On the Mechanism of Photocycloaddition of Thiobenzophenone at 366 nm[1]

P. de Mayo* and H. Shizuka[2]

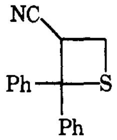
Contribution from the Photochemistry Unit, Department of Chemistry, The University of Western Ontario, London N6A 3K7, Ontario, Canada.

Received December 14, 1972

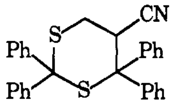
Abstract: The photocycloaddition of thiobenzophenone to acrylonitrile at 366 nm has been studied kinetically. The quantum yields for thietane formation decreased with increasing the concentration of thiobenzophenone and increased with increasing the concentration of acrylonitrile. It has been shown, using biacetyl quenching, that the reactive state at 366 nm is the second excited (π,π^*) singlet. Its lifetime is the order of magnitude of 10^{-11} sec. It has been found that the 1,3-dithiane is the only intermediate to give the thietane under the experimental conditions used ($0.5 \geq [S_0] \geq 0.05$ *M*), and that the energy wasting process partly responsible for the low quantum yields was the reaction of the immediate precursor for 1,3-dithiane formation with the ground state of thiobenzophenone.

The study of aromatic ketones dates back to the earliest days of organic photochemistry and has continued with increasing enthusiasm for the last 50 years. In contrast, the corresponding thioketones have, until recently, been virtually ignored. Nonetheless such compounds and their alicyclic equivalents do give rise to many interesting reactions: photocycloaddition,[3-6] photocyclization,[7] photodimerization,[5a,8] photooxidation, and photoreduction.[9]

Ohni, Tsuchihashi, and their coworkers reported that the photoaddition of thiobenzophenone to acrylonitrile induced by excitation in the π,π^* band (366 nm) yielded a thietane (**1**), but that at longer wavelength, that is by excitation through the n,π^* band, no reaction was observed.[4a] Our own studies confirmed the obtention of **1** in high yield at short wavelength, but showed, further, that the thietane (**1**) was not the primary product, but derived from the thermal breakdown of the unstable 1,3-dithiane (**2**).[5] Under such circumstances, arguments deriving from the stereospecificity in the addition which were used to support the contention that the reaction was a singlet process required reinterpretation.[4a] We were also able to show that products were obtained by irradiation at long wavelength (>500 nm) and that these products, the 1,4-dithiane (**3**) and the thiatetrahydronaphthalene (**4**), were different from those obtained at short wavelength.



1



2

Support for the hypothesis that the short wavelength excitation led to the reaction of the second excited singlet of thiobenzophenone was forthcoming from Liu and Ramamurthy.[10] These authors showed that the quantum yield of addition appeared to decrease with increased thiobenzophenone concentration, and interpreted this phenomenon as being due to S_2–S_0 energy transfer and quenching. At the concentrations of thiobenzophenone used, this implied an exceptionally long lifetime for the S_2 state of thiobenzophenone, but such seemed not excluded *a priori* because of the very large energy gap (~50 kcal/mol) between the π,π^* and n,π^* states.

In any event, no detailed kinetic study of any aromatic thione reaction having been previously reported, we have investigated the reaction in some detail with the expectation that these observations will have a general significance for the photochemistry of these types of compounds. As will be seen, the results indicate several, and important, differences from the now reasonably well-understood behavior of aromatic ketones. Our studies on the mechanism of the reaction at long wavelength will be reported presently.

Experimental Section

Materials. Thiobenzophenone was prepared by the procedure reported by Aberles, *et al.*[11] Acrylonitrile was purified by distillation. Ether was an analytical reagent grade product of Mallinckrodt Chemical Works and was used without further purification. Biacetyl was purified by fractional distillation.

Radiation Source and Actinometry. A high-pressure Hg resonance lamp (a HBO 200-W lamp) was used as the 366-nm radia-

---

(1) Photochemical Synthesis. 49. This is the ninth in a sequence on thione photochemistry. Publication No. 66 from the Photochemistry Unit, The University of Western Ontario.

(2) On leave from Gunma University, Kiryu, Gunma, Japan.

(3) (a) E. T. Kaiser and T. F. Wulfers, *J. Amer. Chem. Soc.*, **86**, 1897 (1964); (b) K. Yamada, M. Yoshioka, and N. Sugiyama, *J. Org. Chem.*, **33**, 1240 (1968).

(4) (a) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 161 (1969); *J. Amer. Chem. Soc.*, **91**, 5038 (1969); (b) A. Ohno, Y. Ohnishi, M. Fukuyama, and G. Tsuchihashi, *ibid.*, **90**, 7038 (1968); (c) A. Ohno, T. Koizumi, T. Ohnishi, and G. Tuschihashi, *Tetrahedron Lett.*, 2025 (1970); (d) A. Ohno, N. Kito, and T. Koizumi, *ibid.*, 2421 (1971); (e) A. Ohno, T. Koizumi, and Y. Ohnishi, *Bull. Chem. Soc. Jap.*, **44**, 2511 (1971).

(5) (a) D. R. Kemp, A. H. Lawrence, C. C. Liao, R. O. Loutfy, P. de Mayo, A. A. Nicholson, and S. Paszyc, *Pure Appl. Chem.*, Plenary Lectures, IUPAC (Boston), 367 (1971); (b) P. de Mayo and A. A. Nicholson, *Isr. J. Chem.*, **20**, 341 (1972); (c) P. de Mayo and H. Shizuka, unpublished results.

(6) (a) H. J. T. Bos, H. Schinkel, and Th. C. M. Wijsman, *Tetrahedron Lett.*, 3905 (1971); (b) H. Gotthardt, *ibid.*, 2345 (1971); (c) H. Gotthardt, *Chem. Ber.*, **105**, 2008 (1972).

(7) R. Lapouyade and P. de Mayo, *Can. J. Chem.*, **50**, 4068 (1972).

(8) C. C. Liao and P. de Mayo, *Chem. Commun.*, 1525 (1971).

(9) (a) G. Oster, L. Citarel, and M. Goodman, *J. Amer. Chem. Soc.*, **84**, 703 (1962); (b) N. Kito and A. Ohno, *Chem. Commun.*, 1338 (1971); (c) D. R. Kemp and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 233 (1972).

(10) R. S. H. Liu and V. Ramamurthy, *Mol. Photochem.*, **3**, 261 (1971).

(11) R. H. Aberles, R. F. Hulton, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **79**, 712 (1957).

Table I. Quantum Yields for the Thietane Formation at 366 nm

Run no.	Thiobenzophenone concn, *M*	Acrylonitrile[a] concn, *M*	Irradiation temp, °C	Irradiation time, hr	Thietane concn × 10^3 *M*	Conversion, %	Φ_0^E
1	0.05	7.6	30	2	7.4_5	15	0.077 ± 0.005
2	0.05	7.6	−70	2	5.1_0	10	0.053 ± 0.004
3	0.1	7.6	30	1	3.2_0	3.2	0.066 ± 0.004
4	0.1	7.6	30	2	6.3_7	6.4	0.066 ± 0.004
5	0.1	7.6	30	3	9.6_0	9.6	0.066 ± 0.004
6	0.1	7.6	−70	2	4.4_4	4.5	0.045 ± 0.003
7	0.1	7.6	30	2	6.5_6	6.6	0.067 ± 0.004
8	0.1	7.6	−70	2	4.5_4	4.5	0.046 ± 0.003
9	0.2	7.6	30	2	4.7_3	2.4	0.049 ± 0.003
10	0.2	7.6	−70	2	3.1_8	1.6	0.031 ± 0.003
11	0.3	7.6	30	2	3.8_7	1.3	0.040 ± 0.003
12	0.3	7.6	−70	2	2.2_2	0.74	0.023 ± 0.003
13	0.4	7.6	30	2	3.0_9	0.77	0.033 ± 0.003
14	0.4	7.6	−70	2	1.6_4	0.41	0.018 ± 0.003
15	0.4	7.6	30	3	4.1_0	1.0	0.033 ± 0.003
16	0.5	7.6	30	2	2.8_0	0.56	0.029 ± 0.003
17	0.1	15.2	30	1	4.6_5	4.6_5	0.096 ± 0.006
18	0.1	7.6	30	2	6.4_0	6.4_0	0.066 ± 0.004
19	0.1	4.34	30	4	8.1_2	8.1_2	0.042 ± 0.003
20	0.1	2.54	30	5.25	7.3_5	7.3_5	0.029 ± 0.002

[a] Ether solution.

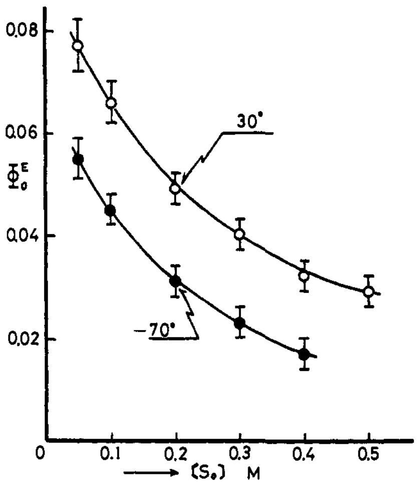


Figure 1. The quantum yields for the thietane formation Φ_0^E at 366 nm in ether as a function of the concentration of thiobenzophenone $[S_0]$, where [A] = 7.6 *M*.

tion source with Corning glass filters (CS-52 and CS-7-60). A merry-go-round irradiation apparatus was also used in the measurements of biacetyl quenching at 366 nm. The cells were enclosed and exposed to the light only through narrow center slits.

Actinometry at 366 nm was carried out using a ferric oxalate solution.[12]

Degassing Procedure and Product Analysis. The solutions were made up in a nitrogen glove box and were thoroughly degassed on a high-vacuum line to less than 5×10^{-5} Torr residual pressure by the freeze-pump-thaw method. The photoproduct (**1**) at 366 nm was quantitatively measured by vapor phase chromatography. The vpc apparatus (a UNILAB 400) was used with a 3% poly-A glass column, with injection temperature 240°, column temperature 190°, and helium pressure 7.5 psi. Flavone was used as the calibrating standard compound in the measurements of vpc. With irradiations conducted at low temperature, time was allowed[5] for the conversion of **2** to **1**.

Results

Quantum Yields for the Thietane Formation at 366 nm. Table I shows the quantum yields for the thietane formation in ether at 366 nm, at 30 and −70°. The quantum yields did not change with variation of the irradiation time in the initial stages of the reaction. However, the quantum yields at 366 nm depended considerably upon the initial concentration of the ground state of thiobenzophenone, $[S_0]$, and of acrylonitrile, [A]. The quantum yield at 30 and −70° decreased with increasing $[S_0]$, when [A] was maintained at 7.6 *M*, as shown in Figure 1. Figure 2 shows the quantum yields of thietane formation at 366 nm and 30° as a function of [A], where $[S_0]$ was maintained constant at 0.1 *M*. The values of Φ increased with increasing [A].

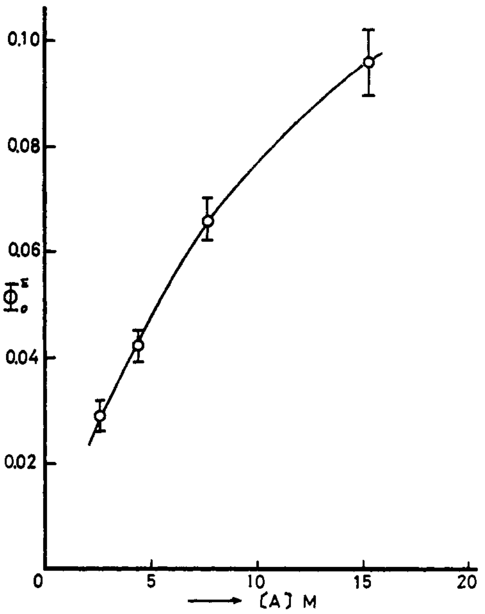


Figure 2. The quantum yields Φ_0^E at 366 nm and 30° in ether as a function of the concentration of acrylonitrile [A], where $[S_0]$ = 0.1 *M*.

Biacetyl Quenching at 366 nm. The quantum yield of thietane was measured at varying biacetyl concentrations using concentrations of 0.1 *M* for thiobenzo-

---

(12) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

phenone and 7.6 *M* for acrylonitrile in ether at 30°. The results are listed in Table II. The quantum yields for the reaction decreased with increasing biacetyl concentration, [B]. It was unfortunately not possible to detect the induced fluorescence from biacetyl because of reabsorption by ground-state thiobenzophenone.[13]

Table II. Biacetyl Quenching at 366 nm and 30°[a,b]

[Biacetyl]	Φ_0/Φ
0	1.0
0.0594	1.02 ± 0.02
0.119	1.04 ± 0.02
0.238	1.07 ± 0.03
0.475	1.18 ± 0.04
0.950	1.33 ± 0.05

[a] $[S_0]$ = 0.4 *M* and [A] = 7.6 *M*. [b] The light absorbed by biacetyl was less than 1% of total incident light.

Solvent Dependence of Thietane Quantum Yield. The quantum yields were measured in a variety of solvents (Table III); very little variation was observed.

Table III. Quantum Yield of Thietane in Various Solvents at 366 nm and 30° [a]

Solvent	Φ_{thietane}	Dielectric constant of solvent
Cyclohexane	0.075 ± 0.006	2.02[b]
Benzene	0.060 ± 0.005	2.28[b]
Ether	0.066 ± 0.004	4.34[b]
CH_3OH	0.058 ± 0.007	32.63[b]
CH_3CN	0.076 ± 0.006	38.8[c]
$CH_2{=}CHCN$ neat	0.096 ± 0.005	

[a] $[S_0]$ = 0.1 *M* and [A] = 7.6 *M*. [b] "Handbook of Chemistry and Physics," Chemical Rubber Co., Cleveland, Ohio, 1969. [c] "The Merck Index," Merck and Co., Rahway, N. J., 1960.

Discussion

Excitation into S_2 of thiobenzophenone leads to products, as mentioned which are different from those obtained from excitation into S_1 (n,π*). We have shown the latter to be derived from the lowest triplet state of the thione.[5c] We have shown that at −78° the (S_2) primary product is the 1,3-dithiane[5b] (**2**) and that at room temperature this decomposes quantitatively to generate the thietane and one molecule of thiobenzophenone. For reasons outlined below, we believe that the reaction at room temperature follows the same pathway.

Our observations at 366 nm appear to require the following extensive, but minimum, set of equations

$$S_0 + h\nu\ (366\ \text{nm}) \longrightarrow S_2 \tag{0}$$

$$S_2 \xrightarrow{k_1} \longrightarrow S_0 \tag{1}$$

$$S_2 + A \longrightarrow M_1 \tag{2}$$

$$S_2 + S_0 \xrightarrow{k_3} \longrightarrow 2S_0 \tag{3}$$

$$S_2 + B_0 \longrightarrow S_0 + B_1 \tag{4}$$

$$M_1 + S_0 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} M_2 \xrightarrow{k_5'} \longrightarrow 2S_0 + A \tag{5}$$

$$M_1 \longrightarrow \mathbf{1} \tag{6}$$

$$M_1 \longrightarrow S_0 + A \tag{7}$$

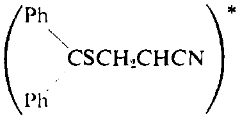
$$M_2 \longrightarrow \mathbf{2} \tag{8}$$

$$\begin{aligned} M_2 + S_0 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} M_3 \longrightarrow & \xrightarrow{k_9'} \longrightarrow 3S_0 + A \\ & \llcorner\!\xrightarrow{k_9''[S_0]} 4S_0 + A \end{aligned} \tag{9}$$

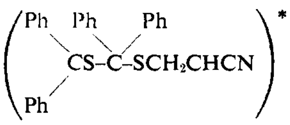
$$\mathbf{2} \longrightarrow \mathbf{1} + S_0 \tag{10}$$

where S_0 and S_2 are the ground state and second excited singlet state of thiobenzophenone, A is the ground state of acrylonitrile. B_0 and B_1 refer to the ground state and first singlet of biacetyl, and M_1, M_2, and M_3 are singlets of the type

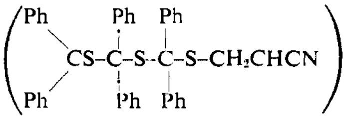
M_1:



M_2:



M_3:



with no commitment as to the electron distribution. Equation 6 is included for the sake of formality because, we believe, under our conditions (0.5 ⩾ $[S_0]$ ⩾ 0.05 *M*[5b,c]), $K_6 \ll k_5[S_0]$ since we are unable to detect direct thietane formation at low temperature. It was in principle possible that the reaction might proceed differently at room temperature, but the parallel effects of concentration variation at the two temperatures, 30 and −70°, shown in Figure 1 lead us to conclude that such is not the case.

Equation 1 requires further explanation. The decay of S_2 is, presumably, to S_1. The latter will react or decay or intersystem cross, of course, in the same manner as if generated directly. However, *since the quantum yields of products from T_1 derived from S_1 are of the order of 1% of those from S_2,*[5c] *under the conditions of the experiment we would not observe any products derivable from S_1*, although they are, no doubt, formed. Hence decay of S_2, though probably *via* S_1, is a nonproduct forming process.

The intermediate, M_2, is required for the obtention of **2**, but the inclusion of M_3 may require some comment. It will be seen shortly that some energy wasting step is required. Our results will show that eq 3, the quenching process postulated by Liu and Ramamurthy,[10] while extant, is insufficient to explain the rather strong quenching. This is, of course, because of the very short lifetime of S_2, and this short lifetime may be judged directly by the massive concentrations of biacetyl needed to induce quenching. Since the concentrations of thiobenzophenone are lower, eq 3 cannot be expected to be very important. Some other species must, then, be trapped and the most likely species is M_2. It is, of course, implied that there may be an M_4, M_5 present in decreasing concentrations, but the result is kinetically indistinguishable from the present representation.

---

[13] (a) P. Brocklehurst and A. Burawoy, *Tetrahedron*, **10**, 118 (1960); (b) O. Korver, J. U. Veenland, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **81**, 1031 (1962); *ibid.*, **84**, 289 (1965).

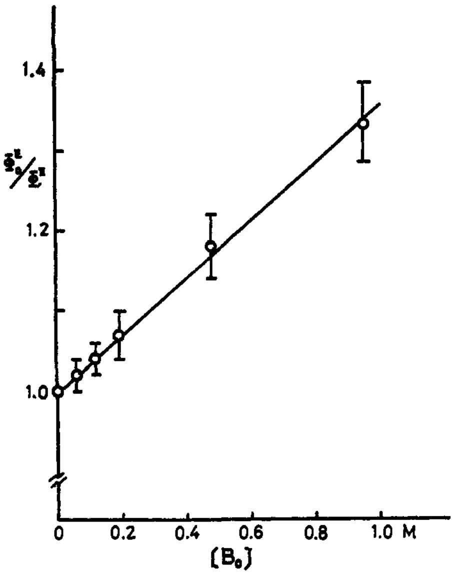


Figure 3. The Stern–Volmer plot of Φ_0^E/Φ^E *vs.* the concentration of biacetyl, $[B_0]$.

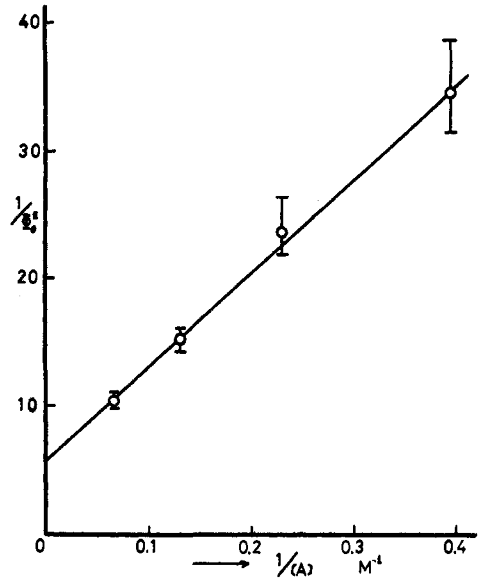


Figure 4. Plot of $1/\Phi_0^E$ *vs.* [A].

Using the usual steady-state approximation, the quantum yield of thietane formation is given by expression

$$\Phi = \frac{k_2[A]}{K_1 + K_2[A] + K_3[S_0] + k_4[B_0]} f(S_0) \quad (11a)$$

where $f(S_0)$ is defined in eq 11b. The corresponding

$$f(S_0) = \frac{k_5[S_0]}{k_5[S_0]\left(1 - \dfrac{k_{-5}}{k_{-5} + k_5' + k_8 + k_9[S_0] \times \{1 - k_{-9}/(k_{-9} + k_9' + k_9''[S_0])\}}\right) + k_6 + k_7} \times \left(\frac{k_8}{k_{-5} + k_5' + k_8 + k_9[S_0] \times \{1 - k_{-9}/(k_{-9} + k_9' + k_9''[S_0])\}}\right) \quad (11b)$$

Stern–Volmer equation is therefore

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_4[B_0]}{k_1 + k_2[A] + k_3[S_0]} = 1 + k_4\tau_{S_2}[B_0] \quad (12)$$

where τ_{S_2} denotes the lifetime of S_2 in the absence of biacetyl and at concentration $[S_0]$ of thiobenzophenone

$$\tau_{S_2} = 1/(k_1 + k_2[A] + k_3[S_0])$$

and Φ_0 is the quantum yield for thietane formation in the absence of biacetyl.

It may be seen that the Stern–Volmer plot of biacetyl quenching (Figure 3) shows good linearity up to the highest concentration utilizable. The value of the quenching constant, $k_4\tau_{S_2}$, is determined from the slope in Figure 3

$$k_4\tau_{S_2} = 0.34\ M^{-1} \quad (13)$$

where $[S_0] = 0.1\ M$ and $[A] = 7.6\ M$ at 30°.

The lifetime measurements for the excited singlet states of organic compounds have been reported by, among others, Dubois, *et al.*[14] They have shown that electronic energy transfer from the excited singlet state of a donor molecule, resulting in the excitation of a singlet level of an acceptor molecule, is diffusion controlled, when an acceptor having a low extinction coefficient, such as biacetyl, is used. Under these conditions, the long-range singlet–singlet energy transfer due to dipole–dipole interaction of the transferring species may be avoided. The excited singlet lifetimes of diphenylamines, for instance, have been estimated by this method.[15] If it be assumed that in this system the energy transfer to biacetyl to generate the n,π* singlet (64 kcal/mol) is also diffusion controlled, then this may be approximated using the modified Debye equation.[16]

It is assumed, here, that biacetyl is, indeed, acting only by an energy transfer quenching process. Interaction with another intermediate such as M_1 in an unspecified way could lead to similar observations, and hence to a misinterpretation of lifetimes. Since we have no reason to suspect the existence of such a process we have, with the above understanding, interpreted our observations as indicated in eq 4.

From eq 13 under the concentration conditions specified

$$\tau_{S_2} = 3.1 \times 10^{-11}\ \text{sec} = 1/(k_1 + k_2[A] + k_3[S_0]) \quad (14)$$

The reciprocal of the quantum yield, from eq 11, may be expressed as

$$\Phi^{-1} = \frac{1}{f(S_0)}\left[1 + \frac{k_1 + k_3[S_0]}{k_2[A]}\right] \quad (15)$$

and a plot of Φ^{-1} *vs.* $[A]^{-1}$ with $[S_0]$ constant should be linear. That this is so is seen in Figure 4 for a concentration of 0.1 *M* thiobenzophenone. In this curve

---

[14] (a) J. T. Dubois and M. Cox, *J. Chem. Phys.*, **38**, 2536 (1963); (b) F. Wilkinson and J. T. Dubois, *ibid.*, **39**, 377 (1963); (c) J. T. Dubois and R. L. V. Hemert, *ibid.*, **40**, 923 (1964).

[15] H. Shizuka, Y. Takayama, I. Tanaka, and T. Morita, *J. Amer. Chem. Soc.*, **92**, 7270 (1970).

[16] (a) P. Debye, *Trans. Electrochem. Soc.*, 82, 265 (1942); (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1967, p 626. The modified Debye equation is given by $k_{\text{diff}} = 8RT/3000\eta$, where k_{diff} is in units of M^{-1} sec^{-1} when η, the viscosity of the solvent, is in units of poise. The value of k_{diff} for 7.6 *M* acrylonitrile in ether at 30° was $1.14 \times 10^{10}\ M^{-1}$ sec^{-1} where η was equal to 0.262 cP.

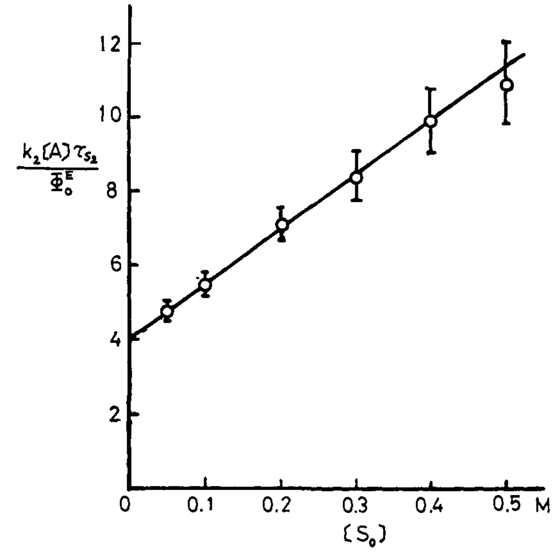


Figure 5. Plot of $k_2[A]\tau_{S_2}/\Phi_0^E$ *vs.* $[S_0]$.

the slope and intercept are respectively

$$(k_1 + 0.1k_3)/k_2f(0.1) = 73\ M \qquad (16)$$

and

$$1/f(0.1) = 5.6 \qquad (16')$$

Substitution of (16′) in (16) gives

$$k_1 + 0.1k_3 = 13.1k_2 \qquad (17)$$

from (14)

$$k_2 = 1.55 \times 10^9\ M^{-1}\ \text{sec}^{-1} \qquad (18)$$

and

$$k_1 + 0.1k_3 = 2.13 \times 10^{10}\ \text{sec}^{-1} \qquad (19)$$

The self-quenching process in eq 3 should also, as in the case of biacetyl, be diffusion controlled, whence with this assumption k_1 can be estimated as $\sim 2.0 \times 10^{10}$ sec^{-1} giving the lifetime of the second excited singlet of thiobenzophenone in the absence of self-quenching as $\sim 5.0 \times 10^{-11}$ sec.

The interpretation of eq 18 is certainly not clear. It is expressed in terms of a bimolecular rate constant in the same way as when two species migrate toward each other and subsequently react. However, at the concentration of olefins used (necessary because of the short lifespan of the excited state) there is always a molecule of olefin in the nearest neighbor relationship to the excited thioketone. It may, thus, be more meaningful to interpret the rate as indicating an orientation probability. The implication would then be that only certain specific mutual orientations lead to reaction, and that with greater accumulation of olefin molecules about the excited thione there is a correspondingly greater probability of one having the desired orientation. With this uncertainty, which regards the existence of contact complexes in the ground state (complexes having essentially no binding energy and no perturbed absorption spectra), the precise interpretation of eq 18 escapes us, and we are left with a disquieting fuzziness.

We have ignored the possibility of the excitation of a ground-state complex with binding energy to an excited complex. Whilst we have no direct method for excluding this possibility there was no spectroscopic evidence in favor of it. However, it appears reasonable that such association would be dependent on the dielectric constant of the medium,[17] and, as may be seen by inspection of Table III no relationship, and very little effect, was obtained with solvent changes.

The lifetime of thiobenzophenone here obtained is very much shorter than that reported for azulene which is 1.4×10^{-9} sec^{-1}.[18] In the latter substance the S_2–S_1 energy separation is about 40 kcal/mol, about 10 kcal/mol less than thiobenzophenone. A number of reasons may be adduced for this shorter lifetime than azulene, but longer than normal aromatic hydrocarbons. These include the important difference that the lowest state of thiobenzophenone is n,π^* in contrast to the π,π^* of azulene, and that the intersystem crossing process may be enhanced by the presence of the heavy atom. The effects of self-quenching by ground-state thione on the lifetime may be seen in Table IV.

Table IV. Estimated Values of τ_{S_2}[a]

$[S_0]$	$\tau_{S_2} \times 10^{11}$ sec	$[S_0]$	$\tau_{S_2} \times 10^{11}$ sec
0	3.14	0.3	2.84
0.05	3.09	0.4	2.75
0.1	3.04	0.5	2.67
0.2	2.93		

[a] [A] = 7.6 *M* at 30°.

It is of interest to pursue the energy wasting processes a little further with the kinetic situation here described. From the lowness of the quantum yields one interpretation is that $k_q[S_0] \gg k_{-5}$ and k_5'. They represent the nonuseful ways of disposing of M_2. If this be assumed, and that M_3 has little tendency to regenerate M_2, *i.e.*, $k_9''[S_0] + k_9' \gg k_{-9}$ where $0.5 \geq [S_0] \geq 0.05\ M$, then we obtain from eq 11 that

$$\frac{k_2[A]\tau_{S_2}}{\Phi} = \left(1 + \frac{k_7}{k_5[S_0]}\right)\left(1 + \frac{k_{-5} + k_5'}{k_8} + \frac{k_q[S_0]}{k_8}\right) \qquad (20)$$

Now a plot of $k_2[A]\tau_{S_2}\Phi^{-1}$ against $[S_0]$, as may be seen in Figure 5, shows good linearity. This suggests that $k_5[S_0] \gg k_7$ and, if so, we may obtain from the slope of Figure 5 the ratio of k_9 to k_8 as 15 M^{-1}. On the other hand, the intercept gives the ratio of the sum of $k_5' + k_{-5}$ to k_8 as 3. We would not wish to press this analysis further since other assumptions might also lead to the pseudolinearity shown in Figure 5.

In summary, the foregoing evidence appears persuasive that in thiobenzophenone we do have an intermolecular reaction of a second excited singlet state. No such equivalent exists unequivocally established in carbonyl photochemistry. This may well be no more than a consequence of the longer lifetime of S_2, and even so very high concentrations of olefin are necessary to observe reaction. The complexity of the mechanism and of kinetics, however, have presumably nothing to do with the excited state involved since eq 3 is not important at usual concentrations of thioketones. They derive from the fact (an important

[17] See, for example, H. Bouas-Laurent and R. Lapouyade, *Chem. Commun.*, 817 (1969).

[18] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 103.

difference from ketones) that thiobenzophenone and presumably other thiones are excellent radical traps.[19]

We have observed the same phenomenon on long wavelength irradiation of the thiobenzophenone–acrylonitrile system,[5c] and there are indications[5a] that the same may be true for alicyclic thiones also.

---

(19) G. Tsuchihashi, M. Yamauchi, and A. Ohno, *Bull. Chem. Soc. Jap.*, **43**, 968 (1969).

Photochemical Ring Expansion of Cyclic Aliphatic Ketones. Cyclobutanones and Cyclopentanones[1a]

Douglas R. Morton[1b] and Nicholas J. Turro*

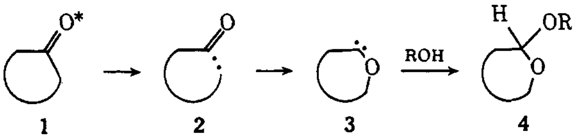
Contribution from the Department of Chemistry, Columbia University, New York, New York 10027.

Received November 6, 1972

Abstract: The solution phase photochemical transformations of several substituted cyclobutanones and cyclopentanones are described with emphasis placed on the mechanism and scope of the photochemical ring expansion reaction. For cyclobutanone, ring expansion appears to be a singlet state reaction, and the extent to which it occurs is found to depend upon the nature and position of substituents on the four-membered ring (Table I). For example, the following yields of ring-expanded acetals are obtained from the designated ketones in methanol: 2,2-bis(trifluoromethyl)-3-phenylcyclobutanone (0%); cyclobutanone (8%); 2,2-dimethyl-3-phenylcyclobutanone (82%); 2-isopropylidenecyclobutanone (100%). The results can be interpreted in terms of an intermediary oxacarbene in equilibrium with a singlet biradical (Scheme II). For monocyclic cyclopentanones, ring expansion is only observed for spiro[2.4]heptan-4-one (**56**). Quantum yield and kinetic and product analyses demonstrate that ring expansion for **56** is a triplet state reaction. These results suggest that substituents capable of stabilizing the oxacarbene intermediate favor ring expansion.

During the past several years, considerable research effort has been directed toward an understanding of the chemistry of electronically excited aliphatic ketones, both acyclic and alicyclic.[2] Analysis of the data obtained from this research has revealed that aliphatic ketones are capable of undergoing four general types of reactions in condensed media:[3] (1) photoreduction, (2) cycloaddition to olefins, (3) intramolecular photoreduction or type II cleavage,[4] and (4) α cleavage or type I cleavage. The latter two processes are unimolecular reactions of electronically excited ketones and, as such, are capable of producing isomeric and fragmentation products. For cyclic aliphatic ketones, in particular, the α-cleavage reaction is known to give rise to products of decarbonylation in addition to products of intramolecular disproportionation (acyclic aldehydes and ketenes). In the case of cyclobutanones, β cleavage (fragmentation to form olefin and ketene products) is a commonly observed reaction. In special cases, another type of reaction, photochemical ring expansion, is also observed, and it is this reaction upon which we focus our attention in the present investigation.

Perhaps because of the rarity of its occurrence, the photochemical ring expansion reaction is one of the least studied excited state transformations of cyclic aliphatic ketones. Nevertheless, it has been shown to be a general reaction of cyclobutanones[5] and tricyclo[2.1.0^{2,6}]heptan-3-ones.[6] At the initiation of this work, the commonly accepted mechanism was that initially suggested by Yates and Kilmurry.[6,7] This mechanism involves initial α cleavage of the excited cyclic ketone (*e.g.*, **1**) to an acyl alkyl biradical intermediate **2** which then undergoes electronic rearrangement and rebonding to afford an oxacarbene intermediate **3**. Studies have revealed that **3** is most efficiently trapped by alcohols to afford ring expanded acetals **4** as isolable products.[5–7]



1 **2** **3** **4** (1)

In this report, we present additional results from our investigation of the photochemical ring expansion reaction of cyclic aliphatic ketones and suggest a somewhat modified mechanism which is capable of explaining a variety of reported results.

Results and Discussion

Photochemical Ring Expansion of Cyclobutanones. It has been observed that electronically excited cyclobutanones rearrange in alcoholic media to yield products of decarbonylation (carbon moxoxide and cyclopropanes), β cleavage (ethylenes and ketenes), and ring expansion (2-alkoxytetrahydrofurans).[3,5,8–10] Al-

---

(1) (a) The authors at Columbia gratefully acknowledge the generous support of this work by the Air Force Office of Scientific Research (Grant AFOSR-70-1848). (b) National Institutes of Health Predoctoral Fellow, 1968–1971.

(2) For a review, see J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).

(3) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, **5**, 92 (1972), and references cited therein.

(4) P. J. Wagner, *ibid.*, **4**, 168 (1971).

(5) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970), and references cited therein.

(6) P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968), and references cited therein.

(7) (a) P. Yates and L. Kilmurry, *Tetrahedron Lett.*, 1739 (1964); (b) P. Yates and L. Kilmurry, *J. Amer. Chem. Soc.*, **88**, 1563 (1966).

(8) N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1970).

(9) N. J. Turro and D. R. Morton, *ibid.*, **93**, 2569 (1971).

(10) N. J. Turro, D. R. Morton, E. Hedaya, M. E. Kent, P. D'Angelo, and P. Schissel, *Tetrahedron Lett.*, 2535 (1971).