(2) Roger Adams Fellow, University of Illinois, 1969–1970.
(3) D. Y. Curtin and S. Dayagi, *Can. J. Chem.*, **42,** 867 (1964).
(4) This was estimated by assuming that the xylyl homologue (D) would have the same coalescence rate, $k_c = 170\ s^{-1}$, as the mesityl homologue A (i.e., $\Delta\nu$ would be the same). This rate at −60 °C would correspond to $\Delta G^{\ddagger} = 10$ kcal/mol; however, the resonance lines of D had not observably broadened at −60 °C.[5] Presumably the parent hydrocarbon would rotate as freely.
(5) D. Y. Curtin, P. E. Bender, and D. S. Hetzel, *J. Org. Chem.*, **36,** 565 (1971).
(6) D. T. Hefelfinger and D. J. Cram, *J. Am. Chem. Soc.*, **93,** 4767 (1971).
(7) For rotation to be observable in this system, it is necessary to have one substituent on the rotor; however, one substituent should not significantly affect the barrier.
(8) H. O. House, W. J. Campbell, and M. Gall, *J. Org. Chem.*, **35,** 1815 (1970).
(9) The ring separation as measured by the C(1)–C(1)' distance is estimated as ~3.0 Å,[10] 2.84 Å,[10] and 2.45 Å[11] for *cis*-1,2-diphenylcyclopentane, B, and C, respectively; (the reaction center should occur near the line between C(1) and C(1)').
(10) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, **76,** 6132 (1954).
(11) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28,** 2403 (1963).
(12) F. H. Westheimer, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 542 ff.
(13) F. V. Brutcher, Jr., and W. Bauer, Jr., *J. Am. Chem. Soc.*, **84,** 2233 (1962).
(14) S. Chang, D. McNally, S. Shary-Tehrany, S. M. J. Hickey, and R. H. Boyd, *J. Am. Chem. Soc.*, **92,** 3109 (1970).
(15) (a) R. Granger, L. Bardet, C. Sablayrolles, and J.-P. Girard, *C. R. Hebd. Seances Acad. Sci., Ser. C.*, **270,** 1326 (1970); (b) R. Granger, L. Bardet, C. Sablayrolles, and J.-P. Girard, *Bull. Soc. Chim. Fr.*, 391 (1971).
(16) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Am. Chem. Soc.*, **92,** 5013 (1970).
(17) This treatment assumes that *cis*-pentalane consists of two fused, but otherwise normal, C_s cyclopentane rings; the dihedral angle θ for H–C–C–C in the trans isomer was measured from framework models.
(18) J. P. McCullough, *J. Chem. Phys.*, **29,** 966 (1958).
(19) K. B. Wiberg, J. E. Hiatt, and K. Hseih, *J. Am. Chem. Soc.*, **92,** 544 (1970).
(20) From Hooke's law, for an ideal helical spring with n turns, each having force constant k and being stretched s/n, where s is the total deflection, the total potential energy is $E = (k/2)(s/n)^2 \cdot n = (k/2n)s^2$.
(21) H. W. W. Ehrlich, *Acta Crystallogr.*, **10,** 699 (1957).
(22) L. D. Hayward and I. G. Csizmadia, *Tetrahedron*, **19,** 2111 (1963).
(23) The parent hydrocarbon, *cis*-1,2-diphenylacenaphthene, has been prepared[24] by catalytic hydrogenation of the known 1,2-diphenylacenaphthylene. However, the homologous olefin 1-phenyl-2-mesitylacenaphthylene could not be catalytically reduced prior to reduction of the aromatic rings and was inert to borane. The preparation of this interesting olefin is reported in the Experimental Section.
(24) H. J. Richter and W. C. Feist, *J. Org. Chem.*, **25,** 356 (1960).
(25) R. C. Fuson, D. H. Chadwick, and M. L. Ward, *J. Am. Chem. Soc.*, **68,** 389 (1946).
(26) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 214.
(27) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N.Y., 1969, p 368.
(28) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N.Y. 1959, p 223. (b) For a comparison of this method with a more laborious method, see D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Can. J. Chem.*, **42,** 565 (1964).
(29) T. H. Siddall, III, and W. E. Stewart, *J. Org. Chem.*, **34,** 233, (1969).
(30) A. I. Kitaygorodsky, *Tetrahedron*, **9,** 183 (1960).
(31) The space-filling model suggests that the "outside" methyl of rotationally activated mesityl may be partially engaged with the H_3 atom of the acenaphthene ring system. However, an interaction similarly involving the outside methyl group probably also occurs in the transition state of cyclopentane A.
(32) Since both benzylic proton doublets in **9** are equally broadened (by long-range coupling to H_3 and H_8),[33] the bromine atom is at the 5 or 6 position, which is the substitution pattern of acenaphthene.[34] The highest field naphthalene ring-proton absorption, which is superimposed at *ca.* δ 6.8 on phenyl ring protons, is assigned to H_3, which is in the shielding zone of the locked mesityl ring. The spectrum of 5-bromoacenaphthene[35] indicates that the second highest field doublet (δ 7.3, $J = 7.0$ Hz) and the lowest field doublet (δ 7.9, $J = 8.1$ Hz) belong to H_8 and the peri hydrogen, respectively. Comparison with the spectrum of rotamer **10** shows that the remaining lines consist of a doublet at δ 7.6 ($J = 7.2$ Hz) superimposed on a one-proton multiplet. A spin-decoupling experiment at 100 MHz allowed unambiguous assignments. Irradiation at 681 Hz downfield of Me_4Si caused collapse of the doublet at δ 7.6. Therefore, the resonance lines from H_3 and H_4 must constitute an AB quartet. It follows that H_6 is the peri hydrogen and that H_7 corresponds to the multiplet.
(33) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85,** 2704 (1963).
(34) I. K. Lewis, R. D. Topsom, J. Vaughan, and G. J. Wright, *J. Org. Chem.*, **33,** 1497 (1968).
(35) "Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., 1972, No. 8587M.
(36) Varian Associates, Publication No. 87-202-001, Palo Alto, Calif., p 4-2.
(37) A. R. Miller, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1973; available from University Microfilms, Ann Arbor, Mich.
(38) M. Schlosser and V. Ladenberger, *J. Organomet. Chem.*, **8,** 193 (1967).
(39) J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry," Elsevier, Amsterdam, 1963.
(40) The following rotamer nomenclature is employed: with regard to a specific rotor substituent, an "inside" rotamer is one in which said substituent is held over the plane of the stator ring, and, conversely, the "outside" rotamer holds the substituent outside the periphery of the stator ring. Likewise, the substituents themselves are referred to as "inside" (in) or "outside" (out).
(41) J. Marton and P. Martinson, *Acta Chem. Scand.*, **23,** 3187 (1969).
(42) R. C. Fuson and E. C. Horning, *J. Am. Chem. Soc.*, **62,** 2962 (1940).
(43) L. P. Hammett, "Physical Organic Chemistry," 1st ed, McGraw-Hill, New York, N.Y., 1940, pp 102–104.
(44) A. J. Gordon and R. A. Ford, "The Chemist's Companion," Wiley, New York, N.Y., 1972, p 136.

The Effect of Transient Photoproducts in Benzophenone–Hydrogen Donor Systems

Jonathan Chilton, Linda Giering, and Colin Steel*

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154.

Received July 14, 1975

Abstract: Besides benzpinacol, the photolysis of benzophenone results in the formation of unstable photoproducts whenever a hydrogen donor is present in solution. Benzpinacol has a low quenching constant ($4 \times 10^6\ M^{-1}\ s^{-1}$), but the unstable compounds are diffusion-controlled quenchers so that, although they are minor products, their presence can significantly affect quantum yield determinations. The problem becomes more serious with long triplet lifetimes. Fourier transform NMR is a convenient method for following the photochemistry of dilute ketone solutions even in nondeuterated solvents. The results show that benzpinacol is not formed by the reaction of an unstable photoproduct with ground-state benzophenone as has been suggested.

The photochemistry and photophysics of aromatic ketones and aldehydes have been extensively studied for many years. In solution the bimolecular reactions of hydrogen abstraction,[1] oxetane formation,[2-4] and complex formation[5-10] are well characterized. Recently, the determination of the phosphorescence lifetimes as a function of substrate concentration has afforded a simple direct method for determining the interaction rate constants of a large number of ketones in their triplet states.[11-15] The interaction rate constant can be obtained from

$$1/\tau_{RH} = 1/\tau + k_{ir}[RH] \tag{1}$$

where τ and τ_{RH} are the lifetimes in the absence and presence of RH, respectively.[15] Besides its simplicity, the method offers the advantage of not employing high light intensities. Thus, there is no buildup of large steady-state radical concentrations,[16] and no significant amount of chemical reaction takes place. The latter is important because photoreaction can result in phenomena which lead to effects which make the extraction of rate constants and quantum yields difficult (vide infra). Much of the data in the literature has been obtained by steady-state photolysis in which significant photoreaction takes place.

The rate constant determined using eq 1 simply measures the interaction rate constant (k_{ir}) of the substrate with the triplet. In the case of alkanes this should correspond to the rate constant for hydrogen abstraction by the triplet (k_a). In terms of the mechanism

$$Ph_2CO \xrightarrow{h\nu} {}^3Ph_2CO^* \tag{2}$$

$$^3Ph_2CO^* \rightarrow Ph_2CO \tag{3}$$

$$^3Ph_2CO^* + S \rightarrow \text{product(s)} \tag{4}$$

$$^3Ph_2CO^* + RH \xrightarrow{k_a} \text{product(s)} \tag{5}$$

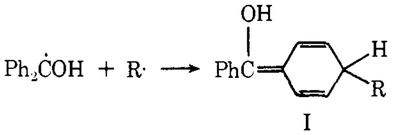
k_a is given by

$$k_a = \frac{1}{\tau}\frac{(\Phi_{RH} - \Phi)}{(1 - \Phi_{RH})}\frac{1}{[RH]} \tag{6}$$

where Φ_{RH} and Φ are the quantum yields of benzophenone consumption in the presence and absence of hydrogen donor. Φ is retained because the solvent (S) may not be completely inert.

Since k_a measures only net chemical reaction, a difference between k_{ir} and k_a could reflect disproportionation of the ketyl and R· radicals, $Ph_2\dot{C}OH + R\cdot \rightarrow Ph_2CO + RH$. The fact that quantum yields less than unity have been reported for benzophenone consumption[17] in neat alkanes indicates that the above reaction is a distinct possibility. In order to see what the relationships between k_{ir} and k_a were, we decided to photolyze benzophenone solutions in "inert" solvents acetonitrile and carbon tetrachloride at various hydrogen-donor concentrations.

It is well known that the photolysis of aromatic ketones in various solvents including 2-propanol and amines can yield unstable photoproducts, often called light-absorbing transients (LAT's), which absorb in the n → π* region of the ketone.[5,18-20] We did not expect to be troubled by LAT's in our systems since Schenck had irradiated benzophenone in carbon tetrachloride, acetonitrile, and hexane and observed no LAT. However, Wagner[21] had shown that the photoreduction of benzophenone by benzhydrol in benzene did result in both the formation of an absorbing photoproduct and a diffusion-controlled quencher which were probably one and the same. He suggested that the quencher was formed by para coupling of a ketyl radical with another radical.



I

If this is so, then LAT formation might be expected to be general for any hydrogen-donating solvent, and so it is surprising that it was not observed by Schenck[18] when he employed hydrocarbons. One possible explanation is that the LAT observed by Wagner arose specifically by the cage reaction of two ketyl radicals.

Experimental Section

Materials. The solvents (acetonitrile, cyclohexane, isooctane, and isopropyl alcohol) were all spectrograde. They were carefully distilled and dried before use. The carbon tetrachloride (Fisher, spectrograde) was purified by the method of Schuster and Weil.[22] Benzophenone and benzpinacol (reagent grades) were recrystallized twice from ethanol and the benzophenone further purified by vacuum sublimation before use.

Method. Five-milliliters samples of 10^{-2}–10^{-4} M benzophenone were degassed by five freeze-pump-thaw cycles in 1-cm fluorescence cells equipped with Fischer-Porter Teflon stopcocks and side degassing bulbs. Solutions of 10^{-2} M benzophenone for NMR experiments were degassed and sealed in the Pyrex inner tube of special coaxial NMR cells purchased from Wilmad Glass Co.

Apparatus. The photolyses were carried out at 366 nm using a Bausch and Lomb high-intensity monochromator with a 200-W high-pressure mercury arc. Irradiation times depended upon the extent of reaction desired and the particular system. The absorption spectra of the degassed samples were recorded on either a Cary 14 or Perkin-Elmer 323 recording spectrophotometer where the sample compartments were extended by means of light-tight boxes to accommodate the cells. A general description of the lifetime apparatus has been given previously.[23] The uncertainty in the measured lifetime is ±5% when the lifetimes are short (<10 μs), but the uncertainty decreases to ±2.5% with longer lifetimes.

The proton magnetic resonance spectra of 10^{-2} M solutions of benzophenone were recorded on a Bruker WH90 Fourier transform spectrometer modified along the lines described previously to suppress the solvent signal.[24] A weak rf pulse is used which is designed not to affect the solvent protons while flipping proton spins of interest 100 or more Hz from the solvent proton resonance. In addition, the NMR spectra of unphotolyzed and photolyzed concentrated (5×10^{-2} M) samples of benzophenone were recorded on a Perkin-Elmer R-32 90-MHz NMR spectrometer.

Results and Discussion

A. Formation of Unstable Photoproducts. Formation of absorbing transients occurs only when a hydrogen donor is present in solution, as can be seen from the following experiments. In agreement with the observations of Schenck and coworkers,[18b] no photoproducts are formed which absorb in the 300–400-nm region when benzophenone at low concentration (10^{-3}–10^{-4} M) is irradiated in carbon tetrachloride. However, when a small concentration of hydrogen donor, for example, cyclohexane, is added to the benzophenone–carbon tetrachloride solutions and the sample is photolyzed, unstable photoproducts are formed. Photolysis of benzophenone in 2-propanol leads to large increases in optical density over the entire n–π* region of benzophenone.[18-20,25] The optical density increases in the case of acetonitrile are not nearly as large as in the case of 2-propanol indicating its relative inertness to hydrogen abstraction, but when a hydrogen donor is added, significant increases in optical density over the entire n–π* region are observed. In the case of alkane solvents, we still observed LAT's, but they absorb less strongly. As can be seen from Figure 1, the LAT absorption maxima are blue shifted from the n → π* absorption of benzophenone so that consumption of benzophenone is observed at long wavelengths, while formation of unstable photoproducts can be observed at shorter wavelengths. This is very similar to what Wagner[21] obtained. We have also observed unstable photoproducts with acetophenone in similar systems.

B. Decay of Unstable Photoproducts. From the data in Figure 1, it is clear that the LAT's are unstable and that several days are required for the dark reaction (disappearance of unstable photoproducts) to come to completion. Even then there is absorption which cannot be accounted

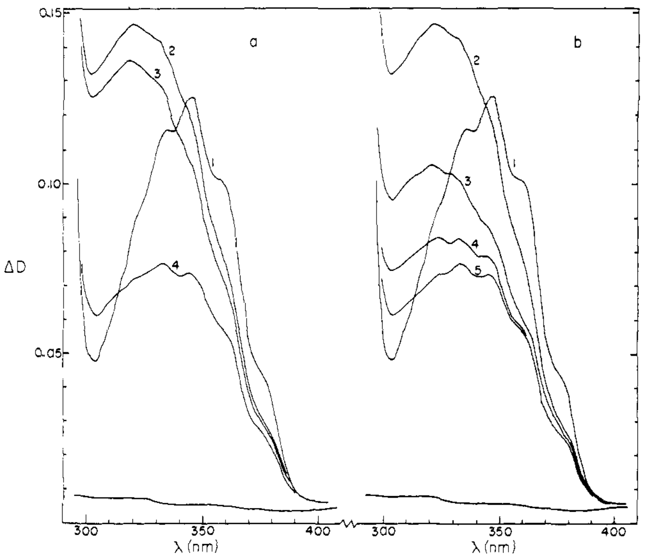


Figure 1. (a) Absorption spectra of 1.04×10^{-3} M benzophenone in cyclohexane: (1) before irradiation, (2) after photolysis (2 min), (3) after 60 min of dark reaction, (4) after 1.0×10^4 min (t_∞). (b) Absorption spectra of 1.04×10^{-3} M benzophenone in cyclohexane: (1) before irradiation, (2) after photolysis (2 min), (3) after adding oxygen immediately after photolysis, (4) after 60 min of dark reaction in the presence of oxygen, (5) after 1.0×10^4 min (t_∞) in the presence of oxygen.

for in terms of the residual benzophenone and the known photoproducts, benzpinacol and bicyclohexyl.[26] The detailed kinetics for the decay in another alkane solvent, isooctane, are shown in Figure 2. The major part of the decay can be fitted by a first-order process whose half-life is 1.7 h. However, there does seem to be a contribution from a much slower process whose half-life is about 27 h. The full-line curve was generated from the equation, $\Delta D_{\text{LAT}} = (\Delta D_t - \Delta D_\infty) = 0.030e^{-t/2.5} + 0.011e^{-t/38.5}$, where ΔD_t is the absorbance at the absorption maximum ($\lambda_{\max}$) of the photoproduct at time t (h) after termination of photolysis, and ΔD_∞ is the corresponding absorbance at the end of the dark reaction. For optical densities less than 0.01, there are significant systematic errors that are indicated by the large error bars.

The unstable photoproducts formed in the above system show sensitivity to oxygen. If two identical samples of benzophenone in alkane solvent are prepared and photolyzed under the same conditions and one cell is opened to the air immediately after photolysis, the following is observed (see Figure 1). The optical density of the aerated sample decreases rapidly. Most of the reaction is over within 1 h, but it requires several days for the terminal (i.e., time invariant) spectrum to be reached. The corresponding data for the decay of the aerated LAT in isooctane are shown in Figure 2. Again it can be seen that most of the decay is over within an hour. Similar decay behavior and oxygen sensitivity is observed in the case of acetonitrile and 2-propanol.

C. Correlation of Triplet Lifetimes with Concentration of LAT's. A very interesting correlation appears if the optical density in the region of LAT absorbance and the triplet lifetime are plotted as functions of time. The data in Figure 3 are for benzophenone in acetonitrile. As the unstable photoproducts build up in solution, they act as quenchers of the benzophenone triplet, and as they disappear, the lifetime recovers though not totally, and the absorption spectrum never fully recovers to benzophenone. A similar pattern for the lifetime and optical density change as a function of time is observed when benzophenone is irradiated in alkane solvents. The lifetime limitation of our flash system prevented the study of the triplet lifetime of benzophenone in cyclohexane ($\tau = 3.0 \times 10^{-7}$ s)[13] as a function of photolysis. However, we were able to study the variation of the benzophenone triplet lifetime in the less reactive isooctane[15] during photolysis and observe its recovery (see Table I). In carbon tetrachloride there is no change of the benzophenone triplet lifetime on photolysis, but once a hydrogen donor (cyclohexane) is added, the triplet lifetime decreases on photolysis and recovers as the unstable photoproducts disappear.

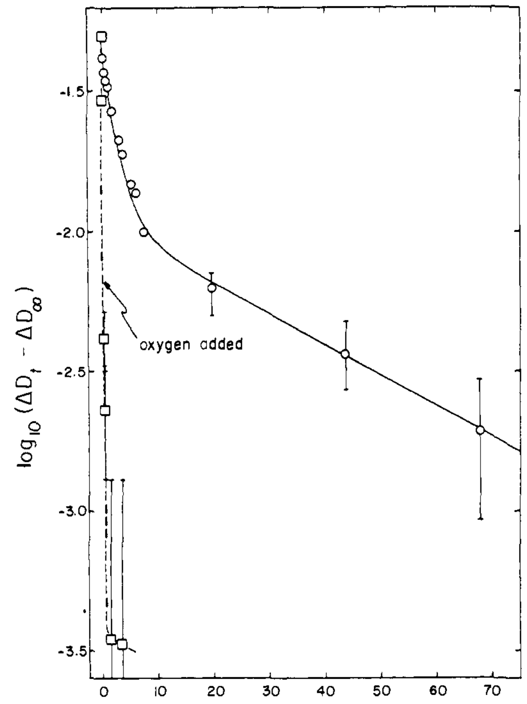


Figure 2. Decay of absorbing photoproducts (LAT) as a function of time. ΔD_t is the absorbance at the absorption maximum ($\lambda_{\max}$) of the photoproduct at time t (h) after termination of photolysis; ΔD_∞ is the corresponding absorbance at the end of the dark reaction. (○) Ph_2CO (1.16×10^{-3} M) in isooctane, $\lambda_{\max} = 325$ nm; (□) Ph_2CO (1.16×10^{-3} M) in isooctane, $\lambda_{\max} = 325$ nm, oxygen added immediately after zero-time dark reaction absorption spectrum. The full-line curve was generated from the equation $\Delta D_{\text{LAT}} = (\Delta D_t - \Delta D_\infty) = 0.030e^{-t/2.5} + 0.011e^{-t/38.5}$.

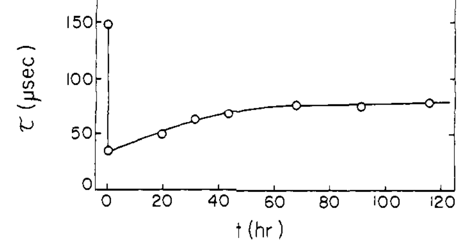


Figure 3. Correlation of triplet lifetime with formation and decay of absorbing photoproducts for Ph_2CO (1.04×10^{-4} M) in acetonitrile. The optical density was measured at 345 nm.

Table I. Variation in Lifetime of Benzophenone Triplet with Formation and Decay of Unstable Photoproducts[a]

Sample	Solvent	τ, μs[b]	τ_{LAT}, μs[c]	τ_∞, μs[d]	t_∞, h[e]
1×10^{-4} M Ph_2CO	Acetonitrile	180	31.7	63	50
1×10^{-3} M Ph_2CO + 0.015 M cyclohexane	CCl_4	47.2	18.0	24.4	80
1×10^{-3} M Ph_2CO + 0.15 M cyclohexane	CCl_4	11.5	4.6	7.2	80
1×10^{-3} M Ph_2CO	Isooctane	2.74	2.14	2.5	16

[a] Temperature is 25°. [b] Triplet lifetime before photolysis. [c] Triplet lifetime immediately after photolysis. [d] Triplet lifetime after completion of dark reaction. [e] Time to complete dark reaction, i.e., no further observable change in absorbance or in τ over a 24-h period.

In order to see if the quenching of benzophenone could be accounted for by the formation of benzpinacol, the interaction rate constant (k_{ir}) for benzpinacol with benzophenone was measured and found to be 4×10^6 M^{-1} s^{-1} in acetonitrile. Using entry 4 in Table I as a particular example, the maximum concentration of benzpinacol that could be formed, based on the fact that 65% of the benzophenone was consumed, is $1 \times 10^{-3} \times (0.65/2)$ M. This quencher concentration together with the above rate constant is two orders of magnitude below that required to explain the variation in lifetime using eq 1.

D. Nature of Photoproducts. Benzpinacol is the major benzophenone derived product from the photolysis of benzophenone in a hydrogen-donating solvent.[17,27-29] The reaction sequence is generally given by

$$Ph_2CO^* + RH \rightarrow Ph_2\dot{C}OH + R\cdot \quad (7)$$

$$2Ph_2\dot{C}OH \rightarrow (Ph_2COH)_2 \quad (8)$$

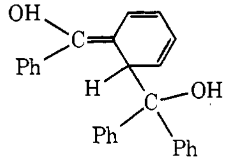
However, on the basis of their studies of the photoreaction of benzophenone in isopropyl alcohol, Filipescu and Minn[25] suggested that benzpinacol formation actually occurs via the slow dark reaction of an intermediate Ia [R = $\dot{C}(CH_3)_2OH$] with another molecule of benzophenone. In aerated solution, Ia reacted with oxygen to regenerate benzophenone. This implies that the optical density in the n-π^* region of two photolyzed samples should be different if one sample is allowed to stand in the absence of oxygen and the other is oxygenated immediately after photolysis. The results in Figure 1 and our experiments in 2-propanol do not support this proposed mechanism, since the aerated terminal spectrum is identical with the degassed terminal spectrum in both cases. Since the mechanism proposed by Filipescu and Minn did not correctly predict the outcome of the photolysis of acetone by benzhydrol, Weiner[30] has also criticized the above scheme and has indicated that Ia could not go onto the observed products at a rate consistent with his results.

In order to get more information about this problem, we decided to analyze photolysis samples using NMR. The advantages of this technique are (a) the samples do not have to be opened to air (oxygen) before analysis, (b) labile products will not be affected as could, for example, be the case in chromatographic analysis, and (c) uv spectral analysis can be carried out using the sealed NMR tubes. Standard NMR spectrometers require concentrations greater than 0.1 M in benzophenone to get good spectra in reasonable times. However, the use of Fourier transform NMR, modified as described in the Experimental Section, enabled us to observe the reaction in nondeutrated solvents at low ketone concentrations (10^{-2} M) within 3 min after the termination of photolysis. Within this time, no significant decay of the LAT occurs. In Figure 4, the results of the NMR experiments in 2-propanol are shown. The correspondence of the resonances in the photolyzed sample of benzophenone in 2-propanol (spectrum c), with those in the spectrum of a mixture of benzophenone and benzopinacol is 2-propanol (spectrum b), and the good agreement with the solid lines in spectrum c, which represent the benzpinacol resonances obtained in 2-propanol-d_8, support the conclusion that benzpinacol is formed immediately and not by a slow dark reaction as has been suggested.[25] The results in cyclohexane (Figure 5a-d) further confirm the fact that benzpinacol is formed immediately. The photolyzed solution is stable with no change in the benzpinacol concentration after several weeks.

The NMR method offers a direct and convenient way for measuring benzophenone consumption. In a series of experiments, the consumption measured in this way was about 20% greater than the values obtained by uv analysis. This discrepancy is not surprising since there is still some absorbing product(s) in the terminal absorption spectrum (see Figure 1).

In order to expand the range of the NMR spectra so that the complete spectral region of δ 0-10 could be observed, photolyses were also carried out using deuterated cyclohexane. Again, no resonances besides those attributable to benzpinacol and benzophenone could be detected.

It would therefore appear that LAT's represent a small fraction of the total photoproduct. The LAT's, whose most likely formulae are "isobenzpinacol" structures I (R = $\dot{C}(Ph)_2OH$) and II such as suggested by Schenck and coworkers,[18] would be expected to have low triplet energies and to be diffusion-controlled quenchers.[21,31]


II

As an example of the latter, the measured quenching of triplet benzophenone by naphthalene in isooctane has a value of 9.5×10^9 M^{-1} s^{-1}.[12] Substituting this value and the data in entry 4 (Table I) into eq 1 yields a value of 1.1×10^{-5} M for the concentration of LAT. Since the sample had been photolyzed to 65% completion, this concentration represents about 2% of the benzophenone consumed and is comparable to the 2% pair coupling observed by Nelsen and Bartlett[32] for cumyl radicals. It would appear that benzpinacol and LAT formation occur by parallel rather than sequential reactions.

E. Effect of LAT's on Quantum Yields. Returning to the problem of determining quantum yields, we see that LAT's can affect the yields not only by their inner-filter effect but also because they are effective quenchers. The ratio of the quantum yield in the presence ($\Phi_{RH}{}^{LAT}$) and in the absence (Φ_{RH}) of quenchers (LAT) is given by

$$(\Phi_{RH})/(\Phi_{RH}{}^{LAT}) = (\tau_{RH})/(\tau_{RH}{}^{LAT}) \quad (9)$$

where the lifetimes are measured in the absence (τ_{RH}) and the presence ($\tau_{RH}{}^{LAT}$) of quencher. From the data in Table I, it can be seen that after 65% consumption in isooctane $\tau_{RH}/\tau_{RH}{}^{LAT} = 1.3$. This means that the observed quantum yield, which is an average of Φ_{RH} and $\Phi_{RH}{}^{LAT}$, will be less than the "ideal" value, Φ_{RH}. This could be a reason why the reported quantum yield for the photoreduction of benzophenone in alkane solvent is less than unity.[10] Of course, if RH

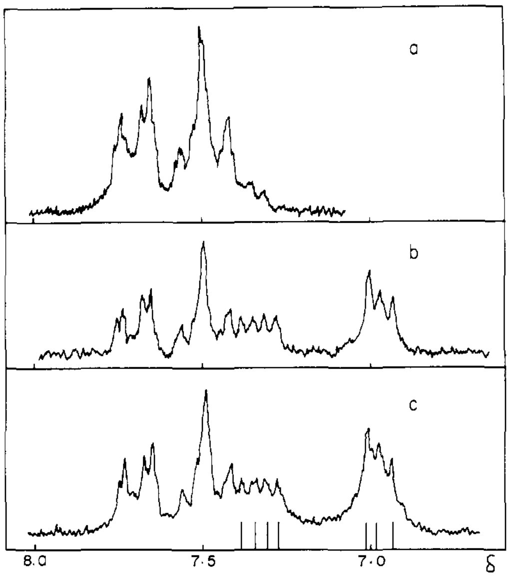


Figure 4. NMR spectra of (a) 4.7 × 10^{-2} M Ph_2CO; (b) 2 × 10^{-2} M Ph_2CO + 1 × 10^{-2} M $(Ph_2COH)_2$; (c) 4.7 × 10^{-2} M Ph_2CO photolyzed for 7.5 min. Spectra a–c in 2-propanol. The solid lines in c correspond to the benzpinacol resonances in 2-propanol-d_8. Spectra a–c were recorded on a Perkin-Elmer R-32 90 MHz NMR spectrometer. The spectrum of benzpinacol in 2-propanol-d_8 was recorded on a Bruker WH 90 Fourier transform spectrometer.

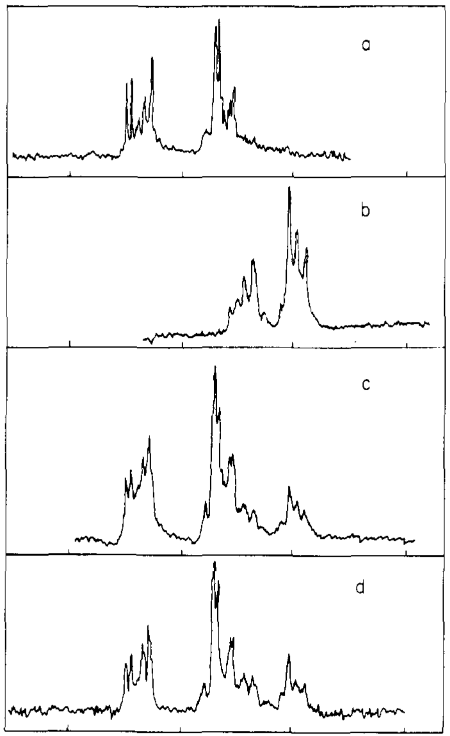


Figure 5. NMR spectra of (a) 1.2 × 10^{-2} M Ph_2CO; (b) 5.0 × 10^{-3} M $(Ph_2COH)_2$; (c) 1.0 × 10^{-2} M Ph_2CO + 1.0 × 10^{-3} M $(Ph_2COH)_2$; (d) 1.2 × 10^{-2} M Ph_2CO photolyzed. Spectra a–d in cyclohexane. Spectra were recorded on a Bruker WH 90 Fourier transform spectrometer.

is sufficiently reactive and its concentration is sufficiently large, then the value of $k_{ir}[RH]$ may be large enough that the value of τ_{RH} and hence φ_{RH} is not significantly affected by the presence of LAT.[5] Also, in competition studies,[26] since the LAT is common to both substrates, relative rates can still be obtained in the presence of significant concentration of LAT. However, when the initial lifetimes are long (see Table I), then the effect of LAT is sufficiently strong as to make the application of eq 6 of dubious value. In addition to the lifetime effects, since the LAT's undergo thermal dark decay at significant rates, the uncorrected experimental quantum yields can depend upon the time of photolysis and time after photolysis before analysis is carried out and whether oxygen is or is not added before benzophenone consumption is measured spectrally.

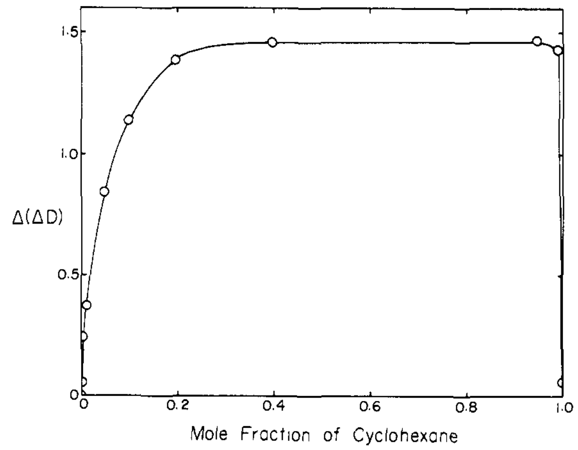


Figure 6. Change in optical density at 310 nm for photolysis of Ph_2CO (1.1 × 10^{-3} M) in carbon tetrachloride solution with added cyclohexane. In all cases the incident light intensity was 5 × 10^{-8} einstein/s, and the period of photolysis was 5 min.

The LAT problem is obviously a complex one, and although statements about the general nature of their effects can be made, the details are very dependent on the exact nature of the solvent. This can be seen quite clearly if one considers the photolysis of a series of solutions in which the solvent is varied from pure carbon tetrachloride to pure cyclohexane. As mentioned above, in pure carbon tetrachloride, no LAT's are formed while there is some LAT formation in pure cyclohexane. However, for intermediate compositions, the extent of LAT formation, as judged by the extent of transient absorbance, is more extreme than for pure cyclohexane. This is shown in Figure 6. Apparently, cyclohexane is required as a hydrogen donor to produce radicals which can then react readily with carbon tetrachloride (or some trace impurity) yielding the light absorbing transients.

Acknowledgment. The authors thank Dr. A. Redfield for his help with the NMR experiments. Support from the National Science Foundation through Development Grant GU 3852 and Grant GP 35980-X is gratefully acknowledged.

References and Notes

(1) J. C. Scaiano, *J. Photochem.*, **2**, 81 (1973).
(2) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).
(3) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).
(4) N. C. Yang, *Photochem. Photobiol.*, 7, 767 (1968).
(5) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973).
(6) D. I. Schuster and B. R. Brizzolara, *J. Am. Chem. Soc.*, **92**, 4359 (1970).
(7) J. Saltiel, H. Curtius, and B. Jones, *Mol. Photochem.*, **2**, 331 (1970).
(8) D. I. Schuster, T. M. Weil, and M. R. Topp, *Chem. Commun.*, 1212 (1971).
(9) D. I. Schuster, T. M. Weil, and A. M. Halpern, *J. Am. Chem. Soc.*, **94**, 8248 (1972).
(10) M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, **3**, 539 (1972).
(11) C. A. Parker and T. A. Joyce, *Chem. Commun.*, 749 (1968); C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **65**, 2823 (1968).
(12) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Am. Chem. Soc.*, **91**, 5413 (1969). W. D. K. Clark, A. D. Litt, and C. Steel, *Chem. Commun.*, 1087 (1969).
(13) G. Porter and M. R. Topp, *Proc. R. Soc. London, Ser. A*, **315**, 163 (1970).
(14) H. Lutz, E. Breheret, and L. Lindqvist, *J. Phys. Chem.*, 77, 1758 (1973).

(15) L. Giering, M. Berger, and C. Steel, *J. Am. Chem. Soc.*, **96**, 953 (1974).
(16) N. C. Yang and S. L. Murov, *J. Am. Chem. Soc.*, **88**, 2852 (1966).
(17) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2039 (1963).
(18) (a) G. O. Schenck, W. Meder, and M. Pape, *Proc. Int. Conf. Peaceful Uses At. Energy*, **29**, 352 (1958); (b) G. O. Schenck, M. Czlesla, K. Eppinger, G. Matthlas, and M. Pape, *Tetrahedron Lett.*, 193 (1967).
(19) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Reckenwald, and R. P. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).
(20) H. L. J. Backstrom, K. L. Appelgren, and R. J. V. Niklasson, *Acta Chem. Scand.*, **19**, 1555 (1965).
(21) P. J. Wagner, *Mol. Photochem.*, **1**, 71 (1969).
(22) D. I. Schuster and T. M. Weil, *Mol. Photochem.*, **4**, 447 (1972).
(23) C. Steel and T. F. Thomas, *Chem. Commun.*, 900 (1966).
(24) A. G. Redfield and R. K. Gupta, *Adv. Magn. Reson.* **5**, 181 (1971).
(25) N. Filipescu and F. L. Minn, *J. Am. Chem. Soc.*, **90**, 1544 (1968).
(26) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 336 (1965).
(27) G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900); **34**, 1541 (1901).
(28) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).
(29) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).
(30) S. Weiner, *J. Am. Chem. Soc.*, **93**, 425 (1971).
(31) S. G. Cohen and J. I. Cohen, *Isr. J. Chem.*, **6**, 757 (1968).
(32) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966).

Activation Volumes and Volumes of Reaction for the Proton-Transfer Reaction between 4-Nitrophenylnitromethane and 1,1′,3,3′-Tetramethylguanidine in Some Aprotic Solvents

Colin D. Hubbard,*[1] Christopher J. Wilson, and Edward F. Caldin

Contribution from the University Chemical Laboratory, Canterbury, Kent, England.
Received February 24, 1975

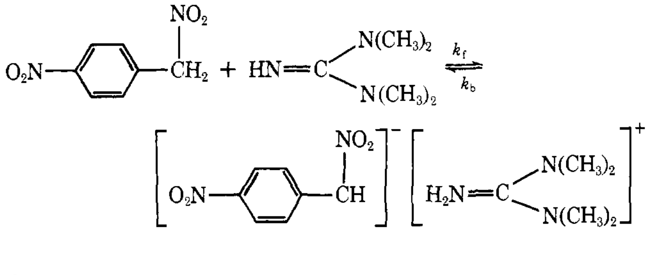
Abstract: Volumes of activation ($\Delta V^{\ddagger}$) and of reaction (ΔV°) have been determined by means of a laser apparatus with a high-pressure cell for the fast proton-transfer reaction between 4-nitrophenylnitromethane and 1,1′,3,3′-tetramethylguanidine in five aprotic solvents (mesitylene, *o*-xylene, toluene, anisole, and chlorobenzene). The values of $\Delta V_f^{\ddagger}$ are around −15 cm³ mol⁻¹ and do not vary by more than twice the standard deviations; those of ΔV° are larger and differ more (−16 to −29 cm³ mol⁻¹), the ratio $\Delta V_f^{\ddagger}/\Delta V^{\circ}$ ranging from 0.56 to 0.84. An electrostatic treatment is not adequate to explain the results; specific solvation changes are also involved. The near constancy of $\Delta V_f^{\ddagger}$ is consistent with the explanation previously put forward for the large tunneling correction found for the reaction in these solvents; during the proton transfer, the solvation changes involve only electron polarization and not motion of solvent molecules.

The proton-transfer reaction (eq 1) between 4-nitrophenylnitromethane (4-NPNM; $NO_2C_6H_4CH_2NO_2$) and a base B in aprotic solvents produces a yellow solution, with λ_{max} approximately 450 nm, containing an ion pair.[2-5] The observed rate constant k depends on the concentration of base b (in large excess) in the way expected from the reaction scheme of eq 1 (eq 2). The reaction with the strong base,

$$NO_2C_6H_4CH_2NO_2 + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NO_2C_6H_4CHNO_2^- \ HB^+ \text{ (ion pair)} \quad (1)$$

$$k = bk_f + k_b \quad (2)$$

1,1′,3,3′-tetramethylguanidine [TMG; $HN{=}C(NMe_2)_2$], has recently been studied by the stopped-flow method.[3,4] In solvents of low polarity (dielectric constant <6), the kinetic deuterium isotopic effects and in particular the ratio of the preexponential factors (A^D/A^H) are exceptionally large and indicate a large tunneling correction:[6,7] for instance, in toluene, k^H/k^D at 25 °C is 45 ± 2, ($\Delta H^{\ddagger D} - \Delta H^{\ddagger H}$) is 4.3 ± 0.3 kcal mol⁻¹, and A^D/A^H is 32 ± 14. Application of Bell's equation[8,9] for tunneling through an unsymmetrical parabolic barrier, on the assumption that the mass of the particle transferred is that of the proton or deuteron (m^H = 1, m^D = 2 amu), allows determination of the barrier dimensions that give the best fit to the experimental data; the result is that the barrier height is solvent dependent, but the barrier width is nearly constant. In solvents of higher polarity (dielectric constant >7), the isotopic differences are smaller but still indicative of tunneling. It was found possible to fit the data to Bell's equations either on the assumption that m^H = 1 and m^D = 2 amu, in which case the resulting barrier widths are solvent dependent and larger than for the less polar solvents; or with the assumption only that $m^D - m^H = 1$, in which case the best fit is obtained with barrier widths that are nearly constant and equal to those for the less polar solvents, while the effective mass is increased (m^H = 1.17 to 1.27). Other bases gave similar though smaller effects.[5]



The interpretation that was suggested for these solvent-dependent results is as follows. The transfer of the proton leads to a separation of charge and therefore to a strong electrostatic field with which the solvent must interact. In the solvents of higher polarity, the field produces a torque on the polar solvent molecules, whose motion is therefore coupled to that of the proton, thus increasing the effective mass; while in the less polar solvents (which are also the