group, indicating the importance of the resonance structure II. The theory thus states that these radicals are more analogous to the allyl radicals than to the methyl radicals, and indicates a danger of conjecturing the electronic nature of this type of radicals in terms of the hyperfine coupling constants to the protons only.

Extinction Coefficient and Recombination Rate of Benzyl Radicals. I.[1] Photolysis of Sodium Phenylacetate

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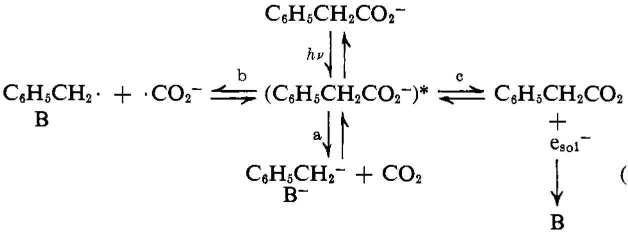
Abstract: The photolysis of sodium phenylacetate in methanol at 26° gives the following products (Φ): in the absence of oxygen, $C_6H_5CH_3$ (0.03), CO_2 (0.031), $(C_6H_5CH_2)_2$ (0.0007), C_6H_5CHO (<0.0001); in the presence of oxygen, $C_6H_5CH_3$ (<0.0001), CO_2 (~ 0.03), $(C_6H_5CH_2)_2$ (<0.0001), C_6H_5CHO (~ 0.028). It is proposed that the primary process in methanol yields benzyl anion and carbon dioxide, and that the minor path ($<5\%$) involves benzyl and carboxylate ($\cdot CO_2^-$) radicals. The photolysis of sodium phenylacetate in water yields mostly polymer and carbon dioxide, very little toluene, and some bibenzyl; in flash experiments, transient benzyl radicals and hydrated electrons are detectable; we therefore propose that a photoionization mechanism dominates here. By following the growth and decay of the transients in water, we have been able to compute the extinction coefficient (ϵ_B) of the benzyl radical at $2000 \pm 500\ M^{-1}\ cm^{-1}$ and its recombination rate constant, $2k_R = 8 \times 10^9\ M^{-1}\ sec^{-1}$.

This is one of three studies on the photoproducts and -mechanisms of compounds related to phenylacetic acid.[2] Although the photoprocesses differ, they all involve, to some degree, the benzyl radical (**B**). Besides working out the details of the decomposition of sodium phenylacetate, we estimate the recombination rate constant k_R as well as a value for the still controversial extinction coefficient, ϵ_B (λ_{max} 318 nm), of **B** in this paper.



$$\begin{tikzcd}
 & C_6H_5CH_2CO_2^- \arrow[d, shift right, "h\nu"'] & \\
\underset{\mathbf{B}}{C_6H_5CH_2\cdot} + \cdot CO_2^- \arrow[r, shift left, "b"] & (C_6H_5CH_2CO_2^-)^* \arrow[l, shift left] \arrow[u, shift right] \arrow[r, shift left, "c"] \arrow[d, shift right, "a"'] & \begin{array}{c} C_6H_5CH_2CO_2\cdot \\ + \\ e_{sol}^- \end{array} \arrow[l, shift left] \arrow[d] \\
 & \underset{\mathbf{B}^-}{C_6H_5CH_2^-} + CO_2 \arrow[u, shift right] & \mathbf{B}
\end{tikzcd} \qquad (1)$$

Of the numerous (>20) photocleavage steps open to a carboxylic acid derivative,[2a] only a few have been observed with the salts to date. Equation 1 outlines the overall photodecarboxylation mechanism for several arylacetates, *e.g.*, 1-naphthylacetate, thymine-1-acetate, or 2-pyridylacetate, although significant photodecomposition may be initiated at sites not involving carboxylate.[3] Concerning the steps of eq 1, the formation of the anion ($\mathbf{B}^-$) appears to predominate among mono- and dinitrophenylacetates,[4] the ejection of the solvated electron (step 1b) was noted for the series $C_6H_5(CH_2)_nCOO^-$ (n = 0 to 4),[5] and the homolysis to give **B** and carboxylate radical anion (step 1b) will be discussed presently. Missing from eq 1 are steps leading to carbon monoxide, which are important in the photolysis of phenylacetic acid and its esters,[2a] or benzyl ketones,[6] but which turn out not to be significant for our salt.

Benzyl is an important species which continues to evoke general interest.[7] This radical and its substituted analogs have been generated by a variety of techniques, among them γ-radiolysis,[8] pulse radiolysis,[9] electric discharge,[10a] electrolysis,[10b,c] thermolysis,[10d–i] and rad-

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(1) Taken from the Ph.D. thesis of T. O. M., Illinois Institute of Technology, 1970. Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract No. PHYS-13. Financial support from the Federal Water Pollution Control Administration in the form of a fellowship for T. O. M. and on Public Health Service Grants GM7021 and EY-516 is gratefully acknowledged.

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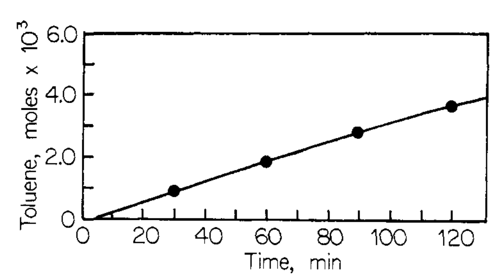

Figure 1. Toluene formation during photodecomposition of sodium phenylacetate (7.34×10^{-2} M) at 26° in methanol.

ical attacks.[10j–l] The formation of B by photolyses from phenylacetic acid,[2a] sodium phenylacetate,[5] phenylacetate esters,[2b,10m,n] benzyl esters,[2b,10m,o] benzyl sulfides,[10p] benzyl ketones,[6] benzylsulfonium salts,[10q] etc.,[5,10r–v] and possibly from benzylammonium salts,[10w] has been recorded (see also Table II). In many of these studies, B was not observed directly, but the nature of the products, *e.g.*, bibenzyl (BB), indicates that B probably was an intermediate. Of the spectral measurements, ir, visible, uv, and esr, that have been made on B,[11] the electronic spectrum (uv) has probably been most studied.[12] A number of different investigators have attempted to determine ϵ_B (λ_{max} 317 nm) and have produced a wide range of values from 1100 to 10^6 M^{-1} cm^{-1}.[8,9,12–16] As far as can be determined, B largely disappears by bimolecular combination to form BB. This rate, which is usually followed at ~317 nm, is dependent upon an accurate knowledge of ϵ_B; of necessity, the wide range in values for ϵ_B leads to a wide range in k_R, 8×10^7–2×10^9.[9,14,15] A measurement of k_R by the rotating sector method, which is independent of ϵ_B, has resulted in a value of 1.8×10^9 M^{-1} sec^{-1} in benzene.[17] We shall return to the question of ϵ_B and k_R.

Experimental Section

Our materials, apparatus, analytical methods, steady irradiation technique, and instrumentation have been recorded.[2a]

Flash Photolysis. The apparatus has been described.[5,18] A flash, 30 μsec overall, was produced by a fused silica xenon lamp (700 J). Transient absorptions were monitored by light from a xenon spectroflash lamp (65 J) having an overall duration of *ca.* 20 μsec. The spectroflash was triggered by a phototube monitoring the main flash and timed with a Tektronix 545 A oscilloscope. Transient spectra were recorded on a Hilger E 498 quartz prism spectrograph on Kodak I-N and 103-0 spectroscopic plates. These plates were shown to have a "linear" photographic response by calibration with quartz neutral density filters; the photographic density difference is given by $\Delta PD = \gamma \Delta OD$. The photographic density changes on the developed plates were measured with a Baird-Atomic Model SD-1 scanning microdensitometer. With the Kodak I-N plates, γ = 1.23 at 720 nm and 1.13 at 314 nm. Kinetic spectrophotometric measurements were made with a RCA 1P28 photomultiplier detector in a Hilger E720 scanning unit monitoring the light from a 200W Xe/Hg lamp. The photomultiplier signal was displayed on a Tektronix 545A oscilloscope and photographed with Polaroid high-speed film.

The sample cell, constructed from a fused silica tube 1.5×20.5 cm, had a capacity of 29 ml. A coaxial outer quartz jacket was filled with water to minimize temperature changes, or with 20% aqueous acetic acid which also absorbed light below 250 nm. Oxygen was removed from the sample prior to irradiation either by purging with an inert gas, *e.g.*, argon, for 40 min or evacuating to 10^{-5} Torr with shaking. Either method proved equally effective, since reproducible yields of radicals or electrons were obtained. Nitrous oxide was added to a number of samples to test for electron scavenging. After several flashes to demonstrate electron production, the samples were reevacuated. Nitrous oxide was then admitted and the solution successively frozen, thawed, and pumped several times to remove traces of oxygen and to saturate with nitrous oxide.

In the analysis of the kinetics, the experimental transient absorption decay curves were analyzed by simulating the flash photolysis experiments on a nonlinear expanded EAI Model TR-20 analog computer. The unit was equipped with "high accuracy" Type 7.137 quartersquare multipliers. The computer simulations were drawn out on a Moseley Model 2S, X-Y recorder.

Results and Discussion

Photolysis Products. Phenylacetic acid is completely converted to the salt above pH 9. In basic methanol solutions, the salt was found to undergo slow photodecomposition to produce high yields of carbon dioxide and, in the absence of oxygen, high yields of toluene. The results from typical steady irradiations in the presence and absence of oxygen are shown in Table I; quantum yields (Φ) are based on the initial rates of product formation. The rate of toluene formation is illustrated in Figure 1, where the falloff in the rate is ascribed to light absorption by the increasing concentrations of photoproducts. (Margerum notes incidentally that $\Phi(CO_2) \simeq 0.009$ at 250 nm for phenylacetate ions.[4a,b]) The Φ's were sensitive to temperature changes (Table I): a drop of *ca.* 13° decreased the yields of carbon dioxide and toluene by about one-third.

Table I. Products Formed during Photodecomposition of Sodium Phenylacetate (7.34×10^{-2} M) in Methanol

Photoproduct	O_2 present	Temp, °C	Φ^a	Product yield, %[b]
$C_6H_5CH_3$	No	26	0.030	97
		12	0.019	
CO_2	No	26	0.031	100
		12	0.021	
$C_6H_5CH_2CH_2C_6H_5$	No	26	0.0007	2
C_6H_5CHO	No	26	<0.0001	
$C_6H_5CH_3$	Yes	26	<0.0001	
CO_2	Yes	26	~0.030	
$C_6H_5CH_2CH_2C_6H_5$	Yes	26	<0.0001	
C_6H_5CHO	Yes	26	~0.028	
$C_6H_5CH_2OH$	Yes	26	~0	

[a] Average quantum yield at 210–280 nm. [b] Based on sodium phenylacetate consumed.

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When pure oxygen was bubbled through methanolic salt solutions during irradiation, the yield of carbon dioxide did not change (Table I). The yield of toluene now approached zero and appreciable amounts of benzaldehyde were formed. No benzaldehyde was formed in the absence of air or oxygen. Although the yields were not quantitated, toluene and small amounts of BB were definitely produced in several experiments carried out with methanolic salt solutions saturated with nitrous oxide.

The products resulting from photocleavage of sodium phenylacetate in methanol are markedly different from those obtained by decomposition of the parent acid. Photolysis of phenylacetic acid yields BB, carbon dioxide, carbon monoxide, an acidic polymer in substantial amounts, and only traces of toluene.[2a] Having characterized the decomposition of the acid as a homolytic process,[2a] we are compelled to seek alternatives for sodium phenylacetate. We propose that the major primary process is step 1a to form B^- and carbon dioxide. The presence of oxygen does not change the yield of carbon dioxide, which indicates that oxygen has no quenching effect on the excited state that leads to decarboxylation. Even more significant is the formation of benzaldehyde and little or no toluene. Although benzaldehyde is photolytically unstable, the initial Φ indicates that roughly the same amount of benzaldehyde is formed in the presence of oxygen as toluene in the absence of oxygen. Apparently, both toluene and benzaldehyde are formed from a common intermediate, B^-. If this is the case, then competition will take place between oxygen and the solvent for B^-, as in eq 2.

$$C_6H_5CH_3 + CH_3O^- \xleftarrow[a]{CH_3OH} \underset{B^-}{C_6H_5CH_2^-} \xrightarrow[b]{O_2} \longrightarrow C_6H_5CHO + OH^- \quad (2)$$

These competing reactions allow us to estimate the rate of neutralization of B^-. Since benzaldehyde is found only in oxygen saturated solutions, $k_{2a}(O_2) > 4k_{2b}[CH_3OH]$. If we assume that the reaction with oxygen is diffusion controlled, then $k_{2a} \simeq 5 \times 10^9\ M^{-1}\ sec^{-1}$. Using 25 M as the concentration of methanol and $5 \times 10^{-3}\ M$ as the concentration of oxygen, then $k_{2b} \leqslant 2.5 \times 10^5\ M^{-1}\ sec^{-1}$. In methanol, the pseudo-first-order decay rate would be $6.25 \times 10^6\ sec^{-1}$ which would give B^- a half-life of 0.1 μsec or more. Since this is below the time resolution of the flash photolysis apparatus used in this study, it is reasonable that we did not detect B^- in our flash experiments.

Margerum and Petrusis have found that nitro-substituted phenylacetate ions readily decarboxylate in aqueous solution apparently by an ionic mechanism.[4b] Their observation of transient absorption spectra of corresponding nitro-substituted benzyl anions during flash photolysis provides support for an ionic process.[4a] Resonance stabilization of the anions by the electron-withdrawing nitro group makes these species fairly long-lived, which is not the case for B^-. This anion has been shown to absorb at 350 nm with $\epsilon = 3.3 \times 10^3\ M^{-1}\ cm^{-1}$ in frozen tetrahydrofuran (THF).[19] Although we looked for but did not find this absorption in flash photolysis of sodium phenylacetate solutions, B^- remains the most likely intermediate leading to toluene.

Our observation of the B absorption spectrum during flash photolysis of methanolic sodium phenylacetate indicates that the decomposition reaction proceeds partly by a free radical pathway. Since no electron (e_{solv}^-) spectrum was observed during flash decompositions in absolute methanol, it is probable that process 1c can be excluded and that the most likely source of B is reaction 1b, through cleavage of the CH_2–CO_2 bond. This reaction accounts for *ca.* 5% of the total decomposition, if all B forms bibenzyl (BB). In the presence of oxygen, B is presumably converted to benzaldehyde, analogous to its oxidation when generated chemically or electrochemically.[10c,t] The fate of the carboxyl radical anion generated in (1b) is not known, though it may undergo electron or proton transfer reactions[20] similar to those proposed for homolytic photocleavage of phenylacetic acid,[2a] *e.g.*

$$\underset{BB}{(C_6H_5CH_2)_2} \longleftarrow B \xrightarrow{O_2} \longrightarrow C_6H_5CHO + \cdot OH \quad (3)$$

$$CH_3OH + CO_2\cdot^- + C_6H_5CH_2COO^- \longrightarrow \cdot C_6H_6CH_2COO^- + CO_2 + CH_3O^- \quad (4)$$

The photochemical generation of B and B^- and the formation of BB from the former and toluene from the latter each have a parallel. These transients are generated electrochemically in one- or two-electron reductions of benzyltrimethylammonium nitrate in dimethylformamide at an aluminum cathode and they then produce BB and toluene, as in eq 2 and 3.[10i]

The course of the decomposition is drastically different in water and methanol. Although we found small amounts of toluene and BB during irradiation in water, the major product was a polymeric material which ultimately absorbs all the light. Upon acidification, the polymer precipitates as a yellowish viscous solid. Infrared spectra indicated a polyacid (ν_{CO} broad); the equivalent weight of one sample was found to be 300.

The small yield of toluene indicates that the formation of B^- is not an important reaction in aqueous solution. There is also no evidence to show whether reaction 1b leading to the carboxyl radical anion is important either. But these results do indicate that photoionization or reaction 1c becomes the major primary decomposition pathway in water. Flash photolysis of toluene produces little or no electron, whereas flash photolysis of the anions of the type $C_6H_5(CH_2)_nCOO^-$ all produce the electron.[5] In the case of the phenylacetate anion, electron ejection from the carboxyl group would leave a phenylacetate radical which should rapidly dissociate to B and carbon dioxide.

Almost all e_{aq}^- formed in step 1c should react with the solute (or similar aryl species), since the rate constant for this reaction is *ca.* $1.4 \times 10^7\ M^{-1}\ sec^{-1}$.[21] Such electron additions would be followed by proton transfer from the solvent and could ultimately lead to

$$C_6H_5CH_2CO_2^- + e_{aq}^- \longrightarrow {}^-C_6H_5CH_2CO_2^- \xrightarrow{HOH} \cdot C_6H_6CH_2CO_2^- + OH^- \quad (5)$$

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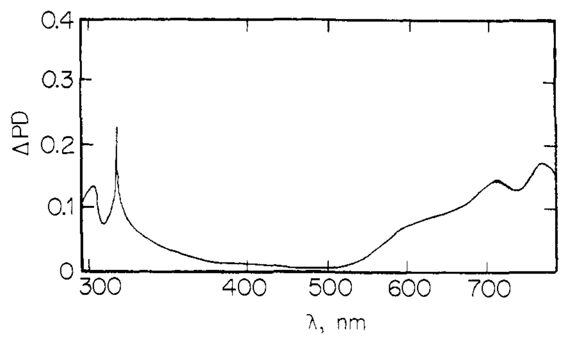


Figure 2. Flash spectrum (5 μsec) of sodium phenylacetate (5 mM) in deoxygenated water; ΔPD = (1.13 to 1.23)ΔOD.

the polymer product. Similar reduced species are formed during decomposition of phenylacetic acid, and it is not surprising that the physical properties of these polymers are similar.[2a] The hydrated electron may react with water or undergo recombination to form hydrogen and hydroxide ions (eq 6).[22]

$$k = 4.1 \times 10^2\ M^{-1}\ \text{sec}^{-1} \qquad e_{aq}^- + H_2O \longrightarrow H + OH^- \qquad (6a)$$

$$k = 6.4 \times 10^9\ M^{-1}\ \text{sec}^{-1} \qquad e_{aq}^- + e_{aq}^- \longrightarrow H_2 + 2HO^- \qquad (6b)$$

The first process is relatively slow and the second, which is very fast, can only be important at high yields of electrons.[22]

In concluding this section, we single out in eq 1 three of the dozen or so mechanistic alternatives available to the photodecarboxylations of dissolved carboxylates.[2a] Step 1a applies to the nitrophenylacetate ions,[4] steps 1a and b probably apply to sodium phenylacetate in methanol, and steps 1a and 1c probably apply to this salt in water.

We believe that discussions of photodecarboxylation have not given steps 1b and 1c the attention they deserve. On the one hand, Joschek and Grossweiner have shown that a wide variety of aromatic substrates, particularly those with electron-donating substituents, yield e_{aq}^- on flash photolysis.[5] On the other hand, the carboxyl radical ion ($CO_2\cdot^-$) and neutral radical ($CO_2H\cdot$) are now fairly easy to generate, observe, scavenge, etc.;[20,23] since $CO_2H\cdot$ is relatively stable ($\Delta G = -51$ kcal/mol),[2a] can be used as a carboxylating agent,[20] is produced by the radiolysis of sodium formate,[23] and is the probable photolytic product of phenylacetic acid,[2a] it appears that step 1b could plausibly apply to some acid salts.

It has been suggested recently that the pattern of step 1a dominates *all* of the following photodecarboxylations: 2-, 3-, or 4-nitrophenyl-, 2-, 3-, or 4-pyridyl-, 2-, 3-, or 4-chlorophenyl-, 1-naphthyl-, 3-indole,- and 1-thymineacetate ions,[3,10u,v] This cannot be correct. The primary photoprocess with the chlorophenylacetic acids probably involves carbon–chlorine bond scission to give **1**; decarboxylation may or may not occur in a later step.[10u,24] Since 3-indoleacetate and other indoles yield e_{aq}^- on flash photolysis,[5] photoionization is presumably followed by a step from **2**, but it is not obvious whether CO_2 or $CO_2\cdot^-$ is ejected to give (eventually) 3-methylindole, indole, etc.[10v]

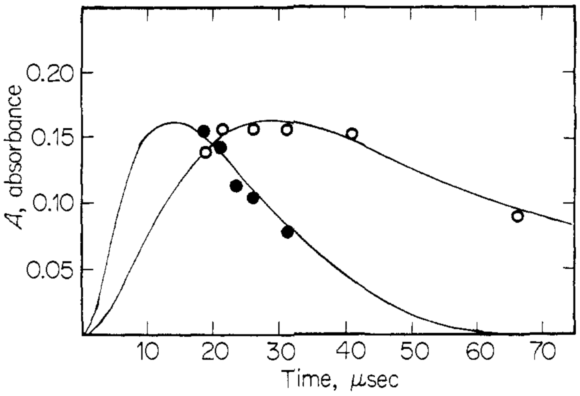
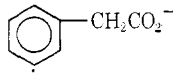


Figure 3. Formation and decay of hydrated electron (λ 720 nm) and benzyl radical (λ 314 nm) absorptions from sodium phenylacetate (0.005 M) in water. The curves were drawn to best fit the points by an analog computer: open circles, $C_6H_5CH_2\cdot$; filled circles, e_{aq}^-.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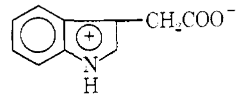
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As for the thymine[3c] and naphthalene acetates,[3a] these could photolyze by path 1a but this is not assured. Going farther afield, the fact that the photolysis of aqueous sodium butyrate yields carbon dioxide (as HCO_3^-) and propane as the major product is a good indication of a path *via* the carbanion, as in step 1a.[25a] But the "free radical" products obtained from sodium acetate or sodium formate, *e.g.*, hydrogen,[25b] or sodium nicotinate, *e.g.*, 2-(3-pyridyl)pyridine-5-carboxylate,[25c] could arise from paths like 1b or 1c, but probably not 1a.

Properties of the Benzyl Radical. Flash photolysis of sodium phenylacetate solutions in water produces transients that have been identified by Joschek and Grossweiner[5] and confirmed by us (Figure 2). Three absorbing species are in evidence by their decay characteristics. The broad absorption in the visible region with maximum at 720 nm decayed in less than 40 μsec and is attributed to e_{aq}^-.[22] In the presence of good electron scavengers, *e.g.*, N_2O, this absorption completely disappeared. The two absorptions at 302 and 314 nm are attributed to B which decayed in 200 μsec. There is also a broad characterless absorption which decreases to longer wavelengths and which we ascribe to a permanent product. This spectrum was also observed in methanol solution, but the absorption of e_{solv}^- was absent. The electron absorption was clearly evident, however, in 25% aqueous methanol and increased in intensity with increasing water content.

These transient absorptions produced from flash decomposition of aqueous sodium phenylacetate have been used to calculate ϵ_B.[26] Decay of the absorptions at 720 and 314 nm during a typical flash decomposition of the salt are shown in Figure 3. The permanent absorption at 314 nm has been subtracted to leave only

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Table II. Extinction Coefficient at ~318 nm of the Benzyl Radical (B)[a]

Source	Method[b]	Solvent[c]	Basis[d]	ϵ, M^{-1} cm^{-1}	Ref
$BCOO^-$	Flash	H_2O	e_{aq}^-	2000	*e*
BCOOB	Flash	CH_3OH	Prod	1500 (900)	2b
BCl, BBr	Flash	Vapor	Prod	$\leqslant 10^6$	16
BCl	Pulse	C_6H_{12}	Prod	12,000	9
BH	Steady	EPA (77°K)	Prod	19,200	15
BCl	Pulse	EtOH–glycerol	Prod	1100	14
BCl	γ	MTHF (77°K)	$Naphth^-$	18,000	8
CH_3COOB	γ	EtOH (77°K)	Prod	18,000	13
BCl	γ	MP (77°K)	$TMPD^+$	12,000	13

[a] λ_{max} for B is solvent dependent. [b] Methods: flash photolysis; pulse radiolysis; steady irradiation; γ-radiolysis. [c] Ambient temperature, unless otherwise noted. EPA = ether–isopentane–ethanol (5:5:2). MTHF = 2-methyltetrahydrofuran. MP = 3-methylpentane. [d] The quantity of B observed was based on stable compounds, *e.g.*, BB, CO_2, HCl, etc., or on other transients, *e.g.*, $Naphth^-$ = naphthalenide ion, $TMPD^+$ = *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine cation. [e] This study.

that of B. The curves in Figure 3 were drawn by the analog computer programmed to simulate the electron and radical decays and have been matched to the experimentally observed values. We assume that e_{aq}^- and B are formed in one reaction and that their yields are identical. Since ϵ of e_{aq}^- is known,[22] the total

$$C_6H_5CH_2CO_2^- \xrightarrow{h\nu} B + CO_2 + e_{aq}^- \quad (7)$$

yield can be calculated from the electron absorption taken from photographic plates.

The rate expression for formation and decay of the hydrated electron is

$$\frac{d}{dt}(e_{aq}^-) = \Phi I(t) - k_1(e_{aq}^-) - 2k_2(e_{aq}^-)^2 \quad (8)$$

Here we have assumed that the electron disappears by two processes, namely by a first-order reaction with the medium (k_1) and a second-order recombination of electrons (k_2). Using $\epsilon_{e^-} = 1.58 \times 10^4\ M^{-1}\ \text{cm}^{-1}$ at 720 nm and $k_2 = 6.4 \times 10^9\ M^{-1}\ \text{sec}^{-1}$,[22] and simulating the observed intensity profile of the flash lamp $I(t)$, we have two adjustable parameters to match to the observed growth and decay. The fit shown in Figure 3 was obtained by setting $\Phi = 0.0467$ and $k_1 = 5.35 \times 10^5\ \text{sec}^{-1}$. It should be noted that $k_1[e_{aq}^-] \gg 2k_2[e_{aq}^-]^2$ under the experimental conditions and that variations in the value of ϵ or k_2 for e_{aq}^- [22] will not affect our treatment significantly. Moreover, the reaction of e_{aq}^- with the "medium," characterized by $k_1 = 5.35 \times 10^5\ \text{sec}^{-1}$, involves *more* than process 5, for which the pseudo-first-order constant $k_\psi = 7 \times 10^4\ \text{sec}^{-1}$ at $[C_6H_5CH_2COO^-] = 5 \times 10^{-3}$. The formation of polymer and decreased yields of BB, as will be noted later, may be associated with the enhanced rate of disappearance of e_{aq}^-.

The B formed in reaction 7 is assumed to react only by recombination so that the change with time is given by the differential expression

$$d[B]/dt = \Phi I(t) - 2k_R[B]^2 = 1.92 \times 10^{-5}\epsilon_B - 4.88 \times 10^{-9}k_R A^2/\epsilon_B \quad (9)$$

After converting the radical concentration to absorbance, inserting the cell length $b = 20.5$ cm and Φ calculated above, and adjusting the computer simulation to the experimental values (Figure 3), we obtain $\epsilon_B = 2.02 \times 10\ M^{-1}\ \text{cm}^{-1}$ and $k_R = 4.14 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. Since these values are calculated by a "best fit" procedure, the expected accuracy can only be estimated from the "goodness" of the fit and the consistency of the experimental data. The probable error in the electron extinction coefficient used in these calculations is only good to ±10%,[22] and the flash absorption spectra were reproducible to *ca.* ±10%. After allowing for some variation in the computer fitting, we estimate that ϵ_B is accurate to *ca.* ±25%.

From the decay curves in Figure 3, it is evident that the electron absorption must be larger than the radical absorption, since the electron reacts so much faster. This immediately suggests that ϵ_B is much smaller than ϵ of e_{aq}^-, possibly an order of magnitude smaller, which is close to our calculated value.

This approach to measuring ϵ_B is based on the assumption that photoionization leads to $[e_{aq}^-]_0 = [B]_0$. Considering the results in methanol solution, we can conceive of B arising from cleavage of the CH_2–CO_2 bond (*e.g.*, step 1b). If this reaction were important, then the observed absorption would result from a higher [B] than originally considered; this would mean that the true $\epsilon_B \leqslant 2020\ M^{-1}\ \text{cm}^{-1}$.

Previous studies of ϵ_B have emphasized product analysis as the basis for determining the radical concentrations (see Table II). These studies were based on various assumptions as to how the radical reacts to form the measured products, but a detailed knowledge of the radical reactions was not always available. The photocleavage of the phenylacetate ion provides a system in which the radical concentration can be determined directly, without recourse to product analysis. During flash photolysis, both the electron and radical absorptions can be seen simultaneously, and differences in cell geometry, light paths, etc., are eliminated.

In the companion paper we give the results of an independent determination of ϵ_B and k_R. Our result of 1500 M^{-1} cm^{-1} [2b] is within experimental error of our value of 2020 M^{-1} cm^{-1} which is based on the properties of e_{aq}^-. Our results are compared in Table II with the results from other workers. The ϵ_B's fall into two distinct groups, namely, values between *ca.* 1000 and 2000 M^{-1} cm^{-1} and those between *ca.* 10,000 and 20,000 M^{-1} cm^{-1}. We are at a loss to explain this discrepancy of an order of magnitude among values in liquid or solid solution, even if allowances are made for variations in solvent and temperature. It should be pointed out that ϵ_B based on a product yield will be high when the optical density is increased by the presence of extraneous transients and when the measured yield is less than the true yield of product. However, high yields are hard to fault. On this basis, we believe that our systems, whose photodecomposition products and mechanisms are now characterized, are perhaps more favorable for the determination of ϵ_B.

The B recombination rate k_R in water was found to be $4.1 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. However, the low yields of BB and high yield of polymer observed during irradiations in water suggest that most B's are intercepted by the polymer or other species. For this reason, the rate of disappearance as measured should actually be taken as an upper limit to the true recombination rate. The lower value, $6.8 \times 10^8\ M^{-1}\ \text{sec}^{-1}$, of the companion paper appears to be more reliable.[2b]

Acknowledgment. We wish to thank Dr. W. D. Brennan for assistance with the calculations leading to Figure 3.

Extinction Coefficient and Recombination Rate of Benzyl Radicals. II.[1] Photolysis of Several Benzyl Phenylacetates in Methanol

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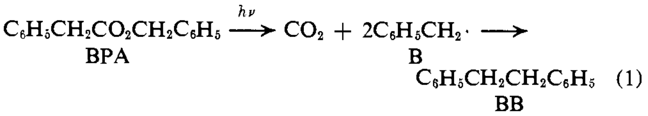
Received February 11, 1972

Abstract: In the absence of oxygen, Φ for the photolysis of benzyl phenylacetate (BPA) in methanol is 0.19; the products (per cent yield) were carbon dioxide (85), bibenzyl (91), and carbon monoxide (3). Comparable yields of carbon dioxide and bibenzyls are obtained from the photolyses of the *p*-methyl-substituted BPA's. In oxygen-saturated methanol, $\Phi \simeq 0.05$, benzaldehyde is formed, and the yield of carbon dioxide remains high, but that of bibenzyl falls to 36%. We consider that the mechanism of photocleavage of BPA involves formation of the radical pair, $C_6H_5CH_2CO_2\cdot\ \cdot CH_2C_6H_5$, which generally dissociates and ejects carbon dioxide to form benzyl radicals; it appears that little (<20%) of the bibenzyl formed arises from cage recombination. By following the growth and decay of the benzyl radical (B) by flash spectroscopy and monitoring the amount of bibenzyl formed, we have found the extinction coefficient $\epsilon_B = 1500 \pm 300\ M^{-1}\ \text{cm}^{-1}$ (λ_{max} 314 nm) and the recombination rate constant $2k_R(B) = 1.36 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at 25°.

In a previous paper, we have listed some 24 photodecomposition routes available to a carboxylic acid or ester. Of these, phenylacetic acid and its methyl ester in methanol favor two homolytic paths, namely, cleavage either to carbon monoxide or to carbon dioxide.[2a] Sodium phenylacetate yields carbon dioxide and benzyl anion (B^-) in methanol, but B, carbon dioxide, and the hydrated electron (e_{aq}^-) in water.[2b] The photolysis of BPA differs from that of many other esters in that it produces relatively clean homolysis, eq 1



$$\underset{\text{BPA}}{C_6H_5CH_2CO_2CH_2C_6H_5} \xrightarrow{h\nu} CO_2 + 2\underset{\text{B}}{C_6H_5CH_2\cdot} \longrightarrow \underset{\text{BB}}{C_6H_5CH_2CH_2C_6H_5} \quad (1)$$

(the advantages of BPA and related compounds as favorable substrates were realized independently by another group[3]). Here we report on this photocleavage as well as on the fate of benzyl radical (B) which is generated in the process.

Aspects of ester photolysis, *e.g.*, distribution of products, properties of intermediates, mechanisms, spectroscopy, etc., continue to attract attention.[2a,3,4] The simplicity of process 1 gave us the opportunity to focus on B, an important species in which there is considerable interest.[5] Published values of the optical extinction coefficient (ϵ_B) of B are widely discrepant.[2b] By flash photolysis studies of BPA, we were able to obtain a new value of ϵ_B as well as to determine its recombination rate constant k_R.

Experimental Section

Our steady irradiation and flash photolysis methods, *e.g.*, apparatus, lamps, actinometry, product analyses, instrumentation, and some of our materials, have been described.[2] The products of the steady irradiations were identified by nmr, after the solutions were concentrated. Since no low molecular weight products were detected, apart from those in Table I, we ascribe losses in material to the formation of polymer. Quantitative estimates on the bibenzyls were obtained by gc: either a known amount of internal standard, *e.g.*, biphenyl, was added to the solution and the peak heights were compared, or the comparison was made after successive (and careful) injections of aliquots of solutions of product and standard.

The benzyl phenylacetates were prepared by the following general procedure: the appropriate acid (1 equiv) was treated with

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[1] Taken from the Ph.D. thesis of T. O. M., Illinois Institute of Technology, 1970. Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract No. PHYS-13. Financial support from the Federal Water Pollution Control Administration in the form of a fellowship for T. O. M. and on Public Health Service Grants EY-516 and GM 7021 is gratefully acknowledged.

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