THE POSITIVE RAY ANALYSIS OF NITRIC OXIDE AND COLLISIONS OF THE SECOND KIND

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Abstract

Using an apparatus previously described, in which ions formed by impact of electrons of definite energy are analyzed by Dempster's positive ray method, the relative numbers of the ions NO^+, N^+ and O^+ were measured over a large range of pressures and electron energies. The percentages of N^+ and O^+ increased gradually with increase in pressure from approximately 4 and 1.5 percent at zero (extrapolated) pressure to 9 and 3 percent, respectively, at 0.01 mm. Evidence is thus given that impact electrons of sufficient energy can ionize the molecules forming NO^+ ions some of which spontaneously dissociate forming N^+ and O^+, and others of which are disrupted on collision with gas molecules into the atomic ions. The ionization potentials for the formation of NO^+, N^+ and O^+ were found to be 9, 21 and 22 volts, respectively. The second, together with the ionization potential of the oxygen atom, gives 7.5 volts (175,000 cal. per mol) for the heat of dissociation of nitric oxide.

In mixtures of NO and A and of NO and He, increase in the relative intensities of NO^+ with increase in pressure gave definite evidence of collisions of the second kind: $NO+A^+=NO^++A$ and $NO+He^+=NO^++He$.

SINCE the discovery, by Franck, of collisions of the second kind, numerous experiments have given evidence of energy interchange in collisions of excited with normal atoms and molecules. To this the present paper adds evidence, from positive ray analysis, of second kind collisions involving collisions of ions with neutral molecules, the energy interchange being here accompanied by an electron transfer. The paper also discusses the positive ray analysis interpretation of the electron impact ionization of NO in continuation of a series of studies by the authors.[1] Reference thereto may be made for details of the apparatus and experimental procedure.

Positive Ray Analysis and Ionization Potentials of NO

The nitric oxide was prepared by the interaction of aqueous sodium nitrite and an acid solution of ferrous sulfate, was dried with phosphorus pentoxide, and then solidified in a liquid air trap whence it was distilled into the storage reservoir.

Positive ions. The products of ionization were found to be NO^+, N^+, and O^+. The relative numbers of these ions vary slightly with the pressure, as is shown by Fig. 1, in which the percentage of each of the ions (as measured by the relative heights of the peaks $m/e=30$, 14 and 16, respectively) are plotted as ordinates, the pressure as abscissas. Since the N^+ and O^+ curves extrapolate to finite quantities at zero pressure, evidence is given that in nitric oxide electron impact with 60-volt electrons can result either

[1] Hogness and Lunn, Proc. Nat. Acad. Sci. **10,** 398 (1924); Phys. Rev. **26,** 44 (1925); **26,** 786 (1925); **27,** 732 (1926).

in the formation of the molecular ions or in the dissociation of the molecules with the formation of atomic ions. Further, since N^+ and O^+ ions are both observed with impact electrons having velocities too small to dissociate a molecule and ionize, simultaneously, both of its atoms (see below), it follows that:

$$NO = NO^+ + \epsilon \quad (1)$$
$$NO = N^+ + O + \epsilon \quad (2)$$
$$NO = O^+ + N + \epsilon \quad (3)$$

all occur as independent primary processes and that (2) is more probable than (3), the probability of (1) being, of course, the greatest.

But the slope of the curves in Fig. 1 shows the occurrence of secondary processes of ionization, the nature of which is indicated by other results. In his work on hydrogen, Smyth[2] observed two peaks having apparent m/e ratios of 1/2 and 3/2. He attributed these to the disruption, on collision

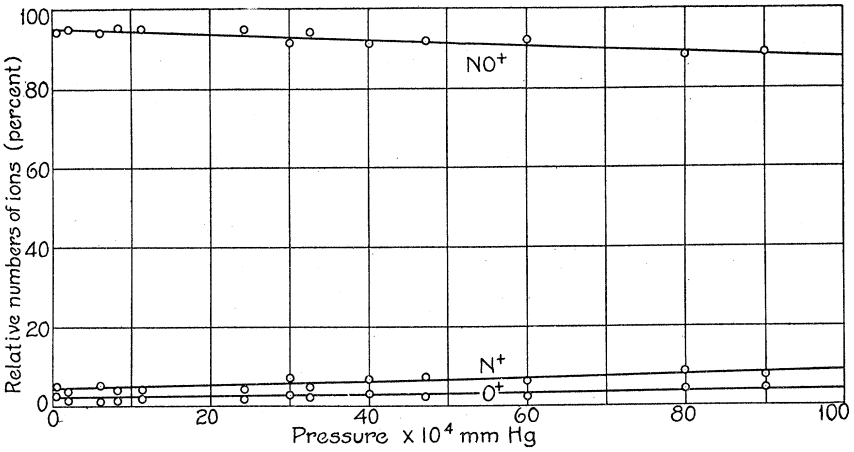

Fig. 1. Percentages of NO^+, N^+, and O^+ as functions of the pressure.

with gas molecules, of the molecular ions H_2^+ and H_3^+ which had fallen through the full positive ray analyzing field. If such a process occurred in NO the products of disruption—N^+ and O^+—would appear as peaks having m/e's of 6.53 and 8.53. A search for such ions at a pressure of 0.01 mm showed a broad band extending roughly from masses 9.5 to 5 and coming to a definite peak near 6.5. While this result only shows the instability toward collision of NO^+ ions with a velocity of 650 volts, slow speed ions may also be unstable. If NO^{++} ions disrupt in the ionization chamber, the N^+ and O^+ would, of course, appear with the peaks $m/e = 14$ and 16 which were measured for Fig. 1. It seems probable, then, that some of the NO^+ ions are unstable toward collision with gas molecules, and on collision dissociate into either N^+ or O^+:

[2] Smyth, Phys. Rev. **25**, 452 (1925).

$$NO^+ = N^+ + O + \epsilon \quad (4)$$
$$NO^+ = O^+ + N + \epsilon \quad (5)$$

and that it is these processes which cause the increase in the percentages of N^+ and O^+ with increase in pressure shown in Fig. 1. Since NO is thermodynamically unstable with respect to N_2 and O_2 and may be dissociated by the hot filament, it might be supposed, however, that some, or all, of the N^+ and O^+ ions arise from ionization of N_2 and O_2 resulting from such thermal dissociation. But the measurements of the intensities of N_2^+ and O_2^+ indicate that the partial pressures of N_2 and O_2 were far too small to account for the numbers of N_1^+ and O_1^+ ions actually observed. From their study of the ionization of NO, Bazzoni and Waldie[3] concluded that dissociation by the hot filament played such a large part in the ionization processes as to obscure the ionization due to NO itself. Thermal dissociation is minimized in the present apparatus by the rapid flow of gas, the low filament temperature and the low gas pressure.

It may be recalled that in studying nitrogen and oxygen it was not possible to establish the presence of doubly-charged molecular ions because of the identity of their specific charges and those of the corresponding atomic ions. In nitric oxide this difficulty is not met with. However, the peak at $m/e = 15$ was so small even with electron energies up to 450 volts as to make it uncertain whether it was due to NO^{++} or to an impurity. If the ion NO^{++} is formed it does not exist as such for an appreciable time.

Negative ions. With the magnetic field and the fields V_3 and V_4 reversed evidence was found of extremely small amounts of NO^-, N^- and O^-, the atomic ions being the more numerous. Because of the unfavorable arrangement of fields necessary in studying negative ions the significance of these observations is very doubtful.

Ionization potentials. The ionization potentials for the formation of NO^+, N^+ and O^+ were determined by comparing their disappearing potentials with that of argon or of helium in essentially the manner previously employed —the molecular potential by comparison with argon, the atomic potentials by comparison with helium. Taking 15.4[4] and 24.5[5] volts as the ionization potentials of argon and helium, the resulting ionization potentials for the formation of NO^+, O^+ and N^+ are 9, 21 and 22 volts respectively.[6]

The above value of 9 volts for the ionization potential of NO^+ agrees well with the more accurate values of Hughes and Dixon[7] and of Mackay,[8] 9.3 and 9.4 volts respectively.

[3] Bazzoni and Waldie, J. Franklin Inst. **197,** 57 (1924).

[4] Hertz and Kloppers, Zeits. f. Physik **31,** 463 (1925).

[5] Lyman, Science **56,** 167 (1922).

[6] The latter potentials were previously (Phys. Rev. **28,** 849 (1926)), through arithmetical error, given as 20 and 21 volts. However, the experimental error is probably greater than one volt.

[7] Hughes and Dixon, Phys. Rev. **10,** 495 (1917).

[8] Mackay, Phys. Rev. **24,** 319 (1924).

This ionization potential is that for the formation of the molecular ion (process (1)) ; the other potentials are associated with processes (2) and (3) respectively :

$$NO = O^+ + N + \epsilon \text{ ; 21 volts} \quad (4)$$

$$NO = N^+ + O + \epsilon \text{ ; 22 volts} \quad (5)$$

These, together with Hopfield's[9] values for the ionization potentials of the oxygen atom (13.56 volts) and the nitrogen atom (14.48 volts), give 7.5 volts (175,000 cal. per mole) as the heat of dissociation of NO. This is in reasonable agreement with the value of 7.9 of Birge and Sponer.[10] The one volt difference in the ionization potentials for processes (2) and (3) agrees with the difference (.92 volts) found by Hopfield for the atomic ions.

In an earlier paper we have shown that the oxygen molecule ion having 20 volts energy is unstable and dissociates spontaneously. This we explained on the basis of a recent theory of Franck.[11] This explanation was strengthened by the conclusions, from spectroscopic observation, of Birge and Sponer. The process of the spontaneous dissociation of some of the NO^+ ions is presumably substantially the same as that given for O_2^+ except that the probability of the transition to the state beyond the convergence limit of the vibrational states is not as great in the case of NO^+ as in O_2^+. The disruption of NO^+ is not to be explained in the same way as was the larger effect for nitrogen. The nitrogen molecule ion, having 24 volts energy, is unstable but, we believe, needs a rearrangement of its electron system before dissociation is possible. This is effected through collision with a second molecule. In the case of NO^+, since some spontaneous dissociation does take place, the collision perhaps merely serves to give the requisite vibrational energy to cause disruption of those NO^+ ions which, immediately after their formation by electron impact, did not possess sufficient energy of vibration to disrupt spontaneously.

Nitric oxide conforms to the rule previously given that molecules with "odd" electrons have low ionization potentials. The NO molecule has one "odd" electron and, compared with other diatomic gases, has a very low ionization potential.

Collisions of the Second Kind Involving Ions

In an investigation incidental to the positive ray analysis of NO we have sought evidence for collisions of the second kind involving ions instead of excited atoms or molecules. To this end the ionization in equimolal mixtures of NO and A and of NO and He was studied. The gas mixtures were ionized with 60-volt impact electrons and the relative numbers of NO^+ and A^+ in the one case and of NO^+ and He^+ in the other were determined as a function of the total pressure. The results are given in Fig. 2 in which the circles

[9] Hopfield, Phys. Rev. **21,** 710 (1923).
[10] Birge and Sponer, Phys. Rev. **27,** 641 (1926).
[11] Franck, Trans. Faraday Soc. (1925).

represent the observed percentages of the NO^+ and A^+ ions from an approximately equimolal mixture of NO and A, the crosses, similarly, the observed percentages of the NO^+ and He^+ ions from an approximately equimolal NO–He mixture. If these ions were formed only by the primary process of

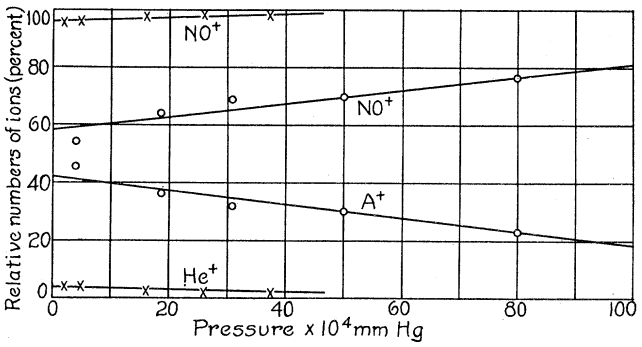

Fig. 2. Percentages of the respective ions from NO-A and NO-He mixtures as functions of the pressure.

electron impact these four curves would, obviously, be straight lines parallel to the axis of abscissas. The observed change in the relative numbers of the two different ions with increase in pressure gives, then, definite evidence for a type of collision of the second kind in which the ion robs the molecule of one of its electrons :

$$A^+ + NO = NO^+ + A \quad (6)$$

$$He^+ + NO = NO^+ + He \quad (7)$$

Since the potentials for the formation of A^+ and He^+ are higher than the ionization potential of NO, the processes (6) and (7) take place with evolution of energy—as radiation, kinetic energy or both. Smyth and Harnwell[12] have observed this same type of second-kind collision in He-Ne and A-Ne mixtures.

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April 11, 1927.

[12] After beginning this aspect of our studies we learned that Smyth and Harnwell of Princeton University were investigating the same general problem. As a result of correspondence with them a preliminary report embodying the results of both laboratories was published, jointly, in Nature, Jan. 15, 1927.