PHYSICAL REVIEW
LETTERS

VOLUME 20 | 5 FEBRUARY 1968 | NUMBER 6

CHARGE-TRANSFER CROSS SECTIONS FOR THE REACTION $N_2^+ + O_2 \rightarrow O_2^+ + N_2$ AT VERY LOW ENERGIES*

D. E. Golden, G. Sinnott, and R. N. Varney
Lockheed Palo Alto Research Laboratory, Palo Alto, California
(Received 15 December 1967)

The charge-transfer cross section for $N_2^+ + O_2 \rightarrow O_2^+ + N_2$ has been measured by a drift-tube technique in the formerly inaccessible energy region from 0.05 to 1 eV in the center-of-mass system. In this energy region the charge-transfer cross section σ may roughly be represented by $\sigma = 2.2\ \text{Å}^2/(\text{c.m. energy in eV})^{1/2}$. This expression is consistent with a model dominated by the induced dipole interaction, and it connects smoothly thermal-energy measurements to ion-beam measurements at several eV.

The charge-exchange reaction $N_2^+ + O_2 \rightarrow N_2 + O_2^+$ has been subject to extensive study[1-3] both because of the light it sheds on the subject of nonresonant exchange processes and because of its importance in atmospheric processes. The present report on this reaction spans the energy range from nearly thermal to about 1 eV in the center-of-mass system, a range in which the cross section proves to fall off rapidly with increasing kinetic energy, and one which has heretofore not been examined.

The apparatus consisted of an electron-collision-type ion source, a double-shutter drift-speed device,[4] and after differential pumping, a quadrupole-type mass spectrometer with electron-multiplier detector. Details are being provided in another paper[5]; the principles are embodied in several other publications.[6,7] Dry air was admitted to the source after passing through a trap cooled with liquid nitrogen. Hence numerous ions including N_2^+, O_2^+, N^+, and O^+ emerged from the source, and appreciable amounts of NO^+ were formed by collision processes not identified positively in the present investigation. Since the formation of ions in excited states was a potential concern, as 50-eV electrons were used in the source, a drift space was provided in which a minimum of ten ion-molecule collisons could be expected to occur at the lowest pressures used and considerably more collisions at higher pressures. It was believed that these collisions served to de-excite the excited states before the ions reached the principal drift space where speeds were measured. The ion currents were modulated and phase-sensitive detection was used in order to minimize effects due to stray secondary electrons, ultraviolet radiation, and metastables.

The reaction cross section (or rate) of the subject reaction was measured simply by noting the decline in the percentage of N_2^+ current relative to total current reaching the electron-multiplier detector with increasing pressure. To assure that the N_2^+ was indeed exchanging charge with O_2 and that this process was therefore the one being studied, the corresponding growth of the percentage of O_2^+ in the total current was also noted and found to agree to with-

in 6%. From simple substitutions in the equation defining two-body reaction rates, the rate constant K was calculated. The result is plotted in Fig. 1 against both E/p_0 and E/N, the ratios of electric field strength to pressure (reduced to 0°C equivalent density) and of electric field strength to gas density.

There are, however, two additional features of the reaction to be shown, the reaction cross section σ and its relation to the center-of-mass kinetic energy ϵ. The rate constant K is related to the cross section σ and the speed v of the ion relative to the molecule, at large atomic-scale distances before collision. The relation is $K = \langle \sigma v \rangle_{av}$, the averaging to be performed over the speed distribution. The slow variation of K with ϵ (see Fig. 1) in the energy range of the present investigation makes the approximation $K = \sigma v$ reasonably valid and permits calculating σ as K/v.

The evaluation of ϵ as a function of E/p_0 or E/N is achieved by use of the drift-speed measurement v_d. For the present work, this interrelation has been set up by the use of Wannier's theory,[8] taking note of the fact that this theory predicts essentially the same results as were computed by Varney[9] from correlation of thermal data with E/p_0 values. The relationship takes the form $\epsilon = \frac{1}{2} m_g v_d^2 + \frac{3}{2} k T_g$, where m_g is the mass of the gas, k is the Boltzmann constant, and T_g is the gas temperature. The graph of σ vs ϵ is shown in Fig. 2 by the squares.

There is some interest in noting that, while the relationship $\sigma = K/v$ is not perfectly an inverse first power one because of the change of K indicated in Fig. 1, the decrease of K with ϵ is relatively small over the range studied so that the simple inverse form $\sigma = \text{const}/v$ is nearly valid. This relationship using a mean value of K of 0.78×10^{-10} cm^3/sec read from Fig. 1 is plotted as the curve in Fig. 2. It is the one that Stebbings, Turner, and Rutherford[2] used to interpolate between their lowest energy point $\sigma \simeq 2$ Å^2 at $\epsilon = 2.7$ eV and Goldan et al.'s thermal data[1] giving $\sigma \simeq 11.4$ Å^2 at $\epsilon \simeq 0.04$ eV. The present results furnish experimental justification for Stebbings' procedure, a procedure which was not strictly justifiable as an extrapolation of his experimental data but which is compatible with the Gioumousis and Stevenson[10] solution for collisions obeying inverse fifth-power attractive forces characteristic of ion-induced dipole interactions. In fact, if an average, constant value of K from the present data is assumed, the resulting values of σ suggest that a fraction 0.12 of the collisions occurring as a result of the ion-dipole interaction results in charge exchange.

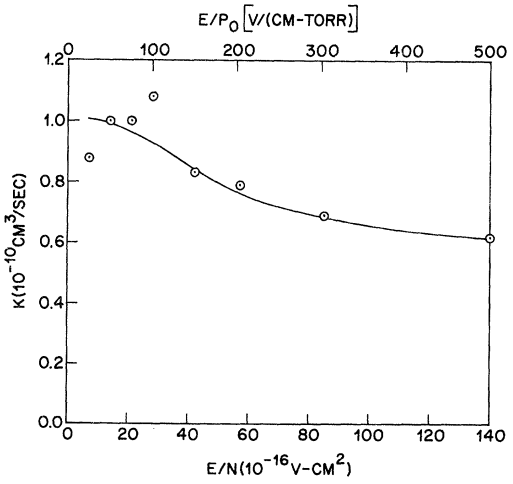

FIG. 1. Reaction rate constant versus E/p_0 and E/N for the process $N_2^+ + O_2 \rightarrow N_2 + O_2^+$. The points are actual readings; the curve is an approximation to the points based in part on the observation that the point at lowest E/N had greater probable error than the others.

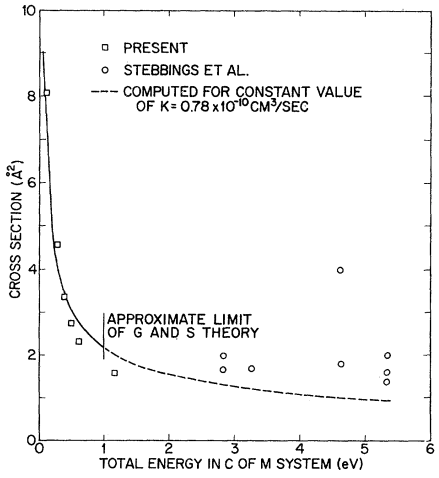

FIG. 2. Charge-transfer cross sections for the process $N_2^+ + O_2 \rightarrow N_2 + O_2^+$ as a function of the relative kinetic energy of the colliding bodies at large distances (atomic scale) prior to impact. The solid curve shows a $1/v$ relationship characteristic of the perfect ion-dipole interaction law using a constant of 0.78×10^{-10} cm^3/sec. The limiting energy at which this type of interaction determines the cross section is at about 1 eV. The abscissa values of Stebbings, Turner, and Rutherford (Ref. 2) are altered from lab energies to center-of-mass energies.

One may conclude from this work that the gross variation of the charge-transfer cross section is consistent with a model based on the formation of a complex N_2^+-O_2 due to the induced-dipole interaction.

*Work supported by Lockheed Independent Research Funds.

[1]P. D. Goldan, A. L. Schmeltekopf, F. C. Fehsenfeld, H. I. Schiff, and E. E. Ferguson, J. Chem. Phys. 44, 4095 (1966).

[2]R. F. Stebbings, B. R. Turner, and J. A. Rutherford, J. Geophys. Res. 71, 776 (1966).

[3]P. Warneck, J. Chem. Phys. 46, 502 (1967).

[4]See, for example, G. Sinnott, Phys. Rev. 136, A370 (1964).

[5]D. E. Golden, G. Sinnott, and R. N. Varney, to be published.

[6]M. Saporoschenko, Phys. Rev. 139, A352 (1965), has an extensive reference list.

[7]E. W. McDaniel, Collision Phenomena in Ionized Gases (John Wiley & Sons, Inc., New York, 1964), pp. 452-454.

[8]G. H. Wannier, Phys. Rev. 83, 281 (1951), and 87, 795 (1952).

[9]R. N. Varney, J. Chem. Phys. 31, 1314 (1959).

[10]G. Gioumousis and D. P. Stevenson, J. Chem. Phys. 29, 294 (1958).

CROSS SECTION FOR THE PRODUCTION OF SINGLY IONIZED HELIUM BY ELECTRON IMPACT AT LOW ENERGIES*

C. E. Brion and G. E. Thomas
Chemistry Department, University of British Columbia, Vancouver, Canada
(Received 17 July 1967)

For an adequate understanding of electron-atom and electron-ion interactions, it is necessary that reliable experimental data from inelastic collision studies be available for comparison with theoretical results calculated using various models. This Letter reports the results of a direct experimental investigation of the energy dependence of the cross section for the formation of singly charged helium positive ions resulting from inelastic collisions between neutral helium atoms and electrons having a narrow energy bandwidth.

Because of the wide Maxwell-Boltzman energy distribution of thermionically emitted electrons, a detailed study of the exact form of ionization cross sections and threshold laws is impossible with conventional electron-impact sources. Clarke[1] has reviewed many of the problems involved in this type of work. The retarding potential difference (RPD) pseudo-monoenergetic electron source has been used by Fox and his co-workers[2] to study the ionization of helium in an attempt to determine the exact shape of the ionization efficiency curve. Fox reported a linear dependence for He^+ formation to within 0.2 V of the threshold. The RPD result, however, must be open to question in view of the possibility of space-charge-induced relaxation as pointed out by Marmet[3] and also because of the fact that the difference currents near threshold are subject to largest errors. On the other hand, any attempt to deconvolute[4] a conventional ionization efficiency curve would involve an exact knowledge of the electron energy spread. Because of the possibility of electron beam relaxation, surface charging, and electron optical effects, a simple knowledge of the cathode temperature is unlikely to provide the correct energy distribution function.[5]

A more direct approach having fewer objections is the use of an electron beam, energy selected by means of a monochromator. Using this technique, McGowan et al. have recently reported a study of the ionization of atomic hydrogen, finding a 1.127-power law in the region close to the threshold.[6] In the present work, we have used a 127° electrostatic energy selector[7] of the Marmet type[8] to produce an electron beam of about 3×10^{-8} A with an energy width at half-height of about 50 mV. Ions produced by electron impact are mass analyzed in a monopole mass filter and detected with an electron multiplier and vibrating-reed electrometer, the output of which is connected to a multichannel analyzer and data-processing system. Full details of the experimental arrangement will be published later.[9] The sample gas pressure is 8×10^{-6} mm mercury and the observed ion currents are a linear function of gas pressure. The ionizing electron current is found to be independent of electron energy in the range studied. Electron energy distributions are obtained by scan-