(3) is confirmed, as is the explanation of the splittings in terms of the static and correlation fields. The splittings range from 2.5–11 cm^{-1}, compared to 3–7 cm^{-1} in the Raman spectrum (5). The weaker bands, resulting from activity induced by the perturbing crystal field, are readily assigned by reference to the Raman data and the normal coordinate analysis (3): the sharp symmetric peak at 214 cm^{-1} is the predicted i.r. singlet for ν_2; the other bands are broader, and represent the unresolved triplets of ν_9 (78 cm^{-1}), ν_8 (149 cm^{-1}), and ν_{10} (442 cm^{-1}). The absence of lattice modes indicates that their interaction with the electromagnetic field is a factor of at least 20 less than that of the intramolecular fundamentals, which is not unusual for such a symmetric molecule.

A final point of interest is that a comparison of the frequencies of bands observed in both i.r. and Raman shows evidence for coincidences within experimental error. This is especially noticeable for ν_6, and the only exception is ν_4, where there is a 4 cm^{-1} difference. From spectroscopic evidence alone, one might conclude that the crystal does not possess a center of symmetry, whereas the X-ray data show that the opposite is true (6). Infrared and Raman data are often used to aid in crystal structure determinations, especially of hydrogenic molecules, when X-ray, electron, or neutron diffraction measurements are not available (10). The above result shows that this procedure must be used with extreme caution, if spurious deductions are to be avoided.

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1. G. Herzberg. Infrared and Raman spectra. D. Van Nostrand, New York. 1945. p. 271.
2. R. B. Barnes. Phys. Rev. **39**, 570 (1932).
3. D. W. Scott, J. P. McCullough, and F. H. Kruse. J. Mol. Spectry. **13**, 313 (1964).
4. G. W. Chantry, A. Anderson, and H. A. Gebbie. Spectrochim. Acta, **20**, 1223 (1964).
5. A. Anderson and Y. T. Loh. Can. J. Chem. **47**, 879 (1969).
6. B. E. Warren and J. T. Burwell. J. Chem. Phys. **3**, 6 (1935).
7. C. Lu and J. Donohue. J. Am. Chem. Soc. **66**, 818 (1944).
8. A. T. Ward. J. Phys. Chem. **72**, 4133 (1968).
9. A. Anderson and H. A. Gebbie. Spectrochim. Acta, **21**, 883 (1965).
10. R. Savoie and A. Anderson. J. Chem. Phys. **44**, 548 (1966).

Thermal reactions of O_2^+ and O^- ions in gaseous ammonia

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The reaction channels and rate coefficients for the reactions of O_2^+ and O^- ions with NH_3 have been determined at 21.4 °C in a flowing afterglow of pure oxygen and a mixture of helium and oxygen. Charge-transfer was found to be the dominant O_2^+ reaction channel whereas hydrogen atom abstraction was found to be the dominant O^- reaction channel. The secondary NH_3^+ ions were found to react further with NH_3 by hydrogen abstraction to yield NH_4^+ ions, which readily associated with NH_3 to yield cluster ions. The further reaction of secondary OH^- ions with NH_3 was not observed suggesting that the electron affinity of NH_2 may be less than 1.10 eV.

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The flowing afterglow technique developed in the Environmental Science Services Administration Research Laboratories principally for the investigation of thermal ion–molecule reactions of interest on the earth's ionosphere has recently been employed to study the reactions of O_2^+ and O^- ions in gaseous ammonia.

Details of the operation of the flowing afterglow system and the related data analysis have been described elsewhere (1). In the present experiment, pure oxygen or a helium–oxygen

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TABLE I

Measured rate constants

Reaction	*k*
$O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$	2.6 (−9)* cm³/s
$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$	1.6 (−9) cm³/s
$NH_4^+ + NH_3 + O_2 \rightarrow NH_4^+ \cdot NH_3 + O_2$	1.8 (−27) cm⁶/s
$O^- + NH_3 \rightarrow OH^- + NH_2$	1.2 (−9) cm³/s

*(−9) denotes 10^{-9}.

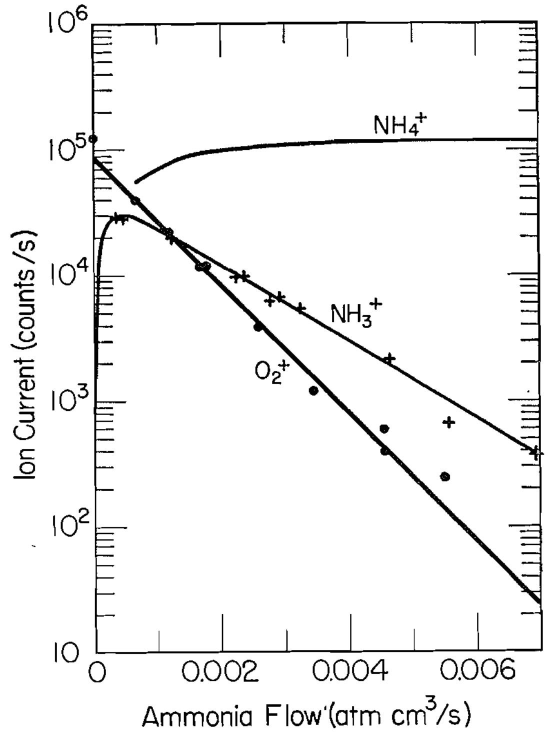

FIG. 1. Ion currents for reactions of O_2^+ and NH_3^+ with NH_3 in an oxygen ion afterglow.

mixture is introduced into the excitation region of the flow tube. The gas is excited by the energetic electrons from an electron gun producing O^- and O_2^+ by electron impact with O_2. In addition some O_2^+ is produced by reaction of O_2 with O^+ and excited and ionized helium.

In the region following the excitation region the secondary reactions forming O_2^+ go to completion. Also, O_2^+ ions formed in electronically or vibrationally excited states are de-excited. The O^- and O_2^+ ions are carried with the flowing gas past a downstream port where measured quantities of ammonia are added. In the region following this reactant inlet the characteristic reactions between the ions and ammonia take place. This reaction region is terminated by the sampling port of a quadrupole mass spectrometer. The decline of the primary ion signal and the increase of the secondary ions as a function of the rate of addition of the ammonia allows the determination of a reaction rate constant and reaction channel designation. The rates so determined by this technique should possess an absolute accuracy of 30% with a relative accuracy of better than 10%.

Figure 1 shows a sample run of data for the reaction sequence beginning with O_2^+ in reaction with ammonia. This data was taken at a gas temperature of 21.4 °C. Pure oxygen was introduced into the excitation region and the steady state gas pressure was 0.224 Torr. As the ammonia is added the O_2^+ signal declines and there is a corresponding rise in the NH_3^+ signal due to the reaction

$$[1] \qquad O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$$

The reaction channel between NH_3 and O_2^+ to produce NH_2^+ and O_2H is endothermic at room temperature for ground state O_2^+ and was not observed.

The NH_3^+ product signal peaks and then declines corresponding to the production of NH_4^+. Since the decline of the NH_3^+ signal is slower than that of the precursor ion O_2^+, a rate coefficient may be determined for the reaction

$$[2] \qquad NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$$

from the slope of the NH_3^+ signal. With large additions of NH_3 the cluster ions $NH_4^+ \cdot (NH_3)$, $NH_4^+ \cdot (NH_3)_2$, and $NH_4^+ \cdot (NH_4)_3$ were observed, and the rate constant for the first step in the formation of these clusters

$$[3] \qquad NH_4^+ + NH_3 + O_2 \rightarrow NH_4^+ \cdot NH_3 + O_2$$

was determined. Table I lists the rate coefficients determined for [1], [2], and [3], along with the rate coefficient for the fast reaction between O^- and NH_3 found to proceed by hydrogen abstraction to form OH^-. The product ion OH^- accounted for essentially 100% of the disappearing O^- ions. Electron transfer will not compete since NH_3 has no affinity for electrons (2). Also, there was no indication of a residual signal at $m/e = 16$. This means that no NH_2^- was produced by the reaction and suggests that this channel for the reaction is endothermic at room temperature, implying that the electron affinity of NH_2^- is less than 1.61 eV. This observation is compatible with the electron affinity of NH_2 of 1.21 eV reported by Vedeneyev *et al.* (3). The further reaction of OH^- with NH_3 to yield NH_2^- and H_2O was not observed suggesting that the electron affinity of NH_2 may be less than 1.10 eV.

Gupta *et al.* (4) have measured the thermal (or zero field) rate constant for reaction [2] using a pulsed-beam technique. The rate of 1.0×10^{-9} determined by Gupta *et al.* at 373 °K is somewhat smaller than the value of 1.6×10^{-9} determined in the present experiment at 295 °K. There are no other published rates for the other reactions with which we may compare.

1. E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf. Advances in atomic and molecular physics. Vol. 5. Academic Press, Inc., New York. 1969; F. C. Fehsenfeld, A. L. Schmeltekopf, P. D. Goldan, H. I. Schiff, and E. E. Ferguson. J. Chem. Phys. **44**, 4087 (1966).
2. H. O. Pritchard. Chem. Rev. **52**, 529 (1953).
3. V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev, and Ye. L. Frankevich. Bond energies, ionization potentials, and electron affinities. St. Martin's Press, Inc., New York. 1966.
4. S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher. Can. J. Chem. **45**, 3107 (1967).

Thermal reactions of O^- ions with saturated hydrocarbon molecules

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The thermal energy reactions of O^- ions with saturated hydrocarbon molecules have been investigated in a flowing afterglow of pure oxygen and a mixture of helium and oxygen. Hydrogen atom abstraction was found to be the dominant reaction channel. The reaction probability was found to increase for the higher members of the homologous series. The further reaction of the product OH^- ions with saturated hydrocarbon molecules was not observed. This result was used to estimate an upper limit to the electron affinity of the free radicals CH_3, C_2H_5, C_3H_7, and C_4H_9.

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The flowing afterglow technique developed in the Environmental Science Services Administration Research Laboratories has been used extensively for the study of thermal energy ion–neutral reactions of interest in aeronomy, and has been employed to investigate the reactions of O^- ions with the homologous hydrocarbon series C_nH_{2n+2}, $n = 1$ to 4. The results suggest a fairly general behavior which is that the reaction of O^- ions with saturated hydrocarbon molecules proceeds by hydrogen atom abstraction

$$[1] \qquad O^- + RH \rightarrow OH^- + R$$

and that the reaction probability for this process increases for higher members of the homologous series.

The details of the experimental apparatus, its operation, and the related data analysis have been described in detail elsewhere (1). The flow system is a stainless steel tube about 100 cm long and 8 cm in diameter in which the products of an electron impact ion source are pumped down the tube at a velocity of about 10^4 cm/s. In the present experiments either pure O_2 or O_2 in small fractional quantities in a helium buffer gas is introduced into the excitation region. The O^- ion is then produced by the dissociative ionization reaction, $e + O_2 \rightarrow O^- + O^+ + e$, and, probably to a lesser extent, the dissociative

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