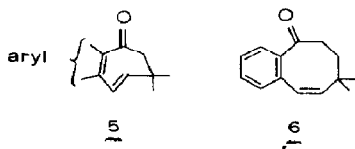


Nevertheless, the primary photochemical process in all cases appears to be identical. These reactions proceed via a trans cycloheptadienone **5** or an excited state with a similarly twisted geometry. This conclusion is supported by the results of trapping experiments and of product studies on the eight-membered ring analog, **6**.



The dimerization mechanisms will be discussed. The wide structural variation of the dimers is a consequence of subtle reactivity differences in the reactive species and in the substrates with which they react. These results will be compared with previous studies on strained seven [2] and eight-membered [3] rings. [4]

We thank the National Institutes of Health for a grant (GM-15997) in support of this research.

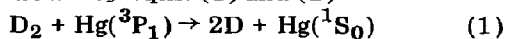
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- 2 E. J. Corey, M. Tada, R. LeMahieu and L. Libit, *J. Am. Chem. Soc.*, **87** (1965) 2051; P. E. Eaton and K. Lin, *ibid.*, **87** (1965) 2052; H. Nozaki, M. Kurita and R. Noyori, *Tetrahedron Lett.*, (1968) 2025; H. Nozaki, and M. Kurita, *ibid.*, (1968) 3635.
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F1

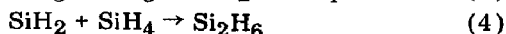
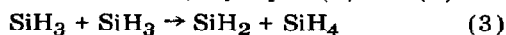
Mercury Photosensitized Reactions of Silyl Radicals

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Deuterium atoms, formed by mercury photosensitization in a flow system coupled to a mass spectrometer, react with monosilane to form silyl radicals and hydrogen-d₁ as shown by eqns. (1) and (2)



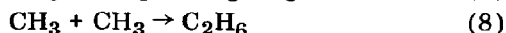
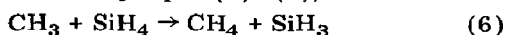
With only deuterium and monosilane present in the flow system, the silyl radicals react with each other to form disilane, which is the only significant product observed. When mixtures of monosilane-d₀ and monosilane-d₄ are subjected to D-atom attack via eqn. (2), isotopically labelled disilane is produced. Detailed mass spectrometric studies of the dependence of this isotopic distribution on ionizing electron energy show the virtual absence of Si₂D₃H₃ and thus confirm recent reports [1, 2] that disilane is formed from silyl radicals solely by eqns. (3) and (4).



In the presence of methyl chloride the rapid abstraction of chlorine atoms by silyl radicals (5) competes effectively with eqn. (3) so that monochlorosilane is formed simultaneously with disilane. Under the conditions of our experiments



methane, methylsilane and ethane are observed in comparable amounts. This suggests that the methyl radicals formed in (5) are consumed by eqns. (6) - (8), viz.



The relative rates of formation of disilane and chlorosilane are such that, with the assumption that k_3 is equal to the specific collision rate of SiH₃ radicals, a value of $k_6 \sim 2 \times 10^{-16} \text{ cm}^3/\text{s}$ is obtained. This rather large rate constant at 300 °K is consistent with the fact that the Si-Cl bond is much stronger than the C-Cl bond.

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F5

Vacuum UV Photoisomerization of *cis*-2-Butene in the Presence of Sulfur Hexafluoride

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At 8.4 eV (xenon resonance lamp), the quantum yield of the isomerization of *cis*-Butene-2 is of the order of 0.08. In the presence of 10% SF₆, the quantum yield is 0.90. Addition of methane (70 Torr) to the *cis*-Butene-2 : SF₆ mixture (1:0.1 Torr) results in a yield of 0.10.

At 10.0 eV (krypton resonance lamp), the quantum yield Φ (*trans*-Butene-2) obtained with the *cis*-Butene-2:O₂: SF₆ mixture is of the order of 270 ± 50 and is not altered by the presence of ammonia or nitrous oxide (0 - 0.06 Torr). The progressive addition of carbon tetrachloride gradually reduces the isomerization yield. On the other hand, the isomerization disappears (Φ (*trans*-Butene-2) = 1.0) in the presence of dimethylamine, trimethylamine, or 1,3-pentadiene (0.05 Torr). The isomerization depends on the dose rate: Φ (*trans*-Butene-2) = $\alpha 1/(I)^{1/2}$.

All these results can be explained on the basis of an ionic mechanism involving at least a negative ion.

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F8

Role of O₂ (¹Σ_g⁺, ¹Δ_g) in the Photosensitized Oxidation of Diphenylamine

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Methylene blue, Rose Bengal and eosine sensitized photo-oxidation of diphenylamine (DPA) leads to the formation of *N*-phenyl-*p*-benzoquinonimine as primary pro-

duct just as the reaction of O₂ (¹Δ_g) generated *in situ* by the reaction of NaOCl + H₂O₂. NaOCl reacts with DPA but under controlled conditions there is no apportioning of NaOCl between DPA and H₂O₂. In the dye sensitizations energy transfer to DPA does not occur and diphenyl nitroxide to which triplet DPA is a precursor is not formed. The rate of oxidation decreases in the presence of allylthiourea and semiquinone radical is not an intermediate. Quenching by singlet O₂ quenchers fits into Stern-Volmer equation suggesting participation of O₂ (¹Σ_g⁺, ¹Δ_g). The effect of dielectric and viscosity of the medium on both dye sensitized and NaOCl + H₂O₂ systems confirms the presence of singlet O₂ as oxidizing agent in these reactions.

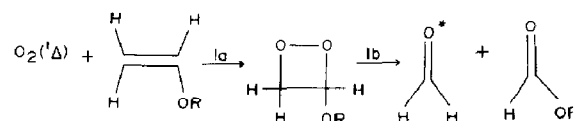
F9

Chemiluminescence Study of the Reactions of O₂ (¹Δ_g) with Vinyl Ethers

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The gas phase reaction of O₂ (¹Δ) with ethyl vinyl ether has been shown to produce formaldehyde (A → X) chemiluminescence via: [1]



where R = C₂H₅

Our earlier study has been extended to include the series methyl, ethyl and n-butyl vinyl ethers. In all three reactions, only H₂CO* chemiluminescence was observed and the upper state vibronic populations are very similar (Fig. 1). Equilibrium statistical mechanics predicts that the carbonyl fragment having the higher vibronic density of states at the available energy will be formed preferentially. We observe essentially identical quantum yields for H₂CO* production for all three reactions in spite of the great increase in the density of states of the HCOOR product in progressing through the series from methyl to n-butyl. This is strong evidence that the electronic energy is partitioned in a non-