Clustering of Sulfur Dioxide and Water Vapor about Oxonium and Nitric Oxide Ions

Abstract. *The mobilities of ions produced in electrical discharges in the presence of trace quantities of water vapor and sulfur dioxide are generally lower than those expected for simple ions. Mass spectrometric identification reveals that species composed of water vapor and sulfur dioxide molecules clustering about common atmospheric ions are formed under these conditions. The identification of these clusters provides an explanation for the effect of trace gases on the mobilities of ions.*

Interest in the nature and properties of small ion clusters has increased during the last few years. Although this interest was first prompted by the discovery of water clustering on oxonium ions in the D-region of the ionosphere (*1*), recent attention has focused on the nature of tropospheric ions as well (*2*). In addition, it has been suggested (*3*) that ion clusters may in fact play a role in atmospheric nitrogen fixation after lightning discharges.

The possibility that ions play a role in initiating nuclei-producing reactions in air after exposure to ionizing radiation is suggested by the work of Megaw and Wiffen (*4*), among others. They found that both the humidity and the SO_2 content of air that had undergone preliminary filtration had an effect on the extent of production of large nuclei. Similar but more extensive studies of this phenomenon have been made by Bricard *et al.* (*5*). Their results lend further support to the conclusion that, under some conditions, interactions between small ions and trace constituents of air can lead to the production of ions of low mobility as well as particles.

As part of their work to elucidate the nature of these ions, Bricard *et al.* (*6*) have initiated a study of the mobility of small ions produced in air by corona discharge. Using a time-of-flight method, they observed six groups of ions having mobilities ranging from 2.1 cm^2 $volt^{-1}$ sec^{-1} down to a terminal value of 0.4 cm^2 $volt^{-1}$ sec^{-1}. Bricard *et al.* observed that groups with mobilites of 2.1 and 1.9 cm^2 $volt^{-1}$ sec^{-1} successively shifted toward groups of lower mobilities upon addition of H_2O vapor or SO_2. Loeb (*7*) has quoted Varney as suggesting that the ions in air having a mobility of 1.9 cm^2 $volt^{-1}$ sec^{-1} may be the stable $H_9O_4{}^+$ ion. Loeb has also pointed out that the ions $O_2{}^+$, $NO_2{}^+$, NO^+, H_3O^+ and their hydrates should be formed in a corona discharge, although he doubts that the hydrates of $NO_2{}^+$ and NO^+ are predominant ions. On the basis of a hard-sphere model, the ions with a mobility of 0.4 cm^2 $volt^{-1}$ sec^{-1} would represent clusters of tens to hundreds of H_2O molecules. However, Loeb (*7*) has suggested that the ion clusters may have a long chain-like structure and be composed of only a few molecules.

Recently, we have initiated a study of the chemistry of ions and molecular clusters formed in an electrical discharge in the presence of SO_2 and H_2O vapor. Using mass spectrometry, we have observed that both SO_2 and H_2O vapor cluster on atmospheric ions.

The apparatus employed in this study consisted of a discharge chamber and a reaction cell, both constructed of stainless steel and surrounded by a single cooling-water jacket. The discharge chamber consisted of a platinum filament, shaped like a pointed hairpin, surrounded by a cylindrical stainless steel repeller. The filament extended to the upper region of the repeller, which was fitted with an insert ring. At this point the filament and repeller ring were separated by a distance of approximately 1 mm, and the ions were produced by electrical discharge across this gap. A stable discharge was usually maintained with the filament potential set at − 360 volts and the repeller potential set at + 140 volts. The ions produced in the discharge were focused into the electrically field-free reaction cell (1 cm long). Argon served as a carrier gas for the introduction of reactants composed of air, H_2O vapor, and SO_2 in varying proportions. After the reaction, the ions and associated clusters drifted out of the cell into a vacuum through a 100-μm leak orifice and were extracted into a quadrupole mass spectrometer. We established the energy of the ions entering the mass filter by applying a potential of + 5.9 volts to the reaction cell and orifice plate.

Experiments were carried out for total system pressures ranging from 1 to 4 torr. In the absence of SO_2 and appreciable quantities of H_2O vapor, the predominant ions were $O_2{}^+$, NO^+, and $O_4{}^+$, as expected. The appearance of hydrates of nitric oxide, $NO^+(H_2O)_m$, where m is $\leqslant 4$, and of oxonium and higher hydrated proton clusters, $H_3O^+(H_2O)_n$, where n is $\leqslant 4$, was observed as the concentration of H_2O vapor increased. Hydrated oxonium ions arise as a result of the following reactions (*8*):

$$O_4{}^+ + H_2O \rightarrow O_2{}^+(H_2O) + O_2 \qquad (1)$$

$$O_2{}^+(H_2O) + H_2O \rightarrow H_3O^+ \cdot OH + O_2 \qquad (2)$$

$$H_3O^+ \cdot OH + H_2O \rightarrow H_3O^+(H_2O) + OH \cdot \qquad (3)$$

The rate constants given for these reactions (in cubic centimeters per molecule per second) are: $k_1 = 1.3 \times 10^{-9}$, $k_2 = 0.9 \times 10^{-9}$, and $k_3 \geqq 10^{-9}$, respectively.

Under conditions of very low H_2O vapor content, SO_2 addition led to for-

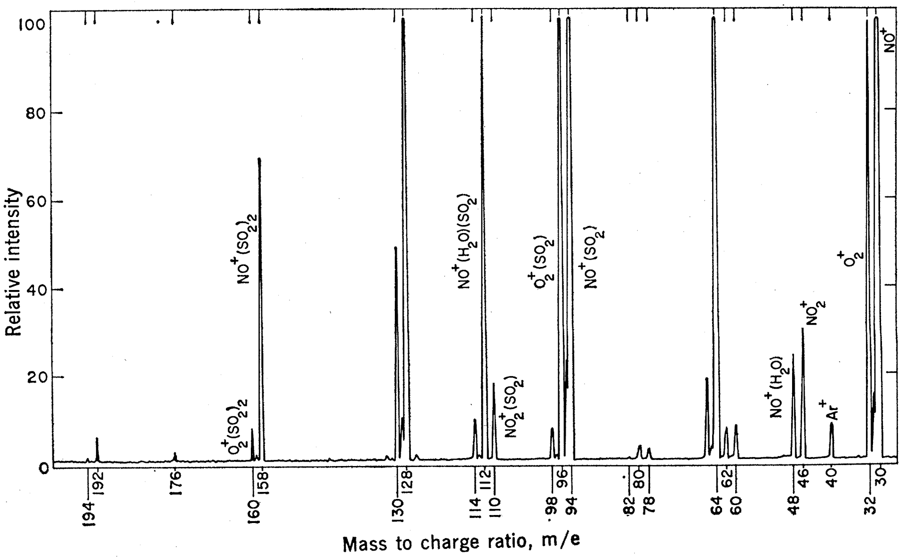

Fig. 1. Clustering of SO_2 on nitric oxide ions in dry argon.

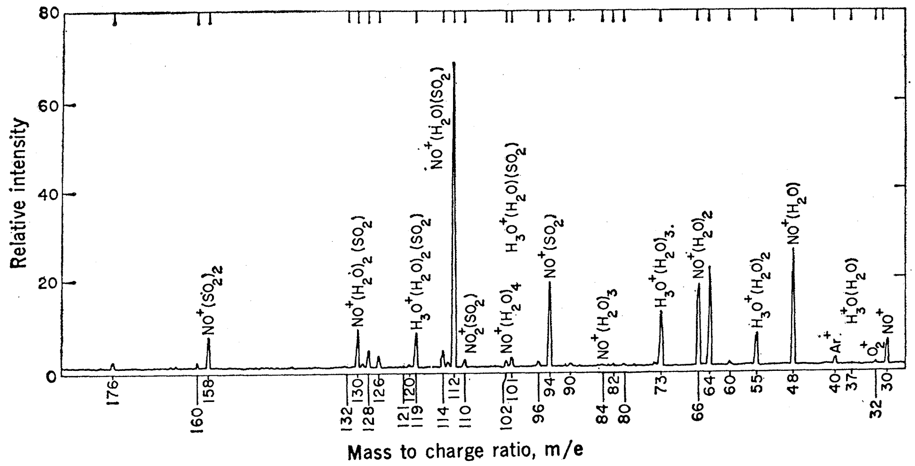

Fig. 2. Clustering of SO_2 and H_2O on oxonium and nitric oxide ions.

mation of the following hitherto unobserved species: $NO^+(SO_2)$, $NO^+(SO_2)_2$, $NO^+(SO_2)_3$, $NO^+(H_2O)(SO_2)$, $NO^+(H_2O)(SO_2)_2$, and $NO_2^+(SO_2)$. A typical recorder tracing for the mass spectrometer output is shown in Fig. 1. The sulfur-containing species were conclusively identified as a result of the doublet in the appropriate spectrum owing to the presence of both the ^{32}S and ^{34}S isotopes. Other species that were observed included $O_2^+(SO_2)$, also reported by Adams *et al.* (*9*), and $O_2^+(SO_2)_2$, as well as the known species NO^+, O_2^+, and $NO^+(H_2O)$. In experiments made in the absence of SO_2, $NO_2^+(H_2O)$ was found, which suggests that the peak observed at a mass-to-charge ratio (*m/e*) of 128 is partially due to $NO_2^+(H_2O)(SO_2)$. The relative contributions of SO_2^+ or O_4^+ to the peak at *m/e* 64 and corresponding clusters with SO_2 molecules contributing to the peak at *m/e* 128 have not been established. Likewise, the peak at *m/e* 192 may be due to both $SO_2^+(SO_2)_2$ and $NO_2^+(H_2O)(SO_2)_2$.

Additional experiments were carried out to establish the identity of the major species formed in air containing both H_2O vapor and SO_2 at concentrations up to 1 percent. During the course of this work, we discovered species involving mixed clusters of both hydrated protons and SO_2. As shown in Fig. 2, the species $H_3O^+(H_2O)_n(SO_2)$ where *n* is equal to 1 and 2, are clearly visible at *m/e* 101 and 119. The mixed cluster $NO^+(H_2O)(SO_2)$, as well as other species also seen in Fig. 1, are present in the spectrum shown in Fig. 2. Other species that have been reported by earlier investigators (*9*) are included. Preliminary results obtained from the work presented here indicate that the stabilities of the species $NO^+(H_2O)_2$, $NO^+(H_2O)(SO_2)$, and $NO^+(SO_2)_2$ are nearly equal; the respective standard free energies of formation are ~14 kcal/mole.

De Paz *et al.* (*10*) have made theoretical calculations on the basis of molecular-orbital theory and have shown that chainlike structures for the hydrated protons are equally as feasible as symmetrical clusters resulting from electrostatic-dipole interactions of water molecules with a central ion. By analogy, the mixed SO_2 and H_2O vapor clusters may also have chainlike structures. This reasoning, together with the fact that the mass of the mixed clusters is relatively large owing to the presence of SO_2, leads one to expect that the mobilities of the mixed clusters would be rather small.

The results presented here have established the existence and identity of mixed clusters of H_2O and SO_2 about common ions such as NO^+ and H_3O^+ which are present in electrical discharges. These results provide an explanation for the heretofore unexplained observations reported in the literature (*6, 7*). However, the observed clusters are part of a complex ion-molecule reaction sequence and would not necessarily be terminal ions under all conditions.

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References and Notes

1. R. S. Narcisi and A. D. Bailey, *J. Geophys. Res.* **70**, 3787 (1965).
2. V. Mohnen, in *Planetary Electrodynamics*, S. C. Coroniti and J. Hughes, Eds. (Gordon & Breach, New York, 1970), pp. 197–206; R. Siksna, in *ibid.*, pp. 207–230; K. G. Vohra and P. V. N. Nair, *J. Aerosol Sci.* **1**, 127 (1970); V. A. Mohnen and J. P. Lodge, Jr., in *Proceedings of the 7th International Conference on Condensation and Ice Nuclei* (Academia, Prague, 1970), pp. 69–91; V. J. Schaefer, *Science* **170**, 851 (1970).
3. E. E. Ferguson and W. F. Libby, *Nature* **229**, 37 (1971).
4. W. J. Megaw and R. D. Wiffen, *Geofis. Pura Appl.* **50**, 118 (1961).
5. J. Bricard, F. Billard, G. Madelaine, *J. Geophys. Res.* **73**, 4487 (1968).
6. J. Bricard, M. Babane, G. Madelaine, in *Planetary Electrodynamics*, S. C. Coroniti and J. Hughes, Eds. (Gordon & Breach, New York, 1970), pp. 243–247.
7. L. B. Loeb, *Advan. Geophys.* **13**, 223 (1969).
8. A. Good, D. A. Durden, P. Kebarle, *J. Chem. Phys.* **52**, 222 (1970).
9. N. G. Adams, D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld, E. E. Ferguson, *ibid.*, p. 3133.
10. M. De Paz, S. Ehrenson, L. Friedman, *ibid.*, p. 3362.
11. We thank Prof. D. R. Olander and Dr. W. J. Siekhaus of the University of California, Berkeley, for helpful suggestions regarding the design of ion optics. This work was performed under the auspices of the U.S. Atomic Energy Commission.

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Reversible Osmotic Opening of the Blood-Brain Barrier

Abstract. *Reversible breakdown of the blood-brain barrier is produced by a class of electrolytes and nonelectrolytes which have little or no lipid solubility but which differ in chemical and ionic properties. These agents may osmotically shrink barrier cells, possibly the vascular endothelium, and reversibly open spaces between them. Lipid-soluble nonelectrolytes damage the barrier irreversibly.*

It has been hypothesized (*1*) that the blood-brain barrier can be opened by osmotically shrinking barrier cells and opening spaces between them to the passage of ions and large molecules. In this report we show, in the rabbit, that a group of electrolytes and relatively lipid-insoluble nonelectrolytes will open the barrier reversibly to the intravascular Evans blue–albumin complex. The action of these substances on the barrier conforms to four experimental conditions (*1, 2*) which are required if they should act osmotically: (i) the agent should open the barrier independently of a specific chemical or drug action, (ii) its effect on the barrier should increase with increasing osmolality or concentration, (iii) its effect should be related inversely to its ability to penetrate the cell membrane, and (iv) its effect should be reversible.