Figure 2. Variation of decomposition rate with pH for the peroxymonosulfate–cyclohexanone system. Reactions were conducted at 2.7 × 10^{-3} M HSO_5^-, 10^{-2} M cyclohexanone, 28°, and $\mu = 0.15$. Solid line is calculated assuming $K_a = 2.3 \times 10^{-10}$ mol/l., $k_1 = 6.9 \times 10^4$ $l.^2$ mol^{-2} sec^{-1} and $k_2 = 3.0 \times 10^{-2}$ l. mol^{-1} sec^{-1}.

Table II. Effect of Cyclohexanone Concentration on the Observed Rate of Decomposition of Peroxymonosulfate[a]

Ketone concentration, M	10^3 k (Obsd),[b] sec^{-1}
1.0×10^{-3}	0.99
3.0×10^{-3}	2.7
5.0×10^{-3}	4.5
7.5×10^{-3}	6.1
10.0×10^{-3}	8.4

[a] At 2.7 × 10^{-3} M HSO_5^-, pH 9.0, $\mu = 0.15$. [b] A linear regression analysis of log k_{obsd} vs. log concentration gave $n = 0.92$.

the theoretical yield of oxygen is evolved.[4] However, with the quaternary ketone I very little oxidation would be expected and greater than 90% yield of oxygen is obtained.[4]

Small amounts of ketone can decompose large quantities of peroxymonosulfate indicating that the ketone is indeed a catalyst. For example, the turnover number (defined as the number of peroxide molecules decomposed for each ketone molecule oxidized) for ketone I is about 40. No loss of acetone is observed during the course of a decomposition run with this ketone and thus the turnover number for acetone must be very large. Also turnover numbers of greater than 1 are indicated for the other ketones shown in Figure 1.

The kinetics of the decomposition reaction have been studied and the rate law was found to be
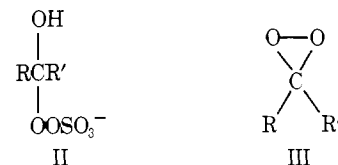
$$-d[HSO_5^-]/dt = k_1 [HSO_5^-][\text{ketone}][OH^-]$$

The loss of HSO_5^- is pseudo-first-order when ketone concentration and pH are held constant (the uncatalyzed reaction is second order in peroxide[5]); plots of log $[HSO_5^-]$ against time are linear through two half-lives which indicate this kinetic order in peroxide concentration. Variation in ketone concentration showed that at low ketone concentration the rate was essentially proportional to the amount of ketone present (Table II).

A plot of log rate against pH is shown in Figure 2. This profile also differs from the symmetrical profile found for the uncatalyzed decomposition reaction [5]At no point is the slope exactly one; however, HSO_5^- is half ionized near pH 9.5 and this results predictably in a leveling-off beginning at this pH. Below pH 8 another leveling begins; as yet the nature of this less important process is unestablished. The shape of this profile can be explained by the use of the K_a value for HSO_5^- of 2.3 × 10^{-10} mol/l., a k_1 value of 6.9 × 10^4 $l.^2$ mol^{-2} sec^{-1}, and a k_2 value of 3.0 × 10^{-2} l. mol^{-1} sec^{-1}, where k_2 is a constant for the possible rate term $(-d[HSO_5^-]/dt = k_2 [HSO_5^-][\text{ketone}])$. Below pH 11

the agreement is good; however, these rate terms do not explain the small decline in rate observed above pH 11. Above pH 11 the enolization of the ketone may become important.

The rate law for the oxidation reactions appear to be more complicated than that for the decomposition reaction although the rate is dependent on peroxide, ketone, and pH in a manner similar to that found for decomposition. The rate of oxidation of reductant S also depends on reductant concentration. For $S^- = Cl^-$, the yield of oxygen production (decomposition of peroxide) decreases[4] with increases in $[Cl^-]$ suggesting Cl^- and HSO_5^- compete for a reactive intermediate. In no case, however, was it possible to obtain 100% yield of hypochlorite. At a Cl^- to HSO_5^- molar ratio of about 40 only a 75% yield of hypochlorite is obtained. The failure to achieve 100% yield may be due to a side reaction (i.e., chlorination of ketone).

The Polar Blue oxidations when followed by dye color disappearance showed apparent first-order behavior in dye concentration; however, this is open to several interpretations. Nonetheless, these results also suggest the involvement of an unusually reactive intermediate. The initial step in all three reactions is believed to be the nucleophilic addition of peroxymonosulfate to the carbonyl carbon to form an adduct (II). This adduct is analogous to the stable adduct 2-hydroxy-2-hydroperoxypropane formed in aqueous alkaline solutions of hydrogen peroxide and acetone.[6] It is unlikely though that adduct II is the reactive intermediate. Smitherman's ^{18}O isotopic work[7] which will be published later clearly indicates that the dioxirane compound III is an intermediate in the decomposition reaction. Whether this is involved in the oxidation reactions is not known at this time.

$$
\begin{array}{ccc}
\text{OH} & & \text{O—O} \\
| & & \diagdown \diagup \\
\text{RCR}' & & \text{C} \\
| & & \diagup \diagdown \\
\text{OOSO}_3^- & & \text{R} \quad \text{R}' \\
\text{II} & & \text{III}
\end{array}
$$

References and Notes

(1) A. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899); R. Robinson and L. H. Smith, *J. Chem. Soc.*, 371 (1937); C. H. Hassall in "Organic Reactions," Vol. IX, R. Adams, A. H. Blatt, A. C. Cope, D. Y. Curtin, F. C. McGrew, and C. Niemann, Ed., Wiley, New York, N.Y., 1957, Chapter 3, p 73.
(2) N. A. Milas and A. Golubovic, *J. Amer. Chem. Soc.*, **81**, 6461 (1959); J. Hine and R. W. Redding, *J. Org. Chem.*, **35**, 2769 (1970).
(3) P. D. Bartlett and J. R. Vincent, *J. Amer. Chem. Soc.*, **57**, 1596 (1935).
(4) E. P. Gosselink, personal communication.
(5) D. L. Ball and J. O. Edwards, *J. Amer. Chem. Soc.*, **78**, 1125 (1956); J. F. Goodman and P. Robson, *J. Chem. Soc.*, 2871 (1963).
(6) M. C. V. Sauer and J. O. Edwards, *J. Phys. Chem.*, **75**, 3004 (1971).
(7) H. C. Smitherman, to be submitted for publication.

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**Molecular Twisting as a Mode of Excited State Decay.
Mechanistic Organic Photochemistry[1,2]**

Sir:

Many years ago we noted that most photochemical reactions proceed directly to ground state of product.[3] In the case of n–π* reactions this was revealed by following the

Table I. Lifetimes, Quantum Yields, and Derived Rates for the 1-Phenylcycloalkenes

| Compd	Temp, °K	τ, nsec	$^1k_{dt}$, sec^{-1}	ϕ_f	k_f, sec^{-1}	ϕ_{isc}	k_{isc}	$^3k_{dt}$, sec^{-1}	k_{ic}, sec^{-1}
4	300	15.89 ± 0.58	6.29×10^7	0.27	1.7×10^7	0.004	0.25×10^6	280	4.6×10^7
	77	23.45 ± 0.64	4.26×10^7	0.62	2.64×10^7				1.6×10^7
5	300	14.01 ± 0.50	7.14×10^7	0.43	3.07×10^7	0.11	7.9×10^6	1700	3.3×10^7
	77	17.38 ± 0.68	5.75×10^7	0.72	4.14×10^7				0.98×10^7
6	300	1.44 ± 0.12	69.4×10^7	0.03	2.08×10^7	0.0008	0.56×10^6	6,300	67×10^7
	77	15.84 ± 1.86	6.31×10^7	0.4	2.52×10^7				3.8×10^7
7	300	0.28 ± 0.04	357×10^7	0.016	5.71×10^7	0.0016	5.7×10^6	30,000	351×10^7
	77	9.33 ± 0.68	10.7×10^7	0.42	4.49×10^7				6.2×10^7
8	300	$\begin{cases}11.41 \pm 0.55^a \\ 3.01 \pm 0.13^a\end{cases}$	$\begin{cases}8.76 \times 10^7 \\ 33 \times 10^7\end{cases}$	$\begin{cases}0.03 \\ 0.08\end{cases}$	$\begin{cases}0.25 \times 10^7 \\ 2.64 \times 10^7\end{cases}$	0.01	$\begin{cases}0.88 \times 10^6 \\ 3.3 \times 10^6\end{cases}$	150,000	$\begin{cases}8.5 \times 10^7 \\ 3.0 \times 10^7\end{cases}$
	77	12.35 ± 0.21	8.10×10^7	0.46	3.72×10^7				4.3×10^7

^{a} Double exponential decay observed.

electronic configuration in three dimensions.[3a–d,4] For electrocyclic reactions we noted[5] that in excited state "allowed" reactions a degeneracy occurs along the reaction coordinate, that Jahn–Teller distortion results,[6] and that internal conversion to ground state at this point along the reaction coordinate is optimized.

Excited state decay plays a major role in most photochemistry. Our recently described computer controlled single photon counting-reiterative convolution measurements of ultrarapid rates[8] has allowed investigation of singlet rates of rearrangement and overall decay.

Presently we were interested in evaluating the importance of one mode of decay, that arising from twisting about a π bond which has often been qualitatively discussed as a decay mode.[9]

In the present communication we report (A) the direct measurement of the total decay rates of the excited singlets of the four- to eight-membered 1-phenylcycloalkenes (4–8), (B) the dissection of these overall rates into the component rates (k_f, fluorescence; k_{isc}, intersystem crossing; k_{ic}, internal conversion), (C) the temperature dependence of these rate constants, (D) the corresponding rates of triplet decay, (E) a remarkable parallelism between the singlet and triplet decay rates, (F) a relationship between molecular flexibility and internal conversion, and (G) evidence that ring constraint precludes access to twisted configurations from which decay occurs.
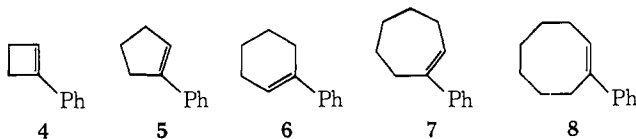
The total excited singlet decay rates (*i.e.*, the k_{dt}'s) were obtained using our method for rapid rates[8] and are given in Table I. We then proceeded to dissect $^1k_{dt}$.

$$^1k_{dt} = k_f + k_{isc} + k_{ic} \tag{1}$$

To obtain k_f's, we measured fluorescence quantum yields relative to a biphenyl standard[10] and used eq 2 along with the determined $^1k_{dt}$'s.

$$\phi_f = k_f/^1k_{dt} \tag{2}$$

The rates of intersystem crossing (the k_{isc}'s) were derived using the method of Wilkinson and Dubois[11] and Sandros.[12] Here a plot of the reciprocal of biacetyl phosphorescence *vs.* the reciprocal of biacetyl concentration was made for each of the 1-phenylcycloalkenes and for a biphenyl standard. The ratio of intercepts gave the ratio of ϕ_{isc}'s for any two compounds, and ϕ_{isc} for biphenyl is known as 0.81.[13] Thus, the ϕ_{isc}'s in Table I were obtained, and using eq 3 the k_{isc}'s were derived.

$$\phi_{isc} = k_{isc}/^1k_{dt} \tag{3}$$

With all rates in eq 1 known except for the rate of internal conversion, the dissection was possible. The k_{ic} values are included in Table I.

Table I includes measurements of rates for both room temperature and 77°K. In the case of k_{isc}, the room temperature values were quite small and the still smaller 77° values were not significant.

Inspection of Table I reveals that the k_f's are temperature independent. While this has precedent[14] for planar aromatics, this more general result is important for use of our "magic multiplier"[8] in determining very rapid rates of singlet reactions.

The k_{ic}'s increase with increasing ring flexibility.[15] Most dramatically, all k_{ic}'s decrease and converge toward a limiting value of *ca.* 3.6×10^7 sec^{-1} at 77°K in 4:1 MCIP, a value close to the room temperature value of $k_{ic}^{300} = 4.6 \times 10^7$ sec^{-1} found for the relatively rigid 1-phenylcyclobutene (4). This, along with the observation that the greatest change in ϕ_f occurred at the matrix melting–freezing temperature upon warming–cooling, provides evidence that molecular rigidity inhibits decay.

Additionally, the slope to intercept ratios of the biacetyl plots cited above gave, following the literature treatment,[11,12] $^3k_{dt}/k_{ET}$. Here $^3k_{dt}$ is the decay rate of the triplet and k_{ET} is the rate of energy transfer, assumed to be diffusion controlled (*i.e.*, $k_{ET} = 1.5 \times 10^{10}$ l. mol^{-1} sec^{-1}). The rates of triplet decay are included in Table I.

There is a remarkable parallelism between the rates of singlet decay and that for triplet decay. For example, the ratio of k_{ic} for the seven- to four-ring compounds is *ca.* 76 while that for $^3k_{dt}$ is 107. However, the singlet decay[15] has a rate advantage of *ca.* 10^5 as a consequence of multiplicity forbiddenness of the triplet decay.

Thus, it is seen that twisting about an excited π bond is important to both singlet and triplet excited state decay. This corresponds to the free rotor effect we hypothesized previously.[16] Its greater importance in inhibiting triplet reactions is now seen as necessarily due to the often slow rates for triplet processes and their greater susceptibility to decay competition.

The results obtained bear on photochemical reactivity as well as decay; the relationship between decay and reaction is often close.[8] Twisting about a π bond is involved not only in the decay processes described here but also in cis–trans isomerization of acyclic alkenes. Evleth has noted[17] that ethylene twisting is a ground state forbidden process and photochemically allowed. Thus here decay and reaction are closely related.

This is then another example where a Jahn–Teller effect is anticipated at that point along the reaction coordinate

where bonding and antibonding MO's cross,[5] this resulting from the one-electron degeneracy. As a consequence efficient conversion to ground state should occur.[5,18]

References and Notes

(1) This is paper 91 of our photochemical series.
(2) For paper 90 of the series, note H. E. Zimmerman and B. R. Cotter, *J. Amer. Chem. Soc.*, in press.
(3) (a) H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., 1961, Abstracts; (b) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961); (c) *ibid.*, **84**, 4527 (1962); (d) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (e) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Amer. Chem. Soc.*, **90**, 4892 (1968).
(4) L. Salem, *J. Amer. Chem. Soc.*, **96**, 3486 (1974), has presented correlation diagrams for these processes and has assigned configurations in terms of symmetries corresponding to our "circle-dot-y" notation. Interestingly, he has found that the ground state reactant curve leads to excited state of product with crossing of states.
(5) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); (b) *ibid.*, **88**, 1566 (1966); (c) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971); (d) *ibid.*, **5**, 393 (1972).
(6) This point has been made more recently by Dewar, *et al.*,[7] who has apparently overlooked some earlier literature.[5] Thus, ref 5b pointed out that at points of degeneracy along a correlation diagram Jahn–Teller vibrations may be available and with the correct symmetry and geometry to enhance radiationless transition of excited states to ground states. The Jahn–Teller effect has been discussed in further detail in ref 5d with exploration of surfaces in the vicinity of crossing points. Similarly, that forbidden ground state reactions has been noted several times as in ref 5c. Also overlooked was our point in ref 5b that the noncrossing rule is not inviolate.
(7) M. J. S. Dewar, *et al.*, *J. Amer. Chem. Soc.*, **96**, 5240, 5242, 5244, 5246 (1974).
(8) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Amer. Chem. Soc.*, **96**, 439 (1974).
(9) (a) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964); (b) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, **62**, 2975 (1940); (c) W. J. Potts, *J. Chem. Phys.*, **23**, 65 (1955); (d) S. Sharafy and K. A. Muszkat, *J. Amer. Chem. Soc.*, **93**, 4119 (1971).
(10) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N.Y., 1965.
(11) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).
(12) K. Sandros, *Acta Chem. Scand.*, **23**, 2815 (1969).
(13) (a) Sandros' value of $\phi_{isc} = 0.81 \pm 0.04$ was chosen,[12] it will provide upper limits for ϕ_{isc} in compounds 4–8. The alternative literature value is $\phi_{isc} = 0.51 \pm 0.20$;[13b] (b) W. Heinzelmann and K. Labhart, *Chem. Phys. Lett.*, **4**, 20 (1969).
(14) (a) W. R. Dawson and J. L. Kropp, *J. Phys. Chem.*, **73**, 693 (1969); (b) J. L. Kropp, W. R. Dawson, and M. W. Windsor, *ibid.*, **73**, 1747 (1969).
(15) (a) All of the 1-phenylcycloalkenes decayed as single falling exponentials, except 8 which decays as the sum of two falling exponentials at room temperature but as a single exponential at 77°K. We attribute the double decay to cis and trans excited singlets. The abnormally long lifetime of 8 (slower decay rate than the pattern of 4–7 would predict) is attributed to the increased hydrogen–hydrogen nonbonded interaction in this medium-sized ring, inhibiting the twist which allows the molecule to reach conformations from which decay is facile. That the cyclooctane is abnormally strained is shown by the heat of hydrogenation of cyclooctene which is considerably lower than that of cyclohexene or cycloheptene;[15b] (b) R. W. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).
(16) (a) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969). (b) It should be recognized that presently we focus attention on one mode of decay which seems dominant, namely twisting. However, other molecular vibrations must interact in the decay process. Thus, for example, the slightly inverted rates of the four- and five-ring 1-phenylcycloalkenes (4 and 5) may result from more ready phenyl twisting in the four-ring case.
(17) E. Evleth, *Chem. Phys. Lett.*, **3**, 122 (1969).
(18) Note the discussion and review by J. Michl in "Chemical Reactivity and Reaction Paths," G. Klopman, Ed., Wiley, New York, N.Y., 1974, p. 301, where such excited state–ground state "energy funnels" are considered. This was also discussed by J. Michl, 5th International IUPAC Photochemistry Symposium, Enschede, Holland, July 21–26, 1974.

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Effect of Heteroatom Electronegativity on the Development of Diatropic Character in *cis,trans,cis,trans,cis,trans*-Aza[13]annulenes

Sir:

We recently reported on the title system, **1**, **2**, and stressed that whereas parent amine **1a**[1] is "aromatic" by nmr, acetamide **2a** and carbamate **2b** are best classed as polyenes under the same criterion.[2] Presently, we should like to briefly relate our experience with the conjugate base of **1a**, the *cis,trans,cis,trans,cis,trans*-aza[13]annulenyl anion, as well as with three choice N-substituted derivatives whose properties yield basic information with regards to the skeletal and π-electronic effects controlling the development of "aromatic" character.

Potassium aza[13]annulenide (**1b**) was generated for purposes of direct observation on overnight low-temperature (−78°) exposure of its conjugate acid (**1a**) to potassium mirror in THF-d_8. It is a dark red, extremely heat sensitive species rearranging cleanly and almost instantaneously to **3a** (nmr)[3] on warming to 0°.[4] As a result, it was necessary to record the nmr spectrum of **1b** at an undesirably low temperature (*ca.* −70°) with consequent loss of resolution due to increased medium viscosity. Nonetheless, one can still readily discern in this spectrum two well-separated doublets due to the α protons, one showing at τ 1.8 with $J \sim 7$ Hz ("outer" proton bound to a cis link) and the other appearing at τ 12.5 with $J \sim 13$ Hz ("inner" proton bound to a trans link). The wide separation (over 10 ppm!) between these two doublets is clearly implicative of the presence of a strongly diatropic frame in **1b**.

Next, we posed the question as to whether the system will retain its diatropic character when sterically encumbered with an electron-*releasing* N substitutent such as methyl.[5] The desired derivative, **1c**,[6] was prepared on consecutive low-temperature (−78°) treatment of **1a** with methyllithium and methyl iodide and was isolated as a yellow air-sensitive liquid characterized by the following spectral data: $\lambda_{max}(C_6H_{14})$ 300 and 360 nm in a ratio of *ca.* 7:1;[7] nmr (100 MHz, acetone-d_6, 0°) τ 3.1–4.3 (9 H, m), 6.29 (1 H, dd, $J = 15.5$, 9.0 Hz; "inner" proton), 6.43 (3 H, s; meth-

A   B

1a, X = NH
b, X = N̈K̇⁺
c, X = NMe

A   B
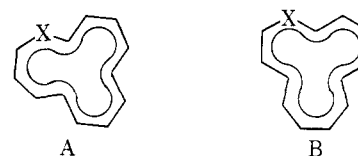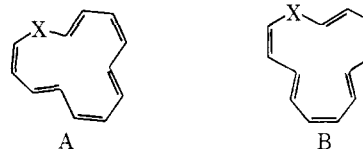
2a, X = NAc
b, X = NCOOMe
c, X = NCF=CF₂
d, X = NCON(Me)₂

3a, X = N̈K̇⁺
b, X = NH