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Photodissociation of Trimethylene Sulfoxide. Energy Partitioning and the Possible Formation of SO($^1\Delta$)

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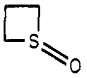
On direct photolysis or Hg($^3P_1$) sensitized decomposition trimethylene sulfoxide (I) undergoes fragmentation in the gas phase to yield ethylene, propylene, and cyclopropane. There is a nonrandom distribution of the available energy in the cyclopropane-forming reaction which is interpreted to indicate that, in order to conserve spin angular momentum, this reaction channel may be driven to produce SO($^1\Delta$) during direct photolysis, and SO($^3\Sigma^-$) during Hg($^3P_1$) sensitized decomposition. There is a comparison of some aspects of the photochemistry of trimethylene sulfoxide to cyclobutanone photochemistry.

Introduction

We have extended our work on the gas-phase photochemistry of sulfoxides[1] to include this study of trimethylene sulfoxide (I).



I

The photochemistry of this system is particularly interesting because on photolysis in the gas phase it yields the same hydrocarbon as does cyclobutanone[2] (ethylene, propylene, and cyclopropane). However, in contrast to the cyclobutanone system where the ground electronic state of the CO fragment is a singlet, the ground electronic state of SO that must be produced in the channel that yields C_3H_6 is a triplet ($^3\Sigma^-$). This molecule has electronic excited states,[3] SO($^1\Delta$) and SO($^1\Sigma^+$), that are 6150 (17.6 kcal mol^{-1}) and 10 510 cm^{-1} (30.0 kcal mol^{-1}), respectively, above its electronic ground state, and reaction channels leading to these excited states of SO are energetically allowed during the photofragmentation of I. Therefore, the photochemistry of trimethylene sulfoxide is richer in potential reaction channels than the cyclobutanone system, and the comparisons of their photochemistry might prove interesting. In addition, since more than one product spin state is accessible, the system offers the potential to observe how the conservation of spin angular momentum might drive a photochemical reaction to produce specific product electronic states. Moreover, if a trimethylene biradical proved to be an intermediate in the cyclopropane forming reaction, the spin state of this intermediate would be a reflection of the spin state of the electronically excited reactant and SO product.

Our work to date has been confined to dealing with the photochemistry of I and the partitioning of energy to the cyclopropane fragment produced on photolysis of I. The energy partitioning results suggest that SO($^1\Delta$) is produced when I is photolyzed to give cyclopropane, but ground electronic state SO is the produce when I undergoes decomposition to cyclopropane subsequent to its excitation by Hg($^3P_1$) sensitization.

Experimental Section

Materials. Trimethylene sulfoxide was prepared by oxidation of trimethylene sulfide according to the method given in ref 4. It was identified by IR, NMR, and mass spectral analysis. The product was purified by GLC and then subjected to trap-to-trap distillation in the vacuum apparatus. The purified material was stored at −78 °C. The reactant was kept free of C_2H_4 and C_3H_6 impurities by occasionally pumping on it at room temperature, and periodic GLC analysis after no light experiments were used to check for interfering impurities. Several experiments carried out under conditions of constant pressure but with reactor surface area/volume ratios that changed by a factor of 2.8 indicated that the product composition was not influenced by the surface. It did appear, however, that attempts to photolyze I when its partial pressure was near its vapor pressure, and there was a hydrocarbon diluent in the reactor, lead to somewhat erratic results. Isopentane was the diluent for most of this work. All chemicals were checked for interfering impurities. The products were identified by comparison of their GLC retention times with known samples. Product analyses were carried out by use of a 60-ft GLC column (0.125-in. diameter) composed of 20% dimethylsulfolane on 80 mesh Chromosorb.

Equipment. All gas handling was carried out on a conventional mercury-free vacuum apparatus fitted with greaseless stopcocks. Photolyses were carried out in Suprasil or commercial grade cylindrical quartz cells. The mercury, Hg($^3P_1$), sensitization experiments were done in spherical Vycor cells using an alternate vacuum apparatus for gas handling. The light sources used for the experiments included Cd (229 nm), Zn (214 nm), and low-pressure Hg (253.7 nm) sources. Attempts to observe fluorescence were carried out on a Varian SF-330 spectrofluorometer fitted to handle a gas cell. Spectra were recorded by use of a Cary 17 spectrometer.

The measurement of the quantum yield for product formation at 254 nm was accomplished by photolyzing mixtures of cyclopentanone and I. In these experiments the UV spectra of I, and the spectra of a mixture of I and cyclopentanone, were recorded before photolysis. Using the known relative quantum yield for formation of cyclobutane from 254-nm photolysis of cyclopentanone,[5] ϕ = 0.39, and our measured value for the relative quantum yield of cyclopropane formation at 254 nm, we are able to deduce the quantum yield for $C_2H_4 + C_3H_6$ formation, ϕ_D, during 254-nm photolysis of I. The average value of ϕ_D resulting from these experiments carried out in the pressure range of 0.5–37 torr was 0.16 ± 0.04.

Results and Discussion

General Features of the Photochemistry. The gas-phase absorption spectrum of I is illustrated in Figure 1. The extinction coefficient, ϵ, is ~74 (±30%) L mol^{-1} cm^{-1} at 230 nm. The relatively large uncertainty is due to the

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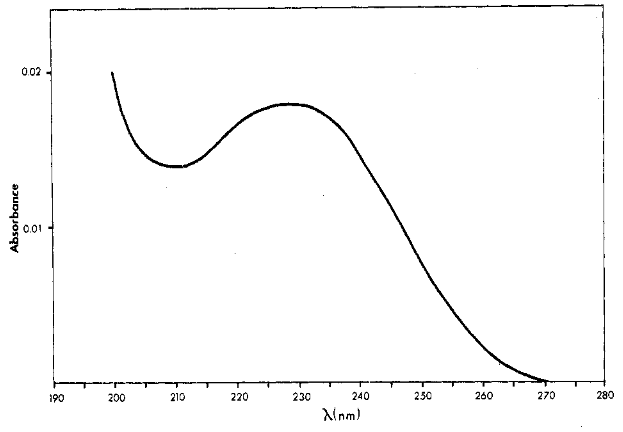
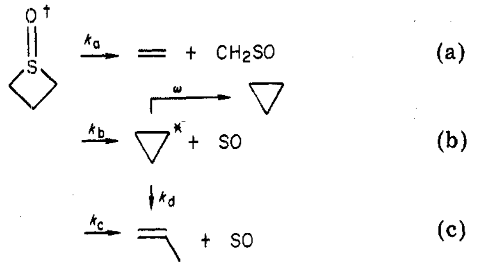


Figure 1. The gas-phase absorption spectrum of ~0.45 torr of trimethylene sulfoxide in a 10-cm path length cell at 296 K.

Scheme I



uncertainty in the vapor pressure of I. Since the oscillator strength for the transition is ~2 × 10^{-3}, it is somewhat forbidden, and it is likely that we are dealing with the $\pi^* \leftarrow n$ transition of I.

We could not observe fluorescence emission by I. Using benzene emission as a standard,[6] we estimate that the fluorescence quantum yield of I must be $<10^{-2}$ when it is excited by 254- or 229-nm radiation in the gas phase. This in turn implies that the lifetime of the S_1 state of I must be $<2 \times 10^{-9}$ s.

The hydrocarbon product distribution that is observed when I is photolyzed in the gas phase can be described by Scheme I.

In Scheme I we intend to imply that some, but not all, of the cyclopropane formed in reaction b contains sufficient vibrational energy such that it can undergo unimolecular isomerization to propylene with an average rate constant k_d, unless it is deactivated by energy transfer through collisions at a rate ω with the bath molecules. The dagger indicates an electronically excited species; the asterisk indicates a vibrationally excited molecule. It is interesting to note that only reaction a is observed during thermolysis of I.[7]

The total quantum yield for $C_2H_4 + C_3H_6$ formation at 254-nm excitation was 0.16 and was independent of pressure up to 37 torr of isopentane added to the reaction mixture. We have not measured the quantum yield at any other wavelength of excitation, nor have we searched for products other than hydrocarbons. The fate of the SO and CH_2SO will have to be left to future work with this system.

The dependence of the C_3H_6/C_2H_4 product ratio on mode of excitation and pressure is illustrated in Figure 2. We have also summarized these date in Table I. During direct photolysis the product ratio clearly depends on excitation energy; lower excitation energy favors ethylene formation relative to the C_3H_6 pathways. While the C_3H_6/C_2H_4 ratio is dependent on excitation energy, its pressure dependence appears at pressures greater than roughly 10 torr. The pressure dependence of this product ratio also indicates that the lifetime of the S_1 state is sufficiently short such that photofragmentation occurs more rapidly than collisional vibrational energy transfer in the pressure region below ~10 torr. Since fragmentation of I to ethylene and sulfine has been observed during thermolysis,[7] one might suspect that the pathway yielding C_2H_4 during photolysis is indicative of a $S_0 \leftarrow S_1$ internal conversion process. Ethylene formation in cyclobutanone photolysis is a result of "hot" ground-state decomposition.[2] However, there is no pressure dependence in the total quantum yield for decomposition of I up to 40 torr with isopentane as a diluent, and the data in Table II indicate that there is no significant pressure dependence in the quantum yield with pressures up to 530 torr of oxygen in the system. However, the unimolecular rate constant for decomposition of a vibrationally excited trimethylene sulfoxide with internal energies in excess of 113 kcal mol^{-1} might be greater than 10^{10} s^{-1}, and we simply have not reached pressures high enough to quench this reaction channel. We cannot make estimates of this rate constant because the thermal kinetic data are unavailable. However, decomposition of cyclobutanone[2a] with internal vibrational energies in excess of 113 kcal mol^{-1} has rate constants $\geq 10^{10}$ s^{-1}. In summary, our data do not shed an unambiguous answer to the question of whether C_2H_4 formation is indicative of a $S_0 \leftarrow S_1$ internal conversion process during the photolysis of I.

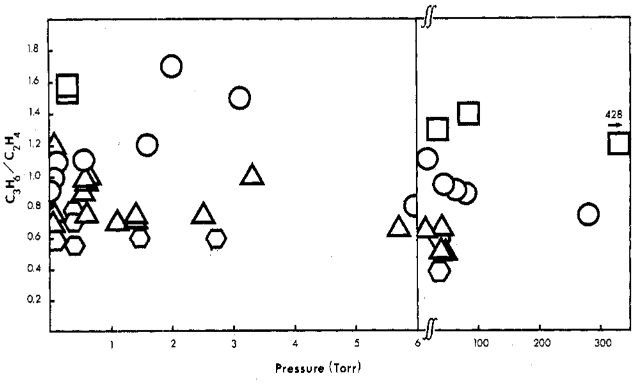


Figure 2. The C_3H_6/C_2H_4 product ratio as a function of pressure and excitation: (○) = 214-nm photolysis; (△) = 228-nm photolysis; (□) = 254-nm photolysis; (□) = Hg($^3P_1$) sensitization.

TABLE I: Product Ratio Produced by Photodecomposition of Trimethylene Sulfoxide[a]

	C_3H_6/C_2H_4	
excitation	press. ≤6 torr	press. ≥6 torr
214 nm	1.1 ± 0.3	0.9 ± 0.1
229 nm	0.83 ± 0.14	0.56 ± 0.06
254 nm	0.63 ± 0.07	0.48 ± 0.10
Hg($^3P_1$)	1.6 ± 0.1	1.3 ± 0.1

[a] The diluent in the direct photolysis experiments is isopentane; the diluent in the Hg($^3P_1$) sensitization experiments is helium.

TABLE II: Effect of Oxygen on Total Quantum Yields and Product Ratios—Trimethylene Sulfoxide Photolysis at 229 nm

total press., torr	diluent	relative total product, $\phi(O_2)/\phi(He)$	(propylene + cyclopropane)/ C_2H_4	propylene/ cyclopropane
261	He	1.0	0.80	0.22
223	O_2	1.08	1.15	0.23
532	O_2	0.79	1.34	0.19

The data in Figure 2 and Table I illustrate that Hg($^3P_1$) sensitized decomposition of I does more greatly favor formation of C_3H_6 relative to C_2H_4 than does direct pho-

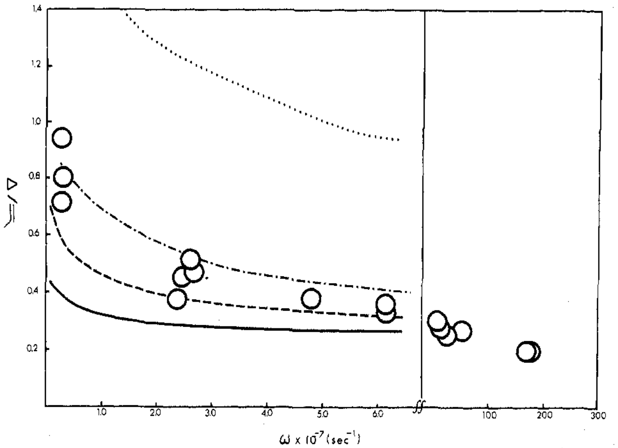


Figure 3. The propylene/cyclopropane ratio as a function of the collision rate of cyclopropane, 229-nm photolysis. The lines are calculated curves for E^+ = 99 kcal (•••), E^+ = 89 kcal (-•-); E^+ = 86 kcal (- - -), and E^+ = 81 kcal (—).

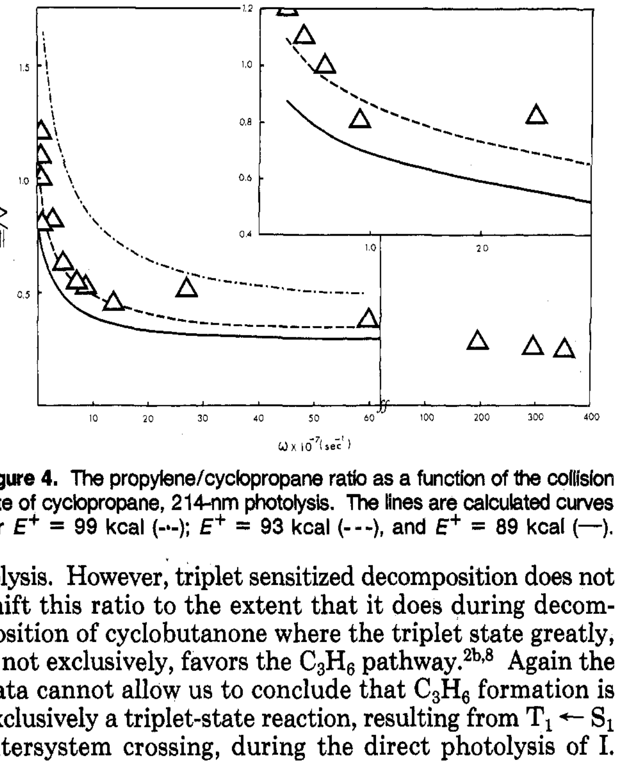


Figure 4. The propylene/cyclopropane ratio as a function of the collision rate of cyclopropane, 214-nm photolysis. The lines are calculated curves for E^+ = 99 kcal (-•-); E^+ = 93 kcal (- - -), and E^+ = 89 kcal (—).

tolysis. However, triplet sensitized decomposition does not shift this ratio to the extent that it does during decomposition of cyclobutanone where the triplet state greatly, if not exclusively, favors the C_3H_6 pathway.[2b,8] Again the data cannot allow us to conclude that C_3H_6 formation is exclusively a triplet-state reaction, resulting from $T_1 \leftarrow S_1$ intersystem crossing, during the direct photolysis of I. Oxygen quenching experiments (Table II) indicate that if C_3H_6 formation does occur by decomposition from the T_1 state during direct photolysis, the lifetime of that state must be $\leq 10^{-10}$ s. The decarbonylation pathway that occurs on direct photolysis of cyclobutanone results from decomposition from both the S_1 and T_1 states; the relative amount of the two states involved depends on energy of excitation.[2]

Energy Partitioning. In Figures 3 and 4 we illustrate the dependence of the propylene/cyclopropane ratio on the collision rate, ω, of the cyclopropane with the bath molecules. These data illustrate that a fraction of the cyclopropane formed during the photofragmentation of I subsequent to its excitation by 229- and 214-nm radiation carries enough internal vibrational energy such that it can undergo unimolecular isomerization to propylene unless it is stabilized through energy transfer by collisions with the bath molecules. Isopentane is the diluent in these experiments, and the collision rate, ω, is calculated from eq 1, where P is the total pressure during the experiment.

$$\omega\ (\mathrm{s}^{-1}) = 4.38 \times 10^7 P\ (\mathrm{torr}) \qquad (1)$$

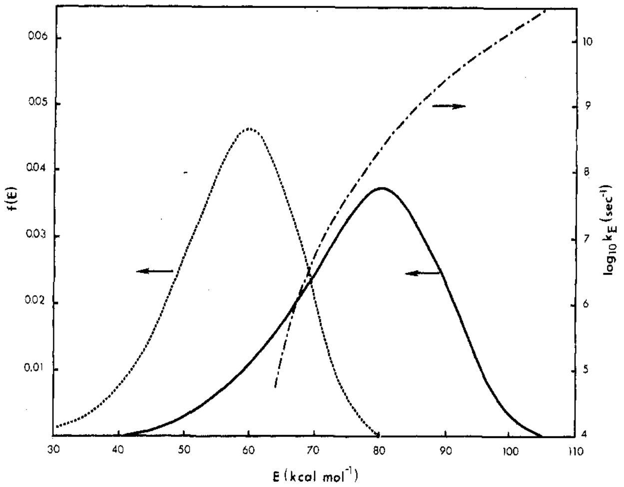


Figure 5. The value of k_E for cyclopropane isomerization to propylene (-•-), and examples of two statistical energy distribution functions: E^+ = 81 kcal (•••) and E^+ = 107 kcal (—).

In calculating the collision rate we have assumed hard-sphere collision diameters of 0.5 and 0.58 nm, respectively, for cyclopropane and isopentane. Moreover, we have corrected these hard-sphere diameters by estimating the Lennard-Jones potential function constants and the $\Omega^{(2,2)}$ integral for the cyclopropane–isopentane pair.[9] Finally, as we explain below, we used a model that assumes that there is statistical intramolecular energy relaxation of the available energy during the separation of the cyclopropane and SO fragments as a reference point for understanding the experimental data. We must then consider that there is energy released along the degree of freedom of the "transition state" that becomes relative translation of the separating fragments; therefore, the cyclopropane would have translational energy in excess of the normal thermal distribution of energies. This would imply that the collision rate would be between 1.75 and 1.96 times (depending on the amount of available energy) the collision rate that cyclopropane would have if it had a thermal distribution of translational energies at 296 K.[10,11] We chose an average value of 1.85 for these calculations.

Experimentally one can characterize the propylene/cyclopropane product ratio with eq 2.

$$\text{propylene/cyclopropane} = (k_d/\omega)\{1 + k_c/k_b\} + k_c/k_b \qquad (2)$$

The experimentally observed rate constant, k_d, is related to the microscopic rate constant, k_E, for unimolecular isomerization of cyclopropane to propylene by reaction 3,

$$k_d = \omega \frac{\sum[k_E/(k_E + \omega)]f(E)}{\sum[\omega/(k_E + \omega)]f(E)} \qquad (3)$$

where f(E) is the distribution function for the internal energies of the vibrationally excited cyclopropane formed on photolysis of I. The values of k_E for cyclopropane structural isomerization have been calculated by using RRKM theory,[12-14] they are illustrated in Figure 5.

We have used a statistical model for energy relaxation in the photofragmentation of I to cyclopropane.[14-16] The distribution function is therefore calculated from eq 4.

$$f(E) = \frac{N(E^+ - E_R)\sum^{E_R} P_R(E_R)}{\sum P^+(E^+)} \qquad (4)$$

In eq 4, $N(E^+ - E_R)$ is the density of energy eigenstates for those internal degrees of freedom of the "activated complex" for the decomposing trimethylene sulfoxide that will be associated with the internal degrees of freedom of the cyclopropane fragment. The sum term in the numerator is the sum of states over those degrees of freedom of the "activated complex" that are to become the SO stretching vibrational degree of freedom, and the three relative translational and two rotational degrees of freedom of the newly formed products. The term in the denominator is a normalization term which is a sum over all of the degrees of freedom of the activated complex, but allowing one of the vibrational modes to be associated with translation of the separating fragments. In order to calculate f(E), we constructed a vibrational frequency assignment for a fragmenting trimethylene sulfoxide by using the known assignments for cyclobutanone,[17] cyclopropane,[18] dimethyl sulfoxide,[19] and SO[3]. The results of the calculation of f(E) are somewhat insensitive to the details of the vibrational frequency assignment that goes into the model.

The amount of energy that is available to be distributed to the degrees of freedom of the products, E^+, includes the sum of the absorbed light energy and the thermal energy of the reactant minus the endothermicity of the reaction at 0 K. We have estimated the standard enthalpy of formation of trimethylene sulfoxide in the gas phase at 298 K from the methods and data provided by Benson.[20,21] If we assume that the strain energy of I is the same as the strain energy of trimethylene sulfide,[20] 19.4 kcal mol^{-1}, we calculate ΔH_f^0(298) of I to be −15 kcal mol^{-1}. If, however, the strain energy of I is closer to the value observed for molecules such as cyclobutanone, cyclobutane, trimethylene oxide, and azetidine (26.0 ± 0.3 kcal mol^{-1}),[20] the ΔH_f^0(298) of I would be closer to −9 kcal mol^{-1}. This uncertainty in the energetics becomes relatively important in discussing the implications of the energy partitioning results. After extrapolating the enthalpy of formation of each of the compounds in reaction b to 0 K through comparison with known data for similar compounds, and estimating the thermal vibrational energy of I at 296 K to be 1.4 kcal mol^{-1}, we estimate the energy available to be partitioned to the degrees of freedom of the cyclopropane and ground electronic state SO($^3\Sigma^-$) products on photolysis of I, E^+, to be 86 kcal mol^{-1} at 254-nm excitation, 99 kcal mol^{-1} at 229-nm excitation, and 107.5 kcal mol^{-1} at 214-nm excitation. These values assume that the strain energy of I is 19.4 kcal mol^{-1}; the available energy could be as much as 6–7 kcal mol^{-1} greater if the strain energy in I is closer to the 26 kcal mol^{-1} value. In Figure 5 we have included samples of f(E) calculated for two different values of E^+.

In Figures 3 and 4 we illustrate the calculated pressure dependence of the propylene/cyclopropane ratio as a function of ω using the statistical model for energy relaxation outlined above with different values of E^+. The data are illustrated for 229- and 214-nm photolysis of I. One can see that there is a nonrandom distribution of all of the available energy in that the curve that best fits the experimental data for 229-nm photolysis corresponds to $E^+ \approx 87$ kcal mol^{-1} (most probable energy, E_{mp}, is 64.5 kcal mol^{-1}); and the calculated curve that best fits the 214-nm photolysis data has $E^+ \approx 93$ kcal mol^{-1} ($E_{\mathrm{mp}} = 69$ kcal mol^{-1}). A significant point is that although there is a nonrandom distribution of all of the available energy, the increase in available energy on going from 229- to 214-nm photolysis is apparently randomly distributed in the fragmentation process.

The energetics used to calculate E^+ above refer to the production of ground electronic state SO($^3\Sigma^-$). It is unlikely that the missing energy is due to vibrationally excited SO($^3\Sigma^-$) being produced since the vibrational frequency and the bond distance of the SO group change very little on going from reactant to product.[3,19] Since SO($^1\Delta$) lies 6150 cm^{-1} (17.6 kcal mol^{-1}) above its ground electronic state,[3] reaction channels which yield electronically excited SO are energetically allowed. The difference between the total available energy and the values of E^+ that best fit the experimental data is 12–14 kcal mol^{-1}. This number could be as much as 18–20 kcal mol^{-1} if the strain energy of I is as great as 26 kcal mol^{-1}. Therefore, it is possible that reaction b actually produces electronically excited SO and the remainder of the available energy is randomly distributed to the degrees of freedom of the products. The fragmentation reaction may occur from a singlet state of I, and the reaction is driven to produce SO($^1\Delta$) in order to conserve spin angular momentum.

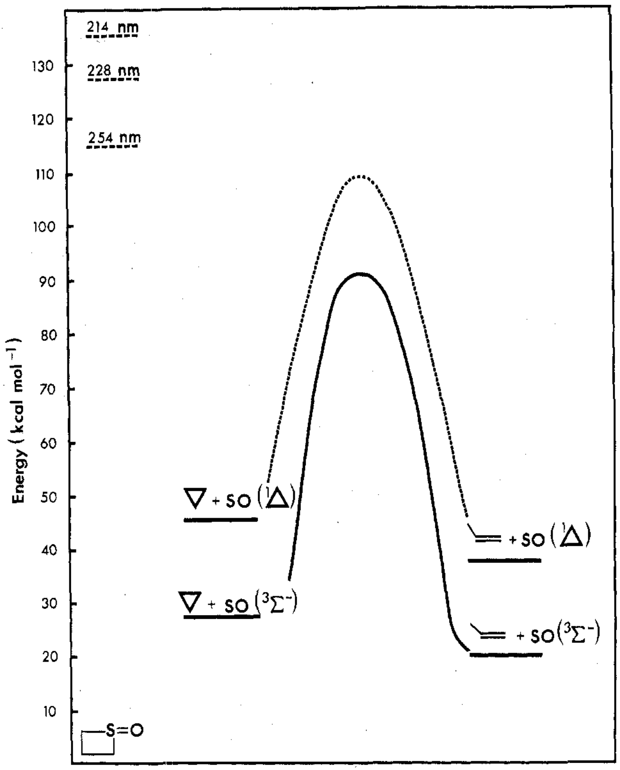


Figure 6. A schematic illustration of the energetics of the trimethylene sulfoxide system. Trimethylene sulfoxide is taken as the zero of energy, and the barrier is to indicate the magnitude of the critical energy for isomerization of cyclopropane to propylene.

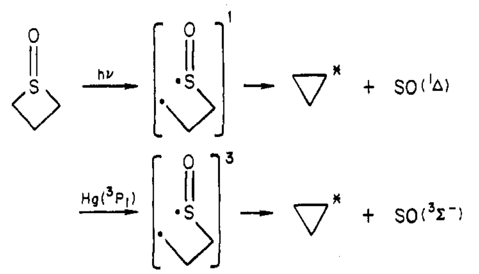
This explanation is supported by the pressure dependence of the propylene/cyclopropane ratio that is observed when I is photolyzed by 254-nm radiation as compared to the pressure dependence of this ratio observed on Hg($^3P_1$) sensitized decomposition. The energetics of the system are diagramed in Figure 6. One can see that during direct photolysis by 254-nm radiation there is sufficient energy available ($E^+ = 86$ kcal mol^{-1}) to produce some vibrationally "hot" cyclopropane with enough internal energy such that they can surmount the energy barrier for isomerization to propylene ($E_0 \approx 63.5$ kcal mol^{-1})[14] if ground electronic state SO($^3\Sigma^-$) is the product. However, if SO($^1\Delta$) is the product, the available energy is insufficient to yield cyclopropanes with enough internal energy such that one could observe a pressure dependent propylene/cyclopropane ratio. The data in Table III illustrate that while Hg($^3P_1$) sensitization does yield a pressure dependent propylene/cyclopropane ratio, direct photolysis at 254 nm does not. It is likely that, in order to conserve spin angular momentum, direct photolysis produces SO($^1\Delta$) and cyclopropane, whereas for triplet sensitized decomposition

TABLE III: Propylene/Cyclopropane Ratio; Hg($^3P_1$) vs. Direct Photolysis of Trimethylene Sulfoxide

press., torr	diluent	propylene/ cyclopropane
Hg($^3P_1$) Sensitization ($\leqslant$0.3 torr of I)		
~0.3	0	0.54
~0.3	0	0.54
21	He	0.27
34	He	0.32
86	He	0.18
263	He	0.12
360	He	0.22
428	He	0.17
Direct Photolysis (254 nm)		
0.11	isopentane	0.26
~0.5	0	0.28
1.9	isopentane	0.27
2.7	isopentane	0.24
37	isopentane	0.18

the products are SO($^3\Sigma^-$) and cyclopropane.

We can propose a mechanism that involves initial rupture of a C–S bond to produce a diradical intermediate which could undergo intramolecular randomization of the available energy while it is decomposing to cyclopropane and SO($^1\Delta$) or SO($^3\Sigma^-$):



However, to really understand the details of this system, including a better characterization of the reaction that produces ethylene, one should likely extend these studies. A study of the *cis*- and *trans*-dimethyl isomers of trimethylene sulfoxide might prove helpful in elucidating if a trimethylene biradical is an intermediate as well as allowing some better insight about the cleavage reaction channel.

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Effect of Solvent on the Ion-Pair Dissociation Constant of Tetramethoxybenzene Cation Radical Ion Pairs

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The equilibrium constant for the dissociation of the cation radical ion pair of 1,2,4,5-tetramethoxybenzene with I_3^- has been determined at −20 °C in acetonitrile and dichloromethane. Equilibrium constants were measured from solvent mixtures with nitromethane by following the changes in *g* value on addition of varying amounts of I_3^- to solutions of the free radical and extrapolating to pure secondary solvent (acetonitrile or dichloromethane).

Introduction

In order to interpret the solvation phenomena involving the formation of ion pairs, one should consider two very important factors. One is a purely electrostatic factor, from which the well-known equations which relate the ion-pair dissociation constant to the dielectric constants (ϵ) of the solvents were derived.[1,2] The other is an empirical approach to solute–solvent interactions which states that all solvents, at least in principle, possess both nucleophilic and electrophilic properties.[3] These properties have been summarized by the Guttmann donor[4] and acceptor numbers.[5] Thus, a solvent with a relatively high dielectric constant and a low donor or acceptor number could lead to the formation of ion pairs. Table I shows these properties for some common solvents. As an example, hexamethylphosphoramide (HMPA) has a moderate dielectric constant (29.6) but an unusually high donor number (38.8), thus making it an excellent cation solvator. This property makes HMPA a very good solvent for the generation of essentially free ions,[6] but, because of the fact that the anions in HMPA are poorly solvated (acceptor number = 10.7), it is possible under some conditions to form ion pairs.[7]

On the other hand, nitromethane (MeNO$_2$) has a larger

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