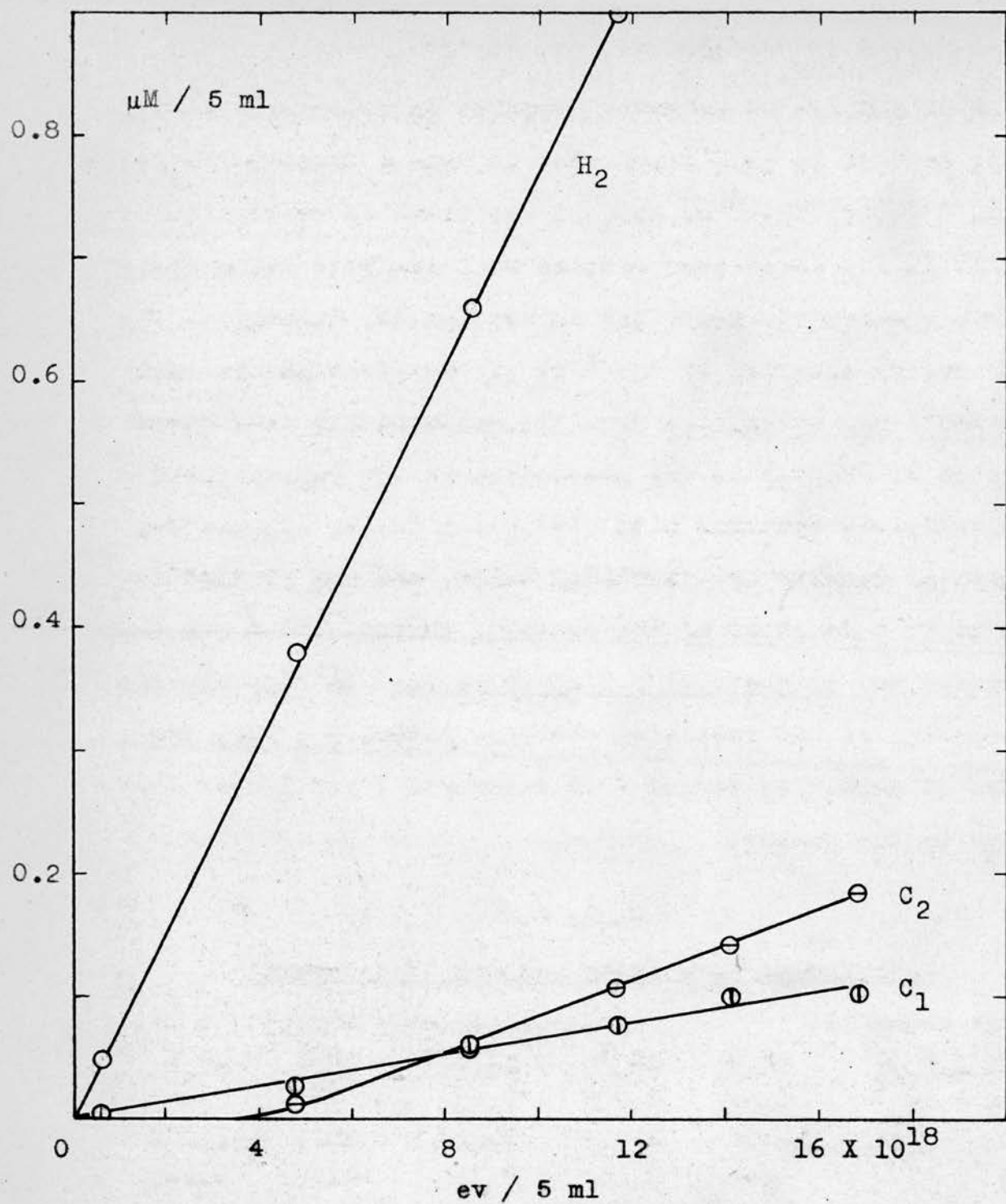


Fig. 15. A plot of the data for H₂, C₁ and C₂ in Table 6. opposite. The amounts of C₃ and C₄ hydrocarbons are too small to be plotted.

5. Radiolysis of n-hexane by ^{60}Co γ -rays:

5 ml samples of n-hexane prepared as described in Chapter I, section 2. were irradiated in Type A irradiation cells (Fig. 3) with the ^{60}Co sources described in section 1. of Chapter I. The irradiated samples were analyzed using the apparatus and methods described in section 3., Chapter I. The γ -ray energy absorbed by the 5 ml of liquid hexane in each experiment was calculated from the actinometric data given in Table I, Chapter I.* The absorption in the vapour phase was negligible compared with absorption in the liquid. The analytical results are tabulated below, and are plotted in Fig. 15 as a function of the absorbed energy, which has been expressed as ev absorbed / 5 ml of hexane to simplify the calculation of the radiation chemical yield, G , i.e. the number of molecules formed (or destroyed) per 100 ev absorbed by the hexane.

Table 6.

Analyses of irradiated samples of n-hexane:

Energy absorbed: <u>ev / 5 ml</u>	Gaseous products formed / 5 ml:				
	$\mu\text{M H}_2$	$\mu\text{M CH}_4$	$\mu\text{M C}_2\text{H}_6$	$\mu\text{M C}_3$	$\mu\text{M C}_4$
0.64×10^{18}	0.05	0.005	0.002	-	-
4.9	0.38	0.027	0.012	0.01	0.002
8.5	0.66	0.060	0.057	0.002	0.002
11.6	0.90	0.078	0.104	0.002	0.002
14.1	1.10	0.10	0.142	-	0.005
16.9	1.32	0.10	0.185	-	0.005

N_2 was less than $0.001 \mu\text{M} / 5 \text{ ml}$ in all samples.

* See, however, note at foot of Table I (p. 14).

Evidently H_2 is the chief gaseous decomposition product of the irradiation of liquid hexane. CH_4 and C_2H_6 are formed in relatively much smaller quantities, the latter being the only 'C₂' product. As discussed in section 3., Chapter I, C_2H_2 , C_2H_4 and unsaturated 'C₃' and 'C₄' hydrocarbons were sometimes found, but it was later established that these were formed from hexane vapour thermally decomposed on hot Pyrex when samples were sealed off without adequate precautions to cool the hexane to $-196^\circ C$.

The results above lead to the following values of \underline{G} for the products:

$G_{H_2} = 4.86$	$G_{CH_4} = 0.40$	$G_{C_2H_6} = 0.68$
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The yield of C_2H_6 was calculated from the slope of the curve for C_2H_6 in Fig. 15 after the induction period. The yields of the higher hydrocarbons are negligibly small, at least in the initial stages of the decomposition which are considered here.

In Table 7 below the values of \underline{G} just found are compared with values calculated from data in the literature. The comparison is made with reservations, since the published data are meagre and much of the work is semi-quantitative. The results from early work with Rn α -particles have the disadvantage that the primary decomposition was allowed to proceed to such an extent that secondary reactions must have contributed appreciably to the results. In this work and in the work with 170 KV electrons an un-

satisfactory feature of the results lies in the uncertainty which must be attached to the estimation of the absorbed energy (84). The value of G_{H_2} for 170 KV electrons in Table 7 is an assumed one, and the assumption implies that only 4% of the electron energy was dissipated in the hydrocarbon. Reference to Glockler and Lind (B 6, p.75) will show that the fraction of the energy available may have been of this order. Undoubtedly the most valid comparison is to be made between the present work and that of Forsyth, Weber and Schuler. Unfortunately, they report only the H_2 evolved.

Table 7.

Values of G for hydrocarbon radiolysis:

<u>Hydrocarbon:</u>	<u>Radiation:</u>	G_{H_2}	G_{CH_4}	$G_{C_2H_6}$	<u>Reference:</u>
n-C ₄ H ₁₀ gas	Rn α 's	4.1	0.73	0.77	Lind and Bardwell (72).
..	..	4.3	0.54	1.0	Honig and Sheppard (110).
..	8 Mev d's	5.5	0.32	1.5	..
n-C ₆ H ₁₄ liq.	170 KV e's	(4.7)	0.47	?	Schoepfle and Fellows (106).
n-C ₇ H ₁₆ liq.	⁶⁰ Co γ 's	5.4	?	?	Forsyth, Weber and Schuler (41).
..	.3Å X-rays	4.3	?	?	
n-C ₆ H ₁₄ liq.	⁶⁰ Co γ 's	4.86	0.40	0.68	This work.

The radiolysis of n-butane referred to in Table 7 yielded a relatively large amount of a liquid product of general composition C_nH_{2n} (110). A liquid of higher molecular weight was also found as the main product of the vapour phase radiolysis of n-hexane by Henri and coworkers (53).

This confirms the qualitative result established by earlier workers (B6,p.149) that radiolysis of the paraffin hydrocarbons leads to the formation of H_2 and a substance of higher molecular weight than the original hydrocarbon.

Lind and Bardwell found ' C_3 ', ' C_4 ' and ' C_5 ' hydrocarbons as well as the products listed in Table 7 from the radiolysis of CH_4 , C_2H_6 and C_3H_8 by Rn α -particles in the gas phase (excluding, of course, the appropriate parent hydrocarbon in each case). They noted the absence of unsaturation even among the gaseous products of higher molecular weight. Honig and Sheppard noted the same absence of unsaturation in the ' C_3 ' fraction from the radiolysis of $n-C_4H_{10}$, as did Schoepfle and Fellows for the gaseous products of the radiolysis of liquid n-hexane which were non-volatile at $-183^\circ C$. It should be mentioned, however, that Dr. R. A. Back, working in this laboratory with techniques more sensitive and reliable than those of the above workers, has found unsaturated products from the vapour phase decomposition of $n-C_5H_{12}$ by ^{210}Po α -particles.

The extent of the agreement among the values of \underline{G} listed in Table 7 is surprising considering the diversity of the sources from which the data were collected. It is evidence for the fundamental simplicity of the reactions involved, and supports the hypothesis that the mechanism of decomposition is independent of the state of aggregation

of the hydrocarbon molecules, at least as regards the products listed in Table 7.

An interesting parallel to the work just described is found in the very extensive studies of the mercury photosensitized decomposition of paraffin hydrocarbons in the gas phase (Steacie, BlO). For these reactions the primary step has been established as one involving the rupture of a C-H bond. The interaction between a hydrocarbon molecule, \underline{RH} , and a mercury atom excited to the $6(3P_1)$ level (2537 Å) may be represented as:



\underline{R}^\bullet and \underline{H}^\bullet represent respectively the free radical and the hydrogen atom resulting from the primary C-H rupture. These entities are highly unstable, since each has an unshared electron, and have a correspondingly short lifetime in the reaction. (i) above is followed immediately by



since \underline{RH} is always present in great excess. At room temperature the radicals disappear by reaction (iii).



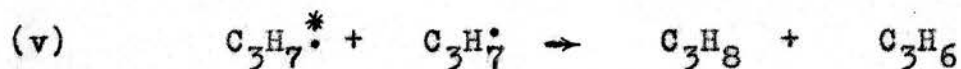
These reactions account for the experimental fact that the mercury photosensitized decomposition of the paraffin hydrocarbons yields, at moderate temperatures, only H_2 and the appropriate dimer (or polymer). Thus Hay and Winkler obtain from the mercury photosensitized decomposition of $n\text{-C}_4\text{H}_{10}$ at room temperature only H_2 and compounds with

carbon numbers 8 and 12 (52). The same result was found by Bywater and Steacie for n- and iso-C₄H₁₀ at temperatures up to 250 °C (24). At still higher temperatures CH₄, 'C₂' and 'C₃' hydrocarbons were found in amounts which increased with increasing temperature. This result corresponds to the thermal degradation of the radicals, \underline{R}^{\bullet} , before they can react by (iii) above. Bywater and Steacie have studied this phenomenon (24,25,26) and have assigned energies of activation to several of the steps of the thermal degradation. Those proceeding by C-C rupture require an energy of activation of 20 Kcal/mol (roughly 1 ev), while those involving a C-H rupture require approximately twice this energy.

Groth and Scharfe (49) have recently studied the direct photolysis of C₃H₈ in the gas phase by the Xe lines at 1470 and 1295 Å. They favour a primary step in the photolysis similar to (i) above, namely,



The propyl radical so formed may be in an electronically excited state. Groth and Scharf propose the following reaction to account for the formation of propylene in their experiments:



It is uncertain whether the extra electronic energy is required by (v), since reactions of this type, i.e. 'disproportionations', are known to occur in the liquid phase in the chain terminating steps of ordinary polymerizations (11).

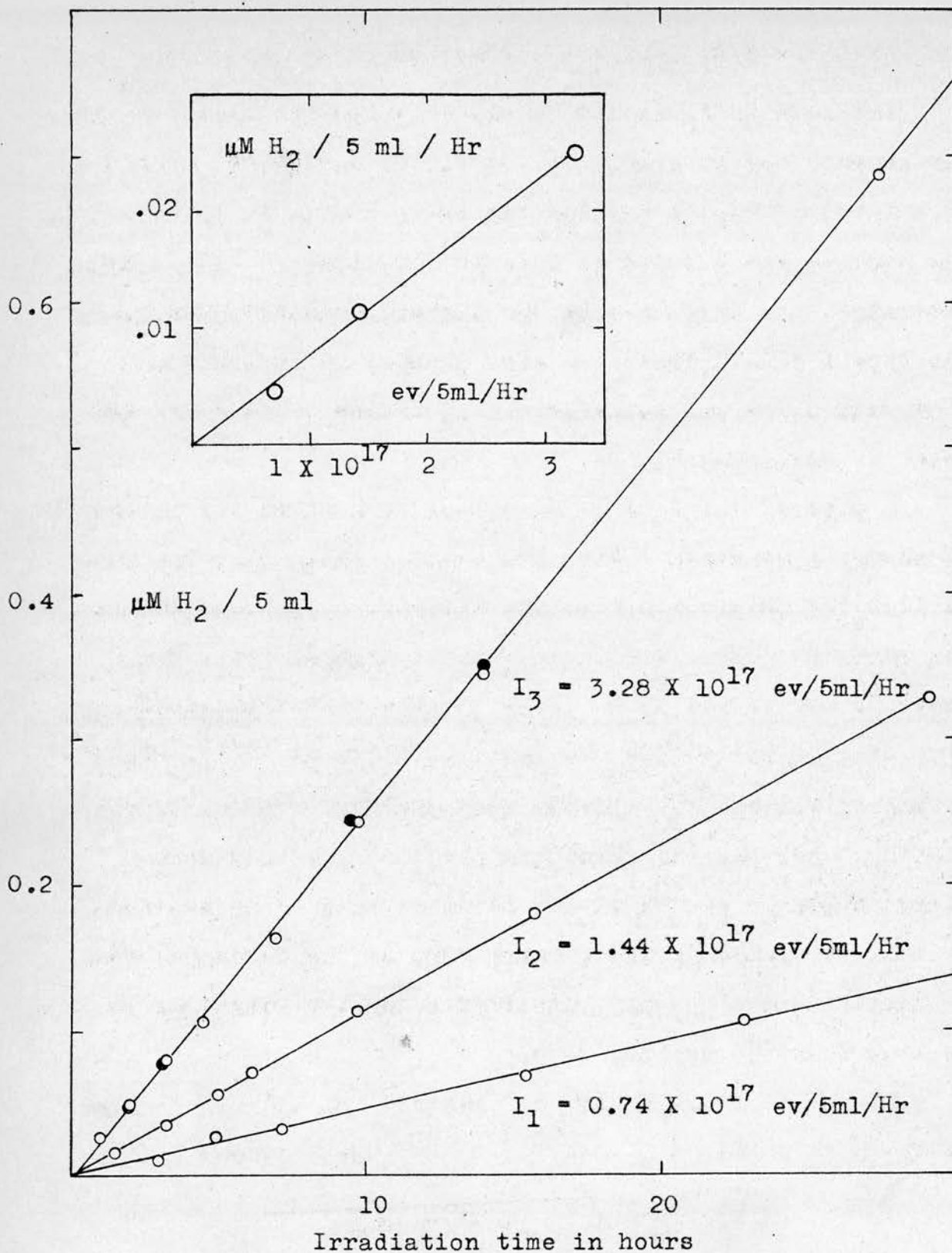


Fig. 16. Measurements of the rate of H₂ evolution from irradiated hexane at three different intensities of energy absorption. Open circles are from Type C cell measurements; filled circles from measurements with Type A cells (see Fig. 3).

5a. Radiolysis of n-hexane; Effect of γ -ray Intensity:

The rate of H_2 evolution was measured for three different intensities of energy absorption in samples of n-hexane irradiated in Type C irradiation cells (Fig. 3, Chapter I). The results are plotted in Fig. 16 opposite. Several single determinations were made at the highest intensity, using the Type A cells. These are also plotted in Fig. 16, and show that there was satisfactory agreement between the two types of measurements.

A plot of the rate of H_2 evolution against the intensity of energy absorption (Fig. 16, Inset) shows that the rate is directly proportional to the intensity, at least within the range of intensities shown in the figure. While this range is not large, it is ample to show that the dependence upon the intensity does not involve $I^{1/2}$ or $I^{3/2}$. This direct relationship, together with the fact that H_2 is the principal gaseous decomposition product, provides very strong support for the theory advanced in a later section, that H_2 is formed in the primary step of the decomposition of hexane, and not as a product of secondary reactions resulting from the primary step.

The plot of $\mu M H_2/5ml/Hr$ against $ev/5ml/Hr$ yields as the mean value of G_{H_2} for the three kinetic runs:

$$G_{H_2} = 4.78 \pm 0.26$$

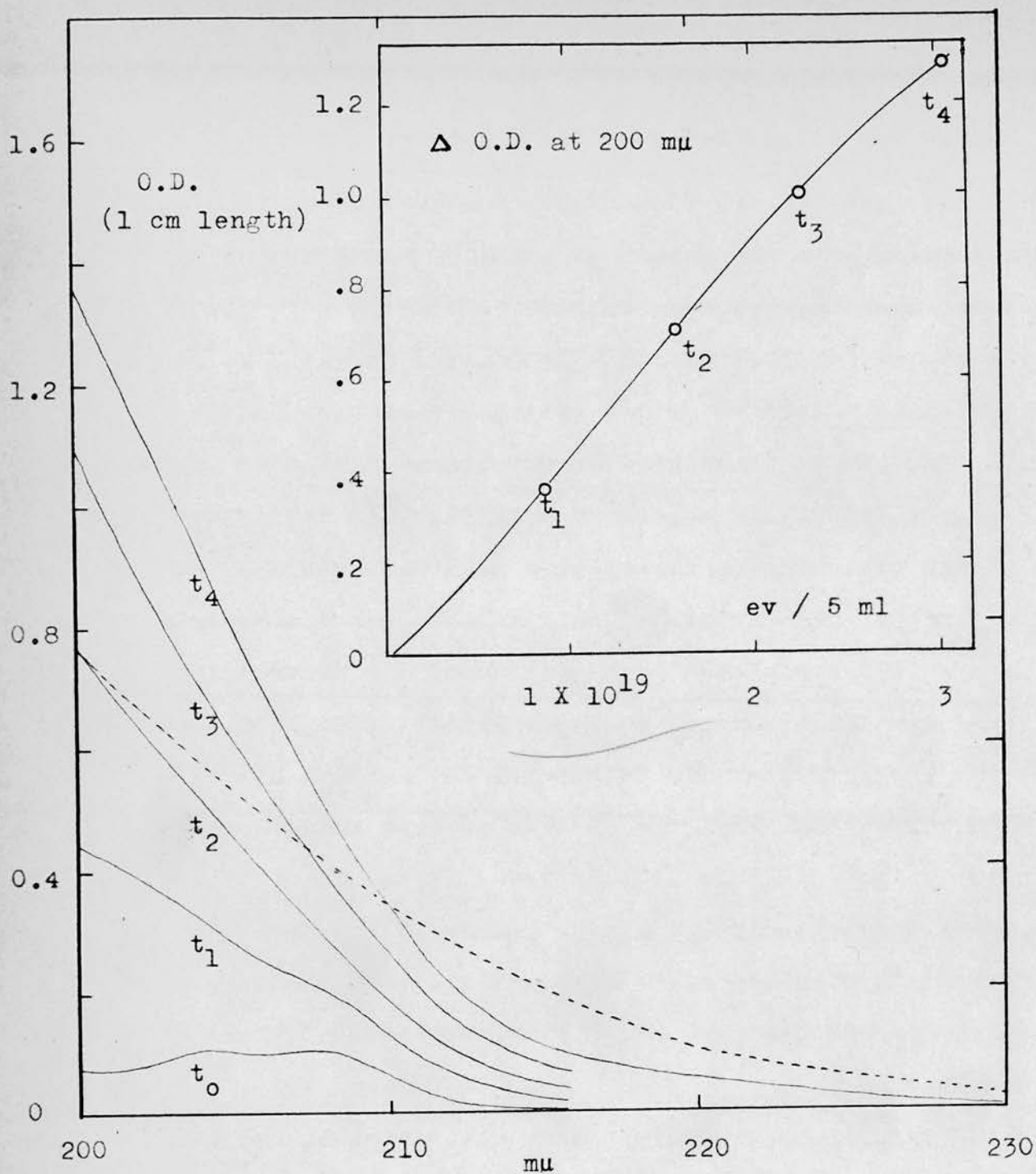


Fig. 17. The effect irradiation with ^{60}Co γ -rays on the absorption spectrum of n-hexane in the far U.V. The optical density (O.D.) is plotted against the wavelength. $t_0 \dots t_4$ refer to increasing total irradiation time. A plot is also shown (Inset) of the change in O.D. at 200 μ as a function of the energy absorbed in $\text{ev}/5\text{ml}$. The irradiation was performed in vacuum using a Type B cell (Fig. 3). aerated hexane.

5b. Radiolysis of n-hexane: Liquid Products:

It was expected, in view of the findings of earlier investigations of the radiolysis of paraffin hydrocarbons in the vapour phase (B7,72,73), that in addition to the gaseous decomposition products from irradiated hexane a polymeric substance would be found, probably dissolved in the liquid. Samples of irradiated hexane did in fact show traces of a material of higher molecular weight, which was deposited on the walls of the irradiation cell upon evaporation of the hexane. The amounts of this material were extremely small, even after prolonged irradiation at the highest intensities available, and an analysis did not seem possible. Moreover, it was preferable to examine the initial stages of the decomposition when the amounts of this product would certainly be too small to be detected. It was found, however, that the transmission of the hexane in the far U.V. was appreciably diminished by irradiation, even after relatively moderate periods, and a study was made of this phenomenon.

Samples of n-hexane were sealed under vacuum in Type B and Type D irradiation cells (Figs. 3 and 9, Chapter I) using techniques described in Section 2 of Chapter I. The absorption measurements were made with the Unicam SP500 spectrophotometer. The results of a typical run are shown in Fig. 17 opposite. The transmission of the sample was

measured relative to air, and was corrected for the reduction in transmission caused by the cell alone. As a matter of interest, it was found that aerated hexane had a much lower transmission in the far U.V. than did hexane sealed under vacuum. This fact undoubtedly accounts for the transmission limit found in the region of 210 μ by Pirlet (88) for the purest hexane which he could prepare.

The absorption spectrum of the deaerated hexane at to in Fig. 17 is probably caused by an unsaturated impurity, possibly hexadiene (91). The partially resolved peaks have a separation of ca 1100 cm^{-1} , which corresponds roughly to a vibrational frequency of the conjugated double bond (94). It is estimated that the concentration of the impurity was roughly $5 \times 10^{-5} \text{ M}$ (compare p.40-41).

The change in the absorption spectrum of hexane caused by irradiation can be attributed to the development of an absorption peak to the short wave side of 200 μ . There is no change in the transmission limit which might correspond to the formation of paraffin hydrocarbons of greater complexity than hexane, the so-called " red-shift " of Klevens and Platt (63). A strong band in the region of 190 μ is, however, characteristic of a number of isomeric hexenes (27,63,113,). The molar extinction coefficients of these compounds at 200 μ vary between 10^3 and 3×10^4 on a decadic scale (27,28,113). Of these, the extinction coefficients of the n-hexenes and of cyclohexene range from

10^3 to 4×10^3 at 200 μ (27,113). These coefficients were determined for solutions in n-heptane.

Tests made with the Type D irradiation cell in which the products of the irradiation could be distilled into the arm carrying the absorption cell as well as transferred directly into it showed that the substance causing the absorption at 200 μ could be separated into a large fraction possessing the same volatility as n-hexane and a much smaller fraction of somewhat lower volatility. If it is assumed that the products were chiefly isomeric n-hexenes with an effective extinction coefficient of 2×10^3 , it is then possible to calculate from the change in optical density (Fig. 17, Inset) the quantity of unsaturated compounds formed, and from this in turn a value for $G_{C=C}$, the number of molecules of unsaturated compounds formed per 100 ev absorbed in the hexane. This is:

$$G_{C=C} = 6$$

$G_{C=C}$ thus determined is in reasonable agreement with the yields of the other products, particularly that of H_2 . Fig. 17, Inset also shows that the unsaturated compounds were formed in amounts proportional to the absorbed energy, at least in the initial stages of the decomposition.

An attempt was made to determine the concentration of unsaturated compounds in irradiated hexane using as a reagent a 5×10^{-3} M solution of iodine in n-hexane. This has a broad absorption band whose maximum is at 524 μ .

The molar extinction coefficient was found to be slightly dependent upon the concentration of I_2 between 10^{-4} Mpl and 10^{-3} Mpl. The average value of the extinction coefficient at 524 $m\mu$ was $760 \text{ Mpl}^{-1}\text{cm}^{-1}$. The absorption was therefore adequate for spectrophotometric analyses with a precision of $\pm 2\%$ in the range of concentrations referred to above.

It was estimated that the concentration of unsaturated compounds in irradiated hexane would be $\sim 5 \times 10^{-4}$ Mpl when the optical density was 1.0 at 200 $m\mu$. An addition of 1 part of iodine reagent to 6 parts the irradiated hexane should yield a solution whose I_2 concentration was $\sim 50\%$ lower than in a solution made in the same proportions with unirradiated hexane, provided the I_2 reacted quantitatively with the unsaturated C=C linkages. It was in fact found that no difference could be detected between the dilution with ordinary hexane and that with hexane in which the concentration of unsaturated compounds was estimated to be about 4×10^{-4} Mpl, and with a second sample in which the concentration was estimated to be 6×10^{-4} Mpl.

These tests were supplemented by some tests with hexane irradiated with a 100 c ^{60}Co source which became available toward the end of this research. Negative results were again found, though the energies absorbed were ten times greater. A possible explanation for these results is considered in the theoretical discussion in Chapter III.

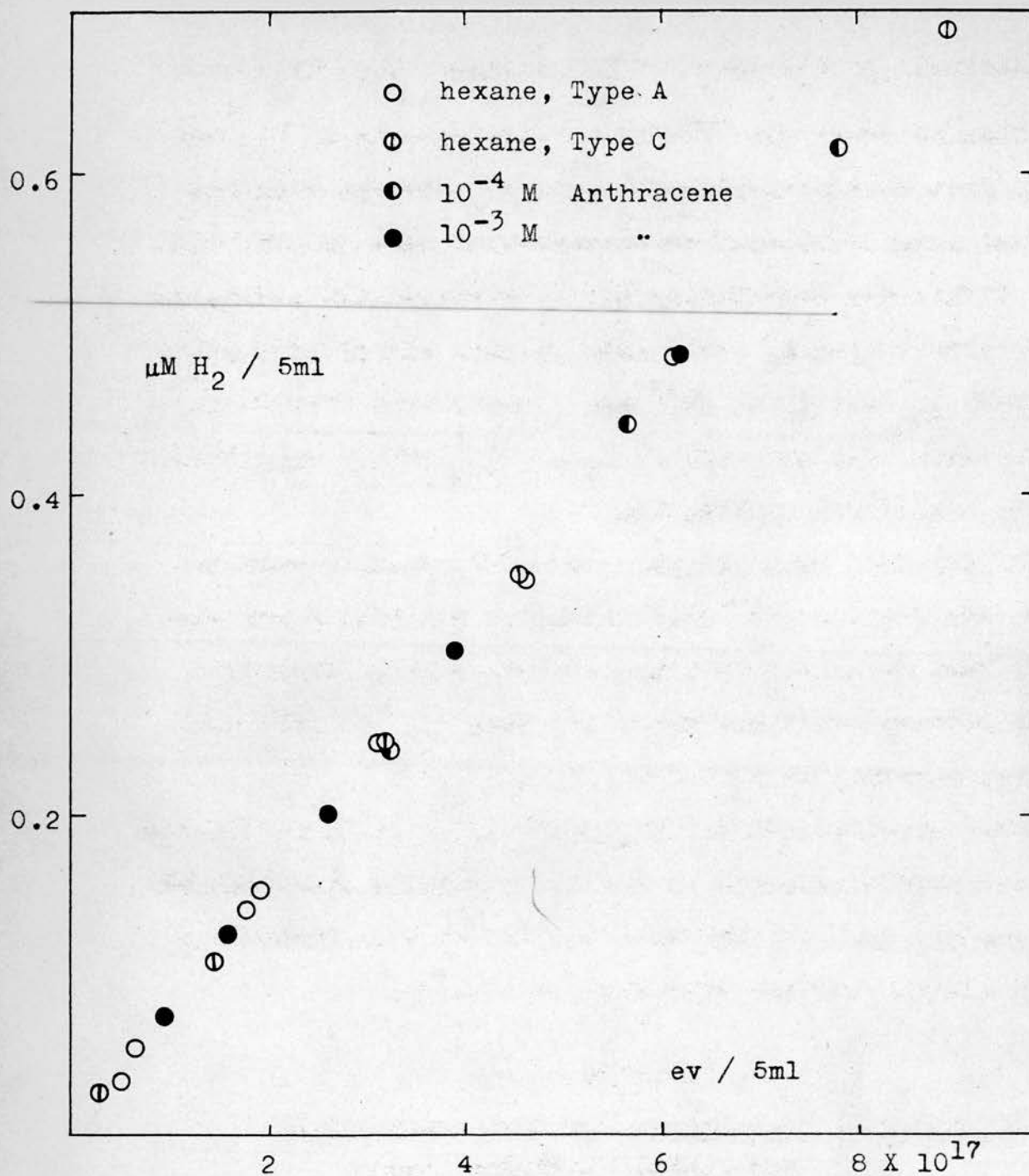


Fig. 18. H₂ evolution from pure hexane and from solutions of anthracene in hexane. Both Type A and Type C measurements are shown for hexane. Measurements for 10⁻⁴ M anthracene were made with Type A cells; for 10⁻³ M with a Type C cell.

6. Radiolysis of Solutions of Anthracene: Gas Evolution:

Fig. 18 shows the results of measurements of H_2 evolution from solutions of anthracene in n-hexane compared with the results of similar measurements made on pure hexane. Within the sensitivity of the measurements anthracene has no effect upon H_2 evolution. A real effect of 5 - 10% (compare G_{H_2} and G_t at 10^{-3} Mpl) would have been detectable between 0.6 and 0.3 $\mu M H_2$. $G_{H_2}(\text{ave}) = 4.84 \pm 0.16$ for the runs shown in Fig. 18.

This result lends support to the contention made by Burton and Patrick (23) that dissolved anthracene and terphenyl have no effect upon the evolution of H_2 from benzene irradiated with 1.5 Mev electrons. G_{H_2} in pure benzene is, however, only 0.036 (23).

Some measurements of CH_4 and C_2H_6 found in samples of irradiated hexane and of hexane containing dissolved anthracene are compared in Table 8., and show an absence of effect similar to that discussed just above.

Table 8.

CH_4 and C_2H_6 from hexane and from solutions of anthracene in hexane:

		pure hexane	5×10^{-4} Mpl A
G_{CH_4}	0.41 ± 0.1	0.44 ± 0.1
$G_{C_2H_6}$	0.69 ± 0.1	0.57 ± 0.1

G (solutions) average of three measurements.

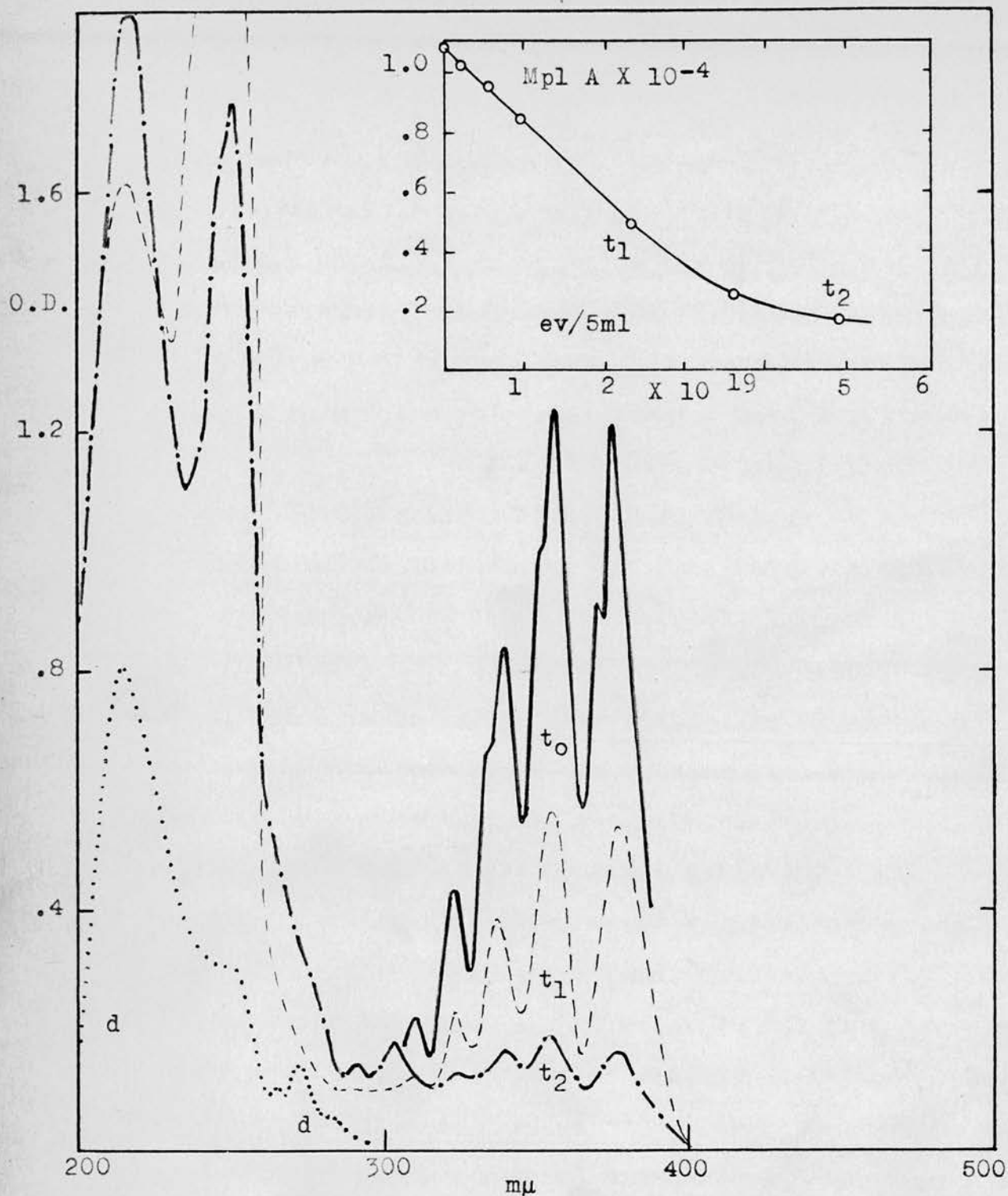
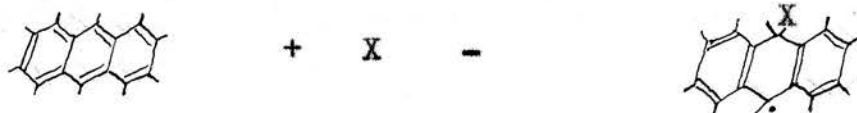


Fig. 19. The effect of γ -radiation on the A-spectrum of anthracene in n-hexane. The optical density (O. D.) measured in a 1 cm cell (Type B, Fig. 3) is plotted against the wavelength in μ for different irradiation periods, t_1 . The concentration is also plotted as a function of the total absorbed energy (Inset) using $\epsilon_{355.5} = 11,800$.
 d.....d is the A-spectrum of dianthracene (Weiss).

6a. Radiolysis of Solutions of Anthracene: Effect on Solute:

The radiolysis of solutions of anthracene was also effected in irradiation cells of Types B and D, and the A-spectrum of the solution was measured at different times during the irradiation. It was found that the characteristic spectrum of anthracene in hexane gradually diminished in intensity during the irradiation. The results of a series of measurements are shown in Fig. 19.

Since the A-spectrum in the region between 300 and 400 m μ is characteristic of the triple-ring system of anthracene, its gradual disappearance must be the result of the gradual destruction of the characteristic anthracene conjugation. It is well known that carbon atoms 9 and 10 of anthracene are most susceptible to attack by chemical reagents. The 9, 10 carbons play the part of a typical diene in the Diels and Alder reaction with phthalic anhydride (35). Anthracene readily forms metallic aryls with sodium, potassium, etc., in which these metals are bound to the 9 and 10 carbons of the molecule (76). The reactivity of anthracene toward methyl free radicals (69) may be assumed to be a property of the 9, 10 carbons. With the exception of the formation of metallic aryls, the reactions above lead to a destruction of the characteristic anthracene conjugation. This effect is, in fact, limited to "addition" reactions, as shown schematically below;



except, of course, when the attack upon the anthracene molecule results in an actual destruction of the ring system and rupture into fragments. To add to anthracene in the manner shown above X must be able to supply an unpaired bonding electron. The resulting compound is unstable, since an electron remains unshared among the remaining carbon atoms. In the scheme above it is shown as a dot at the 10 carbon atom, but could equally be assigned to the 11 or 12 carbon atoms on either side of 9. To achieve stability the compound may a) react with another part of X, as in the diene reaction, b) add a second X at the 10, 11 or 12 carbon atom, most probably the 10, c) react with a second molecule of unstable compound to form a stable dimer.

All of the processes considered above result in stable products in which the altered configuration of the central ring effectively isolates the two outer rings with respect to participation in the electronic resonance characteristic of anthracene, and the products therefore do not have the characteristic anthracene absorption spectrum. Thus 9,10-dihydroanthracene shows only the spectrum of the two isolated benzene rings (B5, p.114). Dianthracene is another such compound, and would be formed by alternative a) above if X represents a second anthracene molecule. The absorption spectrum of dianthracene is also shown in Fig. 19. The spectrum was measured by Weiss and coworkers, and was very kindly supplied by Dr. Weiss.

The decadic molar extinction coefficient of dianthracene at 217 μ is 21,500 (Weiss). Assuming that the unknown absorption peak is that of dianthracene, we calculate that a diminution of 3.2×10^{-5} Mpl of anthracene between t_1 and t_2 is accompanied by a rise of 1.3×10^{-5} Mpl of dianthracene. While this calculation involves some rather arbitrary corrections for the very intense anthracene absorption at 252 μ and the background caused by this in the neighborhood of 217 μ , it shows that the respective concentration changes are of the correct magnitude to account for the disappearance of anthracene by dimerization.

It is well known that the photolysis of anthracene in inert solvents leads in the presence of dissolved oxygen to the formation of photooxides (37), in the absence of oxygen, to the formation of dianthracene (B3,67,121). The reactions occur with excitation in the region of 365 μ , corresponding to the first singlet-singlet transition of anthracene. The reactions probably involve the first triplet level of anthracene (95), i.e. that in which two of the fourteen π -electrons are unpaired. Porter and Windsor (95) have found very strong evidence for a rapid transition from the singlet to the triplet state of anthracene in hexane. It has been demonstrated in earlier sections of this chapter that singlet excited anthracene is formed in solutions exposed to γ -rays. We next examine whether this explains quantitatively the disappearance of anthracene in such solutions by dimerization.

Fig. 19 (Inset) shows the decline in the concentration of anthracene with increasing energy absorbed by the solutions, i.e. with increasing times of irradiation. The initial part of this curve permits the calculation of the initial yield, G_{-A} , of anthracene molecules altered or destroyed per 100 ev of \sqrt -ray energy absorbed by the solution. For the data in question this is 0.90. G_{-A} was found to vary with the starting concentration of anthracene, the values over the concentration range studied being given fairly well by the expression:

$$G_{-A} = 3.6 \frac{3 \times 10^3 C_A}{1 + 3 \times 10^3 C_A} \quad \text{III.}$$

where C_A is the anthracene concentration in Mpl.

Expression III should be compared with expression II on pages 66,67. Values of G_{-A} calculated from III are compared with the experimental values in Table 9 below.

Table 9.
Theoretical and Experimental Values of G_{-A}

C_A , Mpl.	G_{-A} calc'd ⁺	G_{-A} exp'l	Diff.
1.8×10^{-5}	0.19	0.21	- 0.02
3.1	0.31	0.31	0.00
1.1×10^{-4}	0.92	0.90	+ 0.02
1.2	0.95	0.75	+ 0.20
2.0	1.54	1.45	+ 0.09
3.0	1.71	1.65	+ 0.06
2.0×10^{-3}	3.10	3.60	- 0.50
4.8	3.35	3.00	+ 0.35

⁺ from Expression III above.

The values of G_{-A} calculated from Expression III agree with the experimental values - excepting that at 1.2×10^{-4} Mpl - within the experimental error. This increased rapidly above a starting concentration of 5×10^{-4} Mpl because the optical density of the solution could not be measured directly, but only after the solution had been diluted. The type D irradiation cell (Fig. 9) could be used for this measurement, but the dilution error was rather large, i.e. $\pm 10\%$. A second difficulty at the high concentrations lay in the uncertainty as to whether all the anthracene was in solution, the solutions being nearly saturated at these concentrations. The results just obtained are plotted in Fig. 21 in the next section.

The limiting value of G_{-A} is 3.6 . Similarly the limiting value of G_t is ~ 1 . This is the maximum yield of singlet excited anthracene resulting from energy transfer in hexane solutions (p. 71) and therefore the maximum yield of anthracene 'destruction' by dimerization will be ~ 2 . This assumes that dimerization occurs by reaction of a triplet excited molecule with a molecule in the ground state. This yield must actually be less than ~ 2 , since some processes occur (e.g. fluorescence) which do not involve dianthracene formation. Thus while some dianthracene is undoubtedly formed by a process resembling photo-dimerization, this cannot account for more than ca 50% of the reaction involving the disappearance of anthracene. Undue reliance is perhaps placed on the absolute value of G_t in reaching this conclusion, but it does not seem likely that G_t is in error by more than $\pm 25\%$.

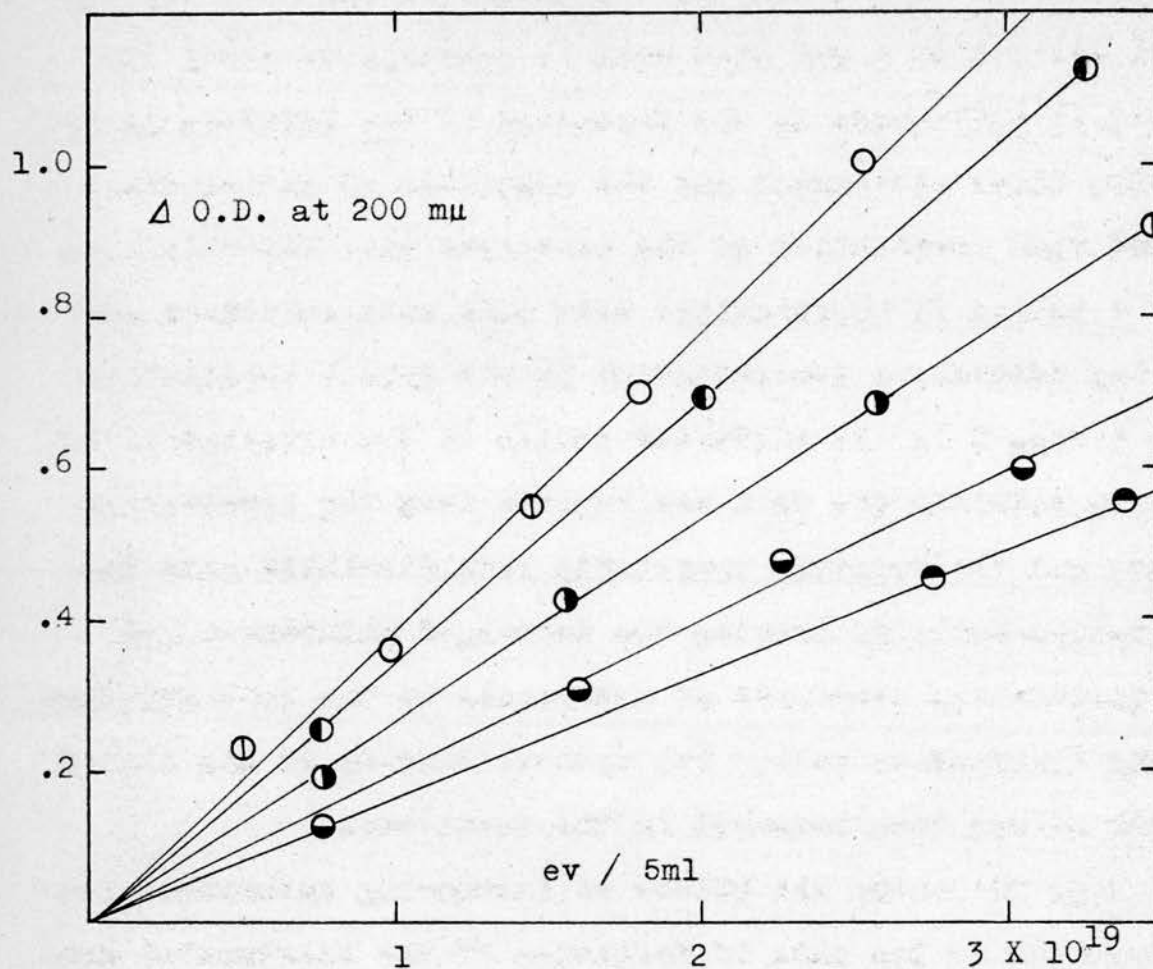


Fig. 20. The effect of anthracene on the formation of unsaturated compounds in the liquid phase. The measurements were made with a Type D irradiation cell in which the unsaturated compounds could be separated from Anth.

- Hexane, products transferred directly.
- ⊙ Hexane, products distilled in abs. cell.
- 5 x 10⁻⁵ M Anth., products distilled.
- 1.8 x 10⁻⁴ M ..
- 8.2 x 10⁻⁴ M ..
- 3.5 x 10⁻³ M ..

6b. Radiolysis of Anthracene Solutions: Liquid Products.

The unsaturated liquid products formed in irradiated n-hexane were of approximately the same volatility as the hexane (Section 5b) and this made it possible to study the effect of anthracene on the formation of the unsaturated compounds, since anthracene and the compounds of anthracene formed upon irradiation of the solutions were non-volatile.*

A series of irradiations were made with solutions of varying anthracene concentration in the Type D irradiation cell (Fig. 9). At different stages of the irradiation of a given solution the cell was removed from the irradiation block, and the volatile components were distilled into the absorption cell, C, leaving the unchanged anthracene and the irradiation compounds of anthracene in the bulb attached to the irradiation cell. The optical density of the liquid at 200 μ was then measured in the usual way.

Fig. 20 shows the effect of increasing anthracene concentrations on the rate of formation of the unsaturated compounds absorbing at 200 μ . The change in optical density is plotted as a function of the γ -ray energy absorbed by the solutions for four different concentrations of anthracene. Evidently anthracene reduces the quantity of unsaturated compounds formed in a given interval of time or of absorbed energy, but the magnitude of this effect approaches a limit

* This fact eliminates a large number of 9,10-addition compounds as possible products, since the majority of these are but slightly less volatile than n-hexane.

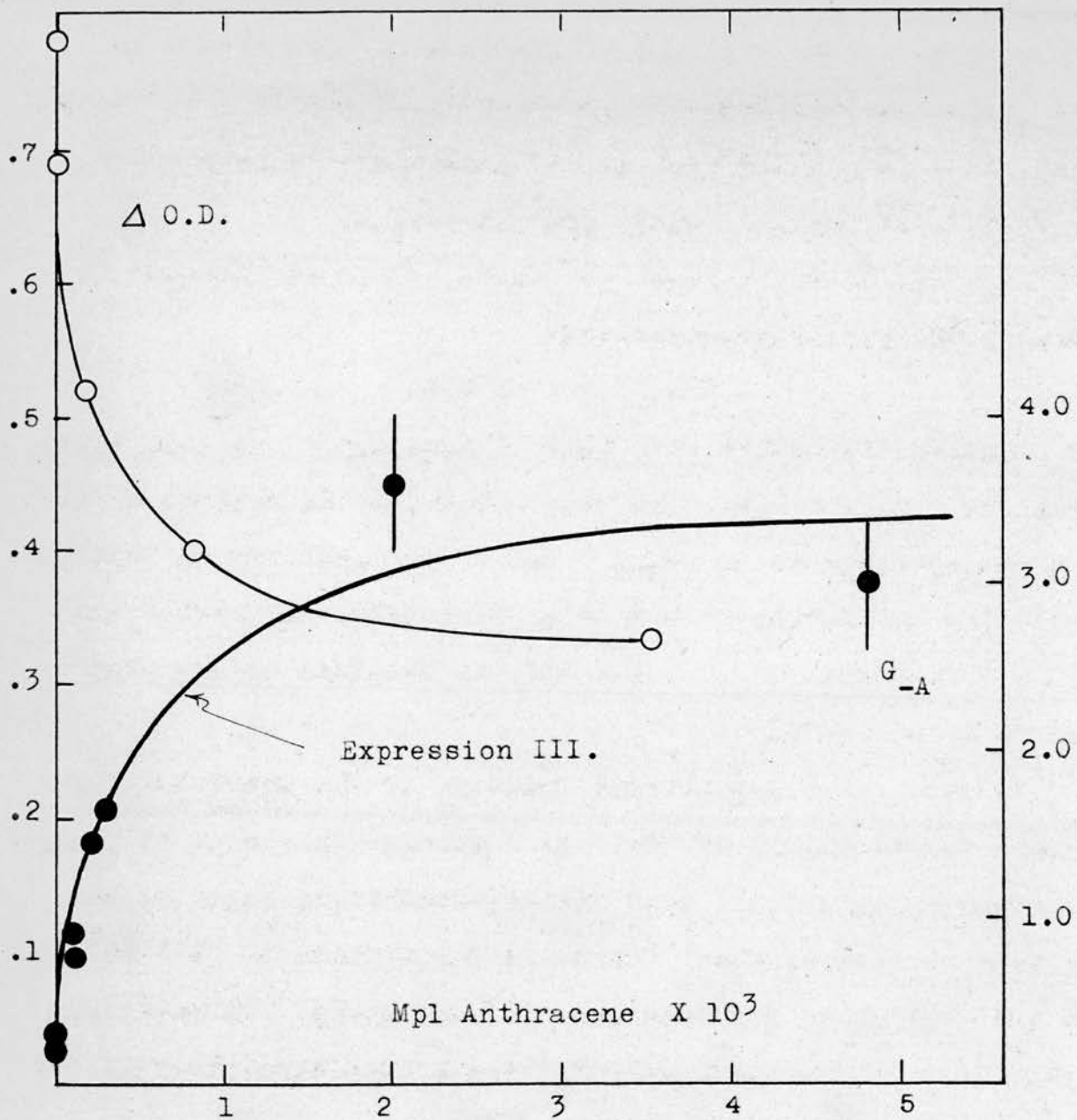


Fig. 21. The increase in optical density at 200 mμ caused by 2×10^{19} ev/5ml (Fig 20) plotted as a function of the initial anthracene concentration (open circles). The yield, G_{-A} , is also plotted against the initial concentration. The curve is given by Expression III, Sec. 6a.

at the higher concentrations of anthracene. The effect is more easily seen in Fig. 21, in which $\Delta O.D.$ for $2 \times 10^{19} \text{ ev/5ml}$ (Fig. 20) is plotted against the anthracene concentration. The results of Table 9 (p.92) are also shown.

G_{-A} approaches a limit of 3.6 . It is of interest to consider the possible equivalence



The limiting diminution in $\Delta O.D.$ (i.e. 0.48) is then equivalent to $\Delta G_{C=C} = 1.8$; so that $\Delta O.D.$ in the absence of anthracene corresponds to $G_{C=C} = 2.9$. A corollary to this is that $\epsilon_{C=C}$ at 200 μ = 4×10^3 . Similarly, the result that $G_{C=C} = 6$ and that $\epsilon_{C=C} = 2 \times 10^3$ is obtained by assuming that $1 A = 1 C=C$.

Further, if a significant fraction of the anthracene disappears independently of $C=C$ by a process analogous to photodimerization (pp.91,93) then the argument above leads to the unlikely conclusion that $\epsilon_{C=C}$ is the minimum at 4×10^3 , and that values of the order of 10^4 may apply. It seems unlikely that 'photodimerization' would affect significantly the stoichiometry considered above.

The considerations suggest, however, that the value of $\epsilon_{C=C}$ previously chosen (p.86) may require an upward revision. This would result in a corresponding diminution of $G_{C=C}$. We will assume for the purpose of theoretical considerations in the next chapter that

$$G_{C=C} = 4 \pm 2$$

7. Summary of Experimental Results:

Before proceeding to the theoretical considerations of the next chapter, we will summarize the experimental results described above. It should be noted that the corrected values of the yields, G , of the different reactions are given in this summary (see Note at foot of page 14).

a. The irradiation of liquid n-hexane with ^{60}Co γ -rays causes its decomposition mainly into H_2 , CH_4 , C_2H_6 and an unsaturated compound (or compounds) with approximately the same volatility as the hexane.

The yields of the principal products are:

$$\begin{aligned} G_{\text{H}_2} &= 4.83 \pm 0.2 \\ G_{\text{CH}_4} &= 0.41 \pm 0.1 \\ G_{\text{C}_2\text{H}_6} &= 0.69 \pm 0.1 \\ G_{\text{C}=\text{C}} &= 4 \pm 2 \end{aligned}$$

b. When solutions of anthracene in hexane are irradiated with γ -rays, the absorption spectrum of anthracene in solution disappears, and is replaced by a spectrum resembling that of dianthracene (p. 89). The yield of this process, G_{-A} , is given by

$$G_{-A} = 3.6 \frac{3 \times 10^3 C_A}{1 + 3 \times 10^3 C_A} \quad (\text{p. 92}).$$

c. The presence of anthracene in the hexane during the radiolysis has no significant effect upon the yields of H_2 , CH_4 , C_2H_6 , but causes a diminution in the

yield of unsaturated products. $G_{C=C}$ decreases with increasing anthracene concentration toward a minimum value of < 2 .

d. Anthracene fluorescence is excited in solutions exposed to γ -radiation by a process which undoubtedly involves energy transfer from solvent to anthracene (see p. 1, et seq.). k' , the coefficient of energy transfer is

$$k' = 610 \pm 60 \text{ Mpl}^{-1}.$$

The absolute efficiency of energy transfer, G_t , in units of anthracene molecules excited per 100 ev of γ -ray energy absorbed by the solution, is

$$G_t = 0.92 \frac{610 C_A}{1 + 610 C_A} \quad (\text{ pp.65,71 })$$

where C_A is the concentration of anthracene.

e. The temperature coefficient of the γ -ray excited fluorescence of anthracene in hexane solutions is approximately three times as great as the temperature coefficient of fluorescence excited by light at 3650 \AA (p. 74).

Chapter III : Theoretical Considerations

1. Primary Processes:

γ -rays lose energy to the medium in which they are absorbed by interaction with the electrons of the medium. The mechanism of interaction depends both upon the energy of the γ -rays and upon the electron density of the absorber. ^{60}Co γ -rays are absorbed in hexane, anthracene and in Pyrex chiefly by the Compton process, in which the electrons of the absorber are ejected from the path of the primary quantum with a continuous distribution of energies ranging from 0 up to the energy of the primary quantum. In contrast to the γ -rays, the ejected electrons have a limited range in the absorber, and hence by far the greatest part of the absorbed energy is dissipated by the electrons (For review see B 9, 33,83,114).

In this discussion we shall be concerned only with those Compton electrons which lose appreciable energy in the hexane. Those which are stopped in the walls probably have relatively little effect upon the hexane, though they may cause the walls to luminesce (p. 56). In hexane the electrons lose energy by inelastic collisions with the electrons of hexane, either with the ejection of an electron from the hexane molecule, i.e. ionization, or with the transfer of a bound electron to an orbital of higher energy, i.e. electronic excitation. Both processes may involve some transfer of kinetic energy to the surrounding molecules, i.e. heat. The Compton electrons

therefore lose energy to the hexane in relatively small, discrete amounts, corresponding to the average energy required to produce an ion or an excited molecule in hexane. The quantity that is usually measured is \underline{W} , the "energy dissipated per ion pair formed in the medium" or simply the "energy per ion pair". This quantity has never been measured satisfactorily for a liquid, but has been determined with reasonable accuracy for several gases.

The lowest ionization potential, \underline{V}_0 , of a molecule is the energy required for the process



in which \underline{M} and \underline{e} are both at rest. Accurate measurements of \underline{V}_0 have been made for many substances in the gas phase, both from spectroscopic data and from the appearance potentials of the ions in a mass spectrometer. \underline{V}_0 and \underline{W} are compared in Table 10 for several substances in the gaseous state.

Table 10.

Comparison of \underline{V}_0 and \underline{W} for gases :

<u>Gas</u>	<u>\underline{V}_0, ev</u>	<u>\underline{W}, ev</u>	<u>Diff., ev</u>	<u>Ref*</u>
H ₂	15.422	38.0 ± 2	22.6	(B8a,p.459)
N ₂	15.576	37.0 ± 1	21.4	..
CH ₄	13.1	29.1	16.0	(112)
C ₂ H ₆	11.6	27.0	15.3	(118)
n-C ₆ H ₁₄	10.1	-	(15.0) ?	(64)

* The values of \underline{W} are from a list compiled by Dr. T. J. Hardwick from measurements made at Chalk River (priv.com.).

Table 10 shows that more than 50% of the energy expended per ion pair is dissipated in processes other than ionization. We shall assume that \underline{W} for n-hexane is 25.0 ev, and that this amount is expended per ion pair formed in the liquid as well as in the gas. This last assumption, while difficult to justify theoretically, is customarily made and is probably not greatly in error (114). On this basis there are, on the average, 4 ion pairs formed per 100 ev dissipated in the hexane.

Table 11 lists the more important ions formed in gaseous hexane by electron impact.

Table 11.

Appearance potentials of various ionized fragments of n-hexane: (64)

Electron energy (ev):	10.1	10.9	11.0	11.4	
Positive ion :	C_6H_{14}	C_6H_{13}	C_5H_{10}, C_4H_8	C_4H_9	
Elect. en.:	11.5	12.5	14.1	14.8	20.4
Pos. ion :	C_3H_6	C_3H_7	C_3H_4	C_2H_5	C_2H_4

Many fragments of hexane can evidently be formed on impact with electrons of energy only slightly greater than that of the minimum ionization potential of hexane in the gaseous state. This situation should be contrasted with the relative simplicity of the products found in the radiolysis of liquid hexane (Chap. II, Sec. 7).

The energy in excess of V_0 , which is required to produce an ion pair in hexane (p.99) may produce electronically excited molecules or be dissipated as heat. Both ionization and excitation probably occur inefficiently, i.e. with some excess energy. Table 11 shows that some of the excess energy may bring about the dissociation of the primary ions.

Concerning the excited electronic levels of the paraffin hydrocarbons very little is known. The A-spectra of these compounds are found in the vacuum U. V. between 1200 and 1600 Å, and probably correspond to the excitation of an outer electron to levels lying below the photo-ionization limit (27,38,91,93, 115). The lowest ionization potentials of these compounds lie between 10 ev and 13 ev, corresponding to photo-ionization limits in the range from 1240 to 950 Å. In the paraffin hydrocarbons every outer electron is a bonding electron, and there should exist a strong coupling between the electronic and vibrational states. However, no vibrational structure has been detected in the few bands which have been observed.

Duncan and Howe (38) have suggested all the levels to which transitions can occur may be repulsive, and this has much support from photochemical evidence. Groth (48) and Groth and Scharfe (49) have photolyzed, respectively, methane and propane with the 1470 and 1295 Å lines of the Xe discharge. The primary photochemical process in each case appeared to be



This process might have been expected when $RH = \text{methane}$, but

is surprising when $RH = \text{propane}$, since the primary absorption undoubtedly occurs in one of the C-C bonds of the molecule. The absorption is associated with the most weakly bound electrons in the molecule (91,92,93,94,96) and in propane these are the electrons forming the C-C bonds. The strength of these bonds is less than the C-H bond strength by about 1 eV (118,138). There is also evidence from measurements of the transmission limits of a series of paraffin hydrocarbons (63) that the first absorption band shifts to longer wave lengths with an increasing degree of substitution about a central C-C bond. The band cannot, therefore, be associated with the C-H bond, and it is a matter of fundamental interest that in propane a C-H rupture should occur preferentially. The effect might be explained if a transition to a repulsive C-H configuration could be made from the excited level of the C-C bond. Such a transition is purely speculative, but finds a counterpart in the 'intersection' of the $^2\Sigma_g$ and $^3\Pi_g$ states of the hydrogen molecule described by Magee and Burton (79) in a discussion of the processes subsequent to charge neutralization of the H_2^+ ion by electron capture.

The selection rules which determine the primary absorption process in the photolysis of the paraffin hydrocarbons probably do not apply to excitation by secondary electrons, and in the latter instance repulsive levels of the C-H bond to which transitions are normally forbidden may be directly excited. That such repulsive levels exist not far above the

ground state is demonstrated by the fact that a C-H split can be induced in paraffin hydrocarbons by collisions with $6(^3P_1)$ mercury atoms (4.89 ev). The results of mercury photosensitized photolysis have been described in Chapter II, Sec. 5 (p. 81 et seq.). The excitation of hexane by Compton electrons may therefore lead to dissociation into a hexyl radical and a hydrogen atom (compare reaction (i) p. 81) by a process requiring as little as 5 ev. Reference to Table 11 (p. 100) shows that dissociation into a radical-ion and a hydrogen atom may occur upon impact with electrons of 10.9 ev energy. If 5 ev is required for the dissociation, \underline{V}_0 for the hexyl radical must be approximately 6 ev, or 4 ev less than \underline{V}_0 for the hexane molecule. That the ionization potentials of free radicals are considerably lower than the potentials of the parent molecules is well known (75).

Table 11 also shows that a C-C rupture in hexane can be caused by impact with electrons of only slightly higher energy than 10.9 ev. It is therefore to be expected that some primary dissociations of this type will occur during the radiolysis.

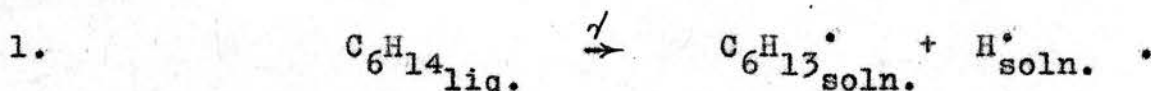
A somewhat different type of dissociation may be expected as a result of charge neutralization of molecular ions by electron capture, a process which has been considered in some detail for the hydrogen molecule (79). The neutral molecule resulting from electron capture possesses energy of excitation

equivalent to V_0 . For the H_2 molecule this is ca 15 ev, i.e. an amount which is greatly in excess of the H-H bond energy (4.70 ev). The dissociation proceeds by



A transition occurs from the excited state resulting from electron capture ($^2\Sigma_g$) to a repulsive ($^3\Pi_g$) state yielding upon dissociation a normal H atom and one possessing about 10 ev of excitation energy (Lyman 1215Å⁰). Both atoms have at least 0.5 ev kinetic energy. Magee and Burton (79) consider this to be the most important process subsequent to charge neutralization. They state that similar processes are probable for hydrocarbons (79,p.1971) without, however, considering the possibility of interaction between C-C and C-H excited levels.

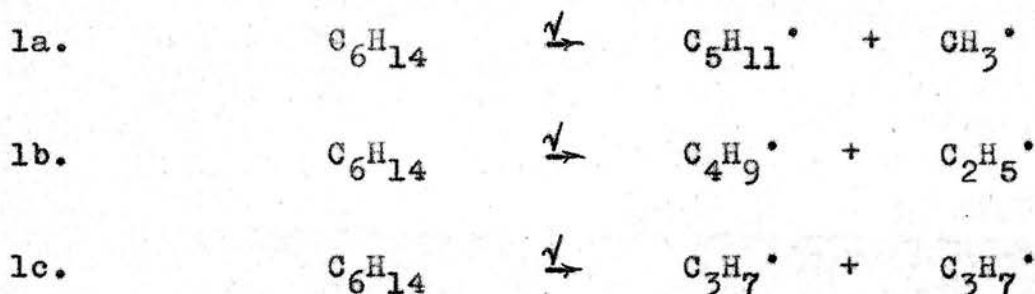
Despite the evidence in Table 11 it seems possible to explain the main results of the radiolysis of liquid hexane on the assumption that the principal primary process is



It will not be necessary to consider the role of the molecular ions in the discussion which follows because electron capture occurs within a time (ca 10^{-13} sec) which is short compared with the time required for the processes to be considered (132a). Reaction 1. above represents the net effect of the dissociative processes discussed just above, i.e. dissociation corresponding to the normal process of photo-

dissociation, dissociation resulting from excitation to repulsive (normally forbidden) levels, and dissociation resulting from charge neutralization by electron capture.

Though 1. is considered to be the most important primary process, the results suggest that the following processes may occur to a lesser extent:

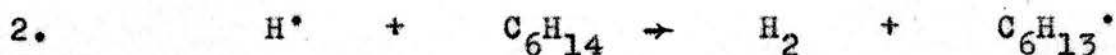


2a. Subsequent Reactions: Hexane.

The reactions subsequent to the primary dissociation proposed above are merely those characteristic of H atoms and hydrocarbon free radicals. Though such reactions have been studied in the liquid phase only to a limited extent, they have been intensively studied in the gas phase (B11). The results of gas phase studies form an adequate basis for the discussion of reactions in the present system if it is assumed that the solutions of the reactants are ideal (B10, Chap. I). This assumption is not greatly in error for solutions in hexane near its boiling point (i.e. at room temperature). Hexane is a non-associated liquid which is inert to most reagents.

As a solvent for most reactants it merely provides a medium of relatively high viscosity compared to that of gases. This has the effect of altering the distribution-in-time of collisions between reactants, but probably has little effect upon energies of activation and steric factors (B10,B11). We shall devote some consideration to the mechanism of a reaction in hexane as a spherical close-packed liquid in a later section. In the paragraphs immediately below we consider the probable reactions of H atoms and hydrocarbon free radicals on the basis of reactions which have been established in the gas phase.

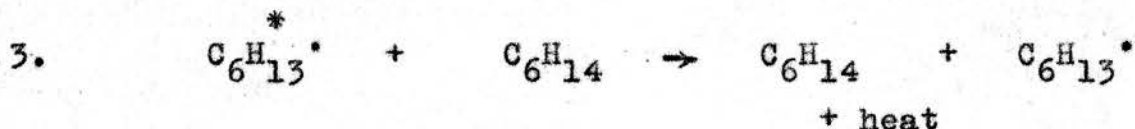
H atoms formed by reaction 1. probably react at once with the surrounding hexane.



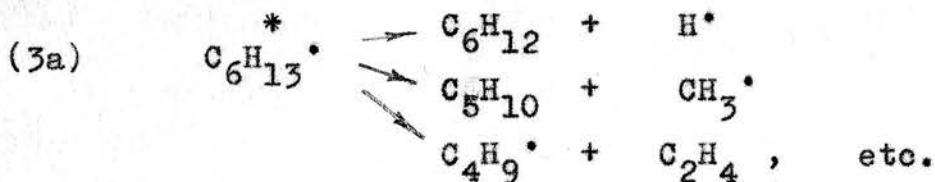
This reaction is considered to be the source of H_2 in the radiolysis of hexane. It is exothermic by about 0.5 ev (B11,118,138), and in the gas phase requires an activation energy of ~ 0.4 ev at room temperature (125). If dissociation occurs via the process of charge neutralization (79), it seems likely that energies considerably in excess of 0.4 ev may be imparted to the H atom. The reaction is therefore energetically feasible.

A reaction between the hexyl radical and hexane analogous to reaction 2., though not ruled out on energetic grounds, would undoubtedly be very much slower because of steric restrictions.

The reaction would produce, in any event, no net change in the system. Should the hexyl radical be formed in a highly excited state - as would be likely in dissociations following charge neutralization - the following process would involve a net change;



It should be noted that though the excited levels of the hexane molecule may be repulsive, the hexyl radical possesses an unshared electron whose electronic states resemble (like those of the H atom) the electronic states of the π -electrons of mono-olefins (92,93,94). The excited states may therefore have a relatively long life (10^{-9} - 10^{-8} sec) provided reaction 3. is inefficient. The same steric restrictions apply as above. Furthermore the excited level of the hexyl radical has no counterpart in normal hexane, and hence an exchange of electronic energy without reaction is impossible. There is, however, the possibility of dissociation analogous to that proposed by Groth and Scharfe above (pp.82,101) for the excited propyl radicals formed by the direct photolysis of propane (49).



The first of these alternatives might account for the

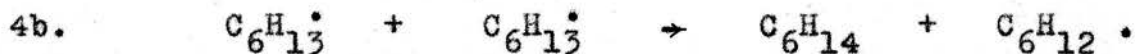
fact that H_2 and $C=C$ are main products in the radiolysis. It is, however, difficult to reconcile a mechanism of this kind with the effect of anthracene on $C=C$, to be considered in a later section. The second alternative could account for the methane formed, but the third is unlikely for the reason that no ethylene was detected, though very sensitive analytical techniques were employed (See Table 2, p.32). Similar objections may be levelled against the other possible alternatives, and it may be concluded that reaction (3a) is unimportant to the present scheme. The reason for this may lie in the comparative efficiency of reaction 3.

It will be of later importance to consider the energy of the excited hexyl radical resulting from charge neutralization and dissociation. The energy of the neutral molecule will be 10.1 ev (Table 10, p.99). The energy required for C-H rupture is between 4.1 and 4.3 ev (138). The resulting hexyl radical may therefore have between 5.8 and 6.0 ev of excitation energy. If about 1 ev is imparted to the fragments as kinetic energy, this figure must be diminished accordingly, and it seems likely that excitation energy of the order of 5 ev may be retained by the radical. This would correspond to emission at a wavelength of 2300 Å.

The ultimate fate of the hexyl radicals - in the absence of competing reactions - will be a) dimerization (11,24-26,52)



and b) disproportionation (11,24-26,133b),

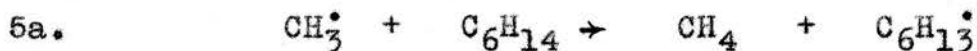


Compounds of higher molecular weight have always been found, together with H_2 , as the principal products of the radiolysis of hydrocarbons (B7, p.149-, 53, 72, 110, etc.) The formation of unsaturated compounds of approximately the same volatility as hexane is evidenced in this work by the appearance of a strong absorption band at ca 1900 Å in the irradiated hexane (Chap. II, Sec. 5b). The failure to generate sufficient quantities of the unsaturated compounds to be identified by the I_2 reagent by using the 100 c ^{60}Co source may be attributed to the following reaction, which undoubtedly becomes important at high radiation intensities, or on long exposures:



leading eventually to the reduction of the concentration of $\text{C}=\text{C}$ to a low steady state value when the rate of destruction by the reactions above was balanced by the primary formation of $\text{C}=\text{C}$. Here R^\bullet may be the hexyl radical, or may be a smaller radical generated by reactions 1a - 1c.

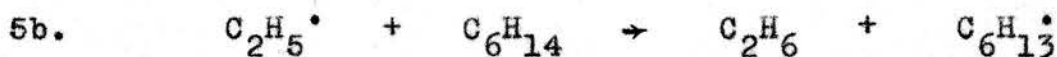
Reactions analogous to reaction 2. may occur for the radicals formed by reactions 1a - 1c. The reaction



occurs in the gas phase with an activation energy of 8.1 Kcal/mol

and with a normal frequency factor (117) of 2×10^{11} (126).

Similarly, ethane may be formed by



with approximately the same activation energy, but at a slower rate owing to steric restrictions (24). The induction period observed for the evolution of ethane (Fig. 15, p. 77) might be explained as the result of a competitive reaction between the ethyl free radicals and a residual impurity in the hexane, e.g. that causing the residual absorption in the U.V.

To account for the virtual absence of 'C₃' and 'C₄' hydrocarbons among the products, it must be assumed that reactions such as 5a. and 5b. involving propyl and butyl radicals are very efficient owing, presumably, to steric restrictions. It should be noted that there is no evidence for reaction 1c., aside from the traces of propane found, although the reaction involves the rupture of the weakest bond in the molecule.

2b. Some Consequences of the Theory:

Before proceeding farther, we shall consider briefly some of the consequences of the theory just proposed.

a) It was assumed (p.100) that $W_{liq} = W_{vapour}$. W_s for the light paraffin hydrocarbons are not greatly different from W_{vapour} for hexane. The same reactions are assumed to occur in the liquid as in the gaseous phase. It therefore

follows that the yields of the various products of the radiolysis of the lighter hydrocarbons in the gas phase should approximate to the yields of the same products in liquid hexane. That this is so is shown in Table 7 (p.79).

b) On the basis of reactions 1 - 5, the yield of free hexyl radicals, G_R , in liquid hexane is given by

$$\begin{aligned} G_R &= 2G_{H_2} + G_{CH_4} + G_{C_2H_6} \\ &= 10.9 \text{ radicals/100 ev.} \end{aligned}$$

On the same basis, the yield of radicals of all kinds must be at least 12/100 ev.

Magat and co-workers (97) have measured G_R by a method sensitive to all the radicals for a number of organic liquids. They list the following values for the paraffin hydrocarbons:

<u>Liquid</u>	G_R
n-heptane	9.9
n-octane	11.4
cyclohexane	14.3

c) Since $G_R \approx 12$ and $G_{C=C} \approx 4$, the yield of the dimer, R_2 , must be

$$G_{R_2} \approx 2.$$

The relative yields of dimerization and of disproportionation are different from those determined by Ivin and Steacie for ethyl radicals in the gas phase (2dim:1dis). Though part of this difference may lie in the uncertainty attached to $G_{C=C}$, a real difference may exist owing to difference in structure (11). Dimerization should, however, be favoured in solution.

2c. Subsequent Reactions: Solutions.

In solutions of anthracene in hexane absorbing γ -radiation, a reaction between anthracene molecules, A, and the radicals, R*, can compete with reactions 4. and 5. (p.89).



R* may be any reactive species (e.g. an H atom) but in view of the unaltered yields of H₂, CH₄ and C₂H₆ in solutions of anthracene (p.88) it seems probable that only reactions with hexyl radicals are important. The reaction is shown as a 9-addition (p.89) involving a transition from the singlet ground state to the lowest triplet state of anthracene. Szwarc (123) has recently demonstrated the feasibility of reactions of this type. In this instance the reaction requires not more than 0.5 ev activation energy, and possibly less than 0.3 ev.

A reaction between R* and A in which R* abstracts an H atom from A (analogously to reactions 2.,3.,5a.,5b.) while energetically feasible, does not appear to be important, possibly because of a high activation energy.

Reaction 6. must compete with the radical recombination reactions 4a. and 4b. which, though somewhat restricted by a steric consideration, proceed with 0 activation energy. That it does so at all effectively is due to the relatively high concentrations of anthracene present at all times. Even at the highest intensities of γ -rays employed, 3×10^{17} ev/5ml/hr,

the rate of generation of hexyl radicals was ca 10^{-10} Mpl/sec, and the instantaneous concentration of radicals was probably not greater than ca 10^{-9} Mpl, both quantities being calculated on the basis of uniform distribution of the radicals throughout the solution. Such a calculation is, of course, a simplification because the radicals are formed in the tracks of the Compton electrons and secondaries and may initially be in local concentrations much higher than 10^{-9} Mpl. The problem in non-homogeneous reaction kinetics which this situation raises has been considered in detail by Dewhurst, Samuel and Magee (132a) but is beyond the scope of the present work. If the above simplifying assumption is made, and it is further assumed that the energy of activation of reaction 6. is 0.4 ev and that the steric factors for reactions 4a., 4b. and 6. are identical, then we find that these reactions should proceed at the same rate at anthracene concentrations of the order of 10^{-4} Mpl. This agrees very well with the magnitude of the anthracene concentrations for which an appreciable diminution in $G_{C=C}$ was found, as is to be seen in Fig 21, p.95.

The compound, RA^{\bullet} , is a new free radical, stabilized to some extent by resonance, but requiring an additional electron for chemical stability (p.90). Neglecting the unlikely event in which R is a diradical, there are only two reactions by which RA^{\bullet} may be stabilized;



RAR and RAAR are both compounds with A-spectra resembling that of dianthracene (pp.90,91). Reactions 6a. and 6b. both require little or no activation energy, and are therefore relatively rapid, probably comparing in velocity with reactions 4a. and 4b. Reaction 6. is the slow, or rate-determining reaction of this group.

It will be noted that the formation of RAR corresponds to the equivalence, $1 A = 1 C=C$, considered on p. 95 above. The formation of RAAR similarly corresponds to the equivalence, $2 A = 1 C=C$. No account has been taken of the effect of anthracene on G_{R_2} in this consideration (p.111). If $G_{R_2} = \frac{1}{2} G_{C=C}$, as found above, and a reduction in G_{R_2} equal to the reduction in $G_{C=C}$ is brought about in the presence of anthracene, considerations like those on p.95 lead to the conclusion that a reasonable value for $\epsilon_{C=C}$ is obtained only for the case that $1 A = 1 C=C$, i.e. when reaction 6a. predominates. Such considerations are somewhat speculative, since G_{R_2} has not been measured directly.

3. A Mechanism of Energy Transfer:

A theory of energy transfer in solutions must meet the following criteria:

- 1) Transfer must be complete in ca 10^{-10} seconds. (p.5)
- 2) It occurs with the same efficiency in such diverse solvents as hexane and xylene, (p.67) i.e. $k'_h = k'_x$
- 3) It occurs in solution over distances of 2 molecular diameters. (p.72)
- 4) It probably has an appreciable negative temperature coefficient. (p.74)

An ingenious mechanism of indirect excitation by ionizing radiation, due to Weiss (131), was omitted from the discussion in the Introduction. It is considered here. Weiss points out that there is a small range of energies for the secondary electrons - near the end of the electron track - in which the electron has insufficient energy to excite the solvent, but may still excite optical levels of the solute. This mechanism meets 1) and 3) above, but fails to meet 2) and 4). The electronic spectra of hexane and anthracene are widely separated, while those of xylene and anthracene strongly overlap. On Weiss's theory the efficiency of excitation in hexane should be greater because of the greater range of energy available to the electron. The only significant effect of temperature, a slight variation of the intensities of the spectra (87), cannot account for the coefficient in 4) above.

A second theory, that due to Reid (p.3,ref.85,86), regards energy transfer in solution as a process occurring within a complex between the solute and solvent molecules. The properties of such a system would probably fulfill all four requirements above. There is evidence, however, that the benzenoid solvents interact much more strongly with anthracene than does hexane. The 0-0 separation of the A- and F-spectra (pp.9,10) is almost twice as great in the former solvents as in hexane (104). The greater electronic coupling should, on this theory, result in more efficient transfer.

The Birks, or photon transfer mechanism (p.2,B2,12) does not appear to be applicable to solutions of anthracene in hexane. The solvent is non-fluorescent, the excited electronic levels being repulsive.

Two mechanisms to be considered require a collision between an 'active' solvent molecule and the solute molecule, the charge transfer mechanism due to Haynes (p.2,R1), and the mechanism involving excited solvent molecules due to Furst and Kallmann (pp.2,3,ref.44). We consider briefly below whether a collisional mechanism can account for the velocity and the range of energy transfer in solution.

A collision mechanism in solution differs from that in gas by the fact that the collision partners are "hemmed in" by molecules of the solvent (B10,Chap.I,16,42). The partners are contained in a cage of solvent molecules in which several collisions may occur between the partners before one of them escapes from the cage, i.e. diffuses away. Such

groups of collisions have been termed encounters. A consequence of encounters in solution is that if the probability of a reaction between two molecules is not negligibly small per collision, each encounter may lead to reaction. The rate of the reaction is then the rate at which the reactants diffuse together in solution, i.e. the rate is diffusion controlled. The quenching of fluorescence in solution is a type of diffusion controlled reaction (16,17,127). A mechanism of the same kind might account for the reverse of quenching, i.e. excitation. The reverse process is in fact inherent, since the quencher may be excited.

For the discussion which follows we will adopt as a model of hexane a spherical -close-packed liquid similar to that which has been considered in some detail by Fowler and Slater (42). The effective diameter, \underline{d} , of the hexane molecules in such a liquid is 6.7 Å. The model is not seriously divergent from current theories of the structure of liquids (46).

In close packing, each molecule of hexane is contained in a cage formed by twelve of its neighbors, the linear dimensions of the cage being of the same order as \underline{d} . At room temperature each molecule makes 7×10^{12} collisions per second with the walls of the cage (42). In a majority of these the molecule is simply reflected back into the cage, but in collisions in which the molecule has energy greater than a critical amount, it will 'escape' from the cage by exchanging positions with one of the molecules forming the wall. It thus

it thus moves a distance \underline{d} in diffusion. This process is then repeated in a new cage, each successive displacement, \underline{d} , being in a direction independent of that of the preceding displacement. The molecule therefore executes Brownian movement in which the $\overline{\text{mean}}^2$ displacement per diffusive 'jump' is given by Einstein's expression (B4)

$$\overline{\Delta X}^2 = d^2/3$$

The critical energy for a diffusive collision in hexane is ~ 2 Kcals/mol (B10,p.12). Hence at room temperature the fraction of the collisions, 0.03, result in an escape from the cage*. In an interval of 10^{-10} seconds 7×10^2 collisions are made, ~ 20 of which result in a random displacement, \underline{d} . Using Einstein's expression for the $\overline{\text{mean}}^2$ displacement, we find that in 10^{-10} seconds the molecule under consideration has suffered a mean displacement of 17.5 \AA . It thus moves a distance of between 2 and 3 molecular diameters.

Though the model above would have to be modified if, instead of the motion of a molecule, the motion of an ion or excited molecule were to be considered (i.e. these are respectively smaller and larger than the normal hexane molecule), the model shows that energy transfer by collisions is well within the realm of possibility. Unfortunately, the mechanisms under consideration fall down for other reasons.

* It is assumed that the molecular energies have a Boltzmann distribution (42).

To be effective, the charge transfer mechanism requires that the solvent ions have a lifetime of at least 10^{-10} seconds, whereas they are neutralized by electron capture in probably less than 10^{-13} seconds (132 a). The mechanism due to Furst and Kallmann requires long-lived excited states of the hexane molecule, and hence cannot be applied to the present system.

These criticisms, which apply to ions and excited molecules, do not apply to the excited hexyl free radicals, $C_6H_{13}^*$, formed by dissociation after charge neutralization. These may have a natural lifetime equal to those of most fluorescent molecules, i.e. 10^{-9} - 10^{-8} seconds (p.107). They are, however, probably efficiently quenched by reaction 3. (p.107), and it is doubtful whether they would survive for 10^{-10} seconds, as required by a collisional mechanism. Collisions are, however, not required for energy transfer. It has been estimated that the excited radical may have an energy of excitation in the region of 5 eV (i.e. somewhat below the ionization potential of the radical). This may be emitted as fluorescence in the region of 2300 \AA within the natural lifetime. Anthracene absorbs strongly in this region (Fig.6,p.43). A strong coupling of the electronic states of anthracene with those of the excited radical can therefore exist, and energy transfer by resonance of the type described by Förster (B6, 40,also19,43) can occur. Förster has shown (40) that the time required for energy transfer varies as the sixth power

of the distance between the molecules engaged. The time for transfer becomes equal to the natural fluorescence time at a critical distance, \underline{d}_0 , determined by the extent of overlap between the electronic spectra of the molecules. For the extent of overlap envisaged here $d_0 \sim 100 - 150 \text{ \AA}$. The time required for transfer over 2 to 3 molecular diameters is therefore $1/10^6$ times the natural decay time, or 10^{-15} to 10^{-16} seconds, i.e. a time which is short even compared with the time of molecular vibrations, 10^{-13} seconds. Transfer could therefore occur before the excitation energy of the free radical was quenched.

The calculations just made are perforce approximate, and the balance between energy transfer and quenching may be finer than the above results indicate. Thus the effect of temperature could be determining by increasing the probability of quenching and correspondingly reducing the probability of transfer.

It may also be surmized that transfer would occur with about the same efficiency in both hexane and xylene (p.67) since it is not the electronic spectra of the solvents which are involved, but the spectra of the free radicals, or more accurately the spectrum of the unshared electron in the solvent radical. On this basis also the increased efficiency observed with terphenyl may be associated with the greater degree of overlap between the A-spectrum of this molecule and the emission spectrum of the radicals. An increase in

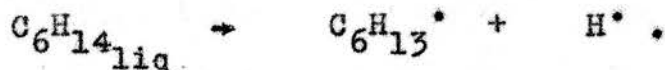
overlap is to be expected because the A-spectrum of terphenyl is at shorter wave lengths than that of anthracene (B5, No.171).

Magat et al (97) have measured G_R , the yield of free radicals, in m-xylene and ethylbenzene and find values of G_R equal to 6.3 and 9.0 respectively. These values are lower than $G_R = 10.9$ estimated for hexane above (p.111), but it is uncertain to what extent this comparison is significant, since the yields of excited radicals may not be in proportion to G_R . The transfer coefficient, k' , is in any event determined, not by G_R , but by the velocity of reaction 3.

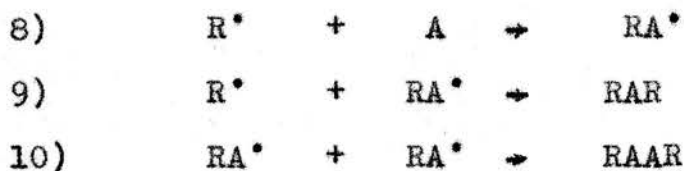
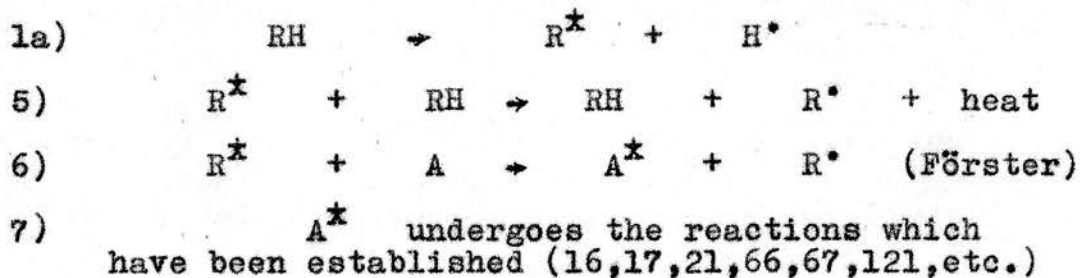
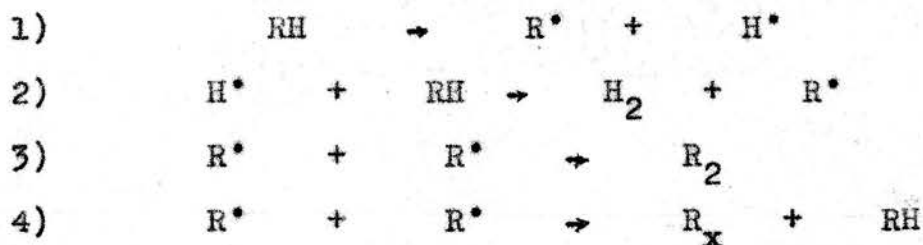
Much work has yet to be done before a firm conclusion can be drawn as to the precise nature of energy transfer in solvents other than hexane. In hexane it has been shown that anthracene molecules may be excited by at least two types of energy transfer; a) optical excitation by background radiation in the hexane (in this instance probably Čerenkov radiation) and b) excitation by a radiationless process attributable to resonance of the Förster type (40) between molecules of anthracene and electronically excited hexyl radicals. The latter are formed by the primary dissociation of hexane molecules absorbing ionizing radiation. The mechanism of energy transfer to anthracene is but part of a general scheme of reactions proposed to explain the effects of \sqrt -rays on dilute solutions of anthracene in hexane.

4. Summary:

The experimental results summarized at the end of Chapter II (p.96) can be explained by a theory built upon the assumption that the primary radiation chemical process in liquid hexane is



The subsequent reactions are summarized below in a simplified scheme in which RH = hexane, R^{\bullet} = hexyl radical, R_x = hexene and R^{\star} = excited radical. Reactions yielding CH_4 and C_2H_6 are omitted. A represents anthracene.



The excitation of anthracene to fluorescence occurs by reaction 6) above which is thought to involve resonance transfer of the Förster type (40,B6). $G_{t \text{ max}}$ for this process is 0.9 whereas G for the primary rupture is 4.9. Thus the number of excited radicals formed is rather less than one fifth of the total formed by the primary rupture. As there are four ions formed per 100 ev dissipated in hexane (p.100) this result suggests that there may be an excited radical formed independently of the ions, i.e. by a process of direct excitation, but this conclusion is highly speculative.

Reaction 6) is in competition with reaction 5). If it is assumed that the reduction in the intensity of the fluorescence caused by a rise in temperature is due to the increased velocity of 5), then using the temperature data we may calculate an approximate value of the activation energy for reaction 5). Using the data in Fig. 14 (p.74) we find an energy of activation for 5) of 3-4 Kcals/mol, a value which would appear to be reasonable for this process.

Reactions 8-10) account for the transformation of anthracene to compounds resembling dianthracene. They compete with reactions 3) and 4). The minimum value of $G_{G=C}$ is probably not less than two, even when the reactions 8-10) become saturated. Such a result can only be explained on the basis of non-homogeneous kinetics (p.113). It is hoped this problem will receive serious attention in the future, since it is fundamental to the kinetics of radiation chemistry.

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Edinburgh, April 5, 1955

Books Referred to in the Thesis

- B 1 F. Bayer: Gasanalyse: Methoden der Arbeitspraxis.
Enke, Stuttgart, 1941.
- B 2 J. B. Birks: Scintillation Counters.
Pergamon, London, 1953.
- B 3 E. J. Bowen: The Chemical Aspects of Light.
Clarendon, Oxford, 1946.
- B 4 A. Einstein: The Brownian Movement.
Methuen, London, 1926.
- B 5 R. A. Friedel and M. Orchin: U. V. Spectra of Aromatic
Compounds. Wiley, New York, 1951.
- B 6 Th. Förster: Fluorescence of Organic Compounds.
Vandenhoeck, Göttingen, 1951.
- B 7 G. Glockler and S. C. Lind: The Electrochemistry of
Gases and other Dielectrics.
Wiley, New York, 1939.
- B 8 G. Herzberg: Molecular Spectra and Molecular Structure.
2nd Ed. Van Nostrand, New York, 1950.
- B 9 D. E. Lea: Action of Ionising Radiations on Living
Cells. U. P. Cambridge, 1946.
- B 10 E. A. Moelwyn-Hughes: Kinetics of Reactions in Solution.
2nd Ed. U. P. Cambridge, 1947.
- B 11 E. W. R. Steacie: Atomic and Free Radical Reactions.
Reinhold, New York, 1947.
- B 12 Y. K. Syrkin and M. E. Dyatkina: Structure of Mole-
cules. Butterworths, London, 1950.

Reviews

- R 1 Latest developments in scintillation counting.
Nucleonics, 10, No. 7, 32 (1952)

References

1. M. Ageno, M. Chozziotto and R. Querzoli:
Scintillations in liquids and solutions.
Phys. Rev. 79, 420 (1950)
2. M. Ageno and G. Cortellessa:
Fluorescence excited in stilbene by α -particles.
Il Nuovo Cim. IX, 196 (1952)
3. M. Ageno, G. Cortellessa and R. Querzoli:
An instance of aging in liquid scintillators.
Il Nuovo Cim. IX, 1242 (1952)
4. M. Ageno and R. Querzoli:
The mechanism of scintillations in solutions.
Il Nuovo Cim. IX, 282 (1952)
5. P. Alexander and A. Charlesby: Energy transfer in
macromolecules exposed to ionizing radiation.
Nature 173, 578 (1954)
6. P. Alexander, A. Charlesby and M. Ross:
Degradation of polymethylmethacrylate by radiation.
Proc. Roy. Soc. A 223, 392 (1954)
7. E. H. Belcher: The luminescence of aqueous
solutions of radioactive isotopes.
Proc. Roy. Soc. A 216, 90 (1953)
8. H. A. Benesi and J. H. Hildebrand: A spectroscopic
investigation of interaction of I_2 with hydrocarbons.
J. Am. Chem. Soc. 71, 2703 (1949)
9. A. Bernanose, T. Bremer and P. Goldfinger:
Free radical mechanism of chemiluminescence.
Bull. Soc. Chim. Belg. 56, 269 (1947)
10. M. Berthelot:
Coloration of glass by emanation.
Compt. Rend. 145, 710 (1907)

11. J. C. Bevington, H. W. Melville and R. P. Taylor:
Termination reaction in radical polymerization.
J. Polymer Sci. XII, 449 (1954)
12. J. B. Birks:
Energy transfer in organic phosphors.
Phys. Rev. 94, 1567 (1954)
13. J. B. Birks and G. T. Wright:
F-spectra of organic crystals.
Proc. Phys. Soc. B 69, 657 (1954)
14. J. B. Birks and M. E. Szendrei:
Absolute scintillation efficiency of anthracene.
Phys. Rev. 91, 197 (1953)
15. E. J. Bowen:
Luminescence of organic substances.
Nucleonics 10, No.7, 14 (1952)
16. E. J. Bowen: Fluorescence quenching
in solution and in the vapour state.
Trans. Farad. Soc. 50, 97 (1954)
17. E. J. Bowen, H. W. Barnes and P. Halliday:
Bimolecular quenching processes in solution.
Trans. Farad. Soc. 43, 27 (1947)
18. E. J. Bowen and R. J. Cook:
Temperature coefficients of fluorescence.
J. Chem. Soc. (1953) 3059.
19. E. J. Bowen and R. Livingston: Experimental
studies of energy transfer in liquid solutions.
J. Am. Chem. Soc. 76, 6300 (1954)
20. E. J. Bowen, E. Mikiewicz and F. W. Smith:
Resonance transfer of energy in organic crystals.
Proc. Phys. Soc. A 62, 26 (1950)
21. E. J. Bowen and A. Norton:
Quenching of fluorescence in solution.
Luminescence, Disc. Farad. Soc. (1939) 44.

22. E. J. Bowen and K. K. Rohatgi:
Photochemical reaction of anthracene with CCl_4 .
Disc. Farad. Soc. 14, 147 (1953)
23. M. Burton and W. N. Patrick:
Radiation chemistry of luminescent solutions.
J. Chem. Phys. 22, 1150 (1954)
24. S. Bywater and E. W. R. Steacie: Mercury $6(^3P_1)$
sensitized photolysis of n-butane and isobutane.
J. Chem. Phys. 19, 172 (1951)
25. of ethane at high temperature.
ibid. 19, 326 (1951)
26. of propane at high temperature.
ibid. 19, 319 (1951)
27. E. P. Carr and M. K. Walker: U. V. A-spectra
of simple hydrocarbons: I, n-heptene-3, etc.
J. Chem. Phys. 4, 751 (1936)
28. E. P. Carr and G. F. Walter:
II, in liquids and solutions.
ibid. 4, 756 (1936)
29. E. P. Carr and H. Stücklen:
III, vapour in Schumann U. V.
ibid. 4, 760 (1936)
30. P. Čerenkov: Visible luminescence
from pure liquids irradiated with γ -rays.
C. R. Akad. Sci. USSR 2, 446 (1934)
see also ibid. 2, 469 (1934)
ibid. 3, 413 (1936)
31. C. Chéchan: Inhibiting effect of O_2
on the fluorescence of solutions.
Compt. Rend. 222, 80 (1946)
32. S. G. Cohen and A. Weinreb: Energy transfer
in organic solutions under U. V. illumination.
Phys. Rev. 93, 1117 (1954)

33. F. S. Dainton:
Chemical reactions induced by ionizing radiation.
Ann. Rep. Chem. Soc. 45, 5 (1949)
34. C. J. Danby, B. C. Spall, F. J. Stubbs and C. N. Hinshelwood:
Modes of decomposition of n-pentane.
I. Proc. Roy. Soc. A 223, 421 (1954)
II. ibid. A 223, 429 (1954)
35. O. Diels, K. Alder and S. Beckmann:
Diene synthesis of anthracene. Anthracene formula.
Ann. der Chemie 486, 191 (1931)
36. D. M. Donaldson and N. Miller:
Quantitative studies of radiation induced reactions.
J. Chim. Phys. (in press)
37. C. Dufraise and I. Gillet: A spectrographic
study of photoöxyanthracene.
Compt. Rend. 225, 191 (1947)
38. A. B. F. Duncan and J. P. Howe:
The U. V. absorption of methane.
J. Chem. Phys. 2, 851 (1934)
39. A. G. Flieger:
Use of palladium in gas analysis.
Ind. Eng. Chem. Anal. Ed. 10, 544 (1938)
40. Th. Förster:
Energy migration and fluorescence.
die Naturwiss. 30, 166 (1946)
41. P. F. Forsyth, E. N. Weber and R. H. Schuler: Radia-
tion induced reaction between I₂ and n-heptane.
J. Chem. Phys. 22, 66 (1954)
42. R. H. Fowler and N. B. Slater:
Collision numbers in solution.
Reaction Kinetics, Disc. Farad. Soc. (1937) 81.

43. J. Franck and R. Livingston: Remarks on
intra- and intermigration of excitation energy.
Rev. Mod. Phys. 21, 505 (1949)
44. M. Furst and H. Kallmann: Energy transfer by
collisions in solutions under γ - and U.V. excitation.
Phys. Rev. 94, 503 (1954)
45. M. Furst, H. Kallmann and B. Kramer: Absolute
light emission efficiency of crystalline anthracene.
Phys. Rev. 89, 416 (1953)
46. R. Fürth:
The structure of liquids.
Science Progress 37, 202 (1949)
47. S. Gordon and M. Burton:
Radiation chemistry of pure organic compounds.
Disc. Farad. Soc. 12, 88 (1952)
48. W. Groth: Photochemical studies in the
vacuum U. V., 5. Photolysis of methane.
Z. f. phys. Chem. B 38, 366 (1937)
49. W. Groth and G. Scharfe:
10. Photolysis of propane.
ibid. 2, 142 (1954)
50. F. B. Harrison:
Large area scintillation counters.
Nucleonics 10, No.6, 40 (1952)
51. F. B. Harrison and G. T. Reynolds: Spectral
emission from scintillating solutions and crystals.
Phys. Rev. 79, 732 (1950)
52. A. W. Hay and C. A. Winkler: Mercury photo-
sensitized decomposition of n-butane.
Can. J. Res. B 21, 149 (1943)

53. V. P. Henri, C. R. Maxwell, W. C. White and D. C. Petersen: α -bombardment of 'C₆' hydrocarbons.
J. Phys. Chem. 56, 153 (1952)
54. C. J. Hochanadel and J. A. Ghormley: Calorimetric determination of absorbed γ -ray energy.
J. Chem. Phys. 21, 880 (1953)
55. S. Hustrulid, P. Kusch and J. T. Tate: Dissociation of benzene, pyridine and cyclohexane by electrons.
Phys. Rev. 54, 1037 (1938)
56. P. D. Johnson and F. E. Williams: Efficiency of organic crystals and solutions.
Phys. Rev. 81, 146 (1951)
57. R. N. Jones: U. V. A-spectra of polynuclear hydrocarbons.
J. Am. Chem. Soc. 67, 2127 (1945)
58. H. Kallmann: Scintillation counting with solutions.
Phys. Rev. 78, 621 (1950)
59. H. Kallmann and M. Furst: Fluorescence of solutions bombarded with high energy radiation.
Part I: Phys. Rev. 79, 857 (1950)
60. Part II: *ibid.* 81, 853 (1951)
61. M. F. and H. K. Part III: *ibid.* 85, 816 (1952)
62. H. Kersten and C. H. Dwight: Solarization of glass by soft X-rays.
J. Chem. Phys. 1, 627 (1933)
63. H. B. Klevens and J. R. Platt: U. V. transmission limits of some liquids and solids.
J. Am. Chem. Soc. 69, 3055 (1947)
64. M. B. Koffel and K. A. Lad: Ionization and dissociation of paraffin hydrocarbons by electron impact.
J. Chem Phys. 16, 420 (1948)

65. G. Kortüm and B. Finckh:
Fluorescence of polyatomic molecules.
Z. f. phys. Chem. B 52, 263 (1942)
66. K. Lauer and M. Horio:
A-spectrum of anthracene in various solvents.
Ber. 69 B, 130 (1936)
67. K. Lauer and R. Oda:
Photochemical action (anthracene \rightarrow dianthracene).
Ber. 69 B, 139 (1936)
68. D. J. Leroy: An apparatus for low
temperature fractionation of small gas samples.
Can. J. Chem. 28 B, 492 (1950)
69. M. Levy and M. Szwarc:
"Methyl affinities" of aromatic compounds.
J. Chem. Phys. 22, 1621 (1954)
70. S. H. Liebson:
Decay times of organic phosphors.
Nucleonics 10, No.7, 41 (1953)
71. S. C. Lind: Chemical effects of elec-
trical discharge through gaseous hydrocarbons.
Trans. Am. Electrochem. Soc. 157, 165 (1931)
72. S. C. Lind and D. C. Bardwell: The chemical action
of gaseous ions produced by α 's. IX. Sat'd Hydrocarb.
J. Am. Chem. Soc. 48, 2335 (1926)
73. E. G. Linder:
Electron bombardment of hydrocarbon vapours.
Phys. Rev. 33, 1080 (1929)
74. E. G. Linder:
Bombardment of octane with 120 volt electrons.
J. Chem. Phys. 1, 129 (1933)
75. F. P. Lossing, K. U. Ingold and I. H. S. Henderson:
Free radicals by mass spectrometry.
J. Chem. Phys. 22, 621 (1954)

76. L. E. Lyons:
The electron affinities of some aromatic molecules.
Nature 166, 193 (1950)
77. A. G. Maddock: A contribution
to the discussion on radiolysis of organic liquids.
Disc. Farad. Soc. 12, 124 (1952)
78. J. L. Magee: Charge neutralization
by reaction between positive and negative ions.
Disc. Farad. Soc. 12, 33 (1952)
79. J. L. Magee and M. Burton: Elementary pro-
cesses in radiation chemistry. I. Electron capture.
J. Am. Chem. Soc. 72, 1965 (1950)
80. M. J. Marshal and G. Constabaris: An apparatus
for microanalysis of gas mixtures.
Can. J. Chem. 31, 843 (1953)
81. H. W. Massey:
Gaseous ions and their reactions.
Disc. Farad. Soc. 12, 24 (1952)
82. W. R. McDonell and S. Gordon:
Decomposition of methyl alcohol by ^{60}Co γ -rays.
J. Chem. Phys. 23, 208 (1955)
83. N. Miller: Quantitative studies of radiation
induced reactions. I. Ferrous sulfate oxidation.
J. Chem. Phys. 18, 79 (1950)
84. N. Miller and J. Wilkinson:
Actinometry of ionizing radiation.
Disc. Farad. Soc. 12, 50 (1952)
85. M. M. Moodie and C. Reid:
Energy transfer between complex molecules.
J. Chem. Phys. 19, 986 (1951)
86. M. M. Moodie and C. Reid:
Inter- and intramolecular energy transfer.
J. Chem. Phys. 22, 1126 (1954)

87. R. Passerini and I. A. Ross: Temperature dependence of A-spectrum of naphthalene in solution. *J. Chem. Phys.* 22, 1012 (1954)
88. G. Pirlot: Purification of hexane for U. V. spectroscopy. *Bull. Soc. Chim. Belges* 56, 291 (1947)
89. G. Pirlot: Purification of solvents for spectroscopy. *Bull. Soc. Roy. Sci. Liege* 18, 115 (1949)
90. J. N. Pitts, Jr., D. D. de Ford and G. W. Recktenwald: A microgasanalysis apparatus. *Anal. Chem.* 24, 1566 (1952)
91. J. R. Platt and H. B. Klevens: Spectroscopy of organic molecules in the vacuum U. V. *Rev. Mod. Phys.* 16, 183 (1944)
92. J. R. Platt, H. B. Klevens and W. C. Price: A-spectra of ethylenes and acetylenes in vacuum U.V. *J. Chem. Phys.* 17, 466 (1949)
93. W. C. Price: Advances in spectroscopy of the vacuum U. V. *Rep. Prog. Phys.* XIV, 1 (1951)
94. W. C. Price and A. D. Walsh: U. V. spectra of conjugated dienes. *Proc. Roy. Soc. A* 174, 220 (1940)
95. G. Porter and M. W. Windsor: Triplet states in fluid solvents. *Disc. Farad. Soc.* 17, 178 (1954)
96. W. J. Potts, Jr. A-spectra of olefins in the farther U. V. *J. Chem. Phys.* 23, 65 (1955)
97. A. Prevot-Bernas, A. Chapiro, C. Cousin, Y. Landler and M. Magat: Radiolysis of organic liquids. *Disc. Farad. Soc.* 12, 98 (1952)

98. R. W. Pringle, L. D. Black, B. L. Funt and S. Sobering:
New quenching effect in liquid scintillators.
Phys. Rev. 92, 1582 (1953)
99. W. J. Ramler and M. S. Friedmann:
Scintillation efficiency of anthracene for electrons.
Rev. Sci. Instr. 21, 784 (1950)
100. C. Reid:
Decomposition in liquid scintillation systems.
J. Chem. Phys. 22, 1947 (1954)
101. G. T. Reynolds:
Solid and liquid scintillation counters.
Nucleonics 10, No.7, 46 (1952)
102. L. Roth:
F-spectrum of anthracene by high energy radiation.
Phys. Rev. 75, 983 (1949)
103. D. D. Saksena and L. M. Pant:
Cathode luminescence of crystalline quartz.
J. Chem. Phys. 19, 134 (1951)
104. S. Sambursky and G. Wolfsohn: Fluorescence of
solutions and dielectric properties of solvents.
Phys. Rev. 62, 357 (1942)
105. H. I. Schiff and E. W. R. Steacie: Reaction of
H and D atoms on hydrocarbons.
Can. J. Chem. 29, 1 (1951)
106. C. S. Schoepfle and C. H. Fellows:
Effect of cathode rays on pure hydrocarbons.
Ind. Eng. Chem. 23, 1396 (1931)
107. C. C. Schubert and R. H. Schuler:
Effect of iodine on the radiolysis of hydrocarbons.
J. Chem. Phys. 20, 518 (1952)
108. R. H. Schuler and A. O. Allen:
Radiation chemical studies with cyclotron beams.
J. Am. Chem. Soc. 77, 507 (1955)

109. R. K. Sheline, D. E. Sharp and W. J. Arner:
Color centres in glass.
J. Chem. Phys. 19, 1422 (1951)
110. C. W. Sheppard and R. E. Honig: Chemical effects
of α -particles on methane and n-butane.
J. Phys. Chem. 50, 119 (1946)
111. C. W. Sheppard and R. E. Honig: Theoretical
analysis of chemical effects of α 's and deuterons.
J. Phys. Chem. 50, 144 (1946)
112. L. G. Smith:
Ionization and dissociation of molecules. Methane.
Phys. Rev. 51, 263 (1937)
113. C. P. Snow and C. B. Allsopp:
Some levels of the C=C double bond.
"Free Radicals" Disc. Farad. Soc. (1933) 93.
114. F. W. Spiers: Radiation absorp-
tion and energy loss by primary and secondary particles.
Disc. Farad. Soc. 12, 13 (1952)
115. H. Sponer and E. Teller:
U. V. A-spectra of hydrocarbons.
Rev. Mod. Phys. 13, 75 (1941)
116. J. Stark, W. Steubing, C. J. Enklaar and P. Lipp:
U.V. A-spectra of the resonance bond in hydrocarbons.
Jahrb. d. Rad. u. Elektronik 10, 139 (1913)
117. E. W. R. Steacie and M. Szwarc:
Temperature independent factor of elementary reactions.
J. Chem. Phys. 19, 1309 (1951)
118. D. P. Stevenson:
On the strength of C-C and C-H bonds.
J. Chem. Phys. 10, 291 (1942)
119. D. P. Stevenson: Mass spectrometric
studies. Ionization potentials of butane, isobutane.
J. Am. Chem. Soc. 64, 1588 (1942)

120. D. P. Stevenson: Benzyl-hydrogen
bond energy from electron impact measurements.
J. Chem. Phys. 22, 151 (1954)
121. M. Sudzuki:
Mechanism of bianthracene (i.e. dianth.) formation.
Bull. Chem. Soc. Jap. 18, 146 (1943)
122. R. K. Swank and W. L. Buck:
The scintillation process in plastic solid solutions.
Phys. Rev. 91, 927 (1953)
123. M. Szwarc:
Singlet-triplet energies of aromatic compounds.
J. Chem. Phys. 23, 204 (1955)
124. A. W. Tickner and F. P. Lossing: Measurement
of vapour pressures with a mass spectrometer.
J. Phys. Coll. Chem. 55, 733 (1951)
125. W. R. Trost and E. W. R. Steacie:
Reactions of H atoms with paraffin hydrocarbons.
J. Chem. Phys. 16, 361 (1948)
126. A. F. Trotman-Dickenson:
The reactions of methyl radicals.
Quart. Rev. Chem. Soc. VII, 198 (1953)
127. J. Q. Umberger and V. K. LaMer:
Kinetics of diffusion controlled molecular reactions.
J. Am. Chem. Soc. 67, 1099 (1945)
128. S. I. Weissman:
Intramolecular energy transfer in europium complexes.
J. Chem. Phys. 10, 214 (1942)
129. P. Wagner and A. B. F. Duncan:
A-spectrum of cyclopropane in the vacuum U. V.
J. Chem. Phys. 21, 516 (1953)
130. H. W. Webb and H. A. Messenger:
Phosphorescence in fused quartz.
Phys. Rev. 34, 1463 (1929)

131. J. Weiss: Excitation of optical levels by particles of relatively low energy.
Nature 174, 78 (1954)

Supplementary References

132. H. A. Dewhurst and F. H. Krenz: Oxidation of ferrous sulfate by ^{60}Co γ -rays.
J. Chem. Phys. 17, 1337 (1949)
- 132a. H. A. Dewhurst, A. H. Samuel and J. L. Magee: Radiation chemistry of water: Theoretical survey.
Radiation Res. 1, 62 (1954)
- 132b. H. A. Dewhurst: Oxidation of ferrous sulfate in presence of organic compounds.
J. Chem. Phys. 19, 1329 (1951)
133. J. Hollander, I. Perlman and G. T. Seaborg: Table of Isotopes.
U.C.R.L.-1928 (rev.) Berk. 1952
- 133a. J. I. Hopkins: Electron studies with the anthracene scintillation counter.
Rev. Sci. Instr. 22, 29 (1951)
- 133b. K. J. Ivin and E. W. R. Steacie: Disproportionation of ethyl radicals.
Proc. Roy. Soc. A 208, 25 (1951)
134. F. H. Krenz: Energy transfer in polystyrene-anthracene.
Trans. Farad. Soc. 51, 172 (1955)
135. R. M. Lazo, H. A. Dewhurst and M. Burton: Calorimetric determination of $G(\text{Fe}^{3+})$ for γ -rays.
J. Chem. Phys. 22, 1370 (1954)

136. R. F. Post:
Scintillation decay times of organic phosphors.
Nucleonics 10, No.6, 56 (1952)
- 136a. R. F. Post and L. I. Schiff:
Resolving time of scintillation counters.
Phys. Rev. 80, 1113 (1950)
137. O. Stern and M. Volmer:
On the decay time of fluorescence.
Phys. Z. 20, 183 (1919)
138. M. Szwarc:
Energies of C-C and C-H bonds.
Disc. Farad. Soc. 10, 336 (1951)
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RADIOLYSIS OF LIQUID *n*-HEXANE AND SOLUTIONS OF ANTHRACENE IN *n*-HEXANE

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A STUDY has been made in this laboratory of the radiolysis in vacuum of pure, liquid *n*-hexane and of solutions of anthracene in hexane by γ -rays from a cobalt-60 source. The principal products of the radiolysis of the hexane were hydrogen, methane, ethane and an unsaturated hydrocarbon with approximately the same volatility as *n*-hexane. C_3 - and C_4 -hydrocarbons were also detected, but in amounts which were negligible compared with those of the principal products. A C_6 fraction was never satisfactorily separated from hexane, but did not appear to contain any important product.

Hydrogen, methane, ethane and the unsaturated liquid hydrocarbon were formed in amounts which were directly proportional to the energy absorbed from the γ -rays up to the highest concentrations of products measured (c. 10^{-4} M). The yields, G , in terms of the molecules of products per 100 eV. of γ -ray energy absorbed by the hexane (determined by ferrous sulphate actinometry, using $G_{Fe^{3+}} = 15.5$) were :

$$\begin{array}{ll} G_{H_2} = 4.89 \pm 0.2 & G_{C=C} = 4 \pm 2 \\ G_{CH_4} = 0.41 \pm 0.1 & G_{C_2H_4} = 0.69 \pm 0.1 \end{array}$$

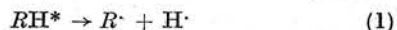
The radiolysis in vacuum of solutions of anthracene in hexane showed that anthracene in concentrations up to 10^{-3} M had no measurable effect upon the yields of hydrogen, methane or ethane, but caused a diminution in the yield of unsaturated products. $G_{C=C}$ decreased with increasing anthracene concentration toward a minimum value of approximately 2. The radiolysis of the solutions was accompanied by 'fading' of the anthracene absorption spectrum. The bands between 300 and 380 $m\mu$ gradually disappeared, and were replaced by a new spectrum between 200 and 280 $m\mu$, superimposed upon the very intense anthracene band at 256 $m\mu$. The new spectrum closely resembled that of dianthracene (Weiss, J., private communication; I am indebted to Dr. Weiss for the absorption spectrum of dianthracene in

ethanol). G_{-A} , the number of anthracene molecules disappearing per 100 eV. of γ -ray energy absorbed by the hexane, was described within the experimental error by the function:

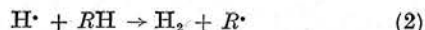
$$G_{-A} = 3.6 \left\{ \frac{3 \times 10^3 M}{1 + 3 \times 10^3 M} \right\}$$

where M is the concentration of anthracene in moles per litre.

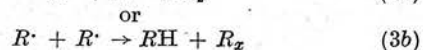
The results above are explained by a simple mechanism resembling that which has been established for the mercury-photosensitized photolysis of paraffin hydrocarbons in the gas phase¹. The principal primary step in the radiolysis of hexane is considered to be



RH^* represents an electronically excited molecule of hexane resulting from primary absorption processes², $R \cdot$ a hexyl radical and $H \cdot$ a hydrogen atom formed by the rupture of a C—H bond in hexane. The rupture may impart considerable kinetic energy to the fragments, particularly to $H \cdot$, which probably reacts immediately with the surrounding hexane:



The hexyl radical must disappear, in the absence of competing reactions, by



R_2 is the dimer, dodecane, and R_x is an unsaturated compound formed by the disproportionation of two hexyl radicals, that is, it is one of several possible isomeric hexenes.

The relatively small amounts of methane and ethane found among the products may result from (a) the primary rupture of a C—C bond in RH , (b) $H \cdot$ atom 'cracking' of hexane³ as an alternative to reaction (2), or (c) dissociation of an excited radical produced in the primary step (1). The methyl or ethyl radicals so formed probably undergo reactions analogous to (2), forming methane and ethane respectively⁴. The reason for the relative unimportance of processes of this type is not apparent.

In solutions of anthracene, reactions (3a) and (3b) must compete with the following reaction:



Here A represents a molecule of anthracene, and $RA \cdot$ is a new free radical resulting from the addition of $R \cdot$ to A , probably at the 9- or 10-position. $RA \cdot$ may react with a second $R \cdot$ to form $RAAR$, or may form a dimer analogous to R_2 , namely, $RAAR$. In either case a stable product is formed having an electronic structure similar to that of dianthracene.

The results summarized above are in substantial agreement with the results of earlier studies of the radiolysis of paraffin hydrocarbons⁵, and the theory successfully describes the earlier results. The yield, G_R , of free hexyl radicals given by the theory is

$$G_R = 2 G_{H_2} + G_{CH_4} + G_{C_2H_6} \\ = 10.9$$

On the same basis, the yield of radicals of all kinds (excluding $H \cdot$ atoms) is at least 12. These values are in agreement with values of G_R ranging from 9.9 to 14.3 recently found by Magat and co-workers⁶ for *n*-heptane, *n*-octane and cyclohexane, using an independent method of measurement.

More recently, Schuler and Allen⁷ have noted that the yield, G_{H_2} , of hydrogen from liquid cyclohexane decomposed by energetic radiation was independent of the linear ion density of the radiation. Such an effect is explained in terms of reactions (1) and (2) above, since the separation between successive ionizations (or excitations) would have to be of molecular dimensions before recombination of atoms could compete effectively with reaction (2).

A complete account of the present work has been submitted for publication in the *Canadian Journal of Chemistry*. I am grateful to Prof. N. Feather for support and encouragement and to Drs. N. Miller and R. A. Back for much help and advice in the course of the work.

¹ Steacie, "Atomic and Free Radical Reactions" (Reinhold, New York, 1947). Bywater and Steacie, *J. Chem. Phys.*, **19**, 172, 319, 326 (1951).

² Dainton, Ann. Rep. Chem. Soc., **45**, 5 (1948). Magee and Burton, *J. Amer. Chem. Soc.*, **72**, 1965 (1950).

³ Schiff and Steacie, *Can. J. Chem.*, **29**, 1 (1951).

⁴ Trotman-Dickenson, *Quart. Rev. Chem. Soc.*, **7**, 198 (1953).

⁵ Lind and Bardwell, *J. Amer. Chem. Soc.*, **48**, 2335 (1926). Schoepfle and Fellows, *Indust. Eng. Chem.*, **23**, 1396 (1931). Honig and Sheppard, *J. Phys. Chem.*, **50**, 119 (1946).

⁶ Prévot-Bernas, Chapiro, Cousin, Landler and Magat, *Disc. Farad. Soc.*, **12**, 98 (1952).

⁷ Schuler and Allen, *J. Amer. Chem. Soc.*, **77**, 507 (1955).