that region can be seen, namely 990 cm.$^{-1}$ and 1083 cm.$^{-1}$. The 958 cm.$^{-1}$ line had been unassigned. The 990 cm.$^{-1}$ band is assigned to the out-of-plane twisting motion.

2. The weak line at 889 cm.$^{-1}$ which had been assigned to the out-of-plane twisting motion seems actually to be slightly lower, about 863 cm.$^{-1}$. It is now unassigned.
3. The weak broad line at 411 cm.$^{-1}$ was resolved into two lines at 395 cm.$^{-1}$ and 444 cm.$^{-1}$. It had been assigned to the A_g center and terminal angle bending modes. The 444 cm.$^{-1}$ line is assigned to the terminal angle bending mode, and the 395 cm.$^{-1}$ line is reassigned to the B_g skeletal bending mode.
4. The line at 347 cm.$^{-1}$ is polarized and cannot be the B_g mode as previously assigned. It therefore is assigned to the A_g center angle bending vibration.
5. The assignments of the lines at 1187 cm.$^{-1}$ and 1238 cm.$^{-1}$ were switched as noted in the text.

At the same time the infrared spectra of the liquid and vapor were taken on a Perkin–Elmer Model 421 spectrometer. No essential differences from the previously reported work[3b] were noted. Table IV gives the complete assignment of *trans*-hexatriene utilizing the remeasured infrared and Raman spectra and the changed Raman assignments.

Special thanks go to Dr. Derek Steele and Mr. Francis Powell of the University of Maryland for assistance in this work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Ionic and Free Radical Processes in the Radiolysis and Sensitized Photolysis of Benzene Solutions[1]

BY WILLIAM VAN DUSEN, JR., AND WILLIAM H. HAMILL

RECEIVED JANUARY 26, 1962

The gamma radiolysis of various binary liquid mixtures, mostly with benzene as one component, has been observed over the complete range of composition, for the primary purpose of correlating chemical effects with dissociative electron attachment and also to obtain evidence for positive charge exchange. Parallel measurements of benzene photosensitized decomposition at 2537 Å. were also performed to establish the quantum efficiency of energy transfer. Systems included various alkyl chlorides, bromides and iodides as well as chloroform, carbon tetrachloride, phenylacetyl chloride and benzyl acetate, all with benzene, as well as chlorobenzene–chloroform and methyl iodide–carbon tetrachloride. In conjunction with other evidence (P. S. Rao, *et al.*, *J. Am. Chem. Soc.*, **84**, 500 (1962)) the results support the hypothesis that dissociative electron attachment is an important primary process in the radiation chemistry of liquid systems with components which can readily attach slow electrons in the low pressure gas. Attachment can produce a large sensitized radiolysis of a minor component of the system. Positive charge transfer is indicated by a marked depression of G(product) from carbon tetrachloride, chloroform or benzyl acetate for small additions of benzene. It is concluded that evidence from luminescence of solutes demonstrates the very minor role in radiation chemistry of energy transfer from singlet states.

Introduction

The work reported here extends previous studies[2-4] which are concerned with distinguishing between ionic and other processes. It also attempts to assess the contributions of excited states and the corresponding energy transfer, exclusive of ionic processes.

These studies are concerned, in particular, with chemical consequences of dissociative electron attachment. Organic halides are expected to be suitable for this purpose, if the results of mass spectrometry may be used as a tentative guide. If chemical effects attributable to electron attachment can be demonstrated, it would also be desirable to measure their relative reactivities with various solutes and the approximate number of molecules they encounter before recapture.

Chemical evidence alone cannot ordinarily furnish conclusive evidence for dissociative electron attachment since similar dissociative processes presumably occur concurrently by other routes. The ultimate stable products of ionic reactions are largely those which arise subsequent to charge neutralization, *i.e.*, they are products of atom and free radical reactions. It is also particularly important to distinguish between the reactions of electrons and of H-atoms. By examining a sufficient number of solutions in benzene as a common component and by choosing for solutes, as far as possible, molecular species of characterizable reactivity toward electrons, we hope to accumulate sufficient evidence to demonstrate our working hypothesis, *viz.*, that ionic processes play an important role in radiation chemistry.

It appeared desirable to maintain one common hydrocarbon component throughout this work. Because of the considerable G(H) for cyclohexane and other alkanes, the use of benzene was indicated because of its reported relative stability under gamma radiation.[5,6] Some of the systems studied in this work have been investigated previously by Magat, Bouby and Chapiro,[7-9] using diphenylpicryl-

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(1) This article is based on a thesis submitted by W. Van Dusen, Jr., in partial fulfillment of the requirements for the Ph.D. degree in the University of Notre Dame, June, 1961. The Radiation Laboratory is operated under Atomic Energy Commission contract AT (11-1)-38.

(2) R. R. Williams, Jr., and W. H. Hamill, *Radiation Research*, **1**, 158 (1954).

(3) H. A. Gillis, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 17 (1961).

(4) L. J. Forrestal and W. H. Hamill, *ibid.*, **83**, 1535 (1961).

(5) S. Gordon and M. Burton, *Discussions Faraday Soc.*, **12**, 88 (1952).

(6) S. Gordon, A. Van Dyken and T. Doumani, *J. Phys. Chem.*, **62**, 20 (1958).

(7) M. Magat, L. Bouby, A. Chapiro and N. Gislon, *Z. Elektrochem.*, **62**, 307 (1958).

(8) L. Bouby and A. Chapiro, *J. Chim. Phys.*, **52**, 645 (1955).

hydrazyl to measure G(radicals). In this work, one or more radiolytic products arising from the added reagent have been measured.

Experimental

Materials.—Benzene, Eastman research grade, was purified by three crystallizations. Analysis by gas–liquid (g.l.) chromatography showed 0.1% impurity initially, none after purification.

Methyl and ethyl iodides of reagent grade were purified as described[4]; refractive indexes were $n^{20}D$ 1.5307 and $n^{20}D$ 1.5136, respectively.

Chloroform of C.P. grade was further purified,[4] $n^{20}D$ 1.4580. No impurities were detected by g.l. chromatography.

Ethyl bromide and carbon tetrachloride of reagent grade and Eastman white label toluene and benzyl acetate were used as received since no impurity was detected by g.l. chromatography.

All propyl halides, Eastman white label, were purified by distillation.[4]

Methyl and ethyl chlorides from the Matheson Co., with stated purity of 99.5 and 99.99 mole %, were distilled trap-to-trap several times. No impurities appeared by mass analysis. Iodine was resublimed.

Triphenylmethane, Eastman white label, was used as received.

Naphthalene, purified for scintillation measurements, was kindly supplied by Dr. J. Kropp.

Methods.—Pyrex cells 16 mm. o.d. × 14 cm. equipped with breakseals were used for gamma radiolysis. A Vycor cell 13 mm. o.d. × 14 cm. was used for photolysis. Liquid samples of 10 ml. were outgassed by repeated freeze-pump-thaw cycles followed by trap-to-trap distillation while evacuating. Iodine and triphenylmethane, when used, were introduced directly into the cell before sealing to the vacuum line and were held a $-70°$ during evacuation. Benzyl acetate was added similarly and evacuated first at room temperature and finally at *ca.* 50°. Filled, evacuated cells were finally sealed.

Radiolyses were performed with a Co^{60} source previously described,[10] which was calibrated by Fricke dosimetry. Dose rates varied from 1.9×10^{17} to 1.2×10^{17} e.v. ml.$^{-1}$ min.$^{-1}$ over the period of these experiments. The average dose was 2×10^{20} e.v.

Apparatus and procedures for photolysis at 2537 Å. were substantially those previously described.[11] The light flux through 10 ml. samples was 5.4×10^{19} quanta min.$^{-1}$. Extinction coefficients of the substances used in mixtures were measured at 2537 Å. using a model 14 Cary or a model D. U. Beckman spectrophotometer. Values obtained for the materials used were: benzene, 89.8; ethyl iodide 427.5; carbon tetrachloride 0.49; chloroform 0.02; benzyl acetate 126.3; phenylacetyl chloride 484 l. mole^{-1} cm.$^{-1}$.

Product Gas Recovery.—Quantitative recovery of very small gas samples from liquids (*ca.* 10^{-6} mole/ml.) is not feasible by customary freeze-pump-thaw cycles. The use of a small still in the vacuum line is faster and much more efficient. The microstill used in this work comprised a 50 ml. r.b. boiling flask, a 1.0 cm. o.d. × 50 cm. column with a 6 mm. concentric glass rod. The column head was 1.5 cm. o.d. × 8 cm. with a re-entrant cold finger 1.0 cm. o.d. × 6 cm., connected at its upper end through stopcock A to 25 cm. of 8 mm. o.d. tubing in the shape of a U-trap and provided with two 2 mm. stopcocks, and leading through stopcock B to a Saunders–Taylor gas collecting device. The U-trap was cooled to retain most of the solvent and negligible gaseous product.

In operation, the radiation cell was sealed to the 50 ml. distilling flask, the still was evacuated, stopcock A closed, and the sample transferred to the still through a breakoff seal. The cold finger was cooled by a copper rod immersed in toluene at the bottom and suitably cooled (by Dry Ice) at the top. Pot temperature was chosen to maintain a vapor pressure of 10–20 cm. After 5 min. at total reflux, stopcock A was opened momentarily, and accumulated gas and some vapor in the still head was collected. A cold bath was placed around the U-trap and stopcock B opened, the gas expanded into the Saunders–Taylor apparatus and P–V–T measured. This cycle was repeated until collection was substantially completed. Gaseous samples were analyzed on a CEC 21–103A mass spectrometer. High boiling products, when reported, were measured by g.l. chromatography.

Hydrogen halide was measured by titrating aqueous extracts of irradiated samples with 0.01 N sodium hydroxide, CO_2-free, with brom cresol purple. Iodine was titrated against 0.01 N sodium thiosulfate using potassium iodide as indicator.

Results

Radiolysis.—We find average values of $G(H_2) = 0.038$ and $G(C_2H_2) = 0.018$ for benzene, unaffected by 0.05 M iodine or 0.05 M triphenylmethane. Also, $G(C_6H_5I) = 0.27$ in 0.05 M iodine, which has not been reported previously, while G(biphenyl) = 0.08 is unaltered. With 0.02–0.05 M iodine in water-saturated benzene, $G(HI) = 1.35$ as the average of 3 runs, somewhat larger than reported.[12] Other yields agree with prior reports.[6,13] Values of G(radicals) of 1.8 and 0.8 have been reported,[14,15] but these measurements were not considered entirely free of possible complicating effects.

Benzene–Methyl Iodide.—The compositions in this and other series are expressed in electron per cent., hereafter $e\%$. All solutions in this series (see Fig. 1) were 0.03 M in hydrogen iodide and $G(CH_4)$ is the measure of $G(CH_3)$. This technique was tested by one run with 19.7 $e\%$ methyl iodide-d_3 in benzene containing 0.03 M hydrogen iodide for which $G(CD_3H)$ was 3.68. For a parallel run with 18.9 $e\%$ methyl iodide, $G(CH_4)$ was 3.80. Hydrogen yields are not reported because hydrogen iodide reacts with mercury to liberate hydrogen and measurements of hydrogen are unreliable. For all these solutions $(CH_3I) >> (HI)$ and at the end of any run $(HI) >> (I_2)$. In one run (95 $e\%$ CH_3I) the addition of 0.15 M naphthalene did not alter $G(CH_4)$. The results in Fig. 1 and several others to be described, exhibit a marked indirect effect, *i.e.*, the yield of product increases much more rapidly than a linear dependence with added reagent. Addition of triphenylmethane as a free radical scavenger does not affect $G(HI)$ of these solutions. Samples were extracted with water immediately following irradiation, but the results must still be considered to represent minimal values of $G(HI)$. In one anhydrous sample containing 34 $e\%$ of methyl iodide, g.l. chromatographic analysis showed a very small yield of toluene.

Benzene–Ethyl Iodide.—The results in Figs. 2, 3 refer to mixtures with no minor solutes present. Ethane and ethylene, in nearly constant ratio 1:1.2 are the major gaseous products; yields of hydrogen iodide were not measured. The results in Figs. 2, 3 are expressed only as the combined $G(C_2H_4) + G(C_2H_6)$ since this is a measure of the yield of C–I bonds broken.[3] Parallel runs at 9, 27 and 94 $e\%$ of ethyl iodide in benzene and in toluene (Fig. 2) gave substantially the same yields

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(9) L. Bouby, Ph.D. thesis, Université de Paris (1957).

(10) M. Burton, J. A. Ghormley and C. Hochanadel, *Nucleonics*, **13**, 74 (1955).

(11) R. F. Pottie, W. H. Hamill and R. R. Williams, Jr., *J. Am. Chem. Soc.*, **80**, 4224 (1958).

(12) G. Meshitsuka and M. Burton, *Radiation Research*, **10**, 449 (1959).

(13) R. Schuler, *J. Phys. Chem.*, **60**, 381 (1956).

(14) A. Prevost-Bernas, A. Chapiro, C. Cousin, Y. Landler and M. Magat, *Discussions Faraday Soc.*, **12**, 98 (1952).

(15) W. Wild, *ibid.*, **12**, 127 (1952).

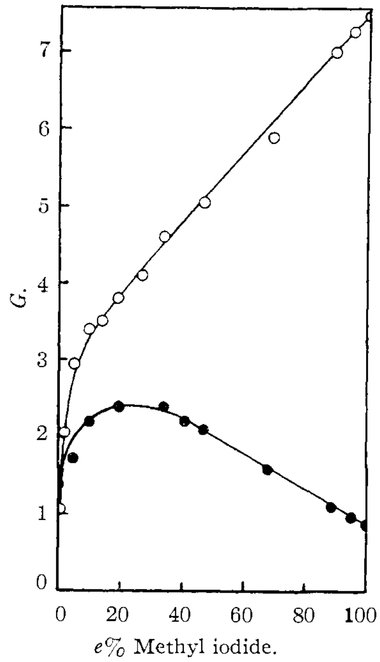

Fig. 1.—Radiolysis of methyl iodide–benzene: ○, $G(CH_4)$ *vs.* e% CH_3I with 0.03 *M* HI; ● G(HI) *vs.* e% CH_3I with 0.03 *M* I_2.

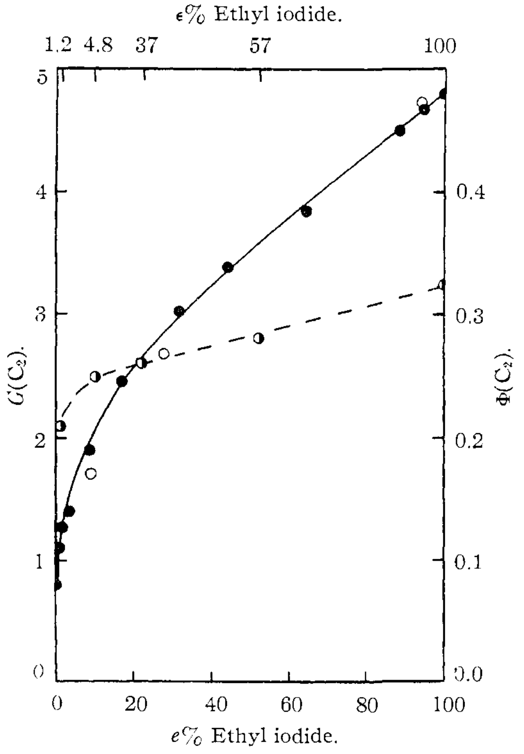

Fig. 2.—Radiolysis and photolysis of ethyl iodide-benzene or toluene: ● $G(C_2H_4 + C_2H_6)$ in benzene, ○ $G(C_2H_4 + C_2H_6)$ in toluene *vs.* e% C_2H_5I; ◑ $\Phi(C_2H_4 + C_2H_6)$ *vs.* ε% (top) or e% (bottom) C_2H_5I.

of products, as did 0.09 *M* naphthalene to 9 e% of ethyl iodide in benzene.

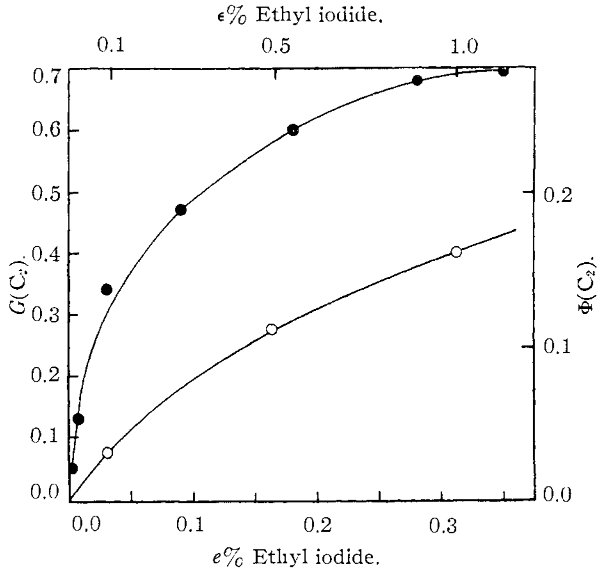

Fig. 3.—Radiolysis and photolysis of ethyl iodide in dilute solutions of benzene: ● $G(C_2H_4 + C_2H_6)$ *vs.* e% C_2H_5I; ○ $\Phi(C_2H_4 + C_2H_6)$ *vs.* ε% (top) or e% (bottom) C_2H_5I.

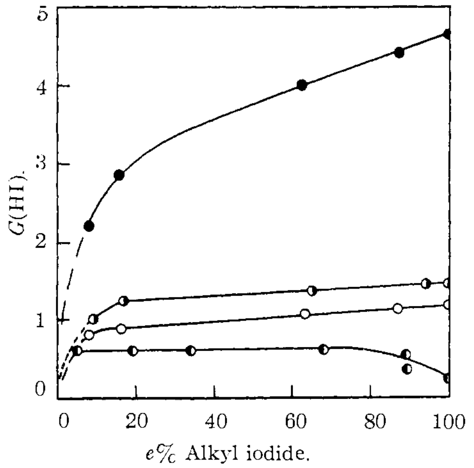

Fig. 4.—Radiolysis of alkyl iodides in benzene; G(HI) *vs.* e% RI for ● s-C_3H_7I, ○ n-C_3H_7I, ◑ C_2H_5I, ◐ CH_3I.

Benzene–Alkyl Iodides.—Values of G(HI) for solutions containing methyl, ethyl, 1-propyl or 2-propyl iodides with added water and triphenylmethane (but without added iodine) appear in Fig. 4. The much greater G(HI) for 2-propyl iodide is, in part, characteristic of the β-effect.[16]

Benzene–Alkyl Bromides.—Values of G(HBr) for systems with ethyl, 1-propyl and 2-propyl bromides, together with water and triphenylmethane, appear in Fig. 5. An indirect effect at low concentrations of alkyl bromides appears in each system.

Benzene–Methyl Chloride.—In the presence of 0.03 *M* hydrogen iodide, $G(CH_4)$ was 0.33 and 0.36 at 3.4 and 5.6 e% methyl chloride, respectively. These yields are strikingly less than corresponding yields from solutions of methyl iodide (Fig. 1).

Benzene–Chloroform.—These mixtures were analyzed for hydrogen chloride only. In one (the earliest) series of runs, no minor solutes were added. In a subsequent series with water also present,

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[16] E. L. Cochran, W. H. Hamill and R. R. Williams, Jr., *J. Am. Chem. Soc.*, **76**, 2145 (1954).

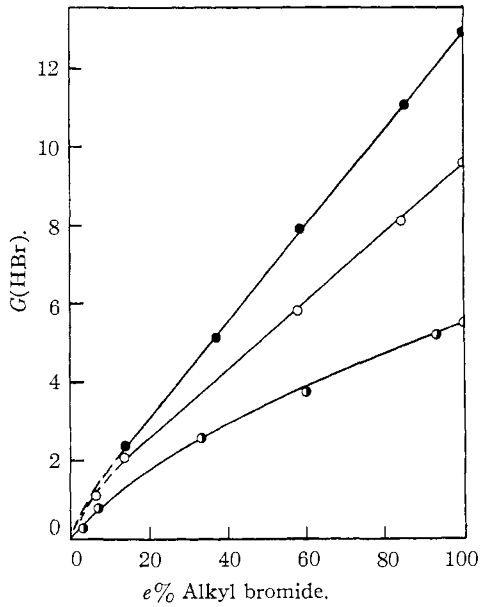

Fig. 5.—Radiolysis of alkyl bromides in benzene: G(HBr) *vs.* e% RBr for ● n-C_3H_7Br, ○ s-C_3H_7Br, ◑ C_2H_5Br.

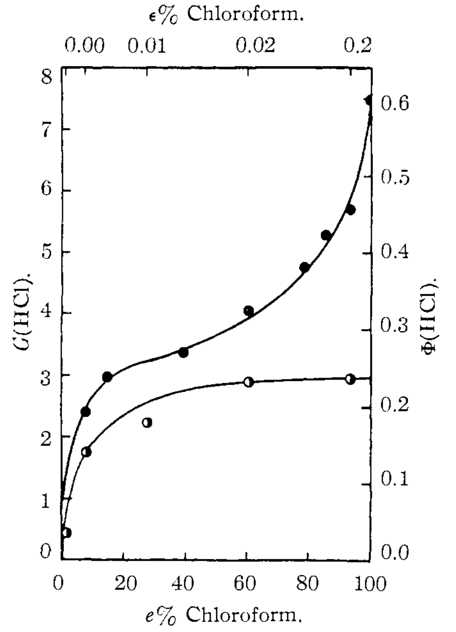

Fig. 6.—Radiolysis and photolysis of chloroform in benzene: ● G(HCl) *vs.* e% $CHCl_3$; ◑ Φ(HCl) *vs.* ϵ% (top) or e% $CHCl_3$ (bottom).

the yields were appreciably increased. Finally, in a third series, both water and 0.05 M triphenylmethane were added, with additional large increments in G(HCl). These last results appear in Fig. 6. It is our interpretation that triphenylmethane effectively converts Cl atoms to HCl, thereby preventing loss by addition to benzene. Water is assumed to act, as for systems containing hydrogen iodide,[3,4] by converting molecular hydrogen halide to the less reactive ionic form. Both water and triphenylmethane were subsequently used in all systems in which Cl or Br atoms were expected to form.

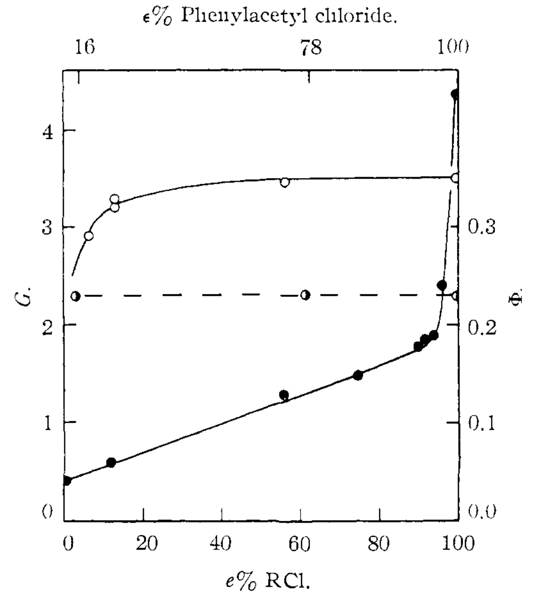

Fig. 7.—Radiolysis and photolysis of phenylacetyl chloride–benzene: ○ G(CO) *vs.* e% $C_6H_5CH_2COCl$; ◑ Φ(CO) *vs.* ϵ% (top) or e% $C_6H_5CH_2COCl$ (bottom). Radiolysis of chlorobenzene-chloroform: ● G(HCl) *vs.* e% $CHCl_3$.

Other aspects of the radiolysis of this system have been studied previously.[9,17]

Chlorobenzene–Chloroform.—The results in Fig. 7 correspond qualitatively to those of Bouby[9] but are quantitatively much lower. Since neither water nor triphenylmethane was added, the results in Fig. 7 have qualitative significance only.

Benzene–Carbon Tetrachloride.—The results for these mixtures, all of which contained water and triphenylmethane, appear in Fig. 8 and are qualitatively similar to those of Bouby's measurements of G(radical), using DPPH.[9] Since his reported values of G(radical) are much larger than our G(HCl), it appeared advisable to test the efficiency of triphenylmethane. In three consecutive runs at 61.9 e% carbon tetrachloride and constant dose, with 0.04, 0.05 and 0.08 M triphenylmethane, the G(HCl) was 4.15, 4.10 and 4.14, respectively.

Benzene–Alkyl Chlorides.—Results for these mixtures, in Fig. 9, are characterized by strikingly small G(HCl) at low concentrations of additive, relative to the results with added carbon tetrachloride, under similar experimental conditions. There is no indication of indirect effect at low concentrations of chlorides.

Benzene–Phenylacetyl Chloride.—This system was chosen in the expectation that C-Cl rupture would be followed by an efficient decomposition of the phenyl acetyl radical, since resonance stabilized $C_6H_5CH_2$ and CO would result. The quantitative reliability of all previously mentioned yields in this report is somewhat to be doubted because free radicals, halogen atoms and hydrogen halides as products of radiolysis may react with benzene or its radiolytic products, despite the precautions which were taken.

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[17] A. Henglein and H. Mohrhauser, *Z. physik. Chem.* (Frankfurt), **18**, 43 (1958).

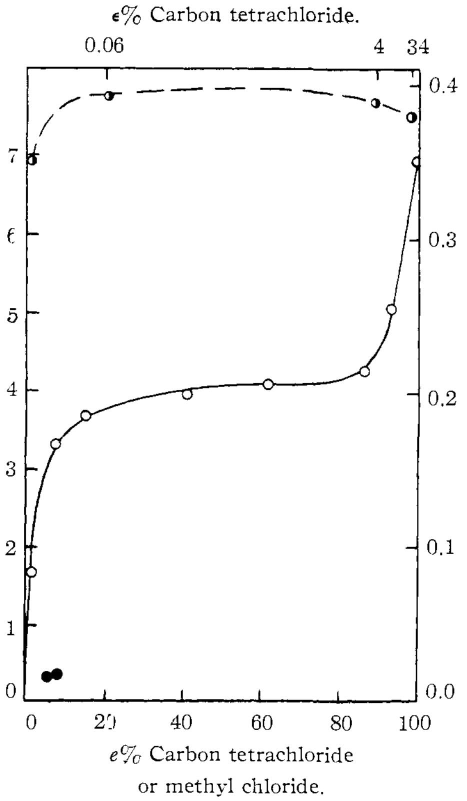

Fig. 8.—Radiolysis of carbon tetrachloride and of methyl chloride and the photolysis of carbon tetrachloride in benzene: ○ G(HCl) *vs.* e% CCl_4; ◑ Φ(HCl) *vs.* ε% (top) or e% (bottom) CCl_4; ● $G(CH_4)$ *vs.* e% CH_3Cl, with 0.03 *M* HI.

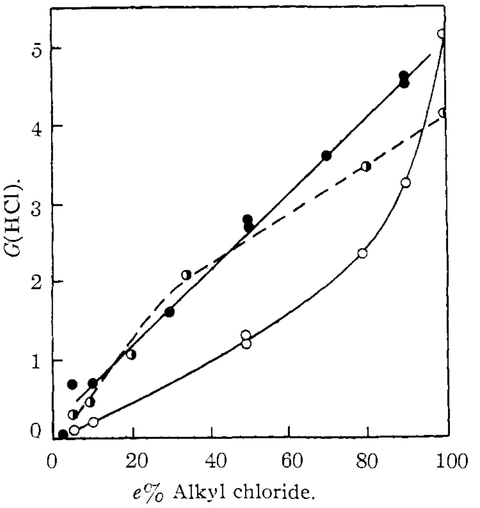

Fig. 9.—Radiolysis of alkyl chlorides in benzene: G(HCl) *vs.* e% RCl for ◑ C_2H_5Cl, ● *n*-C_3H_7Cl, ○ *s*-C_3H_7Cl.

This system is of interest because there is a marked indirect effect which saturates at 10 e%. There is little or no direct effect leading to formation of carbon monoxide. Results appear in Fig. 7.

Benzene–Benzyl Acetate.—This additive was chosen because dissociative electron attachment yielding $CH_3CO_2^-$ has been observed mass spectrometrically.[18] Efficient decomposition was expected because of $C_6H_5CH_2$ resonance stabilization and the high electron affinity of CH_3CO_2.[19] Also, one expects that charge neutralization will be followed by a very prompt decomposition of acetoxy radicals.[20] Measurement of $G(CO_2)$ has, therefore, the advantages just mentioned for an unreactive molecular product. The results in Fig. 10 at high concentrations of benzyl acetate, *viz.*, $G(CO_2)/G(CH_4)$ is not constant, suggest that there are two mechanisms for producing methyl radicals. Addition of 0.03–00.7 *M* iodine greatly decreases $G(CH_4)$, indicating a free radical precursor of methane, presumably the methyl radical.

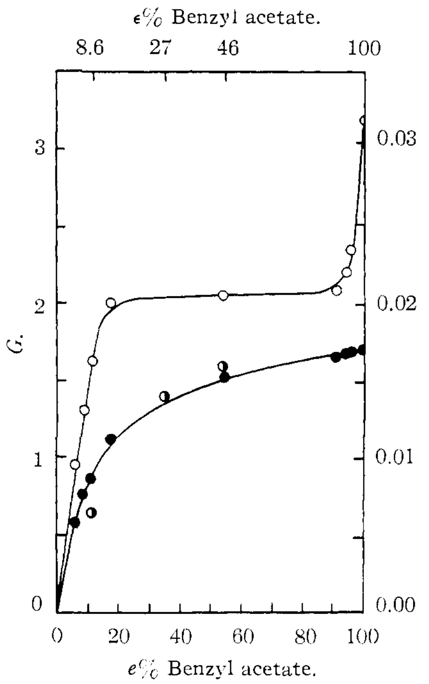

Fig. 10.—Radiolysis and photolysis of benzyl acetate–benzene: G(product) *vs.* e% $C_6H_5CH_2OCOCH_3$ for ○ CO_2, ● CH_4; ◑ $\Phi(CO_2)$ *vs.* ε% (top) or e% (bottom) $C_6H_5CH_2OCOCH_3$.

Benzene–Methyl Chloride Vapor.—Mass spectrometric observations of ion-molecule reactions between C_6H_6 and CD_3^+, CCl_3^+ or $CHCl_2^+$ to give secondary ions of the type $C_7H_{7-m}X_m^+$ and $C_6H_{5-n}X_n^+$ indicate the formation of tropylium secondary ions.[21] To determine the possible role of ion-molecule reactions in radiation chemistry, a gaseous mixture of benzene with 75 e% methyl chloride was irradiated at 25° and 490 mm. with 1 m.e.v. electrons at a dose of 2 × 10^{21} e.v. The absorption spectrum of the aqueous extract did not correspond to that for tropylium carbinol[22] and G(tropylium) < 0.12; none could be detected. Since electron attachment yielding Cl^- may be critical for the success of this test and since CH_3Cl appears not to attach thermal electrons,[23] a second run was made with benzene,

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(18) T. Moran, this Laboratory.

(19) L. Jaffe, E. J. Prosen and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

(20) J. Nash, W. H. Hamill and R. R. Williams, *J. Phys. Chem.*, **60**, 823 (1956).

(21) L. P. Theard and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 1131 (1962).

(22) W. E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

methyl chloride (66 $e\%$) and carbon tetrachloride (8 $e\%$). Again, no tropylium carbinol could be detected in the aqueous extract.

As an independent test for tropylium ion formation, liquid samples in benzene with 20 $e\%$ methyl iodide-d_3 and 0.03 M iodine were irradiated. If $C_7H_{7-m}D_m^+$ forms and decomposes to $C_5H_{5-n}D_n^+$, D-labeled acetylenes would be eliminated. None ($G < 10^{-3}$) could be detected. If $C_7H_6D_3^+$, forms and decomposes to $C_7H_{7-m}D_m^+$, HD would result. Values of G(HD) were 0.015 and *ca.* 10^{-3}, respectively.

Methyl Iodide–Carbon Tetrachloride.—Solutions of these two halides, also containing *ca.* 0.035 M hydrogen iodide, were measured for methane. The results appear in Fig. 11. For comparison, one mixture each of 19 $e\%$ dichlorofluoromethane and one of 14 $e\%$ trichlorofluoromethane in methyl iodide were also irradiated.

Photolysis.—Efficient photosensitized decomposition of ethyl iodide in benzene or hexane–naphthalene solutions has been observed.[24,25]

Since the phenomena of interest in the radiolyses described in this report may be induced by ionic processes, by free radical attack or by energy transfer it appeared desirable to examine photosensitized decomposition in several of the same systems.

It has been suggested that formation of hydrogen iodide from the radiolysis of benzene solutions of iodine arises from an excited state of benzene reacting with iodine, rather than from scavenging of atomic hydrogen.[26] To test this possibility a solution of 0.01 M iodine in benzene was exposed with the result that $\Phi(\mathrm{HI}) = 5 \times 10^{-4}$. To compare with the results of Fig. 1 the illumination of methyl iodide in benzene gave values of Φ(HI) equal to 0.005, 0.003 and 0.000 at 3, 60 and 100 mole % methyl iodide.

Results for the photolysis of benzene–ethyl iodide mixtures appear in Figs. 2, 3, in terms of the combined quantum yields of ethane–ethylene, $\Phi(C_2)$. The reported quantum yields for all systems refer only to the contribution from energy transfer obtained by subtracting from the observed total yields the calculated contribution expected from direct absorption, except that yields reported for pure substances are values observed. Such calculations, when applied, involve the assumption that the quantum yield for direct absorption does not change with environment. The percentage amount of the absorbed light which is absorbed by the substrate is shown by the scale above the figures as $\epsilon\%$. In fact, the gross quantum yields and those calculated for the photosensitized reactions do not differ significantly.

Results for the photolysis of solutions of chloroform and of carbon tetrachloride in benzene appear in Figs. 6, 8. Since Φ(HCl) was to be measured, triphenylmethane and water also were added.

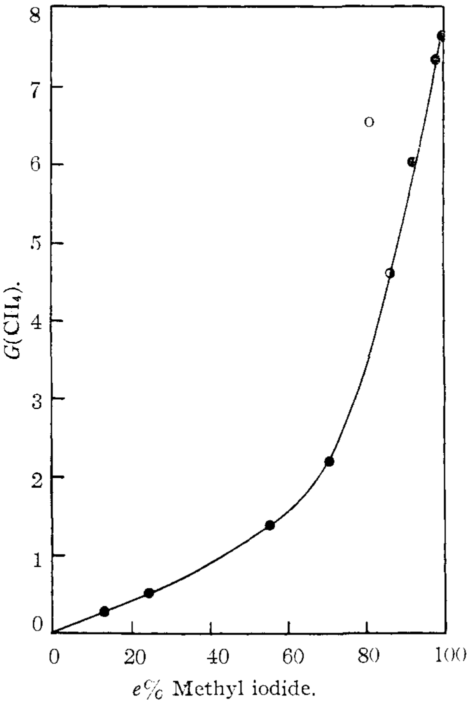

Fig. 11.—Radiolysis of methyl iodide–RCl with 0.03 M HI: $G(CH_4)$ *vs.* $\epsilon\%$ RCl for ● CCl_4; ○ $CHCl_2F$; ◑ CCl_3F.

For solutions containing phenylacetyl chloride or benzyl acetate, the yields Φ(CO) and $\Phi(CO_2)$ appear in Figs. 7, 10. No other solutes were present. Yields of methane from benzyl acetate were substantially less than those of carbon dioxide.

As a rough test of the reactivity of H-atoms toward benzene, a solution of 0.05 M hydrogen iodide was photolyzed. The iodine-to-hydrogen mole ratio was approximately 6.

Discussion

Energy Transfer.—A disproportionately large chemical effect in a component of a gamma irradiated solution may be due to transmission of energy as electronic excitation, of matter by atom and free radical reactions and of electric charge by transfer and electron attachment. The first two mechanisms have been intensively studied. We shall consider particularly evidence for the third. The fates of very high energy states of liquid benzene are entirely unknown experimentally, and there are not even estimates of the distribution of energy among processes of ionization, internal conversion, inter-system crossing, decomposition or energy transfer. The present theory of energy transfer excludes consideration of internal conversion or other competitive processes and so cannot be invoked.[27]

The emission spectrum of scintillators in benzene solutions is the same for ultraviolet and for gamma excitation, as is the energy transfer parameter Q; the quenching constants are nearly equal.[28a] These facts alone establish a qualitative

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(23) V. Dibeler and R. Reese, *J. Res. Natl. Bur. Standards*, **54**, 127 (1955).

(24) W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

(25) W. West and W. E. Miller, *J. Chem. Phys.*, **8**, 849 (1940).

(26) M. Burton, J. Chang, S. Lipsky and M. P. Reddy, *Radiation Research*, **8**, 203 (1958).

(27) Th. Forster, "Comparative Effects of Radiation," Eds. M. Burton, J. S. Kirby-Smith and J. L. Magee, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 300.

(28) (a) S. Lipsky and M. Burton, *J. Chem. Phys.*, **31**, 1221 (1959). (b) F. H. Brown, M. Furst and H. Kallmann, *Discussions Faraday Soc.*, **27**, 43 (1959).

but not a quantitative correspondence. The quantum efficiency of energy transfer following ultraviolet illumination is large and sometimes approaches 100%,[28b] while the energy efficiency of most scintillators in gamma irradiated organic liquid solutions is much less than 1%.[29] *Such experiments demonstrate, therefore, not the importance of energy transfer in the gamma irradiated systems, but rather the contrary.* Specifically, such experiments demonstrate that the yield of $^1B_{2u}$ states in gamma irradiated liquid benzene, whether formed directly or by internal conversion, accounts for a rather small part of the absorbed energy. For the same reasons one concludes that theoretical calculations indicating relatively high yields for excitation to the lowest excited (singlet) levels cannot be valid.[30]

Electron Attachment.—The indirect chemical effects reported here contrast with luminescence phenomena in that a relatively high yield ($G \sim 3$) is approached in the limit, and in that the limiting G is approached at a fairly high concentration, typically 10 e%. Another evident difference between the two phenomena is shown by their solvent effects. The relative efficiencies reported by Sangster and Irvine[29] for energy transfer to *p*-terphenyl in the following gamma irradiated solvents are: toluene 9.3, benzene 7.8 and phenyl ether 8.2 (all referred to crystalline anthracene as 100). At *ca.* 9 e% solute, $G(C_2H_4 + C_2H_6)$ from ethyl iodide in several solvents is: toluene 1.7, benzene 1.9 and methyltetrahydrofuran 5.2[31]; G(CO) from phenylacetyl chloride in benzene is 3.0; in methyltetrahydrofuran it is 5.0.[31] G(HCl) from carbon tetrachloride is much less in 3-methylpentane than in methyltetrahydrofuran.[31] Enhanced yields in the latter solvent are not due to reduction by H-atoms since it is itself an efficient H-atom scavenger in irradiated cyclohexane. It does not appear that excited states dominate these gross chemical phenomena. The facts do suggest that solvolysis by polar solvents promotes radiation-induced dissociative electron attachment.

According to the theory of Samuel and Magee,[32] electrons produced by high energy radiation in liquid water are recaptured by parent ions and therefore do not encounter very large numbers of molecules. This conclusion does not depend critically upon the values of the parameters and presumably applies to non-aqueous liquid or glassed systems. It is not possible to interpret our results quantitatively in this context, but it is quite evident that no significant yield of electrons reaches steady state conditions. If this were the case, electrons would encounter very large numbers of molecules and could be detected by chemical effects at very small solute concentrations.[33]

We postulate that reactions of dissociative electron attachment with a solute contribute importantly to an indirect effect in the lower solute concentration range whenever the mass spectrometric appearance potential for fragment negative ions from the solute molecule is not appreciably greater than kT. In each of the systems reported here which exhibits a marked initial rise of product from solute, there is good reason to expect dissociative electron attachment, and conversely. Thus, the iodides and bromides, as well as carbon tetrachloride, all show gamma radiation sensitized decomposition in benzene. In contrast, the alkyl chlorides do not. Correspondingly the appearance potentials for Cl^- from CCl_4 and CH_3Cl are 0.20 e.v.[34] and 9 e.v.[23] respectively, while that for Br^- from CH_3Br or I^- from CH_3I are both zero.[23]

Although there are no reports on appearance potentials for other alkyl halides, we might expect them to approximate that of the corresponding methyl halide. This assumption is supported in part by absence of measurable electron attachment in alkyl chloride vapors.[35] These considerations, we repeat, apply to the indirect effect, which is arbitrarily taken as the yield of product in excess of that corresponding to the straight line passing through the origin and G(HCl) for pure RCl, and analogously for other systems. This difference depends, of course, upon the concentration units chosen, and no justification of descriptions in terms of e% is implied by its use here. The differences between alkyl chlorides and alkyl iodides are qualitatively evident and independent of this choice.

The preceding interpretations are strongly supported by other studies in this Laboratory.[36] Gamma irradiation of 0.10–1 e% naphthalene or biphenyl in rigid organic media at −196° produced the well known anion spectra. The limiting $G(C_{10}H_8^-)$ approximates 4. There is related evidence for electron attachment by carbon tetrachloride, giving CCl_4^- in hydrocarbons and Cl^- in polar media. An important conclusion from this work, which is not as evident from chemical studies,[4] is that the yield of attached electrons has already attained a value approximating unity at solute concentrations of *ca.* 0.1 e%. This effect is not peculiar to rigid media and is also observed in organic liquids when reduction by e^-

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(29) R. C. Sangster and J. W. Irvine, Jr., *J. Chem. Phys.*, **24**, 670 (1956), report C_0-gamma energy efficiencies for ten organic scintillators in benzene solutions. The most efficient of these is 1,2-di-(α-naphthyl)-ethylene which is 12.3% as efficient as crystalline anthracene. According to these authors, the consistently higher relative efficiencies reported by H. Kallmann and M. Furst, *Nucleonics*, **8**, No. 3, 32 (1951), are probably due to determinate errors. Sangster and Irvine found an absolute energy efficiency for anthracene crystal luminescence approximating 3.5% and, considering other reported values, take 4% as the best value. The highest value of 10% was obtained by M. Furst and H. Kallmann, *Phys. Rev.*, **89**, 416 (1953). The absolute energy efficiency for 1,2-di-(α-naphthyl)-ethylene in benzene is probably 0.5%, and possibly 1.2%. In terms of 2.6 e.v fluorescence quanta, and presumably of benzene $^1B_{2u}$ states, G is 0.2 or 0.5.

(30) M. Inokuti, *Isotopes and Radiation* (Tokyo), **1**, 82 (1958).

(31) J. P. Guarino and M. R. Ronayne, this Laboratory.

(32) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **12**, 1080 (1953).

(33) J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720 (1961), have observed appreciable lowering of $G(H_2)$ from methanol with as little as 2×10^{-6} M anthracene. When both the positive hole and the electron become trapped in a good dielectric, as $CH_3OH_2^+$ and e^--solvated, the electron may escape its parent ion following dielectric relaxation. Quite small solute concentrations may then be effective.

(34) W. Hickham and D. Berg, *J. Chem. Phys.*, **29**, 517 (1958).

(35) J. C. Devins and O. H. Leblance, Jr., *Nature*, **187**, 409 (1960).

(36) P. S. Rao, J. P. Nash, J. P. Guarino, M. R. Ronayne and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 500 (1962).

and H-atoms can be distinguished. As one example, the results for ethyl iodide (Fig. 2, 3) indicate an appreciable yield of attached electrons in dilute solution (below 0.1 $e\%$) as well as continuing reaction at higher concentration (above 1 $e\%$). Reduction by H-atoms should make only a limited contribution to C_2-products below 0.1 $e\%$ of ethyl iodide in benzene. As another and clearer example, $G(H_2)$ is 0.8 for 0.01 M hydrogen iodide in cyclohexane-d_{12}.[37] This remarkably large yield may be compared with the combined ethane–ethylene $G(C_2) = 0.5$ at the same concentration of ethyl iodide in benzene (Fig. 3). The ratio of quantum yields, $\Phi(H_2)/\Phi(C_2)$, for the corresponding photolyses is *ca.* 0.9/0.3. Since the latter yields depend upon diffusion controlled processes and cage effects,[38] we suggest that efficiency of dissociative electron attachment in the condensed phase may also be decreased by the same effects which would either prevent attachment (if RX^- cannot exist) or favor non-dissociative attachment. The formation of CCl_4^- is an example.[36] It is plausible that molecular anions may not decompose during subsequent charge neutralization. These effects explain in part the larger chemical yields in polar solvents for a given solute,[31] since solvolysis of molecular anions overcomes the inefficiency due to cage effects.

Benzene.—The net chemical changes in irradiated benzene are fairly complex and the primary reactive entities have not been identified. Hydrocarbon products (C_{12} or higher) account for $G(-C_6H_6) = 0.93$,[6,39] while our $G(HI) = 1.35$ indicates a still larger $G(-C_6H_6)$. Simple C—H bond rupture followed by H-atom scavenging can make only a limited contribution since $G(C_6H_5I)$ amounts to 0.27.[40] For the same reason one cannot postulate that a reaction of iodine with excited benzene contributes a major effect. The ratio of rate constants for H-atom scavenging by iodine

$$C_6H_6^* + I_2 \longrightarrow C_6H_5 + HI + I$$

and by benzene is 10^2.[41] At iodine concentrations 0.02, 0.03 and 0.05 M in benzene, approximately 17, 23 and 33% of H-atoms should react with iodine, the rest with benzene. The measured values of $G(HI)$ were 1.27, 1.38 and 1.40. It appears that although most of the H-atoms react initially with benzene, the ultimate $G(HI)$ is unaffected.[42] We are led to postulate that such reactions as 1–3

$$C_6H_6 \rightsquigarrow C_6H_5 + H \tag{1}$$

$$C_6H_6 + H \longrightarrow C_6H_7 \tag{2}$$

$$C_6H_5 + C_6H_6 \longrightarrow C_6H_5\text{–}C_6H_6 \tag{3}$$

are followed by reactions of the type 4 and 5

$$C_6H_7 + I_2 \longrightarrow C_6H_6 + HI + I \tag{4}$$

$$C_6H_5\text{–}C_6H_6 + I_2 \longrightarrow C_6H_5\text{–}C_6H_5 + HI + I \tag{5}$$

In the absence of iodine we might expect such reactions as

$$2C_6H_7 \longrightarrow C_6H_6 + C_6H_8 \tag{6}$$

$$\longrightarrow C_6H_7\text{–}C_6H_7 \tag{7}$$

Considering that $G(C_6H_5I)$ is small while biphenyl is a minor product even at high LET,[43] it may be that H arises from ionic reactions such as[44]

$$C_6H_6^+ + C_6H_6 \longrightarrow C_{12}H_{11}^+ + H \tag{8}$$

Since only *ca.* 3 e.v. would be released by charge neutralization of $C_{12}H_{11}^+$, further decomposition is unlikely. We can thus understand phenylcyclohexene, phenylcyclohexadiene and bicyclohexadienyl as products in irradiated benzene,[6,43b] as well as $G(HI)$ rather greater than $G(C_6H_5I)$. Post-radiative addition of iodine dehydrogenates phenyl cyclohexadienes to biphenyl[43b] and also contributes to $G(HI)$. Pre-radiative addition of iodine augments G(biphenyl), giving both a maximum and a minimum,[43b] thus providing partial support for reaction 8. It should be observed that reaction 4 is quite plausible on thermochemical grounds. On the other hand, the corresponding reaction involving an alkyl iodide would be more endothermic by about 18 kcal. and probably would not contribute.

Photolysis Radiolysis of Mixtures.—The results in Figs. 1–11 include many examples of gamma radiation-induced indirect effects. The system benzene–carbon tetrachloride in Fig. 8 demonstrates two striking effects, in contrast to the data for alkyl chlorides in Fig. 9 which show no comparable indirect effects. The combined effect of H-atoms and electrons, which cannot be distinguished by these results, approaches saturation at 15 $e\%$ carbon tetrachloride and no other important contribution appears up to *ca.* 85%. In addition to reactions 1–8 we expect these

$$CCl_4 + e \longrightarrow CCl_4^- \tag{9}$$

$$\longrightarrow CCl_3 + Cl^- \tag{10}$$

$$M^+ + CCl_4^- \longrightarrow CCl_4 + ? \tag{11}$$

$$M^+ + Cl^- \longrightarrow M + Cl \tag{12}$$

$$M^+ + e \longrightarrow \text{Products} \tag{13}$$

$$CCl_4 + H \longrightarrow HCl + CCl_3 \tag{14}$$

Analogous mechanisms presumably apply to benzene with added chloroform, phenylacetyl chloride, alkyl iodides and bromides and possibly benzyl acetate over the lower concentration range.

A few per cent of benzene in carbon tetrachloride markedly suppresses $G(HCl)$. Energy transfer cannot be excluded on the basis of the results with 2537 Å. illumination since quite pure carbon tetrachloride has a much smaller extinction coefficient at 2537 Å. than our value.[45] Whether or not energy

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(37) J. Nash and W. H. Hamill, *J. Phys. Chem.*, **66**, 1097 (1962).

(38) D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **78**, 6228 (1956).

(39) J. R. Nash, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **82**, 5974 (1960).

(40) Phenyl iodide is apparently the major stable organic iodide since G(stable iodide) = 0.3 according to A. T. Fellows and R. H. Schuler, *J. Phys. Chem.*, **65**, 1451 (1961).

(41) Based upon the competition of H-atoms for iodine/cyclohexane (ref. 4) and benzene/n-hexane, from the work of T. J. Hardwick, *J. Phys. Chem.*, **65**, 101 (1961).

(42) (a) In support of this interpretation, Mr. J. Roberts observed that addition of 5 $e\%$ benzene to cyclohexane also containing 0.015 M iodine does not significantly diminish $G(HI)$, although it appreciably affects $G(H_2)$. (b) P. J. Dyne, W. M. Jenkinson and J. Denhartog, Document *AECL*-1416, Atomic Energy of Canada Limited, have reported $G(HD) = 6.84 \times 10^{-3}$ for 3.96 mole % c-C_6D_{12} in C_6H_6 and $G(HD) = 0.057$ for 4.63 mole % C_6D_6 in c-C_6H_{12}. These and other results suggest a fairly large yield of H-atoms from benzene, not induced by iodine.

(43) (a) T. Gäumann and R. H. Schuler, *J. Phys. Chem.*, **65**, 703 (1961); (b) T. Gäumann, *Helv. Chim. Acta*, **44**, 1337 (1961).

(44) R. Barker, *Chem. and Ind.* (London), 233 (1960).

(45) Prof. M. Magat, private communication.

transfer contributes, the possibility of charge exchange deserves consideration. We note first that a similar effect appears for benzene added to chloroform and to benzyl acetate, as well as benzyl chloride in chloroform (see Figs. 6, 7, 8, 10). Although a similar effect was not found in Forrestal's work,[4] it has been observed recently for 1–10 *e*% cyclohexane in fluorotrichloromethane[46] and is not, therefore, peculiar to benzene or aromatic hydrocarbons. We interpret the effect of benzene or cyclohexene in cyclohexane[47] as due to charge exchange, apart from H-atom scavenging. There is fairly direct evidence for charge exchange from the observed enhancement of G(anions) in rigid hydrocarbon media resulting from additives of lower ionization potential than molecules of the matrix. Such solutes are thought to trap positive holes which otherwise migrate to anions.[36] Hole migration and positive charge exchange to solute should not occur in media whose molecules undergo ion-molecule reactions, since these processes lower the potential of the ion and trap it.

The mass spectral patterns of the polyhaloalkanes exhibit very little or no molecular ion, *viz.*, CCl_4^+, $CHCl_3^+$, CCl_3F^+. The most abundant ions are CCl_3^+, $CHCl_2^+$, CCl_2F^+, and we assume that the same situation holds in liquids. The relevant ionization potentials are: $I(CCl_3) = 8.78$[48] or 8.28 e.v.[49]; two breaks in the ionization efficiency curve (by the RPD method) for the process

$$CCl_3F + e \longrightarrow CCl_3^+ + F + 2e$$

indicate higher states of CCl_3^+ at 1.5 and 2.7 e.v. above the ground state[49]; $I(CCl_2F) = 8.69$ e.v.[49] and, although no structure appears in the ionization efficiency curve, it is rounded to *ca.* 1.5 volts above threshold, a result indicating higher states; $I(CHCl_2) = 9.30$ e.v.,[50] and it is not known whether higher states contribute. The ionization potentials of benzene and cyclohexane are 9.24 and 9.88 e.v. respectively.[51]

Reactions of the type

$$M^+ + X \longrightarrow M + X^+$$

are not always controlled by the relative ionization potentials but rather by the *recombination energies*,[52] which may be less because of Franck–Condon restrictions. Although we cannot now predict when charge exchange can occur, we see that within the limits of available information marked protection of carbon tetrachloride and chloroform by benzene and not by cyclohexane and protection of fluorotrichloromethane by cyclohexane can all be attributed to charge exchange.

There is little mass spectrometric information for benzyl acetate from which the possibility of charge exchange can be judged. A single measurement of $I(C_6H_5CH_2CO_2CH_3) = 8.6$ e.v.[53] would argue against charge exchange.

Finally we must consider why G(HX), *etc.*, from alkyl halides are not also markedly decreased by benzene, with the exception of *s*-propyl chloride, since ionization potentials of alkyl halides are generally greater than those of benzene. The molecular ions are prominent in the mass spectra of RI and RBr and might therefore be expected to exchange charge. On the other hand, molecular ions are minor components of mass spectral patterns of the alkyl chlorides. The typical ionization potentials are $I(RI) = 9.4$ e.v., $I(RBr) = 10.3$ e.v. and $I(RCl) = 11$ e.v. All RI and RBr which have been observed in the mass spectrometer undergo several ion-molecule reactions.[21] Only one secondary ion has been observed (from *s*-C_3H_7Cl) for alkyl chlorides.

Lack of protection by benzene for iodides and bromides can be understood either in terms of too little recombination energy to ionize benzene or of ion–molecule reactions involving little molecular reorganization which might still occur in liquids, as

$$RX^+ + RX \longrightarrow R_2X^+ + X$$

No secondary ion R_2X^+ could undergo charge exchange with benzene since at least 2.5–3 e.v. of potential has been expended on chemical change. Another possibility is that, following electron attachment, dielectric relaxation solvates all RX^+, and solvent reorganization would now be required for charge exchange to benzene. If the cation-anion pair are not separated by more than 15–20 Å. initially, charge recombination may intervene.

The photolyses of pure methyl and ethyl iodides differ because geminate (CH_3 + I) can only separate or recombine while (C_2H_5 + I) can also disproportionate to C_2H_4 + HI. The results for the photolysis and the radiolysis of ethyl iodide resemble each other considerably, but whereas $\Phi(CH_4)$ and $\Phi(I_2)$ for methyl iodide are very small, and Φ(HI) is zero, $G(CH_4)$ is large and G(HI) is appreciable. These similarities and differences can be understood in terms of electron impact and ion-molecular processes.[3] Benzene greatly enhances G(HI) from methyl iodide in the presence of 0.03 *M* iodine (Fig. 1) and the extrapolated yield at 0 *e*% iodide exceeds 3. Since no such effect was found for the photolysis of methyl iodide in cyclohexane,[11] we may either attribute the results for G(HI) of Fig. 1 to competition between C_6H_6 and CH_3I for H-atoms or, possibly, to an ionic process of the type

$$MH^+ + I^- \longrightarrow M + HI$$

where MH^+ arises from benzene. If M is a molecule, then the reaction would be rather exothermic even for neutral reacting species.

The results for G(HI) from methyl iodide in Figs. 1 and 4 differ because 0.03 *M* iodine was present in the former series, but not in the latter. Within the series described in Fig. 4, we can understand in part the quantitative differences in terms of the corresponding photochemistry. That is, the efficiency of disproportionation between an alkyl radical and iodine atom geminate pair is

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(46) J. Roberts, this Laboratory.

(47) J. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952); G. R. Freeman, *J. Chem. Phys.*, **33**, 71 (1960); *Can. J. Chem.*, **38**, 1043 (1960)

(48) J. B. Farmer, I. H. S. Henderson, F. P. Lossing and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

(49) R. K. Curran, *ibid.*, **34**, 2007 (1961).

(50) F. P. Lossing and J. B. DeSousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

(51) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(52) H. von Koch and E. Lindholm, *Arkiv. f. Fysik*, **19**, 123 (1961), and earlier papers.

(53) We are indebted to Dr. R. F. Pottie for this measurement.

proportional to the number of H-atoms in β-position relative to the free valence.[16]

It is rather remarkable that $G(C_2H_4)/G(C_2H_6)$ is substantially independent of composition for the runs of Figs. 2 and 3. Excepting only the two most dilute solutions, for which the ratio drops below unity, the averages and average deviations are 1.23, a.d. 0.03, and 1.17, a.d. 0.05, for the runs above and below 10 e% ethyl iodide, respectively. By analogy with the explanation of the large G(HI) from solutions of methyl iodide, we must also attribute part of G(HI) from ethyl iodide to reaction with products from irradiated benzene, and only part to C_2H_5–I disproportionation. There would be a corresponding enhancement of $G(C_2H_6)$, without a concomitant increase of $G(C_2H_4)$. The invariance of the ethylene–ethane ratio with composition may be due to a fortuitous equivalence of radiation-produced hydrogen iodide in benzene-rich systems and in pure ethyl iodide[3] by mechanisms other than disproportionation.

The value of $\Phi(C_2H_4)/\Phi(C_2H_6)$ for pure ethyl iodide, or its solution in cyclohexane, is 1.5.[38] For the photosensitized decomposition, $\Phi(C_2H_4)/\Phi(C_2H_6)$ rises gradually from 1.55 for pure ethyl iodide to 1.65 for its one mole % solution in benzene, and then rises rapidly to 2.1 at 0.1 % and to 3.8 at 0.02%. The ratio scarcely changes as the primary act of light absorption by ethyl iodide is almost completely replaced by absorption in benzene; even $\Phi(C_2H_6)$ and $\Phi(C_2H_4)$ are unaltered. The dramatic change in the value of the ratio occurs in dilute solutions of nearly constant environment and in the range of nearly complete light absorption by benzene. It would be impossible to account for the effect observed if a single mode of energy transfer were involved. The trivial process of absorption of benzene fluorescence by ethyl iodide is quantitatively insignificant and would, in any event, have no other effect than to diminish slightly the quantum yields of products. There is no evidence whatever for a change in mechanism over this interval of wave lengths. Only one possibility remains, that of intersystem crossing of singlet to triplet benzene, followed by energy transfer to ethyl iodide. The internal conversion can only become important at small concentrations of ethyl iodide because it is a slow (forbidden) process, but it is still detectable because reversion of $^1B_{2u}$ to the ground state is also somewhat forbidden. The requirement of spin conservation for the sensitized decomposition leads one to suggest the process

$$C_6H_6^* \text{ (triplet)} + C_2H_5I \longrightarrow C_6H_6 + C_2H_4^* \text{ (triplet)} + HI$$

The lowest triplet state of ethylene has been estimated at 52 kcal./mole,[54] while that of benzene is 85 kcal./mole. The reaction is therefore exothermic by 7 kcal.

The marked difference in the concentration dependences of $G(C_2H_4)/G(C_2H_6)$ and $\Phi(C_2H_4)/\Phi(C_2H_6)$ demonstrates empirically that energy transfer does not contribute importantly to the radiolysis of dilute solutions of ethyl iodide. To the extent that one may apply the results of scintillator studies to chemistry, the indications are the same. If we take $G(^1B_{2u}) \lesssim 0.5$,[29] the quantum yield for energy transfer to ethyl iodide as unity and the quantum yield for net decomposition of ethyl iodide as 0.3, because of cage effects,[38a] then we predict $G(—C_2H_5I) \lesssim 0.15$ from energy transfer. The value for other solutes should be comparable. *It is certainly not possible to assign a significant role to energy transfer in the radiation chemistry of solutions on the basis of the evidence from scintillators.*

The extrapolated values of G(HBr) in Fig. 5 approximate to unity for all three alkyl bromides, although yields for the pure substances are rather unequal. The relatively smaller extrapolated G(HBr), compared to G(HI), is probably not related to the reactivities of I· and Br· toward benzene since the limiting G(HCl) from carbon tetrachloride is large, although Cl· is very reactive.

In contrast to the alkyl iodides and bromides, the alkyl chlorides (Fig. 9) give extrapolated values of G(HCl) close to zero. Since G(HCl) from carbon tetrachloride and $G(CH_4)$ from methyl chloride in Fig. 8 are quite different at comparable concentrations and give large extrapolated values of G(HCl), the effect is not attributable to loss of Cl-atoms by addition to benzene. Qualitatively the alkyl halides exhibit radiation effects which are consistent with predictions based upon the appearance potentials of X^- from CH_3X.[23]

The results in Fig. 11 for mixtures of methyl iodide–carbon tetrachloride suggest that the marked decrease of $G(CH_4)$ with added carbon tetrachloride may be due to a more efficient electron attachment by carbon tetrachloride. This supposition is not necessarily in disagreement with the observation that in benzene-rich mixtures these two halides react with very nearly equal efficiencies, since charge exchange may compete with dissociation

$$CH_3I^- + CCl_4 \longrightarrow CH_3I + CCl_4^-$$

of the anion. In rigid media there is good evidence for stabilized CCl_4^- and also for more efficient attachment by carbon tetrachloride.[36] Yields of hydrogen chloride from carbon tetrachloride and fluorotrichloromethane in cyclohexane are very similar at similar concentrations, while those from added fluorodichloromethane are decidedly less.[46] These three halides show the same relative efficiencies in competition with methyl iodide (Fig. 11), and both results correlate with the reported appearance potentials for Cl^-; 0.20 e.v. for CCl_4; 0.10 e.v. for CCl_3F and 0.90 e.v. for $CHCl_2F$.[23]

The radiation yields of carbon dioxide from solutions of benzyl acetate are roughly what one might expect if dissociative electron attachment occurs. In support of this interpretation, the yields of naphthalene and biphenyl anions in rigid organic media were observed to be diminished by the addition of *ca.* 0.2% benzyl acetate prior to gamma irradiation.[31,55]

In marked contrast to radiolysis, the photolytic yields from benzyl acetate are quite small (Fig. 10). In this and other cases where the photosensitized

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[54] J. E. Douglas, B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

[55] Similarly good correlations were found with several other solutes employed in the present work. Alkyl chlorides were very inefficient.[31]

decomposition has been measured, the utility of comparison with gamma radiation is restricted by lack of information of the higher excited states. It has been generally assumed that higher states in aromatic molecules undergo very rapid (10^{-13} sec.), efficient internal conversion.[56,57] Since the yield of the lowest excited singlet state of benzene has been established by scintillation measurement as only $G(^1B_{2u}) \lesssim 0.5$, we must then conclude that the yield of higher singlet states *in toto* is even smaller. If internal conversion is as efficient as claimed, then the rule-of-thumb that high energy radiation produces roughly equal primary yields of excited states and of ion pairs must be incorrect. There is, however, some recent evidence that radiationless transitions can intervene,[58] and one must therefore consider dissociative and energy transfer processes from high energy states which may compete with internal conversion. "This important process (of internal conversion) deserves more careful study from the theoretical and experimental point of view, instead of being taken for granted as is commonly done."[59]

In summary it may be said that, at this time, the significant primary indirect effects in gamma irradiated organic solutions are consistently interpretable in terms of ionic processes.

Acknowledgment.—The authors are indebted to Professor John L. Magee for many helpful discussions.

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(56) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

(57) H. Sponer, *Radiation Research*, Supplement **1**, 558 (1959).

(58) J. Ferguson, *J. Mol. Spectroscopy*, **3**, 177 (1959).

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[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, QUARTERMASTER RESEARCH AND ENGINEERING CENTER, U. S. ARMY, NATICK, MASSACHUSETTS]

A Flash Photolysis Study of 2-(2',4'-Dinitrobenzyl)-pyridine in Water

BY GUNNAR WETTERMARK[1]

RECEIVED FEBRUARY 17, 1962

The phototropism of 2-(2',4'-dinitrobenzyl)-pyridine in liquid water solution at 24 ± 0.5° has been studied by the flash photolysis method. The solution turns blue when exposed to light and is restored to the initial colorless form in the dark reaction. The fading reaction followed the kinetics of a first order reaction with a 10^5 fold variation in the rate constant over the pH range 2 to 12. The great change in reaction rate has been interpreted to be due to the existence of two dissociation stages of the compound in this pH range. At high pH values where the colored compound is largely in the form of a negative ion, the rate of the fading reaction is constant with a rate constant of 0.1 sec.$^{-1}$. At lower pH values where the equilibrium is shifted to a higher population in a zwitterion form the rate of the fading reaction is increased and shows the characteristics of a general acid catalyzed process.

Introduction

2-(2',4'-Dinitrobenzyl)-pyridine is known to show phototropism both in the crystalline state and in solution.[2] The pure compound is colorless when kept in the dark but turns blue when exposed to light. Hardwick, *et al.*, studied the fading reaction and found that the compound was restored to its original colorless form. By using a cryostat together with a Cary spectrophotometer, they were able to make measurements on the fading reaction in dilute liquid solutions with isopropyl alcohol as the solvent at −10° to −60°. Compounds with a structure similar to 2-(2',4'-dinitrobenzyl)-pyridine have been reported not to be phototropic and it has thus been thought that the behavior of the compound was specific.[2b] Exploratory work in this Laboratory has shown, however, that many derivatives of *o*-nitrotoluene also are phototropic.

Flash photolysis has provided an excellent tool for detecting and studying the above effects since the colored form produced by exposure to light is in many cases so short-lived as not to be detected by low intensity techniques. As part of an investigation of these reactions in depth, we have investigated the kinetics of the fading reaction of 2-(2',4'-dinitrobenzyl)-pyridine in considerable detail. Information has been obtained about the mechanism of the process in water under different conditions of pH where the compound is found to be largely in ionic or molecular form.

Experimental

Flash Apparatus.—A detailed description of the flash light source is to be published in the near future[3]; hence only some specific data are given here. The electrical energy discharged to produce the flash in four straight quartz tubes was 2400 joules at about 28 kilovolts. The flash duration was 5 μsec. (1/*e* time). The lamp tubes were arranged symmetrically around a cylindrical quartz reaction vessel provided with optically flat end windows 20 cm. apart. A 0.5 cm. layer of aqueous filter liquid, containing 200 g. of $CuSO_4 \cdot 5H_2O$ per liter, surrounded the solution under investigation. The filter absorbed all light of wave lengths shorter than approximately 3100 Å. A fresh reaction solution was prepared for each experiment and flashed only once. All measurements were made at 24 ± 0.5°. A single beam absorption spectrophotometer recorded the light absorption changes in the system. The spectrophotometer consisted in part of a Bausch and Lomb grating monochromator and an E.M.I. 9552B photomultiplier tube. The signal from the tube was fed through a cathode follower to a Tektronix 535A oscilloscope. The light source for the spectrophotometer was a xenon arc; its light of wave lengths shorter than approximately 5200 Å. was cut off with Corning color filter 3486 in order to prevent the sample from being excited by the light of shorter wave length from this arc. The filter also served as a cut off for the secondary pass band of the grating.

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(3) L. Lindqvist, Institute of Physical Chemistry, Uppsala, Sweden.