PHYSICAL REVIEW A VOLUME 23, NUMBER 5 MAY 1981

Charge-transfer reaction $Ar^+ + N_2 \rightleftarrows N_2{}^+ + Ar$ at thermal energies

D. Smith and N. G. Adams
Department of Space Research, University of Birmingham, Birmingham B15 2TT, England

(Received 18 July 1980)

The results are presented of a study of the forward and reverse rate coefficients (k_f and k_r) at thermal energies for the reaction $Ar^+(^2P_{3/2}) + N_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ar + N_2{}^+(\nu = 0,1)$. The data were obtained in a selected ion flow tube. It is shown that at 300 K the forward reaction proceeds predominantly via the $N_2{}^+(\nu = 1)$ product channel and at 80 K via the $N_2{}^+(\nu = 0)$ channel. k_r is large for $N_2{}^+(\nu = 1)$ which probably explains the anomalies in previous studies of k_f in afterglows in which Ar and N_2 coexisted.

I. INTRODUCTION

The rate coefficient for the charge-transfer reaction of Ar^+ with N_2 has been determined in many laboratories using a variety of techniques during the last fifteen years (a summary of the previous data is given in the accompanying paper[1]). Much greater differences are apparent in the reported rate coefficients than are usual in ion-molecule reaction-rate studies, this being due to the rather rare combinations of energy states involved in the reaction, the relevant energetics being

$$Ar^+(^2P_{3/2}) + N_2 \rightarrow N_2{}^+\ (\nu = 0) + Ar + 0.179\ \text{eV} \tag{1a}$$

$$\rightarrow N_2{}^+\ (\nu = 1) + Ar - 0.090\ \text{eV}\,, \tag{1b}$$

$$Ar^+(^2P_{1/2}) + N_2 \rightarrow N_2{}^+\ (\nu = 0) + Ar + 0.357\ \text{eV} \tag{1c}$$

$$\rightarrow N_2{}^+\ (\nu = 1) + Ar + 0.088\ \text{eV}\,, \tag{1d}$$

where the N_2, $N_2{}^+$, and Ar are in their ground electronic states. Thus, the simultaneous presence of both the spin states of Ar^+ in a reaction cell which also contains both N_2 and Ar means that at 300 K ($\bar{\epsilon} \sim 0.04$ eV), reaction channels a, c, and d are energetically allowed and channel b could also proceed at a significant rate. Also, very significantly, the presence of vibrationally excited $N_2{}^+$ allows the reverse reaction with Ar to proceed which, as has been reasoned by Lindinger *et al.*[1] (accompanying paper), has caused many of the problems in afterglow measurements.

In order to clarify the situation we have studied both the forward and reverse of reaction (1) at thermal energies using a selected ion flow tube (SIFT) at and below 300 K. Lindinger *et al.*[1] have made a parallel, more detailed study using an injected ion drift tube over an ion-to-neutral center-of-mass kinetic-energy range from near thermal to a few electron volts.

II. EXPERIMENTAL

The SIFT technique has been described in detail previously[2-4] and therefore will only be alluded to here. Ions are created in a remote ion source and after mass filtering are injected into a fast flowing carrier gas where they thermalize by collisions while being convected down a flow tube. Reactant gases are added to the carrier gas at controlled rates and reaction-rate coefficients and product-ion distributions are obtained by correlating the rate of change of the primary and product-ion count rates at a downstream mass-spectrometer detection system with the rate of flow of the reactant gas.

In the experiments described here Ar and N_2 were the only ion source and reactant gases used. Most data were obtained at 300 and 80 K but one measurement was performed at 140 K. More details of the techniques adopted in this study are given as appropriate in the following sections.

III. RESULTS

A. $N_2{}^+ + Ar$

It is convenient to discuss first the reverse of reaction (1). The $N_2{}^+$ ions were generated in an electron impact ion source containing N_2 at a pressure of about 1 mtorr and injected into the carrier gas (helium at ~0.5 torr typically), Ar was added, and the $N_2{}^+$ count rate was observed at the downstream detection system. Data obtained at 300 K for an ion-source electron energy of 100 eV are shown in Fig. 1(a). Treatment of these data according to the methods described in detail by Glosik *et al.*[5] indicates that two differently reacting species are present: a rapidly reacting one (~40% of the total $N_2{}^+$) and one which reacts extremely slowly. The rate coefficient for the fast reaction is 4×10^{-10} cm^{3}s^{-1}, i.e., a major fraction of the collisional limiting (Langevin) value[6] $k_L = 7 \times 10^{-10}$ cm^{3}s^{-1}, whereas that for the very slow reaction is approximately 2×10^{-13} cm^{3}s^{-1}.

It is well known that low-pressure ion sources can generate large fractions of positive ions in metastable electronic states and it is known that $N_2{}^+$ possesses at least two such states with appearance potentials approximately within the range

21–22 V.[7] The electron accelerating voltage in the ion source was therefore reduced below these values to 18 V and the experiment repeated. The results obtained were essentially identical to those shown in Fig. 1 (but with reduced signal levels). The lowest possible source voltage we were able to use was 16.5 V before the injected N_2^+ current became prohibitively low. At this voltage the electron impact energy is only about 1 eV above the threshold energy for production of N_2^+ (i.e., 15.5 eV) yet the data obtained under these ion-source conditions were again essentially identical to those obtained for 100-eV electrons. We therefore conclude that the "excited state" of N_2^+ present in the flow tube is not an electronically excited state but a vibrationally excited state(s) of N_2^+ in its ground electronic state, and that the unreactive component is N_2^+ $(\nu = 0)$, the reaction of which with Ar is endothermic at 300 K [see Eq. (1a)].

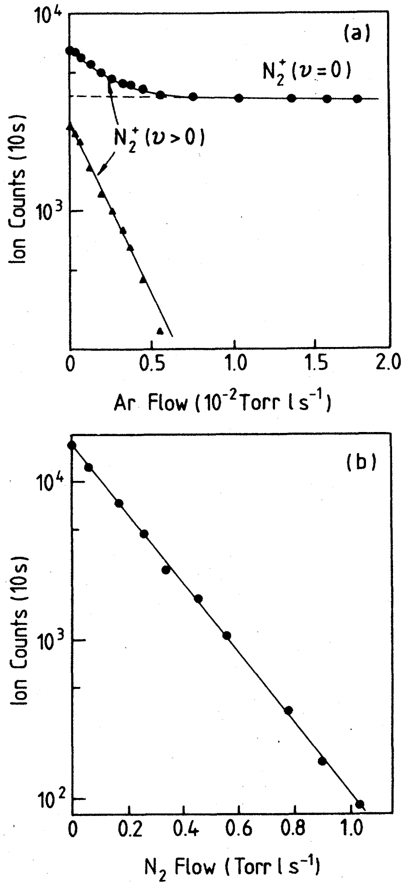

FIG. 1. (a) Data for the reaction of N_2^+ with Ar. The decline of the N_2^+ count (ten-second sampling period) for small Ar flows is due to the rapid reaction of the N_2^+ $(\nu=1)$ component. The linear plot from which the rate coefficient for the N_2^+ $(\nu=1)$ reaction is obtained is derived by subtracting the relatively unreactive N_2^+ $(\nu=0)$ from the total N_2^+ count rate. The rate coefficient for the N_2^+ $(\nu=0)$ reaction is obtained from the almost imperceptible decline of the N_2^+ count rate at larger Ar flows. (b) Data for the reaction of Ar^+ with N_2. The linearity of the plot over more than two decades in Ar^+ count rate coupled with the small rate coefficient for the reaction (see text) is an indicator that only one state of Ar^+ is effectively involved in the reaction which we reason to be the $^2P_{3/2}$ state.

The fraction of the excited to ground states present in the helium carrier gas at 300 K was independent of the helium pressure. From this observation we deduce that the rate coefficient for relaxation of the vibrationally excited N_2^+ in collisions with helium atoms is less than 10^{-15} cm^3s^{-1}. When the carrier gas was cooled to 80 K, the fraction of the excited state in the SIFT was again ~40% and the rate coefficient for its reaction with Ar remained at 4×10^{-10} cm^3s^{-1}. The rate coefficient for the slower reaction was now immeasurably small ($\lesssim 10^{-13}$ cm^3s^{-1}), as would be expected for the reverse of reaction (1a) at this low temperature. Evidence which suggests that the vibrationally excited state of N_2^+ is the $\nu=1$ state is given in Sec. C below.

Some evidence is also available which suggests that vibrationally excited ions are rapidly relaxed in collisions with their parent neutral molecules.[8] To investigate this phenomenon for the N_2^+ $(\nu > 0)$ present in these experiments is a straightforward procedure. Ar is used as a "monitor gas" for the excited state (thus distinguishing it from the ground state) by adding Ar to the flow at a position just upstream of the ion-detection-system sampling orifice. The presence of Ar^+ ions is then an indicator of N_2^+ $(\nu > 0)$. By the controlled addition of N_2 upstream of the Ar addition port, the quenching-rate coefficient for the reaction

$$N_2^+ (\nu > 0) + N_2 \rightarrow N_2^+ (\nu = 0) + N_2^* \qquad (2)$$

can readily be determined. Reaction (2) is indeed fast, the rate coefficient being $\sim 6\times10^{-10}$ cm^3s^{-1}, that is, a large fraction of the collisional rate coefficient (8×10^{-10} cm^3s^{-1}). Thus in a gas containing appreciable amounts of N_2, vibrationally excited N_2^+ ions will be rapidly quenched.

It is worthy of note that the presence of the vibrationally excited component of N_2^+ was not apparent during our previous studies of the reactions of N_2^+ ions with several molecular gases[9] implying that the N_2^+ $(\nu > 0)$ was either quenched or more likely reacted at the same rate as N_2^+ $(\nu = 0)$ for these more exoergic reactions.

B. $Ar^+ + N_2$

Ar^+ ions were generated in the electron impact ion source containing Ar at a pressure of about 1 mtorr. We therefore presume that both the $^2P_{3/2}$

and the higher energy $^2P_{1/2}$ states were initially created approximately in the ratio of their statistical weights (2:1) as we have clearly shown to be the case for both Kr^+ and Xe^+ produced in this source.[10] Separation and identification of the two spin states of Kr^+ and Xe^+ is a relatively simple procedure by virtue of the appreciable energy differences between the spin states which is manifest in their greatly differing reactivities with several molecular gases. Thus we were able to investigate the reactions of each state separately by using "chemical filtering."[10] However, this is not possible for the Ar^+ spin states which are separated in energy by only 0.18 eV and so the identification of the spin state(s) present must necessarily be more indirect.

A typical data curve obtained for this reaction is given in Fig. 1(b). Measurements were made at 300, 140, and 80 K and the decay curves were linear over more than two decades in Ar^+ decay. This linearity coupled with the small rate coefficient for the reaction(s) of 1×10^{-11} cm^{3}s^{-1} [$k_L = 7.7(-10)$ cm^{3}s^{-1}] indicates almost certainly that only a single reacting ion species is present in the flow tube. The very unlikely, but not unknown, circumstance [for example, $Xe^+(^2P_{3/2,1/2}) + O_2$[10]] is that two species are present which react with N_2 at identical rates. However, data have been obtained by McGowan *et al.*[11] in a low-pressure experiment which indicates that $Ar^+(^2P_{3/2})$ reacts with N_2 at a rate some three times greater than does the $Ar^+(^2P_{1/2})$ state. It is interesting to note that the lower-energy spin states ($^2P_{3/2}$) of both Kr^+ and Xe^+ react more rapidly with a wide variety of molecular gases.[10] However, this apparently general rule for Kr^+ and Xe^+ does not hold for the reaction of Ar^+ with H_2 for which Tanaka *et al.*[12] have found that the $^2P_{1/2}$ state reacts 50% more rapidly than the $^2P_{3/2}$ state over a center-of-mass energy range from near thermal to about 0.5 eV. So it appears that in the present experiment only one state of Ar^+ is involved, this presumably being the lower-energy $^2P_{3/2}$ state. This implies the $^2P_{1/2}$ state is being collisionally relaxed either in the source in collision with electrons or the Ar source gas (the latter being unlikely since the quenching rate with Ar has been shown to be very small[13]), or in the helium carrier gas or in unreactive (non-charge-transfer) collisions with N_2, viz.,

$$Ar^+(^2P_{1/2}) + N_2 \rightarrow Ar^+(^2P_{3/2}) + N_2^* . \qquad (3)$$

If reaction (3) is occurring at the Langevin rate, it would be some 100 times more efficient than the very low probability reaction (1c), the latter having a rate coefficient of about 30% of that for the $^2P_{3/2}$ state reaction (1a),[11] i.e., $\sim3\times10^{-12}$ cm^{3}s^{-1}.

Additional evidence that the Ar^+ ions injected into the SIFT are the $^2P_{3/2}$ state is obtained by observing their reactivity with Ar. We have shown that the Ar^+ ions readily associate with Ar forming Ar_2^+, whereas Liu and Conway[13] have shown that the $^2P_{1/2}$ state does not associate with Ar at temperatures of 200 and 300 K. So the body of evidence indicates that the Ar^+ ions being studied here are in the $^2P_{3/2}$ state.

C. State of the N_2^+ generated in the $Ar^+(^2P_{3/2}) + N_2$ reaction

Utilizing the information gained from the above experiments it is now possible to determine the fraction, if any, of vibrationally excited N_2^+ ions which is formed in the $Ar^+(^2P_{3/2}) + N_2$ reaction. Thus Ar^+ was injected into the SIFT and sufficient N_2 was added upstream in the flow to produce an appreciable signal of N_2^+ at the downstream detection system, but insufficient N_2 to significantly relax any N_2^+ ($\nu > 0$). In practice this permitted a reduction in the primary Ar^+ signal by only about 2% from its initial value. Ar was then added downstream as a detector of N_2^+ ($\nu > 0$).

At 300 K the results indicated, somewhat surprisingly, that the majority (>70%) of the N_2^+ product ions are vibrationally excited. For $Ar^+(^2P_{3/2})$ primary ions, the highest vibrational level accessible is $\nu = 1$. So the slightly endoergic reaction channel (1b) is favored at 300 K rather than the exoergic reaction channel (1a). A similar result was obtained in the Innsbruck drift tube experiment.[1] The relatively small rate coefficient for the $Ar^+ + N_2$ reaction at 300 K (see Sec. B) indicates that only about 1% of the ion-molecule collisions result in a charge transfer. This can be seen now in terms of a very small probability for the exoergic channel (1a) and a much larger (~unity) probability for charge transfer into N_2^+ ($\nu = 1$) for the small fraction of interactions which, by virtue of the finite temperature, are energetically allowed to resonantly transfer charge.

At 80 K, the $Ar^+ + N_2$ rate coefficient is 1×10^{-11} cm^{3}s^{-1}, i.e., within error equal to the 300-K value, but the N_2^+ product was seen to be almost totally formed in the $\nu = 0$ state. At this temperature very few interactions are sufficiently energetic to overcome the endoergicity in channel (1b) which explains the absence of N_2^+ ($\nu = 1$). However, it is surprising that the overall rate coefficient does not reduce significantly below the 300-K value. In an attempt to understand this, the overall rate coefficient was measured at an intermediate temperature of 140 K and a small but significant reduction was observed ($k \sim 8\times10^{-12}$ cm^{3}s^{-1}). The total errors involved in the rate coefficients at 300, 140, and 80 K are such that a detailed discussion is unwarranted. However, it appears that the rate coefficient for the $Ar^+ + N_2$ reaction does pass through a shallow minimum between 80 and 300 K and could indicate a different reaction mechanism in the two temperature regimes.

The rate coefficient for the reaction with Ar of the N_2^+ ($\nu = 1$) derived from the $Ar^+ + N_2$ reaction could not be determined as accurately as usual because of the small N_2^+ signals available. The value obtained was $(3 \pm 1) \times 10^{-10}$ $cm^3 s^{-1}$ which is within error equal to that obtained for the reaction with Ar of the N_2^+ ($\nu > 0$) created in the ion source and this can be taken to indicate that this N_2^+ is largely in the $\nu = 1$ state. Thermodynamic evidence that this long-lived state is the $\nu = 1$ state is given in the accompanying paper.[1]

IV. CONCLUSIONS

The evidence presented in this short paper indicates that previous studies of the $Ar^+ + N_2$ reaction at 300 K have most probably been complicated by the reverse reaction ($N_2^+ + Ar$) since the N_2^+ product is formed predominantly in the $\nu = 1$ state, viz.,

$$Ar^+(^2P_{3/2}) + N_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ar + N_2^+ \ (\nu = 1) \, . \qquad (4)$$

k_r is seen to be very large and since the N_2^+ ($\nu = 1$) appears to be long lived, then the rate of the back reaction can be large. However, the N_2^+ ($\nu = 1$) is efficiently quenched to N_2^+ ($\nu = 0$) in collision with N_2 and so the presence of N_2 effectively inhibits the back reaction. The rate of loss of Ar^+ ions is therefore influenced in a complicated way by the N_2 concentration in the reaction cell. In the accompanying paper[1] this situation is treated quantitatively in relation to a previous flowing afterglow experiment.

The initial presence of $Ar^+(^2P_{1/2})$ in a collision-dominated reaction cell would also lead to complications, but the evidence suggests that this state is efficiently quenched to $Ar^+(^2P_{3/2})$ in collisions with electrons, neutral atoms, or molecules and so only the $Ar^+(^2P_{3/2})$ need be considered as taking part in the charge-transfer reaction. However, in single-collision ion-beam experiments there exists a greater probability that both spin states will be involved depending, of course, on the nature of the ion source in which the Ar^+ ions are generated.

The rate coefficients and product-ion states for the $Ar^+(^2P_{3/2}) + N_2$ reaction at 300 K indicate a high probability for the production of N_2^+ ($\nu = 1$) and a very small probability for the production of the N_2^+ ($\nu = 0$). The channel leading to N_2^+ ($\nu = 0$) becomes increasingly more efficient at the lower temperatures at which the N_2^+ ($\nu = 1$) state is inaccessible.

ACKNOWLEDGMENT

We are grateful to Professor W. Lindinger and his colleagues for many helpful suggestions and comments.

---

[1] W. Lindinger, F. Howorka, P. Lukac, S. Kuhn, H. Villinger, E. Alge, and H. Ramler (accompanying paper) Phys. Rev. A 23, 2319 (1981).

[2] N. G. Adams and D. Smith, Int. J. Mass Spectrom. Ion Phys. 21, 349 (1976).

[3] N. G. Adams and D. Smith, J. Phys. B 9, 1439 (1976).

[4] D. Smith and N. G. Adams in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1979), Vol. I, p. 1.

[5] J. Glosik, A. B. Rakshit, N. D. Twiddy, N. G. Adams, and D. Smith, J. Phys. B 11, 3365 (1978).

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

[7] M. Tichy, A. B. Rakshit, D. G. Lister, N. D. Twiddy, N. G. Adams, and D. Smith, Int. J. Mass Spectrom. Ion Phys. 29, 231 (1979).

[8] D. L. Albritton, in *Kinetics of Ion-Molecule Reactions*, edited by P. Ausloos (Plenum, New York, 1979), p. 119.

[9] D. Smith, N. G. Adams, and T. M. Miller, J. Chem. Phys. 69, 308 (1978).

[10] N. G. Adams, D. Smith, and E. Alge, J. Phys. B 13, 3235 (1980).

[11] J. W. McGowan, P. Marmet, and L. Kerwin, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland, Amsterdam, 1964), p. 854.

[12] K. Tanaka, J. Durup, T. Kato, and I. Koyano, J. Chem. Phys. 73, 586 (1980).

[13] W. F. Liu and D. C. Conway, J. Chem. Phys. 62, 3070 (1975).