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FLASH PHOTOLYSIS-SHOCK TUBE STUDIES

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FLASH PHOTOLYSIS-SHOCK TUBE STUDIES OF BIMOLECULAR REACTIONS

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Since its inception,[1] this project has concentrated on the measurement of thermal bimolecular reactions of atomic species with stable molecules. The flash or laser photolysis-shock tube (FP- or LP-ST) method involves first creating the atomic species by photolysis and then monitoring the atomic concentration with atomic resonance absorption spectrometry (ARAS) as a function of the reactant molecular concentration. Studies on H-, O-, and D-atoms have already been carried out with this apparatus. During the past year, two additional studies of this type have been completed. This first is with O-atoms, and the second is with N-atoms. Additionally, experiments designed to measure the curve of growth for Cl-atoms and studies on the thermal decomposition of CH_3Cl have been completed. Lastly, a new type of experiment is described in which radicals are first pyrolytically created and then react with a photolytically produced concentration of an atomic species. The method is called the pyrolysis photolysis-shock tube (PP-ST) technique and has been applied to the $O + CH_3$ reaction between 1609-1972 K.

In the first study, rate constants for the reaction,

$$O + CH_3Cl \rightarrow OH + CH_2Cl, \qquad (1)$$

have been measured over the temperature range, 556-1485 K.[2] Two different techniques have been used, (1) the LP-ST technique at Argonne (Lim and Michael) over the temperature range, 916-1485 K, and (2) the HTP technique at Rensselaer Polytechnic Institute (Ko and Fontijn) over the temperature range, 556-1291 K. Over the range of common temperature overlap, the rate constants are in excellent agreement. Therefore, the entire database has been analyzed together, and the results can be described by the three parameter expression,

$$k_1 = 2.57 \times 10^{-11}\, T^{0.31} \exp(-5633\ K/T)\ cm^3\ molecule^{-1}\ s^{-1}, \qquad (2)$$

for $556 \leq T \leq 1485$ K.

In the second study, rate constants for the reaction,

$$N + NO \rightarrow N_2 + O, \qquad (3)$$

have been measured over the temperature range, 1251-3152 K, with the LP-ST technique. N-atoms have been monitored by the ARAS technique. The data do not show T-dependence over this range and can be represented by,

$$k_3 = (3.7 \pm 0.9) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}, \qquad (4)$$

This result is in satisfactory agreement with recent shock tube results by Davidson and Hanson[3] and Koshi et al.[4] who have used a similar technique It also agrees with results obtained between 196-400 K.[5] This wide invariance with temperature shows that this reaction is one of the simplest addition-elimination reactions of second row elements.

The thermal decomposition of CH_3Cl has been studied by observing the buildup of Cl-atoms with the ARAS technique. The results are shown in Fig. 1 and can be represented by the Arrhenius expression,

$$k_5 = 9.6 \times 10^9 \exp(-27449\ K/T)\ s^{-1}. \quad (5)$$

Kondo, et al.[6] have previously studied this reaction, and the present results do not agree with their conclusions. k_5 has been used along with literature rate constants for the $CH_3 + CH_3$ reactions to provide profiles of $[CH_3]$. Subsequently, SO_2 has been introduced into the system, and the reactions of Cl-, H-, and O-atoms with it have been experimentally checked for importance. It appears that SO_2 is a spectator molecule at the concentrations, temperatures, and densities that are used. After CH_3Cl has had time to significantly decompose, the delayed photolysis of SO_2 then provides a pulse of O-atoms which are then subsequently monitored by the ARAS technique. The only process of sufficient rate to remove O-atoms under the present conditions is the reaction,

$$O + CH_3 \rightarrow H_2CO + H \text{ or } H_2 + CO + H. \quad (6)$$

Fits to O-atom profiles under a variety of conditions gives the T-independent rate constant value,

$$k_6 = (1.4 \pm 0.3) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}. \quad (7)$$

This value agrees well with lower temperature determinations between 294-900 K.[7]

Additional atom with molecule reaction studies and, also thermal decomposition investigations, are in the planning stage at the present time. The reactions that will be studied will either be of theoretical interest to chemical kinetics or be of practical interest in hydrocarbon combustion.

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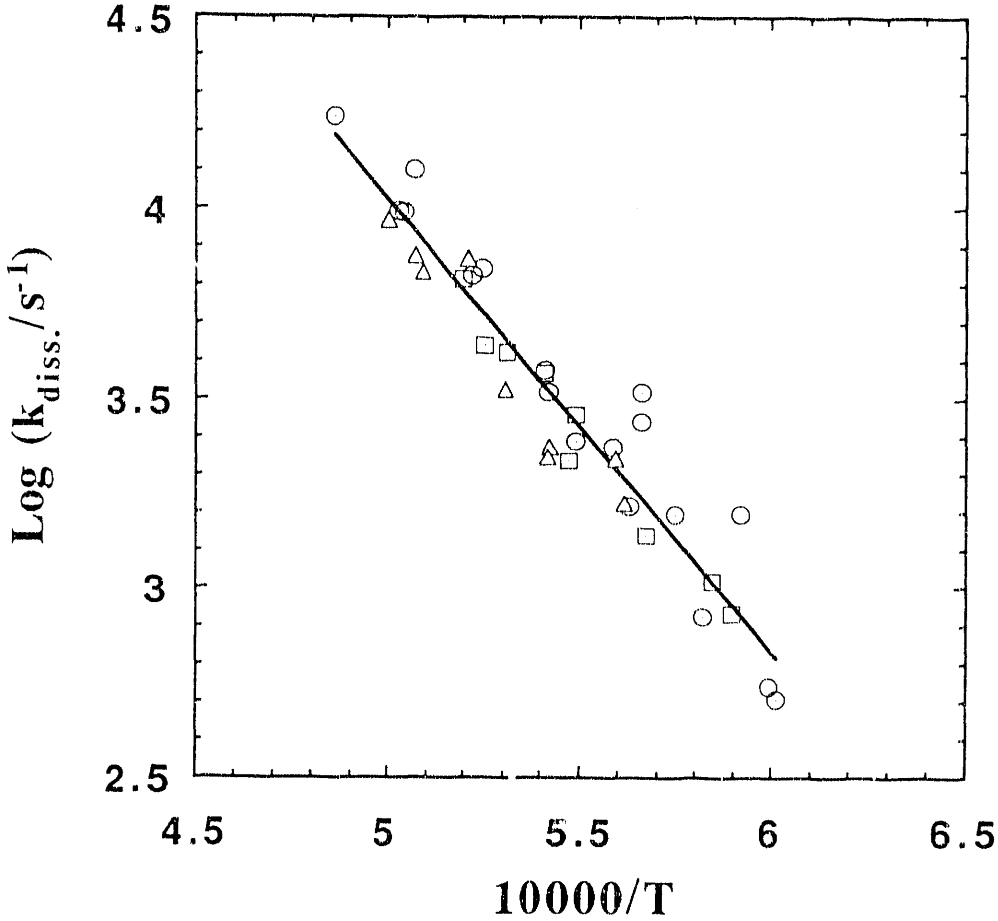

Figure 1: Rate data for $CH_3Cl \rightarrow CH_3$ + Cl. Circles are with P_1 = 15 torr, squares are with P_1 = 10 torr, and triangles are with P_1 = 6 torr. The line is calculated from eq (5).

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