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Abstract: Rate constants for the reaction O^- + N_2O were measured using a temperature variable selected ion flow drift tube apparatus. The rate constants depend only upon total energy, not upon the form of that energy, i.e., whether internal or translational. The pure temperature dependence of the rate constants is $T^{-0.5}$. The dominant product channel is NO^- + NO.

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ISOTOPE STUDIES AND ENERGY DEPENDENCES OF RATE CONSTANTS FOR THE REACTION $O^- + N_2O$ AT SEVERAL TEMPERATURES

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Rate constants for the reaction $O^- + N_2O$ were measured using a temperature variable-selected ion flow drift tube (SIFDT) instrument. The reaction was studied as a function of kinetic energy at four temperatures: 143, 196, 295, and 515 K. The product branching ratios of the reactions $^{16}O^- + {}^{14}N^{15}N^{16}O$ and $^{18}O^- + {}^{14}N^{15}N^{16}O$ were measured at two temperatures: 143 and 298 K.

The experiment employs a temperature varible flow tube with which to control the thermal energy of the reagents as well as an electric drift field to increase independently the kinetic energy of the ionic reactant. This permits fixing the overall center of mass collision energy while varying the relative contributions to that collision energy from the thermal energy of the reagents (due to temperature) and from the additional ion kinetic energy due to the electric field of the drift tube. Thus, reactions of monatomic ions (no internal modes) can be probed for the effects of the internal energy of the reactant neutral (Viggiano et al., 1988).

Figure 1 shows the rate constants for the reaction $O^- + N_2O$ plotted versus center-of-mass collision energy. The energy dependences of the rate constants measured at different experimental temperatures fall on the same curve within experimental uncertainty. Therefore, there appears to be little or no effect of the internal energy of the N_2O reactant on the rate constant. In other words, the rate constant appears to depend only upon total energy and not on the particular type of energy. The pure temperature dependence of the rate constant is shown in the figure as a solid line and can be represented as $T^{-0.5}$.

* Air Force Geophysics Scholar

Nonequilibrium Effects in Ion and Electron Transport
Edited by J. W. Gallagher *et al.*, Plenum Press, New York, 1990

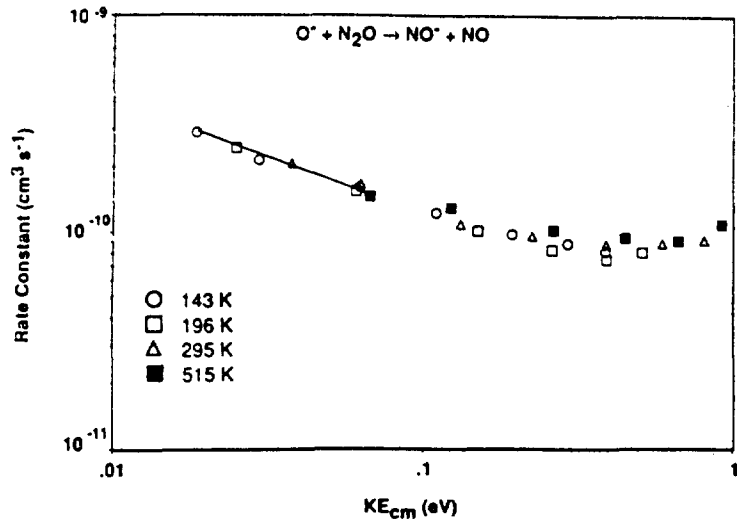

Fig. 1. Rate constants for the reaction O^- + N_2O plotted as a function of center-of-mass kinetic energy.

The dominant product channel at the energies accessible in the experiment is that producing NO^- + NO. For the reaction of O^- with $^{14}N^{15}NO$, the ratio of the ionic products, $^{14}NO^-/^{15}NO^-$, approached unity at zero $^{14}N^{15}NO$ flow rate but decreased below unity with increasing $^{14}N^{15}NO$ flow rate. It is suggested that the decrease is due to the secondary reaction $^{14}NO^- + {}^{14}N^{15}NO \longrightarrow {}^{15}NO^- + {}^{14}N^{14}NO$, which we have measured to occur with a rate constant of 1 X 10^{-11} cm^3s^{-1}.

For the reaction $^{18}O^- + {}^{14}N^{15}N^{16}O$, the O^- exchange product, $^{16}O^-$, was observable and represents a major product channel along with that producing NO^- + NO. All four NO^- isotopic products were observed: $^{14}N^{16}O^-$, $^{15}N^{16}O^-$, $^{14}N^{18}O^-$, and $^{15}N^{18}O^-$. The secondary reactions of both the exchange product $^{16}O^-$ and the various NO^- products with N_2O complicate the interpretation of the product spectra. Computer modeling of the coupled reactions and the resulting product branching ratios measured at the two experimental temperatures will be discussed.

REFERENCES

Viggiano, A. A., R. A. Morris, and J. F. Paulson, 1988, J. Chem. Phys. 89, 4848; ibid. (in press, 1989).