

RECENT ADVANCES IN THE CHEMICAL KINETICS OF THE ATMOSPHERE AND EFFECTS ON CHEMICAL POLLUTION ESTIMATES

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In the field of chemical kinetics new and better data are constantly being obtained. In many cases, the new measurements verify existing data and assure the chemical kineticist that this measurement technique is accurate. Occasionally, however, repetition of previous experiments using different techniques produces unexpected results which may force a radical change in generally accepted scientific viewpoints. One example of such an occurrence is the finding that the reaction



exhibits a pressure dependence and that the rate of this reaction is more than twice as fast at high atmospheric pressures than had been previously believed. The initial reports of this result by Cox *et al.* [1] and Sie *et al.* [2] have been substantiated by later studies which show that the pressure dependence is also a function of the diluent gas used in the experiment [3]. These data indicate that this reaction occurs much faster at tropospheric pressures; thus the new experimental data have a substantial impact on the understanding of the global CO cycle.

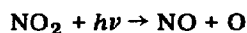
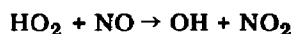
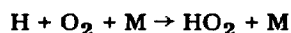
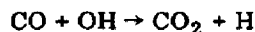
Another recent development which has had profound importance in atmospheric chemistry is the direct measurement of the reaction rate of



which was reported by Howard and Evenson [4] to proceed much faster than indirect measurements had indicated. Some of the consequences of this increased reaction rate are the following:

- (1) effluents from supersonic aircraft flying in the stratosphere may not be as damaging to the ozone layer as had been previously believed;
- (2) the budgets of the nitrogen oxides ($\text{NO} + \text{NO}_2$) in the troposphere have become much less certain;
- (3) catalytic destruction of ozone via free chlorine in the stratosphere is most likely enhanced.

In addition, the combined effect of the rate increases of reactions (1) and (2) indicates that an important photochemical source of ozone in the troposphere may exist through the sequence of reactions



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The impact of these reactions on the global cycle of tropospheric ozone is substantial. Recent studies suggest that this *in situ* photochemical production of ozone may be the largest source of ozone in this region of the atmosphere [5] and that the total ozone column in the atmosphere may have increased by as much as 10% because of anthropogenic activity [6].

Thus it is clear that the atmospheric budgets of carbon monoxide, ozone, nitrogen oxides and odd hydrogen radicals are quite interdependent. Furthermore, our understanding of these interactions has changed considerably in the past year because of the new chemical kinetics data which have appeared recently in the literature.

- 1 R. A. Cox, R. G. Derwent and P. M. Holt, *J. Chem. Soc., Faraday Trans. 1*, 72 (1976) 2031.
- 2 B. K. T. Sie, R. Simonaitis and J. Heicklen, *Int. J. Chem. Kinet.*, 8 (1976) 85.
- 3 R. A. Perry, R. Atkinson and J. N. Pitts, Jr., *J. Chem. Phys.*, 67 (1977) 5577.
- 4 C. J. Howard and K. M. Evenson, *Geophys. Res. Lett.*, 4 (1977) 437.
- 5 J. Fishman and P. J. Crutzen, *Nature*, in the press, 1978.
- 6 E. Hesstvedt and I. S. A. Isaksen, paper presented at WMO Symposium on the Geophysical Aspects and Consequences of Changes in the Composition of the Stratosphere, Toronto, June 1978.

CHEMILUMINESCENT ION-MOLECULE REACTIONS

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Chemical reactions with charged reactants, traditionally called "ion-molecule reactions", have been studied for a long time using mass spectrometers. Recently optical detection of the reaction products has been introduced to this field. One studies the emission spectrum for electronically excited products, thereby exploiting the high energy resolution inherent in optical spectroscopy to obtain detailed information on the reaction mechanism. Luminescence from simple charge transfer, e.g. $\text{A}^+ + \text{BC} \rightarrow \text{A} + \text{BC}^{\dagger*}$ or $\text{A}^* + \text{BC}^+$, has been investigated quite extensively, while the optical study of "true" ion-molecule reactions, which proceed by exchange of an atom (rather than just an electron), is a new development. In this report reactions of the type $\text{A}^+ + \text{BC} \rightarrow \text{AB}^{\dagger*} + \text{C}$ or $\text{AB}^* + \text{C}^+$ will be dealt with, which one might call Chemi-Luminescent Ion-Molecule Atom-EXchange (CLIMAX) reactions.

Systems studied so far include reactions of C^+ , O^+ and N^+ ions with hydrogen and hydrocarbons [1 - 5], the reaction $\text{C}^+ + \text{O}_2 \rightarrow \text{CO}^{\dagger*} + \text{O}$ [6] and the reaction $\text{N}^+ + \text{NO} \rightarrow \text{N}_2^{\dagger*} + \text{O}$ [7]. (The last example is a case where the $\text{N}_2^{\dagger*}$ product was first identified optically, and later mass spectrometrically.) The experiments were done using the