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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) = α $1/(I)^{1/2}$.

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.
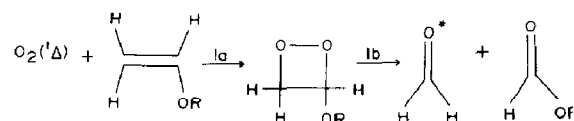
F9
Chemiluminescence Study of the Reactions of $O_2(^1\Delta_g)$ with Vinyl Ethers

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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-
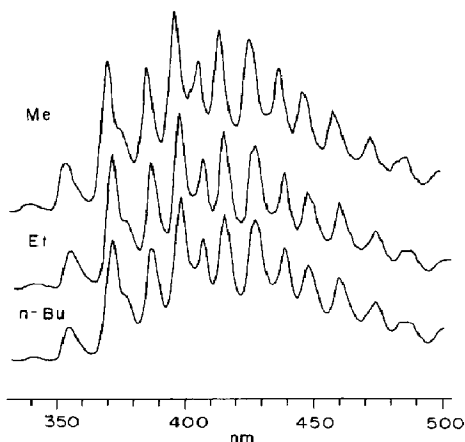
Fig. 1. Formaldehyde (A $^1A_2 \rightarrow$ X $^1A_1$) *che-miluminescence from the reactions of vinyl ethers with* $O_2(^1\Delta_g)$. *Pressure: 4 Torr; temperature: 550 K; spectral slit width: 2 nm.*

statistical and perhaps exclusive fashion to the formaldehyde product.

The chemiluminescence showed an Arrhenius activation energy of 12 to 13 kcal/mole, the methyl value being higher than ethyl or n-butyl. The low activation energy suggests that (1a) is rate limiting since the thermal activation energies for dioxetane decompositions are known to be ca. 25 kcal/mole.

Experiments have been reported measuring the rate of decomposition of the adduct of $O_2(^1\Delta_g)$ plus ethyl vinyl ether relative to its rate of collisional stabilization [1]. Our most recent experiments, reported here, establish the adduct lifetime at $\leq 10^{-8}$ sec for all three vinyl ether reactions and there was no evidence of collisional stabilization.

In summary, the observed behavior of these systems is consistent with a two step mechanism involving formation of a vibrationally excited dioxetane intermediate which then decomposes very rapidly to give the products H_2CO^* plus HCOOR.

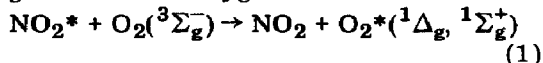1 D. J. Bogan, R. S. Sheinson, R. G. Gann and F. W. Williams, J. Am. Chem. Soc., 97 (1975) 2560.

F11
Excitation of Singlet Molecular Oxygen by Energy Transfer from NO_2 and HO_2

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The quenching of electronically excited NO_2 by O_2 is known [1 - 4] to produce singlet molecular oxygen

$$NO_2^* + O_2(^3\Sigma_g^-) \rightarrow NO_2 + O_2^*(^1\Delta_g, {}^1\Sigma_g^+) \quad (1)$$

NO_2^* excited by absorption of radiation yields predominantly [1] $O_2(^1\Delta_g)$. Some evidence [3, 4] suggests that addition of NO to O, $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ increases $[O_2(^1\Sigma_g^+)]$, although the mechanism of enhancement was not established. We wished to see whether quenching by O_2 of NO_2^*, excited by the recombination of O and NO, formed mainly $O_2(^1\Sigma_g^+)$.

We measured simultaneously the intensities of the air afterglow, the $O_2(^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-)$ (λ = 760 nm) and the $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)(\lambda$ = 1.26 μm) emission in a discharge flow system. Using a microwave discharge in an O_2/He flow as the source of O, it was shown that $[O_2(^1\Sigma_g^+)]$ increased in the presence of NO beyond that accounted for by the energy pooling reaction

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \rightarrow O_2(^1\Sigma_g^+) + O_2 \quad (2)$$
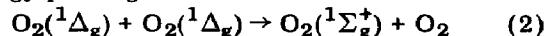
This result means that there is a genuine enhancement of $O_2(^1\Sigma_g^+)$, rather than a *suppression*, in the presence of NO, of the loss of $O_2(^1\Sigma_g^+)$ in reaction with O_3 from the discharge.

The kinetic data show that the "additional" $O_2(^1\Sigma_g^+)$ (i.e. beyond that from reaction (2) is formed at a rate proportional to $[NO_2^*]$ and approximately proportional to $[O_2]$. However, $[O_2(^1\Delta_g)]$ is also nearly proportional to $[O_2]$ so that $O_2(^1\Sigma_g^+)$ could be excited either in reaction (1) or in the process

$$NO_2^* + O_2(^1\Delta_g) \rightarrow NO_2 + O_2(^1\Sigma_g^+) \quad (3)$$

In diagnostic experiments, where O was generated by the N + NO reaction, and O_2 added separately, neither $O_2(^1\Sigma_g^+)$ nor $O_2(^1\Delta_g)$ was observed. This result favours reaction (3) as the source of $O_2(^1\Sigma_g^+)$ in the O_2 discharge experiments. We are currently trying to establish unequivocally whether reaction (3) yields $O_2(^1\Sigma_g^+)$ and to determine the absolute efficiency of excitation.