Vol. 63

4.1) that nothing in the present state of the model would lead to the expectation that the  $\bar{\zeta}$  value for "24 Mev." X-rays should exceed that for Co<sup>60</sup>  $\gamma$ -

### TABLE IV

Values of the "Exponent,"  $\overline{\zeta}$ , for Different Radia-

	Scav	Scavenger	
Radiation	CI-	- Br-	
"24 Mev." X-rays	0.38	0.38	
$\mathrm{Co}^{60} - \gamma$	. 34	.32	
50 kev. max. X-rays	.26	.26	
3.4 Mev. $\alpha$	. 15	. 15	

#### Conclusion

In many respects the data for effect of scavenger in the radiolysis of water show results in agreement with the Ganguly-Magee and Magee treatment of the expanding-spur theory. However, more detailed quantitative examination of the results show curious discrepancies which will ultimately require some refinement of the mode and which may reveal some presently unexpected features of the mechanism of the radiolysis of liquid water.

It appears clear that both ions and excited molecules contribute to free-radical formation in the cases studied but that some reverse reaction of free radicals occurs so rapidly that it is inaccessible to the effect of scavenger.

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# **RADIATION CHEMICAL PROCESSES IN RIGID SOLUTIONS**

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Gamma radiolysis of rigid solutions of aromatic molecules in paraffin solution at 77°K. results in the formation of aromatic radicals which have been trapped and identified by means of their electronic absorption spectra. Studies of the radicals which result from the radiolysis of toluene and a number of its derivatives show that although the primary fission processes are very similar to those which follow irradiation at 2537 Å, there are also significant differences. G-values of formation of triphenylmethyl from solutions of triphenylmethane have been determined and it is shown that dissociation of the solute is brought about principally by energy transferred from the solvent and that the efficiency of this transfer is 800 l. solvent/mole solute.

The absorption of ionizing radiations is an unspecific process and most of the energy taken up by a dilute solution is absorbed by the solvent. The matrix isolation technique therefore appears less promising for the study of primary radiation chemical processes than for photochemical processes since, in the former case, the trapped primary products which are observed might be expected to arise principally from the matrix rather than from the solute. For this reason, although studies of the free radicals which result from the photochemical dissociation of a solute in a dilute rigid solution are of great value in the elucidation of primary photochemical processes<sup>1-3</sup> most radiation chemical studies using the trapped radical technique have been concerned with pure substances.<sup>4,5</sup>

A system which has proved particularly appropriate for the study of primary photochemical processes is one in which an aromatic molecule, especially toluene or one of its derivatives, is dissociated by ultraviolet irradiation in dilute solutions at low temperatures. Most of the benzyl type radicals which result from such dissociations have

G. N. Lewis and D. Lipkin, J. Am. Chem. Soc., 64, 2801 (1942).
 I. Norman and G. Porter, Proc. Roy. Soc. (London), A230, 399 (1955).

(3) G. Porter and E. E. Strachan, Trans. Faraday Soc., 54, 1595 (1958).

(4) C. F. Luck and W. Gordy, J. Am. Chem. Soc., 78, 3240 (1956).
(5) M. S. Matheson and B. Smaller, J. Chem. Phys., 23, 521 (1955).

been identified spectroscopically and the main features of the primary photochemical dissociation at the  $\beta$ -bond have been elucidated.<sup>3</sup> In the present work we have extended this type of study to the primary processes of radiation chemical dissociation. Contrary to the considerations of the last paragraph we have found that the species which are trapped and observed under these conditions are few in number and remarkably specific. It appears that energy absorbed by the solvent results in dissociation of the solute, even when the latter is in concentrations as low as  $10^{-3}$  M and when the solvent is quite rigid. Further, of the many primary products of solute dissociation which are energetically possible, only one is observed in most cases.

### Experimental

The basic experimental technique was that of Norman and Porter<sup>2</sup> except that the ultraviolet source was replaced by one for  $\gamma$ -irradiation.

A quartz cell of 12.5 mm. path length was used to contain the solutions which were always outgassed before freezing in liquid nitrogen. The cell could be clamped rigidly in a fixed position in a large Dewar flask of liquid nitrogen which was placed in front of a Co-60 $\gamma$ -ray source of approximately 70 Curie. Dose rates of up to 2.6  $\times$  10<sup>4</sup> rad./hr. could be obtained and were measured by means of the standard ferrous sulfate dosimeter.<sup>6</sup> After irradiation, the cell containing

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<sup>(6)</sup> G. Weiss, "Peaceful Uses of Atomic Energy," 14, 179, United Nations (1956).

the frozen solution was transferred to a Dewar vessel containing liquid nitrogen, the design of which is shown in Fig. 1. It is made up of several easily replaceable parts and has a number of advantages over the original all quartz spectroscopy Dewar of Norman and Porter.

Spectra were recorded using a Hilger E484 spectrograph and Selochrome plates in conjunction with either a tungsten lamp or a hydrogen discharge lamp. For the quantitative work on triphenylmethane a Unicam SP500 spectrophotometer, which had been modified to take a pair of spectroscopic Dewars in place of the normal quartz cells, was used. Super purity quartz, which does not discolor when irradiated, eventually was used for the cells. In earlier runs, where the super purity quartz could not be used, correction for the quartz absorption was applied and any discoloration was removed by heating the cell at the completion of each experiment.

The solvents used to form glasses were E.P.A. (ether, isopentane and ethanol in the proportions 5:5:2 by volume) and M.P. (methylcyclohexane and isopentane in the proportions 2:3 by volume). They were carefully purified and dried.<sup>2</sup> Pure samples of a number of solutes used in similar photochemical work<sup>3</sup> were supplied by Dr. E. Strachan, namely benzhydrol, benzyl chloride, benzylamine, benzo-trichloride, diphenylmethane, triphenylmethane, t-butylbenzene and isopropylbenzene. Ethylbenzene was purified by the method of Vogel<sup>7</sup> and other solutes by fractional distillation or recrystallization.

### Results

Preliminary Observations.-Irradiation of the pure solvents E.P.A. and M.P. at  $-196^{\circ}$ , with doses similar to those used in the later work on solutions (4  $\times$  10<sup>5</sup> rad.), produced no permanent change which could be detected by ultraviolet spectroscopic or chromatographic analysis of the liquid after warming to room temperature. The rigid E.P.A. glass, after irradiation, showed an intense absorption throughout the visible and ultraviolet region which remained as long as the glass was held at  $-196^{\circ}$ . The glass was violet in color after short irradiations and became guite opaque in a 1 cm. path after a dose of  $10^5$  rad. The color disappeared completely as the temperature of the glass was raised to softening point. The absorption spectrum extended from 7000 A. to shorter wave lengths and may arise from "trapped electrons" or from radicals such as CH<sub>3</sub>CHOH.<sup>8</sup> The E.P.A. glass is clearly unsuitable for the ultraviolet spectroscopic study of  $\gamma$ -irradiated solutions.

The pure hydrocarbon M.P. glass showed no such effect on irradiation at  $-196^{\circ}$  and remained quite transparent throughout the visible and quartz ultraviolet region of the spectrum after a dose of  $4 \times 10^5$  rad. It was therefore used for all subsequent investigations.

Irradiation of solutions of various aromatic molecules in M.P. glass at  $-196^{\circ}$ , followed by spectroscopic investigation at the same temperature, showed characteristic sharp banded absorption spectra which disappeared when the glass was brought to room temperature and which closely resembled the spectra of benzyl and its derivatives, found after photolysis of the same compounds. The spectra were, in most cases, more intense than the strongest absorptions so far obtained in photochemical studies of rigid solutions, using the same path length and were comparatively free from other diffuse absorption spectra such as those of hexa-

(7) A. I. Vogel, J. Chem. Soc., 607 (1948).

(8) M. C. R. Symons and M. Townsend, J. Chem. Phys., 25, 1299 (1956).



Fig. 1.—G = quartz/Pyrex graded seal;  $J_1, J_2$  = standard joints; Q = quartz windows; T = vacuum tap. Optical dewar vessel used for ultraviolet absorption spectroscopy.

triene derivatives. The spectra of these solutions showed no measurable permanent change after warming, except for some small continuous absorption at shorter wave lengths in a few cases which was, however, generally much smaller than in the corresponding photochemical experiment, in spite of the greater concentration of radicals originally present in the irradiated glass.

On warming the glassy solutions after irradiation. the rise in temperature was accompanied by an emission of light, readily visible in subdued daylight. The glow was quite separate and readily distinguishable from that of quartz, being more intense, of different color and observed over a different temperature range. Furthermore, the warmup glow of the solutions varied in color from one solute to another. For example the luminescences of solutions of toluene, benzyl chloride and ethylbenzene solutions were green, whilst those of tbutylbenzene and diphenylmethane were pale yellow. The warm-up glows must therefore involve the solute molecule or its products but their origin is not yet known. There is no correlation with the observed radical spectra since not only solutions of benzene and chlorobenzene but also the pure M.P. solvent showed a luminescence after irradiation. On the other hand no phosphorescence of comparable intensity was observed on warming irradiated E.P.A. glass. Attempts to record the spectrum of the warm-up glow were not successful.

Identification of the Absorption Spectra and Dissociation Processes.—As already mentioned, the solutions investigated showed absorption spectra which closely resembled those obtained after ultraviolet irradiation under the same conditions. There were, however, significant differences. For example rigid carbon disulfide solutions, which yield the CS radical after short exposure to ultraviolet light, showed no such spectrum after  $\gamma$ -irradiation, although some changes took place as evidenced by a weak continuous absorption, a green color of the solution which disappeared on warming, and a smell of garlic in the products. Again, rigid solutions of



Fig. 2.—Radical spectra resulting from the radiolysis of aromatic molecules at 77°K. In each case the first spectrum is recorded before and the second after irradiation of the rigid solution.

benzene which, when subjected to ultraviolet irradiation, yield intense absorption bands attributed to hexatriene, showed no such spectrum after  $\gamma$ -irradiation.

On the other hand toluene and its derivatives gave strong banded absorption spectra when irradiated with  $\gamma$ -rays in M.P. solution at  $-196^{\circ}$ . Their assignments and relationships to spectra observed under similar conditions after photolysis provide information concerning the primary processes taking place. Three classes of compound have been investigated in which the hydrogens of the methyl group of toluene are successively substituted by phenyl, chlorine and methyl, respectively. Typical spectrographic records of the glasses before and after irradiation are shown in Fig. 2.

**Phenylmethanes.**—These compounds, and the related molecule benzhydrol, gave absorption spectra whose main bands were identical, within the limits of measurement, with those obtained from the photochemical dissociation of the same compounds in M.P. glass. The identity was confirmed by direct comparison of the plates and, in the case of triphenylmethane, by spectrophotometric measurements. Wave lengths of band maxima, with approximate relative intensities on a scale of ten, are given in Table I. The measurements were made independently on each plate and the error in wave length is estimated at about  $\pm$  5 Å. for the sharp bands and  $\pm$  10 Å. for the broader bands.

The assignments of the main absorption bands to benzyl, diphenylmethyl and triphenylmethyl can be made with confidence in view of the evidence already put forward in support of those assignments by Porter and Strachan.<sup>3</sup> The assignment of the radical from benzhydrol to diphenylmethyl cannot however be considered definite until the spectrum of the semipinacone is known. Some of the weaker unidentified bands may also belong to the same radicals since the absorption was stronger in the  $\gamma$ -ray work and the weakest bands would have been below the limit of detection in the photochemical experiments. In at least one case, that of toluene, there are bands at longer wave lengths which are absent after photochemical dissociation and which cannot be attributed to the benzyl radical.

Chlorine Substituted Derivatives.—The radical spectra from the three compounds of this class, as well as from toluene itself, were very similar, consisting principally of one strong band and a weaker doublet at shorter wave lengths. The spectra derived from benzal chloride and benzotrichloride were identical within the accuracy to which plates could be compared. The spectrum derived from benzyl chloride was definitely different from these and from that of benzyl. These facts, and comparison with the wave lengths of the radical spectra previously measured, lead to the assignments of radicals formed which are given in Table II.

There were very few additional bands from the chlorinated molecules but a weak band at 3179 Å. obtained from benzyl chloride may indicate that a small amount of benzyl also is formed.

Comparison with the photochemical dissociation processes of these molecules reveals that, unlike the previous class of phenylmethanes, the chlorine compounds show differences in their behavior to  $\gamma$  and to ultraviolet irradiation. The clearest example of this difference is found in benzyl chloride which with 2537 Å. irradiation, yields benzyl whilst, with  $\gamma$ -rays, little or no benzyl is found and C<sub>6</sub>H<sub>5</sub>CHCl is the main product observed. Only in toluene and benzotrichloride are the products the same with both kinds of irradiation. The  $\beta$ -bond fission processes of these molecules therefore depend on the type of irradiation. With  $\gamma$ -irradiation the H atom separates in preference to the chlorine atom whilst the converse is true with ultraviolet irradiation.

Ethyl-, Isopropyl- and t-Butylbenzenes.—The band maxima of radicals derived from these hydrocarbons, with their probable assignments, are given in Table III. These spectra were weaker and more diffuse and there were also some relatively intense additional bands so that the assignments are less definite than in the two previous classes of compound. Again, however, the spectra from isopropyl- and t-butylbenzene were quite different

		TABLE I			
	Band max. assigned			Unassigned band	
Molecule	to radical λ (Å.)		Radical	max. λ (Å.)	
$C_6H_bCH_3$	3179(10)  3071(3)	3044(3)	$C_{6}H_{5}CH_{2}$	3339(4)	3242(2)
$(C_6H_a)_2CH_2$	3365(10)  3314(2)		$(C_6H_5)_2CH$	3270(2)	3237(2)
				3121(6)	3015(2)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOH	3377(10) 3333(2)		(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH	3252(1)	3141 (6)
(-00)2	( (,		( 00)2	3067(1)	. ,
$(C_6H_5)_3CH$	3425(10) 3293(2)		$(C_6H_5)_3C$	2790-2800 (6)	
		TABLE II			
	Band max. assigned			Unassigned band	
Molecule	to radical λ (Å.)		Radical	max. λ (Å.)	
$C_{6}H_{5}CH_{3}$	3179 (10) 3071 (3)	3044(3)	$C_6H_5CH_2$	3339(4)	3242(2)
$C_6H_5CH_2Cl$	3225 (10) 3112 (3)	3075(3)	$C_6H_bCHCl$	3179(2)	2994(1)
				2959(1)	
$C_6H_5CHCl_2$	3243 (10) 3131 (3)	3105(3)	$C_6H_5CCl_2$	3334(1)	
$C_6H_5CCl_3$	3243 (10) 3137 (3)	3101 (3)	$C_6H_5CCl_2$		
		TABLE III			
	Band max. assigned			Unassigned band	
Molecule	to radical λ (Å.)		Radical	max. λ (Å.)	
$\mathrm{C_6H_5CH_2CH_3}$	3236(10) 3163(2)	3098(2)	$C_6H_5CHCH_3$	3355(2)	3328(6)
	3078(4)				
$C_6H_5CH(CH_3)_2$	3245(10)		$\mathrm{C_6H_5C(CH_3)_2}$	3439(4)	3325 (10)
$C_6H_5C(CH_3)_3$	· · · ·			3313 (10)	3228(7)

from benzyl derived from toluene whilst the radical spectrum derived from ethylbenzene was unique and showed no bands of benzyl. The corresponding spectra obtained after ultraviolet irradiation of these substances are also relatively weak and have been measured in E.P.A. solution only, but it seems probable that the principal processes of  $\beta$ -bond fission are the same with both types of irradiation and that the hydrogen atom separates in preference to the methyl group.

All the  $\beta$ -bond fission processes discussed and given in Tables I, II and III are summarized by the following statement. The  $\gamma$ -irradiation of solutions of toluene and its derivatives in rigid M.P. solution leads to fission of a  $\beta$ -bond, and, when more than one type of  $\beta$ -bond is present in such a molecule, the probability of separation of a hydrogen atom is greater than that of CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> or a chlorine atom.

This is the same as was found for ultraviolet irradiation under similar conditions with the important exception that the order of probabilities of fission of C–H and C–Cl bonds is reversed.

G-Values and their Concentration Dependence. —The G-values of radical formation have been studied for the formation of triphenylmethyl from triphenylmethane. This particular case was chosen first because its photochemical quantum yield has been determined under similar conditions and second because triphenylmethyl is the only one of the radicals which we have studied whose absolute extinction coefficient is known, having been measured at 77°K. by Chu and Weissman.<sup>9</sup>

Solutions of triphenylmethyl in M.P. were irradiated for 16 hours under identical conditions at  $-196^{\circ}$  and the concentration of the triphenylmethyl radical formed was measured in the modified Unicam spectrophotometer, the comparison cell containing an identical solution which had not been irradiated. The dose rate in these runs, deter-

(9) T. L. Chu and S. I. Weissman, J. Chem. Phys., 22, 21 (1954).

mined by standard ferrous sulfate dosimetry, was  $2.6 \times 10^4$  rad./hr. and the total dose was  $4.2 \times 10^5$  rad After small corrections for the different absorption coefficients of the solutions this leads to a *G*-value of triphenylmethyl formation from a 5.33  $\times 10^{-3}$  molar solution of triphenylmethane of 0.17 radicals/100 e.v.

The G-value of 0.17 is calculated per 100 e.v. of energy absorbed by the solution. Most of this energy is absorbed in the first place by the solvent, the proportion absorbed by the solute, calculated on the basis of absorption of energy by Compton scattering, is equal to the ratio of electron densities in solute and solvent and is  $1.7 \times 10^{-8}$  for a 5.33  $\times 10^{-8} M$  solution. The energy used in the dissociation of the solute must therefore be derived mainly from energy originally absorbed by the solvent.

Further evidence that energy transferred from the solvent is mainly responsible for dissociation of the solute was obtained from studies of the radical yield as a function of solute concentration. Owing to the fact that the  $\gamma$ -ray source is no longer available to us we have not yet been able to obtain as complete data on this important factor as we would wish. The data so far available are, however, sufficient to show that the radical yields are not proportional to solute concentration, as would be the case if only energy absorbed by the solute were utilized for dissociation, but tend to a limiting value at higher concentrations, indicating that the process of energy transfer from the solvent is approaching unit efficiency. The radical yields, as a function of solute concentration, are shown in Fig. 3.

### Discussion

There is much previous evidence to show that radiation chemical change in a solute may be brought about as a result of energy originally absorbed by the solvent. The particular significance of studies of such effects in rigid solutions,



Fig. 3.—Variation of triphenylmethyl radical concentration with triphenylmethane concentration at constant dose.

apart from the directness of the observation of the intermediate products, lies in the fact that processes involving molecular diffusion are eliminated.

The energy absorbed by the matrix or solvent M appears as potential energy of separation of ions  $M^+$  and electrons and of free radicals, as electronic excitation of matrix molecules and as residual kinetic energy of these products, particularly as sub-excitation electrons.<sup>10</sup> At least one of these forms of energy must be transferred, in the present experiments, to the solute molecules which are in relatively low concentration in the rigid solvent. We shall describe the energetic product or products whose energy is transferred to the solute by the symbol  $X^x$  and all other products derived from irradiation of the solvent by P

$$\begin{array}{ccc} \mathbf{M} & & & \mathbf{M} \\ M & & & \mathbf{M} \\ M & & & \mathbf{P} \end{array} \qquad \begin{array}{c} k_1 \\ k_2 \end{array}$$

Now  $X^x$  may lose its energy by the matrix or may transfer it in some way to the solute A

$$X^{x} + M = X + M$$
 or other products  $k_{3}$   
 $X^{x} + A = X + A^{x}$   $k_{4}$ 

and  $A^x$  may dissociate to give the observed radical R or undergo some other change not forming R

A×

$$A^{x} = R \qquad k_{5}$$
  
= A or other products  $k_{6}$ 

Finally, in more concentrated solutions, radicals may be formed by direct irradiation of the solute

$$A \longrightarrow R k$$

Steady-state treatment of this scheme leads to the following expression for the concentration [R] of radicals formed in unit time

$$[\mathbf{R}] = \frac{k_1 k_4 k_5 [\mathbf{A}] [\mathbf{M}]}{(k_5 + k_6) (k_3 [\mathbf{M}] + k_4 [\mathbf{A}])} + k_7 [\mathbf{A}]$$

when  $k_1$  and  $k_7$  are the rates of reactions 1 and 7 for unit concentrations of M and A, respectively.

In dilute solution  $k_7[A] < < k_1[M]$  and the second

(10) R. L. Platzman, Radiation Research, 2, 1 (1955).

term in this expression is negligibly small. Then

$$\frac{1}{[\mathbf{R}]} = \frac{k_3}{k_1 k_4 [\mathbf{A}]} + \frac{k_3 k_6}{k_1 k_4 k_5 [\mathbf{A}]} + \frac{1}{k_1 [\mathbf{M}]} + \frac{k_6}{k_1 k_6 [\mathbf{M}]}$$

A plot of 1/[R] versus 1/[A] should therefore be linear for dilute solutions and

$$\frac{\text{Intercept}}{\text{Slope}} = \frac{k_4}{k_3[\text{M}]} \text{ l. mole}^{-1} = P_0$$

 $P_0$  is the energy transfer probability for unit solute concentration.

The data of Fig. 3. are in accord with this relation and lead to the value

 $P_0 = 830 \text{ l. mole}^{-1} = 7000 \text{ molecules solvent/molecule solute}$ *i.e.*, the probability of transfer of the energy to a molecule of triphenylmethane is approximately 7000 times greater than that of its degradation by a solvent molecule.

In addition to the efficiency of the energy transfer process from  $X^x$  to A there are indications that the intermediate  $X^x$  must be formed efficiently in process 1 and is a major product of the primary processes. The quantum yields of photochemical dissociation of aromatic hydrocarbons are usually small and the quantum yield of the particular process under consideration, viz., the dissociation of triphenylmethane to triphenylmethyl radicals in a rigid glass at  $-196^{\circ}$ , has been measured and found to be 0.01 at 2537 Å.<sup>3</sup> If A<sup>x</sup> in our present scheme were identical with the excited triphenylmethane formed by 2537 Å. irradiation, i.e., the lowest excited singlet state, it would follow that the G-value of formation of  $A^x$  at high concentrations of A was  $\sim 20$  and that since the excitation potential of the first singlet state in triphenylmethane is 4.6 e.v.,<sup>11</sup> more than half the total energy absorbed by the solution is used in excitation of the solute. In fact A<sup>x</sup> probably contains considerably more energy than the molecule excited by 2537 Å. light and may therefore have a somewhat greater dissociation probability.

Although molecular diffusion processes are eliminated in the present experiments several alternative explanations of the energy transfer mechanism are possible. Discussion of these will be postponed until further data on the concentration dependence of radical yield become available. The results of this present investigation show that studies of trapped radicals formed by radiolysis of dilute rigid solutions provide a promising approach to the study of primary radiation chemical processes and energy transfer.

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(11) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.