PHYSICAL REVIEW VOLUME 125, NUMBER 3 FEBRUARY 1, 1962

Formation of NO_2^- by Charge Transfer at Very Low Energies*

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(Received September 25, 1961)

The formation of NO_2^- by charge transfer of various negative ions of near 0-ev kinetic energy in NO_2 has been observed. The explanation of the very large cross section observed for the charge transfer process may possibly be found in the proposal of Rapp and Magee for the enhancement of the charge transfer cross section for nonresonant systems at low energy by the influence of the polarization of the target molecule by the incoming ion. A lower bound of 3.82 ev is placed on the electron affinity of NO_2.

PREVIOUS work by Fox[1] on negative-ion formation in NO_2 showed that NO_2^- can be formed by electron impact in NO_2. In the work of Fox it appeared that the NO_2^- current was proportional to the pressure squared, but due to the very weak NO_2^- signal this could not be considered as definitely established.

Using the same mass spectrometer as was used by Fox, modified with a low-conductance partition between the source and the pumping lead to allow much higher source pressures, the NO_2^- signal was large enough so that accurate measurements could be made on the dependence of the NO_2^- ion current on pressure and electron energy. Figure 1 shows a plot of $\log p$ vs $\log I_-$ normalized to constant electron current. The solid line is a line of slope 2. The pressure was measured with an ion gauge whose linearity was confirmed by the linearity of a plot of ion gauge current vs the NO_2^+ ion current measured by the mass spectrometer. There seems to be no doubt that in the pressure range observed the NO_2^- ion current is proportional to the square of the pressure. Figure 2 shows the dependence of the NO_2^- ion current on electron energy. The electron retarding curve determines the zero of the electron energy scale. The average of the appearance potential measurements was 1.40±0.05 ev.

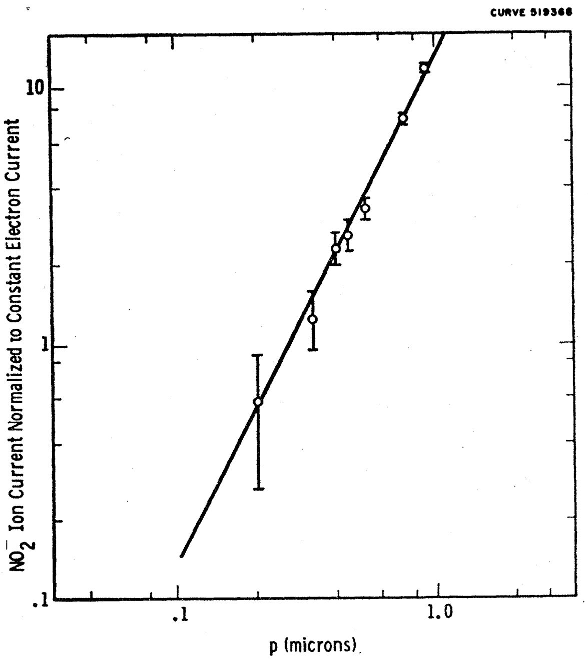

FIG. 1. Pressure dependence of NO_2^- ion current.

Three processes may be postulated to give a pressure squared dependence for the NO_2^- ion. They are

$$e+N_2O_4 \rightarrow NO_2^- + NO_2, \qquad (1)$$

$$\begin{aligned} &e+NO_2 \rightarrow (NO_2^-)^*, \\ &(NO_2^-)^* + NO_2 \rightarrow NO_2^- + NO_2^*, \end{aligned} \qquad (2)$$

$$\begin{aligned} &e+NO_2 \rightarrow O^- + NO, \\ &O^- + NO_2 \rightarrow NO_2^- + O. \end{aligned} \qquad (3)$$

Process (1) is unlikely as the pressures used in the source would require a cross section of the order of 10^{-12} cm^2 for this process if the N_2O_4 was at its equilibrium value. That the N_2O_4 was at its equilibrium value in the ion source was indicated to be the case since the NO_2^- current for constant electron current and ion source pressure was found to be independent of gas sample pressure for a variation of sample pressure from atmospheric pressure to 1 mm of Hg. Process (2) would require a very large three-body attachment coefficient of about 10^{-26} cm^6/sec. The process is unlikely as it would require a very strong resonance between an excited state of NO_2 and the excited state of NO_2^-. Process (3) appears to be the most plausible interpretation of the mechanism for NO_2^- formation. The O^- ion is formed[1] in NO_2 at an energy of 1.35 ev. A comparison of the energy dependence of the NO_2^- ion current observed here and that observed by Fox[1] for the O^- ion formed in NO_2 show them to be identical. The correctness of this interpretation was verified by observing NO_2^- ions formed when mixtures of NO_2 and various "foreign" gases were introduced into the mass spectrometer. In addition to the NO_2^- ion formed by the O^- ion from NO_2 at 1.35 ev additional NO_2^- ion currents were observed for electron energies at which the "foreign" gases formed negative ions. The negative ions and their parent gases for which an NO_2^- was observed were O^-/CO_2, O^-/O_2, SF_6^-/SF_6, SF_5^-/SF_6, and Cl^-/CCl_4.

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* This work supported in part by the Advanced Research Projects Agency and the Office of Naval Research.

[1] R. E. Fox, J. Chem. Phys. 32, 285 (1960).

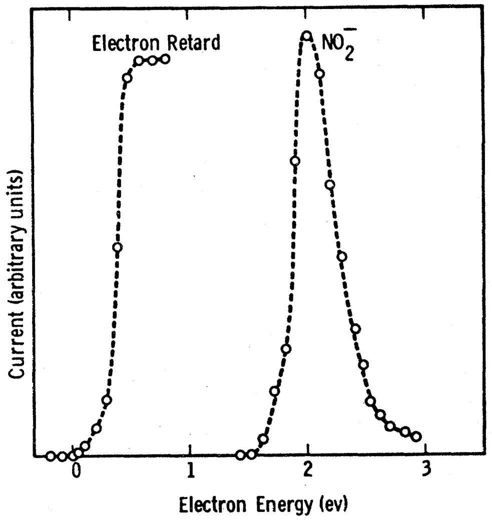

FIG. 2. Electron energy dependence of NO_2^- ion current formed from O^-/NO_2.

The cross sections were estimated from the ratio of the NO_2^- ion peak to the primary ion peak. The cross sections for charge transfer of O^-, SF_6^-, SF_5^-, and Cl^- with NO_2 ranged from 8×10^{-16} cm^2 to 7×10^{-15} cm^2. The mass spectrometer is arranged such that the ion collector is at the same potential as the exit slit of the ion source. This defines the region between the electron beam and the exit slit as the region of NO_2^- formation. The ions moving in this region have very low energy. They are accelerated towards the exit slit where they have at most 0.5 ev kinetic energy in addition to any kinetic energy of formation. In order for process (3) to be energetically possible, the electron affinity of NO_2 must be greater than the electron affinity of the incident negative ion. Cl had the largest electron affinity, namely[2] 3.82 ± 0.06 ev. Thus a lower limit of 3.82 ev may be put on the electron affinity of NO_2.

The explanation of the very large cross section observed at the very low energies of the interacting particles may possibly be found in the proposed[3] enhancement of the charge transfer cross section for nonresonant systems at low energy by the influence of the polarization of the target molecule, in this case NO_2, by the incoming ion. It should be pointed out that the cross section observed for a process such as (3) may be less than that calculated considering only the effect of polarization since any competition due to a rearrangement resulting from the collision or from detachment of the electron from the collision complex would make the measured cross section lower.[4] A competitive process of detachment is energetically possible whenever the electron affinity of the incoming negative ion is less than the dissociation energy of the neutral complex formed by the incident ion and target molecule on removal of an electron.

Charge exchange processes similar to that reported here have also been observed by Kraus *et al.*[5] for negative ions moving in their parent gas.

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[2] H. O. Pritchard, Chem. Revs. **52**, 529 (1953).

[3] D. Rapp and J. L. Magee, *Second International Conference on the Physics of Electronic and Atomic Collisions* (W. A. Benjamin, Inc., New York, 1961), p. 52.

[4] A. V. Phelps (private communication).

[5] K. Kraus, W. Müller-Duysing, and H. Neuert, *Fifth International Conference on Ionization Phenomena in Gases*, Munich, Germany, August 28, 1961 (unpublished).