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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% SF_6, the quantum yield is 0.90. Addition of methane (70 Torr) to the *cis*-Butene-2 : SF_6 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:O_2: SF_6 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 O_2 ($^1\Sigma_g^+$, $^1\Delta_g$) 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 product just as the reaction of O_2 ($^1\Delta_g$) generated *in situ* by the reaction of NaOCl + H_2O_2. NaOCl reacts with DPA but under controlled conditions there is no apportioning of NaOCl between DPA and H_2O_2. 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 O_2 quenchers fits into Stern–Volmer equation suggesting participation of O_2 ($^1\Sigma_g^+$, $^1\Delta_g$). The effect of dielectric and viscosity of the medium on both dye sensitized and NaOCl + H_2O_2 systems confirms the presence of singlet O_2 as oxidizing agent in these reactions.

F9

Chemiluminescence Study of the Reactions of $O_2(^1\Delta_g)$ with Vinyl Ethers

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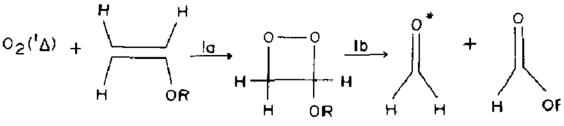
The gas phase reaction of $O_2(^1\Delta)$ with ethyl vinyl ether has been shown to produce formaldehyde (A → X) chemiluminescence via: [1]



where R = C_2H_5

Our earlier study has been extended to include the series methyl, ethyl and n-butyl vinyl ethers. In all three reactions, only H_2CO^* 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 H_2CO^* 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-