GRANT/NASA IN-46
71107-CR
P.4

University of Pittsburgh

Pittsburgh, PA 15260

Final Technical Report Submitted to

National Aeronautics and Space Administration

for Grant No. NGR 39-011-161 entitled

LABORATORY STUDIES OF THE KINETICS OF TROPOSPHERIC AND STRATOSPHERIC ATOM AND RADICAL REACTIONS

Principal Investigator: Dr. Michael F. Golde

For the Period: March 1, 1985 to February 28, 1987

Michael F Golde
Michael F. Golde
Associate Professor
(412) 624-8380

David M. Hercules
David M. Hercules, Chairman
Department of Chemistry
(412) 624-8300

Peter Koehler
Peter F. M. Koehler, Dean
Faculty of Arts & Sciences
(412) 624-6091

Ruthann A. Mangelsdorf
Ruthann A. Mangelsdorf, Head
Grants & Contracts Administration
(412) 624-7400
5/22/87

(NASA-CR-180590) LABORATORY STUDIES OF THE KINETICS OF TROPOSPHERIC AND STRATOSPHERIC ATOM AND RADICAL REACTIONS Final Technical Report, 1 Mar. 1985 - 28 Feb. 1987 (Pittsburgh Univ.) 4 p Avail: NTIS HC
N87-22330
Unclas
G3/46 0071107

A. Laboratory Studies of the Kinetics of Tropospheric and Stratospheric Atom and Radical Reactions.

B. Principal Investigator: Frederick Kaufman, University Professor of Chemistry (d. July 6, 1985).

Acting Principal Investigator: Michael Golde, University of Pittsburgh, Pittsburgh, PA 15260.

C. Abstract of Research Objectives: The research objectives are three-fold: (a) to provide direct measurements of reaction rate constants and branching fractions for elementary reactions necessary in the modeling of the troposphere or stratosphere; (b) to further elucidate details of reaction mechanisms by studying pressure and temperature dependences of reactions, as well as by use of isotopic labels; (c) to improve measurement techniques for radical species in the laboratory, expanding our capabilities for laboratory studies as well as future field studies.

D. Summary of progress and results.

1. The study of the NH_2 + NO reaction has been deferred after the identification of severe problems arising from use of the F + NH_3 generating reaction in the double-injector flow system. The early measurements using this system reproduced rate constants obtained in other flow-tube studies. However, with continued work, the Teflon wall coating eroded, producing OH radicals and causing an increase in the effective measured rate constant. In an uncoated flow tube, much secondary chemistry was observed, including NH and NF chemiluminescence. Clearly reliable product yields cannot be obtained under these conditions.

   This study will be continued in a separate apparatus, where NH_2 will be generated by the clean and very rapid reaction:

   $$Xe^* + NH_3 \rightarrow Xe + NH_2 + H,$$

   and monitored by laser-induced fluorescence. The very low radical concentrations in this system should reduce the importance of secondary chemistry.

2. Evaluation of the results of our study of H + O_2 recombination has led to a reappraisal of the correct form of the 'collision rate' to be used in determining the efficiency of the third body for stabilizing the nascent HO_2 molecule. Troe proposed a formula for this rate, which consists of a modification of the hard sphere collision rate by multiplication by the reduced collision integral appropriate for viscosity. We have concluded that the theoretical foundations of this formula are shaky at best. As an alternative, we propose use of the total quantum mechanical scattering rate. Semiclassically, this rate includes all collisions which are deflected by an angle larger than the Heisenberg uncertainty associated with the trajectory. For a 6-12 potential, this rate is easy to calculate. For the more difficult 12-6-3 potential we have performed calculations using JWKB and JB approximations which allow us to parameterize the rate, thus making calculation of scattering rates for 12-6-3 potentials equally straightforward.

Use of this rate as a reference collision rate is found to account for most of the difference in third body efficiencies observed in the $H + O_2 + M$ reaction. Additionally, the collision efficiencies were all less than 1, which is often not the case when Lennard-Jones collision rates are used.

A paper documenting the development of the total scattering rate, and its application to several collisional studies is in preparation.

3. We have briefly examined the $ClONO_2 + HCl$ reaction. Preliminary results from Molina's lab suggested that $k = 5 \times 10^{-16}$ cm^3/s at room temperature, large enough to have a dramatic effect on the calculated stratospheric ozone reduction. Our measurements, using mass spectrometric detection of product Cl_2, indicated that the heterogeneous wall reaction was two orders of magnitude faster than the proposed homogeneous reaction rate, precluding our measurement of the homogeneous component. Indeed, recently published work from Molina's lab supports this observation and provides an upper bound for the homogeneous, gas phase reaction rate constant of 10^{-19} cm^3/s.

4. Good progress has been made in characterizing sources of CH_3O and in studying its reaction with NO. The reactions of OH and F atoms with CH_3OH have been examined as possible sources of the CH_3O radical. The rate constants of $OH + CH_3OH$ and deuterated analogs were measured by OH laser-excited fluorescence and suggest that the yield of CH_3O is of the order of 10%. The latter reaction was examined more directly using mass spectrometry, by comparing the HF and DF yields from reactions of F with CH_3OD and CD_3OH. Consistent results were obtained, implying a branching fraction of 0.68 ± 0.05 for formation of CH_3O radicals. Previous measurements range between 0.24 and 0.75, but are mostly considerably less direct than the present study.

   A kinetic study of the reaction of CH_3O with NO is nearing completion. CH_3O is produced in this study by the sequence:

$$F + CH_4 \rightarrow CH_3 + HF$$

$$CH_3 + NO_2 \rightarrow CH_3O + NO,$$

   and is monitored by laser-excited fluorescence in excess NO. Measurements span the temperature range 223-473K and the pressure range ($M = He$) 0.75-4 Torr. At 297K, the second-order rate coefficient is $\sim 4 \times 10^{-12}$ $cm^3\ s^{-1}$, but shows a small positive pressure dependence, indicating a contribution from a 3-body combination channel. The reaction shows a small inverse temperature dependence, also consistent with reaction via a bound intermediate.

   The combination product is expected to be methyl nitrite, CH_3ONO. Mass spectrometry indicates peaks at m/e 61 (parent) and 60, but the amplitude ratio differs markedly from that given by pure CH_3ONO in our system. We find the spectrum to be closer to that of nitromethane, CH_3NO_2. Preliminary analysis of the mass spectra of these species and of the reaction products suggests that, at a pressure of 0.5 Torr, the precursor reaction, $CH_3 + NO_2$, yields CH_3NO_2 with a branching fraction of ~ 0.03, and $CH_3O + NO$ yields CH_3ONO with a branching fraction of ~ 0.12.

E. Journal Publications:

1. "Kinetics of the Reactions of OH with C_2H_6, CH_3CCl_3, $CH_2ClCHCl_2$, $CH_2ClCClF_2$, and CH_2FCF_3," K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).

2. "Rate Constant of the OH + HO_2 Reaction from 252 to 420 K," U. C. Sridharan, L. X. Qiu, and F. Kaufman, J. Phys. Chem. 88, 1281 (1984).

3. "Kinetics of Elementary Radical Reactions in the Gas Phase," F. Kaufman, J. Phys. Chem. 88, 4909 (1984).

4. "Detailed Course of the O + HO_2 Reaction," U. C. Sridharan, F. S. Klein, and F. Kaufman, J. Chem. Phys. 82, 592 (1985).

5. "Kinetics of the Isotope Exchange Reaction of ^{18}O with NO and O_2 at 298 K," S. M. Anderson, F. S. Klein, and F. Kaufman, J. Chem. Phys. 83, 1648 (1985).

6. "Rates of Elementary Reactions: Measurement and Applications," F. Kaufman, Science 230, 393 (1985).

7. "Rate Constants for H + O_2 + M at 298 K for M = He, N_2 and H_2O," K.-J. Hsu, J. L. Durant and F. Kaufman, J. Phys. Chem. 91, 1895 (1987).