J. Am. Chem. Soc. 1982, 104, 5673-5679

Photochemistry of Benzophenone in Micelles. Formation and Decay of Radical Pairs[1]

J. C. Scaiano,* Elsa B. Abuin,[2] and Laura C. Stewart[3]

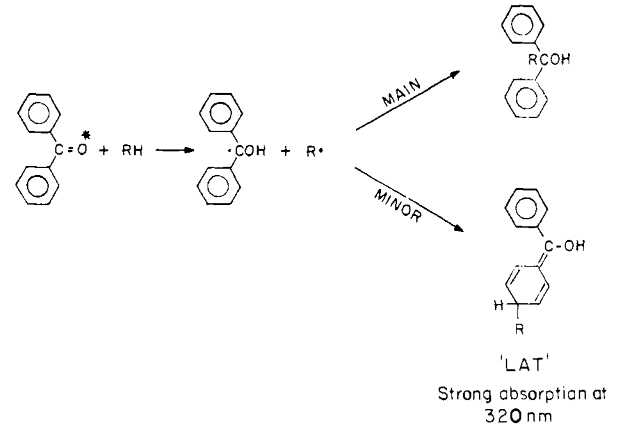
Contribution from the Division of Chemistry, National Research Council, Ottawa, Ontario, Canada K1A 0R6.
Received November 30, 1981

Abstract: The photoreduction of benzophenone triplets in micellar solution leads to the generation of isolated radical pairs, whose behavior resembles that of biradicals. Radical-pair decay is controlled by intersystem crossing and by radical exit from the micelle. For example, the $(C_6H_5)_2\dot{C}OH$-cyclohexadienyl triplet radical pair in CTAC micelles undergoes intersystem crossing with $k_{ISC} = 1.7 \times 10^6\ s^{-1}$ and radical escape (sum for both radicals) with $k_- = 1.6 \times 10^6\ s^{-1}$. Application of moderate magnetic fields leads to a dramatic enhancement of the fraction of radicals that escapes from the micelles. The photolysis of benzophenone in micelles in the absence of added hydrogen donors leads to a radical pair formed by a $(C_6H_5)_2\dot{C}OH$ and a surfactant-derived radical. The partition of this radical pair into products is strongly influenced by the micellar environment and by the application of magnetic fields. The importance of taking these effects into account in the study of radical processes in organized assemblies using magnetic fields (NMR, EPR, etc.) is emphasized.

Organized assemblies continue to attract the interest of photochemists.[4-9] Recent reports have demonstrated that a considerable degree of product control can be achieved by working in organized systems such as micelles; the control exerted on the reaction can range from changes in the nature of the products or their distribution[10-13] to several examples of isotope enrichment recently reported by Turro and co-workers.[14-19] The interest in the field is further reinforced by the fact that understanding photoprocesses in simple organized assemblies can in turn lead to a better understanding of similar processes in biological systems.

In the case of carbonyl compounds, some of the aspects that have received attention in micelles include their photoreduction,[20-23] dimerization,[11] Norrish type I[8,12,13,15-19,24] and type II reactions,[25-27] the dynamics of exit and entry processes,[27,28] their spectral properties,[29,30] and energy migration phenomena.[27] Despite the wide range of areas that this list seems to cover, detailed quantitative studies have been scarce. A few recent reports from Hayashi's,[21,22,24] Turro's,[31,32] Braun's,[32] and our laboratory[23,27,28] have used laser flash techniques in the study of carbonyl triplets in micelles, thus leading to the first direct time-resolved examination of their dynamic behavior. The picture that emerges from these experiments clearly shows that the understanding of the behavior of radical pairs is at least as important as the role of the precursor excited states and, in fact, far more sensitive to the microenvironment.

Scheme I



In this study we have used laser flash photolysis techniques to address some of the problems mentioned above. In particular, we consider the possibility of triplet product formation, the control

---

[1] Issued as NRCC 20590.

[2] Visiting Scientist from Universidad de Santiago, Chile.

[3] NRCC summer student, 1981.

[4] Whitten, D. G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 440-450.

[5] Thomas, J. K.; Grieser, F.; Wong, M. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 937-949.

[6] Thomas, J. K. *Chem. Rev.* **1980**, *80*, 283-299.

[7] Turro, N. J.; Grätzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675-696.

[8] Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369-377.

[9] Kalyanasundaram, K. *Chem. Soc. Rev.* **1978**, *7*, 453-472.

[10] de Mayo, P.; Sydnes, L. K. *J. Chem. Soc., Chem. Commun.* **1980**, 994-995.

[11] Lee, K. H.; de Mayo, P. *Photochem. Photobiol.* **1980**, *31*, 311-314. Avenir, D.; Johnston, L. J.; de Mayo, P.; Wong, S. K. *J. Chem. Soc., Chem. Commun.* **1981**, 958-959.

[12] Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7431-7432.

[13] Kraeutler, B.; Turro, N. J. *Chem. Phys. Lett.* **1980**, *70*, 270-275.

[14] Turro, N. J.; Chow, M.-F. *J. Am. Chem. Soc.* **1980**, *102*, 1190-1192.

[15] Turro, N. J.; Kraeutler, B. *J. Am. Chem. Soc.* **1978**, *100*, 7432-7434.

[16] Turro, N. J.; Kraeutler, B.; Anderson, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 7435-7437.

[17] Turro, N. J.; Anderson, D. R.; Kraeutler, B. *Tetrahedron Lett.* **1980**, *21*, 3-6.

[18] Kraeutler, B.; Turro, N. J. *Chem. Phys. Lett.* **1980**, *70*, 266-269.

[19] Turro, N. J.; Chow, M.-F.; Kraeutler, B. *Chem. Phys. Lett.* **1980**, *73*, 545-549.

[20] Breslow, R.; Kitabatake, S.; Rothbard, J. *J. Am. Chem. Soc.* **1978**, *100*, 8156-8160.

[21] Sakaguchi, Y.; Nagakura, S.; Hayashi, H. *Chem. Phys. Lett.* **1980**, *72*, 420-423.

[22] Sakaguchi, Y.; Nagakura, S.; Minoh, A.; Hayashi, H. *Chem. Phys. Lett.* **1981**, *82*, 213-216.

[23] Scaiano, J. C.; Abuin, E. B. *Chem. Phys. Lett.* **1981**, *81*, 209-213.

[24] Hayashi, H.; Sakaguchi, Y.; Nagakura, S. *Chem. Lett.* **1980**, *1149*-1152.

[25] Turro, N. J.; Liu, K.-C.; Chow, M.-F. *Photochem. Photobiol.* **1977**, *26*, 413-415.

[26] Worsham, P. R.; Eaker, D. W.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 7091-7093.

[27] Scaiano, J. C.; Selwyn, J. C. *Photochem. Photobiol.* **1981**, *34*, 29-32.

[28] Scaiano, J. C.; Selwyn, J. C. *Can. J. Chem.* **1981**, *59*, 2368-2372.

[29] de Mayo, P.; Miranda, J.; Sothers, J. B. *Tetrahedron Lett.* **1981**, *22*, 509-512.

[30] Menger, F. M.; Jerkunica, J. M.; Johnston, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4676.

[31] Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Tanimoto, Y.; Weed, G. C. *J. Am. Chem. Soc.* **1981**, *103*, 4574-4578.

[32] Braun, A. M.; Krieg, M.; Turro, N. J.; Aikawa, M.; Gould, I. R.; Graf, G. A.; Lee, P. C.-C. *J. Am. Chem. Soc.* **1981**, *103*, 7312-7316.

0002-7863/82/1504-5673$01.25/0

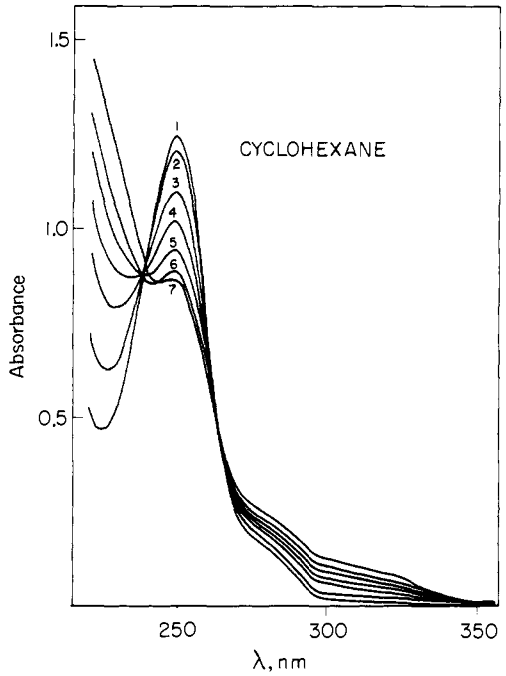


Figure 1. Irradiation of 2.8 × 10^{-4} M benzophenone in cyclohexane at 20-s intervals (22 °C).

exerted by the environment on the partition of radical pairs into products, the dynamics of radical exit and radical-pair intersystem crossing in micellar solution, and the effect of external magnetic fields.

Results and Discussion

It is generally accepted that radical reactions in micelles lead to the formation of ground-state products.[8] Naturally, for most systems in which the formation of triplet products would be highly endothermic, one can safely assume that this is a good postulate. However, there are systems in which one can conceive that some reaction paths could be energetically feasible even if the products are formed in the triplet state. Since a triplet-derived radical pair confined to a micelle may persist in this spin state for hundreds of nanoseconds (vide infra), one could conceive that such a reaction path could play an important role in product formation.

The photoreduction of benzophenone is well-known to occur by the mechanism of Scheme I.[33,34] The para-coupling product (or ortho coupling) is usually referred to as an "LAT", which stands for light absorbing transient.[34-42] While for the sake of consistency with earlier reports we will use the same nomenclature in this paper, it should be noted that this is a rather unfortunate choice of name, since the product is not a transient but in fact quite stable. We found that in the absence of oxygen and traces of acid, LATs can be preserved from a few hours to at least several days. LATs probably account for 1–2% of the products in homogeneous solution.

A simple examination of the structure of LATs and comparison with those of many other molecules with low-lying triplets[43] suggest that their triplet energy should be around or below 50 kcal/mol. Consistent with this, their fluorescence spectrum peaks at ~400 nm.[42] Since the C–C bond energy of the bond being formed can be expected to exceed 50 kcal/mol,[44] one can conclude that, from an energetic point of view, formation of triplet LATs would be feasible. The next section addresses this question.

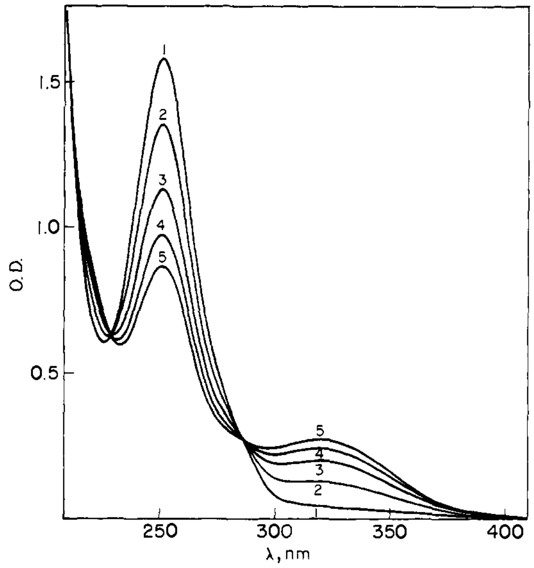


Figure 2. Irradiation of 3.2 × 10^{-4} M benzophenone in SDS (0.1 M) at 20-s intervals (22 °C).

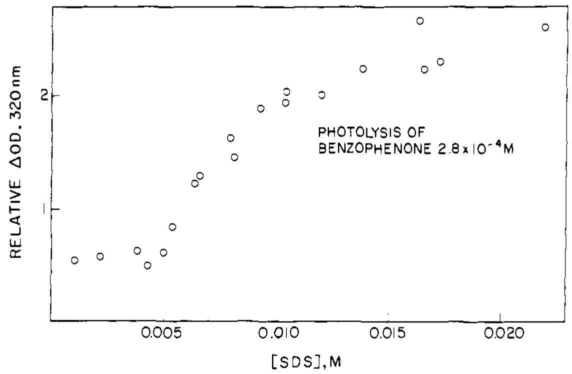


Figure 3. Relative initial yields of LATs upon irradiation of 2.8 × 10^{-4} M benzophenone in water in the presence of variable SDS concentrations (22 °C).

On the Origin of LATs. Two samples containing benzophenone in cyclohexane and in sodium dodecyl sulfate (SDS) micelles were irradiated for several 20-s intervals. The UV spectra of the samples were recorded at the beginning of the experiment and after each irradiation period. The results are shown in Figures 1 and 2; the *initial* rate of LAT generation is around ten times larger in micellar solution, where it also leads to better-defined isosbestic points. In alcohol solutions, the behavior is intermediate, leading to two or three times the yield observed in cyclohexane, depending on the alcohol.

In the system of Figure 2, the surfactant, SDS, is not only the micelle-forming agent but also the reagent donating a hydrogen in the photoreduction of benzophenone. Thus, it seemed important to establish that the enhancement of the yields of LATs was the result of the properties of SDS as a surfactant rather than as a reagent. Figure 3 shows a plot of the yield of LATs (in arbitrary units) as a function of SDS concentration. Quite clearly, the marked increase in yield occurs around the cmc,[45] thus supporting

---

[33] For a review on photoreduction, see: Scaiano, J. C. *J. Photochem.* **1973**, *2*, 81–118.

[34] Chilton, J.; Giering, L.; Steel, C. *J. Am. Chem. Soc.* **1976**, *98*, 1865–1870.

[35] Weiner, S. A. *J. Am. Chem. Soc.* **1971**, *93*, 425–429.

[36] Bäckström, H. L. J.; Appelgren, K. L.; Nikasson, R. J. V. *Acta Chem. Scand.* **1965**, *19*, 1555–1565.

[37] Pitts, J. N.; Letsinger, R. L.; Taylor, R. P.; Patterson, J. M.; Recktenwald, G.; Martin, R. P. *J. Am. Chem. Soc.* **1959**, *81*, 1068–1077.

[38] Schenck, G. O.; Cziesla, M.; Eppinger, K.; Matthias, G.; Pape, M. *Tetrahedron Lett.* **1967**, 193–198.

[39] Schenck, G. O.; Matthias, G. *Tetrahedron Lett.* **1967**, 699–702.

[40] Filipescu, N.; Minn, F. L. *J. Am. Chem. Soc.* **1968**, *90*, 1544–1547.

[41] Wagner, P. J. *Mol. Photochem.* **1969**, *1*, 71–87.

[42] Lemire, A.; Mar, A.; Maharaj, U.; Dong, D. C.; Cheung, S.-T.; Winnik, M. A. *J. Photochem.* **1980**, *14*, 265–268.

[43] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; Table 2-1.

[44] For example, see: Darwent, B. de B. "Bond Dissociation Energies of Simple Molecules". *Natl. Bur. Stand.* **1970**, NSRDS-NBA No. 31; also ref 43, Section 8.

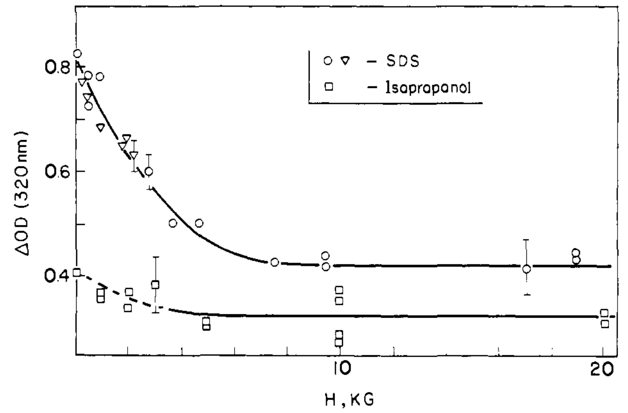
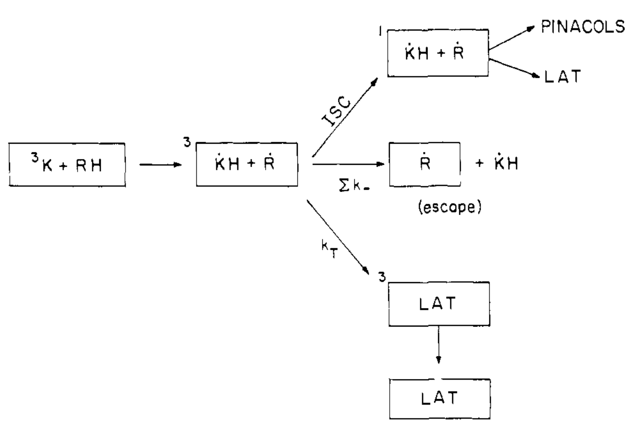


Figure 4. Effect of external magnetic fields on the yield of LATs obtained upon irradiation of 2 × 10^{-3} M benzophenone in 0.22 M SDS (▽ and ○) and in 2-propanol (□). Two different magnets were used in the surfactant system (22 °C).

Scheme II



the idea that the enhancement reflects the formation of micelles.[46] It should be noted that the plot does not show—and cannot be expected to show—the sharp features common in other cmc plots;[47] this is due to the double role of SDS as both surfactant and reagent.

The results given above naturally encouraged our expectations of a triplet reaction path. In order to further elaborate our analysis of the system, we need to have a model mechanism on which to test the different possibilities. Scheme II shows the reaction paths considered. The photoreduction is assumed to occur exclusively from the triplet state and to lead to the formation of triplet radical pairs; these can lead to "conventional" products (which include LATs) following intersystem crossing. Exit of *either radical* from the micelle would destroy the germinate radical pair. Finally, we consider the possibility of LAT formation directly in the triplet state.

A relatively simple experiment can help us decide on the relative importance of the triplet reaction path. Application of moderate magnetic fields should lead to Zeeman splitting of the triplet sublevels. This splitting should be sufficient to slow down considerably radical-pair intersystem crossing from the T_+ and T_- sublevels.[8] Thus, a reduction of intersystem crossing would be expected to enhance the relative efficiency of reaction paths not requiring intersystem crossing such as radical exit and our hypothetical triplet LAT formation. In other words, if LATs come from a triplet path, their yield should be increased in a field, while it would decrease if LATs reflect the chemistry of singlet radical pairs. Figure 4 illustrates the results of a series of experiments of this type. Also included in the same figure are the results in 2-propanol, in which the change is minimal, if any at all. We note at this point that studies of this type are subject to many experimental complications, which are discussed in some detail in the Experimental Section. The results of these experiments conclusively show that LATs result mainly from singlet radical pairs, just as they do in homogeneous solution. This still leaves us in need of an explanation for the enhancement of LAT yields in micellar solution. We propose that the ketyl radicals generated in the decay of benzophenone triplets reside in the micelle in a highly polar environment, probably with the hydrogen-bonded hydroxyl group in or near the Stern layer in the same way in which type II biradicals do.[27] The counterradical R· has the option of reacting at the central carbon atom or at the para position in the aromatic ring. The latter are expected to be located in a less polar environment. Since in our example the R· radical will be located in the hydrophobic part of the surfactant molecule, one could anticipate an enhancement of those reaction paths compatible with this characteristic, i.e., LAT formation.

Table I. Effect of Bromide Ions on the Lifetime of Benzophenone Triplets in CTAC/CTAB Micelles

% Br^-	lifetime, ns
0	310 (CTAC)[a]
0.26	270
1.26	214
1.99	200
2.96	172
100	17 (CTAB)

[a] CTAC = 0.0502 M.

In micelles derived from other surfactants such as cetyltrimethylammonium bromide (CTAB) and chloride (CTAC), our results parallel those in SDS. In all cases we observe a decrease in LAT yields upon application of a magnetic field. The initial yields of LATs are about 20 times higher in CTAC compared with CTAB. The result is entirely consistent with the change in benzophenone triplet lifetimes observed in these two surfactants. Table I shows the triplet lifetimes obtained by using laser flash photolysis in CTAC, CTAB, and when a fraction of the Cl^- counterions is replaced by Br^-.[48] The shortening of the triplet lifetime in CTAB is attributed to benzophenone triplet quenching by Br^- and is consistent with the benzophenone molecule residing near the micellar surface. The slow rate of formation of LATs in CTAB micelles is then attributed to the predominance of triplet quenching.

Finally, laser flash photolysis experiments of the type to be described in the following sections show that the 320-nm absorptions due to LATs are formed in the same time scale (100–1000 ns) in which ketyl-radical decay takes place.

Transient Phenomena in the Absence of Added Hydrogen Donors. The previous section deals exclusively with the question of LAT formation when benzophenone is irradiated in anionic or cationic micelles. When similar samples are examined by using laser flash photolysis techniques, the results are indicative of complex reaction mechanisms. At 540 nm, where both the ketyl radical and the benzophenone triplet absorb, one observes relatively "clean" decay traces leading to a residual absorption that can be attributed to ketyl radicals. In earlier studies,[28] we have indicated that the yield of ketyl radicals in SDS (as measured by this residual absorption) is only ~7% of the value expected for quantitative photoreduction. As far as the decay trace is concerned, they could be reasonably fitted with first-order kinetics, even if, with hindsight (see below), one could argue that this should not be the case. When we recorded a series of transient spectra at different times after the laser pulse, we found that the initial spectrum (at the maximum in Figure 5A) clearly corresponds to that of triplet benzophenone, with λ_{max} ~525 nm. As one "slides down the

---

[45] Mysels, K. J.; Princen, L. H. *J. Phys. Chem.* **1959**, *63*, 1696–1700.

[46] A similar type of behavior has been observed when the intensity of benzophenone phosphorescence is plotted against the concentration of surfactant.[32]

[47] See, for example: the plots presented in ref 11.

[48] Bromide anions are expected to bind more strongly than chloride anions.[49]

[49] Bartet, D.; Gamboa, C.; Sepúlveda, L. *J. Phys. Chem.* **1980**, *84*, 272–275.

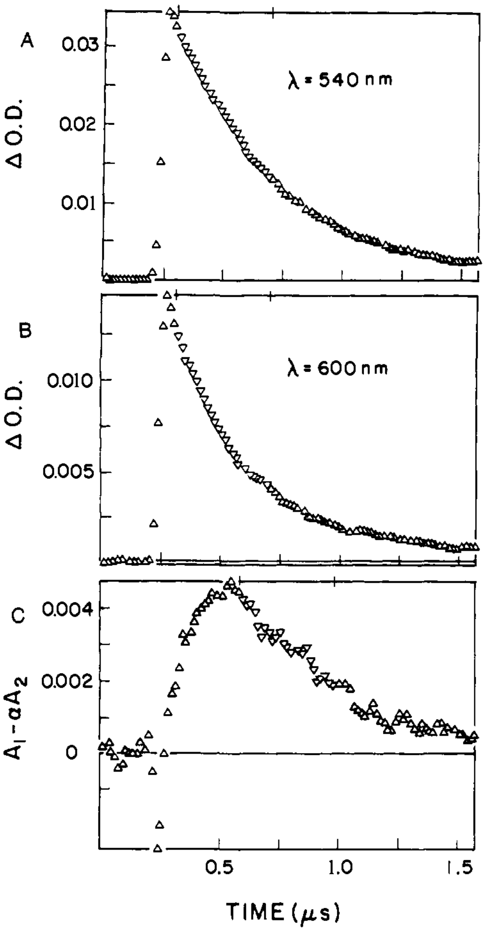


Figure 5. Transient absorptions observed upon laser excitation of benzophenone in SDS (0.22 M). Traces obtained at 540 and 600 nm (A and B) and deconvoluted trace (C, see eq 2) showing a profile for the time evolution of the ketyl radical concentration (27 °C).

trace", one observes a gradual evolution toward the ketyl spectrum (λ_{max} 540 nm). An analysis of these data suggested that substantial ketyl absorptions may be underlying the decay trace of Figure 5A. We note at this point that the traces obtained by us are consistent with similar ones obtained by Hayashi[21] and by Braun, Turro, et al.[32,50] We found that the triplet lifetimes can be obtained with less complications by monitoring the evolution of the signal at ~600 nm. We have shown earlier that at this wavelength the triplet state shows absorptions that (even if weak) are far larger than those due to the ketyl radical.[28,51] In experiments of this type, we measured a triplet lifetime, τ_T = 320 ns.

In earlier work from this laboratory, we have demonstrated that in a system in which two transients overlap extensively, it is possible to deconvolute the signals if two wavelengths can be found in which the ratio of extinction coefficients for the two transients differ considerably.[52] Equations 1a and 1b give the transient optical

$$A_1 = \epsilon_1{}^T C^T + \epsilon_1{}^K C^K \qquad (1a)$$

$$A_2 = \epsilon_2{}^T C^T + \epsilon_2{}^K C^K \qquad (1b)$$

densities per unit optical path (A_1 and A_2) at two different wavelengths (600 and 540 nm, respectively, in this example). C^T and C^K are the concentrations of the triplet state and the ketyl radical, respectively, and the various ϵ represent the extinction coefficients of each species at each wavelength. Multiplying eq 1b by the ratio of triplet extinction coefficients (α) and subtracting from eq 1a leads to

$$A_1 - \alpha_2 = (\epsilon_1{}^K - \alpha\epsilon_2{}^K)C_K \qquad (2)$$

where

$$\alpha = \epsilon_1{}^T/\epsilon_2{}^T \qquad (3)$$

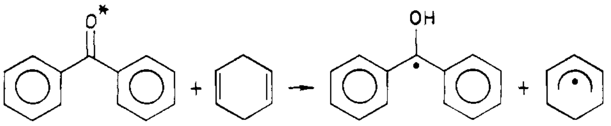
Thus, a plot according to eq 2 will show a time profile proportional to the concentration of ketyl radicals. Figure 5C shows the corresponding plot for SDS micelles. We note that the value of α is simply the ratio of experimental optical densities at 600 and 540 nm before significant triplet decay takes place.

The ketyl concentration profile of Figure 5C provides conclusive proof that ketyl radicals are formed in good yields but that the majority of the radical pairs decay during, or overlapping with, the triplet-state process. Previous studies, while recognizing the problem, did not provide a time-resolved analysis of the evolution (formation and decay) of ketyl radicals.[21,22,32]

In principle, the deconvoluted traces can be analyzed by using a mechanism including a first-order formation step and a decay combining chemical processes and exit from the micelle. In our view, an analysis of this type cannot be expected to lead to accurate kinetic parameters. The alternative approach, preferred by us, consists of addition of a good hydrogen donor to the micelle so that triplet decay becomes fast enough that for all practical purposes it can be ignored. This approach is presented in the next section.

In order to provide at least an estimated value for k_{ISC} for the radical pair formed by reaction of triplet benzophenone with SDS, we evaluated the integral under the curve in Figure 5C and then used the approach described in earlier studies[53] that allows for comparable rates of formation and decay of the transient of interest. The value estimated was $k_{ISC} \sim 3 \times 10^6$ s^{-1}.

Transient Phenomena in the Presence of 1,4-Cyclohexadiene.[54] The selection of a substrate that would photoreduce benzophenone triplets in micellar solution proved to be a rather difficult task. While many molecules are known to react with benzophenone triplets,[33] few of them can be expected to be largely resident in the micellar phase and to be sufficiently good quenchers that a few molecules would compete favorably with 60–100 surfactant molecules. A series of molecules bearing allylic hydrogens have recently been shown to photoreduce benzophenone efficiently;[51] among them, 1,4-cyclohexadiene quenches with $k_q = 2.9 \times 10^8$ M^{-1} s^{-1} in homogeneous solution, and 94% of the quenching events lead to ketyl radical formation, reaction 4.



(4)

In the case of 0.22 M SDS, we found that 0.023 M 1,4-cyclohexadiene reduces the lifetime of triplet benzophenone to only 19 ns (as monitored at 600 nm). Under these conditions, the traces at 540 nm can be regarded as a direct measure of the behavior of the ketyl radical. Under these conditions, the yields of LATs are depressed considerably.

A few characteristics of the decay of the radical pair produced in reaction 4 deserve some comment. First, there is the question of dimensionality; radical–radical reactions in homogeneous solution are usually bimolecular *and* second order. In relatively short time scales in micellar solution, these decay processes will still be bimolecular, but they will be expected to follow first-order kinetics. These ideas have been developed in considerable detail in a recently published stochastic model for reactions in micellar solution.[55,56] From a conceptual viewpoint, we find it useful to

---

(50) During a recent conference, we had the opportunity to compare our data with the results obtained by Braun, Turro, and co-workers.[32] It is quite clear that where the experiments overlap, the agreement of the raw data is excellent.

(51) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *102*, 6393–6397.

(52) Mendenhall, G. D.; Stewart, L. C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5109.

(53) Scaiano, J. C. *J. Photochem.* **1981**, *16*, 71–74.

(54) A preliminary account of this part of the work has been published.[23]

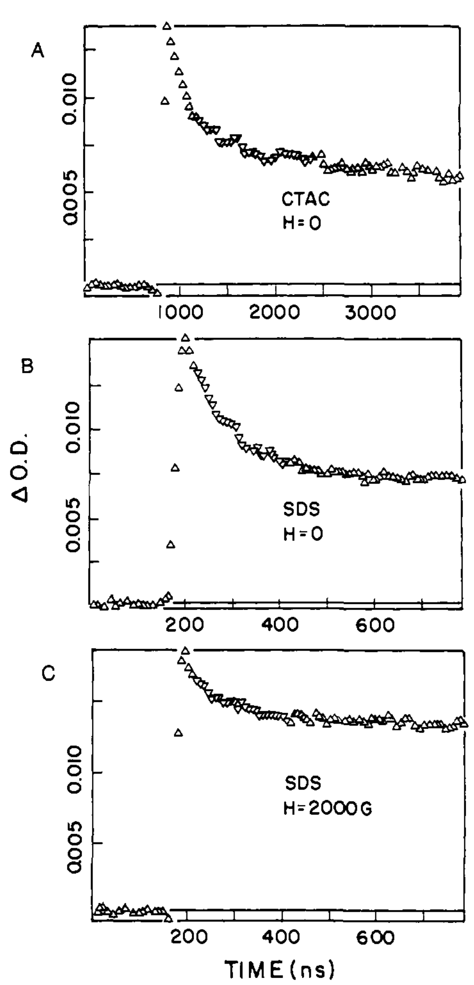


Figure 6. Decay traces observed at 540 nm for benzophenone in surfactant solutions in the presence of sufficient 1,4-cyclohexadiene to quench quantitatively the triplet state: (A) CTAC (0.043 M), $H = 0$; (B) SDS (0.22 M), $H = 0$; (C) SDS (0.22 M), $H = 2000$ G (27 °C).

think about the confined radical pair as a biradical in which the radical sites are held in close vicinity by a physical boundary rather than a molecular framework. In this sense the interpretation of the predicted (and observed) first-order decay is straightforward.

Second, there is the consideration of radical exit processes ($\sum k_-$ in Scheme II); the germinate radical pair is effectively destroyed when *either* radical exits from the micelle. We refer to these as escape processes. However, escape processes do not destroy the chromophore monitored in our experiments, i.e., the ketyl group. In other words, escape processes destroy the germinate nature of the radical pair, while at the same time they make the detectable chromophore long-lived enough that in the time scale of our experiments, it can be regarded as a stable species. In fact, the kinetic analysis of such a system is straightforward and mathematically identical with the case of Norrish type II biradicals reacting with hydrogen donors that have been discussed in detail elsewhere.[57] Figure 6A shows a representative trace obtained in CTAC micelles and monitored at 540 nm. The decay part of the trace obeys first-order kinetics and leads to a rate of decay, $k_{\text{exptl}} = 3.3 \times 10^6\ \text{s}^{-1}$, that corresponds to the sum of the different decay processes, i.e.:

$$k_{\text{exptl}} = k_{\text{ISC}} + \sum k_- \qquad (5)$$

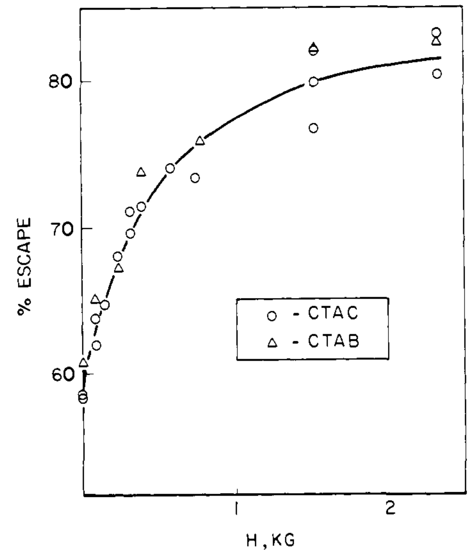


Figure 7. Escape plot for Ph$_2\dot{\text{C}}$OH radicals in CTAC (○) and CTAB (Δ) micelles as a function of the external field (27 °C).

The long-lived absorption observed after the initial decay is complete and corresponds to the fraction of radical pairs that underwent escape processes. Thus, the ratio of end (or plateau) to initial absorption is a measure of the importance of escape processes according to eq 6 (see Scheme II).[58] Combination of

$$\frac{\text{(end or plateau OD)}}{\text{(initial OD)}} = \frac{\sum k_-}{k_{\text{ISC}} + \sum k_-} \qquad (6)$$

eq 5 and 6 leads to rates of escape ($\sum k_-$) of 1.6×10^6 and $4.4 \times 10^6\ \text{s}^{-1}$ for CTAC and SDS, respectively. For the rate constants for intersystem crossing, the values are 1.7×10^6 and $5.8 \times 10^6\ \text{s}^{-1}$, respectively.

As in the case of LAT formation, a good test of the mechanism is the application of magnetic fields. For practical reasons our laser flash photolysis experiments are limited to fields below 2500 G. Examination of the mechanism of Scheme II, ignoring triplet LAT formation for the reasons given before, suggests that a slowdown of intersystem crossing (due to Zeeman splitting of triplet sublevels) should lead to an increase in the fraction of radicals that undergoes escape processes. Such an enhancement is indeed observed, as shown in Figure 7 for CTAC and CTAB micelles. It is important to note that while benzophenone triplets behave quite diferently in CTAC and CTAB micelles (see Table I), the radical pairs show essentially identical behavior (Figure 7). This supports our proposal that the effect of magnetic fields is largely on the radical pair, not on the triplet state. In this sense, it should be noted that triplet-state lifetimes were not affected (±10%) by application of magnetic fields ($H \leq 2500$ G) in SDS, CTAC, or CTAB micelles. A plot of "escape" vs. H for SDS micelles shows essentially the same features as that in Figure 7 but with substantially lower dispersion of the data; a plot of this type has been included in an earlier communication.[23]

An interesting observation in these experiments is that while the fraction of ISC vs. escape changes substantially with the application of a field (compare Figure 6, B and C), the experimental rate constant associated with the decay is virtually the same at zero or 2000 G. This is in fact to be expected if applied fields around 2000 G completely prevent intersystem crossing from T_+ and T_-, while the process from T_0 remains unaffected. At low fields (a few hundred gauss), apparently slower kinetics can be expected and are indeed observed.[59]

---

(55) Hatlee, M. D.; Kozak, J. J. *J. Chem. Phys.* **1980**, *72*, 4358–4367.

(56) Hatlee, M. D.; Kozak, J. J.; Rothenberger, G.; Infelta, P. P.; Grätzel, M. *J. Phys. Chem.* **1980**, *84*, 1508–1519.

(57) Encinas, M. V.; Wagner, P. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 1357–1360.

(58) The slow component in the case of CTAC tends to show some decay (not entirely flat) even in this time scale. Conceivably, this may be due to traces of electron-acceptor impurities in the surfactant. In SDS (see ref 23 for representative traces), the slow component shows no decay in the submicrosecond time scale.

(59) No attempt is made to fit quantitatively the data in this intermediate (e.g., ~400 G) range, since the decay processes are clearly a combination of several different kinetic steps.

Table II. Summary of Kinetic and Escape Data for the Benzophenone Ketyl-Cyclohexadienyl Radical Pair at 27 °C

surfactant	field and carbonyl	k_{exptl}/ 10^6 s^{-1}	escape fraction, %
SDS (0.22 M)	0, ^{12}C	10.2 ± 0.5	43
SDS (0.22 M)	2000, ^{12}C	10.3 ± 0.7	73
SDS (0.22 M)	0, ^{13}C	11.2 ± 0.5	39
SDS (0.22 M)	2000, ^{13}C	10.6 ± 0.7	73
CTAC (0.05 M)	0, ^{12}C	3.3 ± 0.7	58
CTAC (0.05 M)	2000, ^{12}C	3.0 ± 1.0	81
CTAB (0.043 M)	0, ^{12}C	2.2 ± 1.0	61
CTAB (0.043 M)	2000, ^{12}C	3.0 ± 1.0	83

Table II summarizes the kinetic and escape data obtained under different experimental conditions. A few experiments using benzophenone-^{13}C in SDS have also been included. The effect of magnetic isotopes is quite small, as could be expected from the small value of the ^{13}C hyperfine coupling constant in the radical $Ph_2\dot{C}OH$ in comparison with other radicals (such as $Ph\dot{C}H_2$ or $PhCH_2\dot{C}O$)[60] in which magnetic isotope effects are considerably larger.[8]

It is interesting to note that the yield of radical escape that can be achieved at relatively high fields is limited by the model (see Scheme II) to the amount at zero field plus two-thirds of the difference with 100%. For example, in SDS micelles, in which 43% of the radical pairs undergo escape processes at zero field, only 81% at most could escape at high field.[61] The measured escape at 2000 G is 73%. A number of factors may contribute to make this yield lower than the theoretical value: i.e., the earth's magnetic field is not zero (which leads to overestimates of the theoretical value); the "plateau" may not be fully reached at 2000 G; hyperfine mechanisms[8] that could become of importance at high fields and when Δg is large may somewhat increase k_{ISC} from the T_0 level; some $Ph_2\dot{C}OH$ radicals may be lost in side reactions within the micelle; or the extinction coefficient of $Ph_2\dot{C}OH$ may be slightly different for the escape radicals. While all these effects are expected to be small, their composite effect may be responsible for the observed difference.

In the case of CTAC and CTAB micelles (see Figure 7), the theoretical limit is 86% escape and the observed value around 82%. In general, the data in this system are subject to considerably more error than in the case of SDS; this is due to the lower surfactant solubility, which requires lower benzophenone concentration to maintain low occupancy levels, and in the case of CTAB, part of the triplets are lost via bromide quenching, which also reduces the signal-to-noise ratio.

Dynamics of Radical Pairs in Micelles

To understand the behavior of the radical pairs presented in the previous three sections, one must realize that their generation under our experimental conditions occurs almost exclusively in the micellar aggregates. For benzophenone triplet in SDS, the ratio of entry (k_+) and exit (k_-) rate constants has been estimated as ~26 000 M^{-1}. Since for [SDS] = 0.22 M the micellar concentration is 3.4 × 10^{-3} M, one can estimate that only around 1% of the ketone triplets will reside in the aqueous phase. Aqueous photoprocesses seem unlikely to play a role in our experiments. In the case of CTAC and CTAB experiments, our surfactant concentrations were lower than for SDS, but the rates of exit from the micelle are known to be substantially smaller in CTAC and CTAB,[62] thus compensating for the decrease in micellar concentrations.

In the case of 1,4-cyclohexadiene, the values of the exit–entry parameters have not been reported, but if we assume them to be similar to those for 1,3-cyclohexadiene,[63] then about one-half of the molecules can be expected to be resident in the micelle. This does not in itself represent a complication, since the molecules of 1,4-cyclohexadiene play a role *only* when they react with a benzophenone triplet. The location of the latter will therefore determine the site where the radical pairs are generated. It should, however, be noted that if uncorrected occupancy levels for 1,4-cyclohexadiene are calculated directly from our data, they will be about twice the true value.

The radical pairs will then be generated in the highly polar intramicellar environment in which the ketone resides,[27–29,64] probably near the Stern layer, as suggested by de Mayo[10] and by the efficient quenching by bromide anions (see Table I). In the absence of added donors, the radical pair will consist of a ketyl radical and a surfactant-derived radical. The sum of exit rate constants for those two radicals in SDS will equal 7% of the rate of radical-pair decay, i.e., ~2 × 10^5 s^{-1}. Thus, the exit rate of 4.4 × 10^6 s^{-1} measured when 1,4-cyclohexadiene is added to the micelle must be almost entirely due to the exit of the cyclohexadienyl radical. The value compares well with values of 5.6 × 10^6 s^{-1} for 1,3-cyclohexadiene[63] and 4.4 × 10^6 s^{-1} for triplet benzene.[62,65] Fair agreement is also obtained in the case of CTAC micelles, where the exit rate of 1.6 × 10^{-6} s^{-1} compares well with the value of 7.5 × 10^5 s^{-1} reported for benzene in CTAB.[62]

The rate constants obtained for radical-pair intersystem crossing (ketyl–cyclohexadienyl) of 5.8 × 10^6 and 1.7 × 10^6 s^{-1} in SDS and CTAC, respectively, compare well with many biradical lifetimes obtained for Norrish type II biradicals in which similar radical centers are involved.[27,66,67] The values also agree well with the rate constant for intersystem crossing of 5.3 × 10^6 s^{-1} measured by Closs and Miller[68] for the biradical derived from 6,6-dimethyl-7,8,9,10-tetrahydro-5(6*H*)-benzocyclooctenone, in which the radical centers are located in 1,8 relative position. We were rather surprised by the parallel between the rates of escape and of intersystem crossing (CTAC and SDS) that lead to comparable values for the escape fraction in various surfactants (see Table II). At this point (with only two values), it is not clear whether this parallel is fortuitous or whether it simply reflects an increase in micellar volume from SDS to CTAC or CTAB.

The increase in LATs yields, observed in micellar solution and to some degree in polar solvents, must reflect the orientation of the ketyl radical and the solvation of the hydroxy group that combine to make the reaction at the ring positions more favorable.

LAT formation, while an interesting process in itself, is a complicating factor in the study of benzophenone photochemistry in micelles. For example, laser photolysis experiments monitored at 320 nm reflect LAT generation rather than the main photoprocesses taking place. In the absence of added hydrogen donors, triplet benzophenone in SDS micelles has a lifetime of ~320 ns, while the radical pair lives ~300 ns. When one considers that the triplet-state and the ketyl-radical spectra overlap extensively,[69] it seems essential to take into consideration these effects to properly understand the behavior of each species.

Finally, it seems reasonable to assume that, while quantitatively different, the same type of qualitative effects could be expected in other organized systems such as microemulsions, vescicles, membranes, liquid crystals, or cells. Therefore, it seems important to emphasize that in systems involving the generation of radical pairs, magnetic fields could be dominant factors in determining the dynamics and mechanisms involved; if one considers that

---

[60] Berndt, A.; Fischer, H.; Paul, H. In "Magnetic Properties of Free Radicals", Part B; Fischer, H., Hellwege, K. H., Eds.; Springer-Verlag, Berlin, 1977; Sections 3.2.3, 4.4.4.1, and 4.7.2.2.3.

[61] I.e., 43 + $^2/_3$(100 − 43) = 81.

[62] Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279–291.

[63] Selwyn, J. C.; Scaiano, J. C. *Can. J. Chem.* **1981**, *59*, 663–668.

[64] Menger, F. M.; Bonicamp, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 2140–2141.

[65] Turro et al.[31] have proposed that processes that take place in the 10^{-4} s time scale and involve $Ph\dot{C}H_2$ radicals in CTAC micelles do not compete with exit from the micelle. The apparent inconsistency with our results may be due to an overestimation of the radical scavenging ability of Cu^{2+} ions. Our own experiments indicate that the reaction of $Ph\dot{C}H_2$ and Cu^{2+} in water is substantially slower than diffusion controlled: Ferraudi, G. F.; Scaiano, J. C., unpublished work.

[66] Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126–2136.

[67] Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970.

[68] Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3586–3588.

[69] For example, see: Topp, M. R. *Chem. Phys. Lett.* **1975**, *32*, 144–149.

magnetic fields are frequently applied in studies employing NMR spectroscopy, EPR techniques, or even magnetic stirrers, the evaluation of these effects seems of critical importance.

Experimental Section

Materials. Benzophenone (Aldrich) was recrystallized twice from ethanol; benzophenone-^{13}C (carbonyl ^{13}C), 90% isotopic purity from Merck Sharp and Dohme, was used as received. 1,4-Cyclohexadiene (PCR) was chromatographed on alumina and distilled twice. Gas chromatography showed that it was free from 1,3-cyclohexadiene and benzene; low yields of formation of the latter were observed in the experiments described in this paper. Sodium dodecyl sulfate, SDS (BDH, specially purified), was used as received. Cetyltrimethylammonium chloride, CTAC, was obtained as a 50% solution from K & K and precipitated with acetone. Repeating this procedure did not seem to affect the benzophenone triplet lifetimes. Cetyltrimethylammonium bromide (CTAB) from BDH was used as received.

Steady-State Photolysis. All irradiations were carried out under oxygen-free conditions and by using the same sample cells as in the laser experiments (see below). A Hanovia 150-W Xe/Hg lamp installed in a Bausch & Lomb housing was used for these experiments. Two different magnets were employed: one was a Varian system capable of fields of up to 20 000 G. The other was a home-built magnet capable of fields of up to 2500 G. Both were calibrated by using a Varian E-500 NMR gaussmeter. In both systems the lamp was located 50–80 cm from the center of the magnet. In the high-field system we observed that there was enough leakage to substantially affect the arc in the lamp. A screen was placed past the cell holder and behind the magnet, so as to have a clear projection of the cell and cell holder. We found that frequently this image would reveal dramatic changes in the beam shape and alignment. When this was the case, reversing the field direction would modify substantially the LAT yields measured. We found that the simplest practical solution to this problem (in addition to supplementary magnetic shielding in the lamp housing) was to locate small permanent magnets near or attached to the housing, so that their effect would override any changes due to leakage. In addition, the screen mentioned before provided the means for a simple visual check. Experiments at high fields were always repeated reversing the field direction.

UV spectra were recorded on a Varian 219 spectrophotometer.

Laser Flash Photolysis. The samples, usually 1 or 2 mL, were contained in Suprasil cells made of rectangular (3 × 7 mm) tubing. Oxygen-free nitrogen was used to deaerate the solutions. A Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, up to 10 mJ) was used to excite the samples. Transient absorptions were monitored by using a detection system with nanosecond response. The signals, initially acquired by an R-7912 Tektronix transient digitizer, were processed by a PDP-11/03L computer, which also controlled the experiment and provided suitable storage and hard-copy facilities. Further details have been reported elsewhere.[70] Experiments in a magnetic field were carried out with the home-built magnet mentioned before.

Acknowledgment. Thanks are due to Dr. A. Braun and Professor N. J. Turro for the communication of unpublished results and for valuable discussions, to S. E. Sugamori for his technical assistance, and to Drs. D. F. Williams, J. Park, and A. H. Reddoch for their help with the use and calibration of the magnets.

Registry No. SDS, 151-21-3; CTAB, 57-09-0; CTAC, 112-02-7; $(C_6H_5)_2\dot{C}OH$, 4971-41-9; benzophenone, 119-61-9; bromide, 24959-67-9; 1,4-cyclohexadiene, 628-41-1.

---

(70) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753.

Enthalpies of Formation of Fused Cyclobutane Derivatives

Kenneth B. Wiberg*[1a] and John J. Wendoloski[1b]

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511, and the National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. *Received January 25, 1982*

Abstract: The energies of 1,2- and 1,3-bridged cyclobutanes have been calculated with several basis sets. The differences in energy between isomeric compounds are essentially constant when extended basis sets (6-31G* and 6-31G**) are used. The geometries of the compounds are discussed, and it is concluded that the published structure for bicyclo[2.1.1]hexane must be incorrect. The only unusual geometries are found for *trans*-bicyclo[2.2.0]hexane and "windowpane". The enthalpies of formation are estimated on the basis of the calculated energies along with zero-point energies and the change in enthalpy from 0 to 298 K. The strain energies derived from these results are discussed in the context of the reactions of the compounds.

Cyclobutane derivatives have been of considerable interest with regard to the mechanisms of thermal cleavage of hydrocarbons,[2] the Cope rearrangement,[3] the factors that lead to accelerated solvolysis rates,[4] and the potential function for bond angle deformation.[5] Most of these studies require a knowledge of the enthalpies of formation of the compounds. These data are available for cyclobutane[6] and for some of its derivatives such as cyclobutene[7] and bicyclo[1.1.0]butane.[7] The enthalpies of hydrogenation of bicyclo[2.1.0]pentane and bicyclo[2.2.0]hexane have been determined,[8] and from these data the enthalpies of formation may be obtained. However, such data are not available for most of the compounds in which cyclobutane is fused onto another ring. Some molecular mechanics calculations have been carried out,[9-13] but one cannot be sure that the parameters used are appropriate for compounds that have relatively unusual bond angles. Similarly, some ab initio SCF calculations[14,15] have been

---

(1) (a) Yale University. (b) NRCC. Present address: Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, DE.

(2) Benson, S. "Thermochemical Kinetics"; Wiley-Interscience: New York, 1976. Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981.

(3) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 6268.

(4) Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III. *Carbonium Ions* **1972**, *3*, 1295.

(5) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 1212.

(6) Kaarsemaker, S.; Coops, J. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 261.

(7) Wiberg, K. B.; Fenoglio, R. *J. Am. Chem. Soc.* **1968**, *90*, 3395.

(8) Roth, W. R.; Klarner, F.-G.; Lennartz, H.-W. *Chem. Ber.* **1980**, *113*, 1818.

(9) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.

(10) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.

(11) Baas, J. M. A.; van de Graaf, B.; van Rantwijk, F.; van Veen, A. *Tetrahedron* **1979**, *35*, 421.

(12) Wiberg, K. B.; Olli, L. K. *J. Am. Chem. Soc.* **1980**, *102*, 7467.

(13) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

(14) For general reviews of the application of molecular orbital theory to cyclobutane derivatives, see: Newton, M. D. *Mod. Theor. Chem.* **1977**, *4*, 223. Greenberg, A.; Liebman, J. F. "Strained Organic Molecules", Academic Press: New York, 1978.

(15) Bicyclo[1.1.1]pentane: Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773. Whitman, D. R.; Chiang, J. F. *Ibid.* **1972**, *94*, 1126. Lehn, J.-M.; Wipff, G. *Chem. Phys. Lett.* **1972**, *15*, 450. Bicyclo[2.1.1]hexane: Lehn, J.-M.; Wipff, G. *Theor. Chim. Acta* **1973**, *28*, 223. Bicyclo[2.1.0]pentane (4-21G with geometry optimization): Van Alsenoy, C.; Scarsdale, J. N.; Schäfer, L. *J. Chem. Phys.* **1981**, *74*, 6278.