

10^5 dynes cm.,^{22,23} the above analogy would predict an increased field gradient at the deuteron in ketene relative to formaldehyde. The opposite trend is observed by our work which indicates that eq. 15 is not valid for the nonlinear polyatomic molecules such as formaldehyde or ketene. It is also possible, however, that the assignment of the low C-H force constant in formaldehyde is in error. Salem's²⁰ calculated force constants for linear molecules using eq. 15 are all smaller than the actual force constants which agrees with our results in ketene. Formaldehyde would therefore require a larger force constant to bring it in accord with the present results.

- (22) S. Sundaran and F. F. Cleveland, *J. Chem. Phys.*, **32**, 1554 (1960).
(23) C. B. Moore and G. C. Pimentel, *ibid.*, **38**, 2816 (1963).

The chemical shielding in ketene is also interesting as the experimental average shielding is the largest methylene shift measured.⁸ The large methylene proton shielding in ketene arises from both a large diamagnetic and relatively small paramagnetic contribution. Our results show that ketene has a slightly larger diamagnetic term than formaldehyde but a considerably smaller paramagnetic term leading to a small proton spin-rotation interaction in ketene.

Acknowledgment. The support of the National Science Foundation in this work is gratefully acknowledged. We also wish to thank Professors P. Beak and J. Baldwin for encouragement and help in this research.

A Study of the Benzyl Free Radical and Substituted Benzyl Free Radicals

Joe E. Hodgkins and E. Dennis Megarity

Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas. Received July 12, 1965

The spectra of a series of substituted benzyl free radicals have been taken and the shifts from the unsubstituted radical have been measured. These shifts have been correlated with $\Delta\sigma$, a reaction constant. Substituent effects on α -substituted benzyl radicals have also been measured. These are unusual in that delocalization decreases with an increase in the stability of the radical. The benzyl radical itself seems to form primarily through vibronic excitation involving a C-H stretching mode of the methyl group of toluene. The extinction coefficient of the benzyl radical has been measured by a method that has not been used previously.

Introduction

In the late 1950's Porter, *et al.*,¹⁻⁶ conducted intensive research on the benzyl ($C_6H_5CH\cdot$) and other related radicals. These workers were successful in obtaining the spectrum of the benzyl radical in gas and solution phases and also in solid EPA. Porter and Strachan¹ established the assignment of 3187 ± 5 Å. to the benzyl radical by obtaining the spectrum of the intermediate from a number of different but reasonable precursors. This wave length assignment to the benzyl radical gains support from the theoretical calculations of Dewar, Longuet-Higgins, and Pople.^{7,8} These researchers predicted a value of 2965 Å. in the gas phase, and Bingle⁹ predicted a long wave length band at 4580

- (1) G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).
(2) I. Norman and G. Porter, *Proc. Roy. Soc. (London)*, **A230**, 399 (1955).
(3) G. Porter and F. Wright, *Trans. Faraday Soc.*, **51**, 1469 (1955).
(4) G. Porter and M. W. Windsor, *Nature*, **180**, 187 (1957).
(5) G. Porter and E. Strachan, *Spectrochim. Acta*, **12**, 299 (1958).
(6) G. Porter, Special Publication No. 9, The Chemical Society, London, 1958, p. 139.
(7) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc. (London)*, **A67**, 795 (1954).
(8) H. C. Longuet-Higgins and J. A. Pople, *ibid.*, **A68**, 591 (1955).

Å. Porter and Wright³ obtained the benzyl radical in gas phase and recorded the principal absorption band at 3053 Å. The longer wave length band was obtained by Porter and Strachan,⁵ who assigned a value of 4527 Å. to the radical in matrix at 77°K. These results are in reasonably good agreement with the calculated values.

A number of substituted toluenes were photolyzed by Porter, *et al.*^{1,2} The bands due to the transients were assumed to be result of substituted benzyl radicals because their band shapes were identical with that of the radical obtained from toluene and because the bands disappeared upon warming the matrix.

The purpose of this study was to obtain the spectra of a number of substituted benzyl radicals in hopes to measure the degree of stabilization afforded by the substituents by ultraviolet absorption spectra. In addition, we were interested in determining the extinction coefficient of the benzyl radical and in assigning the particular energy of ultraviolet radiation which was leading to formation of the radical.

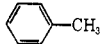
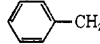
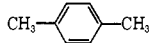
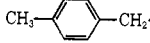


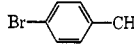
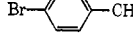
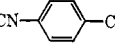

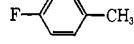
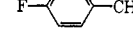
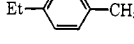
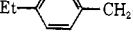
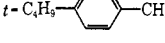
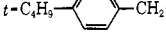
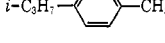
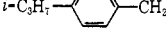
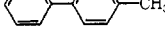
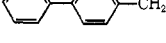
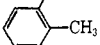
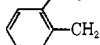

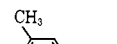
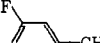
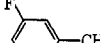
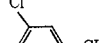
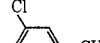
Results and Discussion

Table I indicates the benzyl and substituted benzyl radicals formed by photolysis at 77°K. with their assigned wave lengths. While most of the substituted radicals show a wave length shift to the red in comparison to benzyl, the halogen-substituted radicals show either no stabilization¹⁰ or, in the case of fluorine, a marked destabilization. The relative ease of photolysis, as determined by photolysis times necessary to

- (9) W. Bingle, *Z. Naturforsch.*, **10a**, 462 (1955).

(10) A shift to slightly longer wave lengths of the same transition is normally considered to be stabilization, especially when the compounds differ only slightly in structure. The transitions involved in substituted aromatic compounds are considered to be perturbations of the normal benzenoid transitions.

Table I. Absorption Spectra of Benzyl Radicals in EPA at 77° K.

Parent molecule	Radical	$\lambda \pm 3 \text{ \AA.}$	$\Delta\lambda$ from benzyl $\pm 6 \text{ \AA.}$	$E_D \pm 0.02 \text{ kcal./mole}$
		3182	0	0.0
		3226	+44	+1.23
		3192	+10	+0.28
		3181	-1	0.0
		3238	+56	+1.55
		3150	-32	-0.91
		3223	+41	+1.14
		3221	+39	+1.09
		3221	+39	+1.09
		3260	+78	+2.15
		3232	+50	+1.39
		3224	+43	+1.17
		3167	-15	-0.43
		183	+1	0.0

produce transient absorptions of approximately the same intensity,¹¹ is as follows: *p*-phenyltoluene > xylenes > toluene > *p*-ethyltoluene \geq *p*-isopropyltoluene \geq *p*-(*t*-butyl)toluene > *p*-toluonitrile > *m*-chlorotoluene > *m*-fluorotoluene > *p*-chlorotoluene > *p*-bromotoluene > *p*-fluorotoluene.

Thus, the order of ease of photolysis of the halogen-substituted toluenes, for example, does not follow the order of electronegativity but does follow the degree of red shift from the parent radical. *p*-Toluonitrile is the only exception to this type of behavior.

The fluorine-substituted benzyl radicals were the hardest to form and showed a blue shift of the radical (0,0) band. The blue shift is not shown in the singlet spectra of the parent *p*-fluorotoluene in the 2700-Å region (see Table II), but a blue shift has also been noted in the phosphorescence spectra of *p*-fluorobenzaldehyde.¹² Murrell and Longuet-Higgins¹³ carried out calculations on successively fluorinated benzene in which the wave functions for the excited states were

(11) This is not directly comparable, of course, owing to differences in the molar extinction coefficients, but we felt this to be justified for observing gross differences.

(12) J. Woodyard and J. E. Hodgkins, to be published.

(13) J. N. Murrell and H. C. Longuet-Higgins, *Proc. Phys. Soc. (London)*, **A68**, 329 (1955).

Table II. Comparison of the Absorption of Radicals and Parents

Compound	(0,0) band $\pm 2 \text{ \AA.}$	(0,0) band of radical $\pm 6 \text{ \AA.}$
Toluene	2686	3182
<i>o</i> -Xylene	2702	3232
<i>p</i> -(<i>t</i> -Butyl) toluene	2720	3221
<i>m</i> -Xylene	2722	3224
<i>p</i> -Fluorotoluene	2726	3150
<i>p</i> -Ethyltoluene	2733	3223
<i>p</i> -Xylene	2741	3226
<i>p</i> -Chlorotoluene	2763	3194
<i>p</i> -Bromotoluene	2768	3181
<i>p</i> -Toluonitrile	2791	3238

mixed. Their calculations predicted a blue shift of the short wave length transition. We have been unable to apply these ideas to the benzyl system. Porter¹⁴ has used these types of calculations to predict the blue spectral shifts in going from the benzyl to the phenoxyl to the anilino radicals even though Murrell and Longuet-Higgins state that such calculations are not valid when the mesomeric effect is appreciable, such as might be expected with the free pair electrons of oxygen and nitrogen. In any case, the blue shift caused by the fluoro substituent is in line with its chemical reaction substituent effect (*vide infra*).

By taking the spectra of very dilute solutions of parent compounds in EPA, the (0,0) bands of a number of substituted toluenes were resolved. These band assignments are given in Table II accompanied by the (0,0) bands of the corresponding radicals. It is evident that there is no definite correlation between the wave length of absorption of the toluenes and the resulting radical. While the (0,0) bands of the parent compounds are placed in order of increasing wave lengths, the radical wave lengths are in no particular order. Thus, the stabilization of the benzyl radical is not simply related to the stabilization of the excited states of toluene.

An attempt was made to see if the spectral shifts of the substituted radicals could be correlated with Hammett's σ_p values, without success. Land and Porter¹⁵ independently observed a similar failure to correlate Hammett's constants with the observed shifts of substituted phenoxyl radicals. In some older work, Doub and Vandenbelt,¹⁶ showed that Price's $\Delta\sigma$ values ($\sigma_p - \sigma_m$) rather than Hammett's σ_p values correlate very roughly with the primary band displacement of substituted benzenes. Figure 1 shows clearly that the data for benzyl radical shifts correlate well with $\Delta\sigma$. Taft's σ_R values which are supposed to be a better measure of the pure resonance effect of a substituent showed worse correlation of the observed shifts than did $\Delta\sigma$.¹⁷ As Jaffé and Orchin¹⁸ point out, no really exact correlation between spectral shifts and any parameter measuring a pure resonance effect should be expected since spectral shifts measure total delocalization.

(14) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).

(15) E. J. Land and G. Porter, *ibid.*, **59**, 2027 (1963).

(16) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(17) R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5342 (1949).

(18) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 259.

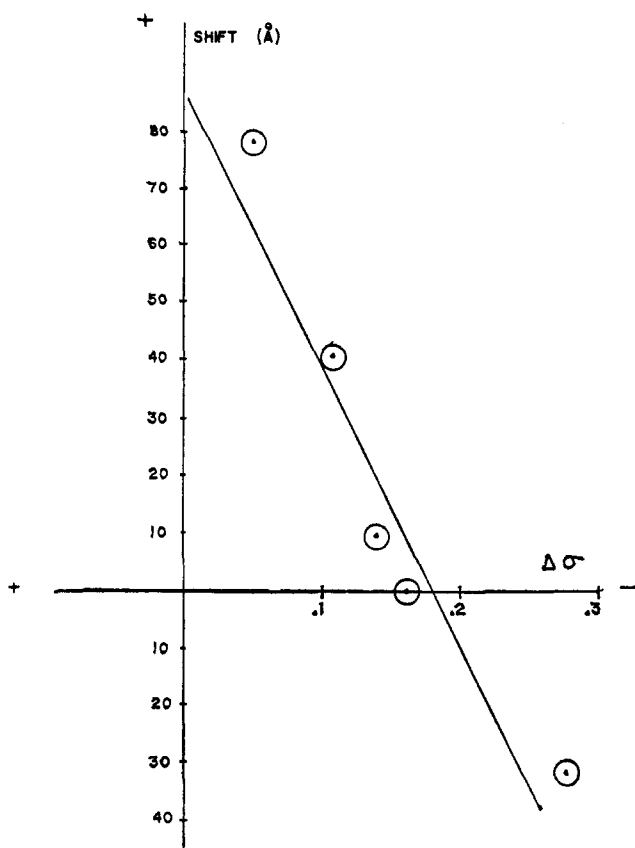


Figure 1. Substituent shifts in the benzyl radical vs. $\Delta\sigma$.

Nonetheless, as Figure 1 indicates, it is possible to measure fairly accurately the $\Delta\sigma$ reaction constant, which is more closely related to total delocalization, with a simple spectral measurement.

The (0,0) bands of the transients resulting from the photolysis of ethylbenzene and isopropylbenzene were less intense than the band formed upon photolysis of toluene and were much more difficult to produce. This is probably due to the fact that the C-C bond, being weaker than the C-H bond, is broken to a greater extent and thereby dissipates the absorbed energy. Recombination in this case, however, is exceedingly high because the $\text{CH}_3\cdot$ would diffuse out of the matrix cage at a much slower rate than $\text{H}\cdot$. Thus, isopropylbenzene in EPA glass required 5 min. of photolysis to produce a transient band having about one-tenth the intensity of the bands produced by irradiating toluene or *p*-xylene for 1 min. A similar situation existed when comparing the (0,0) band of the transient arising from the photolysis of ethylbenzene with that of the transient arising from toluene. Therefore, the intense band produced by short irradiation of *p*-isopropyltoluene and *p*-ethyltoluene must have been due to the substituted benzyl radical. We did not observe or attempt to form, by extended irradiation, the other possible radical.

Porter, *et al.*,^{1,2} have also taken the spectra of the methylphenylcarbinyl radical (I) and the dimethylphenylcarbinyl radical (II) in matrix, prepared from ethylbenzene and isopropylbenzene, respectively. The matrix technique was also employed in this work to trap and obtain the spectra of radicals I and II as well as a number of substituted radicals of this type. These are listed in Table III.

Table III. Methylphenylcarbinyl and Dimethylphenylcarbinyl Radicals

Parent molecule	Molar concn. $\times 10^3$	Radical	λ \pm 3 Å.	λ^a \pm 6 Å.
	3.76		3221	0
	9.4		3242	+21
	3.76		3239	+18
	3.76		3245	+24
	3.76		3250	+29
	3.76		3240	0
	3.76		3253	+13

^a From nonsubstituted radical.

While it is known that a particular substituent may cause variable amounts of shift when attached to different types of structures, such as conjugated ethylenes, aliphatics, aromatics, and carbonyls,¹⁹ it is generally accepted that a certain substituent will show the same amount of shift when substituted on several different members of a like group.^{20, 21} Table IV shows

Table IV. Effects of Individual Substituents on a Series of Radicals^a

Substituent shifts	Radicals		
	Benzyl	I	II
<i>p</i> -Ethyl	+41	+21	...
<i>p</i> -Isopropyl	+39	+18	-4.9
<i>p</i> - <i>t</i> -Butyl	+39	+24	+13

^a Shifts are shown in Å.

a comparison of the shifts caused by the same substituents attached to the *para* position of different radicals. (It was found not to be possible to prepare the *p*-ethylphenyldimethylcarbinyl radical since only the *p*-isopropylphenylmethylcarbinyl radical would form. Ethylbenzene is somewhat easier to photolyze than isopropylbenzene, giving some justification for this result. Either a statistical argument or an argument based on an increased number of vibrational modes, dissipating the absorbed energy, could be employed to explain this behavior.) Considering the information given in this table, one can easily see that the higher the energy of a given radical, the greater the degree to which it is stabilized by an aliphatic *para* substituent. The red shifts decrease 50% (for a given substituent) in going from the benzyl radical to radical I and radical II (see Table IV and Figure 2). There is a definite indication that the degree of stabilization of an aromatic free radical by a given aliphatic *para* substituent is dependent upon the stability of the radical.

(19) K. Bowden, E. A. Brande, and E. R. H. Jones, *J. Chem. Soc.*, 948, (1946).

(20) M. Margoshes and V. A. Fassel, *Spectrochim. Acta*, 7, 14 (1955).

(21) L. E. Lyons, *Research (London)*, 2, 589 (1949).

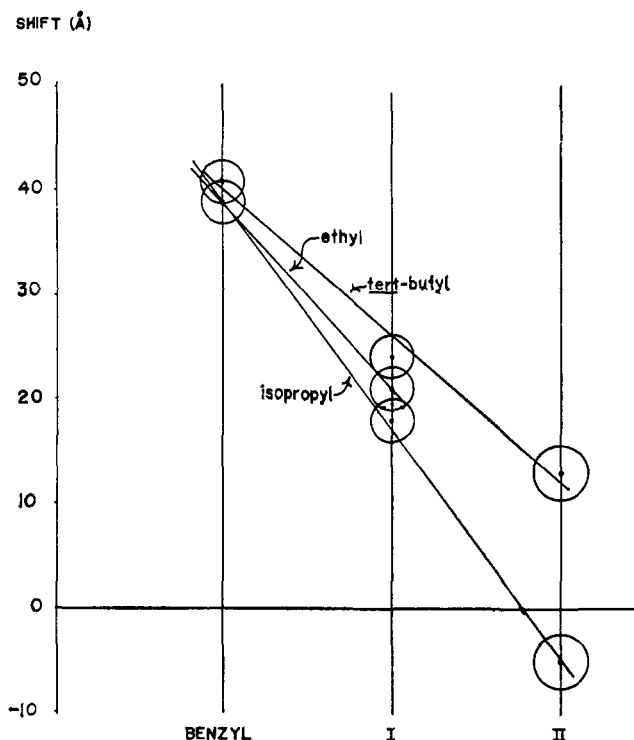


Figure 2. Comparative shifts of the *p*-ethyl, *p*-isopropyl, and *p*-*t*-butyl substituents on the benzyl, methylphenylcarbinyl, and dimethylphenylcarbinyl radicals.

Bindley, Watts, and Walker²² have also obtained the spectra of some substituted radicals of this type (I and II), although their work with substituted radicals duplicated the work described here in the case of only one radical. They assigned the (0,0) band of the *p*-ethylphenylmethylcarbinyl radical as being 3295 Å., as taken in a matrix of 2:3 methylcyclohexane-isopentane at 77°K. The wave length assignment of this radical as given in Table III is 3242 Å., taken in EPA; and no band was noted in the 3280–3300 Å. region. Evidence that Bindley, Watts, and Walker are in error in their assignment or that matrix interactions are far greater than suspected is as follows. In considering the benzyl radical, one notes that the substitution of either a *p*-ethyl or *p*-isopropyl group results in approximately a 40-Å. red shift (see Table IV). Further, our investigation showed that the substitution of a *p*-isopropyl group on radical I resulted in a red shift of 24 Å., roughly half the amount of red shift caused by the substitution of this group on the benzyl radical. It therefore seems unreasonable for the *p*-ethylphenylmethylcarbinyl radical to have a (0,0) band at 3895 Å. This value indicates a red shift of over 70 Å. as compared to the unsubstituted radical. One would expect, rather, that the *p*-ethyl group would stabilize radical I to approximately the same degree as the *p*-isopropyl group, since both of these substituents effect the same amount of red shift on the benzyl radical. This investigation indicates a red shift of 18 Å. upon substituting radical I with a *p*-ethyl group.

The Monochromator Study. The absorption spectra of a dilute solution of toluene in solid EPA were taken in order to resolve the principal vibrational modes. Toluene was then photolyzed in the same matrix at a

(22) T. F. Bindley, A. T. Watts, and S. Walker, *J. Chem. Soc.*, 4327 (1962).

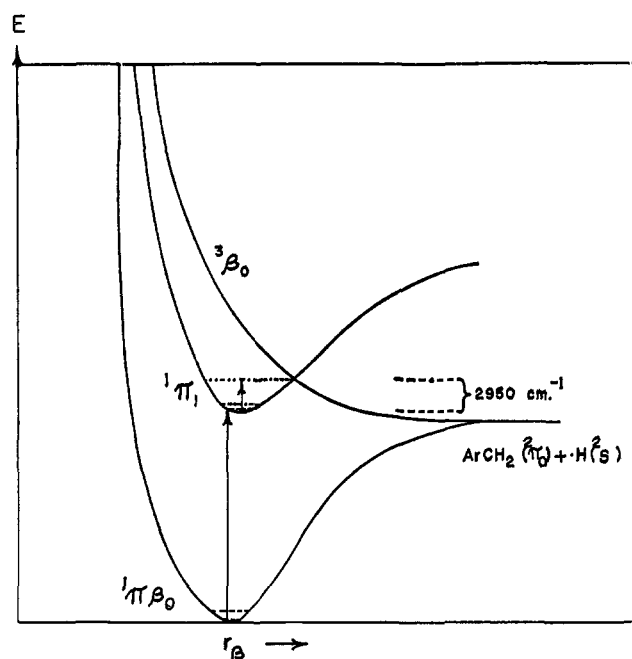


Figure 3. Energy diagram for the dissociation of toluene: $1\pi\beta_0$ = ground state, $1\pi_1$ = first excited electronic state, $3\beta_0$ = repulsive state of C-H bond.

number of different wave lengths, corresponding to the vibrational modes, in order to determine which of the vibrational levels of the first excited state was leading to the rupture of the C-H or β bond.⁶ The wave length at which the radical was formed to a much greater extent than all the others was 2490 ± 10 Å. Conversion to cm^{-1} and subtraction from the (0,0) frequency of toluene gives a frequency of 2950 ± 170 cm^{-1} . This value lies in the vibrational range for a methyl group (neglecting the possibility of this being a combination mode).²³ Pitzer and Scott²⁴ have carried out a vibrational analysis of toluene and have calculated a vibrational frequency for the methyl group at 2950 cm^{-1} .

It is believed that the dissociation of molecules usually takes place by excitation from the lowest vibrational level of the ground electronic state to a vibrational level of the first excited state, which subsequently leads to bond fission.²⁵ Porter has drawn a conventional Morse potential well diagram to depict this theory of β -bond cleavage,⁶ and he proposes that the molecule undergoes a predissociative process by an intersystem crossing from a first excited vibronic level to a repulsive or triplet state of the β bond. Figure 3 is a general reproduction of Porter's diagram. The point at which the repulsive state crosses the excited state can now be assigned, as shown in Figure 3. Thus, as might be expected, vibronic excitation involving the stretching of the C-H bond near 2950 cm^{-1} leads to fission and formation of the benzyl free radical.

The Extinction Coefficient. McCarthy and MacLachlan²⁶ have reported that the molar extinction coefficient of the benzyl radical is 1100. This low value

(23) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 5.

(24) K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, 65, 803 (1943).

(25) F. Daniels and R. A. Alberty, "Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 540.

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

suggests that the transition is symmetry forbidden. Land and Porter¹⁵ have, however, indicated that the 3182 Å. band is an allowed transition, and that the extinction coefficient should be considerably higher, perhaps 10,000–20,000. Careful analysis of the method by which the 1100 value was measured leads to several objections. Firstly, the radical was generated with an electron beam, the use of which could cause radical formation from a number of molecules other than the progenitor of the benzyl radical, *i.e.*, solvent. Secondly, the total products of photolysis, including radical combination with solvent radicals, were taken as indicative of the concentration of benzyl radical during the time in which the ultraviolet absorption was recorded. Thus, it would appear that solvent radicals were created by the electron beam since it is thermodynamically an unfavorable situation in which a relatively low energy radical, such as the ground-state benzyl radical, would abstract hydrogen from aliphatic hydrocarbon solvents. Further, Steacie²⁷ has indicated that the benzyl radical dimerizes essentially 100%. This fact is the basis for the toluene carrier technique used by Szwarc.²⁸ Other workers^{6, 29} have also noted the tendency of benzyl to form dibenzyl rather than react with other molecules. (Since atomic hydrogen atoms are very small and diffuse rapidly through the matrix dimerizing to yield H₂, one would not expect the recombination effect of the benzyl radical and H· to be appreciable.)

Nonetheless, we have also noticed small amounts of solvent-radical interaction products, using a more conventional method of radical generation, that of ultraviolet irradiation. We did not include these products in the calculation of the benzyl radical concentration because of the known stability of the benzyl radical—and the following argument. If the benzyl radical were an excited-state radical of higher energy than a resulting solvent radical, owing to the intense ultraviolet irradiation, then it could abstract H· from solvent. These products would not, however, show an increase in the concentration of the radical since toluene would be the product after hydrogen abstraction, and combination of benzyl and solvent radicals should take place relatively easily even in the frozen matrix. (Small radicals cannot be trapped in EPA matrix.) The benzyl radical would remain excited only as long as the high-energy source was being applied and not during the ultraviolet spectrometry. Thus, the absorption spectra would be the absorption spectra of the ground-state benzyl radical, which could only react with another benzyl radical, leading to dibenzyl. The solvent-radical products would be formed during irradiation and not after melting the glass. If this more logical approach is taken, the molar extinction coefficient of the benzyl radical is found to be $19,200 \pm 20\%$. This value seems to be much more reasonable than 1100 for an allowed transition.

Experimental Section³⁰

The absorption spectra were taken with a medium Hilger spectrograph (E-498). A Beckman spectro-

(27) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, p. 74.

(28) M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949).

(29) A. F. Trotman-Dickenson, "Free Radicals," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 14.

photometer Model DK-2 was used routinely to determine if radical was present in a matrix. A Texas Instruments continuous optical pumping system, equipped with an Osram 1600-w. high-pressure xenon bulb with a 24-in. ellipsoidal focusing mirror, was used as a high-intensity light source. The monochromator used was a Bausch and Lomb grating instrument equipped with a 200-w. super pressure mercury lamp. A Joyce-Lobel Model MK-III C double beam recording microdensitometer was used for photometry of the photographic plates. The film used was Ilford R-50 and FP-4. Acufine and Rodinal developers were employed. Vapor phase chromatography was accomplished using a Perkin-Elmer Model 800 gas chromatograph equipped with a 15-ft. copper column packed with 5% Apiezon L grease on Chromosorb. The carrier gas was nitrogen at a flow rate of 35 cc./min.

The dewars employed were similar to those described by Porter³ except that the light path was constructed to be at the bottom of the cell rather than in the middle. The cells were of two types, square and round. The round cells showed much less breakage than the square cells but were difficult to position to take spectra. Solvents were mixed using spectroquality ether and isopentane. The ethyl alcohol was prepared by the method of Lund and Bjerrum.³¹ All liquid samples were distilled on a column packed with glass helices or Helipak. The solids were repeatedly recrystallized.

A copper arc was used to calibrate the printed scale of wave lengths on the Hilger spectrograph. The plate was expanded 50× with a microdensitometer, and a graph constructed of the scale *vs.* the true wave length of the scale divisions as determined by the copper arc. A mercury pen lamp emission spectrum was recorded on each plate. As small shifts were noted, proper corrections were made in the wave length assignments.

Determination of the Molar Extinction Coefficient. A round cell was employed in this experiment and was positioned so that the complete height of the matrix was exposed to the light and was rotated so that an even photolysis would be obtained. After measurement of the intensity of absorption, the matrix was allowed to melt and a measured portion was evaporated to a smaller known volume and injected in a gas chromatograph. The size of the dibenzyl peak was noted and matched with a known sample of dibenzyl dissolved in chromatographic quality acetonitrile. The concentration of dibenzyl in the melted matrix was thus obtained, and this value was doubled to obtain radical concentration. Beer's law was then employed in the normal fashion to determine the extinction coefficient, taking into consideration shrinkage of the matrix and background absorption. The complete experiment was repeated five times and the resulting values averaged.

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(30) A very detailed experimental description of our research is available on request: E. D. Megarity, M. A. Thesis, Texas Christian University, 1964.

(31) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).