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Photochemistry of Diphenylketyl Radicals: Spectroscopy, Kinetics, and Mechanisms[1]

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Abstract: The photochemistry of the diphenylketyl radical has been examined in nonpolar solutions. Transient studies using two-laser techniques yield an excited-state lifetime of 3.9 ns in toluene at room temperature, while for diphenylketyl-*O*-*d* the lifetime is 8.7 ns. Dye laser irradiation (515 nm) in the ketyl's visible absorption band leads to efficient photobleaching with $\Phi_{\text{bleach}} = 0.27 \pm 0.06$ for the parent radical and 0.39 and 0.26 for the 4-methyl and 4-chloro derivatives, respectively. The photobleaching reaction involves the cleavage of the O–H ketyl bond to yield benzophenone and hydrogen atoms; in cyclohexane the latter abstract hydrogen from the solvent to produce molecular hydrogen, which was characterized by Raman spectroscopy. In accordance with this mechanism, two-laser experiments produce lower yields of photoreduction products than the one-laser experiments in which the ketyls are not photobleached. When the ketyl radicals are generated by reaction of *tert*-butoxy radicals with benzhydrol, dye laser irradiation leads to a large increase in the yield of benzophenone (now a product), although the mechanism here is somewhat more complex due to the quenching of excited ketyl radicals by di-*tert*-butyl peroxide ($k_q = 1.9 \times 10^9\ M^{-1}\ s^{-1}$). Detailed studies of the fluorescence, isotope effects, temperature effects, and products are also included.

The photophysics and photochemistry of excited reaction intermediates such as free radicals, biradicals, and carbenes have received considerable attention recently.[4,5] Much of this interest has been prompted by the realization that laser excitation can often lead to dramatic differences when compared with conventional lamp irradiation at a similar wavelength. It is not uncommon for laser excitation to produce a sufficient concentration of intermediates to compete with the precursor for exciting photons and, thus, to lead to photochemistry of the intermediates.

Fluorescence from excited radicals in solution at room temperature is readily observable for radicals such as diphenylmethyl,[6,7] 1-naphthylmethyl,[8,9] 9-anthrylmethyl,[10] and various diphenylketyl[11-15] and acetophenone ketyl radicals.[5] Although the parent benzyl radical does not fluoresce at room temperature, its luminescence is readily detectable at low temperature.[16] The unusual temperature dependence of benzyl and a number of its substituted analogues has recently been examined.[16] Absorption spectra of excited radicals are usually more difficult to obtain than emission spectra, but a few have been observed.[6-8,15]

The intermolecular reactivity of several excited radicals with relatively long lifetimes (e.g., diphenylmethyl, 260 ns;[6] 1-naphthylmethyl, 35 ns[8]) has been examined. However, the short lifetimes of most other excited radicals frequently limit such investigations. Among the radicals studied, triphenylmethyl[7] and diphenylketyl[15] are known to undergo irreversible decomposition upon photoexcitation in solution. Such processes have also been shown to occur for other excited intermediates.[5]

The excited diphenylketyl radical has been studied by several groups.[11-15,17,18] Its fluorescence is readily detectable with $\lambda_{max} \sim 575$ nm, depending on the solvent, and with typical lifetimes of ca. 4 ns.[11-15,18] An absorption spectrum ($\lambda_{max} \sim 350$ nm) has been reported,[15] and there are also several measurements of its quenching by substrates such as methyl methacrylate and a variety of electron acceptors.[14] Irreversible bleaching of the ketyl radical has been observed upon excitation in either its UV or visible absorption band.[15] This bleaching has been suggested to result from product formation, which is in turn responsible for the short excited-state lifetime.[15,18] However, this has not been confirmed by product studies.

We report herein the results of our studies on the photochemistry and photophysics of diphenyl ketyl radicals under conditions of two-photon laser excitation. The results demonstrate that excitation of the radical results in a decreased yield of radical-derived products with concomitant production of hydrogen and benzophenone. A preliminary account of our results on the fluorescence of diphenylketyl radicals has been published.[18]

Results

Unless otherwise indicated all our experiments were carried out at room temperature in deaerated samples.

Generation of Ketyl Radicals. Diphenylketyl radicals were usually generated by photoreduction of benzophenone in a hydrogen-donating solvent (reaction 1). For example, in cyclohexane

$$Ph_2CO^* + RH \rightarrow Ph_2\dot{C}OH + R^{\bullet} \qquad (1)$$

triplet benzophenone decays with a lifetime of 180 ns to produce the ketyl radical. Figure 1 shows spectra in two time windows after 308-nm excitation; the early ketyl spectrum contains some triplet ketone, while the later one shows only the radical. Two decay traces showing triplet decay at 610 nm (where the ketyl radical is transparent) and triplet plus ketyl decay at 545 nm (the ketyl maximum) are shown in the inset. Similar results are obtained in other hydrogen-donating solvents; for example, in toluene the ketyl radical has a growth lifetime of 220 ns. Addition of 1,4-cyclohexadiene as a hydrogen donor was used for solvents

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Table I. Fluorescence Spectra, Lifetimes at Room Temperature, and Arrhenius Parameters (−90 to +20 °C) for Substituted Ketyl Radicals in Toluene

radical	solvent	λ_{max}, nm	τ, ns	E_a, kcal/mol	log A	ref
$(C_6H_5)_2\dot{C}OH$	toluene	574	3.9	1.11 ± 0.05	9.22 ± 0.05	18
	benzene		3.9			this work
	cyclohexane		2.7			this work
	cyclohexane-d_{12}		3.3			this work
$(C_6H_5)_2\dot{C}OD$	toluene-d_8	570	8.7	1.75 ± 0.16[a]	9.4 ± 0.1	18
$(C_6D_5)_2\dot{C}OH$	toluene		4.2			18
$(C_6D_5)_2\dot{C}OD$	toluene-d_8	570	10.5			18
$(4\text{-}CH_3C_6H_4)_2\dot{C}OH$	toluene	588	3.1	1.20 ± 0.06	9.39 ± 0.05	this work
$(4\text{-}ClC_6H_4)_2\dot{C}OH$	toluene	596	5.9	1.55 ± 0.07	9.19 ± 0.07	this work
$4\text{-}CNC_6H_4\dot{C}OH(C_6H_5)$	toluene	613	7.8	1.5 ± 0.2	9.23 ± 0.06	this work
$(4\text{-}CH_3OC_6H_4)_2\dot{C}OH$	toluene	623				this work
$(C_6H_5)_2\dot{C}OCH_3$	toluene	587	3.5	1.55 ± 0.08	9.5 ± 0.1	this work

[a] A temperature-independent lifetime is observed below ca. −40 °C.

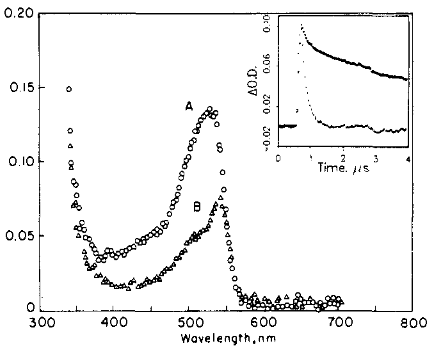

Figure 1. Transient absorption spectra obtained by 308-nm excitation of 5.5 mM benzophenone in toluene and recorded 150 ns (A) and 1.5 μs (B) after the laser pulse. Inset: Decay traces for the above sample monitored at 545 nm (top, ▽) and 610 nm (bottom, +); trace at 610 nm expanded by a factor of 3.5.

in which photoreduction was slow or for cases for which it was desirable to shorten the triplet lifetime to ≤20 ns.[19]

An alternate source for ketyl radicals in some of our experiments was hydrogen abstraction from benzhydrol by *tert*-butoxy radicals produced by photolysis of di-*tert*-butyl peroxide (reaction 2).

$$Ph_2CHOH + t\text{-}BuO^\bullet \rightarrow Ph_2\dot{C}OH + t\text{-}BuOH \qquad (2)$$

Reaction 2 occurs with a rate constant of 6.9×10^6 M^{-1} s^{-1}.[20] For a benzhydrol concentration of 0.1 M this leads to a lifetime for the ketyl growth of 790 ns, when other forms of decay for the *tert*-butoxy radical[21] are taken into consideration.

Methoxydiphenylmethyl radicals were produced by photolysis of α-phenylbenzoin methyl ether (reaction 3). The triplet state of α-phenylbenzoin is very short-lived, and for practical purposes reaction 3 provides an instantaneous source of the radicals.

$$PhCOC(OCH_3)Ph_2 \xrightarrow{h\nu} Ph\dot{C}O + Ph_2\dot{C}OCH_3 \qquad (3)$$

Ketyl Radical Fluorescence. For fluorescence measurements the ketyl radicals were excited by using 337-nm laser irradiation. The details of the characterization of the fluorescence spectra for $(C_6H_5)_2\dot{C}OH$, $(C_6H_5)_2\dot{C}OCH_3$, and a variety of deuteriated diphenylketyls have been reported in our preliminary communication.[18] We have also now examined a variety of sustituted ketyl radicals, all of which show spectra that are similar to that of the parent radical (Figure 2). The fluorescence λ_{max} values for several representative radicals are listed in Table I.

The lifetime of the ketyl radical has been shown to be considerably lengthened by deuterium substitution at the hydroxylic position (3.9 vs 8.7 ns for OH vs OD, Table I), although substitution on the ring has a more modest effect.[18] Deuteriation of the solvent has essentially no effect on the lifetimes (for radicals generated from ketone plus 1,4-cyclohexadiene in toluene-d_8). Similarly, substitution of 4-chloro or 4-cyano groups lengthens the lifetime, while a 4-methyl group leads to a small decrease, as does replacement of hydrogen by methyl at the oxygen center (Table I).

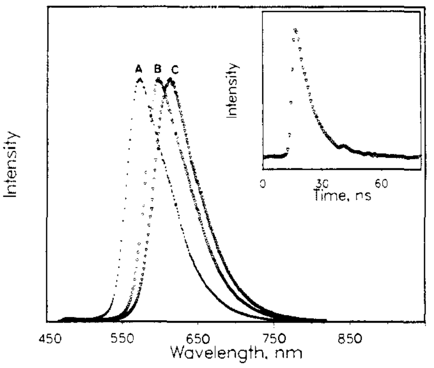

Figure 2. Fluorescence spectra for radicals in toluene at 291 K: A, $(C_6H_5)_2\dot{C}OH$; B, $(4\text{-}ClC_6H_4)_2\dot{C}OH$; C, $4\text{-}CNC_6H_4\dot{C}(OH)C_6H_5$. Inset: Fluorescence decay trace for $4\text{-}CNC_6H_4\dot{C}(OH)C_6H_5$ in toluene at 277 K.

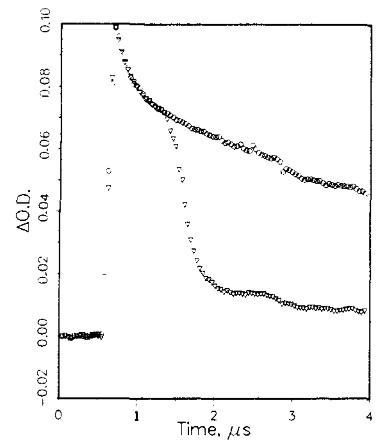

Figure 3. Decay of transients produced from benzophenone in cyclohexane and monitored at 545 nm for 308-nm excitation (○) and 308-nm excitation followed by a 515-nm dye laser pulse (▽).

Arrhenius parameters for the ring-substituted ketyl radicals and for $(C_6H_5)_2\dot{C}OCH_3$ in toluene are similar to those previously reported for the parent radical (Table I). There was no evidence for leveling off of the lifetime at low temperature, as has been observed for $(C_6H_5)_2\dot{C}OD$[18] and various benzyl radicals.[16]

Bleaching of Ketyl Radicals. Diphenylketyl radicals produced by 308-nm excitation of benzophenone in the presence of a hydrogen donor were excited in their visible absorption band by using a dye laser (λ_{exc} ~ 515 nm). It should be noted that while this is not the same band excited in the fluorescence studies, it is the

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[19] The rate of hydrogen abstraction by benzophenone from 1,4-cyclohexadiene is 2.9×10^8 M^{-1} s^{-1} in benzene: Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

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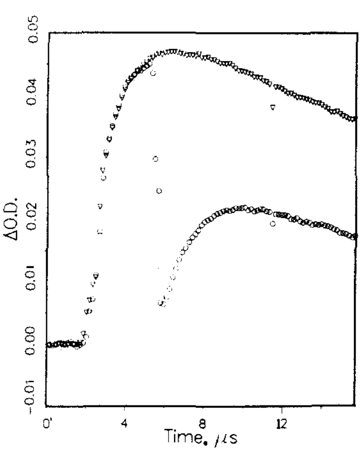

Figure 4. Formation and decay traces at 545 nm for diphenylketyl radicals generated from 0.27 M di-*tert*-butyl peroxide and 0.1 M benzhydrol in benzene for 308-nm excitation (▽) and 308-nm excitation followed by a 515-nm dye laser pulse (○).

absorption band corresponding to the fluorescence from the radical. Further, studies by Nagarajan and Fessenden have shown that a similar bleaching can be obtained by irradiating either the UV or visible band.[15] Dye laser excitation at 515 nm leads to efficient and irreversible bleaching of the ketyl radical, as shown in Figure 3 for cyclohexane as solvent. Similar results were observed in toluene by monitoring the visible or UV absorption band of the ketyl radical. In neither case was there any evidence for formation of additional transients or detectable recovery of the ketyl absorption following the dye laser pulse. Note that the recovery associated with the 3.9-ns excited ketyl lifetime is undetectable in our system due to the 250-ns pulse width of the dye laser. This long pulse width and resulting moderate power (typically ~100 mJ/pulse, i.e., ~0.4 MW) makes the bleaching process equivalent to a continuous irradiation. Several substituted ketyls were also examined; $(C_6H_5)_2\dot{C}OD$, $(C_6H_5)_2\dot{C}OCH_3$, and ketyls formed from 4-chlorobenzophenone and 4-methylbenzophenone all showed efficient and irreversible bleaching.

Somewhat different results were observed upon dye laser excitation of the parent diphenylketyl radical when benzhydrol plus *tert*-butoxy radicals in benzene was used as the radical source. In this case there was a slow partial recovery following the dye laser pulse (Figure 4). This growth was absent when the dye laser was not preceded by the 308-nm synthesis pulse, so it does not arise from dye laser excitation of the ground-state precursors. Several experiments were carried out to determine the origin of this effect. First, the growth kinetics following the dye laser pulse were similar to those for the initial production of the ketyl radical, and both were shown to depend upon the benzhydrol concentration. Second, no transients other than the ketyl radical were observed after the dye laser pulse. For example, there was no evidence of formation of benzophenone triplet at 610 nm. Third, when the radical was generated from benzophenone plus 1,4-cyclohexadiene in benzene and then excited at 515 nm, irreversible bleaching was observed with no secondary growth at 545 nm. Similarly, the growth following the dye laser was absent when benzophenone plus benzhydrol in benzene was used as the ketyl source. These results suggest that the growth observed in Figure 4 is due to the production of additional ketyl radical and that the process requires the presence of di-*tert*-butyl peroxide and of benzhydrol.

Quantum Yields. The quantum yield for the bleaching of the ketyl radical was measured by using Aberchrome-540 actinometry. The use of this actinometer for measuring two-laser quantum yields and transient extinction coefficients has been recently developed in our laboratory and is described in detail in the accompanying paper.[22]

Measurement of the bleaching quantum yield requires the determination of the ketyl radical extinction coefficient ϵ_K. This was measured in cyclohexane by using Aberchrome-540 in toluene as the actinometer. The yields of ketyl radical and the colored form of the actinometer were measured at 550 and 494 nm, respectively, as a function of the laser dose for samples of benzophenone and Aberchrome-540 with matched optical densities at the laser wavelength (308 nm). Although 550 nm is not the maximum for the ketyl radical, ϵ_K was measured at this wavelength as it was more convenient for the bleaching experiments outlined below. Since both ketyl radical and triplet benzophenone absorb at 550 nm, the optical densities at this wavelength had to be corrected for triplet interference.[23] An alternate approach involved the addition of sufficient 1,4-cyclohexadiene to shorten the triplet lifetime to ≤10 ns and eliminate any interference from the triplet.[24] Similar results were obtained for either method. By use of the method outlined in the accompanying paper a value of 3300 ± 700 M^{-1} cm^{-1}[25] was obtained for $\epsilon_K\Phi_K$, where Φ_K is the quantum yield for ketyl formation. The value of Φ_K may be taken as 1.0 in this system.[26] The value of ϵ_K is in line with those reported in the literature.[26]

Measurement of the quantum yield for ketyl radical bleaching requires matching the optical densities for the radical and the colored form of Aberchrome-540 at the dye laser wavelength (515 nm) and at the time of the dye laser pulse. This was again done by measuring the signals for each as a function of the 308-nm laser dose. Bleaching of the radical and the Aberchrome-540 colored form by the dye laser pulse was then measured at 550 and 494 nm, respectively, as a function of the 308-nm laser dose. The dye laser power was adjusted to obtain between 20 and 45% bleaching of the transient. It should be noted that there is no interference due to absorbing product formation at 550 nm, since the amount of bleaching was constant for various wavelengths in the visible band of the ketyl radical and no new transients were observed at other wavelengths. Furthermore, the bleaching process was shown to be monophotonic, since the amount of bleaching showed the expected dependence on the dye laser power. The quantum yield was then calculated from the ratio of ΔOD_{bleach}(Aberchrome) and ΔOD_{bleach}(ketyl) by the method outlined in the preceding paper[22] and led to a value of $\Phi_{bleach} = 0.27 \pm 0.06$.[27]

The quantum yields for bleaching of the ketyl radicals from 4-methylbenzophenone and 4-chlorobenzophenone in cyclohexane were also estimated. A single determination for each ketone led to values of $0.39\Phi_K$ and $0.26\Phi_K$. Assuming that Φ_K can be expected to be approximately 1 for these two ketyls, the efficiency of bleaching is not particularly sensitive to ring substitution of the ketyl. Note that any differences are well within the estimated ±30% error limits for single determinations.

The relative quantum yields for bleaching of $(C_6H_5)_2\dot{C}OH$ and $(C_6H_5)_2\dot{C}OD$ were estimated by matching the optical densities for the two radicals at the dye laser wavelength and measuring the amounts of bleaching for each. The ketyl radicals were generated from benzophenone in toluene or toluene-d_8. This experiment yielded a value of ca. 2.7 for $\Phi_{bleach}(OH)/\Phi_{bleach}(OD)$, assuming the same extinction coefficient for the two ketyls at the dye laser wavelength. Furthermore, the longer lifetime of triplet benzophenone (690 ns) in toluene-d_8 (compared with 220 ns in toluene) leads to more interference from triplet signals in monitoring the ketyl radical and results in a larger error for measuring the bleaching for ketyl OD.

Temperature Effects on Ketyl Radical Bleaching. The bleaching of the ketyl radical was measured at 293 and 198 K for samples with matched transient optical densities at the dye laser wavelength. A delay of ca. 10 μs was required between the 308-nm laser and the dye laser in the low-temperature measurement to allow for complete decay of the triplet under these conditions. This

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(22) Wintgens, V.; Johnston, L. J.; Scaiano, J. C., preceding paper in this issue.

(23) This involves extrapolation of the ketyl signals to the time of laser excitation; the correction is usually <20%.

(24) Reaction of benzophenone with 1,4-cyclohexadiene involves essentially quantitative hydrogen abstraction.[19]

(25) The reported value is the average of six determinations (two with added 1,4-cyclohexadiene).

(26) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904.

(27) Average of six determinations.

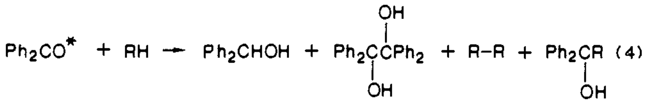
Table II. Product Ratios for Laser Photolysis of Benzophenone in Cyclohexane and Toluene[a,b]

laser(s), nm	solvent	Ph_2CO	$[Ph_2C(OH)]_2$	Ph_2CHOH	$Ph_2C(OH)R$	RR	ROH
308	cyclohexane	87.0	4.7	0.4	0.24	2.5	*e*
308 + 515	cyclohexane	92.8	1.3	0.3	0.10	5.7	*e*
515 + 308	cyclohexane	88.6	4.7	0.4	0.25	2.9	*e*
308	toluene	*d*	4.7	0.37	0.51	2.9	0.40
308 + 515	toluene	*d*	1.4	0.40	0.25	1.8	1.1
515 + 308	toluene	*d*	4.4	0.25	0.54	2.3	0.80
308	toluene-d_8	*d*	2.7	0.28	0.26	2.1	1.0
308 + 515	toluene-d_8	*d*	1.1	0.51	0.14	1.5	1.5

[a] R = $PhCH_2$, in toluene; R = c-C_6H_{11}, in cyclohexane. [b] Products (mol %) are based on starting ketone concentration except for $Ph_2C(OH)R$, which is relative to added internal standard. [c] Determined by HPLC analysis except for RR in cyclohexane where GC analysis was used. [d] Not determined due to interference by solvent in HPLC analysis. [e] Trace amounts; not determined.

experiment led to a value for $\Phi_{bleach}(293\ K)/\Phi_{bleach}(198\ K)$ of ca. 2.2, assuming that ϵ_K's at 550 and 515 nm are temperature independent in this range.

Product Studies. Photolysis of degassed solutions of 5 mM benzophenone in either toluene or cyclohexane with 300-nm Rayonet lamps gave the expected photoreduction products (reaction 4; R = benzyl, cyclohexyl). Small amounts of alcohols (ROH) derived from the trapping of the solvent-derived radicals by residual oxygen were also detected. A minor amount of a compound tentatively identified as benzylbenzophenone (either ortho or para) by LC/MS was also observed. Similar products derived from addition of solvent-derived radicals to the aromatic ring of the ketyl radical have been observed for benzophenone photoreduction in alcohols.[28]



$$Ph_2CO^* + RH \rightarrow Ph_2CHOH + Ph_2\underset{OH}{C}\overset{OH}{C}Ph_2 + R{-}R + Ph_2\underset{OH}{C}R \quad (4)$$

Samples of benzophenone in toluene or cyclohexane were then irradiated with both one and two lasers to determine what, if any, new products were formed as a result of the efficient bleaching observed in the transient experiments. Each experiment involved irradiation of three aliquots of a 5–6 mM solution of benzophenone with (a) 500 308-nm laser shots, (b) 500 pairs of 308- and 515-nm dye laser shots with the 308-nm laser preceding the dye pulse by ~1 μs, and (c) 500 pairs of laser shots as in (b) but with the laser sequence reversed. The latter serves as a control to demonstrate that any differences between (a) and (b) do not result from thermal effects or from irradiation of products by the dye laser. The results are summarized in Table II. We note that while the use of a continuous stream of nitrogen during the experiment unavoidably leads to some oxidation products (due to traces of oxygen), this remains the preferred experimental technique, since several tests in this type of experiment indicated that continuous stirring of the samples is critical if a quantitative comparison of the various laser sequences is desired.

In cyclohexane, 308-nm laser excitation led to the same products as did lamp irradiation. Similarly, no appreciable yields of new products were observed in either the 308-nm plus dye laser irradiation or in the reversed two-laser experiment. However, lower yields of ketyl radical derived products were observed for 308-nm plus dye laser irradiation, and there was an increase in the amount of unreacted benzophenone compared with one-laser irradiation. In this experiment the yield of solvent-derived radical products was increased for the two-laser photolysis. It should be noted that the known disproportionation to combination ratio of $k_d/k_c = 1.1$[29] for cyclohexyl radical is consistent with the lower yield of dicyclohexyl compared with ketyl radical products for the 308-nm photolysis. The disproportionation product cyclohexene is not detectable under our experimental conditions.

In toluene, the solvent of choice for many of our experiments due to its wide liquid range, no new products were obtained under conditions of one- or two-laser irradiation, in comparison with the case of lamp irradiation. However, a considerable change in the product distribution was again observed in the case of the 308-nm plus dye laser irradiation. A decreased yield of ketyl radical derived products was observed, with the amount of benzpinacol being approximately three times lower for the 308-nm plus dye irradiation. However, the products from the benzyl radical changed very little for the three different experiments. Unfortunately, in toluene the HPLC analysis for recovered benzophenone was complicated by interference from the solvent.

Table III. Product Yields (mol %) for Laser Photolysis of 0.082 M Benzhydrol plus 0.27 M Di-*tert*-butyl Peroxide in Benzene

laser(s), nm	Ph_2CO	$[Ph_2C(OH)]_2$
308	1.67	1.4
308 + 515	3.04	0.47
515 + 308	1.94	1.2

A comparison of one- and two-laser irradiations for benzophenone in toluene-d_8 gave results qualitatively similar to those in the undeuteriated solvent (Table II). This suggests that similar reactions are involved in the bleaching of the ketyl OH and ketyl OD radicals, despite the fact that the bleaching process is more efficient for the former. It should be noted that the product studies for the two radicals were not done under matched conditions and, therefore, cannot be used to estimate the relative efficiencies.

Laser product studies were also carried out using benzhydrol plus *tert*-butoxy radicals as the ketyl source to confirm independently that benzophenone is indeed a product of dye laser excitation of the ketyl radical. The results shown in Table III indicate that an increased yield of benzophenone does occur upon dye laser excitation.

Detection of Hydrogen as a Product of Two-Laser Photolysis of Ketyl Radicals. The above results suggest that benzophenone is the product produced by bleaching of the diphenylketyl radical. Since molecular hydrogen is obviously also a possible product of this reaction, we attempted to detect its presence in the reaction mixture with Raman spectroscopy. Accordingly, two identical samples of 6.6 mM benzophenone in cyclohexane were irradiated with (a) 750 308-nm pulses and (b) 750 pairs of 308-nm plus 515-nm pulses, the latter being delayed by 1 μs. The gas above the solution was then examined by Raman spectroscopy. The two-laser sample showed the presence of bands at 587, 1035, and 4156 cm^{-1} characteristic of molecular hydrogen.[30] None of these were present in the "blank" one-laser sample, confirming that hydrogen is a product of the photolysis of the ketyl radical.

Comparison of the relative areas (A) of the 587-cm^{-1} hydrogen band and the 801-cm^{-1} cyclohexane band in combination with the known cross-sections (σ)[30,31] for each and the vapor pressure of cyclohexane (100 mm at 25.5 °C)[32] gave a semiquantitative estimate of the amount of hydrogen (eq 5). The value of $P_{H_2} \approx$ 32 mm was then compared with the difference in the amount of

$$P_{H_2} = \frac{A_{H_2}}{A_{C_6H_{12}}} \frac{P_{C_6H_{12}}\sigma_{C_6H_{12}}}{\sigma_{H_2}} \quad (5)$$

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(30) Schrötter, H. W.; Klöckner, H. W. In *Raman Spectroscopy of Gases and Liquids*; Weber, A., Ed.; Springer: New York, 1979; p 123.

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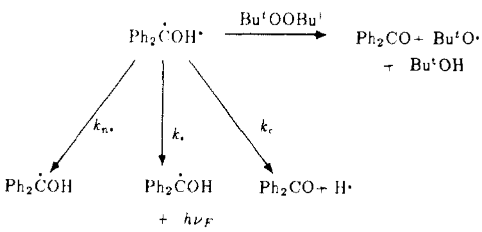
Scheme I



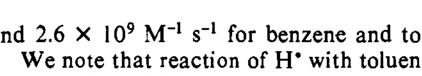
benzpinacol formed in the one- and two-laser experiments. Assuming that each ketyl radical that does not produce pinacol in the two-laser photolysis loses a hydrogen atom that reacts with solvent to give a hydrogen molecule, at least 1.3 μmol of hydrogen would be produced. This number would be somewhat higher if all the products were considered. Taking into account the gas volume of the cell used, we obtain a calculated value of $P_{H_2} \sim 14$ mm. The agreement between this number and that obtained from the Raman experiment is gratifying given the complex nature of the two determinations.

Fluorescence Quenching by Di-*tert*-butyl Peroxide. The quenching of the fluorescence from diphenylketyl radicals by di-*tert*-butyl peroxide was examined in benzene by using a Stern–Volmer type of approach. The importance of this experiment will become evident in the Discussion section as we try to interpret the transient data in peroxide-containing systems. A Stern–Volmer plot of the integrated fluorescence intensity as a function of [peroxide] yielded a value of $k_q\tau_K = 7.3$ M^{-1}, from which, assuming $\tau_K = 3.9$ ns (Table I), we obtain $k_q = 1.9 \times 10^9$ M^{-1} s^{-1}. The ketyl radical in this experiment was generated from ketone plus sufficient 1,4-cyclohexadiene to quench >95% of the ketone triplets even at the highest peroxide concentration (0.22 M) used.

Exploratory Experiments in Acetonitrile. Dye laser excitation of the ketyl radical (from benzophenone plus 1,4-cyclohexadiene) in acetonitrile showed the expected bleaching at 550 nm. However, in this solvent there was an additional transient formed by the dye laser pulse. The new species showed a broad absorption at long wavelengths with a maximum at 710 nm and had a lifetime of ca. 4 μs. No such transient was detected in an identical experiment using benzene as solvent. This transient, while bearing some resemblance to the reported absorptions from solvated electrons[33] and for $Ph_2CO^{\bullet -}$,[34] did not fully agree with either of them.

Discussion

The results from the one- and two-laser preparative irradiations outlined above provide convincing evidence that bleaching of the diphenylketyl radical in toluene or cyclohexane leads to benzophenone plus hydrogen atom (Scheme I). An increased benzophenone yield has been observed in both benzene and cyclohexane. The fate of the hydrogen atom is expected to vary according to the solvent. For example, in either benzene or toluene addition of H$^\bullet$ to the solvent to give a cyclohexadienyl radical should occur (reaction 6). In aqueous solutions k_6 has been determined to be



(6)

1.1×10^9 and 2.6×10^9 M^{-1} s^{-1} for benzene and toluene, respectively.[35] We note that reaction of H$^\bullet$ with toluene involves almost exclusively ring addition (as opposed to hydrogen abstraction).[35] This probably accounts for the failure to observe any increase in the benzyl-derived products in the two-laser experiments in toluene (see Table II).

Reaction of H$^\bullet$ atoms with benzophenone occurs with a rate constant of 5.6×10^9 M^{-1} s^{-1} (again in aqueous media);[36] however, in the presence of 5 mM ketone this reaction could not compete with reaction with solvent in either benzene or toluene.

In cyclohexane, reaction of H$^\bullet$ with solvent will yield a cyclohexyl radical and molecular hydrogen (reaction 7) with the rate constant being 3×10^7 M^{-1} s^{-1} in aqueous solution.[37] Thus,

$$H^\bullet + C_6H_{12} \rightarrow H_2 + C_6H_{11}^\bullet \qquad (7)$$

reaction 7 should be almost 1 order of magnitude faster than reaction of H$^\bullet$ with benzophenone. Product studies in cyclohexane are consistent with this, since an increased yield of solvent-derived product (i.e., dicyclohexyl) is observed for two-laser irradiations. Furthermore, molecular hydrogen has been detected directly as a product of the bleaching of the ketyl radical in cyclohexane.

The shorter lifetime of the excited ketyl radical in cyclohexane (2.7 ns) compared with other solvents has been attributed to hydrogen abstraction from solvent.[15] Our product studies show that similar yields of benzhydrol are produced by both one- and two-laser irradiations in cyclohexane. This suggests that hydrogen abstraction is not a major decay pathway for the excited radical although, based on a slight increase in lifetime for the ketyl in deuteriated solvent, it may make a small contribution.

The situation is more complex when benzhydrol plus *tert*-butoxy radicals is used as the ketyl source. Photolysis of the ketyl radical with the dye laser now leads to a secondary growth of ketyl radical, which has been shown to require the presence of di-*tert*-butyl peroxide and benzhydrol. Two possible explanations for this observation are outlined in reactions 8–11. The first involves

$$Ph_2\dot{C}OH^* \rightarrow Ph_2CO + H^\bullet \qquad (8)$$

$$H^\bullet + t\text{-}BuOOBu\text{-}t \rightarrow t\text{-}BuOH + t\text{-}BuO^\bullet \qquad (9)$$

$$t\text{-}BuO^\bullet + Ph_2CHOH \rightarrow Ph_2\dot{C}OH + t\text{-}BuOH \qquad (10)$$

$$Ph_2\dot{C}OH^* + t\text{-}BuOOBu\text{-}t \rightarrow Ph_2CO + t\text{-}BuO^\bullet + t\text{-}BuOH \qquad (11)$$

cleavage of the excited ketyl radical to yield H$^\bullet$, which reacts with the peroxide to produce a *tert*-butoxy radical that then abstracts hydrogen from benzhydrol (reactions 8–10). The second possibility is direct quenching of the excited radical by peroxide to generate a *tert*-butoxy radical, which then abstracts from benzhydrol (reactions 11 plus 10). Support for the latter mechanism is provided by the fact that the fluorescence from the ketyl radical is quenched by di-*tert*-butyl peroxide with a rate constant of 1.9×10^9 M^{-1} s^{-1}. Furthermore, reaction 9 is not expected to compete with reaction of H$^\bullet$ with benzene solvent (i.e., $k_6 = 1.1 \times 10^9$ M^{-1} s^{-1} for benzene,[35] whereas reaction of H$^\bullet$ with hydrogen peroxide has a rate constant of only 9×10^7 M^{-1} s^{-1} in aqueous media[38]). Thus, quenching of the excited ketyl radical by peroxide to generate *tert*-butoxy radicals that then abstract from benzhydrol appears to best account for the observed results. Further support for this mechanism is obtained from a quantitative analysis of the bleach and recovery data, since eq 12 can be expected to relate these two quantities. The experimental data were found to adhere well to this behavior.[39]

$$\Delta OD_{recovery} \sim \Delta OD_{bleach}\frac{k_q[\text{peroxide}]}{k_q[\text{peroxide}] + \tau_K^{-1}} \qquad (12)$$

The substantial isotope effect on the quantum yield for ketyl radical bleaching provides further support for the cleavage of the excited radical to benzophenone plus hydrogen atom. There is

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(35) Sauer, M. C.; Ward, B. *J. Phys. Chem.* **1967**, *71*, 3971. We note that there may be considerable error in extrapolating these rate constants to other solvents but values for reaction of H$^\bullet$ in organic solvents are not readily available.

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(39) Using the measured values of 1.9×10^9 M^{-1} s^{-1} and 3.9 ns for k_q and τ_K, respectively, and at 0.27 M peroxide, we calculated 67% recovery of bleaching. The fraction of recovery measured in a two-laser transient experiment under these conditions is ~50% at 0.1 M benzhydrol.

also a considerable isotope effect on the rate constant for the sum of radiative and nonradiative decays for the excited radical. Thus, using the measured values for $\Phi_{\text{bleach}}(\text{OH})$, $\Phi_{\text{bleach}}(\text{OD})$, $\tau_K(\text{OH})$, and $\tau_K(\text{OD})$, the rate constants for chemical reaction (k_c) and the sum of radiative and nonradiative decay pathways ($k_r + k_{nr}$) may be calculated (see Scheme I). Values of $k_c = 6.9 \times 10^7$ s^{-1} and $(k_r + k_{nr}) = 1.9 \times 10^8$ s^{-1} were obtained for ketyl OH and $k_c = 1.2 \times 10^7$ s^{-1} and $(k_r + k_{nr}) = 1.0 \times 10^8$ s^{-1} for ketyl OD. This gives an isotope effect of $k_H/k_D = 5.8$ for chemical reaction of the ketyl radical and of $k_H/k_D = 1.9$ for the sum of other radiative and nonradiative decays. The value of 5.8 for the chemical reaction supports that the stretching leading to the elimination of atomic hydrogen is the reaction coordinate in the system. It is rather interesting that the nonradiative decay (since radiative processes are minor, vide infra) would show an isotope effect of 1.9. This may suggest the contribution of radiationless decay paths involving the O–H stretching mode or, alternatively, that some H atom elimination is actually followed by in-cage geminate addition to benzophenone. While the reported rate constant for reaction of H$^\bullet$ with benzophenone of 5.6×10^9 M^{-1} s^{-1} is sufficiently fast to compete with cage escape, the reaction is believed to involve predominantly ring addition and therefore does not provide a significant pathway for ketyl regeneration.[36]

The short lifetime of the excited diphenylketyl radical had previously been attributed to chemical reaction. However, the quantum yields of bleaching of 0.27 ± 0.06 measured herein indicate that this is not the only factor in determining the excited radical lifetime. If we assume that the quantum yield of radical fluorescence of 0.16 at 77 K[17] can be converted to room temperature, assuming that the ratio of fluorescence yields is proportional to the corresponding lifetimes, then we estimate the quantum yield for fluorescence at room temperature as 0.03. This means that approximately two-thirds of the excited radicals undergo radiationless, nonreactive decay.

Several substituted diphenylketyl radicals also undergo efficient chemical bleaching that is assumed to involve loss of H$^\bullet$ to yield the parent ketone, although product studies have not been carried out for these. Thus, the reaction appears to be a general one for excited diphenylketyl radicals. The methoxydiphenylmethyl radical provides a particularly interesting example, as an equivalent excited radical cleavage would yield a methyl radical. Additional experiments are planned to confirm whether this is responsible for the observed bleaching.

Similar Arrhenius parameters are observed for all the radicals examined (Table I). A substantial part of the temperature dependence is presumably due to chemical reaction, although even at 198 K bleaching of the parent radical can still be observed. The relative bleaching and fluorescence quantum yield data at 293 and 198 K lead to the expected lower activation energy for the nonradiative decay process.

Finally, cleavage reactions that generate hydrogen atoms in solution are not common. In this case, the ΔH for reaction of $\text{Ph}_2\dot{\text{C}}\text{OH}$ to give Ph_2CO and H$^\bullet$ is +30 kcal/mol, for the ground-state radical.[40] The excitation energy for the radical can be estimated as 52 kcal/mol, on the basis of the intersection between its absorption and fluorescence spectra, which makes the cleavage process energetically favorable from the excited state of the radical.

Conclusion

Photoexcitation of the diphenyl ketyl radical in solution leads to its strongly fluorescent ($\lambda_{\max} = 574$ nm) excited doublet state. The lifetime of this state is 3.9 ns in toluene at room temperature. The radical decays by a combination of chemical reaction ($\Phi = 0.27$), fluorescence ($\Phi \sim 0.03$), and radiationless decay ($\Phi \sim 0.70$). The chemical component in this decay involves cleavage of the O–H bond to yield benzophenone and a hydrogen atom. When the ketyl radicals are generated by photoreduction of benzophenone by the solvent, the overall reaction is the two-photon sensitized decomposition of the solvent. Isotope studies led to H/D kinetic isotope effects of 5.8 for the chemical decay and 1.9 for the radiationless process; the latter suggests possible important components in the radiationless decay involving O–H stretching and/or cage reaction of hydrogen atom with benzophenone.

Experimental Section

Materials and General Techniques. Benzophenone and substituted benzophenones were recrystallized before use. Benzhydrol was sublimed twice, and di-*tert*-butyl peroxide was passed through an alumina column. α-Phenylbenzoin methyl ether was prepared and purified according to a literature procedure.[42] 1,4-Cyclohexadiene was vacuum distilled. Aberchrome-540 was obtained from Aberchromics Ltd. (Cardiff, U.K.). Benzene, toluene, and cyclohexane (all spectrograde) and toluene-d_8 and cyclohexane-d_{12} (MSD Isotopes) were dried over molecular sieves before use.

GC analyses were done on a Perkin-Elmer 8320 gas chromatograph equipped with a 12-m BPI on vitreous silica capillary column. GC/MS spectra were recorded on a Hewlett-Packard 5995 instrument equipped with a 10-m Ultra 1 (OV-101) capillary column. HPLC analyses were done on a Varian 5000 instrument using a reversed-phase column with methanol/water mixtures as eluent and with UV detection at 215 nm. LC/MS spectra were measured on a Hewlett-Packard 5988A instrument with a similar column and solvent system.

Laser Flash Photolysis. The laser flash photolysis facility and recent modifications required for two-laser experiments have been described in earlier publications.[6,43] A Lumonics TE-860-2 excimer laser with a Xe/HCl gas mixture (308 nm, ~5-ns pulses, ≤20 mJ/pulse) was used as the synthesis laser for the ketyl radical. For fluorescence spectra the ketyl radical was excited by using a Molectron UV-24 nitrogen laser (337.1 nm, ~8-ns pulses, ≤10 mJ/pulse). The spectra were recorded by using an EG & G gated intensified optical multichannel analyzer with a 20-ns gate coincident with the 337-nm laser pulse. For fluorescence lifetime measurements a PRA LN-1000 nitrogen laser (~600-ps pulses, ≤1 mJ/pulse) was used, and the radical emission was monitored at or near its $\lambda_{\max}$. A Candela flash-pumped dye laser (Coumarin 503 dye in 50% aqueous methanol; ~250-ns pulses; ≤400 mJ/pulse) was used for measurements of the bleaching of ketyl radicals and for all two-laser product studies.

Samples were usually contained in 7 × 7 mm^2 quartz cells and were degassed by nitrogen purging. For quantum yield measurements a flow cell was used for both the Aberchrome-540 actinometer and the ketyl radical precursor solutions.

Product Studies. (i) Lamp Irradiation. Samples of benzophenone (5–6 mM) in toluene or cyclohexane were irradiated through Pyrex with Rayonet 3000-Å lamps. Products were identified by comparison of GC/MS and LC/MS spectra with those of authentic samples, except for the two radical cross-coupling products (benzyldiphenylmethanol and cyclohexyldiphenylmethanol) for which standards were not available. The mass spectra for both of these were consistent with the proposed structures.

(ii) Laser Irradiation. Samples of benzophenone (5–6 mM, 2 mL) in the appropriate solvent were purged with nitrogen and irradiated by using (i) 500–308-nm laser shots, (ii) 500 pairs of 308- and 515-nm pulses with a sufficient delay between the two lasers to allow for complete decay of triplet benzophenone, and (iii) 500 pairs of shots as in (ii) but with the laser sequence reversed. The samples were continuously purged with nitrogen during the irradiations to provide sample mixing, which is essential for comparison of the three different experiments. However, this mixing technique leads to some products of radical trapping by oxygen.

Quantitative product analyses were done by HPLC using an internal standard and solutions of known composition for calibration. Analyses for both cyclohexanol and dicyclohexyl were done by GC, since their extinction coefficients were too low at 215 nm for UV/HPLC detection. The experiments in both toluene and cyclohexane were repeated twice (only one set of data for each are listed in Table II).

Similar experiments were carried out for the comparison of one- vs two-laser irradiations for the generation of the ketyl radical from benzhydrol plus di-*tert*-butyl peroxide.

Bleaching Quantum Yields. Quantum yields for bleaching of the diphenylketyl radical and two of its substituted analogues in cyclohexane were measured with Aberchrome-540 in toluene as an actinometer.[22] This required measurement of the extinction coefficients for the radicals, and these were also determined by Aberchrome-540 actinometry. A detailed experimental procedure for this technique is provided in the

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(40) The necessary thermodynamic parameters do not appear to be available in the literature, but a rough estimate is available.[41]

(41) Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans 2* **1972**, 1672.

(42) Werner, A. *Chem. Ber.* **1906**, *39*, 1278.

(43) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

preceding paper in this issue.[22] For extinction coefficient measurements the diphenylketyl radical was generated by either abstraction from cyclohexane solvent or by abstraction from 1,4-cyclohexadiene in cyclohexane. For bleaching quantum yields only the former source of the radical was used in order to eliminate potential problems due to diene quenching of the excited radical.

Detection of Hydrogen by Raman Spectroscopy. Samples of 6.6 mM benzophenone in cyclohexane (2 mL) in 7 × 7 mm^2 quartz cells were nitrogen purged and then irradiated with 750 308-nm laser shots and 750 pairs of 308- and 515-nm pulses. The samples were shaken every 20 shots. The gas above the photolyzed samples was then analyzed by Raman spectroscopy for hydrogen and cyclohexane. The experimental setup for measuring Raman spectra has been previously described.[44]

Acknowledgment. Thanks are due to Drs. H. L. Casal and W. F. Murphy for the Raman experiment, to D. Lindsay for LC/MS measurements, and to S. E. Sugamori for technical assistance.

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Structure Sensitivity of the Marcus λ for Hydride Transfer between NAD$^+$ Analogues[1]

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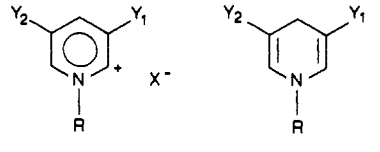
Contribution from the Chemical Dynamics Laboratory, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received December 23, 1986*

Abstract: Thirty-five rate constants, k_{ij}, for transfer of hydride between various pyridinium, quinilinium, acridinium, and phenanthridinium ions spanning a range of over 10^{11} in their equilibrium constants K_{ij} and over 10^6 in k_{ij} have been measured. (All these ions can be regarded as analogues of NAD$^+$.) Calculation of these k_{ij} by conventional Marcus theory, with a constant, averaged value of the intrinsic barrier, λ, gives a fair level of agreement, with an average discrepancy of 0.9 between calculated and observed values of ln k_{ij}. Use of a structure-sensitive λ reduces this discrepancy to 0.5. The structure-sensitive λ is evaluated by using different values of λ, λ_n, for the symmetrical reactions of each cation. The λ_n depend on the ring system in a way that was determined experimentally and on the equilibrium constant for the reduction of the cation by a reference substance, 10-methylacridan, $K_{ij}{}^{\circ}$. The relation between λ_n and ln $K_{ij}{}^{\circ}$ is grounded in Marcus theory and permits the experimental determination of the tightness parameter, τ. In the present case the value of τ, 0.81, suggests the net loss of 19% of the initial carbon–hydrogen binding energy in the critical configuration and 19% excess negative charge on the in-flight hydrogen. The theory also suggests subsets of the data that should give good Brønsted curves and permits the estimation of their slopes, α. The estimated slopes are in reasonable agreement with experiment. The agreement between calculation and experiment supports the Marcus cross relation and the derived relation between λ_n, $K_{ij}{}^{\circ}$, and τ. It also provides some experimental support for the theoretically predicted variation of α with K_{ij}, although the effect is small. The Marcus theory is based on a model in which all the reactions in question proceed through the same general mechanism, involving no high-energy intermediates. Its success strongly suggests that these conditions are met.

In the semiempirical calculation of rate constants for atom or group transfer by Marcus theory[2–7] the rate constants for the related symmetrical (or degenerate) transfer reactions play a key role.[6] In this theory, both in its original form[2–5] (in which it is a quadratic free energy relationship) and in its modified form[6,7] (in which it includes cubic terms), the reactive event is divided into three stages: (1) reactants form a precursor configuration or complex, which may or may not be metastable; (2) the precursor is converted, by passing through a critical configuration,[8] to a successor complex or configuration; and (3) the successor is converted to the ultimate products. The free energy of activation for the second stage is modeled in terms of its free energy of reaction, $\Delta G^{\circ\prime}$, and the free energies of activation for the symmetric analogue reactions, $\lambda_i/4$ and $\lambda_j/4$.

Chart I



1 1H

compd	R	Y_1	Y_2	X
a	$C_6H_5CH_2$	CN	H	Br
b	$C_6H_5CH_2$	$COCH_3$	H	Br
c	$C_6H_5CH_2$	CO_2CH_3	H	Br
d	$C_6H_5CH_2$	$CONH_2$	H	Br
e	CH_3	$CONHCH_2C_6H_5$	H	I
f	CH_3	$CONHC_8H_{17}$	H	I
g	CH_3	CO_2CH_3	CO_2CH_3	I
h	4-$FC_6H_4CH_2$	CN	H	Br
2	4-$FC_6H_4CH_2$	$COCH_3$	H	Br
j	4-$FC_6H_4CH_2$	CO_2CH_3	H	Br
k	4-$FC_6H_4CH_2$	$CONH_2$	H	Br

In this paper we discuss hydride-transfer reactions of the type shown in eq 1, with rate constant k_{ij} ($\tilde{k}$ is Boltzman's constant,

$$A_i{}^+ + A_jH \rightarrow A_iH + A_j{}^+ \tag{1}$$

$$\Delta G^* = W^r + \lambda/4 + \Delta G^{\circ\prime}/2 + \Delta G^{\circ\prime 2}/4\lambda \tag{2}$$

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[1] This work was supported by the National Science Foundation through Grants CHE82-15014 and CHE85-20903 to the University of Minnesota. M.M.K. is also grateful to Prof. J. S. Rowlinson and Dr. R. K. Thomas of the Physical Chemistry Laboratory, Oxford, who provided generous hospitality while this paper was in preparation.

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[5] Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227.

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[8] The term "critical configuration" is used for the structure that, along with the reactant structures, determines the structure-related quantities, such as the Brønsted α and Hammett ρ, obtainable from k_{ij} measurement. It replaces the term "transition state", which we reserve for the structure corresponding to the point of maximum energy on the minimum energy path connecting reactants and products. The critical configuration can be different from the transition state because of tunneling and may not lie on the minimum energy path at all.[27]

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