tion 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 4.1×10^9 M^{-1} 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, 6.8×10^8 M^{-1} 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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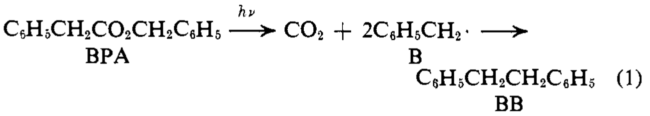
Abstract: In the absence of oxygen, Φ for the photolysis of benzyl phenylacetate (BPA) in methanol is 0.19; the products (per cent yield) were carbon dioxide (85), bibenzyl (91), and carbon monoxide (3). Comparable yields of carbon dioxide and bibenzyls are obtained from the photolyses of the *p*-methyl-substituted 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} cm^{-1} (λ_{max} 314 nm) and the recombination rate constant $2k_R(B) = 1.36 \times 10^9$ M^{-1} 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.

[2] (a) T. O. Meiggs and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 1989 (1972); (b) T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, *ibid.*, **94**, 7981 (1972).

[3] R. S. Givens and W. F. Oettle, *ibid.*, **93**, 3301 (1971).

[4] (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 434 ff; (b) D. Belluš, *Advan. Photochem.*, 8, 109 (1971 ; (c) Y. Odaira, *Kagaku No Ryoiki, Zokan*, (93) 103 (1970); *Chem. Abstr.*, 75, 4865 (1971); (d) R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 2685 (1971); (e) J. E. Gano, *Mol. Photochem.*, 3, 79 (1971); (f) D. Greatorex and T. J. Kemp, *J. Chem. Soc., Faraday Trans. 1*, **68**, 121 (1971); (g) J. Tournon and M. A. El-Bayoumi, *J. Amer. Chem. Soc.*, **93**, 6396 (1971).

[5] *Anon., Chem. Eng. News*, 40 (May 5, 1969); C. L. Angell, *ibid.*, 6 (July 7, 1969).

Table I. Photolysis of Benzyl Esters in Deoxygenated Absolute Methanol at 26°

Ester, *ca.* 4×10^{-2} *M*	$\lambda_{max}^{CH_3OH}$, nm	ϵ, M^{-1} cm^{-1}	Φ[a]	CO_2,[b] %	$ArCH_2$–CH_2Ar',[c] %
$C_6H_5CH_2CO_2CH_2C_6H_5$	256	375	0.19 (0.12)	85	91
			(0.10)[d]	91	56
			(0.04)[e]	109	36
p-$CH_3C_6H_4CH_2CO_2CH_2C_6H_4CH_3$-*p*	263	580	0.25	91	93
$C_6H_5CH_2CO_2CH_2C_6H_4CH_3$-*p*	257	390	0.28	86	88
p-$CH_3C_6H_4CH_2CO_2CH_2C_6H_5$	263	440	0.13	83	74

[a] Based on loss of ester, by saponification and titration.[2a] The figures in parentheses are Φ_{app}'s based on the amount of ester actually decomposed in 1 hr, whereas Φ's were determined from the initial slopes of plots such as Figure 2. [b] Determined by titration or by gc.[2a] [c] Determined on a Micro Tek 2000R chromatograph with an aluminum column at 160° containing 5% OV-101 on 70–80 mesh Anachrom ABS. [d] This solution was saturated with air. [e] This solution was saturated with oxygen.

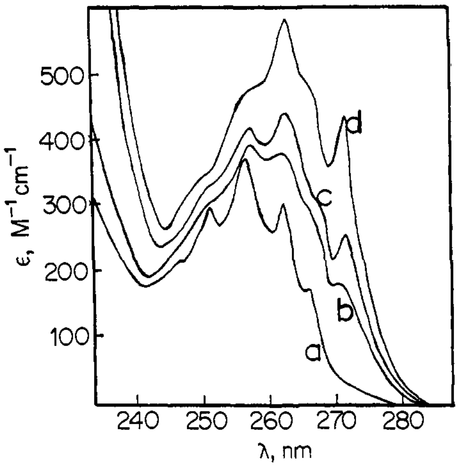

Figure 1. Ultraviolet absorption spectra of benzyl esters in methanol: (a) benzyl phenylacetate; (b) *p*-methylbenzyl phenylacetate; (c) benzyl *p*-methylphenylacetate; (d) *p*-methylbenzyl *p*-methylphenylacetate.

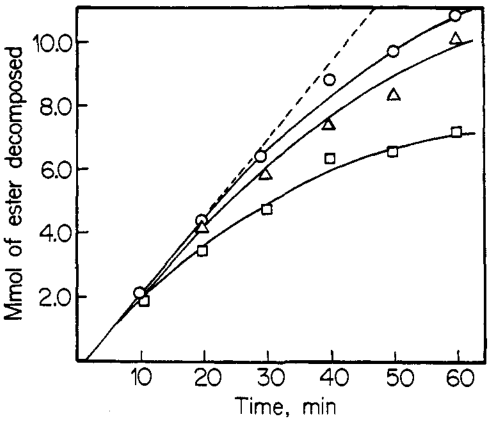

Figure 2. Photodecomposition of benzyl phenylacetate at varying concentrations in deoxygenated absolute methanol: □, 0.02 *M*; △, 0.04 *M*; ○, 0.08 *M*.

potassium ethoxide (1 equiv). After all the acid was dissolved, the excess ethanol and water were removed by heating under vacuum. Acetonitrile (*ca.* 500 ml) and the appropriate benzyl chloride (0.5 equiv) were added to the dry salt. After 17 hr at reflux temperature the solution was cooled, the precipitated sodium chloride removed by vacuum filtration, and the remaining acetonitrile worked up for product. The benzyl ester was purified by fractional distillation; final yields ranged from 60 to 75%. A check of purity was provided by the mass spectrum of each ester, at 70 eV on a MAT CH7 mass spectrometer; in each case, the parent peak was obtained. The uv spectra are given in Figure 1.

Benzyl phenylacetate (BPA) had bp 154° (0.5 mm), n^{35}D 1.5514 (lit.[6] bp 318°, n^{24}D 1.555); τ(neat) 3.41 s (2 H), 4.94 s (2 H), 7.10 s (10 H); $\lambda_{max}^{CH_3OH}$ 256 nm (ϵ 375). Hydrolysis with standard base followed by back-titration indicated that the ester was greater than 98.0% pure.

p-Methylbenzyl phenylacetate had bp 157.5° (0.3 mm), n^{35}D 1.5466; τ(neat) 2.05 s (3 H), 3.38 s (2 H), 4.90 s (2 H), 6.75–7.18 m (9 H); $\lambda_{max}^{CH_3OH}$ 257 nm (ϵ 390). Hydrolysis and back-titration showed the ester to be greater than 99.6% pure.

Benzyl *p*-methylphenylacetate had bp 122° (0.2 mm), n^{35}D 1.5425; τ(neat) 2.11 s (3 H), 3.42 s (2 H), 4.96 s (2 H), 6.85–7.20 m (9 H); $\lambda_{max}^{CH_3OH}$ 263 nm (ϵ 440). The ester was shown to be greater than 99.5% pure by titration.

p-Methylbenzyl *p*-methylphenylacetate had bp 157° (0.3 mm); the liquid slowly crystallized to give a white solid: mp 40.0–40.5°; τ (CCl_4) 2.10 s (6 H), 3.38 s (2 H), 4.90 s (2 H), 6.80–7.13 m (8 H); $\lambda_{max}^{CH_3OH}$ 263 nm (ϵ 580). The ester was shown to be greater than 98% pure by nmr.

Fluorescence Measurements. Dilute samples of BPA in methanol (*ca.* 0.5 μM) were placed in a quartz cuvette and purged with argon to remove all traces of oxygen. The cuvette was stoppered and irradiated with a mercury resonance lamp housed in a Beckman DK-2 fluorescence attachment. No filters were used and some scattered light from the mercury lamp was observed. However, since the mercury lines were rather sharp, the weak fluorescence emission from the ester was easily discernible at λ >280 nm. In order to determine the effect of varying concentrations of oxygen, the samples were exposed to air or flushed with pure oxygen prior to further excitation. Quenching was apparent by a decrease in the fluorescence intensity.

Results and Discussion

Products of Steady Irradiation. Irradiation of methanolic solutions of several benzyl phenylacetates at ≫ 210 nm produces relatively large amounts of ester decomposition in the absence of oxygen (Table I). The ease of ester decomposition appears to have little relationship to their ϵ values, but the uniformly high yields of carbon dioxide and bibenzyls do, however, indicate a common mechanism for photocleavage. Apart from some discoloration after irradiation and some carbon monoxide from the parent ester BPA, no other products were detected in these studies.

In order to determine the quantum yields (Φ) for ester decomposition, the amount of BPA at various times was determined. From the initial linear portion of the decomposition curves (Figure 2), Φ = 0.19 at 26°. The yields decrease with time because the products of reaction absorb the light and reduce the amount absorbed by the ester. However, apparent Φ's could be calculated from the amount of ester actually decomposed, say in 1 hr; these are useful for determining the effect of varying experimental conditions. The curves in Figure 2 indicate that changing the ester concentration by a factor of 4 has little or no effect on the rate of ester loss.

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(6) B. S. Rajyam, C. Haranadh, and C. R. K. Murty, *Ind. J. Pure Appl. Phys.*, 6, 16 (1968).

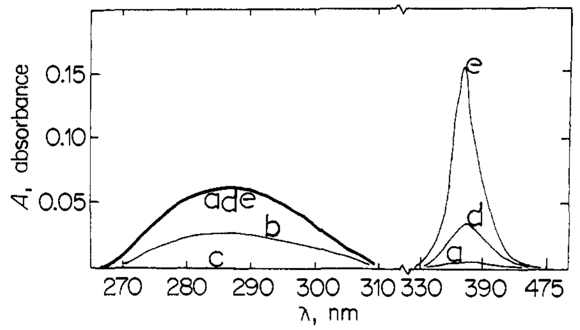

Figure 3. Fluorescence spectra of 1 mM benzyl phenylacetate in methanol at room temperature: (a) aerobic, (b) air saturated; (c) oxygen saturated; (d) aerobic, after 2-min irradiation in the presence of air; (e) aerobic, after 2-min irradiation in the presence of oxgyen, λ_{max} 374 nm.

There is a definite substituent effect, since the Φ's for ester loss vary by more than a factor of 2 depending upon which aromatic nucleus contains a substituent. The results indicate that a *p*-methyl substituent on the alcohol side of the ester greatly increases the decomposition efficiency, whereas a *p*-methyl substituent on the acid side reduces the efficiency. The greater stability and ease of generation of the *p*-methylbenzyl radical over the unsubstituted radical[7] should increase the probability of producing radical pair **1**, thereby increasing the amount of ester decomposition. The same reasoning does not apply when the methyl substituent is on the other aromatic nucleus, presumably because the methyl group neither promotes initial fission nor stabilizes the first product *p*-$CH_3C_6H_4CH_2CO_2\cdot$ (eq 2).

$$\begin{tikzcd}
BPA \arrow[r, shift left, "h\nu"] & (BPA)^S \arrow[l, shift left, "O_2"] \arrow[r] & (BPA)^T \arrow[r, "a"] & \underset{\mathbf{1}}{(C_6H_5CH_2CO_2\cdot\ \cdot H_2CC_6H_5)} \arrow[dl, "c"'] \arrow[dr, "b"] & \\
\underset{\mathbf{3}}{(C_6H_5CH_2\cdot\ \cdot H_2CC_6H_5)} \arrow[d, "e"] \arrow[drr, "f"] & & \underset{\mathbf{2}}{(C_6H_5CH_2\cdot CO_2\ \cdot H_2CC_6H_5)} \arrow[ll, "-CO_2"', "d"] & & C_6H_5CH_2CO_2\cdot + B \arrow[d, "-CO_2"] \\
2B \arrow[rr, "g"] & & BB & & B \arrow[ll, "g"']
\end{tikzcd} \qquad (2)$$

Our choice of the solvent methanol turned out to be fortunate. Reported irradiations in dioxane at 253.7 nm of BPA and *p*-methoxybenzyl *p*-methoxyphenylacetate have Φ = 0.033 and 0.25, respectively, and show lower yields of products (~57%).[3] Since B is generated in both solvents, it appears that dioxane may be reacting with B, while methanol is indifferent to B. Alternatively, the possible incursion of a second mechanism in dioxane, *e.g.*, the formation of carbon monoxide (see below), would have to be checked.

Air-saturated solutions of BPA show a decrease in the apparent Φ of ester photolyzed. An even greater reduction is found in the presence of pure oxygen, where the yield is decreased by almost two-thirds. Now, a weak fluorescence spectrum is shown with BPA in methanol (Figure 3). In the presence of air, fluorescence is reduced, and in the presence of pure oxygen, it is completely quenched.[8a] Thus oxygen is acting to quench (deactivate) the excited state which leads to photocleavage of the ester. This presents the possibilities that either the singlet state producing fluorescence also leads to the photodecomposition or that oxygen is preventing intersystem crossing to the triplet state by quenching the excited singlet. In either case, only a study of the ester phosphorescence will determine which alternative is correct. But since oxygen is known to be a very efficient quencher of triplet states,[8] the most probable state leading to decomposition is the triplet state. The very weak fluorescence observed indicates that radiationless transitions and/or intersystem crossing to a triplet state are favored processes. On the basis of work with quenchers or sensitizers on the photodecarboxylation of their benzyl esters, Givens and Oettle have suggested that the photoproducts derive directly from a triplet state.[3]

Oxygen is not, however, completely efficient in quenching process 1, since some ester is still decomposed: Φ (apparent) = 0.04. This may be due to inhomogeneous oxygen concentrations in the irradiated solution which would lead to inefficient quenching of excited BPA. Rapid consumption of oxygen at the lamp surface, for example, could develop a concentration gradient across the vessel. The presence of measurable quantities of bibenzyl (BB) in the "oxygen saturated" solutions adds support to this idea.

High yields of carbon dioxide are observed in the presence or absence of oxygen, indicating that if any ester is decomposed, it loses carbon dioxide. In contrast, the yields of BB decrease with increasing oxygen concentration, indicating that oxygen interferes with its formation. Indeed, during fluorescence studies, a new product was seen to form in the presence of oxygen. When solutions were first irradiated in the presence of air and the air was removed, a new fluorescence spectrum was observed at 375 nm, Figure 3. Irradiation in the presence of pure oxygen, followed by oxygen removal and fluorescence measurement, showed an even more intense peak centered at 375 nm. This spectrum is identical with that observed for benzaldehyde fluorescence in methanol. These results show that during photocleavage of BPA in the presence of oxygen, benzaldehyde is formed at the expense of BB.

$$B + O_2 \longrightarrow \longrightarrow C_6H_5CHO \xrightarrow{h\nu} (C_6H_5COOH) \qquad (3)$$

Benzaldehyde is not the only new product formed in the presence of oxygen. Following such irradiations, the decrease in ester concentration cannot be determined by the usual saponification technique owing to the formation of an acidic product; a gc method was used instead. Although the identity of the acidic material was not investigated, benzaldehyde is known to be photooxidized readily to benzoic acid.[9]

In the absence of oxygen, the only observed photoproduct besides carbon dioxide and BB was a small amount of carbon monoxide in *ca.* 3% yield. Carbon monoxide has also been found during pulse radiolysis of a substituted BPA,[10] $[CO]/[CO_2] = 0.09$, while we found this ratio to be 0.03. The carbon monoxide presumably arises from acyl cleavage of the ester followed by decarbonylation of the acyl radical. In this scheme, we do not know the fate of the phenylalkoxyl

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[7] R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

[8] (a) I. B. Berlman, "Fluorescence Spectra of Aromatic Molecules," 2nd ed, Academic Press, New York, N. Y., 1971; (b) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 66, 199 (1966); (c) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970, Chapter 6.

[9] M. Niclause, J. Lemaire, and M. Letort, *Advan. Photochem.*, **4**, 25 (1966).

[10] A. A. Miller, *J. Phys. Chem.*, **69**, 1077 (1965).

Table II. Distribution of Bibenzyls from the Photolysis of Methyl-Substituted Benzyl Phenylacetates in Methanol at 26° for ~1 hr[a]

Ester	$(C_6H_5CH_2)_2$	p-$CH_3C_6H_4CH_2CH_2C_6H_5$	$(p$-$CH_3C_6H_4CH_2)_2$	% cage
$C_6H_5CH_2CO_2CH_2C_6H_4CH_3$-$p$	0.90 ± 0.05	2.17 ± 0.10	0.93 ± 0.05	8.5 ± 5
p-$CH_3C_6H_4CH_2CO_2CH_2C_6H_5$	0.73 ± 0.05	2.43 ± 0.10	0.84 ± 0.05	21.5 ± 7

[a] The total yield was normalized to 4.00. The deviation in the amount of *p*-methylbibenzyl from a wholly randomized process was used to calculate per cent cage.

radical. Dibenzyl ether is a possibility, but we do

$$\mathrm{BPA} \xrightarrow{h\nu} (\mathrm{C_6H_5CH_2CO}\cdot\ \cdot\mathrm{OCH_2C_6H_5}) \qquad (4)$$

$$\mathrm{C_6H_5CH_2CO}\cdot \longrightarrow \mathrm{B} + \mathrm{CO}$$

know through gc analysis that no benzyl alcohol, benzaldehyde, or toluene is formed. There was some slight discoloration of the irradiated solution which called to mind formation of polymers from phenylacetic acid, its salt, and methyl ester.[2a] A possible segment of the polymer is $C_6H_5CH_2OC_6H_5CH_2CH_2C_6H_5$–. In fact, continued irradiation gave rise to a permanent absorption whose OD increased toward shorter wavelengths. This can be seen in the flash photolysis spectrum shown in Figure 4; the transient is presumably B.

Photomechanism. Recently, an interpretation of the spectra of phenylacetic acid, ethyl phenylacetate, and related molecules has focused on fluorescence *vs.* phosphorescence or singlet-triplet energy transfer.[4g] But irrespective of the state or states proximate to bond cleavage, there is little doubt that BPA undergoes photodecomposition by a free radical process. Observation of the spectrum of B during flash photolysis is adequate demonstration that it is formed during cleavage of the ester (Figure 4). What happens next? To investigate the problems of induced decomposition (eq 5) and cage *vs.* noncage recombination of B, we

$$\begin{array}{l} \mathrm{ArCH_2}\cdot\ + \\ \mathrm{ArCH_2CO_2CH_2Ar'} \end{array} \xrightarrow{?} \left[\begin{array}{l} \longrightarrow \mathrm{ArCH_2CH_2Ar'} + \mathrm{ArCH_2CO_2}\cdot \\ \longrightarrow \mathrm{ArCH_2CH_2Ar} + \mathrm{Ar'CH_2CO_2}\cdot \end{array} \right. \qquad (5)$$

$$\mathrm{ArCH_2CO_2}\cdot \longrightarrow \mathrm{ArCH_2}\cdot + \mathrm{CO_2}$$

considered the product data of the BPA "labeled" with methyl groups (Table II) within the framework of eq 2 and 5.

With regard to the induced decomposition, if eq 5 were highly efficient, Φ could be >1.0. Our Φ's are <0.3, and the ester decomposition rate is zero order in ester within *ca.* 10% (Figure 2). Further, in eq 5, radical attack would presumably occur preferentially on one side or the other of the carboxyl group of BPA. If such were the case, the amounts of BB and *p,p'*-dimethylbibenzyl from labeled BPA would not have been near equal as observed (Table II). (More direct evidence on process 5 could be obtained, if the appearance of BB were monitored in flash experiments and the rate eq 7 (see below) put to the test.)

Now, suppose eq 2 represents our photolyses. Here certain transients are given in parentheses; if they exist at all, they are relatively shortlived, since B is observed within 5 μsec during flash photolysis of BPA. Photodecomposition of the singly labeled esters would lead to the following proportions, bibenzyl:*p*-methylbibenzyl:*p,p'*-dimethylbibenzyl = 0:4.0:0 for cage recombination, and 1.0:2.0:1.0 for noncage or random recombination of solvent-separated radicals. In Table II, the total yields of bibenzyls were normalized to 4.0 in order to indicate the percentage of cage process, which is certainly <28%. To these data should be added the recent observation that photolysis of *p*-methylbenzyl *p*-methoxyphenylacetate "affords a nearly statistical mixture of the three possible bibenzyls."[3] In some limited series, the "stabilized" radicals may show somewhat greater probability of undergoing cage recombination;[11] therefore, we would guess that the unsubstituted BPA should lead to <10% cage process. In general, we take it as highly probable that the products of process 1 arise chiefly from noncage processes.

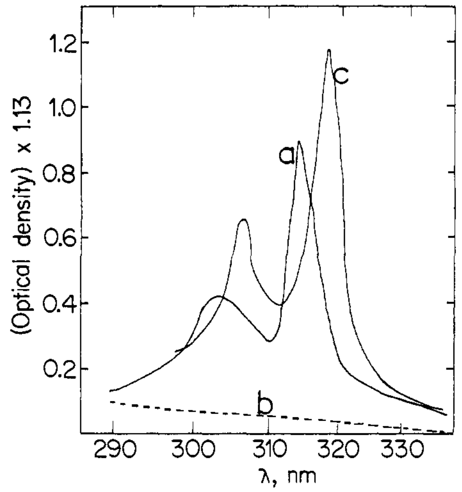

Figure 4. Flash spectrum at 10-μsec delay of benzyl phenylacetate in methanol: (a) transient benzyl radical; (b) permanent product. Flash spectrum at 2-μsec delay of *p*-methyl-*p*-benzylacetate in methanol; (c) transient *p*-methylbenzyl radical.

Both of the unsymmetrical esters should yield an identical caged species (p-$CH_3C_6H_4CH_2\cdot\ \cdot H_2CC_6H_5$), analogous to **3** in eq 2. Since the amount of cage recombination differs, this is evidence for path branching before species **3**, say at **1**. Branch b in eq 2 would lead to 100% randomization. The alternative ejection of carbon dioxide prior to disruption of the radical pairs **2** and **3** allows for cage recombination along step f or randomization following step e in eq 2. It should be noted that photoenergy in excess of 102 kcal/mol is imparted to the ester. This is more than adequate to break almost all single bonds (except C–H) in the ester and to give one or more species possessing more than their ground state energies. It would not be surprising, therefore, that B should break out of the

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(11) A referee (and we) have questioned the idea that the more stable radicals of a series may show a relative preference toward cage recombination, as compared with noncage reactions. W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970), report that in octane at 60° the fraction of cage return is 0.25 for the pair p-$O_2NC_6H_4\cdot\ \cdot C(C_6H_5)_3$ *vs.* 0.29 for the pair $C_6H_5\cdot\ \cdot C(C_6H_5)_3$. Other examples of the type $ArCH_2\cdot\ \cdot OC(CH_3)_3$, in which the fraction ranges from 0.33 (p-CH_3O) to 0.26 (p-Cl), are given in ref 12.

(12) R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654, 657 (1971).

solvent cage before collapsing to BB, as in step b and possibly as in e.

To summarize our suggested mechanism (eq 2), the ester is excited (210–280 nm); most of the excited molecules return to the ground state through various deexcitation processes, but <20% decompose to radical pair **1**; the radicals may diffuse apart into the bulk solvent (step b) or lose carbon dioxide with preservation of a benzyl–benzyl radical pair, **3**; collapse within **3** *vs.* solvent disruption of the pair leads to partitioning into cage *vs.* noncage bibenzyl products, but the latter predominate.

For comparison consider the following reported observations on benzylic species. Greene, *et al.*, has shown that the thermolysis of optically active azo-α-methylphenylethane leads to predominant randomization *within* the cage over recombinaton, disproportionation, and/or cage departure (4:1).[13] For the thermal decomposition of *tert*-butyl *m*-chlorophenylperacetate in solution, Newman and Behar favor two-bond over one-bond homolytic scission as the initial step.[12] The ratio of cage to noncage recombination is 0.26 at 1 atm and 0.82 at 4000 atm in cumene at 79.6°. According to this interpretation radical pairs analogous to **2** or **3** in eq 2 are produced, which favor the noncage route(s) over recombination at low pressure. In the photodecarbonylation of dibenzyl ketones, there is compelling evidence for one bond homolytic cleavage. Phenylacetyl ($C_6H_5CH_2CO\cdot$) and B then leave the cage *before* the former decarbonylates; there is no cage recombination, even if the incident energy is lowered from 254 to 313 nm or if the viscosity (cP, 30°) is increased from 0.56 in benzene to 41.1 in cyclohexanol.[14] In the context of eq 2, this corresponds to decomposition from **1** along step b. These findings support the notion that both cage and noncage recombination may be found when benzyl-related radicals are generated thermally or photochemically and that the noncage process is likely to be favored, particularly for B and especially in photoprocesses.

Properties of the Benzyl Radical. During flash photolysis of methanolic solutions of BPA, B (λ_{max} 314 and 302 nm) was the only transient species observed. A typical example of the transient spectrum is shown in Figure 4. In addition to B, a small amount of permanent product is also formed which produces an absorption that increases gradually in intensity toward shorter wavelengths. Since >90% of B recombined randomly to form BB, reaction 1 appeared to be well suited for measuring k_R (B) and ϵ_B. The *p*-methylbenzyl radical which was also generated by flash photolysis from *p*-methylphenylacetate resembles B in its spectral behavior (Figure 4). Both radical absorptions decayed within 200 μsec.

The benzyl radical decay curves were analyzed by analog computer, as outlined previously.[2b] A detailed description of the computer program appears in the thesis.[1] In brief, the analysis was based on the assumption that all B react to form BB. The decay of B can then be described by the following rate equation

$$d[B]/dt = I(t) - 2k_R[B]^2 \qquad (6)$$

and BB formation by

$$d[BB]/dt = k_R[B]^2 + k_{Ind}[BPA][B] \simeq k_R[B]^2 \qquad (7)$$

Justification for the neglect of the term in eq 7, corresponding to induced decomposition (eq 5) with rate constants k_{Ind}, derives from the observation that Φ for ester decomposition is essentially independent of [BPA] (Figure 2). The absorbance (A) is related to [B] through eq 8, in which b is the cell length. It is a consequence of the second-order dependence of [B] in eq 6 that the flash experiments yield the ratio k_R/ϵ_B. For this reason, the uncertainties in the two quantities involved are not independent.

$$A = [B]\epsilon_B b \qquad (8)$$

In order to calibrate the computer simulation, the amount of BB formed in a given flash was determined by gas chromatography. With [BPA] varying from 0.7 to 2.4 × 10^{-3} M, [BB] formed per flash varied from 1.34 to 3.07 × 10^{-5} M. By comparing the amount of product with the amount of radical actually generated during a flash, the computer simulation can readily solve the differential rate equations. This analysis produced a value of ϵ_B 1.5 × 10^3 M^{-1} cm^{-1} for λ_{max} 314 nm, which we estimate good to ±25%.[15] This value of ϵ_B is discussed in the companion paper where it is compared with several literature values as well as to a new value based on the photolysis of sodium phenylacetate.[2b]

Our value of $k_R = 6.8 \times 10^8$ M^{-1} indicates a rate that is less than diffusion controlled in methanol, and in accord with the predominant noncage radical combination. The difference from $k_R = 4.14 \times 10^9$ M^{-1} sec^{-1}, obtained from the photolysis of sodium phenylacetate in water,[2b] is not surprising, for the fate of B, when generated from the salt, was not entirely known and its capture by other reactive species was indicated. In the BPA photolyses of this work, we know that B reacts almost quantitatively to form BB, so that the measured rate should be closer to the true recombination rate.

It should be appreciated that radical recombination rates have often been difficult to reproduce by different workers or techniques.[11] Consider the few reports on k_R. McCarthy and MacLachlan showed that the halftime (τ, μsec) for the decay B in several solvents at 25° appeared to depend on the viscosity (η, cP) of the solvent: C_6H_{12} (η = 1.2), τ = 13; C_2H_5OH (η = 1.5), τ = 16; ethanol–glycerol (η = 22), τ = 45; glycerol (η = 340), τ = 220.[16] These workers subjected several benzyl compounds to pulse radiolysis and found ϵ_B = 1100 M^{-1} cm^{-1} and $k_R = 4 \times 10^7$ M^{-1} sec^{-1} for ethanol–glycerol (η = 55). From older flash photolysis data,[17] they also estimated $k_R \simeq 8 \times 10^7$ for a paraffin solvent (η = 163). The k_R's of McCarthy and MacLachlan are not directly comparable with the following k_R's of the low viscosity ($\eta \simeq 1$)

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(13) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970).

(14) W. K. Robbins and R. H. Eastman, *ibid.*, **92**, 6077 (1970).

(15) Normally, the decay of B was followed by point to point photographic measurements. If we used a photoelectric measurement of A, lower values of ϵ_B = 900 M^{-1} cm^{-1} and $k_R = 3 \times 10^8$ M^{-1} sec^{-1} were obtained. Although the B absorption at 314 nm is quite sharp, its width of *ca.* 10 nm leads to an average A for this wavelength range. Thus, the computed values of ϵ_B and k_R are expected to be on the low side, but the order of magnitude is reassuring.

(16) R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **56**, 1187 (1960).

(17) G. Porter and M. W. Windsor, *Nature (London)*, **180**, 187 (1957).

solvents, but their τ data do indicate that k_R may reach its diffusion limit in solvents of high viscosity.

Hagemann and Schwartz studied the pulse radiolyses of benzyl chloride in cyclohexane and obtained $\epsilon_B = 12000\ M^{-1}\ cm^{-1}$ and $k_R = 2 \times 10^9\ M^{-1}\ sec^{-1}$.[18] Then Burkhart obtained $k_R \simeq 1.8 \times 10^9$ in benzene and $2.0 \times 10^9\ M^{-1}\ sec^{-1}$ in cyclohexane by the rotating sector method on the reaction of triethyl phosphite and benzyl mercaptan.[19] Although the last two reports agree on $k_R \simeq 2 \times 10^9\ M^{-1}\ sec^{-1}$ for cyclohexane, we believe the Hagemann and Schwartz value of k_R (and ϵ_B) may be high. This is because their yield of product, based on hydrogen chloride rather than on B species, could be low, and because the decay of B, possibly enhanced by the presence of other reactive species such as cyclohexyl, hydrogen, unsaturates, etc., could be high.

We are left with a factor of 3 discrepancy between our k_R and Burkhart's,[19] which we cannot explain. As pointed out above and also in connection with the evaluation of ϵ_B, the errors in flash photolysis generally lead to overestimates of k_R and ϵ_B. We would be reluctant, therefore, to revise our k_R upward. In the same vein, if ϵ_B was actually 10 times larger than our value of 1500 $M^{-1}\ cm^{-1}$, as some authors claim,[2b] then k_R would have been *ca.* $7 \times 10^9\ M^{-1}\ sec^{-1}$. Since this "high" figure corresponds to the calculated diffusion-controlled limit for B,[19b] it is less likely to be correct.

Since they were first detected, interest in isoelectronic benzyl, phenoxyl, and anilino radicals has evolved on many fronts.[5,20,21] By now their chemical and electron spin resonance properties are quite familiar,[22] but beyond simple recognition, there has often been disagreement in their physical description. The summary in Table III does not, of course, disclose the sort of discrepancies which we have pointed out in detail with respect to ϵ_B and k_R(B). These inconsistencies are not uncommon in the work on radicals, the more so when different research groups and/or techniques are used.[2b,11,23] For this reason, we emphasize that some of the figures of Table III may not be final, but we believe that, at least with respect to B, their margin of uncertainty has been considerably reduced.

Table III. Properties of Radicals at ~25°

	λ, nm	ϵ, M^{-1} cm^{-1}	$k_R \times 10^9$ M^{-1} sec^{-1}	Solvent
$C_6H_5CH_2\cdot$	318	1500[a,b]	0.68[b]	CH_3OH
$C_6H_5NH\cdot$	308[c]	4700[c]	1.5[c]	H_2O
$C_6H_5O\cdot$	330[d]	3800[d]	1.4[d,e]	H_2O

[a] Reference 2b. [b] This work. [c] Reference 20. [d] Reference 21. [e] Discrepancies in this figure are found in ref 20–23, because of the confusion of $2k_R/\epsilon$ with k_R/ϵ and possibly because of arithmetic errors. From ref 20 and 21b, we calculate a mean value of $k_R/\epsilon = (3.65 \pm 0.75) \times 10^5$. Using $\epsilon = 3800 \pm 800$ (ref 21a), we calculate $k_R = 1.4 \pm 0.6 \times 10^9\ M^{-1}\ sec^{-1}$. Reference 23 also reports $k_R = 6.3 \pm 2.5 \times 10^8\ M^{-1}\ sec^{-1}$ in C_6H_6 and $k_R = 5.5 \pm 2.2 \times 10^7\ M^{-1}\ sec^{-1}$ in chlorobenzene.

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Reaction of Formazan with Singlet Oxygen[1a]

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Abstract: Singlet molecular oxygen reacts with 1,3,5-triphenylformazan to yield benzoic acid, benzene, phenol, and the tetrazolium cation. Oxidation by singlet oxygen, produced chemically or with a sensitizer of low triplet energy, results in degradative oxidation of formazan. Under both conditions benzene and benzoic acid are produced; in addition phenol is a product of the photochemical reaction. When a sensitizer of high triplet energy is used, the formation of 2,3,5-triphenyltetrazolium, the nondegradative oxidation product of the formazan, is also observed. A mechanism is suggested for these reactions.

The dye-sensitized photooxidation of organic compounds is of interest because it underlies phenomena of great biological importance. Early investigators showed the participation in these reactions of long-lived metastable excited states of the sensitizing dye, and supposed the formation of a dye–peroxide complex as a reaction intermediate.[2,3] Subsequent studies, however, showed that electronically excited (singlet)

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