# Photolysis of Acetyl Benzoyl Peroxide Isolated in an Argon Matrix: The Stability of the **Benzoyloxy and Acetoxy Radicals toward Decarboxylation**

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Exposure of matrix-isolated acetyl benzoyl peroxide to UV light ( $\lambda > 2800$  Å) produces methyl benzoate, the methyl-phenyl radical pair, and carbon dioxide. The results of the low-temperature irradiation reveal that methyl benzoate is formed by recombination of the benzoyloxy-methyl radical pair. Since phenyl acetate was not detected during the low-temperature irradiation, it was concluded that the lifetime of the acetoxy-phenyl radical pair is too short to allow concentrations that could be detected by infrared spectroscopy. Ab initio calculations are used to provide an explanation for the dramatic lifetime differences between the benzovloxy and acetoxy radicals. In addition, it was shown that electronic excitation of the phenyl radical does not induce a chemical reaction with carbon dioxide. Arguments based on experiment and theory are presented to explain this unexpected result.

### Introduction

Due to the rather low energy of the peroxide bond, diacyl peroxides 1 decompose thermally to produce acyloxy 2 and



alkyl radicals 3; as a consequence of this, they are frequently used in industrial processes requiring a free-radical initiator.<sup>1</sup> Acyloxy radicals are, in general, unstable toward decarboxylation.<sup>2</sup> In fact, the thermal stabilities of diacyl peroxides 1 follow the thermodynamic stabilities of the alkyl radicals 3. For example, diacyl peroxides where R is a primary carbon center may be easily prepared. When R is a secondary carbon center, the peroxides tend to slowly decompose at room temperature. However, when the R group is a tertiary alkyl carbon center, the peroxides are very unstable even at temperatures below ambient.

The benzoyloxy radical, the case where R = phenyl, has been studied with EPR<sup>3</sup> spectroscopy and CIDNP.<sup>4</sup> The fact that the benzoyloxy radical could be observed by CIDNP set the lifetime for the radical at about 10<sup>-8</sup> s at room temperature. To our knowledge, no spectroscopic data exist for the case where  $R = CH_3$ , the acetoxy radical; however, of the series of acyloxy radicals with straight hydrocarbon chains, it has the longest lifetime.

Here, we report low-temperature photochemical studies on acetyl benzoyl peroxide and theoretical calculations on the benzoyloxy and phenyl radicals. The former demonstrates the short lifetime of the acetoxy radical relative to the benzoyloxy radical even at very low temperatures: the latter offers an explanation for the rather limited lifetime for the class of acyloxy radicals in general.

#### **Experimental Section**

The low-temperature vacuum and sample handling systems have been described in previous reports.<sup>5</sup>

TABLE I: The (4s,3p) CGTO Basis Set Used for Carbon in the Phenyl Radical

l	exponent	contraction coeff
S	$\begin{array}{r} 3047.42110\\ 457.68720\\ 104.19590\\ 29.35626\\ 9.36054\\ 3.18880\\ 0.52830\\ \end{array}$	$\begin{array}{c} 0.001832\\ 0.014005\\ 0.068332\\ 0.229482\\ 0.463426\\ 1.0\\ 1.0\\ 1.0\end{array}$
р	$\begin{array}{c} 0.16207\\ 9.46452\\ 2.00658\\ 0.54694\\ 0.15197\end{array}$	1.0 0.037978 0.208938 1.0 1.0

TABLE II:	The (3s) CG	TO Basis Set	for Hydrogen
in the Phenyl	Radical		

l	exponent	contraction coeff	
s	13.013372	0.0196781	
	1.962496	0.1379520	
	0.444569	1.0	
	0.121953	1.0	

All infrared spectra were recorded on a Perkin-Elmer 521 spectrometer. The photochemical apparatus consisted of a 1500-W General Electric HBD high-pressure mercury lamp in conjugation with a 20-cm water filter. The spectral region of interest was isolated with standard Corning glass filters. Exposures were performed either with a corning 053 UV filter (0% transmittance for  $\lambda < 2800$  Å) or with no UV filters in the lamp. The intensity of the highpressure mercury lamp was measured with a calibrated Eppley thermopile (Eppley Laboratories, Inc., Newport, RI). The intensity was found to be  $150 \text{ mW}/\text{cm}^2$  when the Corning 053 filter was incorporated in the lamp and 180  $mW/cm^2$  with no UV filters in the lamp. For irradiations, in the extreme UV, an EIMAC VIX-150 xenon highpressure lamp with a total output of 40 mW/cm<sup>2</sup> in the  $\lambda < 2500$  Å region was employed.

The sample concentration used in the matrix isolation experiments was 1/400 (sample to argon). The deposition rate from the 3-L gas-handling system was nominally 0.5 mmHg/min.

The acetyl benzoyl peroxide was prepared by the method outlined by Sheldon and Kochi.<sup>6</sup>

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York, 1973.

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Figure 1. The geometry used for the phenyl radical in the SCF calculation.

TABLE III: The Molecular Orbital Energies for the <sup>2</sup>A. State of the Phenyl Radical (Energy in Hartrees)<sup>a</sup>

1a,	-11.277874	$1b_2$	-11.258959
$2a_1$	-11.258983	$2b_2$	-11.257785
$3a_1$	$-11.257\ 839$	$3b_2$	$-1.026\ 227$
$4a_1$	-11.253506	$4b_2$	-0.835154
5a,	-1.158597	$5b_2$	-0.625908
6a,	-1.011 851	$6b_2$	-0.603 268
7a,	$-0.813\ 514$	$7b_2$	$-0.503\ 262$
$8a_1$	$-0.708\ 504$	1 հ	0 507 562
9a,	$-0.637\ 722$		-0.507 563
10a,	$-0.543\ 514$	201	-0.340710
$11a_1$	$-0.460\ 079$	$1a_2$	-0.344490

<sup>a</sup> Total energy = -229.9565415.

#### **Computational Details and Results**

Phenyl Radical. The contracted Gaussian-type orbital basis sets (CGTO) used for carbon and hydrogen were taken from the compilation of uncontracted GTO basis sets given by Van Duijneveldt.<sup>7</sup> The scheme used for contracting the original basis set is shown in Tables I and II along with the orbital exponents and contraction coefficients. In essence, the original carbon (8s,4p) and hydrogen  $\langle 4s \rangle$  basis sets were contracted to a  $\langle 4s, 3p \rangle$  and a  $\langle 3s \rangle$  basis, respectively.

The ab initio calculations were performed with the joint MOLECULE-ALCHEMY programs.<sup>8</sup>

The  $C_{2\nu}$  geometry used to compute the total energy for the phenyl radical is shown in Figure 1. This standard geometry<sup>9</sup> was not optimized further because obtaining the equilibrium geometry of the ground state would only have a very small effect on the energy of the vertical electronic excitations. The latter quantity has the highest importance for this report.

Table III contains the molecular orbital energies and total energy obtained for the  ${}^{2}A_{1}$  ground state of the phenyl radical. The molecular orbitals with  $a_1$  and  $b_2$  symmetry are all in the plane of the phenyl ring while the  $b_1$  and  $a_2$ orbitals are perpendicular to the plane and, thus, form the  $\pi$ -system of the radical.

The unpaired electron in the phenyl radical resides in the 11a<sub>1</sub> orbital, which is a  $\sigma$ -type orbital. Two low-lying electronic transitions are possible as a result of excitation of  $\pi$ -electrons from the 1b<sub>1</sub> and 1a<sub>2</sub> molecular orbitals to the half-filled 11a<sub>1</sub> orbital. The transitions  ${}^{2}A_{1} \rightarrow {}^{2}B_{1}$  and  $^2\mathrm{A}_1 \rightarrow ^2\mathrm{A}_2$  are best described as  $\pi \rightarrow \mathrm{n}$  transitions. The transition from the  $7b_2$  to the  $10a_1$  orbital is an in-plane transition,  $2A_1 \rightarrow {}^2B_2$ , which could be classified as a  $\sigma \rightarrow$ n excitation. Ab initio calculations were only performed for  ${}^{2}A_{1}$ ,  ${}^{2}A_{2}$ ,  ${}^{2}B_{1}$ , and  ${}^{2}B_{2}$  states in order to compute the energy for these three vertical transitions. Since all of the states involve a half-filled shell, a reasonable accuracy is

TABLE IV: The Computed Vertical Electronic Transitions from the <sup>2</sup>A<sub>1</sub> Ground State of the Phenyl Radical to the  ${}^{2}B_{1}$ ,  ${}^{2}A_{2}$ , and  ${}^{2}B_{2}$  Excited States

excitation	energy, eV
${}^{2}A_{1} \rightarrow {}^{2}B_{1} (\pi \rightarrow n)$ ${}^{2}A_{1} \rightarrow {}^{2}A_{2} (\pi \rightarrow n)$ ${}^{2}A_{1} \rightarrow {}^{2}B_{2} (\sigma \rightarrow n)$	2.93 3.87 7.25

TABLE V: The (5s, 3p) CGTO Basis Used for Carbon in the Benzoyloxy Radical

l	exponent	contraction coeff
s	5240.635258	0.000 937
	$782.204\ 795$	$0.007\ 228$
	178.350830	0.036344
	50.815942	0.130600
	16.823562	0.318931
	6.175776	1.0
	2.418049	1.0
	0.511900	1.0
	$0.156\ 590$	1.0
q	18.841 800	0.013887
•	4.159240	0.086 279
	1,206710	0.288744
	0.385540	1.0
	0.121940	1.0

TABLE VI: The (5s,3p) CGTO Basis Used for Oxygen in the Benzovloxy Radical

	•		
l	exponent	contraction coeff	
s	10 662.284 940	0.000 799	
	$1\ 599.709\ 689$	0.006153	
	$364.725\ 257$	0.031157	
	103.651 793	0.115 596	
	33.905 805	0.301 552	
	$12.287\ 469$	1.0	
	$4.756\ 803$	1.0	
	$1.004\ 271$	1.0	
	0.300686	1.0	
q	34.856463	0.015648	
1	7.843131	0.098 197	
	2.308269	0.307 748	
	0.723164	1.0	
	$0.214\ 882$	1.0	

expected for the energy of the vertical transitions. Excitations not involving promotion of an electron to the half-filled 11a<sub>1</sub> orbital, such as those involving  $\pi \rightarrow \pi^*$ transitions, were not calculated because the final states would have three open shells and, hence, need CI-type calculations to obtain a reasonable accuracy for the vertical transition energies.

The energy for the vertical transitions  $({}^{2}A_{1} \rightarrow {}^{2}B_{1}, {}^{2}A_{1})$  $^{-2}A_2$ , and  $^{2}A_1 \rightarrow {}^{2}B_2$ ), obtained from ab initio SCF calculations, are 2.93, 3.87, and 7.25 eV (see Table IV). Porter and Ward<sup>10</sup> have observed the  ${}^{2}A_1 \rightarrow {}^{2}B_1$  transition and have assigned a value of 2.468 eV for the 0-0 band. Due to the very good agreement between the experimental and theoretical energies for the  $^2A_1 \rightarrow {}^2B_1$  transition, it is expected that the computed energy of the  ${}^2\!A_1 \to {}^2\!A_2$  and  ${}^{2}A_{1} \rightarrow {}^{2}B_{2}$  transitions should also be dependable.

Benzoyloxy Radical. The total energies for the ground state and three lowest excited states of the benzoyloxy radical were computed with the same methods as for the phenyl radical. The CGTO basis sets<sup>7</sup> used for carbon and oxygen are listed in Tables V and VI. The basis set used for hydrogen is identical with the one listed in Table II with the exception that one p orbital with exponent 0.8was appended to the (3s) basis.

<sup>(6)</sup> R. A. Sheldon and J. K. Kochi, J. Am. Chem. Soc., 92, 4395 (1970). (7) F. B. Van Duijneveldt, IBM Report No. RJ945, 1971

<sup>(8)</sup> The MOLECULE integral package was written by Dr. J. Almlöf of the

 <sup>(</sup>a) The MOLECULE Integral package was written by Dr. J. Almito' of the University of Uppsala, Sweden. The ALCHEMY SCF program was written by Dr. P. S. Bagus and Dr. B. Liu of the IBM Research Laboratory.
 (9) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970, pp 111-2.

<sup>(10)</sup> G. Porter and B. Ward, Proc. R. Soc. London, Ser A, 287, 457 (1965).





$$1.3 \text{ eV} \frac{{}^{2}\text{A}_{1}({}^{2}\sigma_{g})}{{}^{2}\text{B}_{2}({}^{2}\sigma_{g})} - \sigma[\text{pO}_{1} + \text{pO}_{2}]$$

$$0.23 \text{ eV} \frac{{}^{2}\text{B}_{2}({}^{2}\sigma_{\mu})}{2\text{A}_{2}({}^{2}\pi)} - \sigma[\text{pO}_{1} - \text{pO}_{2}]$$

$$0.0 \text{ eV} \overline{{}^{2}\text{A}_{2}({}^{2}\pi)}$$

## Total Energy $(^{2}A_{2}) = 417.4516386$ Hartrees

Figure 3. The total energies for the three lowest excited states of the benzoyloxy radical relative to the  ${}^{2}A_{2}$  ground state.

The standard geometry used for the phenyl radical was also used for the phenyl group in the benzoyloxy radical. However, because the two lowest electronic states are so close energetically, the geometry about the carboxyl group was optimized for a  $C_{2v}$  symmetry (Figure 2). Lower symmetries were not considered due to the tendency of SCF wave functions to localize and give incorrect results when bonding situations like those found in the benzoyloxy radical exist.<sup>11</sup>

The results for the total energies of the ground and three lowest excited states are shown and listed in Figure 3. For the  $C_{2\nu}$  geometry, the ground state has a  ${}^{2}A_{2}$  symmetry with the unpaired electron in a  $\pi$  orbital. The next two excited states result from promotion of an electron from the antisymmetric and symmetric combination of  $\sigma$ -molecular orbitals (oxygen lone pairs). The  ${}^{2}B_{2}$  is very close to the  ${}^{2}A_{2}$  ground state while the  ${}^{2}A_{1}$  state is about 1.3 eV above. The next excited state,  ${}^{2}B_{1}$ , is formed by excitation of the unpaired electron in the  $\pi$ -system on the  $-CO_{2}$  group to a higher  $\pi^{*}$  antibonding orbital and thus lies 5.7 eV about the ground state.

A pertinent comment to make at this point regards the ordering of the  ${}^{2}A_{2}$ ,  ${}^{2}B_{2}$ , and  ${}^{2}A_{1}$  states given by the SCF ab initio calculations. Since they are all very close in energy, the ordering should at least be checked with more sophisticated calculations. In fact, McLean et al.<sup>12</sup> have performed CI calculations on the formyloxy radical,  $HCO_2$ , which reveal a significant difference in the ordering of the states. These are summarized in Figure 4. The SCF ordering of the states for  $HCO_2$  is identical with that found for the benzoyloxy radical reported here. However, the CI calculations place the  ${}^{2}B_{2}\Sigma$  state lowest in enery with the  ${}^{2}A_{2} \prod$  state and  ${}^{2}A_{1} \Sigma$  state higher in energy. For the purposes of this report, i.e., insight into the facile decarboxylation of the acyloxy radicals, whether the  ${}^{2}B_{2}$  or  ${}^{2}A_{2}$ state is lower in energy, is not pertinent. The important point is that the  ${}^{2}A_{1}$  state is found to be higher in energy than both the  ${}^{2}B_{2}$  and  ${}^{2}A_{2}$  states for both the SCF and CI calculations.

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Figure 4. The results of SCF and CI calculations on the formyloxy radical.  $^{\rm 12}$ 

Scheme I





#### **Results and Discussion**

The infrared spectrum of acetyl benzoyl peroxide isolated in an argon matrix (concentration  $\approx 1/500$ ) at T = 10 K is shown in Figure 5. The prominent features in the spectrum that characterize the peroxide are the carbonyl absorptions at 1830 and 1790 cm<sup>-1</sup>. Exposure of the matrix-isolated peroxide to UV light emitted from a highpressure xenon lamp fitted with a Corning 053 filter (0% transmittance for  $\lambda < 2800$  Å) and a 10-cm water filter slowly induces photodecomposition. Kinetic plots, such as absorption vs. time, reveal that the decomposition of the peroxide correlates with the formation of the photoproducts, carbon dioxide, methyl benzoate, and the methyl and phenyl radicals. The infrared spectrum after complete photoconversion to the photoproducts is shown in Figure The presence of  $CO_2$  and methyl benzoate in the 6. spectrum is easily verified by comparison with spectra of authentic samples in argon matrices. Evidence for the existence of the methyl radical is based on the well-known feature<sup>13</sup> at 607 cm<sup>-1</sup> which has been assigned to the out-of-plane deformation mode. The proof for the phenyl

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Figure 5. The infrared spectrum of acetyl benzoyl peroxide isolated in an argon matrix (concentration: 1/500).



Figure 6. The infrared spectrum of acetyl benzoyl peroxide after exposure to UV light ( $\lambda > 2800$  Å) for t = 22 h. The intense bands at 2340 and 650 cm<sup>-1</sup> have been assigned to the asymmetric stretching and bending mode of CO<sub>2</sub>. The intense band at 2270 cm<sup>-1</sup> is the asymmetric stretching mode of <sup>13</sup>CO<sub>2</sub>; those at 3700 and 3600 cm<sup>-1</sup> are due to various combination bands of CO<sub>2</sub>. The new absorption at 1740 cm<sup>-1</sup> is due to the carbonyl stretching mode of methyl benzoate. The bands marked with an asterisk are those that appear upon irradiation and thermally disappear in concert with the formation of toluene. The bands at 3170, 1380, and 607 cm<sup>-1</sup> are assigned to the methyl radical; those at 3081, 2927, 1433, 1387, 1222, 1057, 1023, 703, and 406 cm<sup>-1</sup> are assigned to the phenyl radical.

radical is based on the warm-up experiments. Since the radical pair is trapped in an argon cage, then raising the temperature of the matrix allows combination of the radical pair; the synchronous decreases in the IR absorption of the phenyl and methyl radical absorptions are observed with an increase in the absorption of toluene. The thermal reaction is relatively very rapid, begins at 20 K and, in 1 min, is complete at 30 K. Scheme I summarizes the sequence of events thus far.

So that some rational for the low-temperature photochemical experiments in this report can be provided, the kinetic scheme for the decomposition of acetyl benzovl peroxide determined by CIDNP studies<sup>14</sup> will be used. The first step in this mechanism involves the cleavage of the peroxide bond to form the benzoyloxy-acetoxy radical pair. We feel this is a reasonable mechanism because a number of reports indicate that both radicals live long enough to be trapped.<sup>14-18</sup> CIDNP studies<sup>14,16</sup> have established that the lifetime of the benzoyloxy radical is about 10<sup>2</sup> times longer than the acetoxy radical. This also appears to be the case for the low-temperature matrix isolation studies because when the peroxide is exposed to light with  $\lambda >$ 3000 Å, about 50% of the reaction appears to take the path

for formation of methyl benzoate. The path for formation of phenyl acetate, via combination of the phenyl-acetoxy radical pair, has not been observed; at least to the limits of the detection by infrared spectroscopy, phenyl acetate was not observed. This is attributed to the shorter lifetime for the acetoxy radical under the matrix isolation conditions (see Scheme I).

It is conceivable that the methyl benzoate could be formed by another route. Pacansky and Coufal<sup>19</sup> have shown that the ethyl and isopropyl radicals react with carbon dioxide when excited with UV light shorter than 3000 Å. This reaction leads to the formation of an ester, acid, and an olefin which is conveniently explained on the basis that the radical, when excited, produces an acyloxy radical which subsequently combines with the other alkyl radical in the same cavity to form an ester, or disproportionates to produce a carboxylic acid and an olefin. In the case of the phenyl radical, absorption of light via the  ${}^{2}A_{1}$  $\rightarrow$  <sup>2</sup>B<sub>1</sub> ( $\pi \rightarrow$  n) transition at 2.93 eV may lead to formation of the benzoyloxy radical and, hence, to formation of methyl benzoate via combination of the benzoyloxymethyl radical pair. Due to the much longer lifetime of the benzoyloxy radical than say the propionyloxy radical, it is reasonable to expect that, if formed, it should readily combine with a methyl radical. Rather surprisingly, no changes in the infrared spectrum occurred when the photoproducts of the acetyl benzovl peroxide, shown in

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<sup>(18)</sup> K. Tokumaru, A. Ohshima, and T. Nakata, Chem. Lett., 571 (1974).

<sup>(19)</sup> J. Pacansky and H. Coufal, J. Chem. Phys., 71, 2811 (1979); 72, 3298 (1980).



Figure 7. The infrared spectrum of acetyl benzoyl peroxide after t = 22 h of irradiation with UV light ( $\lambda > 2800$  Å) and an additional t = 10h of exposure to the full output of a high-pressure xenon lamp.



Figure 8. The infrared spectrum of the photoproducts of acetyl benzoyl peroxide shown in Figure 7 recorded after warming the argon matrix to 40 K for t = 20 min.

Figure 6, were exposed to UV light with  $\lambda < 2800$  Å for t = 10 h. This infrared spectrum after the short wavelength UV irradiation is shown in Figure 7. The only changes noted are due to an increase in CO absorption at 2140 cm<sup>-1</sup> attributed to some decomposition of methyl benzoate, and a slight decrease in absorption of the phenyl-methyl radical pair. The latter is most likely due to some heating created by exposure to the matrix to the total output of the high-pressure xenon lamp.

Under the conditions of the short wavelength UV exposure, it is highly probable that the phenyl radical is absorbing light with  $\lambda < 2800$  Å. Although photochemistry was not observed, absorption of UV light by the phenyl radical did creat a change. Irradiation with the shorter wavelength UV light altered the structure of the cavity in which the phenyl-methyl radical pair and  $CO_2$  were contained. Previously, we noted that, after conversion of acetyl benzoyl peroxide to the phenyl-methyl radicals with  $\lambda > 2800$  Å, combination of the radical pair by warming the matrix proceeded rapidly and was complete at T = 30K. However, even though exposure of the radical pair to short wavelength UV light ( $\lambda < 2800$  Å) did not create any photochemical changes, drastic thermal conditions were required to initiate the combination of the radicals. In fact, the temperature of the matix was raised to and held at T= 40 K for 20 min, during which the radicals slowly combined to form toluene. Figure 8 contains the IR spectrum of the system recorded after the warm-up period. Analysis of this spectrum reveals that only toluene is formed during the warm-up period. The significance of this is that the short wavelength UV light most likely created a change

in the orientation of the phenyl radical relative to the methyl radical while maintaining the integrity of the cavity in which the radical pair resides. If the phenyl or methyl radical escaped the cavity, then ethane or biphenyl should have been observed. These latter systems were not observed in the IR spectrum shown in Figure 8. The results for the UV photolysis of the peroxide and the phenylmethyl radical pair are summarized in Scheme I.

The ab initio calculations for the phenyl and benzoyloxy radicals given in this report offer an explanation for the experimental observations. The calculations, along with the known  $\Delta H$  for decarboxylation of the benzoyloxyl radical, and the pertinent electronic excitations for  $CO_2^{20}$ are shown in Figure 9. Jaffe et al.<sup>21</sup> estimate that the  $\Delta H$ for thermal decomposition of the benzoyloxy radical to phenyl radical and  $CO_2$  is about zero. As shown in Figure 9, although the ground states for the benzoyloxy and the phenyl- $CO_2$  systems are at the same energy, the symmetries of the ground state are different. In fact, the  ${}^{2}A_{2}$ ground state of the benzoyloxy radical correlates with the  ${}^{1}\Delta_{u}$  excited state of CO<sub>2</sub> which is 8.3 eV higher in energy. Furthermore, since the  ${}^{2}B_{2}$  state correlates with the  ${}^{1}\Sigma_{u}^{+}$  of CO<sub>2</sub>, which is 9.3 eV higher in energy, symmetry considerations imply that the benzoyloxy radical is thermally stable toward decarboxylation. The electronic state of the benzoyloxy radical that does correlate with the  ${}^{1}\Sigma_{e}^{+}$  state

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<sup>(1957).</sup> 



**Figure 9.** A state diagram for the decomposition of the benzoyloxy radical to carbon dioxide and the phenyl radical. The pertinent ground and excited states for the phenyl radical are at the left side of the figure, while those for  $CO_2$  are on the right. The relative energies were obtained by using SCF calculations given in this report. The computational results for the phenyl radical are given to explain the photochemical results for UV exposure of the phenyl–methyl radical pair. Those for  $CO_2$  are given to provide an explanation for the facile thermal decomposition of the benzoyloxy radical.

of CO<sub>2</sub> is the <sup>2</sup>A<sub>1</sub> state that is 1.3 eV above the ground state. Consequently, as shown in Figure 9, the <sup>2</sup>A<sub>1</sub> surface crosses the <sup>2</sup>B<sub>2</sub> and <sup>2</sup>A<sub>2</sub> surfaces but does not interact with the <sup>2</sup>B<sub>2</sub> and <sup>2</sup>A<sub>2</sub> surfaces because of the different symmetries. However, vibrational modes such as an asymmetric stretch of the CO bonds easily break the symmetry restrictions and allow the potential surfaces to interact; as a consequence, a thermal channel for elimination of CO<sub>2</sub> from the ground state of the benzoyloxy radical is opened. Since the energy differences between the <sup>2</sup>A<sub>2</sub>, <sup>2</sup>B<sub>2</sub>, and <sup>2</sup>A<sub>1</sub> electronic states are so close, the barrier for thermal decomposition of the benzoyloxy radical is indeed expected to be small.

Further consideration of this mechanism for loss of  $CO_2$ from the benzoyloxy radical provides an explanation for the very short lifetime of the acetoxy radical. The  $\Delta H$  for the reaction  $CH_3CO_2 \rightarrow CH_3 + CO_2$  is quite exothermic, compared to that for the benzoyloxy radical. The value (-17 kcal/mol) estimate by Jaffe et al.<sup>22</sup> places the relative energy of the thermal products of CH<sub>3</sub>CO<sub>2</sub> much lower than those for the benzoyloxy system. In essence, this lowers the barrier for thermal decarboxylation of  $CH_3CO_2$ by moving the curve crossing much closer to the ground state surface in comparison to that for the benzoyloxy radical (see Figure 9). In addition, the symmetry restrictions on the interaction of the states are less restrictive. At most, only a plane of symmetry is maintained. If, for example (see Figure 10), the plane contains the  $-CO_2$  group and one CH bond, then the  $\sigma$  states (<sup>2</sup>A<sub>1</sub> and <sup>2</sup>B<sub>2</sub> for  $C_6H_6CO_2$ ) have the same symmetry. According to the CI calculations of McClean et al.<sup>12</sup> on HCO<sub>2</sub>, the  ${}^{2}B_{2}\sigma$  state has the lower energy. This same ordering for CH<sub>3</sub>CO<sub>2</sub>, i.e., the ground state having the open shell in the  $\sigma(p_{O_1}-p_{O_2})$ molecular orbital, would have a dramatic effect on the barrier for thermal decomposition. The two  $\sigma$  states would have the same symmetry and, thus, an extensive interaction would occur. This is illustrated in Figure 10. Certainly, these considerations would apply to acyloxy radicals like, for example, those with long carbon chains, where the probability for any symmetry is very small.

In view of the very rapid photochemical reaction observed when the ethyl and isopropyl radicals were excited with UV light, the inability of the electronically excited phenyl radical to react with  $CO_2$  was rather surprising. First of all, the UV light used to decompose the acetyl



**Figure 10.** A schematic illustrating the consequences of a  $C_s$  symmetry on the low-lying electronic states of  $CH_3CO_2$ . The states formed by taking symmetric and antisymmetric combinations of the in-plane oxygen p orbitals interact, thus lowering the barrier for thermal decarboxylation.

benzoyl peroxide consisted of all wavelengths longer than 2800 Å; hence the  $\pi \rightarrow n$  transition of the phenyl radical at 2.93 eV<sup>10</sup> ( ${}^{2}A_{1} \rightarrow {}^{2}B_{1}$ ) was certainly being excited. (The  ${}^{2}A_{1} \rightarrow {}^{2}A_{2}$  transition is dipole forbidden.) As shown in Figure 9, the  ${}^{2}B_{1}$  state of the phenyl-CO<sub>2</sub> system correlates with the  ${}^{2}B_{1}$  state of the benzoyloxy radical at 5.7 eV. The latter state is about 3 eV above that for the phenyl-CO<sub>2</sub> system prohibiting any reaction to proceed. This provides a reasonable explanation for the absence of any reaction of the phenyl radical with CO<sub>2</sub> even when the system was exposed to light ( $\lambda > 2800$  Å) for extended periods after the acetyl benzoyl peroxide was completely destroyed.

The absence of a photoinduced reaction when the phenyl radical was excited with  $\lambda < 2800$  Å is more difficult to explain. As noted above, the shorter wavelength exposure created a physical change of the cavities in which the phenyl-CO<sub>2</sub>-methyl radicals reside; hence, it is certain that the phenyl radical is absorbing light in this region. Furthermore, the phenyl radical should have  $\pi \rightarrow \pi^*$  excited states which are optically allowed and quite similar energetically to those for benzene around 2800 Å. Since this should also be true for the  $\pi \rightarrow \pi^*$  transition in the phenyl ring of the benzoyloxy radical, then these  $\pi \rightarrow \pi^*$  states of the phenyl +  $CO_2$  and benzoyloxy systems, respectively, should correlate to at least make a photoinduced reaction possible. Several speculations may be proposed for the fact that a reaction is not observed. The one that is considered the most likely is due to the nature of the  $\pi \rightarrow \pi^*$  transition in the phenyl radical which, as a first-order approximation, has little effect on the  $\sigma$  C–C bond that must be formed to produce the benzoyloxy radical. If this is the case, then absorption of UV light ( $\lambda < 2800$  Å) would produce a highly excited phenyl radical that upon deexcitation reorients itself in an argon cavity such that combination with a methyl radical is more restrictive. Certainly, an examination of molecular models for the geometry of a cavity in solid argon required for acetyl benzoyl peroxide shows that the cavity is quite irregular. The energy released by a highly excited phenyl radical could easily move an argon atom between the phenyl radical-CO<sub>2</sub>-methyl radical or the phenyl radical could reorient itself. This, in essence, creates a larger obstruction that must be thermally removed for combination of the radical pair. These arguments of course are not unique, but we tend to favor those that involve reorientation of the phenyl radical by UV light over those which require photochemical formation and destruction of the benzoyloxy radical during the irradiation; the compelling reason for this preference is that the latter process requires formation of methyl benzoate which is not observed.

#### **Concluding Remarks**

The UV photolysis of acetyl benzoyl peroxide in an argon matrix produces carbon dioxide, methyl benzoate,

the phenyl radical, and the methyl radical. The observation that the phenyl radical does not react with CO<sub>2</sub> when excited into its  ${}^{2}B_{1}$  state precludes the formation of methyl benzoate via this route. In essence, the experiments only support formation of methyl benzoate by combination of the longer lived benzoyloxy radical with the methyl radical. Furthermore, since phenyl acetate could not be detected in the matrix experiments, it was concluded that the acetoxy radical must have a much shorter lifetime.

Ab initio calculations were reported on the benzoyloxy radical in order to provide an explanation for the much shorter lifetime of the acetoxy radical vs. the benzoyloxy system. The calculations indicate that the facile decarboxylation for both systems, and acyloxy radicals in general, is due to a curve crossing very close to the ground state of the acyloxy radical. The curve crossing moves closer to the minimum on the ground state as the  $\Delta H$  for the decarboxylation becomes more exothermic. The shorter lifetime for the acetoxy radical is attributed to a more negative  $\Delta H$  for loss of CO<sub>2</sub> and to its lower symmetry because, in this case, the barrier for decarboxylation is lowered by an avoided crossing between two surfaces with the same symmetry.

Registry No. Acetyl benzoyl peroxide, 644-31-5; benzoyloxy, 1854-28-0; phenyl, 2396-01-2.

## Photophysics of Tryptophan in $H_2O$ , $D_2O$ , and in Nonaqueous Solvents<sup>1</sup>

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The fluorescence properties of tryptophan in water and deuterated water have been examined. Tryptophan molecules exhibit three distinct fluorescence lifetimes in water which become longer in deuterated water; the two shorter lifetimes are present below the pK of the amino group and the long lifetime appears as the pH is raised through this pK. The steady-state quenching of tryptophan fluorescence by hydrogen ion in the region of pH less than 3 shows a definite wavelength effect, consistent with less-pronounced quenching of the subnanosecond component whose emission maximum is at 330 nm. The Stern-Volmer plots show a marked curvature in the direction of decreasing Stern-Volmer constant as  $[H_3O^+]$  increases. Deuterium ion also quenches tryptophan fluorescence at low pD. A kinetic scheme is proposed which reproduces both the steady-state and lifetime quenching results. Tryptophan in methanol or ethanol exhibits three fluorescence lifetimes; the relative percentage of the long component vs. the intermediate component can be varied by the additon of triethylamine or acid. In dimethyl sulfoxide, tryptophan and tryptophan deuterated at the amino and ring nitrogen positions show identical behavior, both having the same decay parameters. These results are discussed in light of the theories which have recently been proposed to account for the several components in tryptophan fluorescence decay. Solvent interaction is suggested to play a critical role.

#### Introduction

The fluorescence properties of tryptophan and its derivatives in solution have been a subject of interest for a number of years, and they have been used to attempt to explain the fluorescence of tryptophan residues in proteins. Recently there has been particular interest in the time dependence of the fluorescence of tryptophan since it has been established that the molecule does not follow a single exponential decay law at neutral pH.<sup>3-5</sup> Rather, it fluoresces with two lifetimes, of about 0.6 and 3.2 ns. Further, when the anionic form is present at higher pH a third lifetime of about 9.2 ns is observed.<sup>3</sup> These lifetimes are pH independent in the range of pH 4-10.5 where the concentrations of  $H_3O^+$  and  $OH^-$  are kinetically insignificant. Some of the reasons which have been proposed for tryptophan's complex decay behavior are the existence of two uncoupled, close-lying excited states,<sup>6</sup> the existence of different ground-state conformations which are not rapidly interconvertible in the excited state,<sup>4</sup> and a proton transfer from the side chain to the ring which would result in a diffusional transient component in the fluorescence decay.<sup>5</sup> The presence of two pK's in the molecule, that of the carboxylate and the amino groups, is also a complicating factor, as there are thus three possible groundstate species, the cation, the zwitterion, and the anion, the relative concentrations of which depend on the conditions of the experiment.

In this paper, we describe several aspects of the fluorescence behavior of tryptophan in an attempt to determine the extent of solvent involvement: its fluorescence in nonaqueous solvents, deuterated solvents, and its fluorescence in water and deuterated water at low pH. An attempt has been made to show that solvent interaction is an important parameter in the photophysics of tryptophan and perhaps is a critical factor in the determination of its excited-state behavior.

#### **Experimental Section**

L-Tryptophan (Trp) (Aldrich, 99%) was recrystallized once from an alcohol-water solution. Deuterated L-tryp-

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