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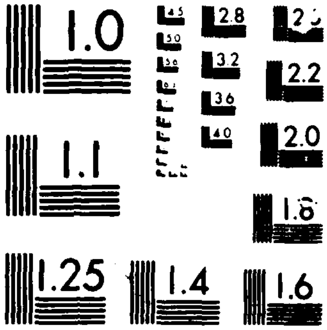
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ATOMIC COLLISIONS AND PLASMA PHYSICS

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Ion-molecule reactions; electron-ion recombination; zirconium ions; three-body association; nitric oxide ions

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Experimental studies have been carried out of ion-molecule reactions and of electron-ion recombination of interest for modelling the normal and disturbed regions of the earth's upper atmosphere. Drift tube and microwave afterglow techniques were employed for these studies. Rates have been determined for the oxidation reactions of zirconium ions, and theoretical models for the temperature dependence of three-body diatomic-ion/diatomic-gas have been developed. The electron temperature dependence of the recombination of NO^+ and O^+ ions has been measured over a wide range of electron temperatures.

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I. Introduction

During the 3-year period of Contract F19628-83-K-0037, we have carried out experimental studies of ion-molecule reactions and electron-ion recombination processes using drift-tube and microwave afterglow techniques.

The studies of ion-molecule reactions focussed on oxidation reactions of metal ions and three-body association of atmospheric diatomic ions. Specifically, we investigated:

a) Reactions of zirconium ions with oxygen, nitric oxide, and carbon dioxide, The details of the measurements and the results of this work are described in an article published in The Journal of Chemical Physics (Appendix I)

b) The dependence on temperature of three-body association of diatomic atmospheric ions with atmospheric gases had been investigated by us in the previous contract period. A theoretical model of the reaction mechanisms underlying the association has been developed and a publication describing this work has been accepted by The Journal of Chemical Physics (Appendix II).

Our experimental studies of electron-ion dissociative recombination involved both simple diatomic ions (NO^+) and clustered species (O_4^+). The principal emphasis was on determining the dependence of the recombination coefficients on electron temperatures via microwave heating of electrons in recombination controlled afterglows. As part of this work extensive computer models of the electron energy loss and gain in afterglow plasmas containing small concentrations of molecular additives (inelastic losses) have been constructed and have been applied in the analysis of the NO^+ and $O_4{}^+$ recombination data. The present measurements and analysis for NO^+ recombination have removed the discrepancy with trapped-ion data and will be submitted to Physical Review A for publication shortly (the abstract is included with this report, see Appendix II).

II. Research published during the grant period

The texts of the following papers appear in the Appendix of this report:

Ion-molecule reactions:

Rate coefficients for the oxidation of zirconium ions with oxygen, nitric oxide, and carbon dioxide. S. Dheandhanoo, B.K. Chatterjee, and R. Johnsen, J. Chem. Phys. 83, 3327 (1985)

Temperature dependence of association of diatomic ions in diatomic gases, R. Johnsen, J. Chem. Phys. xx, xxxx (1986)

III. Research results in preparation for publication:

Electron ion recombination:

Electron temperature dependence of the recombination of electrons with NO^+ ions. J.L. Dulaney, M.A. Biondi, and R. Johnsen. Phys. Rev. A, to be submitted.

Appendix

Text of titles and abstracts of papers published, accepted for publication, or to be submitted shortly in scientific journals during the period of this contract are given on the following pages.

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Rate coefficients for the oxidation reactions of zirconium ions with oxygen, nitric oxide, and carbon dioxide

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(Received 17 May 1985; accepted 20 June 1985)

Rate coefficients for the oxidation reactions of zirconium ions with oxygen, nitric oxide, and carbon dioxide have been determined in the near-thermal energy range (0.04 to about 0.4 eV) using a selected-ion drift apparatus. The reactions are found to proceed with large rate coefficients [$\sim 5(-10)\,\mathrm{cm}^3/\mathrm{s}$ at 300 K]. At elevated ion energies the reactions with NO and CO_2 exhibit smaller rates. The secondary oxidation reactions of ZrO^+ ions with the same reactants have rate coefficients about two orders of magnitude smaller than those for the first oxidation steps. The discharge ion source used to produce the zirconium ions in these experiments is described in some detail.

I. INTRODUCTION

While gas-phase oxidation reactions of metal ions with atmospheric gases are of considerable applied interest, comparatively little experimental results are available. In an earlier series of measurements[1,2] we examined reactions of the type

$$M^+ + O_2 \rightarrow MO^+ + O \tag{1}$$

and

$$MO^+ + O_2 \rightarrow MO_2^+ + O \tag{2}$$

for ions $M^+ = U^+$, Th^+, and Ti^+ and found that the first oxidation step generally occurred with large rate coefficients, while secondary oxidation was usually a slow process. We have extended this work to oxidation reactions of zirconium ions with O_2, CO_2, and NO and present here the measured rate coefficients and their dependence on ion energy in the near-thermal energy range.

The experimental difficulty in such experiments lies primarily with producing the ions, a problem even more severe in the case of the refractory metals. The ion source developed for this work may be applicable to a variety of metals and is described in some detail.

II. EXPERIMENTAL METHODS

The measurements were carried out using a selected ion drift apparatus (SIDA), which except for the Zr^+ ion source had the same configuration as described earlier.[3] The "additional residence time" method[4] employing programmed drift fields to vary the ions' residence time in the drift/reaction region was used to measure the decay of Zr^+ ions in the presence of the reactants, from which the rate coefficients were derived.

It proved difficult to obtain adequate Zr^+ ion currents from ion sources based on the principle of evaporating the metal from heater substrates with subsequent electron impact ionization, a method employed in earlier work.[1,2] In the case of zirconium, such sources were plagued by rapid destruction of the heaters (W wire or indirectly heated tubes of alumina or zirconia were tried) and required too frequent replenishment of the Zr metal samples. A more satisfactory ion source was built in the form of a magnetically confined (Penning) discharge, shown schematically in Fig. 1, which was operated in a mixture of neon and zirconium tetrabromide vapor. It consisted of a cylindrical discharge chamber (5 cm long, 2.5 cm in diameter), formed by a cylindrical, stainless steel anode and two cathode end plates, one containing the ion extraction orifice (0.25 cm in diameter). Mica gaskets served to insulate and seal the anode and cathodes with respect to each other. A permanent magnet surrounding the anode provided the axial magnetic field.

Approximately 1 g of $ZrBr_4$ powder was placed into the discharge chamber and evaporated during operation of the source by heating the entire source assembly to about 160 °C. To obtain a stable discharge, neon gas was passed through the source at pressures of 0.1 Torr and the discharge current was adjusted to typically 0.5 to 1.0 mA. After about 100 h of operation the $ZrBr_4$ supply was exhausted and had to be replenished.

In addition to Zr^+ ions the source produced large ion currents of Ne^+ and Br^+, which were prevented from entering the drift region of the apparatus by the ion-selecting mass

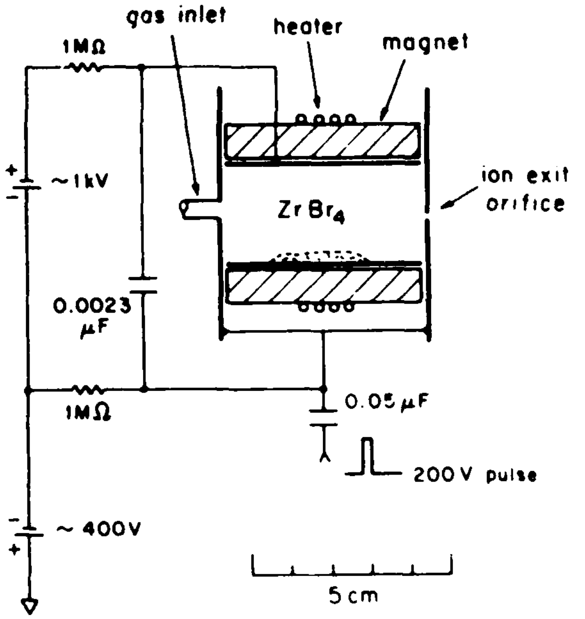

FIG 1 Schematic diagram of the zirconium ion discharge source

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filter. For the measurements pulsed operation of the source was desired. Since it was found to be impractical to achieve pulsing of the discharge by switching the high-voltage supply, the source was dc biased such as to cut off the Zr^+ ion current entering the drift tube. Application of a short ($10\,\mu s$ long) 200 V pulse to the bias network then produced pulsed injection of ions into the drift tube.

III. EXPERIMENTS AND RESULTS

Zirconium ions from the ion source were injected into the drift tube containing typically 0.5 Torr of helium buffer with small admixtures of the reactants O_2, NO, or CO_2 (about 10^{-4} Torr). The ions transmitted through the drift tube were found to consist largely of the Zr^+ parent ions and the ZrO^+ products produced by the reactions:

$$Zr^+ + O_2 \rightarrow ZrO^+ + O, \quad (3)$$

$$Zr^+ + NO \rightarrow ZrO^+ + N, \quad (4)$$

and

$$Zr^+ + CO_2 \rightarrow ZrO^+ + CO. \quad (5)$$

As several minor impurity ions were present in the mass range of interest, the isotopic abundances of both parent and product ions were examined carefully to prevent incorrect identification of the ion species. At higher reactant concentrations, further oxidation of ZrO^+ ions led to the appearance of ZrO_2^+ ions in the mass spectrum.

After having established that the oxidation reactions constituted the dominant loss mechanism of Zr^+ ions, the rate of loss of Zr^+ ions was determined using the additional residence time techniques at several values of the field-to-density ratios E/N, which controls the Zr^+ ions' mean energy. The well known expression given by Wannier[5] was used to infer the mean ion energy from the measured Zr^+ drift velocities. The energy scale shown in the Figs. 2 through 4 corresponds to this energy converted to the Zr^+/reactant center-of-mass system of reference.

The measured rate coefficients for reactions (3), (4), and (5) are shown in Figs. 2 through 4 as function of the Zr^+ center-of-mass energy. The thermal energy (0.04 eV) rate coefficients are close to the limiting Langevin rate coefficients in all three cases, but only the reaction with oxygen exhibits an energy independent coefficient over the energy range covered by the experiments. Fast ion molecule reactions exhibiting rate coefficients near the Langevin limit usually show little or no dependence on ion energy. The reactions of zirconium ions with NO and CO_2 appear to be an exception to this rule, which is somewhat surprising. It is possible that these reactions proceed through an intermediate reaction complex, whose lifetime decreases with increasing ion energy leading to a reduced rate coefficient at higher energies.

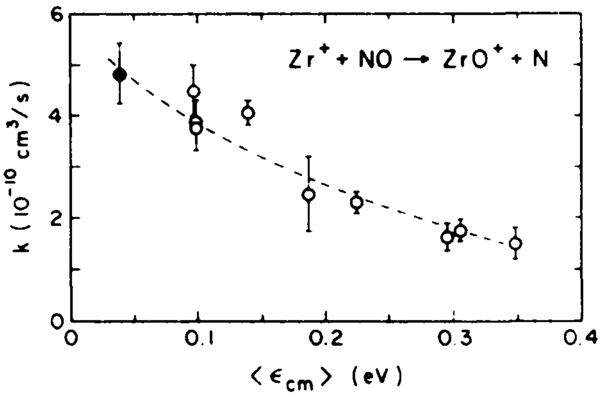

FIG. 3. Measured rate coefficients for the reaction of zirconium ions with nitric oxide as a function of the mean ion energy. Data point at 0.04 eV represents an average of many measurements.

The binding energy of ZrO^+ apparently is not known from other measurements, such that it is difficult to determine the exoergicities for reactions (3), (4), and (5). The occurrence of reaction (4) indicates that the binding energy of ZrO^+ is greater than that of nitric oxide (6.54 eV).[6] The isoelectronic molecule yttrium oxide has a binding energy of 7.02 eV.[6] Thus a similarly large binding energy for ZrO^+ seems plausible.

Secondary oxidation reactions of ZrO^+ ions with O_2, NO, and CO_2 were observed to occur but with rate coefficients two to three orders of magnitude smaller than those

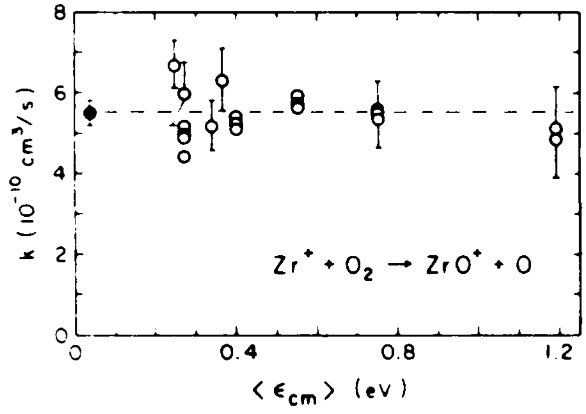

FIG. 2. Measured rate coefficients for the reaction of zirconium ions with oxygen as a function of the mean ion energy. Data point at 0.04 eV represents an average of many measurements.

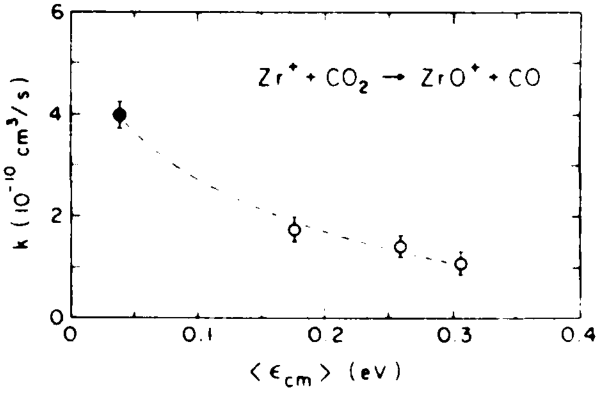

FIG. 4. Measured rate coefficients for the reaction of zirconium ions with carbon dioxide as a function of the mean ion energy. Data point at 0.04 eV represents an average of many measurements.

for the first oxidation steps. Since it was found difficult to obtain experimental conditions suitable for accurate determinations of the secondary rate coefficients only approximate rate coefficients were derived from the observed abundance of the secondary product ZrO_2^+ in the ion mass spectrum.

For the reaction

$$ZrO^+ + O_2 \rightarrow ZrO_2^+ + O \qquad (6)$$

a thermal-energy (300 K) rate coefficient of $(5^{+5}_{-2.5}) \times 10^{-12}$ cm^3/s would be required to explain the observed ZrO_2^+ abundance. Corresponding estimates for the reactions

$$ZrO^+ + NO \rightarrow ZrO_2^+ + N \qquad (7)$$

and

$$ZrO^+ + CO_2 \rightarrow ZrO_2^+ + CO \qquad (8)$$

yielded values of $k(7) = (2.5^{+2.5}_{-1.25}) \times 10^{-12}$ cm^3/s and $k(8) = (1^{+1}_{-0.5}) \times 10^{-12}$ cm^3/s. While the energy dependence of these reactions was not studied systematically, the few measurements that were made indicated that the rate coefficients are likely to decrease with increasing ion energy.

IV. SUMMARY AND CONCLUSIONS

The measurements confirm the expectation that oxidation reactions of zirconium ions with O_2, NO, and CO_2 should be rapid processes with rate coefficients close to the limiting Langevin value. The energy dependence of the reactions with NO and CO_2 appears to indicate that these reactions proceed through an intermediate reaction complex rather than by a direct mechanism.

Secondary oxidation reactions of ZrO^+ proceed with very small rate coefficients and hence may not be important in applications.

ACKNOWLEDGMENT

This work was supported, in part, by Air Force Cambridge/DNA under Grant No. F19628-83-K-0036.

[1] R. Johnsen and M. A. Biondi, J. Chem. Phys. 57, 1975 (1972).
[2] R. Johnsen, F. R. Castell, and M. A. Biondi, J. Chem. Phys. 61, 5404 (1974).
[3] R. Johnsen, Phys. Rev. A 28, 1460 (1983).
[4] J. Heimerl, R. Johnsen, and M. A. Biondi, J. Chem. Phys. 51, 5041 (1969).
[5] G. H. Wannier, Bell Syst. Tech. J. 32, 170 (1953).
[6] *Handbook of Chemistry and Physics*, 54th ed. (Chemical Rubber, Cleveland, 1973/74), p. F-201.

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Temperature dependence of association of diatomic ions in diatomic gases

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(Received 18 April 1986; accepted 24 June 1986)

The temperature dependence of experimental rate coefficients for association of diatomic ions in diatomic gases is compared to model calculations in which the stabilization of the initially formed unstable association complex is assumed to occur by formation of a "super complex." It is shown that acceptable agreement between the model and experimental data on four sample reactions can be obtained with a minimum of plausible assumptions. The agreement indicates that earlier theoretical models may provide an accurate description of the formation and destruction of the association complex, but failed to reproduce the experimental data, because the temperature dependence of the stabilization step was inadequately treated.

I. INTRODUCTION

The association of ions in gases, that is a process of the type

$$A^+ + B + M \rightarrow AB^+ + M \tag{1}$$

has been the subject of many experimental and theoretical investigations, but the problem of reconciling theoretical and experimental results still persists, especially in regard to the dependence of the association rate coefficients on temperature. In one of his many contributions to the theory of ion association, Bates[1] referred to the problem as an "enigma," since it is difficult to identify faults in either the statistical theories of the association mechanism or the experimental data.

Most treatments of the problem[1-9] have focused on the first step in the association mechanism, formation and decay of the intermediate unstable complex. The second, stabilization step is either assumed to proceed with a temperature independent rate coefficient or an essentially *ad hoc* temperature dependence is assigned to the stabilization step in order to obtain agreement of theory with experimental data, a clearly unsatisfactory procedure. In this paper it is suggested that the stabilization of the reaction complex proceeds through a second intermediate complex, called the super complex. It is shown that such a model leads naturally to a strongly temperature dependent complex stabilization and that is capable of reproducing experimental data for diatomic ion association in diatomic gases with acceptable accuracy. The basic steps in the association mechanism are reviewed in order to clarify terms and to state the assumptions on which it is based:

The rate at which the ions A^+ are converted to the associated ions AB^+ is thought to be limited by two distinct mechanisms, formation of an intermediate unstable complex and subsequent collisional stabilization. If either or both A and B are molecular species (we exclude the special case where both are atomic) a fraction of the energy liberated in a collision of A^+ with B may be temporarily absorbed by internal modes of the AB^+ collision complex, i.e.,

$$A^+ + B \rightarrow (AB^+)^{**}, \tag{2}$$

where the symbol ** indicates that the complex has sufficient energy to redissociate into the initial particles:

$$(AB^+)^{**} \rightarrow A^+ + B. \tag{3}$$

The internal dynamics of the highly excited complex is expected to be quite different from that of the corresponding ground state molecule and it is not obvious that a definite geometric structure should be assigned to the complex. Rapid exchange of energy among internal rotations and vibrations will lead to highly irregular motions in the potential well, which one cannot hope to describe in detail. Whether or not the assumption of complete randomness ("chaos") is valid for a particular complex, is a subject of much current debate, but we are here only concerned with the statistical properties of ensembles of such complexes, not the dynamics of a particular complex. If it is assumed that both A^+ and B are members of thermally equilibrated ensembles of particles at a common temperature T and that the unstable reaction complex has no modes of decay in addition to redissociation (e.g., ion–molecule reactions or radiative stabilization), reactions (2) and (3) will lead to equilibrium populations

$$[(AB^+)^{**}]/[A^+] = [B]k(2)/\Gamma, \tag{4}$$

where the square brackets denote concentrations, $k(2)$ is the bimolecular rate coefficient of reaction (2), and Γ the decay rate of an ensemble of unstable complexes [reaction (3)] in thermal equilibrium. The definition of Γ requires some explanation: If, in a hypothetical experiment, after the equilibrium between reactions (2) and (3) have been attained, reaction (2) is made to stop by some means at time t_0, the density $n(t)$ of unstable complexes will initially decay as

$$\frac{dn(t)}{dt} = -\Gamma n(t) \quad \text{at } t = t_0, \tag{5}$$

which defines Γ at $t = t_0$ only, but Γ itself may depend on time, since, for instance, complexes with large total energy may decay first. Thus, the solution of Eq. (5) is not necessarily an exponential function and it is not permissible to identify the reciprocal of Γ,

$$\tau = \Gamma^{-1} \tag{6}$$

with the average lifetime of the ensemble of complexes. The properly defined average lifetime is given by

$$\langle \tau \rangle = \int_{t_0}^{\infty} t \left[\frac{dn(t)}{dt} \right] \frac{dt}{n(t_0)} \tag{7}$$

and may differ greatly from Γ^{-1} or may even be infinite. This formal point has been made earlier.[3] There is nothing wrong with identifying Γ as a reciprocal lifetime in qualita-

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tive discussions, but erroneous conclusions may be drawn, for instance, if one inserts τ as defined by Eq. (6) into equations or inequalities which compare it for instance, to other characteristic times, such as the poorly defined "randomization time" of a particular complex. The time available for accessing specific states of a particular complex may be terminated by collisions (see below) that eliminate it from the ensemble but not by the faster decay of other complexes. The confusion arises only if one fails to distinguish carefully the fate of particular complexes from that of the ensemble to which they belong. In general, the equilibrium of reactions (2) and (3) will be slightly perturbed by stabilizing, energy-transfer collisions of the complex with the ambient gas M,

$$(AB^+)^{**} + M \to (AB^+)^* + M, \tag{8}$$

where the single asterisk is meant to indicate that the AB^+ ion may still be in an excited state but has insufficient energy to dissociate. Reaction (8) is meant to describe the net effect of energy removing collisions including possible collisional reexcitation of highly excited but stable ions to states above the dissociation limit. It does not necessarily represent a single atomic collision process and no elementary cross section should be assigned to it. The experimental data on the density dependence of three-body association indicate that it is valid to represent the stabilization by an effective bimolecular rate coefficient in the low-pressure limit, but they yield little information concerning its magnitude or dependence on temperature.

The low-pressure limit of three-body association is defined by the condition

$$k(8)[M] \ll \Gamma, \tag{9}$$

which is equivalent to the assumption that the equilibrium of reactions (2) and (3) is only negligibly perturbed by stabilizing collisions. In the low-pressure limit the overall rate coefficient for three-body association k may then be written as

$$k = K(T)k(8), \tag{10}$$

where

$$K(T) = k(2)/\Gamma \tag{11}$$

is the temperature-dependent equilibrium constant for reactions (2) and (3). Inequality (9) also implies that the energy distribution of the unstable complexes is only negligibly perturbed by the stabilizing collisions. At higher densities of M, but not in the low-pressure limit, this approximation may become invalid and $k(8)$ will no longer be independent of gas density, i.e., it is not a proper rate coefficient. It is for this reason that it is not entirely correct to extend Eq. (10) to higher gas densities in the form

$$k = K(T)k(8)\Gamma/(\Gamma + k(8)[M]), \tag{12}$$

as is sometimes done.

In order to compare the low-pressure rate coefficient calculated from Eq. (10) with experimental data, it is necessary to obtain the factors $K(T)$ and $k(8)$. Several authors have calculated $K(T)$ by methods based on phase space theory, RRKM theory, or extensions of this approach.[1-9] Of particular interest is the temperature dependence of $K(T)$, for which the following useful "rule of thumb" has been derived (see Ref. 3, Eq. 43). $K(T)$ depends on T in the form

$$K(T) = K(T_0)(T/T_0)^{-x}, \tag{13}$$

where

$$x = \Sigma R_i/2, \tag{14}$$

and R_i represent the rotational degrees of freedom in the reactants A^+ and B. If A and B are diatomic $x = 2$, for instance. Vibrational degrees of freedom may be neglected so long as the vibrational spacing in the reactants is small compared to thermal energy. The simple rule has a simple interpretation. The decay rate Γ is proportional to the product of the internal partition functions of its decay products. Each rotational degree of freedom contributes a factor $T^{1/2}$ to the dependence of Γ on T.

If one assumes that the rate constant for stabilization $k(8)$ is independent on T, it follows at once that k should depend on T as

$$k = k(T_0)(T/T_0)^{-x} \tag{15}$$

in the case of diatomic reactants $x = 2$. As will be seen later, this simple prediction is supported by experimental data only for some but not all reactions. One often finds that the observed dependence on T is stronger than that given by Eq. (15), and it has been common practice to replace x by $x + \delta$ in that equation. The additional $T^{-\delta}$ dependence is sometimes ascribed to the variation of $k(8)$ with T. The practice is not only an unsatisfactory, *ad hoc* addition to theory, but it is also clear that the functional form of the T dependence of $k(8)$ cannot be correct at all temperatures. The Langevin collision rate constant should be an upper bound for $k(8)$, which would be exceeded if the $T^{-\delta}$ dependence remained valid at low temperatures.

II. COMPARISON OF EXPERIMENTAL DATA AND THEORY

The set of reactions chosen for comparing theory and experiment involves diatomic ions and diatomic neutrals. The specific reactions are:

$$N_2^+ + N_2 + N_2 \to N_4^+ + N_2, \tag{16}$$

$$O_2^+ + O_2 + O_2 \to O_4^+ + O_2, \tag{17}$$

$$O_2^+ + N_2 + N_2 \to O_2^+N_2 + N_2, \tag{18}$$

$$NO^+ + N_2 + N_2 \to NO^+N_2 + N_2. \tag{19}$$

All four reactions involve reactants of similar molecular constants, but the stability of the clustered ions decreases from about 1 eV for the first reaction to about 0.2 eV for the last one. Much of the relevant information has been compiled in Table I which also contains references to the published data and power-law fits to the experimental results. Reaction (16) has been measured by many authors in addition to the referenced data. The results are in acceptable agreement (on the order of 30% deviations over the temperature ranges covered) and the temperature exponents range from 1.7 to 2.14.

The rate coefficient of reaction (17) was once believed[11] to exhibit a peculiar maximum at low temperatures. Later experimental data[12] did not show this maximum and Ferguson[21] has pointed out that such a behavior should never be

TABLE I For reactions (16)–(19) (numbered as in Sec. II), the table lists experimental values for the three-body rate coefficients ay 300 K, the exponents x assuming a power-law temperature dependence $k(T) \propto (T/300)^{-x}$, and references to the experimental data. The last two columms give the measured bond energies in eV of the product cluster ions, and references.

Reaction	k(300 K) (cm^6/s)	x	Ref	E_b (eV)	Ref
16	5×10^{-29}	2.14	10	1.0	14
17	4×10^{-30}	2.93	11	0.42	15
18	1×10^{-30}	3.2	10	0.22	16
19	3×10^{-31}	4.4	10	0.18	13

observed. There are few measurements of the remaining two reactions, but one might add that a strong temperature dependence of reaction (19) $(x \simeq 5)$ has also been inferred from ionospheric data.[22]

As is clear from Table I, except in one case the observed values of x differ from $x = 2$, the value expected from the above mentioned rule of thumb. Recently, two attempts have been made to rationalize this departure from simple expectation. Bates,[1] in an attempt to explain the T dependence of reaction (17), made the tentative suggestion that the internal states of the O_4^+ unstable complex might not be fully "randomized" at the higher temperatures. Although his estimates of the additional T dependence due to this effect appeared plausible, he later[2] withdrew his suggestions as untenable in the low-pressure limit of the reaction. His later position is correct. As discussed in Sec. I, departures from a thermal equilibrium distributions in the complex cannot be invoked in the low-pressure limit. In his later paper,[2] Bates also suggested a different reason why some vibrational states in the complex may not be excited at all temperatures, but without detailed further calculations it is difficult to estimate the magnitude of the effect. In one of his earlier papers Bates[5] calculated partition functions for the O_4^+ complex (see Table I in his paper) assuming either absence or presence of vibrational excitation of the constituent molecules. The difference between the two cases was found to be only about 25%, which makes it somewhat unlikely that much additional temperature dependence can arise from vibrational excitation.

Patrick and Golden[6] presented theoretical calculations for reactions (16), (17), and (18) which predicted a T^{-2} dependence for all three reactions. In the case of reaction (18) those authors compared their results only to a subset of the experimental data of Dheandhanoo and Johnsen[10] quoted by Speller *et al.*[20] Even over the limited range of temperatures where the comparison was made, the deviation of the data from a T^{-2} dependence is quite obvious. Since Patrick and Golden's results for reaction (16) gave rate constants considerably higher than the experimental data by Bohringer and Arnold[11] the authors suggested that the experimental data might not have been obtained in the low-pressure limit. Using the expression in Eq. (12), they show that their theoretical results can be made to agree with the experimental data, if the gas pressure in the experiment was on the order of 3 Torr at $T \simeq 65$ K. Although the experimentalists did not clearly state the gas pressures used it is most unlikely that they employed such high pressure at low temperatures: From the figures given in their paper,[11] one can reconstruct the conditions of the experiment and finds that the pressures used at the lowest temperatures must have been less than 0.1 Torr. To give a simpler argument: If the experimentalists had employed a gas pressure of 3 Torr, the reaction would have gone to completion in a time on the order of several nanoseconds, which is orders of magnitude shorter than practical for the experimental method used. Thus, Patrick and Golden's reinterpretation of the experimental data is not convincing.

In the following section, the disagreement between experiment and theory is seen as resulting from the temperature dependence of the complex stabilization rather than from deficiencies in the calculations of $V(T)$.

III. STABILIZATION VIA FORMATION OF A SUPER COMPLEX

Since the temperature dependence of $V(T)$ [Eqs. (13) and (14)] seems to be well established theoretically, the source of the discrepancies between theory and experiment may be found in the temperature dependence of the stabilization step [Eq. (8)]. The detailed mechanism of energy removal from the initially formed unstable complexes is likely to be complicated and possibly involves several collisions with background gas molecules. One may hope that the net effect of the energy exchanging collisions can be described phenomenologically by assuming the existence of super complexes consisting of the unstable complex and an additional third-body molecule. The idea is not new: Herbst[23] applied it to several reactions in which helium was the third body and showed that this model leads to a temperature dependent stabilization efficiency. Formation of super complexes with molecular third bodies, the case of interest here, should be far more likely than with weakly interacting rare gas atoms, such as helium. After all, the existence of stable, higher-order aggregate ions with nitrogen is known from experiments,[20] but one rarely observes ions clustered to helium. The super complexes are assumed to be formed in the reaction

$$(AB^+)^{**} + M \rightarrow (ABM^+)^{**} \tag{20}$$

and to possess two modes of decay, redissociation into the unstable first complex and M:

$$(ABM^+)^{**} \rightarrow (AB^+)^{**} + M \tag{21}$$

or dissociation into a stable $(AB^+)^*$ molecule and M

$$(ABM^+)^{**} \rightarrow (AB^+)^* + M. \tag{22}$$

If we denote the bimolecular rate coefficient of Eq. (20) by k_L and the unimolecular rates of Eqs. (21) and (22) by Γ and Γ, respectively, the overall rate of stabilization k of the first complexes is given by

$$k = k_L(\Gamma/\Gamma)/(1 + \Gamma/\Gamma) \tag{23}$$

In the limit where $(\Gamma/\Gamma) \gg 1$ a dependence of this ratio on temperature will have little effect on k, but in the general case one would have to make assumptions concerning its variation with temperature. Here, we are interested in the temperature dependence of the ratio of two decay modes and

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it seems plausible to assume a temperature dependence of the form

$$(\Gamma_+/\Gamma_-) = (T_c/T)^{-y}. \qquad (24)$$

where T_c is an adjustable parameter to be found by comparison with experimental data and is that temperature for which $k_- = 0.5\,k_L$, i.e., one-half of all collisions result in stabilization. The choice of the exponent y is not obvious. As an estimate one might take y as equal to one-half of the difference of the rotational degrees of freedom of the decay products in reactions (21) and (22). Assuming that free internal rotations are present in the unstable complex but not in the stable molecule and that the latter has a linear structure one obtains $y = 2.5$ and this choice was adopted.

In order to learn if such a model could reproduce the experimental data, three-body rate coefficients were calculated using Eq. (8) and taking $k(8) = k_-$ as defined by Eqs. (23) and (24). The values of $V(T)$ at $T = 300$ K were obtained by interpolating those given by Bates,[5] who numerically calculated absolute values for a number of assumed potential well depths of the product ions assuming free internal rotations in the complex. Adjustments for different rotational and vibrational constants were made using the interpolation table given by Bates[5] and molecular constants from Herzberg[24] and Albritton *et al.*[25] (for NO$^+$).

The Langevin (induced dipole) rate was used for k_L in Eq. (23) taking molecular polarizabilities from the table given by McDaniel and Mason.[26] The exponent y was taken to have a value of 2.5 for all reactions such that T_c remained as the only parameter that depended on the specific reaction.

The results of the model calculations are compared to the experimental data in Figs. 1 to 4. In all cases values of T_c could be chosen such that the calculated values of the three-body rate coefficients agree quite well with the experimental data. The model calculations shown in the figures have the functional forms:

$$k(T) = k(300)\,(300/T)^2\,[1 + (T/T_c)^{2.5}] \qquad (25)$$

with the following parameters:

Reaction (16), $k(300) = 4.6\times10^{-29}$ cm^6/s, $T_c = 1000$ K;
reaction (17), $k(300) = 1.5\times10^{-29}$ cm^6/s, $T_c = 200$ K;
reaction (18), $k(300) = 5.3\times10^{-30}$ cm^6/s, $T_c = 150$ K;
reaction (19), $k(300) = 4.0\times10^{-30}$ cm^6/s, $T_c = 120$ K.

A noticeable deviation from a simple power law ("curvature" in log–log plots of k vs T) is present in the case of reaction (2) (see Fig. 2). The low-temperature data by Rowe *et al.*[12] and Bohringer and Arnold[11] seem to yield a weaker temperature dependence at lower temperatures, but

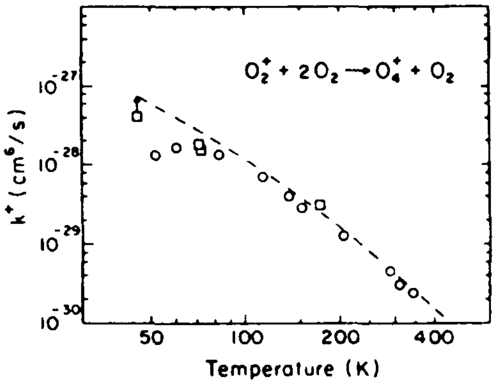

FIG. 2. Rate coefficient for reaction (17) as a function of gas temperature. Open circles: data from Ref. 11. Squares: data from Ref. 12. Dashed line: model calculation.

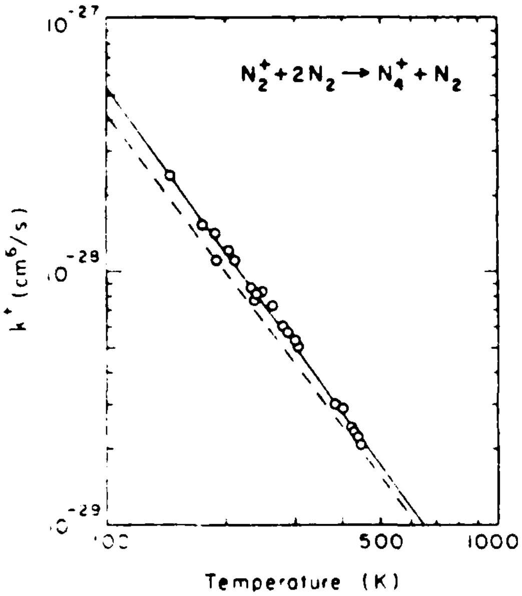

FIG. 1. Rate coefficient for reaction (16) as a function of temperature. Open circles: experimental data from Ref. 10. Dashed line: model calculation.

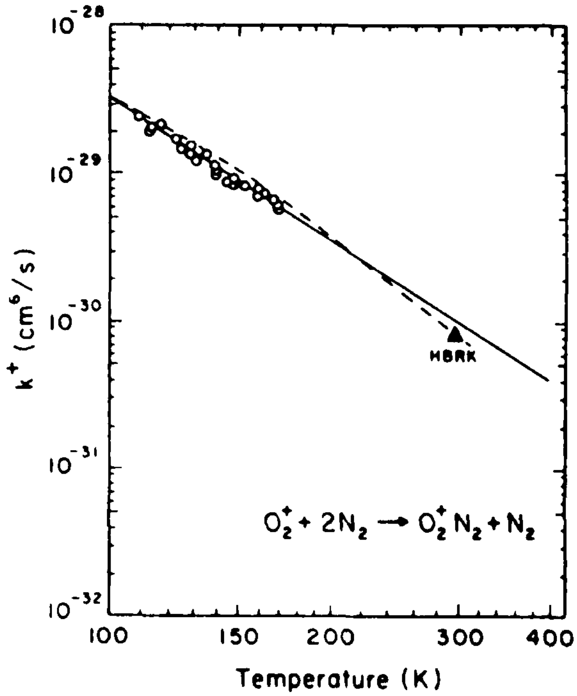

FIG. 3. Rate coefficient for reaction (18) as a function of temperature. Circles: data from Ref. 10. Data point labeled HBRK from Ref. 17. Dashed line: model calculation.

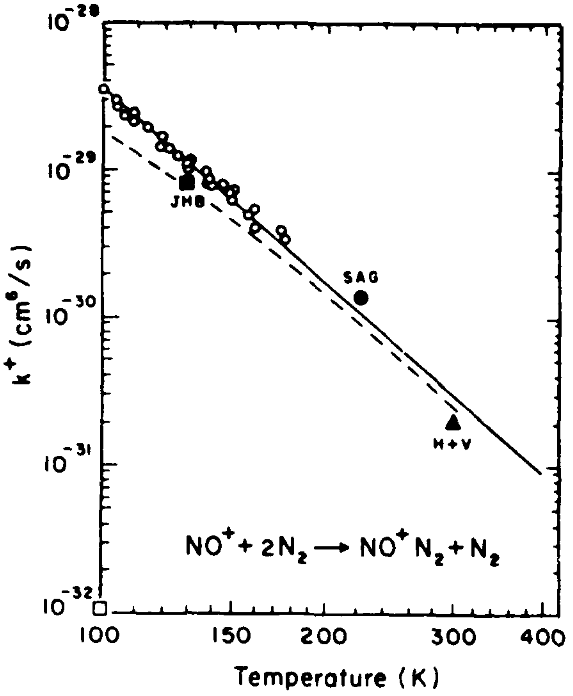

FIG. 4. Rate coefficient for reaction (19) as a function of temperature. Open circles: data from Ref. 10. Points labeled JHB, SAG, and H + V are from Refs. 13, 19, and 18, respectively. Dashed line: model calculations.

unfortunately the experimental data are not sufficiently accurate to permit the statement that the model calculations "explain" this departure from a power law.

It is, of course, not surprising that one can reproduce the experimental data at one temperature by choosing a particular value of T_c, but it seems remarkable that one choice of this parameter yields both an acceptable fit to the absolute value of the rate coefficient and the temperature dependence. The fraction [see Eq. (23)]

$$\beta = (\Gamma^*/\Gamma\quad)/(1 + \Gamma^*/\Gamma\quad), \qquad (26)$$

which may be identified with the usual "complex stabilization efficiency," is near unity for reaction (16) ($\beta = 0.95$) at 300 K, but assumes small values ($\beta = 0.27$, 0.15, and 0.06) for reactions (17), (18), and (19), respectively, at 300 K. As one might have expected, the efficiency of complex stabilization strongly decreases with decreasing stability of the product ion. At very low temperatures β approaches unity for all reactions and the three-body association rates should then vary as T^{-2}. This model prediction still awaits experimental testing.

IV. SUMMARY AND CONCLUSIONS

It has been shown that the measured temperature dependence of several three-body association reactions can be reproduced by modeling the complex stabilization as proceeding through a super complex. It is clear that the theory as presented here is essentially semiempirical since critical parameters are derived from experiment, but it is still remarkable that a minimum of plausible assumptions leads to quite acceptable agreement with experimental data.

The model indicates that ion association rate coefficients may not vary in the form of simple power laws over a wide range of temperatures. Specifically, it is likely to be incorrect to extrapolate experimental data to temperatures much below the range covered by the experiment.

Complex stabilization via formation of a supercomplex is likely to be a poorer approximation in cases where the third body is an atom rather than a molecule. This unfortunately includes the case of helium, the buffergas most often used in flow tube measurements of three-body association.

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[1] D. R. Bates, J. Chem. Phys. **81**, 298 (1984).
[2] D. R. Bates, J. Chem. Phys. **83**, 4448 (1985).
[3] D. R. Bates, J. Phys. B **12**, 4135 (1979).
[4] D. R. Bates, J. Chem. Phys. **71**, 2318 (1979).
[5] D. R. Bates, Proc. R. Soc. London Ser. A **360**, 1 (1978).
[6] R. Patrick and D. M. Golden, J. Chem. Phys. **82**, 75 (1985).
[7] P. A. M. Van Koppen, M. F. Jarrold, M. T. Bowers, L. M. Bass, and K. R. Jennings, J. Chem. Phys. **81**, 288 (1984).
[8] E. Herbst, J. Chem. Phys. **70**, 2201 (1979).
[9] E. Herbst, J. Chem. Phys. **72**, 5284 (1980).
[10] S. Dheandhanoo and R. Johnsen, Planet. Space Sci. **31**, 933 (1983).
[11] H. Bohringer and F. Arnold, J. Chem. Phys. **77**, 5541 (1982).
[12] B. R. Rowe, G. Dupeyrat, J. B. Marquette, and P. Gaucherel, J. Chem. Phys. **80**, 4915 (1984).
[13] R. Johnsen, C. M. Huang, and M. A. Biondi, J. Chem. Phys. **163**, 3374 (1975).
[14] H. H. Teng and D. C. Conway, J. Chem. Phys. **50**, 3864 (1969).
[15] J. H. Yang and D. C. Conway, J. Chem. Phys. **40**, 1729 (1967).
[16] G. S. Janik and D. C. Conway, J. Phys. Chem. **71**, 823 (1967).
[17] C. J. Howard, V. M. Bierbaum, H. W. Rundle, and F. Kaufman, J. Chem. Phys. **57**, 3491 (1972).
[18] J. M. Heimerl and J. A. Vanderhoff, J. Chem. Phys. **60**, 4362 (1974).
[19] D. Smith, N. G. Adams, and D. Grief, J. Atmos. Terr. Phys. **39**, 513 (1977).
[20] C. V. Speller, M. Fitaire, and A. M. Pointu, J. Chem. Phys. **79**, 2190 (1982).
[21] E. E. Ferguson, Chem. Phys. Lett. **101**, 141 (1983).
[22] F. Arnold and D. Krankowski, J. Atmos. Terr. Phys. **39**, 625 (1977).
[23] E. Herbst, Chem. Phys. **68**, 323 (1982).
[24] G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand Reinhold, New York, 1950).
[25] D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare, J. Chem. Phys. **71**, 3271 (1979).
[26] E. W. McDaniel and E. A. Mason, *The Mobility and Diffusion of Ions in Gases* (Wiley, New York, 1973).

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The Electron Temperature Dependence of the Recombination of Electrons with NO^+ Ions

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ABSTRACT

The electron-temperature dependence of the dissociative recombination of NO^- ions with electrons has been re-determined using a microwave afterglow/mass spectrometer apparatus employing microwave heating of electrons in an effort to resolve the discrepancy between previous microwave afterglow measurements of the recombination coefficient $\alpha(NO^+)$ at high electron temperatures made by Huang et. al. ($\alpha \sim T_e^{-.37}$) and the trapped-ion results of Walls and Dunn ($\alpha \sim T_e^{-.85}$). It is found that the electron temperature attained by microwave heating in the experiments of Huang et. al. is lower than calculated by them due to neglect of the effect of inelastic collisions of electrons with minority nitric oxide molecules and that the assumption of spatially uniform electron temperatures is not warranted. An improved data analysis technique is described which allows accurate determination of the recombination coefficient at elevated electron temperatures. Using this analysis, the recombination coefficient is found to follow the relation,

$$\alpha(NO^+) = (4.2 \pm .2)x10^{-7} \ (T_e(K)/300)^{-(.75 \pm^{0.16}_{0.08})} \quad cm^3/s \ ,$$

over the electron temperature range, $295K \leq T_e \leq 4500K$, at $T_+ = T_n = 295K$. The afterglow data now support the trapped-ion results of Walls and Dunn.

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