PRIMARY PHOTOCHEMICAL PROCESSES IN AROMATIC MOLECULES

PART 4.-SIDE-CHAIN PHOTOLYSIS IN RIGID MEDIA

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Two processes of side-chain fission have been identified in the photolysis of substituted aromatic molecules in rigid solvents at low temperatures. One involves fission of a β bond to yield two radicals and the other results directly in the formation of two molecules, one of which is styrene. Quantum yields at 2537 Å in one example of each process, were 1.1×10^{-2} and 3.6×10^{-2} respectively. The radical products have been identified spectroscopically and conditions necessary for their stabilization have been investigated. Generalizations concerning the relative probability of dissociation of different bonds in equivalent positions are applicable to the forty molecules which have been studied.

The primary photolytic bond dissociation processes in aromatic compounds have received relatively little attention owing to the low quantum yields of dissociation and the difficulties of analysis of the complex products which are often formed. Previous studies have been based mainly on analysis of the gaseous products of reaction and the work most relevant to the present discussion is that of Hentz, Sworski and Burton ^{1, 2} who found evidence for fission in the side chain of toluene with a quantum yield of gaseous products of about 1 %.

The method which we have used here is one which eliminates the complexities of secondary reactions. It is based on the observations of Norman and Porter ³ who found that toluene and related molecules dissociate photochemically in rigid media and that aromatic free radicals remain trapped in the matrix at low temperatures, and can be observed spectroscopically. The spectra were first observed following flash photolysis of aromatic vapours by Porter and Wright (part 3) ⁴ and were attributed to benzyl and its derivatives. It has recently been shown that they are also formed during photolysis of ordinary solutions at normal temperatures.⁵ Whilst further studies in gases and liquids will be necessary for the interpretation of the kinetics of the radical reactions, the matrix isolation technique is in many ways more suitable for the identification of the radical spectra and of primary photochemical processes owing to the elimination of most secondary reactions.

EXPERIMENTAL

The apparatus and procedure used in the main part of this investigation were identical with those described by Norman and Porter,³ the cell length being 1.5 cm. In later experiments a different arrangement incorporating a cell 20 cm in length was used to detect weaker transitions.⁶ Spectra were recorded by means of the Hilger medium and small quartz instruments and scanned by microdensitometer. All solvents were spectroscopically pure and were carefully dried in order to prevent crystallization of the glass. The aromatic compounds available as commercial products were purified by fractional distillation, recrystallization or vacuum sublimation and boiling points or melting points in every case were within one degree of those reported in the literature. Some of the particular methods used were : toluene, ethyl benzene, *iso*propyl benzene, benzyl chloride, benzyl cyanide, anisole, phenetole purified by the method of Vogel, 7 benzyl alcohol

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according to Mathews,⁸ aniline according to Knowles,⁹ o-xylene purified by fractional distillation, m- and p-xylenes by fractional crystallization. Phenyl ethyl chloride was prepared from the corresponding alcohol by the method of Norris and Taylor.¹⁰

A high-intensity light source was used in most experiments involving the 1.5 cm cell. This was a 1 kw high-pressure mercury arc, type ME/D (combined with a 2-cm water filter), which emits most lines of mercury, except for the 2537 line which is reversed, and also a continuous spectrum throughout the visible and ultra-violet region. For quantum-yield determinations a low pressure mercury-vapour lamp, combined with a 1-cm filter of 4 N acetic acid was used from which the only significant radiation in the region of aromatic absorption was at 2537 Å. The 20-cm cell was irradiated from the side by two U-tube low pressure mercury-vapour lamps; the length of each limb was 20 cm and the whole apparatus was surrounded by a reflector.

The solvents generally used to form glasses were E.P.A. (ether, *iso*pentane and ethanol in proportions 5:5:2) and M.P. (methyl cyclohexane and *iso*pentane in proportions 2:3). Solutions were always outgassed and sealed off before irradiation and all experiments were performed at -197° C.

RESULTS

Four types of primary dissociation process have been identified in this work. These are as follows.

(i) RING FISSION

This has previously been suggested to explain the formation of hexatriene during photolysis of benzene in rigid glasses.^{11,3.} Spectra very similar to that of hexatriene are also observed in the permanent products of photolysis of toluene and related molecules in rigid glasses and these are probably substituted hexatrienes formed by ring fission followed by abstraction of two atoms from the solvent. The quantum yield of this process in benzene is approximately 0.01 at 2537 Å (Anderton and Porter, unpublished work).

(ii) Electron ejection

This was first clearly established by Lewis and his collaborators in a number of aromatic molecules.¹² We have found spectra of radical cations which must result from this process, after photolysis of many amines. Unlike processes (i), (iii) and (iv), electron ejection (photo-oxidation in the terminology of Lewis) does not readily occur in non-polar glasses (e.g. M.P.), and it is normally encountered only in basic molecules.

(iii) Side-chain dissociation at the β bond

This is exemplified by the formation of the benzyl radical from toluene. Benzyl and its derivatives have strong banded spectra in the near u.-v. region, which are formed on irradiation of rigid solutions, remain as long as the glass is kept rigid and disappear completely and irreversibly on warming.³

(iv) Side-chain dissociation into two molecules, one of which is styrene

This occurs rather generally in compounds of the type $C_6H_5CHXCH_2Y$. Styrene is observed in the rigid glass before warming and is therefore formed in the primary act.

A fifth process, dissociation into two ions, was discussed by Lewis but we have found no evidence for this reaction in any of the systems considered here.

Processes (i) and (ii) will be discussed further in later communications and the present work is concerned mainly with processes (iii) and (iv).

ASSIGNMENTS OF RADICAL SPECTRA

In part 3 arguments were given for assigning the common transient spectrum, observed on photolysis of toluene and other benzyl compounds in the gas phase, to benzyl and it was mentioned that more definite evidence was available from our work in rigid solvents. This will now be given. Common transient spectra, satisfying all energetic requirements, could arise from the primary photochemical dissociation of molecules of formula $C_6H_5CH_2X$ in only three ways :

 $C_6H_5CH_2X \longrightarrow C_6H_5CH_2 + X, \tag{1}$

 $C_6H_5CH_2X \longrightarrow C_6H_5CH + HX, \qquad (2)$

$$C_6H_5CH_2X \longrightarrow C_6H_5 + CH_2X. \tag{3}$$



FIG. 1.—Radical spectra resulting from the photolysis of aromatic molecules at - 197°C. In each case the first spectrum is recorded before and the second after irradiation of the rigid solution for 15 min.

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If we consider the series $C_6H_5CH_3$, $C_6H_5CH_2X$, $C_6H_5CH_2$ and $C_6H_5CX_3$ process (iii) would result in one common spectrum, process (ii) could result in no more than two radical spectra and process (i) in no more than three radical spectra from the four molecules. We have investigated three such series in which X was a chlorine atom, a methyl radical and a phenyl radical respectively. The wavelength maxima of the radical absorption spectra in E.P.A. were as follows.

molecule	max. (Å)	radical	
C ₆ H ₅ CH ₃	3187	$C_6H_5CH_2$	
C ₆ H ₅ CH ₂ Cl	3187	C ₆ H ₅ CH ₂	
C ₆ H ₅ CHCl ₂	3231	C ₆ H ₅ CHCl	
C ₆ H ₅ CCl ₃	3238	$C_6H_5CCl_2$	
C ₆ H ₅ CH ₂ CH ₃	3222	C ₆ H ₅ CHCH ₃	
C ₆ H ₅ CH(CH ₃) ₂	3242	$C_6H_5C(CH_3)_2$	
C ₆ H ₅ C(CH ₃) ₃	3242	$C_6H_5C(CH_3)_2$	
C ₆ H ₅ CH ₂ C ₆ H ₅	3355	C ₆ H ₅ CHC ₆ H ₅	
$C_6H_5CH(C_6H_5)_2$	3415	$C_6H_5C(C_6H_5)_2$	

In each series three distinct spectra were observed, providing excellent confirmation that the dissociation process involved is β bond fission. The spectra can be assigned with some confidence to the above radicals with the exception of the 3231 Å band observed from benzal chloride. This spectrum was rather weak and, although definitely different from any other band of the series, its position and appearance were rather sensitive to concentration and other factors and its assignment should be regarded as uncertain pending further examination.

Further confirmation of the assignments is afforded by the fact that one spectrum in the series, that of triphenyl methyl, was previously well known and established being, in fact, the first free radical spectrum to be observed by Gomberg in 1900.¹³ The colour of this radical is caused by a weaker absorption band at 5110 Å and we have detected this band in the present work by use of the 20 cm cell. Finally we have considered the relationship of the absorption bands of benzyl and its derivatives to the emission spectra of Schuler and his collaborators ¹⁴ and the molecular orbital calculations of Dewar, Longuet-Higgins and Pople ^{15, 16} and of Bingel.¹⁷ This led us to search for the predicted weak long-wavelength system of benzyl and we have recently recorded this spectrum by use of the 20 cm cell.⁶ Comparison of the data from all these sources gives a consistent account of the spectrum of benzyl and final confirmation of our assignments.⁶

Typical free-radical spectra, obtained after 15 min irradiation are shown in fig. 1. The solvent was E.P.A. in each case except α -methyl naphthalene for which the solvent was M.P. The principal absorption maxima of all spectra which we have assigned to neutral free radicals, and the molecules from which they have been observed after photolysis at -197° C are given in table 1. The intensities are visual estimates referred to the strongest band as 10. The wavelength measurements refer to radicals in E.P.A. in all cases except the two naphthyl methyl radicals which were in M.P.

In most cases the bands were sharp and maxima could be estimated to ± 5 Å whilst comparison could be made to about ± 1 Å. The basis of the assignments has been described and although it has not always been possible to obtain a radical from more than one molecule, the close resemblances of the radical spectra in position, band width and structure are strong evidence that radicals of the benzyl type are involved and this is usually sufficient to define the carrier. The spectra all fall in a quite narrow spectral region and some chance coincidences may be expected. The only clear case of coincidence of different radical spectra is found in the three xylyl radicals but, even here, there are distinct differences in band structure; the 3230 Å band in *m*-xylene, for example, is a doublet.

Only spectra attributed to neutral radicals are recorded in table 1 but in all the aromatic amines other transient spectra which we have assigned to the radical cations appeared on photolysis. Our reasons for not attributing these spectra to neutral radicals must be mentioned briefly. The neutral radicals formed from aniline and its N-methyl derivatives were identified in the same manner as benzyl. Thus the three aniline derivatives

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	TABLE 1.—FREE RADICAL SPECTRA			
radical	parent molecule	۶A	vcm ⁻¹	relative intensities
C ₆ H₅CH ₂	C ₆ H ₅ CH ₃ , C ₆ H ₅ CH ₂ Cl, C ₆ H ₅ CH ₂ OH, C ₆ H ₅ CH ₂ NH ₂ , C ₆ H ₅ CH ₂ CN, C ₆ H ₅ CH ₂ COOH, C ₆ H ₅ CH ₂ CH ₂ CH ₂ NH ₂ , C ₆ H ₅ CH ₂ CH ₂ OH, C ₆ H ₅ CH ₂ CH ₂ CH ₂ OH.	3187 3082 3047	31380 32450 32810	10 3 3
C_6H_5CH . CH_3	C ₆ H ₅ CH ₂ CH ₃ , C ₆ H ₅ CHOHCH ₃ ,	3222	31040	10
	C ₆ H ₅ CHNH ₂ CH ₃ , C ₆ H ₅ CH ₂ CH ₂ OH.	3167 3129 3083	31580 31960 32440	5 6 6
C ₆ H ₅ C(CH ₃) ₂	C ₆ H ₅ CH(CH ₃) ₂ , C ₆ H ₅ C(CH ₃) ₃	3242	30840	
(C ₆ H ₅) ₂ CH	(C ₆ H ₅) ₂ CH ₂ , (C ₆ H ₅) ₂ CHOH	3355 3305- 3240 3180 3122	29810 30260 30860 31450 32030	10 8 5 3 4
(C ₆ H ₅) ₃ C	(C ₆ H ₅) ₃ CH	3415 3358 3303	29290 29780 30270	10 8 2
$C_6H_5CH_2CHC_6H_5$	(C ₆ H ₅ CH ₂) ₂	3625	27580	
o-CH ₃ C ₆ H ₄ CH ₂	o-CH ₃ C ₆ H ₄ CH ₃	3230 3170 3100	30960 31550 32260	10 1 1
m-CH ₃ C ₆ H ₄ CH ₂	m-CH ₃ C ₆ H ₄ CH ₃	3230 3100	30960 32260	10 6
<i>p</i> -CH ₃ C ₆ H ₄ CH ₂	p-CH ₃ C ₆ H ₄ CH ₃ p-CH ₃ C ₆ H ₄ CH ₂ Cl	3230 3170 3100 3047	30960 31550 32260 32810	10 1 3 2
1, 3(CH ₃) ₂ 5CH ₂ , C ₆ H ₂	3 1: 3: 5(CH ₃) ₃ C ₆ H ₃	3249 3109 2964	30770 32170 33730	10 6 2
C ₆ H ₅ CHCl	C ₆ H ₅ CHCl ₂	3231 3190 3100	30950 31350 32260	10 5 4
C ₆ H ₅ CCl ₂	C ₆ H ₅ CCl ₃	3238 3108	30880 32180	10 8
CH ₂	CH ₃	3700 3554 3500 3424	27030 28140 28570 29210	7 5 7 10
CH ₂	CH3	3840 3647 3687 3500 3424	26040 27420 27120 28570 29210	7 5 4 8 10
C ₆ H ₅ NH	C ₆ H ₅ NH ₂	3109	32060	

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TABLE 1 - (Cont.)

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radical	parent molecule	٨٩°	v cm ⁻¹	relative intensities
C ₆ H ₅ NCH ₃	$C_6H_5NHCH_3$ $C_6H_5N(CH_3)_2$	3166	31590	
C6H5CH2NC6H5 or C6H5CHNHC6H5	C ₆ H ₅ CH ₂ NHC ₆ H ₅	3745 3635	26700 27510	10 8
C ₆ H ₅ O	C ₆ H ₅ OH, C ₆ H ₅ OCH ₃ C ₆ H ₅ OCH ₂ CH ₃	2870 limit	34840	
p-HOC ₆ H₄O	<i>p</i> -HOC ₆ H₄OH	4140	24150	10
	$O = \underbrace{\frown} = O(+ RH)$	3550	2 <u>8</u> 170	6
	ОН	4220	23700	10
		4041	24740	4
0 0	OH OH	3300	30300	8
ОН	9	5100	19610	10
$\bigwedge \bigwedge$		3830	26110	8
		3531	28320	5
0	0			

can give only two aniline type radicals and the near u.-v. spectra were therefore assigned as follows.

molecule	max. (Å)	radical
C ₆ H ₅ NH ₂	3109	C ₆ H ₅ NH
C ₆ H ₅ NHCH ₃	3166	C ₆ H ₅ NCH ₃
$C_6H_5N(CH_3)_2$	3166	C ₆ H ₅ NCH ₃ .

These spectra were observed in both the polar E.P.A. glass and the non-polar M.P. glass. Other bands were observed in the visible region which were different for each of the three molecules and could not therefore be spectra of the two anilino radicals. Furthermore the visible bands were not observed in gas-phase flash photolysis and were absent or very weak in M.P. glass. Irradiation of N: N'-dimethyl *p*-phenylene diamine in E.P.A. yielded the well-known spectrum of the radical cation ¹⁸ at very high intensity whilst no such spectra were observed after irradiation in the M.P. glass. Other spectra showing these characteristics are therefore also attributed to radical cations and will be discussed in a later communication.

SIDE-CHAIN DISSOCIATION INTO TWO MOLECULES

A number of substances, after photolysis in E.P.A., gave a common banded spectrum which was still present after warming the glass. The spectrum was similar to that of styrene reported in the literature, and its identity was confirmed by comparison with a solution of pure styrene in our solvents both at room temperature and in the glass at -197° C. The substances from which styrene was formed on irradiation in the glass were ϕ CH₂CH₃, ϕ CH₀(OH)CH₃, ϕ CH(NH₂)CH₃, ϕ CH₂CH₂OH, ϕ CH₂CH₂NH₂, ϕ CH₂CH₂Cl and ϕ CH₂CH₂Br. Some of these also gave no radical products which have been discussed; others such as ϕ CH₂CH₂Cl and ϕ CH₂CH₂Br gave no radical products and styrene was the only spectrum observed. Permanent products were also observed

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in the spectra of other compounds, some of which, although they have not been identified, were probably not of the hexatriene type, but no compounds, other than those mentioned above, showed the styrene spectrum. The only substances investigated which gave neither transient spectra nor styrene were benzyl bromide and duroquinone.

DETERMINATION OF QUANTUM YIELDS

Quantum yields of processes (iii) and (iv) were determined in a representative example of each type of decomposition. For process (iii) we had only one possibility—the photolysis of triphenyl methane to give triphenyl methyl—since extinction coefficients of none of the other radicals are yet known. For process (iv) phenyl ethyl bromide was chosen because styrene is the only product detected in the photolysis of this molecule and extinctions can therefore be determined without interference from other products.

The source of radiation in both cases was the filtered low-pressure mercury arc which gave essentially monochromatic light at 2537 Å. The incident intensity was determined by conventional uranyl oxalate actinometry, and the concentrations of products were found by photometry of the photographic absorption spectra.

β bond dissociation in triphenyl methane

A solution of triphenyl methane (2·44 g/l.) in E.P.A. was irradiated for 30 min and the concentration of triphenyl methyl determined from its extinction at 3450 Å using the extinction coefficients given by Chu and Weissman.¹⁹ (These authors used a toluene + triethylamine solvent and the extinction coefficients may therefore differ slightly from those in E.P.A.) Three determinations of quantum yield gave the values $1\cdot10 \times 10^{-2}$, $1\cdot13 \times 10^{-2}$ and $1\cdot08 \times 10^{-2}$ and a mean value,

$$\phi = 1.11 \times 10^{-2}$$
.

STYRENE FORMATION FROM PHENYL ETHYL BROMIDE

A 10⁻³ M solution of phenyl ethyl bromide in E.P.A. was irradiated at the temperature of liquid nitrogen for 2 h and the styrene formed was determined spectrophotometrically after warming the glass to room temperature. The whole spectrum was measured to confirm its identity and quantitative estimation was based on the first absorption maximum at 2905 Å. The parent substance does not absorb at this wavelength. The concentration of styrene was determined by direct comparison with extinction measurements made on solutions of pure styrene in the same solvent. Three determinations of quantum yield gave the values 3.6×10^{-2} , 4.2×10^{-2} and 3.0×10^{-2} and a mean value,

$$\phi = 3.6 \times 10^{-2}$$
.

The similarity of absorption intensities of the benzyl type radicals obtained from different molecules at comparable optical densities and times of irradiation and also of the amounts of styrene formed from the molecules listed in the last section suggest that the quantum yields determined probably represent the order of magnitude of quantum yields of processes (iii) and (iv) in most other molecules investigated.

MATRIX REQUIREMENTS FOR STABILIZATION

All experiments on the stabilization of aromatic radicals have been carried out in glasses at -197° C. The low temperature has the twofold effect of ensuring high rigidity of the glass and so lowering the rate of diffusion and also of reducing the rate of chemical reactions which have a finite activation energy. It is interesting to enquire to what extent a low temperature is necessary for stabilization of benzyl type radicals in matrices which remain rigid at higher temperatures. Two systems were investigated in order to throw light on this question.

(i) Toluene was irradiated in liquid paraffin (nujol) at -78° C at which temperature the glass is quite rigid. No benzyl radical nor any other transient species were observed.

(ii) α -Methyl naphthalene was irradiated in a matrix of polymethyl methacrylate. Solutions of the α -methyl naphthalene in polymethyl methacrylate were cast into films from chloroform and, after outgassing for several days, the film was cut into discs 1 mm thick and 1 cm in diameter. Five of these discs were placed together to form a cylinder 0.5 cm long, and this was irradiated in liquid nitrogen in the same manner as our solutions in E.P.A. or M.P. After irradiation in liquid nitrogen, spectra appeared which were identical with those found in the similar experiment in E.P.A. and described in table 1. On raising the temperature to -78° C the spectra disappeared, although the matrix is of course still rigid in a macroscopic sense, at much higher temperatures. These experiments show that high viscosity of the matrix is not a sufficient condition for stabilization of benzyl type radicals, even at -78° C and that low temperatures are also necessary.

Photolysis of toluene in polymethyl methacrylate in a similar manner was unsuccessful because of the poor transparency of the polymer in the region of toluene absorption. No benzyl radical bands were observed but a region of absorption with maximum at 350 m μ , and half-width 35 m μ , appeared after 5 min irradiation and disappeared completely when the polymer was allowed to come to room temperature. An identical spectrum was obtained from the photolysis, at liquid nitrogen temperature, of polymethyl methacrylate alone. That the transient spectrum was not a product of photochemical dissociation of chloroform, from which the film had been cast, was established by the fact that the identical spectrum was obtained when the polymethyl methacrylate film was cast from ethyl acetate solution and also the photolysis of chloroform in E.P.A. at -197° C gave no transient spectrum. The 350 m μ spectrum is therefore to be attributed to a primary product of photodecomposition of polymethyl methacrylate which is unstable at room temperature. Its assignment must await further investigations on related molecules.

DISCUSSION

Of the forty molecules investigated all except benzyl bromide undergo sidechain fission by process (iii) or (iv) or both, on irradiation in the near ultra-violet region. The fission processes which have been identified are summarized in table 2. Of the two primary products of dissociation, only one has been observed in each case and the other is inferred on the grounds that the process written is probably the only one which is energetically possible.

In both types of dissociation, energy is transferred intramolecularly from an excited π electron to the β bond. Light of wavelength 2537 Å is quite close to the origin of the first singlet-singlet transition in the benzene derivatives and there is therefore little excess energy of vibration in the excited molecule. Side-chain fission must therefore occur by a predissociation mechanism, i.e. a crossing to a second electronic state which is repulsive in the bond parameter concerned. For β bond fission the state concerned is probably the triplet formed by combination of the ground doublet states of the two radicals. The potential energy curves for this process, in particular for toluene, have recently been discussed by one of us.²⁰

Comparison of β bond fission processes in the series of related molecules given in table 2 allows some interesting conclusions to be reached concerning the relative probabilities of dissociation of different bonds at equivalent positions. In order to make such comparisons we shall assume that the extinction coefficients of the benzyl-type radicals are not greatly different so that the optical densities observed are a fair measure of radical concentrations. The spectra in the cases to be considered are so similar as to be nearly indistinguishable so that this assumption is reasonable. Now if we study the radicals which are found after dissociation of those molecules which possess more than one kind of β bond we find, in nearly all cases, that only one of these bonds is dissociated. Furthermore all the data of table 2, including dissociation of the amines as well as the hydrocarbons, are in accordance with the statement that the probability of scparation of a radical at the β bond lies in the order :

$$\begin{bmatrix} OH, NH_2, CI, CN, \\ COOH, CH_2NH_2, CH_2OH, \end{bmatrix} > H > \begin{bmatrix} CH_3, C_2H_5, C_6H_5, C_6H_5CH_2 \\ \end{bmatrix}.$$

This result is somewhat unexpected. It would not have been surprising if no regularities had been found since small differences in potential energy curves could greatly affect crossing probabilities. But, if, as we find, the bonds can be arranged in an order of dissociation probability which is applicable to a large number of different molecules it might be expected that this order would be the order of bond dissociation energies. This is not the case. For example, the bond energies of $C_6H_5CH_2$ —H, $C_6H_5CH_2$ —CH₃ and $C_6H_5CH_2$ —CH₂C₆H₅ in the gas phase are 77.5, 63 and 47 kcal/mole respectively ²¹ and there is little doubt TABLE 2.—SIDE-CHAIN FISSION PROCESSES

 $C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$ $C_6H_5CH_2Cl \rightarrow C_6H_5CH_2 + Cl$ $C_6H_5CH_2OH \rightarrow C_6H_5CH_2 + OH$ $C_6H_5CH_2CN \rightarrow C_6H_5CH_2 + CN$ $C_6H_5CH_2NH_2 \rightarrow C_6N_5CH_2 + NH_2$ $C_6H_5CH_2COOH \rightarrow C_6H_5CH_2 + COOH$ $C_6H_5CH_2CH_2NH_2 \rightarrow C_6H_5CH_2 + CH_2NH_2$ \rightarrow C₆H₅CH=CH₂ + NH₃ $C_6H_5CH_2CH_3 \rightarrow C_6H_5CHCH_3 + H$ $\rightarrow C_6H_5CH = CH_2 + H_2$ $C_6H_5CHOHCH_3 \rightarrow C_6H_5CHCH_3 + OH$ \rightarrow C₆H₅CH=CH₂ + H₂O $C_6H_5CHNH_2CH_3 \rightarrow C_6H_5CH . CH_3 + NH_2$ \rightarrow C₆H₅CH=CH₂ + NH₃ $C_6H_5CH_2CH_2OH \rightarrow C_6H_5CH_2 + CH_2OH$ \rightarrow C₆H₅CH . CH₃ + OH \rightarrow C₆H₅CH=CH₂ + H₂O $C_6H_5CH_2CH_2CH_2OH \rightarrow C_6H_5CH_2 + CH_2CH_2OH$ $C_6H_5CH_2CH_2Cl \rightarrow C_6H_5CH=CH_2 + HCl$ $C_6H_5CH_2CH_2Br \rightarrow C_6H_5CH=CH_2 + HBr$ $C_6H_5CH(CH_3)_2 \rightarrow C_6H_5C(CH_3)_2 + H$ $C_6H_5C(CH_3)_3 \rightarrow C_6H_5C(CH_3)_2 + CH_3$ $C_6H_5CHCl_2 \rightarrow C_6H_5CHCl + Cl$ $C_6H_5CCl_3 \rightarrow C_6H_5CCl_2 + Cl$ $C_6H_5CH_2CH_2C_6H_5 \rightarrow C_6H_5CH_2CHC_6H_5 + H$ $C_6H_5CH_2C_6H_5 \rightarrow (C_6H_5)_2CH + H$ $(C_6H_5)_3CH \rightarrow (C_6H_5)_3C + H$ o-, m- and p-CH₃C₆H₄CH₃ \rightarrow o-, m- and p-CH₃C₆H₄CH₂ + H p-CH₃C₆H₄CH₂Cl \rightarrow p-CH₃C₆H₄CH₂ + Cl $1:3:5(CH_3)_3C_6H_3 \rightarrow 1:3:(CH_3)_25, CH_2 \cdot C_6H_3$ $C_6H_5NH_2 \rightarrow C_6H_5NH + H$ $C_6H_5NHCH_3 \rightarrow C_6H_5NCH_3 + H$ $C_6H_5N(CH_3)_2 \rightarrow C_6H_5NCH_3 + CH_3$ $C_6H_5CH_2NHC_6H_5 \rightarrow C_6H_5CH_2NC_6H_5 + H$ or $C_6H_5CHNHC_6H_5 + H$ $C_6H_5OH \rightarrow C_6H_5O + H$ $C_6H_5OCH_3 \rightarrow C_6H_5O + CH_3$ $C_6H_5OC_2H_5 \rightarrow C_6H_5O + C_2H_5$ $HOC_6H_4OH \rightarrow HOC_6H_4O \cdot + H$ 2:3:5:6-(CH₃)₄1:4(OH)₂C₆ \rightarrow 2:3:5:6(CH₃)₄1, (OH)4(O), C₆ + H α and β CH₃C₁₀H₉ $\rightarrow \alpha$ and β CH₂C₁₀H₉

that the dissociation energy of a β C—H bond in the gas phase is greater, in all the molecules of table 2 than that of a β C—C bond. The probability of dissociation found in this work is, however, consistently greater for the β C—H bond.

There is evidence, very limited at present, that the same will be found to hold for the photolysis of these compounds in solution but not in the gas phase. Thus Porter and Windsor ⁵ found that the flash photolysis of solutions of diphenyl

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methane in paraffin at normal temperatures gave the diphenyl methyl radical but Porter and Wright ⁴ found that flash photolysis of vapours of both ethyl benzene and diphenyl methane gave only the benzyl radical. It seems that photolysis in the gas phase may, for equivalent bonds, occur in accordance with bond-energy (gas-phase) considerations but that in solution, and in rigid solvents at low temperatures, other factors are important. There are two obvious factors which should be considered. First, bond-dissociation energies are almost unknown in solution and may be very different from those in vapours owing to differences in solvation energies of both the parent molecules and the radical products. Secondly, the activation energy of dissociation in solution may exceed the bond energy owing to a cage effect and the additional energy required to separate the dissociation products in the presence of the solvent molecules. This would be greater for the larger radicals and might account for the greater probability of sedaration of the smaller hydrogen atom.

Of the radical dissociation processes listed in table 2 there is one which cannot result directly from β bond fission. This is the formation of the C₆H₅CHCH₃ radical from $C_6H_5CH_2CH_2OH$. The most probable explanation of this observation is that, in addition to fission of the β bond to give benzyl and a type (iv) dissociation to give styrene, this molecule undergoes a γ bond fission by ejection of an OH radical and that the $C_6H_5CH_2CH_2$ radical so formed rapidly isomerizes to the more stable radical $C_6H_5CHCH_3$. Perhaps the most exceptional result in all the molecules investigated is the absence of any radicals from the photolysis of benzyl bromide. This confirms earlier results of Porter and Wright in the gas phase and is now well established since we made many attempts to detect radicals from this substance. The C-Br bond is one of the weakest investigated and therefore our failure to detect benzyl radicals from this substance is remarkable. It may be that dissociation of the β bond does occur but that, because the C-Br bond is exceptionally weak, sufficient energy remains in the benzyl radical after dissociation for this "hot" radical to react with the solvent before thermal equilibration can occur. Alternatively it may be that the increased spin-orbit interaction resulting from the presence of the heavy bromine atom results in rapid deactivation by inter-system crossing.

All molecules which give styrene as a primary product in the rigid glass are characterized by the fact that they can form a 4-centre transition state, dissociation of which leads directly to styrene and a second molecule :

Although intermolecular processes are excluded in the rigid glass the reaction could take place by fission of a single—probably a β bond followed by reaction of radical X within the solvent cage to give styrene and XY. There is no means of distinguishing between this cage reaction and a true intramolecular mechanism in the present experiments but a distinction would be possible in the vapour phase where only the true intramolecular mechanism could be operative. Two molecules of structure C₆H₅CHXCH₂Y did not show styrene in the products of dissociation. In both cases styrene formation would have necessitated the separation of a somewhat more complex molecule, viz., C₆H₆ and CH₃OH.

Hydroquinones dissociate by a β bond fission in the same way as phenols. The semiquinone radical is also formed from quinones but this occurs by hydrogen abstraction from the solvent and is therefore quite separate from the other processes discussed in this paper. It has recently been the subject of a detailed investigation.²²

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PRIMARY PHOTOCHEMICAL PROCESSES

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