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Effect of Vibrational Energy on Elementary O₃ Reactions

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We have recently reported that rate constants for the reactions of ozone with NO, [1, 2] SO, [3] and O₂ (¹Δ) [1] are enhanced considerably when the reactant O₃ 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 O₃. Vibrationally excited ozone is produced in the asymmetric stretch normal mode utilizing a coincident absorption of the P(30) 9.6 μm CO₂ 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 O₃. 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 O₃ 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.

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The Chemiluminescence of Ozone Reactions in the Gas Phase

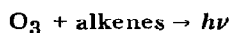
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Many gas phase reactions of ozone are chemiluminescent. Emission has been observed from beyond 2000 nm (O₃ + NO) to wavelengths as short as 225 nm (O₃ + C₂F₄). Unlike liquid phase luminescence, the spectra observed from gas phase reactions usually 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 SO₂*. More recently a new emission was reported and attributed to HSO* or HSO₂* [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 CH₂O. Molecular oxygen did not quench the emission. A more extensive study by Pitts *et al.* [5] showed that O₂ did not quench the CH₂O(¹A'') emission in the reaction of O₂ with eight alkenes studied. On the other hand O₂ largely quenched the Meinel bands from the O₃/C₂H₄ system but not from O₃/*cis*-butene-2 or O₃/isobutene. A mechanism is proposed to account for the observed rate law of O₃/alkene systems and for the inhibiting effect of O₂. In the case of the O₃/C₂H₄ 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-