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Exothermic Ion Molecule Reactions^{*}

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Dissociative charge transfer reactions between rare gas He^+ , Ne^+ ions and diatomic N_2 , O_2 , CO , NO molecules have been studied as a function of reactant ion velocity. N^+ , O^+ and C^+ fragment ions are the major reaction products observed in these exothermic reactions. Experimental cross sections and corresponding rate constants for thermal energy ions are in semi-quantitative agreement with the theoretical rates calculated from the long range ion-induced dipole potential. A reversed repeller technique was used to probe the kinetic energy distributions of the ionic reaction products and the experimental (0.2 to 1 eV) distributions so obtained are well correlated with the heats of the respective reactions. The kinetic energies of the product N^+ and O^+ ions were shifted to lower values when $^3\text{He}^+$ was substituted for $^4\text{He}^+$ ions in the NO and O_2 reactions. This shift in product ion kinetic energy rules out accidentally resonant charge transfer processes involving excited product atoms and is consistent with a two body breakup mechanism of transitory HeN^+ and HeO^+ at low reactant ion velocities.

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INTRODUCTION

Strongly exothermic ion-molecule reactions represent a class of chemical processes in which the potential energy surfaces of reactants and products are widely separated. The probability of collision of charged and neutral reactants can be estimated with fair precision from the Langevin microscopic cross section¹ for low kinetic energy reactant ions. The collision probability is then

$$\sigma(g) = \frac{2\pi}{g} \left(\frac{e^2 \alpha}{\mu} \right)^{1/2}$$

where e is the charge and g the relative velocity of the reactant ion, α the polarizability of the neutral molecule and μ the reduced mass of the reacting system. The mechanism of the ion-molecule reaction is in part revealed by a determination of the collision efficiency or the fraction of collisions which produce reaction products. If product and reactant surfaces are inaccessible over the range of impact parameters operative in most collisions, very small reaction cross sections will be observed.² If relatively high collision efficiencies are observed then it is apparent that in spite of the wide separation of surfaces in initial and final states, surface crossings are possible and significant perturbations of the potential energy of the interacting system take place in the collision process.

The He^+ and Ne^+ ion reactions with neutral molecules are generally highly exothermic because of the relatively large energies available in the neutralization of these inert gas ions. Three types of ion-molecule energy transfer processes may be considered.

Process I is a charge transfer which is generally disfavored unless there is an accidental resonance with an excited state of the product diatomic molecule ion AB^+ . In this case if the energy of the excited state exceeds the bond energy in AB^+ and the excited state is not metastable, process I can feed III with the production of excited species or species with excess kinetic energy. However in the mechanism discussed so far all the energy available in neutralization of X^+ is deposited in AB^+ and none is carried off by the neutral X atom (He or Ne in the particular cases to be reported). The above assertion is based on the assumption that resonant charge transfer processes do not take place with significant transfer of kinetic energy.

Process II represents what is normally considered a conventional ion molecule reaction. This reaction can also produce the products of III if there is sufficient energy available to dissociate the XA^+ or XB^+ product ions. The distribution of energy among the reaction products provides important information on the nature of mechanisms operative if atomic ions are formed via II.

The data of interest in the study of exothermic ion-neutral processes are then the cross sections and their velocity dependences, which measures the accessibility of potential energy surfaces, and the kinetic energy distribution in the reaction products. The production of ionized products with non-thermal kinetic energy distributions introduces serious difficulties in the measurement of ion-molecule reaction cross sections via the use of ordinary mass spectrometer techniques. It is assumed in these measurements that ion collection efficiencies for product and reactant ions are identical. This assumption is clearly not valid if products of strongly exothermic processes are formed with relatively large amounts of kinetic energy. On the other hand, if this is the case, retarding potentials in the mass spectrometer ion source can be used to estimate the kinetic

energy distributions and thus illuminate the reaction mechanism.³

It is the purpose of this paper to report the results of a study of exothermic processes with reactant He^+ and Ne^+ ions. A preliminary report⁴ of the reactions of isotopic ^3He and ^4He ions has been published pointing out the bearing of the reaction mechanism involved on an energy transfer process which can account in part for the escape of helium from the earth's atmosphere. Similar processes with Ne^+ and with other diatomic molecules will be presented and their reaction mechanism will be discussed.

EXPERIMENTAL

Experimental measurements reported in this paper were made with a Consolidated Engineering Corporation 1800, 5 inch radius model 21-103, magnetic field, single focusing mass spectrometer. Instrument settings were: 2500 volts ion accelerating voltage, 10 μa electron beam current, 95 volts electron accelerating voltage and -23 to 23 volts applied to the ion repeller electrodes in the ion source chamber. Course magnetic scanning was used to focus the desired mass which was then scanned electrostatically. The various mixtures were prepared in separate sample bulbs to allow complete mixing before injection into the mass spectrometer. The different gases were individually purified and were free from trace impurities at the highest sensitivities used in this work except for the case of O_2 which contained 0.5% N_2 . Phenomenological cross sections Q were obtained from the relation

$$Q = i_s / i_p n l \quad (1)$$

where i_s represents the collected secondary ion current, i_p the collected primary ion current, n the concentration of neutral molecules in the ion source and l the ion path in the source.

The reproducibility of the experimental ion kinetic energy distributions, as measured by the reversed repeller technique, is directly related to the

cleanliness of the mass spectrometer ion source. A small amount of electrostatic charge can be built up on non-conductive films present on the walls of the ion source previously exposed to hydrocarbon gases at moderate pressures and adversely affect the retarded ion currents at reversed repeller voltages below 0.5 volts. Abrasive, sonic and solvent cleaning in that order were used to remove this film and insure good conductive surfaces. The dependence of the thermal energy X^+ or AB^+ ion intensity as a function of reversed repeller voltage was used to monitor the condition of the ion source since the shape and energy cutoff for retarded ion curves of Maxwellian ions are very sensitive to any extraneous surface charges in the mass spectrometer ion source.

DISCUSSION OF RESULTS

Reaction Cross Sections

The mass spectrometric study of cross sections of reactions of He^+ and Ne^+ which produce atomic ionized and neutral products is complicated by interference from ions of identical mass produced by electron impact on the participating diatomic molecule. A similar problem applies to the observation of accidentally resonant charge transfer processes in which metastable excited diatomic ions are produced. If the assumption is made that the collision probability is determined by the Langevin cross section or that this cross section represents a good approximation to the upper limit of the over-all reaction probability, then practically all of the reaction cross section is accounted for by production of atomic ions in the following systems

Evidence for reactions producing HeN^+ , HeC^+ , NeN^+ , NeO^+ ions or complexes of the type HeN_2^+ , HeNO^+ etc. was sought but not obtained. Experimental measurements of reaction cross sections have been obtained from studies of mass spectra of the various diatomic AB molecules as a function of rare gas ion concentration in the mass spectrometer ion source. The intensity of the bimolecular reaction product A^+ is linear with electron beam current. This linear dependence on electron current eliminates from consideration chemionization reactions between long lived excited AB^*-He^* neutral reactions giving rise to A^+ ionized products. Pressure dependent increases in A^+ atomic ion yields which are proportional to rare gas ion concentration show that these atomic ions are being formed by ion-molecule collision processes as well as by electron impact on AB neutral molecules. The A^+ yield in excess of that produced by electron impact has a first order dependence on rare gas ion concentration and a first order dependence on neutral AB concentration in the mass spectrometer ion source. Plots of the ratio of A^+/AB^+ as a function of He^+ or Ne^+ are characteristic of single bimolecular interactions with intercepts corresponding to the electron impact yield of A^+ from AB. Slopes of these plots are used to calculate phenomenological cross sections Q via equation (1). Experimental Q's so derived from these pressure studies are given in Table I for different reactant ion translational energies.

The experimental cross sections presented in Table I are for the channels of reaction indicated in equations (a)-(d) inclusive. The assumption that these channels account for practically all of the ion-molecule processes is supported by mass spectrometric investigations of ion afterglows⁵ in $\text{He}-\text{N}_2$ and $\text{He}-\text{O}_2$ systems. N^+ and O^+ rather than molecular ions N_2^+ and O_2^+ were found to be the major reaction products of thermal velocity He^+ ions with N_2 and O_2 in radiofrequency discharges. Reaction paths (a) and (e) in He^+-O_2 and He^+-N_2

have also been observed as the prominent reactions with somewhat higher kinetic energy reactant ions in tandem mass spectrometer experiments.⁶ Relatively small yields of O^+ were observed from reactions of He^+ with NO and Ne^+ with NO. These yields were approximately 10-15% of the N^+ yields and could not be measured very accurately because of the comparatively large O^+ yields produced in the electron impact ionization of NO. We find an upper limit of $4 \text{ \AA}^2$ for the endothermic He^+-CO interactions producing O^+ . Our experimental cross sections for C^+ formation in this same system overlap with the measurements of Geise and Maier⁷ at their lowest energies; for example at 10 eV they observe a C^+ formation cross section of $6.5 \text{ \AA}^2$ which is confirmed within limits of experimental error by our value of $8.5 \text{ \AA}^2$ for the same process.

Gioumousis and Stevenson¹ in their theoretical treatment of an isolated ion-molecule interaction have shown the phenomenological cross section Q is given by

$$Q = 2\pi(2m_1\alpha e^2/\mu)^{1/2} (1/eE\ell)^{1/2} \quad (2)$$

where m_1 is the mass of the reactant ion; α is the polarizability of the neutral molecule; μ is the reduced mass of the reacting system; E is the electric field in the ion source; and ℓ is the reactant ion path length in the mass spectrometer ion source. In this treatment it was assumed that every collision is effective in producing product ions. For reactant ions having kinetic energies of less than 10 eV, the applicability of expression (2) in the description of dissociative charge transfer reactions can be assessed by reference to Figs. 1-4. In each of these figures the measured phenomenological cross sections, Q , are plotted against the energy ($eE\ell$) of the primary ion at the ion source exit slit whereas the theoretical cross sections calculated from equation (2) are presented as the solid curves. Within the limits of error inherent in our measurements, there

is a semiquantitative agreement between the experimental data and the calculated cross sections, indicating that the probability of electron transfer in these strongly exothermic reactions is close to unity once the reactant particles are brought into close proximity by means of the long range forces.

The rate constant for reaction of thermal velocity ions has been shown to be related to the phenomenological cross sections by the relation

$$k = (eE\ell/2m_1)^{1/2} Q \quad (3)$$

Substitution of equation (2) into (3) yields the expression

$$k = 2\pi e(\alpha/\mu)^{1/2} \quad (4)$$

originally derived by Eyring, Hirschfelder and Taylor⁸ in their examination of the H_3^+ formation in hydrogen ion-molecule interactions. We have calculated the theoretical rate constants for secondary ion production in the dissociative charge transfer reactions (a) to (e) by means of equation (4) from the molecular polarizability and the reduced mass of the system. In Table II the theoretical rates are compared with the experimental rate constants calculated from (3). These experimental rates were evaluated from Q's in the vicinity of 1 eV as determined by the best curve drawn through the experimental points in the low energy region of the respective reactions. As evidenced in this Table there is reasonable agreement between the calculated and experimental rate constants for these dissociative charge transfer reactions.

The agreement of the experimental results obtained in this study with cross sections computed using the G-S model is of particular interest when compared with data collected in resonant or nearly resonant atomic charge transfer processes.^{9,10} These data are in reasonably good agreement with the total cross sections calculated by means of the impact parameter method.¹¹ In the ^{impact parameter} theoretical treatment the probability of finding the active electron on the impinging ion or the "stationary" target atom oscillates between zero

and unity with an average value approximating 0.5 as the particles approach one another in resonant collisions. It is clear that in molecular collision with low velocity ions, if the electron transfer is an exothermic process a point is reached in the collision process where oscillation of the electron between collision partners is quite different from the motion conjectured in the resonant process. The process becomes practically irreversible and the reaction probability is given by the full value of the collision cross section.

Energy Distribution and Reaction Mechanisms

The reactions of He ions with diatomic N_2 and O_2 molecules are of importance in understanding dissociative charge transfer reactions and the more general problem of energy transfer processes in ion-molecule reactions. These two isolated reactions have received a fair amount of attention from another point of view since they bear on the interesting problem of the escape of helium from the ionosphere. Nicolet¹² noted that the rate of photoionization of helium was similar to the estimated rate of helium escape from the earth's gravitational field and conjectured that the process of He ionization and loss were in some way related. Hanson¹³ suggested that downward diffusion of He^+ in the ionosphere to altitudes where O_2 and N_2 are present could result in ion-molecule reaction forming HeO^+ and HeN^+ . Dissociative recombination of these possible reaction products with electrons would then give resultant He atoms sufficient energy to escape from the exosphere. Later experiments¹⁴ have shown that HeO^+ and HeN^+ are not observed as stable products in the He^+-O_2 and He^+-N_2 interactions. Bates and Patterson¹⁵ have suggested that ion-molecule reactions between He^+ and O_2 molecules may form transitory HeO^+ which could undergo a radiative transition to a repulsive state with the formation of energetic He atoms and O^+ ion. From the energy dependence and magnitude of

the cross sections for O^+ production in the 0.1-2 keV energy range,

Fite and co-workers¹⁴ suggested that the collision process is an accidentally resonant dissociative charge transfer. Our measurements of He^+ -AB interactions at much lower energies, Figs. 1-4, are reasonably well described by the ion induced dipole potential, however the details of the different reaction mechanisms are not brought into sharp focus by the cross section measurements. To further experimentally probe the short range chemical forces we have attempted to measure the energy distributions of the product ions in the respective reactions. The upper limits on these product ion translational energy distributions are determined from heats of the respective reactions, but within these limits the detailed reaction mechanism exerts the controlling influence on the kinetic energy distribution of the products. In Table III the different exothermic X^+ -AB reactions are presented with the manifold reaction possibilities ranging from slightly exothermic He^+ - N_2 reactions to the very exothermic He^+ - O_2 interactions. Along with the heats of the respective reactions we have tabulated the kinetic energies of the product N^+ , C^+ , and O^+ ions that would result if the entire heat of reaction were deposited in the internal modes of the respective diatomic molecule ions with the neutral rare gas atom carrying off little or none of the energy of reaction, e.g. an accidentally resonant dissociative charge transfer process. We have also tabulated the other extreme case of an ion-molecule reaction in which all the heat is deposited in a transitory XA^+ collision complex with the neutral B atom carrying off a trivial amount of the reaction heat as kinetic energy. In this latter case the translational energy of the rare gas He atom resulting from two body breakup of transitory HeA^+ would account for most of the heat evolved in reaction providing a large amount of energy is not lost in radiative processes.

We have used a retarding potential technique in the mass spectrometer ion source to examine the kinetic energy distributions of the product ions. With this retarding field only those ions with sufficient kinetic energy can emerge from the ion source and be collected in the normal manner. Fragment ions produced in the electron impact processes in these systems are experimentally found to have more kinetic energy than the corresponding fragment ions resulting from rare gas ion-neutral molecule interactions and forms the bases of separating the two processes. When He is added to a system undergoing ionization and dissociation by electron impact, the shape of the retarded ion curves (plots of analyzed ion intensity vs. retarding voltage) are perturbed most at low retarding voltages. A typical retarded ion curve is shown in Fig. 5 for the N^+ produced via electron impact ionization of pure NO. As He is added to this system an N^+ ion component, above that produced in the electron impact process, is observed below two volts retarding voltage. The second order pressure dependence of this added component is characteristic of single bimolecular encounters between He^+ and NO. We note that the shape of the N^+ component in the pure gas is independent of NO concentration at the highest pressures used in this work and rules out space charge effects as influencing these measurements. A more stringent test of conditions in the ion source is provided in the retarded ion curves of thermal He^+ or AB^+ ions since the shape and energy cutoff of Maxwellian ions are very sensitive to small voltages in the ion source as mentioned in the experimental section of this paper. Before, during and after each experiment on retarded fragment ion curves, the atomic He^+ and AB^+ retarded ion curves were carefully run to check the voltages

in the ion source and it was experimentally found that these voltages were identical with and without added He^+ .

The separation of the secondary N^+ produced in bimolecular ionic from electron impact produced N^+ interactions is a straightforward process and the retarded ion curve so obtained

is presented in Fig. 6 along with the retarded ion curves for atomic ions produced in the various X^+-AB interactions. We first note that the displacement of the different retarded A^+ ion curves towards higher voltages is correlated with the heats of the respective reactions forming products in ground electronic states.

For a critical test of the applicability of the retarded ion curves to ion kinetic energy distributions we consider the repeller dependent velocity discrimination of thermal velocity ions by the ion source exit slit and the effect of a retarding field on this discrimination. Since there is little momentum transfer in the formation of molecular ions via the electron impact process, their initial kinetic energy distributions are those of the Maxwellian neutral gas at 200°C. With a retarding potential in the source the current density in the ion exit slit is

$$j = \left(\frac{2kT}{m}\right)^{1/2} N \int_0^{2\Theta} e^{-\frac{Q}{kT}} \cos\alpha d\alpha \int_{-\infty}^{\infty} e^{-u_z^2} du_z \int_{-\infty}^{\infty} e^{-u_r^2} u_r du_r \quad (5)$$

where T is the temperature of the ion source, m the mass of the ion, N a constant, divided by kT , Q the electric field potential, k the Boltzmann constant, u_x the x component of velocity

$$u_x = v_x (m/2kT)^{1/2} = u_r \cos\alpha \quad (6)$$

α is the angle between u_r and u_x , and Θ is one half the angle from the point of formation of an ion in a symmetrically placed electron beam to the edges of the ion exit slit. For a given retarding potential the ratio of the current density at the ion exit slit to that at zero field is calculated from eq. (5) to be proportional to $e^{-\frac{Q}{kT}}$. The thermal He^+ and AB^+ retarded ion curves such as displayed in Fig. 6 have the predicted shape within experimental error and the correct retarding voltage cutoff. To check the experimental technique for species with higher kinetic energies we chose the D^+ and T^+ ions resulting from 200 eV electron bombardment of HD, D_2 and HT which have rather well known distributions.¹⁶ The shapes of the retarded D^+ and T^+ ion curves have been calculated numerically

under the assumption of an isotropic distribution of ions formed in the fragmentation process. For an ion having a given kinetic energy we first estimate the solid angle subtended by the ion exit slit to the point of ion formation and the reduction of this effective solid angle as a function of the retarding field which gives the calculated retarded ion curves. Although the shape of the retarded ion curves for D^+ and T^+ are not particularly sensitive to the exact shape of the electron impact distributions, the matching of calculated and observed retarded ion curves is best accomplished when average kinetic energies of D^+ from D_2 , D^+ from HD and T^+ from HT are considered to be 8.5 eV, 5 eV and 4 eV respectively. These kinetic energies are in good agreement with previous experimental measurements on the energetic protons from hydrogen.¹⁶ With good agreement between calculated and observed primary ion distributions we next proceeded to the examination of the retarding curves of the secondary ions resulting from ion-molecule interactions. This analysis is somewhat more complicated since the product ions are not formed in a discrete plane between the repeller and exit slit but rather throughout the path of primary ions in the source. The velocity of primary ions formed in the electron beam increases as they proceed towards the repeller with a decreasing probability of velocity dependent collisions along the path of the reactant ion, and a corresponding decrease in secondary ion formation. The relative spatial distributions of secondary ions resulting from ion-molecule reactions can be calculated for differential segments of the ion path since the

energy dependences of these reactions are known from the cross section measurements presented earlier in this paper. If a significant fraction of the heat of an exothermic reaction is deposited as kinetic energy in the products, and velocity distribution is isotropic, then those ions formed with motion directed toward the ion exit slit may escape the retarding field in the source and be detected after mass analysis.¹⁷ The probability of detecting these ions depends on the respective magnitudes of ion kinetic energy, retarding fields and the collection efficiency of the ion source exit slit for ions formed in various volume elements of the source. With the spatial concentration of products previously calculated and assumed isotropic distribution of velocity vectors in the reaction product, we can find the magnitude of product ion velocity required to fit our experimental curves. In Fig. 7 we present the observed O^+ retarded ion curve along with curves calculated for O^+ product ions having a discrete 1.0 or 1.5 volt kinetic energy. Neither of these assumed O^+ energies of the $He^+ + O_2$ reaction appear to fit the data particularly well but rather an assumed O^+ distribution of 90% - 1.0 volt and 10% - 3.0 volt ions provides a better description of the data. We would thus estimate that most of the O^+ ions resulting from He^+-O_2 interactions have approximately one electron volt kinetic energy.

The O^+ product kinetic energy distribution ions are consistent with formation of electronically excited products in which most of the heat of reaction goes into breakup of O_2^+ as outlined in Table III. This experimental data is also consistent with formation of ground state products in which the excess heat evolved in reaction is deposited in the two body breakup of transitory HeO^+ . We note that the formation of this short lived HeO^+ and its consequent dissociation was postulated by Bates and Patterson¹⁵ to explain the loss of He atoms from the ionosphere. We encounter the same situation in the N^+ resulting from He^+-NO interactions where the retarded product ion curves are

ambiguous in defining the electronic states of the products since both the mechanisms in which the heat of reaction is deposited in two body breakup of NO^+ and also the decomposition of HeN^+ resulting in ground electronic state products are compatible with the measured 0.8 eV N^+ kinetic energy distributions. The kinetic energy of C^+ from $\text{He}^+ - \text{CO}$ interactions at thermal velocities support the mechanism in which most of the heat of reaction is carried off via decomposition of HeC^+ . In the case of N^+ arising from $\text{Ne}^+ - \text{NO}$ and $\text{He}^+ - \text{N}_2$ interactions there is insufficient resolution in our experiments to choose between the different reaction mechanisms which would deposit different kinetic energies in the product N ions as outlined in Table III.

In order to provide a more critical test of reaction mechanism we have substituted $^3\text{He}^+$ in place of $^4\text{He}^+$. If the decomposition path in these dissociative reactions is one in which most of the heat of reaction is converted into translational energy in the two body breakup of HeA^+ , then the A^+ kinetic energy will be shifted to somewhat lower kinetic energies with $^3\text{He}^+$. In Fig. 8 the retarded ion curves of O^+ from $^3\text{He}^+ - \text{O}_2$ and $^4\text{He}^+ - \text{O}_2$ interactions are presented. The retarded O^+ ion curve is shifted approximately 20% lower on the voltage scale in the $^3\text{He}^+$ process, tending to favor ion-molecule interactions in which less of the heat of reaction is found in the O^+ product due to energy and momentum conservation in the two body breakup of transitory HeO^+ . These two experiments were run at the same concentration of reactant species in order to eliminate possible extraneous effects in the measurements of the retarded ion curves. Retarded ion curves for the Maxwellian primary ions given in this same figure are indistinguishable which indicates identical conditions experienced by the two isotopic reactant ions in the source. A small difference in cross sections is expected for the $^3\text{He}^+$ and $^4\text{He}^+$ reactions since for the same retarding voltage the ratio of Q's from equation (2) is

$$Q(^3\text{He})/Q(^4\text{He}) = (m_{^3\text{He}}/\mu)^{1/2}/(m_{^4\text{He}}/\mu)^{1/2} = 0.986$$

however no difference in shape of the O^+ retarded ion curves is expected. The observed shift in O^+ kinetic energy is outside the limits of error in these measurements and supports the formation of transitory HeO^+ which decomposes into He and O^+ via two body breakup. The isotopic substitution of $^3\text{He}^+$ for $^4\text{He}^+$ in the He^+ -NO reactions gives the retarded N^+ ion curves presented in Fig. 9. Experimental conditions identical to those of the He^+ - O_2 reactions were maintained and likewise monitored by the Maxwellian ions. We also observe in this reaction a shift in the N^+ product ion curve with ^3He substitution characteristic of the two body breakup mechanism which implies complex formation for thermal velocity He^+ -NO interactions. The shift in energy of the retarded N^+ ion curve is approximately that expected from interactions in which most of the heat of reaction is deposited in the two body breakup of HeN^+ . Figure 9 also presents the retarded N^+ product ion curve for the less energetic He^+ - N_2 reaction. The maximum shift of 0.01 eV (see Table III) that is predicted for two body breakup of HeN^+ in this reaction is not determined because of the limitations in energy resolution in these measurements but the results are consistent with a very small increase in kinetic energy above a Maxwellian distribution in the products of this ion-molecule reaction.

The product ion kinetic energy distributions in the dissociative charge transfer processes of rare gas ion-diatomic molecule reactions at low velocities are consistent with formation of products in ground electronic states. The absolute kinetic energies of the product ions and their shift with isotopic He^+ shows that the electronic energy available in these reactions is converted

into translational energy in reactive collisions. These data support the concept of complex formation at low velocities of reactant partners in which the heat of reaction is deposited in the rare gas ion-neutral atom bond which decomposes in a two body breakup process.

TABLE I

Experimental cross sections $Q(\text{\AA}^2)$ for dissociative charge transfer

interactions as a function of reactant ion energy (eV)

eV	$Q(\text{\AA}^2)$ $\text{He}^+ - \text{N}_2$	$Q(\text{\AA}^2)$ $\text{He}^+ - \text{CO}$	$Q(\text{\AA}^2)$ $\text{He}^+ - \text{NO}$	$Q(\text{\AA}^2)$ $\text{Ne}^+ - \text{NO}$
0.299	85.8	90.1	52.8	98.6
0.419	77.0	76.6	64.0	70.0
0.598	74.6	54.1	66.0	76.9
0.897	54.1	67.2	66.0	79.3
1.196	38.5	38.2	60.7	59.8
2.390	39.2	34.1	36.9	35.9
3.588	31.1	26.1	31.8	30.0
4.780	29.3	27.8	32.9	27.3
5.980	25.8	20.0	33.5	28.8
7.176	26.0	25.6	26.5	25.7
8.372	22.4	19.6	26.0	29.0
9.568	21.3	18.5	27.8	23.4
10.764	18.2	20.0	25.7	24.5
11.960	18.0	16.2	25.6	21.8

TABLE II

Rate Constants for
Dissociative Charge Transfer Reactions

System	$\times 10^9 \frac{K}{\text{cm}^3/\text{molecule}\cdot\text{sec}}$ Theory	$\times 10^9 \frac{K}{\text{cm}^3/\text{molecule}\cdot\text{sec}}$ Experiment
$\text{He}^+ - \text{N}_2$	1.66	1.69
$\text{He}^+ - \text{CO}$	1.75	1.63
$\text{He}^+ - \text{NO}$	1.62	2.07
$\text{Ne}^+ - \text{NO}$	0.88	0.92

T A B L E I I I

Energetics of Exothermic Ion-molecule Reactions

Reactions	Heat of Reaction $\Delta H(\text{eV})$	Kinetic Energy ^a of Product Ion Formed Via		
		two body breakup of (AB^+)	two body breakup of (XA^+)	two body breakup of ($^3\text{He}A^+$)
$\text{He}^+(2\text{S}) + \text{N}_2(\text{X}^1 \Sigma_g^+) \longrightarrow \text{N}^+(^3\text{P}) + \text{N}(^4\text{S}) + \text{He}(^1\text{S})$	-0.28eV	0.14eV	0.06eV	0.05eV
$\text{Ne}^+(2\text{P}) + \text{NO}(\text{X}^2\Pi) \longrightarrow \text{N}^+(^3\text{P}) + \text{O}(^3\text{P}) + \text{Ne}(^1\text{S})$	-0.52	0.28	0.30	---
$\text{He}^+(2\text{S}) + \text{CO}(\text{X}^1 \Sigma^+) \longrightarrow$	$\text{C}^+(^2\text{P}) + \text{O}(^3\text{P}) + \text{He}(^1\text{S})$ $\text{C}^+(^2\text{P}) + \text{O}(^1\text{D}) + \text{He}(^1\text{S})$	1.26 0.14	0.55 0.06	0.39 0.04
$\text{He}^+(2\text{S}) + \text{NO}(\text{X}^2\Pi) \longrightarrow$	$\text{N}^+(^3\text{P}) + \text{O}(^3\text{P}) + \text{He}(^1\text{S})$	1.89	0.79	0.62
	$\text{N}^+(^1\text{D}) + \text{O}(^3\text{P}) + \text{He}(^1\text{S})$	0.87	0.36	0.29
	$\text{N}^+(^3\text{P}) + \text{O}(^1\text{D}) + \text{He}(^1\text{S})$	0.84	0.35	0.28
$\text{He}^+(2\text{S}) + \text{O}_2(^3 \Sigma_g^-) \longrightarrow$	$\text{O}^+(^4\text{S}) + \text{O}(^3\text{P}) + \text{He}(^1\text{S})$	2.93	1.17	0.92
	$\text{O}^+(^4\text{S}) + \text{O}(^1\text{D}) + \text{He}(^1\text{S})$	1.94	0.78	0.61
	$\text{O}^+(^2\text{D}) + \text{O}(^3\text{P}) + \text{He}(^1\text{S})$	1.27	0.51	0.40
	$\text{O}^+(^4\text{S}) + \text{O}(^1\text{S}) + \text{He}(^1\text{S})$	0.83	0.33	0.26
	$\text{O}^+(^2\text{P}) + \text{O}(^3\text{P}) + \text{He}(^1\text{S})$	0.42	0.17	0.13
	$\text{O}^+(^2\text{D}) + \text{O}(^1\text{D}) + \text{He}(^1\text{S})$	0.28	0.11	0.08

^a Calculated under the assumption that the heat of reaction emerges as translational energy in the two body breakup process.

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- Fig. 1. Total cross sections Q (square angstroms) for the reaction $\text{He}^+ + \text{N}_2 \rightarrow \text{N}^+ + \text{N} + \text{He}$ as a function of He^+ translational energy, eEl.
- Fig. 2. Total cross sections Q (square angstroms) for the reaction $\text{He}^+ + \text{CO} \rightarrow \text{C}^+ + \text{O} + \text{He}$ as a function of He^+ translational energy, eEl. The closed and open circles are the cross sections from two separate measurements and are presented to give a representation of the reproducibility of the experimental data.
- Fig. 3. Total cross sections Q (square angstroms) for the reaction $\text{Ne}^+ + \text{NO} \rightarrow \text{N}^+ + \text{N} + \text{Ne}$ as a function of Ne^+ translational energy, eEl.
- Fig. 4. Total cross sections Q (square angstroms) for the reaction $\text{He}^+ + \text{NO} \rightarrow \text{N}^+ + \text{O} + \text{He}$ as a function of He^+ translational energy, eEl.
- Fig. 5. N^+ ion current plotted as a function of retarding voltage. The lower curve is the N^+ produced in the electron impact ionization of NO while the upper curve contains both N^+ produced in the $\text{He}^+ + \text{NO} \rightarrow \text{N}^+$ ion-molecule reaction as well as the N^+ formed via electron bombardment of NO .
- Fig. 6. Normalized ion intensities are plotted as a function of retarding voltage for various atomic ions resulting from ion-molecule reactions.
- Fig. 7. Normalized O^+ ion intensities are plotted as a function of retarding voltage. The calculated retarded ion curves are those obtained by assuming the product O^+ from $\text{He}^+ - \text{O}_2$ interactions is composed

of the following kinetic energy distributions: a) 1.5eV^{ions}, b) 80%-1eV ions and 20%-3eV ions, c) 90% -1eV and 10% 3eV ions. d) 1.0eV ions.

Fig 8. Normalized ion currents are plotted against retarding voltage.

- represents the product O^+ ions from ${}^4\text{He}^+ - \text{C}_2$ interactions,
- represents the O^+ ions resulting from ${}^3\text{He}^+ - \text{O}_2$ interactions,
- ◻ and ◼ represent the Maxwellian ${}^3\text{He}^+$ and ${}^4\text{He}^+$ ions respectively.

Fig. 9. Normalized ion intensities are plotted as a function of retarding voltage. ● represents the N^+ ions resulting from ${}^4\text{He}^+ - \text{NO}$

- interactions, ○ are the N^+ ions resulting from ${}^3\text{He}^+ - \text{NO}$ interactions,
- ◼ are the N^+ ions resulting from ${}^4\text{He}^+ + \text{N}_2 \rightarrow N^+ + N + {}^4\text{He}$ reaction,
- and ◻ are the N^+ ions resulting from the ${}^3\text{He}^+ + \text{N}_2 \rightarrow N^+ + N + {}^3\text{He}$ reactions.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

FIGURE 9