[CONTRIBUTION FROM THE RADIATION PHYSICS LABORATORY, ENGINEERING DEPT., E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE]

Indirect Chemical Effects of High-energy Radiation in Organic Solutions

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Compounds of the structure $C_6H_5CH_2X$, where X– is Cl, OH, HCOO– and CH_3COO– but not H– or $C_6H_5CH_2$–, when irradiated as solutes (0.1 *M*) in cyclohexane with 2-mev. electrons react with a $G(-\ C_6H_5CH_2X) \cong 4$. Evidence obtained by scavenger studies using iodine and cyclohexene, and by variation of dose, dose rate and solute concentration, indicates that this high radiation yield results from energy transfer to the solute from excited solvent.

Introduction

High-energy radiation imparts excitation energy to organic molecules by interaction with electrons. Such a mode of excitation requires that each molecular species interact directly with the incident beam in proportion to its electron fraction. Any greater amount of excitation that occurs must be the result of some energy transfer process. Secondary reactions involving radicals will tend to obscure determination of the final energy distribution, but by proper choice of conditions the extent of these reactions can be defined.

Evidence for energy transfer, in systems subjected to high-energy radiation, leading to chemical reactions has been reported.[1-7] This paper will present a very favorable system for study of this phenomenon and a preliminary investigation of the mechanism.

For transfer of excitation energy to occur, it is necessary that the ionization potential and/or the excitation energy levels of the donor be at least as great as those of the acceptor. In the case of resonance transfer, the probability is highest when there is maximum overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor.[8] Ultraviolet absorption spectra should be useful as a rough criteria for predicting which compounds will act as energy acceptors or donors. Saturated hydrocarbons having very high excitation levels should be capable of transferring energy to most other organic substances.

For this work benzyl compounds were chosen as solutes because of the high probability of formation of a known radical, as demonstrated by flash photolysis.[9] Cyclohexane was selected as the principal solvent because its radiation chemistry has been studied extensively.[10] The benzyl radical does not abstract a hydrogen atom from the hydrocarbon solvent[11] and thus should destroy itself by dimerization or coupling with any other radicals present in sufficient concentration.

Experimental

Irradiation Procedure.—The radiation source used in these experiments was a 2-mev. Resonant Transformer operated at 1 ma. Samples were placed 20 cm. below the window through which the electron beam emerges from the accelerator. At this point the beam energy distribution has been measured to be flat to within ±5% over the sample area.

Dosimetry was accomplished by means of a flow calorimeter developed in this Laboratory. The error in dosimetry is approximately ±2%. It is estimated that the *G*-values (*i.e.*, the number of molecules altered per 100 e.v. of energy absorbed) in this work are in error by no more than ±10%, which results from a combination of the analytical and dosimetry errors.

Unless otherwise stated, irradiations were carried out using the multiple-cell sample holder previously described.[12] This technique allows five irradiations to be carried out simultaneously under exactly the same conditions. The sample volume in each case is 10 ml. Oxygen-free samples were prepared by successive freezing and thawing cycles on a high-vacuum line (2×10^{-6} mm.). The samples were then transferred to the irradiation cells under a nitrogen or argon atmosphere. In experiments performed in the presence of air, no attempt was made to maintain oxygen saturation during irradiation.

The experimental apparatus used to obtain the data shown in Fig. 2 was as follows: The irradiation cell consisted of a glass vessel (100-ml. volume) with a 0.001-in. thick aluminum cover. Degassing was accomplished by bubbling argon saturated with cyclohexane continuously through the solution. Analysis for amount of benzyl chloride reacted as a function of total irradiation dose was performed by GLC analysis of aliquots taken at various times during the run. Significant points were obtained from approximately 15 to 98% depletion of the original benzyl chloride. The aliquot volumes were maintained as small as possible so that when the final point was taken the total volume change was only 10%.

Reagents.—All chemicals used in this work were reagent grade and were used without further purification unless specified. Benzyl chloride, benzyl formate, benzyl acetate and nitrobenzene were Eastman white label reagents. Toluene and benzyl alcohol were Merck reagent-grade chemicals. Allylphenyl ether was purchased from Matheson, Coleman and Bell, Inc. Cyclohexene was a Phillips "Pure Grade" hydrocarbon. Solute purity in all cases was checked by gas-liquid chromatography. Cyclohexane was Phillips "Pure Grade," benzene was Mallinckrodt "Analytical Reagent" grade, ethanol was U.S.P. absolute and toluene was Merck "Reagent Grade." All solvents were checked for purity by taking their ultraviolet absorption spectra in a Cary Model 14 M spectrophotometer. Compounds used for identification of products produced by radiation were reagent-grade chemicals where possible. Cyclohexanol and cyclohexanone were Eastman white label reagents, benzaldehyde was obtained from Baker Chemical Company and phenylcyclohexyl ketone from Kay–Fries Chemicals, Inc.

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

(5) A. Henglein, C. Schneider and W. Schnabel, *Z. physik. Chem.* (Frankfurt), **12**, 339 (1957); A. Henglein, M. Boysen and W. Schnabel, *ibid.*, **10**, 137 (1957).

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(10) H. A. Dewhurst, *J. Phys. Chem.*, **63**, 813 (1959); H. A. Dewhurst, *J. Chem. Phys.*, **24**, 1254 (1956); A. C. Nixon and R. E. Thorpe, *ibid.*, **28**, 1004 (1958); A. J. Swallow, *Radiation Research*, **9**, 190 (1958).

(11) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, p. 92.

(12) A. MacLachlan, *Kev. Sci. Instr.*, **29**, 790 (1958).

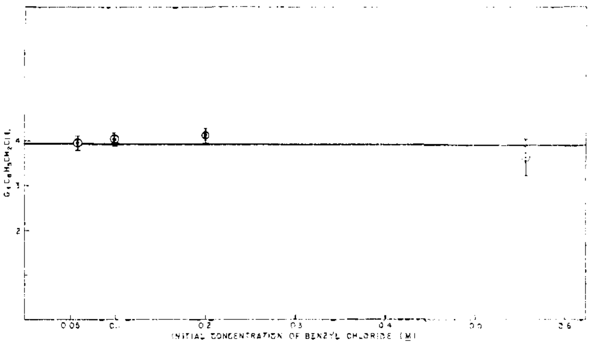

Fig. 1.

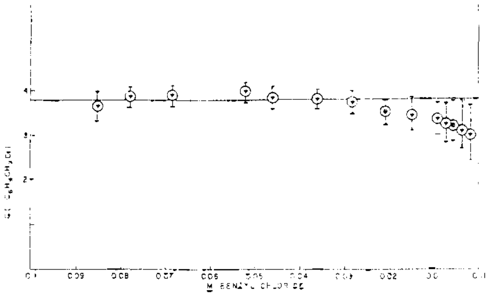

Fig. 2.—$G(-C_6H_5CH_2Cl)$ *versus* remaining concentration of benzyl chloride; total irradiation dose range (2.6–19.5) × 10^{20} ev./ml.

Cyclohexane was purified by repeated refluxing over concentrated sulfuric acid until the acid layer remained almost colorless. The olefin-free cyclohexane was then distilled through a 30-in. column packed with Pyrex helices.

Phenylcyclohexyl methane was prepared by Wolf–Kishner[13] reduction of phenylcyclohexyl ketone. To 270 ml. of triethylene glycol were added 38 g of potassium hydroxide, 38 g. (0.2 mole) of phenylcyclohexyl ketone, and 27 ml. of hydrazine (99%). The solution was refluxed for 1.5 hr., removing the water continuously. The temperature was then raised to 195° and refluxing was continued for 4 hr. more. After cooling, 270 ml. of water was added and the entire solution poured into 160 ml. of 6*N* hydrochloric acid. The crude phenylcyclohexyl methane was then extracted with ether. After removal of the ether the hydrocarbon was distilled under vacuum in a spinning band column. The fraction having a boiling point of 84° (at 5 mm.) was used to prepare standard samples.

Analysis.—Quantitative analysis for the amount of solute decomposed and the amount of products formed was accomplished by means of gas-liquid chromatography (GLC). For the solutes benzylchloride, formate, acetate and alcohol, and allylphenyl ether, as well as the radiation products cyclohexanol, cyclohexanone and benzaldehyde, the *G*-yields were determined using a 5-ft. column of 25% Apiezon N on 30–60 mesh acid-washed Johns–Manville Chromosorb, operated at 120°. Dibenzyl, phenylcyclohexyl methane, dicyclohexyl, diphenyl and dibenzyl ether were determined on the same column, operated at approximately 200°. A Perkin–Elmer Model 154B Vapor Fractometer, equipped with a micro-dipper sampling attachment, was used for the quantitative analysis of all components. By comparison of peak areas with unirradiated samples and with known concentrations of authentic samples of products, yields were easily calculated.

Solutions containing iodine were extracted with a 0.1*M* solution of sodium thiosulfate prior to analysis. The control, containing iodine, was also extracted. By direct comparison with a second control that contained no iodine, it was shown that this extraction did not remove any of the benzyl chloride or benzyl formate. The possibility that iodine might react with the benzyl compounds under the conditions of the experiment in the absence of irradiation was eliminated by always comparing an irradiated iodine-containing sample with an identical non-irradiated sample. In addition, comparison of the control sample containing iodine with a non-irradiated iodine-free sample indicated that iodine did not react appreciably with the solutes during the time necessary for the experiments.

Material Balances.—Material balances for benzyl chloride in cyclohexane, based on determining the *G*-yield for the disappearance of benzyl chloride and the *G*-yields of products, were attempted. Gas-liquid chromatography indicated that the products which could not be detected were high-boiling, high-molecular-weight compounds. This discrepancy prompted an investigation of the residue, with the hope that a knowledge of its structure would more clearly define the complete fate of the benzyl radicals.

For this work 60 ml. of 0.1 *M* benzyl chloride in cyclohexane was irradiated with a total dose of 3.6 × 10^{22} ev. The irradiation cell consisted of a glass vessel with a 0.001-in. thick aluminum cover. Two solutions were irradiated, one saturated with argon and the other with oxygen. Stirring during irradiation was accomplished by means of rotating glass-coated magnets. After irradiation each sample was diluted to 100 ml. Forty-ml. aliquots were then taken and the solvent was removed from each one by blowing argon gently over the solution. This procedure serves to minimize degradation of any products formed during irradiation. Both solutions were tested for peroxides, using potassium iodide acidified with dilute acetic acid. As expected, only the solution that was saturated with oxygen contained peroxides. After evaporation of the solvent a sublimation was carried out on the residue. Each sample was sublimed for 10 hr. at 110° and at a pressure of 0.01 mm. The residue and sublimate from each sample were then taken up in carbon tetrachloride. Infrared and ultraviolet analysis indicated that the high-boiling residues contained ring–ring addition products (λ max. at ~2590 A., with an extinction coefficient >1000). The complete structure of these compounds was not obtained, but it is felt that substituted polyphenyls make up the majority of them.

The total amount of benzyl radical accounted for by products is inadequate to explain the complete fate of the starting material (Table I). Such a result is not surprising in view of Steacie's[14] findings, where it was shown that a fraction of the benzyl radicals leads to products other than dibenzyl. Gas-liquid chromatography designed to uncover all products with boiling points up to 300° indicated that the products not accounted for by dibenzyl, phenylcyclohexyl methane and toluene (traces) are high-boiling, high-molecular-weight materials.

Results

***G*-Yields[15] for Benzyl Chloride.**—Table I presents a summary of the principal analytical data taken in these studies. Benzyl chloride (0.1 *M*) dissolved in cyclohexane reacted with a $G(-C_6H_5CH_2Cl)$ of 3.9. The high-boiling products that are derived from benzyl radicals analyzed by GLC were phenylcyclohexyl methane ($G = 1.15$) and dibenzyl ($G = 0.32$), accounting for a total radical *G*-value, $G(C_6H_5CH_2)$, of 1.79, or 46% of the total benzyl chloride reacted. The expected distribution of energy between benzyl chloride and cyclohexane in the absence of energy transfer is obtained by calculation of the relative stopping powers for the solute and solvent averaged over the electron energies (primary beam plus secondary electrons). No theory is presently available that allows an accurate calculation of this quantity, but an estimate can be

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[13] R. Adams, "Organic Reactions," Vol. IV, Chap. 8, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 391.

[14] H. Blades, A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 298 (1954).

[15] *G*-yield is defined as the number of molecules either produced or reacted for each 100 ev. of energy absorbed by the system. For 0.1 *M* benzyl chloride in cyclohexane (Table I) the proper notation is $G(-C_6H_5CH_2Cl) = 3.9$. A minus sign preceding the formula in parentheses denotes that this compound is used up by the radiation.

TABLE I

G-YIELDS FOR ELECTRON IRRADIATION OF SOLUTES[a]

Solute (S)	Dose × 10^{-20}, ev./ml.	Solvent	*G*-Yields of products $G(-S)$[b]	Dicyclohexyl	Phenyl cyclohexyl methane	Dibenzyl
Benzyl chloride	3.86	Cyclohexane	3.9	0.85	1.15	0.32
Benzyl chloride[c]	5.39	Cyclohexane	4.0	.7	0.95	.29
Benzyl formate	4.83	Cyclohexane	4.1	.59	.83	.37
Benzyl formate[c]	5.39	Cyclohexane	4.2	.32	.53	.35
Benzyl alcohol[d]	4.83	Cyclohexane	3.7	.45	.43	.16
Benzyl acetate	5.39	Cyclohexane	3.1	.47	.98	.35
Toluene	4.83	Cyclohexane	~ .08	1.02	~ .08	..
Benzyl ether[c]	5.38	Cyclohexane	3.8	0.48	.51	
Dibenzyl[e]	6.00	Cyclohexane	~0			
Phenylallyl ether	6.00	Cyclohexane	2.7	0.31		
Diphenyl[c,e]	3.86	Benzene	~0			

[a] Initial concentrations were 0.1 *M*. [b] $G(-S)$ represents one run at the dose given in column 2. The limits of error were established by repeating each run at least three times at similar doses. The product *G*-yields, however, were determined only for the dose given. [c] Irradiation performed in the presence of air. [d] The same $G(-S)$ obtained with air present. [e] Initial concentration was 0.01 *M*.

made by using the valence electron fraction.[16] At 0.1 *M* concentration the valence electron fraction of benzyl chloride is 0.012, corresponding to a true *G*-value for the disappearance of benzyl chloride of 325, when only the fraction of the beam interacting directly with the solute is considered. Assuming that the reaction occurs through carbon–chlorine bond rupture, it can be calculated that 0.3 ev. of energy is expended per bond rupture. The actual strength of this bond is 3.5 ev. This implies that either benzyl chloride has received energy by transfer from excited cyclohexane or some other process is responsible for its reactivity.

The possibility of a chain decomposition of benzyl chloride involving chlorine atoms seems remote, due to the known high reactivity of the chlorine atoms towards cyclohexane and its low reactivity in attacking a hydrogen atom α to a halogen atom.[17] Evidence for the absence of such a process was obtained by varying the radiation intensity over a factor of thirty and noting that the *G*-value for the disapppearance of benzyl chloride remained constant. Table II lists the results obtained. Further verification of this result was obtained by adding scavengers and by varying the solute concentration, both of which are discussed in later sections.

TABLE II

VARIATION OF $G(-C_6H_5CH_2Cl)$ WITH RADIATION INTENSITY[a]

Intensity, ev./ml. sec. × 10^{-18}	Total dose, ev./ml. × 10^{-20}	$G(-C_6H_5CH_2Cl)$
0.356[b]	6.5	4.2
.44	4.2	4.1
.90	4.3	3.7
1.47[b]	6.24	3.8
2.36[b]	5.90	4.0
3.33	4.0	3.9
4.51[b]	5.90	4.0
5.53[b]	5.90	4.4
10.4[b,c]	5.9	3.4

[a] Initial concentration of benzyl chloride was 0.0992 *M*. [b] Oxygen was not excluded for these runs. [c] Due to short irradiation time, the total dose may be high for this run.

Figure 1 presents the results of varying the initial benzyl chloride concentration by a factor of ten. The amount of benzyl chloride decomposed is found to be independent within experimental error of concentration over this range. Figure 2 is a plot of $G(-C_6H_5CH_2Cl)$ as a function of the number of molecules reacted (increasing total dose). The *G*-yield is constant over approximately 80% of the irradiation and then slowly drops to 3 at 97% reaction. A constant *G* again demonstrates the independence of the efficiency of the reaction with solute concentration. At high conversions, products undoubtedly are competing for the energy and account for the downward drift.

Phase Effects.—Irradiation of 0.1 *M* benzyl chloride in cyclohexane as a solid solution at −78° resulted in no detectable decomposition of the solute (total dose = 7.1 × 10^{20} ev./ml.). As a further test of this result, GLC analysis on the high-boiling products was performed and indicated no phenylcyclohexyl methane or dibenzyl were present in the irradiated solid solution. The frozen solutions were crystalline rather than glasses.

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(16) Approximately 50% of the total beam energy is administered to a target by the secondary electrons with energies less than 500 ev. According to the equations of Brandt [W. Brandt, "United States Atomic Energy Commission Nuclear Data Tables," 1959, p. 35, and W. Brandt, *Phys. Rev.*, **104**, 591 (1956); see also W. Brandt, *Health Physics*, **1**, 11 (1958) for a discussion of stopping power as a function of electron energies] the average relative stopping power of benzyl chloride to cyclohexane at energies between 2 mev. and 1000 ev. is 1.25 (1.31 − 1.16), while the same ratio for 100 to 500 ev. electrons is ~1.08. The mean stopping power ratio is therefore ~1.16. Agreement with the valence electron ratio (1.17) of benzyl chloride to cyclohexane is not fortuitous but is a consequence of the similarity of excitation potentials of outer valence electrons for light elements (~12 ev.) and that the secondary electrons because of their low energies relative to the excitation potentials of inner shell electrons (~400 ev.) can only interact with valence shells.

Valence electron fraction of a solute is $Z_B = \dfrac{AZ_A}{AZ_A + BZ_B}$ where Z = number of valence electrons, *i.e.*, one for each hydrogen, four for each carbon and seven for each chlorine, A = solute concentration, B = solvent concentration.

(17) G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4578 (1955).

TABLE III

G-YIELDS FOR IRRADIATION OF SOLID SOLUTIONS IN CYCLOHEXANE AT $-78°$[a,b]

Solute (S)	Conc., M	Dose $\times 10^{-20}$ (ev./ml.)	$G(-\mathrm{S})$	G(Dicyclohexyl)
None	....	4.8	..	1.2
Benzyl formate	0.1015	7.1	~0	1.1
Benzyl alcohol	.1079	7.1	~0	1.1
Benzyl chloride	.101	7.1	~0	0.9

[a] Samples were only 5 ml. [b] Irradiations were carried out in air.

Effect of Dissolved Oxygen.—Table I also contains the results of work performed both in the presence and absence of dissolved oxygen. The most important fact to observe is that the amount of benzyl chloride reacted for a given dose is not altered when the irradiations are carried out in air. Oxygen does have a marked influence on the products formed, as was demonstrated by a detailed analysis of the products. Benzaldehyde, cyclohexanone and cyclohexanol were found when benzyl chloride–cyclohexane mixtures were irradiated in air. The benzyl radical is known to react with oxygen quite readily. Flash photolysis studies[9] have demonstrated that oxygen decreases the lifetime of the benzyl radical and has to be rigorously excluded before the absorption spectrum of the radical can be observed. An indication of the high reactivity of oxygen was obtained by irradiation of 0.1 M benzyl chloride in cyclohexane in the presence of both oxygen and excess iodine. It was found that benzaldehyde and cyclohexanone were still detected in the products.

Effect of Scavengers at High Concentrations.—Consideration of a radical path for the disappearance of solute immediately suggests the technique of adding scavengers. Radical trapping by addition of high concentrations of reactive solutes (iodine, olefins, etc.) undoubtedly introduces complications through the interactions of these additives with excited species of solvent and solute but can still be useful if these possibilities are recognized. Iodine would react with an alkyl radical much more efficiently than any of the benzyl compounds and as shown in Table IV has an appreciable effect on the G-yields. Cyclohexene (0.13 M) has a small effect on the amount of benzyl chloride decomposed, contrary to what might have been expected if radicals were responsible for the reaction.

Equimolar concentrations of benzyl acetate and benzyl chloride (~0.05 M each) in cyclohexane were irradiated to test the effect of competition of similar compounds for energy from the excited solvent molecules. Within the limits of experimental error the results show that there is no selectivity for the transmission of the available energy to these two solutes. If a radical reaction was responsible for the observed effect, some selectivity might be expected.

TABLE IV

EFFECT OF ADDITIVES ON G-YIELDS

Solute (0.1 M)	Dose $\times 10^{-20}$, ev./ml.	Solvent	Additive	Conc. (M)	G-Yields $G(-\mathrm{S})$
Benzyl chloride	5.39	Cyclohexane	Cyclohexene	0.13	3.4
Benzyl chloride	5.39	Toluene			3.7
Benzyl chloride	5.39	Cyclohexane	Toluene	0.50	3.7
Benzyl chloride } [a,b]	5.72	Cyclohexane			1.7
Benzyl acetate }					1.7
Benzyl chloride } [b,c]	6.35	Cyclohexane			3.0
Nitrobenzene }					2.4
Benzyl chloride[b]	6.35	Cyclohexane	I_2	Sat.	3.0
Benzyl chloride[b,d]	5.48	Cyclohexane	I_2	0.03	2.2
Benzyl formate	6.04	Cyclohexane	I_2	Sat.	2.2

[a] Each 0.05 M. [b] Irradiated in air. [c] Each 0.1 M. [d] Concn. = 0.05 M.

A second competition reaction, involving nitrobenzene and benzyl chloride, was performed, and this time some selectivity was obtained (Table IV). This can be seen by noting that $G(-C_6H_5CH_2Cl)$ has been reduced to 3.0 while $G(-C_6H_5NO_2)$ is 2.4. Nitrobenzene is probably depleted by radical reaction, since nitro compounds are well-known inhibitors for radical polymerization.[18] Nitrobenzene is known to be a fluorescence quencher,[19] and it was thought that it might protect the benzyl chloride. Some protection may have occurred, but benzyl chloride appears to be more effective in reacting after "capture" of the excited species.

***G*-Yields for Other Solutes.**—Other solutes, *viz.*, benzyl formate, benzyl alcohol, toluene, benzyl ether, dibenzyl, diphenyl and phenylallyl ether, were studied in cyclohexane, and the G-yields found are listed in Table I. These solutes were not investigated in as great detail as benzyl chloride but the following comparisons can be made. Benzyl acetate, formate, alcohol and ether all have approximately the same G-yield as benzyl chloride at a concentration of 0.1M in cyclohexane ($G \cong 4.0$). Toluene and dibenzyl are essentially inert at these same concentrations and total dose. Benzyl formate and benzyl alcohol were irradiated in solid

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(18) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950).

(19) B. Sveshnikov, *Acta Physicochim. U.R.S.S.*, **4**, 453 (1936); **7**, 755 (1937). The pertinent data for this reference may be found in P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949, p. 331.

cyclohexane at −78° and were found to have undergone no detectable reaction. Table I also demonstrates that oxygen has little effect on the *G*-value, and Table IV exhibits results for other benzyl compounds with respect to the consequence of addition of iodine as a radical scavenger.

The results (except toluene and dibenzyl) are completely analogous to those obtained with benzyl chloride. Table V presents an analysis of the effect of toluene on the products derived from the solvent.

TABLE V

Solute	Conc., *M*	Dose × 10^{-20} (ev./ml.)	*G*(dicyclohexyl)	*G*(cyclohexene)
Toluene	0.0996	4.8	1.02	1.8
None	....	4.8	1.25	2.3

Conclusions

In the presence of a scavenger benzyl chloride reacted with about half the efficiency of the iodine-free irradiation. At 0.1 *M* benzyl chloride in an iodine-saturated-cyclohexane solution the yield was only reduced by one-third. The most unusual aspect of this experiment is that evidently the benzyl chloride is not entirely decomposed by radical attack, *i.e.*

$$C_6H_5CH_2Cl + R\cdot \longrightarrow RCl + C_6H_5CH_2\cdot$$

does not completely account for the disappearance of this solute, but it must be receiving energy in some fashion not effectively inhibited by iodine. In the experiment where the benzyl chloride concentration was 0.05 *M* and the iodine 0.03 *M*, it is seen that the iodine is at best no more effective than benzyl chloride in the competition for the excited species. A lower limit of the *G*-value for the disappearance of benzyl chloride by energy transfer is thus 2.2 at 0.05 *M* and 3.0 at 0.1 *M*.

When no attempt was made to remove oxygen from the solutions during irradiations, it may be seen from Table I that the $G(-C_6H_5CH_2Cl)$ is not affected. This lack of an effect is probably due to the large doses used, relative to the oxygen solubility, although no effort was made to verify this.

Conclusions based on the analysis of the high-boiling products obtained must be made with careful consideration of the possible methods of their formation. Dissociation of an excited benzyl compound leads to the benzyl radical along with a second radical derived from the substituent X. The benzyl radical is very stable and would not abstract a hydrogen atom from the solvent.[11] In many of the compounds studied the substituent radical would undoubtedly abstract a hydrogen atom from cyclohexane and yield a cyclohexyl radical. The chlorine atom from benzyl chloride and hydrogen and methyl radicals from the decomposition of the fragments H COO· and CH_3-COO·, respectively, are in this category. Cyclohexyl radicals formed by this route lead to dicyclohexyl and phenylcyclohexyl methane, just as when they are formed directly by decomposition of excited cyclohexane. Therefore, observation of the dicyclohexyl and phenylcyclohexyl methane yield as a function of solute is not a direct measure of the amount of quenching of excited cyclohexane. In the case of toluene (0.1 *M*) in cyclohexane, such a comparison has some validity. The results summarized in Table V show that *G*(dicyclohexyl) in the absence of toluene is about 20% larger than in its presence, indicating that some quenching may have occurred.

The work already described demonstrated the techniques used in proving that some form of energy transfer was responsible for the high *G*-values obtained from benzyl chloride. Other benzyl compounds gave completely analogous results except when the substituent, X, was hydrogen or carbon, *e.g.*, toluene or dibenzyl. The fact that the *G*-values for many compounds in cyclohexane are ≅4 is strong evidence for the involvement of the aromatic ring in capturing the available energy.

Toluene and dibenzyl undergo very little reaction under these irradiation conditions. Bond strength data, as given in Table VI, do not explain the results.

TABLE VI

BOND DISSOCIATION ENERGIES

Bond	Dissoc. energy, kcal./mole
$C_6H_5CH_2—H$	77–88
$C_6H_5CH_2—CH_2C_6H_5$	47
$C_6H_5CH_2—OH$	73
$C_6H_5CH_2—Cl$	68

When toluene reacts at least 77 kcal. must be supplied. Benzyl chloride and benzyl alcohol have somewhat weaker bonds and it might be expected that these compounds would react more efficiently than toluene. This same argument would predict that dibenzyl should react more readily than benzyl chloride and benzyl alcohol. Experimentally (Table I), it is found that neither toluene nor dibenzyl reacts appreciably, while benzyl chloride and alcohol react to the same extent. It does not appear, therefore, that the amount of energy transferred is limiting, but rather that some explanation other than bond strength differences is required. It should be emphasized that the bond energy data reported here, while they are currently accepted values, suffer from uncertainties. The dissociation energies are for molecules in the gas phase and may be very different from the liquid-phase values. Pyrolysis and photochemical reaction data are often used in calculating bond energies. Such data are often suspect, because of the mechanistic assumptions that must be made.

The π-electron system of the aromatic ring certainly has the attributes of an energy acceptor, regardless of the mechanism of energy exchange, *e.g.*, relatively low electronic levels, low ionization potential and high electron affinity (relative to saturated systems). Irradiation of benzyl chloride in the presence of 0.5 *M* toluene indicates that toluene does not inhibit the reactivity of the benzyl chloride (Table IV). Even more interesting, the *G*-value for the disappearance of benzyl chloride in pure toluene is about the same as it is in cyclohexane. Toluene (0.1 *M*) in cyclohexane (Table I) is only slightly decomposed as measured by both the decrease in toluene concentration and increase in products containing the benzyl fragment. These points demonstrate that there are no radical species present that specifically attack the aromatic ring, while not reacting with cyclohexene or iodine. The aromatic ring is common to all the compounds and probably accepts the excitation energy independent of substituent. This could mean that the substituent controls the amount of reaction by affecting the lifetime of the excited benzyl compound. With toluene (or dibenzyl) the lifetime may be long enough for energy to be degraded thermally with no subsequent chemical reaction. Other solutes, due to electronic interaction of the substituent with the aromatic ring, may suffer bond rupture in a time short compared to the interval necessary to dissipate the energy by other mechanisms. A G of $\cong 4$ for a number of solutes, over a range of concentrations, indicates saturation with respect to capture of the excited species.

While establishing that the large G-yields encountered in these experiments are most certainly not the result of conventional radical reactions, little has been said of what the energy transfer agent might be. Energy may be transferred by collision with an excited solvent molecule (diffusion controlled) by some resonance process,[20] *e.g.*, a long-range transfer, or perhaps one might consider low-energy electrons as suggested by Platzman.[21] This latter mechanism, based on free "subexcitation electrons" having a useful lifetime separated from their cations has many attractive features. However, there appears to be no experimental evidence in favor of this process in solution. Ion molecule reactions, which might be expected to accompany such a mechanism, have not yet been unambiguously demonstrated in solution. The first two mechanisms are well documented in solution, and it seems logical to try to see if evidence can be obtained that will fit one of these two processes.

Differentiation between these two possibilities was attempted by irradiation of both solid and liquid solutions. If the G-yields were unaffected by changing from the liquid to the solid state, then it would seem unlikely that a migrating molecular species was involved. The alternative, *i.e.*, no reaction in the solid state, is ambiguous because either there was no energy transferred or electron capture or energy exchange has occurred, but no reaction is observed due to a cage effect of the solid lattice. Experimentally, the ambiguous case was found and renders further conclusions tenuous (Table III).

The details of the mechanism of energy transfer in liquid systems must still be regarded as vague, but a more extensive study of G-values as a function of temperature and phase (liquid, crystalline and glass) could certainly differentiate among the possible excited species responsible for the observed effects.

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[20] C. Reid, "Excited States in Chemistry and Biology," Butterworth Scientific Publications, London 1957, p. 111.

[21] R. L. Platzman, *Radiation Research*, **2**, 1 (1955).