

## R4

Effect of Vibrational Energy on Elementary  $O_3$  Reactions

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We have recently reported that rate constants for the reactions of ozone with NO, [1, 2] SO, [3] and  $O_2$  ( $^1\Delta$ ) [1] are enhanced considerably when the reactant  $O_3$  possesses excess internal energy in the form of vibration. In this paper we intend to summarize these earlier results and comment about our ongoing studies involving Cl and O atoms.

The reactions have been studied by using chemiluminescence and resonance fluorescence techniques to observe either the real-time or modulated behavior of reactant or product species following laser excitation of the  $O_3$ . Vibrationally excited ozone is produced in the asymmetric stretch normal mode utilizing a coincident absorption of the P(30) 9.6  $\mu m$   $CO_2$  laser line. Reactant species are admitted under steady state or pulsed production and the measurements are initiated.

Typical rate enhancements of one order of magnitude are observed to be associated with one quantum of excess vibrational energy in  $O_3$ . Most recently we have found that, for at least the reaction with NO, the enhancement in the rate constant can be identified with an increased Arrhenius A factor [4]. Thus, the reactions of both thermal and vibrationally excited  $O_3$  with NO exhibit the same activation energy barrier. Studies on a number of other systems are presently being conducted to determine the uniformity of this observation.

- 1 M. J. Kurylo, W. Braun, A. Kaldor, S. M. Freund, and R. P. Wayne, *J. Photochem.*, 3 (1974/75) 71.
- 2 W. Braun, M. J. Kurylo, A. Kaldor, and R. P. Wayne, *J. Chem. Phys.*, 61 (1974) 461.
- 3 A. Kaldor, W. Braun, and M. J. Kurylo, *J. Chem. Phys.*, 61 (1974) 2496.
- 4 M. J. Kurylo, W. Braun, C. Nguyen Xuan, and A. Kaldor, *J. Chem. Phys.*, 62 (1975) 2065.

## R5

## The Chemiluminescence of Ozone Reactions in the Gas Phase

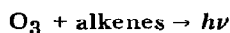
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Many gas phase reactions of ozone are chemiluminescent. Emission has been observed from beyond 2000 nm ( $O_3 + NO$ ) to wavelengths as short as 225 nm ( $O_3 + C_2F_4$ ). Unlike liquid phase luminescence, the spectra observed from gas phase reactions usually contain a wealth of detail giving much information on the nature of the excited intermediates. The systems to be discussed are as follows:



Although ultraviolet luminescence was observed in this system 30 years ago, the first published spectrum appeared in 1971 [1] and the luminescence was attributed to  $SO_2^*$ . More recently a new emission was reported and attributed to  $HSO^*$  or  $HSO_2^*$  [2]. The kinetics of this system have recently been reinvestigated [3] and a mechanism proposed which accounts for the observed rate law and chemiluminescence.



Every system of this type so far investigated emits light. Allene gives a well resolved spectrum in the 340 - 520 nm region which has been identified [4] as singlet excited  $CH_2O$ . Molecular oxygen did not quench the emission. A more extensive study by Pitts *et al.* [5] showed that  $O_2$  did not quench the  $CH_2O(^1A'')$  emission in the reaction of  $O_2$  with eight alkenes studied. On the other hand  $O_2$  largely quenched the Meinel bands from the  $O_3/C_2H_4$  system but not from  $O_3/cis$ -butene-2 or  $O_3/isobutene$ . A mechanism is proposed to account for the observed rate law of  $O_3/alkene$  systems and for the inhibiting effect of  $O_2$ . In the case of the  $O_3/C_2H_4$  system the mechanism gives an explanation for the chemiluminescence and for the observed order of the emitted intensity.



A previously unreported emission has been found for this system. The lumin-

escence is entirely within the ultraviolet region and extends to wavelenths as short as 225 nm (127 kcal/einstein). The identity of the emitter and possible mechanisms for the chemiluminescence will be considered.

- 1 W. A. Kummer, J. N. Pitts, Jr. and R. P. Steer, *Environ. Sci. Tech.*, 5 (1971) 1045.
- 2 K. H. Becker, M. Inocencio and U. Schurath, *Int. J. Chem. Kinet.*, 7 (1975).
- 3 S. Glavas and S. Toby, *J. Phys. Chem.*, 79 (1975).
- 4 S. Toby, *J. Luminescence*, 8 (1973) 94.
- 5 B. J. Finlayson, J. N. Pitts, Jr. and R. Atkinson, *J. Am. Chem. Soc.*, 96 (1974) 5356.

## R6

### Recent Measurements of Stratospheric Water Vapor

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A balloon borne frost-point hygrometer is being used to measure the vertical distribution of water vapor to a height of 30 km. The measurements which were begun in 1964 now provide an 11-year record of the vertical distribution of water vapor for the mid-latitude stratosphere in the northern hemisphere and constitute the only continuous series of measurements over a period of several years. The water vapor to air mass mixing ratio for the stratosphere is found to be approximately constant with height. The total accumulation of data for the 11-year period shows a modal distribution of mixing ratio for the lower stratosphere which is centered at 2.7 ppm with 80 percent of the observations within  $\pm 1$  ppm of the modal value. The times series shows a trend of increase during the first 6 years followed by a step decrease in 1971 with a level trend thereafter. A seasonal cycle is observed in the lowest stratospheric levels with minimums in late winter. The data record provides a reference base for early detection of significant changes in stratospheric water vapor distribution.

Aircraft measurements and balloon soundings since November 1974 show a pronounced decrease in water vapor con-

centration in the low stratosphere between 18 and 16 km. The minimum in the vertical distribution of water vapor coincides with the base of a layer of increased aerosol concentration between 15 and 20 km which was first observed by investigators at mid-latitudes in November 1974.

## R7

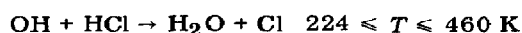
### Laboratory Kinetic Studies of Reactions of Atmospheric Interest Using Resonance Fluorescence Spectroscopy

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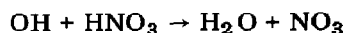
The technique of UV resonance fluorescence detection of reactive atoms and radicals has been coupled with a discharge-flow apparatus to study reactions of OH with  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{D}$ , of  $\text{Cl}$  with  $\text{O}_3$ , and of  $\text{ClO}$  with  $\text{NO}$  and  $\text{O}$ . With the exception of the  $\text{OH} + \text{D}$  exchange reaction all of these are of importance in the photochemistry of the earth's stratosphere.

The sensitivity of the resonance fluorescence technique ( $[\text{OH}] \geq 2 \times 10^9 \text{ cm}^{-3}$ ) has permitted the direct investigation of these reactions under conditions where the observed species' disappearance is unambiguously attributed to the corresponding reaction. The study of the  $\text{OH} + \text{D}$  exchange demonstrates the valuable selectivity of resonance fluorescence such that OH decay could be followed without interference by OD.

The rate constants and temperature dependencies of these reactions studied at total pressure of 1 – 10 Torr of He are:



$$k = 2.0 \times 10^{-12} \times \exp \left[ -\frac{620 \text{ cal/mole}}{RT} \right] \text{ cm}^3 \text{ sec}^{-1} \quad (1)$$



$$295 \leq T \leq 470 \text{ K}$$

$$k = 0.89 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (2)$$