Fig. 1. Formaldehyde (A $^1A_2 \to$ 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 $\leqslant 10^{-8}$ 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.

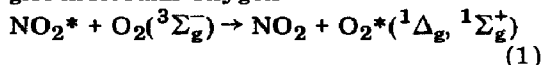1 D. J. Bogan, R. S. Sheinson, R. G. Gann and F. W. Williams, J. Am. Chem. Soc., 97 (1975) 2560.

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

D. J. GIACHARDI, G. W. HARRIS and R. P. WAYNE
Physical Chemistry Laboratory, Oxford (U.K.)

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

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

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 $O_2(^1\Sigma_g^+ \to {}^3\Sigma_g^-)$ (λ = 760 nm) and the $O_2(^1\Delta_g \to {}^3\Sigma_g^-)(\lambda = 1.26 \ \mu m)$ 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

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \to O_2(^1\Sigma_g^+) + O_2 \quad (2)$$
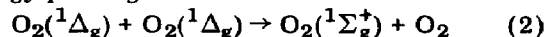
This result means that there is a genuine enhancement of $O_2(^1\Sigma_g^+)$, rather than a *suppression*, in the presence of NO, of the loss of $O_2(^1\Sigma_g^+)$ in reaction with O_3 from the discharge.
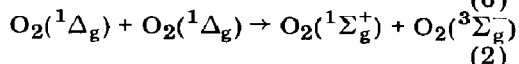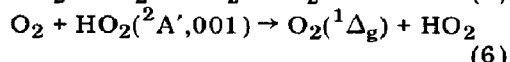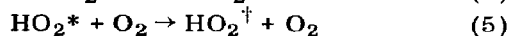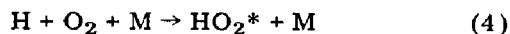
The kinetic data show that the "additional" $O_2(^1\Sigma_g^+)$ (i.e. beyond that from reaction (2) is formed at a rate proportional to $[NO_2^*]$ and approximately proportional to $[O_2]$. However, $[O_2(^1\Delta_g)]$ is also nearly proportional to $[O_2]$ so that $O_2(^1\Sigma_g^+)$ could be excited either in reaction (1) or in the process

$$NO_2^* + O_2(^1\Delta_g) \to NO_2 + O_2(^1\Sigma_g^+) \quad (3)$$
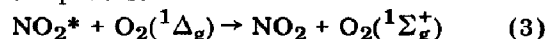
In diagnostic experiments, where O was generated by the N + NO reaction, and O_2 added separately, neither $O_2(^1\Sigma_g^+)$ nor $O_2(^1\Delta_g)$ was observed. This result favours reaction (3) as the source of $O_2(^1\Sigma_g^+)$ in the O_2 discharge experiments. We are currently trying to establish unequivocally whether reaction (3) yields $O_2(^1\Sigma_g^+)$ and to determine the absolute efficiency of excitation.

Energy transfer from $O_2(^1\Delta_g)$ to HO_2 has been reported previously [5]. We now present evidence for the reverse transfer. An H_2/Ar mixture was passed through a microwave discharge and O_2 added just upstream of an observation port. We observe emission bands at 762 nm and 1.26_5, 1.43, 1.51 μm. Replacement of H_2 by D_2 caused the 1.51 μm band to disappear, but all other bands were left unaffected. Thus the 762 nm band seems to be the $O_2(^1\Sigma_g \rightarrow {}^3\Sigma_g^-)$ emission rather than the (possible) $9 \rightarrow 4$ vibrational transition in OH. The other bands are tentatively assigned to the following transitions: $\lambda = 1.26_5$ μm, $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ and/or $HO_2(^2A', 001 \rightarrow {}^2A'', 000)$; $\lambda = 1.43\mu$m, $HO_2(^2A', 000 \rightarrow {}^2A'', 000)$; $\lambda = 1.51\mu$m, $HO_2(^2A'', 200 \rightarrow {}^2A'', 000)$.

The most probable excitation mechanism is

$$H + O_2 + M \rightarrow HO_2^* + M \qquad (4)$$

$$HO_2^* + O_2 \rightarrow HO_2^\dagger + O_2 \qquad (5)$$

$$O_2 + HO_2(^2A', 001) \rightarrow O_2(^1\Delta_g) + HO_2 \qquad (6)$$

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-) \qquad (2)$$

where HO_2^* signifies some undefined excited state of HO_2, and $HO_2^\dagger$ denotes the emitting states ($^2A',001$; $^2A',000$; $^2A'',200$). However, other excitation processes are not excluded, and further experiments are in progress to elucidate the mechanism.

More detailed information on the HO_2 system is published in Chem. Physics Letts., 32 (1975) 586; a description of the NO_2 system will appear in J. Chem.Soc. Faraday Trans.

1 T. C. Frankiewicz and R. S. Berry, J. Chem. Phys., 58 (1973) 1787.
2 I. T. N. Jones and K. D. Bayes, J. Chem. Phys., 59 (1973) 3119.
3 R. J. O'Brien and G. H. Myers, Chem. Phys. Letters, 9 (1971) 544.
4 D. T. Stewart, J. Atmos. Terrest. Phys., 10 (1957) 318.
5 K. H. Becker, E. H. Fink, P. Langen and U. Schurath, J. Chem. Phys., 60 (1974) 4623; Z. Naturforsch., 28a (1973) 1872.

G1
High Resolution Lifetimes in Excited States
E. W. SCHLAG
Institute for Physical and Theoretical Chemistry, Technical University of Munich, 8 Munich 2 (F.R.G.)

We will discuss recent results with naphthalene showing the additional information which can be obtained with high resolution laser experiments. We have demonstrated that it is possible to obtain lifetimes of isolated vibronic states at pressures below 1 Torr with a resolution in the picometer range. For this purpose a tunable high resolution laser is doubled into the U.V. It is shown that a single shot suffices for the entire decay curve hence obviating averaging techniques for these experiments. Isotope effects at high resolution will also be discussed. It will be shown that it is now also possible to populate isolated states in the low pressure limit by two-photon absorption. This allows new states to be reached which have hitherto not even been assigned.

G3
Polarization Effects on Fluorescence Measurements
E. D. CEHELNIK and K. D. MIELENZ
Analytical Chemistry Division, Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234 (U.S.A.)

Polarization effects on fluorescence measurements are a function of four independent variables. The first is $F = S^V/S^H$, the polarization ratio of the exciting light flux S which reaches the sample. The second is r, the emission anisotropy of the sample, which is the polarization "response" of the sample to plane polarized exciting light. The third is $G = T_V/T_H$, the emission detection system, which is the ratio of the responsivities of the emission detection system to vertically and horizontally polarized light. The fourth is α, the viewing angle, which is the angle between the direction of the propagation of the exciting light and the direction from which the emission is being detected.

The equation which defines the overall relative error which can be obtained due to polarization effects is