

Replacing H' by D' increases the product separation mass-weighted displacement (the velocities of D' and H'' are the same during separation, their energies in the ratio 2:1, and mass-weighted velocities (and displacements) in the ratio (2:1)<sup>1/2</sup>), and the contribution of this position to the energy release is increased accordingly. Replacing H'' and H''' with deuterium decreases the product separation mass-weighted displacement of H' (H' has only 1/3 of the energy of the departing HD as opposed to 1/2 in (CH<sub>2</sub>=OH)<sup>+</sup>), and the contribution of H' diminishes. Substituting for all three hydrogens has little effect on the mass-weighted displacements of the departing hydrogens, and hence there is little isotope effect.

It has been suggested that the large energy release in the loss of hydrogen from (CH<sub>2</sub>=OH)<sup>+</sup> is a consequence of the reaction following a concerted orbital symmetry-forbidden route.<sup>13</sup> An earlier molecular orbital calculation<sup>4</sup> on this reaction, and the later qualitative discussion,<sup>13</sup> assume a symmetrical planar transition state and hence that reaction must pass over a barrier imposed by orbital symmetry. Our calculation, in which the potential surface is searched, suggests that the reaction proceeds around this particular barrier. The hydrogen atom H' on the oxygen moves a considerable distance toward the carbon before the transition state is reached. The reaction might be regarded as a 1,2 shift coupled with a 1,1 elimination.<sup>14</sup> The energy barrier surmounted is that for the H' shift, and thereafter H<sub>2</sub> loss is facile. The partition of energy as translation is largely a consequence of the H' motion corresponding quite closely to a motion separating the products.

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- These displacements are proportional to velocities. Using mass-weighted coordinates  $q_i = x_i \sqrt{m_i}$  (see for example, J. C. D. Brand, J. C. Speakman, and J. K. Tyler, "Molecular Structure", 2nd ed, Edward Arnold, London 1975, p 129), velocity and momentum  $p_i$  become equivalent and kinetic energy is given by  $\frac{1}{2} \dot{q}_i^2 = p_i^2$ .
- This idea, which is the essence of our approach, stems from the classic work of M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **35**, 178 (1939).
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- The calculated forward and reverse activation energies are 288 and 171 kJ mol<sup>-1</sup>, respectively (these figures take no account of zero point energies), compared with experimental values of 225 ± 22 and 130 ± 24 kJ mol<sup>-1</sup>, respectively. These experimental activation energies have been obtained from the standard heats of formation of reactants and products and the appearance energy of 14.0 ± 0.2 eV for (CHO)<sup>+</sup> from CH<sub>3</sub>OH (C. Lifshitz, M. Shapiro, and R. Sternberg, *Isr. J. Chem.*, **7**, 391 (1969)). We assume that 14.0 eV represents the minimum energy necessary for the sequence CH<sub>3</sub>OH → (CH<sub>3</sub>OH)<sup>+</sup> → (CH<sub>2</sub>=OH)<sup>+</sup> + H → (CHO)<sup>+</sup> + H<sub>2</sub> + H, in the absence of tunneling. The appearance energy of (CH<sub>2</sub>=OD)<sup>+</sup> from CH<sub>3</sub>OD is 11.66 ± 0.04 eV. See I. Omura, T. Kaneko, Y. Yamada, and K. Tanaka, *J. Phys. Soc. Jpn.*, **27**, 981 (1969).
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- (15) NOTE ADDED IN PROOF. MINDO/3 has recently been applied to the elimination of H<sub>2</sub> from (CH<sub>2</sub>=OH)<sup>+</sup> by M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **99**, 7432 (1977).

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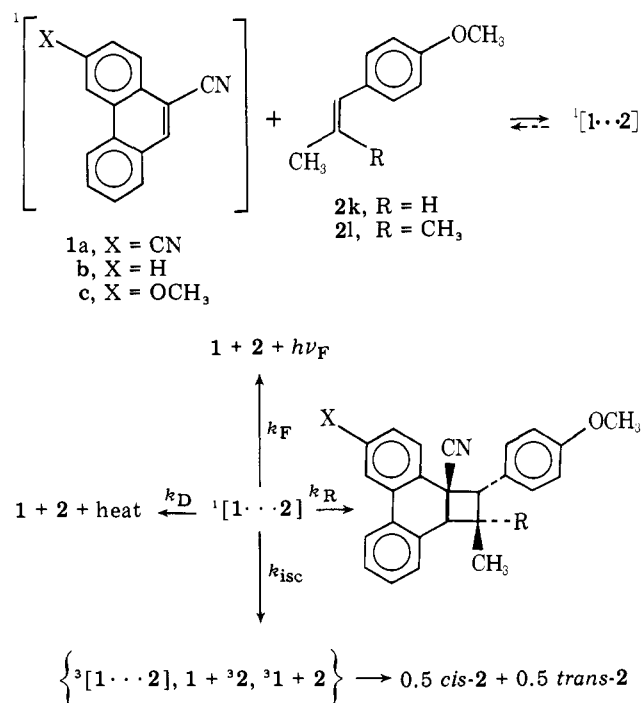
#### Temperature and Substituent Dependence of Photocycloadditions Involving Exciplexes

Sir:

Temperature and substituent effects on reaction rate are ubiquitous probes of mechanism for ground-state reactions. Although a number of temperature dependences of photochemical reactions, including photocycloaddition, have previously been reported,<sup>1,2</sup> we know of no series with systematic variation of substituent, in which each reaction path includes an emissive exciplex. The reactions<sup>3</sup> of substituted 9-cyanophenanthrenes **1a-c** with anethole (**2k**) or anisylisobutylene (**2l**) provide such a series (Scheme I). We have studied four fundamental processes. Rates of cyclobutane formation and internal conversion are affected by both substituent and temperature to a markedly greater extent than are fluorescence and intersystem crossing. Our results suggest a strong similarity in the nature of the cycloaddition and internal conversion processes.

We have determined quantum yields ( $\phi_i$ ) for all four reactions of exciplexes of **1a-c** with **2k** and of **1b** with **2l**. The rate constant  $k_i$  for each process is available as  $k_i = \phi_i \tau^{-1}$  if  $\tau$  is known. We have measured  $\tau$  by laser flash photolysis when  $\tau \geq 9$  ns and have estimated it by oxygen quenching when shorter.<sup>4</sup> In all cases, quantum yields were measured with [**2**] high enough to quench >95% of singlet **1**. For **1c-2k**, results as a function of [**2k**] were extrapolated to [**2k**] = ∞. The  $\phi_{isc}$  values were taken as twice  $\phi_{cis-2k}$ ,<sup>5</sup> and  $k_D$  was computed as  $\tau^{-1} - (k_F + k_R + k_{isc})$ . The cumulative errors make  $k_D$

Scheme I



**Table I.** Activation Parameters<sup>a</sup> for Reactions of Exciplexes

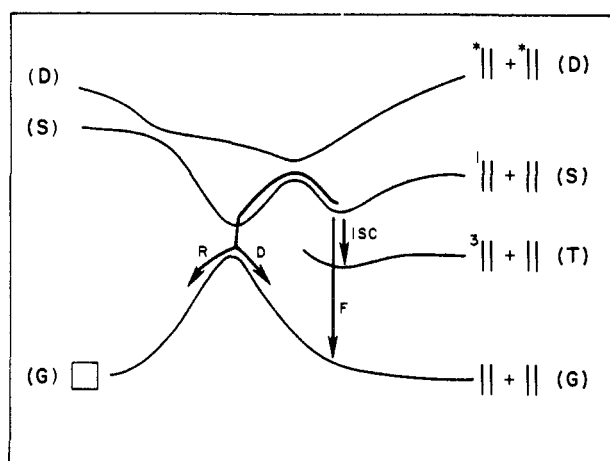
Exciplex	$k_R$		$k_D$		$k_F$ , " $\Delta H^\ddagger$ " <sup>b</sup>	$k_{isc}$ , " $\Delta H^\ddagger$ " <sup>b</sup>
	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$		
1c-2k	2.7 ± 0.6 <sup>c</sup>	-11 ± 2 <sup>c</sup>	2.1 ± 0.7 <sup>c</sup>	-13 ± 2.5 <sup>c</sup>	<i>d</i>	1.6 ± 0.6
1b-2k	2.2 ± 0.6	-16 ± 2	3.0 ± 0.7	-14 ± 2.5	<i>d</i>	-0.6 ± 0.6
1a-2k	4.2 ± 0.6	-14 ± 2	2.2 ± 1.5	-20 ± 4	0.1 ± 0.6	0.6 ± 0.6
1b-2l	4.8 ± 0.7	-16 ± 2			-0.6 ± 0.6	

<sup>a</sup> Values given as  $\Delta H^\ddagger$  (kcal/mol),  $\Delta S^\ddagger$  (cal mol<sup>-1</sup> K<sup>-1</sup>). <sup>b</sup> Since  $\Delta H^\ddagger$  has no meaning for nonadiabatic processes, these values are to be taken as formal and are intended only for comparison of temperature dependence among the four processes. <sup>c</sup> 23 and 65 °C only. <sup>d</sup> Assumed temperature independent.

**Table II.** Rate Constants<sup>a</sup> for Reactions of Exciplexes

Exciplex	<i>T</i> , °C	10 <sup>-6</sup> <i>k<sub>R</sub></i>	10 <sup>-6</sup> <i>k<sub>D</sub></i>	10 <sup>-6</sup> <i>k<sub>F</sub></i>	10 <sup>-6</sup> <i>k<sub>isc</sub></i>
1c-2k	23	280	210	34	34
1b-2k	20.4	42	32	4.3	31
1a-2k	20.5	4.6	4.4	3.6	17
1b-2l	20.1	0.56	<i>b</i>	4.2	<i>b</i>

<sup>a</sup> In s<sup>-1</sup>. <sup>b</sup> 10<sup>-6</sup>(*k<sub>isc</sub>* + *k<sub>D</sub>*) = 26.5; the arguments in text would suggest that *k<sub>isc</sub>* comprises the bulk of this.



**Figure 1.** Schematic state correlation diagram for [2 + 2] photocycloaddition, indicating pathways for fluorescence (F), intersystem crossing (isc), and internal conversion (D), as well as cycloaddition (R) originating from a singlet exciplex.

somewhat less certain (±8–16%) than the other rate constants (±6–8%).

For each exciplex,  $\tau$  decreases with temperature, indicating that its dominant decay processes are activated. The activation parameters in Table I demonstrate a greater temperature dependence for  $k_R$  and  $k_D$  than for  $k_F$  and  $k_{isc}$ . The latter two processes are inherently photophysical, i.e., involve (presumably vertical) interconversion of the two electronic states without recourse to bond reorganization. Minimal temperature dependence is thus not surprising. For the former two, the rather small but real activation enthalpies are consistent with bond reorganization of some sort. Strongly negative values of  $\Delta S^\ddagger$  (-11 to -16 eu) for both  $k_R$  and  $k_D$  suggest substantial ordering in each process. The  $\Delta S^\ddagger$  values are quite reminiscent of those for familiar ground-state unimolecular bond reorganizations with cyclic transition states (e.g., the Cope<sup>6</sup> and Claisen<sup>7</sup> rearrangements, and electrocyclic reactions exemplified by triene<sup>8</sup> and tetraene<sup>9</sup> cyclization). We originally hypothesized that reactive exciplexes are highly ordered.<sup>3</sup> It now appears that much of the organization preceding cycloadduct formation occurs in exciplex collapse. Entropies of exciplex formation are commonly in the range of -13 to -20 eu,<sup>10–12</sup> rather normal for a bimolecular association, and do not themselves suggest extreme ordering.

Table II summarizes the rate constants as a function of reactant structure at (or near) 20 °C. Again,  $k_F$  and  $k_{isc}$  are essentially independent of structure (with one exception), while  $k_R$  and  $k_D$  vary some two orders of magnitude. As the remote phenanthrene substituent is varied from CN to H to OCH<sub>3</sub>, i.e., the order of decreasing CT stabilization expected for the exciplex,  $k_R$  increases sharply. Increase in rate in the face of decreasing CT suggests a transition state for cycloadduct formation markedly less polar than the exciplex. Lewis and Hoyle<sup>13</sup> reached the same conclusion from solvent effects for the diphenylvinylene carbonate-2,5-dimethyl-2,4-hexadiene exciplex. Michl<sup>14</sup> has in fact predicted that the transition state will arise from an avoided crossing of the (polar) singly excited surface with a (nonpolar) doubly excited one and will therefore indeed be less polar than the exciplex.

Variation of  $k_D$  with structure in the reactions of 1a-c with 2k is nearly identical with that for  $k_R$ , a fact shown more directly by the near identity of  $\phi_R$  and  $\phi_D$  (calculated) in the three cases. This, plus the fact that both processes are activated and show similar  $\Delta S^\ddagger$  values (Table I), indicates that *the processes themselves are similar*. Michl<sup>14</sup> has also suggested this similarity previously on theoretical grounds. We can readily summarize our conclusions pictorially using his state correlation diagram. In Figure 1,  $k_R$  and  $k_D$  are shown as substantially the same path, except for partitioning between cycloadduct ( $k_R$ ) and cycloaddends ( $k_D$ ) after reaching the ground surface.

Finally, the success of transition-state theory as an aid in rationalization of the present results encourages its more extensive application in photochemistry. The primary requirement of its applicability is the ability of a single hypersurface (whether ground or excited) to describe the behavior of the system prior to and including passage over the rate-limiting transition state(s). Photochemical [2 + 2] cycloadditions appear to fulfill this criterion.

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- For the short-lived exciplex 1c-2k (1.8 ns, 20 °C), the lifetime at 20 °C was estimated by the oxygen quenching technique, shown to be reliable (±15%) for eight exciplexes for which we have compared oxygen quenching and nitrogen laser experiments for lifetime determination. We further assume that  $k_F$  is essentially temperature independent, by analogy to the longer-lived exciplexes we here describe, and thus that  $\phi_F(T)$ , which we measured, may be used to determine  $\tau(T)$ . The latter assumption was also necessary for 1a-2k at higher temperature.
- The relationship  $\phi_{isc} = 2\phi_{F \rightarrow C}$  follows from the fact that  $\phi_{F \rightarrow C} = 0.49 \pm 0.02$  for benzophenone-sensitized *trans*-anethole isomerization. Evidence that intersystem crossing precedes isomerization derives from the fact that isomerization can be attenuated by concentrations of the triplet quencher isoprene which affect  $\phi_R$  and  $\phi_F$  insignificantly.
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### Structures and Relative Energies of Gaseous CSH<sub>3</sub><sup>+</sup> Ions<sup>1</sup>

Sir:

Recent collisional activation (CA) mass spectral studies of gaseous C<sub>2</sub>SH<sub>5</sub><sup>2a</sup> and C<sub>3</sub>SH<sub>7</sub><sup>2b,3</sup> ions showed that ions of thioalkoxide structures, R<sub>1</sub>R<sub>2</sub>CH—S<sup>+</sup>, rearrange rapidly to the more stable protonated thioaldehyde or thioketone isomers R<sub>1</sub>R<sub>2</sub>C=SH<sup>+</sup>. In contrast, protonated thioformaldehyde, H<sub>2</sub>C=SH<sup>+</sup> (a) has been presumed<sup>4</sup> to be slightly *less* stable than thiomethoxide, H<sub>3</sub>C—S<sup>+</sup> (b), based on the lower appearance potential (AP) of CSD<sub>3</sub><sup>+</sup> vs. CSHD<sub>2</sub><sup>+</sup> from CD<sub>3</sub>SH.<sup>5,6</sup> The latter result implies a dramatic difference between CSH<sub>3</sub><sup>+</sup> ions and their oxygen-containing analogues, for which heats of formation of 169 (H<sub>2</sub>C=OH<sup>+</sup>)<sup>9,10</sup> and ~195 kcal/mol (H<sub>3</sub>C—O<sup>+</sup>)<sup>10,11</sup> have been reported. In light of the importance of these discrepancies in questions concerning sulfur vs. oxygen stabilization,<sup>2,12</sup> we have undertaken a CA study of CSH<sub>3</sub><sup>+</sup> ions generated from a variety of precursors. The results, outlined in this communication, indicate that both a and b are stable under CA conditions (lifetimes >10<sup>-5</sup> s), but that H<sub>2</sub>C=SH<sup>+</sup> (a) is significantly more stable.

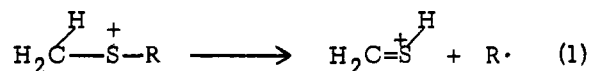
CA spectra of CSH<sub>3</sub><sup>+</sup> ions obtained as described elsewhere<sup>1,2,13</sup> are given in Table I. The spectra of CSH<sub>3</sub><sup>+</sup> produced from several alkanethiols, RCH<sub>2</sub>SH, using 70-eV ionizing electron voltage are identical within experimental error, and are assigned the H<sub>2</sub>C=SH<sup>+</sup> structure (a) based on the likelihood that such ions arise from the well-documented α-

cleavage reaction.<sup>14</sup> CA spectra of CSH<sub>3</sub><sup>+</sup> identical within experimental error are also obtained from methanethiol at low electron energy, from ethyl sulfide (by loss of methyl followed by rearrangement and loss of ethylene), and from a variety of other alkyl sulfides and thiols not listed in Table I.

The 70-eV spectrum of CSH<sub>3</sub><sup>+</sup> from dimethyl disulfide is significantly different from that of a in two regards: the disulfide spectrum has a higher relative abundance of *m/e* 15 (CH<sub>3</sub><sup>+</sup>), and gives a higher ratio of *m/e* 32 to 33 (S<sup>+</sup>/SH<sup>+</sup>). Both features are consistent with the fragmentation pattern expected for CH<sub>3</sub>—S<sup>+</sup> (b), providing firm evidence for the stability of the thioalkoxide isomer. However, the disulfide does not produce b exclusively; its CA spectrum changes to resemble more closely that of a upon going to low energies. The 70-eV ionization of CH<sub>3</sub>SSCH<sub>3</sub> gave the highest value of [b]/[a] found for any CSH<sub>3</sub><sup>+</sup> ions in this study. This CA spectrum was assumed to be that of pure b to analyze CSH<sub>3</sub><sup>+</sup> isomeric mixtures containing lower proportions of b; so these [b] values will represent maxima (Table I). The relative proportion of b was found to decrease on lowering the electron energy for both dimethyl disulfide and methyl methylsulfynylmethyl sulfide.

The apparent higher proclivity for a formation suggests that isomer a is more stable than b. Because this is in apparent contrast to the lower appearance potential observed for CSD<sub>3</sub><sup>+</sup> vs. CSHD<sub>2</sub><sup>+</sup> from CD<sub>3</sub>SH,<sup>4,6</sup> the CA spectra of these ions were examined; ions of both types formed with 70-eV electrons give CA spectra identical (Table I, after correction for shifted *m/e* values) with that of a within experimental error. Low energy spectra are similar, but of lower accuracy due to interference from overlapping CD<sub>3</sub>SH signals. The CA spectrum of CSH<sub>3</sub><sup>+</sup> formed from CH<sub>3</sub>SD at low electron energies also shows no evidence for the formation of b. Despite the larger experimental error in the low energy measurements, it would appear that it is isomer a, not b, that is formed at threshold energies from methanethiol, even for CSD<sub>3</sub><sup>+</sup> formed from CD<sub>3</sub>SH.<sup>15</sup>

The results can be interpreted using an alternative mechanism for the threshold energy loss of H from H<sub>3</sub>CSH to give H<sub>2</sub>C=SH<sup>+</sup> which involves an anchimerically assisted process previously suggested with regard to the C<sub>2</sub>SH<sub>5</sub> and C<sub>3</sub>SH<sub>7</sub> systems<sup>2</sup> (eq 1). For methanethiol (R = H) both this and α-



cleavage H loss would give a; for CD<sub>3</sub>SH the lower AP observed for loss of H could be due to a kinetic isotope effect. For dimethyl disulfide (R = SCH<sub>3</sub>) reaction 1 would compete with S—S cleavage to produce b; as a result of the tightness of the transition state for anchimeric vs. direct-cleavage reactions,

Table I. Collisional Activation Spectra of CSH<sub>3</sub><sup>+</sup> Ions

Compd	<i>m/e</i> of daughter ion <sup>a</sup>							Structure <sup>b</sup>
	12	13	14	15	32	33	34	
CH <sub>3</sub> SH <sup>c</sup>	1.4	3.1	9.0	1.1	35	50	5.3	a
12 eV <sup>d</sup>	1.8	4.7	9.2	1.2	36	48	4.8	a
CH <sub>3</sub> SD, <sup>e</sup> 14 eV (-D)	2.4	3.4	10.6	1.4	34	48	7.1	a
CH <sub>3</sub> CH <sub>2</sub> SH	1.4	2.7	9.3	0.6	35	51	7.4	a
C <sub>2</sub> H <sub>5</sub> SC <sub>2</sub> H <sub>5</sub>	2.0	3.8	10.5	0.8	34	49	6.8	a
CH <sub>3</sub> SSCH <sub>3</sub> <sup>c</sup>	1.8	3.4	8.5	6.2	39	41	8.4	b <sup>f</sup>
12 eV <sup>d</sup>	2.0	3.3	10.3	2.1	37	45	6.0	a (75%), b
CH <sub>3</sub> SOCH <sub>2</sub> SCH <sub>3</sub> <sup>c</sup>	1.6	2.4	7.9	5.1	38	45	5.2	a (20%), b
14 eV <sup>d</sup>	3.1	3.3	13.9	1.6	32	46	7.2	a (85%), b
CD <sub>3</sub> SH (-H) <sup>g</sup>	1.4	3.5	13.1	1.0	29	52	6.9	a
CD <sub>3</sub> SH (-D) <sup>h</sup>	2.0	3.1	11.4	0.6	36	47	5.4	a

<sup>a</sup> Abundances relative to total ion abundance = 100 for all ions shown except *m/e* 34, which is of lower accuracy due to the presence of <sup>34</sup>S from CH<sup>34</sup>S. <sup>b</sup> a, H<sub>2</sub>C=SH<sup>+</sup>; b, H<sub>3</sub>C—S<sup>+</sup>; calculated from [15<sup>+</sup>]/[14<sup>+</sup>], ±15%. <sup>c</sup> Corrected for isotopic contributions to the *m/e* 47 precursor from large peaks at *m/e* 45 and 46. <sup>d</sup> Ionizing electron energy; in other cases 70 eV was used. <sup>e</sup> Contains ~7% CH<sub>3</sub>SH; so only ~55% of CSH<sub>3</sub><sup>+</sup> originates from CH<sub>3</sub>SD. <sup>f</sup> Arbitrarily assumed to be pure b (see text). <sup>g</sup> Spectrum of CSD<sub>3</sub><sup>+</sup>; *m/e* values adjusted for presence of D. <sup>h</sup> Spectrum of CSD<sub>2</sub>H<sup>+</sup>; *m/e* values adjusted for presence of D.