added. The NO rapidly reacts with the atomic nitrogen producing atomic oxygen. The end point of this titration may be detected optically or by the behavior of various ion signals. The measured NO flow at the end point is equal to the total flow of the atomic species. The mixture of N_2 and O then passes into the system. In the region between this inlet and the sampling orifice of the mass spectrometer the reactions between the reactant neutral and the ions take place.

$$\mathrm{Si}^+ + \mathrm{O}_2 \xrightarrow{k_1} \mathrm{SiO}^+ + \mathrm{O}$$
$$k_1 < 10^{-11}$$

$$\mathrm{SiO}^+ + \mathrm{N} \begin{cases} \xrightarrow{k_{2a}} \mathrm{Si}^+ + \mathrm{NO} \\ \xrightarrow{k_{2b}} \mathrm{NO}^+ + \mathrm{Si} \end{cases}$$
$$k_{2a} + k_{2b} \cong 3 \times 10^{-10}\ \mathrm{cm}^3/\mathrm{s},\ k_{2a} \cong 2k_{2b}$$

$$\mathrm{SiO}^+ + \mathrm{O} \xrightarrow{k_3} \mathrm{Si}^+ + \mathrm{O}_2$$
$$k_3 \cong 2 \times 10^{-10}\ \mathrm{cm}^3/\mathrm{s}$$

FIG. 2. The measured reaction rates for Si^+ with O_2 and SiO^+ with atomic nitrogen and atomic oxygen.

Figure 2 lists the measured rate constant for the reaction between Si^+ and O_2 and SiO^+ with the atoms of nitrogen and oxygen. The reaction of SiO^+ with atomic nitrogen is fast. The products of this reaction are Si^+ + NO and NO^+ + Si. The relative intensity of the product ion signals indicates that about two-thirds of the reaction goes to Si^+ while one-third leads to NO^+. This result is not surprising because these reactions are strongly exothermic. The interesting result concerns the fast reaction of SiO^+ with atomic oxygen. Using the published results for the dissociation energy for SiO^+, this reaction should be about 0.5 eV endothermic. The observation of this reaction either indicates that the published dissociation energy of SiO^+ is high, or the SiO^+ that is present in our experiment is in an excited state. However, the fact that the reaction $Si^+ + O_2$ is slow also argues for the exothermicity of the reverse reaction.

In the atmosphere, SiO^+ is probably produced from SiO or SiO_2. These species probably are deposited in this region by meteor ablation. The reactions which have been reported would suggest that SiO^+ would be rapidly converted to Si^+ by atomic oxygen. The ionospheric measurements indicate that there is a significant concentration of SiO^+ relative to Si^+ in the atmosphere. To maintain such a ratio there is probably a rapid reconversion of Si^+ back to SiO^+.

Aeronomic importance of ion–molecule clustering reactions

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A literature survey of observations of ion clusters in mass spectrometers indicates that the association rate constant depends on the number of atoms in the cluster. An altitude profile of estimated apparent bimolecular rates of clustering in the atmosphere is made from this empirical correlation. Experimental measurements of the termolecular rate constant for clusters in formation are reported; the temperature dependence of some of these has been measured.

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The recent mass spectrometric measurements of Narcisi (1) in the D region of the ionosphere have indicated appreciable concentrations of heavy positive ions with masses greater than 45 a.m.u. Some of these heavy ions have been attributed to hydrated cluster ions. The mass 37 ion, presumably the hydrated ion $H_3O^+.H_2O$, was found to be the dominant low-mass positive ion between 60 and 80 km.

Heavy cluster ions have now been identified in many laboratory experiments (2, 3). Recent D region simulation experiments performed in the E.S.S.A. flowing afterglow with air at a temperature of 162 °K and a pressure of 0.1 Torr have yielded evidence for hydrated H_3O^+ ions as

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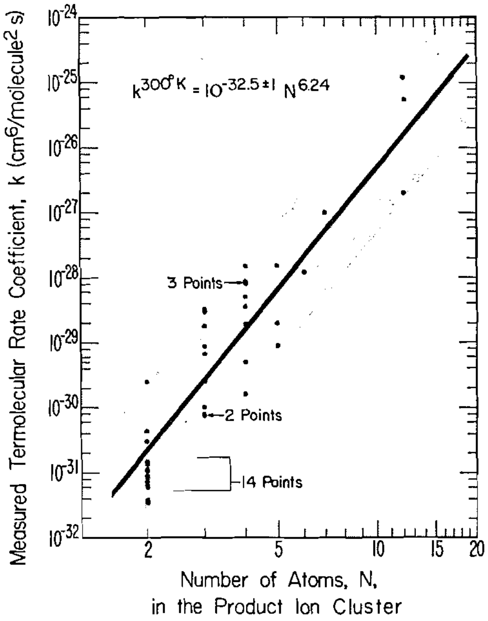

FIG. 1. The measured termolecular rate coefficient plotted as a function of the number of atoms in the product ion cluster.

large as $H_3O^+.6H_2O$, as well as hydrated O_2^+ and NO^+ ions. The cluster ions N_6^+, N_7^+, N_8^+, N_9^+, as well as He_3^+ and Ar_3^+, were identified mass spectrometrically at 82 °K, apparently for the first time (4). Although observations of heavy cluster ions have been numerous, little is known about the magnitude of specific rates of cluster formation and the dependency of these rates on cluster size, temperature, and pressure.

A consideration of all available laboratory data found in the literature on ion–neutral termolecular association in which a stable cluster is formed indicates a surprisingly systematic variation of the termolecular rate coefficient with the number of atoms N in the product ion cluster. This is illustrated in Fig. 1 for 44 measurements of 27 ion–molecule association reactions. The spread in the data may be attributed, in part, to variations in the stabilization efficiency of the third body and the potential energy configuration of the ion cluster. Nevertheless, the following empirical relation, which allows an order-of-magnitude estimation of the specific termolecular rate k of cluster formation at about 300 °K, may be derived from the plot shown in Fig. 1:

$$[1] \qquad k^{300\,°K} = 10^{-32.5\pm1} N^{6.24}$$

An altitude profile of some estimated apparent bimolecular rates of clustering at 300 °K which can be constructed using eq. [1] is given in Fig. 2. A standard reference atmosphere was used to obtain neutral densities (5). The role of ion cluster formation can be seen to be more important at lower altitudes where the apparent bimolecular specific rates are larger. It is evident from Fig. 2 that the three-body formation of heavy ion clusters involving a large number of atoms ($N \gtrsim 10$) may readily compete with the fairly rapid two-body reactions occurring in the D region of the ionosphere. Atomic and molecular ions with very low specific rates of two-body conversion are likely to be bound to polyatomic molecules such as H_2O by the more rapid three-body formation of ion clusters. This would be the case for the terminal ions in the D region such as NO^+ and NO_3^- as well as atomic ions of low ionization potential such as Na^+, Ca^+, Mg^+, Fe^+, and Si^+.

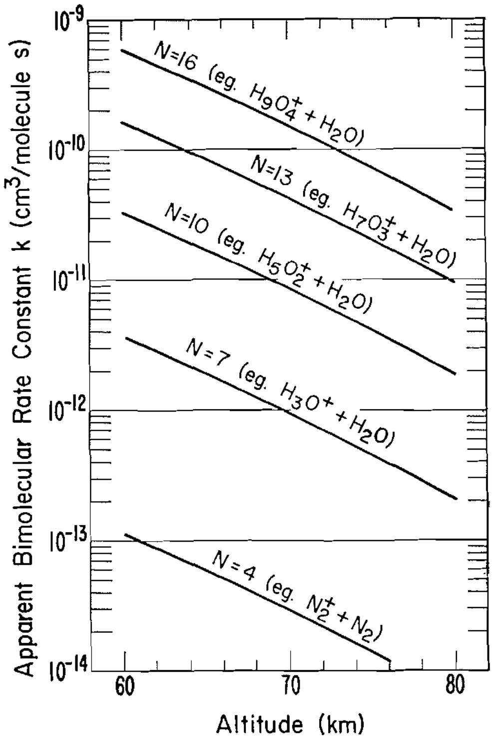

FIG. 2. The estimated apparent rate constant of ion cluster formation at 300 °K plotted as a function of altitude.

Recent experiments conducted in the E.S.S.A. flowing afterglow system have indicated several additional empirical relationships. Table I is a list of some positive and negative three-body

TABLE I

Termolecular rate constants measured in the E.S.S.A. flowing afterglow system

Reaction	Temperature (°K)	Rate constant (cm^6/s)
$O_2^+ + O_2 + He$	82	3.1×10^{-29}
$N_2^+ + N_2 + He$	82	1.2×10^{-28}
	280	1.9×10^{-29}
$O^- + CO_2 + He$	280	1.5×10^{-28}
$O^+ + N_2 + He$	82	5.4×10^{-29}
$N^+ + N_2 + He$	82	7.2×10^{-29}
	280	8.6×10^{-30}
$Ar^+ + Ar + He$	82	1.6×10^{-30}
	290	$\sim 1.3\times 10^{-30}$
$O^- + N_2 + He$	82	1.3×10^{-30}
$Mg^+ + O_2 + Ar$	300	$\sim 2.5\times 10^{-30}$
$Fe^+ + O_2 + Ar$	300	$\sim 1.0\times 10^{-30}$
$Ca^+ + O_2 + Ar$	300	$\sim 6.6\times 10^{-30}$

ion–molecule reactions, the specific rates of which have recently been measured in the E.S.S.A. flowing afterglow at 82 and 280 °K with helium and argon as a third-body over a pressure range 0.1 to 3.0 Torr. At low pressures the kinetics of cluster formation was termolecular at both temperatures, as expected for the ground state ions investigated. The termolecular rate coefficients were found to increase significantly with decreasing temperature. Furthermore, the results indicate that termolecular cluster formation is less strongly dependent upon temperature as the number of atoms N in the product ion cluster increases according to the empirical relation

$$[2] \qquad k_1 = k_0 \left(\frac{T_0}{T_1}\right)^{\frac{N+2}{N}}$$

k_1 and k_0 are the termolecular specific rates at temperatures T_1 and T_0, where $T_0 > T_1$. Equation [2] was derived from the experimental results at the two temperatures 82 and 280 °K for the association of N_2^+ with N_2, N^+ with N_2, and Ar^+ with Ar in helium gas assuming that the termolecular rate coefficient varies as T^{-n}. Therefore, caution must be exercised when invoking eq. [2] to extrapolate the results shown in Figs. 1 and 2 to more realistic D region temperatures.

Finally, the E.S.S.A. flowing afterglow experiments have indicated (6) that the kinetics of the formation of O_4^+ and N_4^+ ion clusters at 82 °K becomes bimolecular above helium pressures of about 1.6 and 0.2 Torr, respectively, as demonstrated in Fig. 3. This result is qualitatively consistent with a clustering process involving a collision sequence of two steps, i.e. initial formation of the intermediate complex followed by stabilization upon collision with a third body. According to such a mechanism, the apparent bimolecular specific rate of ion cluster formation will never exceed the Langevin orbiting rate constant of the initial complex formation, i.e. of two-body ion–molecule reactions. In fact, for the case of O_4^+ and N_4^+ ion cluster formation, the flowing afterglow results at 82 °K indicate an apparent bimolecular specific rate at saturation of only about 7×10^{-12} cm^3/s. It is not yet known whether the apparent bimolecular specific rate of ion cluster formation at saturation is dependent on the gas temperature and on the complexity of the ion cluster.

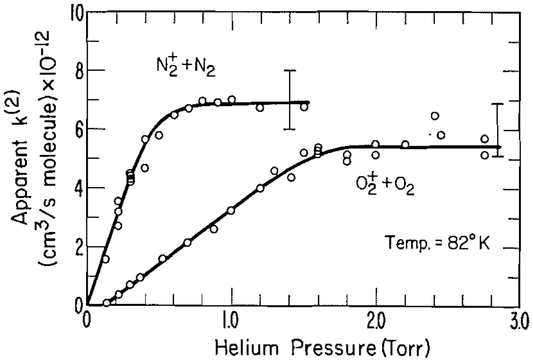

FIG. 3. The experimentally determined bimolecular rate coefficient, $k^{(2)}$, plotted as a function of helium pressure.

A full evaluation of the importance of three-body clustering reactions in the D region of the ionosphere will have to await more laboratory measurements of specific rates at various temperatures and pressures, the complete identification of the large concentrations of heavy positive ions observed in rocket flights, and measurements of neutral concentrations such as principally H_2O and possibly neutral clusters.

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