AIP The Journal of Chemical Physics

Thermal Energy Ion—Neutral Reaction Rates. IV. Nitrogen Ion Charge Transfer Reactions with CO and CO2

F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson

Citation: J. Chem. Phys. **44**, 4537 (1966); doi: 10.1063/1.1726670 View online: http://dx.doi.org/10.1063/1.1726670 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v44/i12 Published by the American Institute of Physics.

Additional information on J. Chem. Phys.

Journal Homepage: http://jcp.aip.org/ Journal Information: http://jcp.aip.org/about/about_the_journal Top downloads: http://jcp.aip.org/features/most_downloaded Information for Authors: http://jcp.aip.org/authors

ADVERTISEMENT



Downloaded 31 Dec 2012 to 152.3.102.242. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

now known has a counterpart with probably identical structure in the phase diagram of Na₂MoO₄.

ACKNOWLEDGMENTS

A portion of this research was carried out in Professor George C. Kennedy's high-pressure laboratory. The author would like to thank him for the use of laboratory equipment. Thanks are due to Martha C.

THE JOURNAL OF CHEMICAL PHYSICS

Pistorius for writing the computer programs and Professor George C. Kennedy, Dr. E. Rapoport, Dr. L. H. Cohen, and Dr. W. Klement for valuable discussions. Mr. T. J. Thomas, Mr. H. Erasmus, and Mr. C. J. Cellarius kept the apparatus in good order. Partial financial support for this research was borne by our contract for Mineral Synthesis, U. S. Office of Naval Research Nonr 233 (28) and NSF GP-3300.

VOLUME 44, NUMBER 12 15 JUNE 1966

Thermal Energy Ion–Neutral Reaction Rates. IV. Nitrogen Ion Charge-Transfer Reactions with CO and CO₂

F. C. FEHSENFELD, A. L. SCHMELTEKOPF, AND E. E. FERGUSON

Institute for Telecommunication Sciences and Aeronomy,* Environmental Science Services Administration, Boulder, Colorado (Received 16 December 1965)

Charge-transfer reaction rates have been measured for N^+ and N_2^+ ions with CO and CO₂ in a pulsed flowing afterglow system. The rates are all very close to 10^{-9} cm³/sec at 300°K, corresponding to essentially a charge transfer on every momentum-transfer collision.

INTRODUCTION

THE flowing afterglow reaction tube that has been L used to measure a number of thermal energy positive ion-neutral reaction rate constants, particularly for reactions of geophysical interest,¹⁻⁸ has been used to measure some additional positive-ion reaction rate constants, which are reported here.

EXPERIMENTAL

The details of operation of the pulsed dc discharge, flowing afterglow system used for the reported measurements are described elsewhere^{1,2} and are only briefly discussed here. Helium gas is introduced into a large reaction tube at a flow rate of $190 \text{ atm} \cdot \text{cm}^3 \text{ sec}^{-1}$. The helium is excited and ionized by a pulsed dc discharge between a large cylindrical cathode and a small

wire anode. The large reaction tube is 7.8-cm i.d. and 100 cm in length. The flow velocity of the helium is 10⁴ cm/sec and the pressure is 0.3 torr. Nitrogen ions are produced by introducing nitrogen gas into the helium afterglow through a small glass jet. The helium ions produce atomic ions by the rapid reaction

$$He^+ + N_2 \rightarrow He + N + N^+ + 0.3 \text{ eV},$$
 (1)

the rate constant being $k_1 = 1.7 \times 10^{-9}$ cm³/sec.^{1,4} The helium triplet metastables produce molecular ions by the Penning reaction,

$$\operatorname{He}(2^{3}S) + \operatorname{N}_{2} \rightarrow \operatorname{He} + \operatorname{N}_{2}^{+} + e, \qquad (2)$$

the rate constant being around 10⁻¹⁰ cm³/sec in this case.9 Reaction (2) produces visible light¹⁰ so that it is easy to see that this reaction [and consequently the faster reaction (1) has gone to completion in a distance down the tube of about 10 cm from the introduction jet.

The neutral reactant to be investigated is introduced downstream at a second jet. It can then react with the nitrogen ions for the remainder of the tube length (\sim 50 cm), or for a time of \sim 5 msec. The N⁺ ions produced by Reaction (1) can only be in the ground electronic state. The N_2^+ from Reaction (2) is largely produced in the $B^{2}\Sigma_{u}^{+}$ zero vibrational state, as determined by absolute intensity measurements of the

^{*} Formerly the Central Radio Propagation Laboratory.

<sup>Formerly the Central Radio Propagation Laboratory.
¹ F. C. Fehsenfeld, A. L. Schmeltekopf, P. D. Goldan, H. I. Schiff, and E. E. Ferguson, J. Chem. Phys. 44, 4087 (1966).
² P. D. Goldan, A. L. Schmeltekopf, F. C. Fehsenfeld, H. I. Schiff, and E. E. Ferguson, J. Chem. Phys. 44, 4095 (1966).
³ F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, J. Chem. Phys. (to be published).
⁴ E. E. Ferguson, F. C. Fehsenfeld, D. B. Dunkin, A. L. Schmeltekopf, and H. I. Schiff, Planetary Space Sci. 12, 1169 (1964).</sup>

^{(1964).} ⁵ F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson,

Planetary Space Sci. 13, 219 (1965). ⁶ F. C. Fehsenfeld, P. D. Goldan, A. L. Schmeltekopf, and

E. E. Ferguson, Planetary Space Sci. 13, 579 (1965). ⁷ E. E. Ferguson, F. C. Fehsenfeld, P. D. Goldan, A. L. Schmeltekopf, and H. I. Schiff, Planetary Space Sci. 13, 823

⁽¹⁹⁶⁵⁾

⁸ E. E. Ferguson, F. C. Fehsenfeld, P. D. Goldan, and A. L. Schmeltekopf, J. Geophys. Res. 70, 4323 (1965).

⁹ E. E. Muschlitz and M. J. Weiss, Atomic Collision Processes

 ⁽North-Holland Publishing Co., Amsterdam, 1964), p. 1073.
 ¹⁰ C. B. Collins, W. W. Robertson, E. E. Ferguson, and F. A. Matsen, J. Am. Chem. Soc. 84, 676 (1962).

TABLE I. Measured rate constants.

	Reaction	Rate constant (cm³/sec) at 300°K
$\overline{\mathrm{N^++CO_2 \rightarrow CO_2^+ + N + 0.75 \ eV}}$		1.3×10-9
$N_2^++CO_2\rightarrow CO_2^++N_2+1.75 \text{ eV}$		0.9×10 ⁻⁹
(a) N ⁺ +CO \rightarrow CO ⁺ +N+0.53 eV		$k_{(a)} + k_{(b)} = 0.9 \times 10^{-9}$
(b)	\rightarrow NO ⁺ +C-0.13 eV	$k_{(a)} > 10k_{(b)}$
$N_2^++CO\rightarrow CO^++N_2+1.57 \text{ eV}$		0.7×10 ⁻⁹

emitted light.⁷ Cermak,¹¹ by retarding potential measurements on the ejected electrons from Reaction (2), has also verified that the N_2^+ is largely produced in the *B* state.

The ion composition of the afterglow is determined by means of a quadrupole mass spectrometer. The decrease in reactant-ion concentration with neutralreactant addition leads to quantitative reaction rate constants.¹⁻³

On the basis of previous analysis,^{1,2} as well as numerous comparisons with reaction rates measured elsewhere, the rate constants are believed reliable to within 30%.

DISCUSSION OF RESULTS

A complete list of the reactions measured is found in Table I. The reactions are unambiguously chargetransfer reactions. The reactions are all quite fast, corresponding to cross sections of ~ 100 Å². There seems to be no correlation between these fast rates and coincidence of electonic energy levels, i.e., electronic energy resonance is not possible without a considerable degree of vibrational excitation in the product molecules.

In the past, it has been usual to predict that reactions requiring an electronic transition (such as charge transfer) will be slow at thermal energies. This has followed from the theoretical result that the cross sections for nonsymmetric resonant electronic transitions approach zero in the zero velocity limit.¹² This in turn is simply an application of the adiabatic principle, which states that transitions between electronic states will not occur when a perturbation is applied sufficiently slowly, in this case the perturbation being the internuclear distance change between the two reactants which comprise the system.

Recent experimental observations, however, show that many thermal energy charge-transfer reactions involving diatomic and larger molecules do occur rapidly at 300°K. Dissociative charge-transfer reactions of atomic helium ions occur with rate constants of about 10^{-9} cm³/sec with O₂, N₂, CO, CO₂, and NO, for example.¹ It is apparent that application of the adiabatic principle in collisions involving molecular species is not as helpful (i.e., predictive) as it has been in the case of atomic collisions.

It is not clear whether the added degrees of freedom for molecules give accidential resonances in many cases, so that the adiabatic region is commonly subthermal, or whether the collision concept needs some altering. In the case of the interaction of an ion and a molecule under the influence of the long-range forces (chargeinduced dipole interaction) the particles spiral about each other in orbits for some time before separating. This spiraling pair may be considered an intermediate reaction complex, and it may be that the exit channels are not sufficiently well determined by the energy levels of the infinitely separated initial reactants to make the consideration of such levels useful in predicting reaction cross sections. It should be pointed out, however, that in the collision of two atomic species, such as He⁺+Ne or He⁺+Ar, intermediate complex formation does not efficiently promote a charge transfer.¹ Moreover, in the molecular case the complex does not result in complete scrambling of the heavy particles in that reaction channels such as

and

$$N_2^+ + O_2 \rightarrow NO^+ + NO$$

$$O_2^+ + N_2 \rightarrow NO^+ + NO$$

involving the breaking of two bonds seem to be effectively closed.

On the basis of thermal energy ion-molecule reaction rates measured to date, it is a better generalization that exothermic charge transfer to molecular species is likely to be fast than slow.

ACKNOWLEDGMENT

This work was supported in part by the Defense Atomic Support Agency.

¹¹ V. Čermák (private communication).

¹² D. R. Bates and N. Lynn, Proc. Roy. Soc. (London) A253, 141 (1959).