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The Effect of the Vibrational and Translational Energies of Ionic Reactant on the Reaction $C_3H_4^+ + NH_3 \rightarrow C_3H_3 + NH_4^+$

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The effect of the internal and translational energies of ionic reactant on the rates of the reactions $C_3H_4^+ + NH_3 \rightarrow C_3H_3 + NH_4^+$ has been examined by producing the reactant ions from propyne, allene, and cyclopropene by photoionization at various wavelengths. The translational energy was varied by changing the repeller voltage in the ionization chamber. The cross sections for all the reactions decreased with an increase in the internal energy at all the translational energies studied. The results have been explained in terms of the complex mechanism.

The roles played by various forms of reactant energy in bimolecular reactions in the gas phase have been the subject of intensive study in recent years, both experimentally and theoretically.1) In ion-molecule reactions, the effect of the vibrational energies of ionic reactants can be studied rather easily since the primary ions can be prepared in various vibrational states with known distributions. Photoionization is particularly suited for this purpose,2) showing well-defined vibrational structure in the ionization efficiency curves. The distribution of ions among vibrational states can be determined precisely by photoelectron spectroscopy. In a favorable case, ions can be prepared in only one particular vibrational state (and even in a rotational state) selectively by making use of autoionization3,4)

Although many investigations have been performed from both experimental and theoretical viewpoints5) on the proton transfer reactions:

$$\begin{aligned} XH^+ + Y &\rightarrow X + HY^+ \\ YH + X^- &\rightarrow Y^- + XH, \end{aligned} \tag{2}$$

the main interest has centered on the comparison of the measured cross section with those predicted from the classical dipole theory; only a few works have been concerned with the effects of reactant vibration and translation. Chupka and Russell6) studied this exothermic reaction:

$$NH_3^+ + NH_3 \rightarrow NH_2 + NH_4^+, \tag{3}$$

by the use of a high-resolution photoionization technique and found that the cross section decreases as the vibrational energy increases at all the translational energies studied. On the other hand, by the use of a flow-drift tube technique, Lindinger *et al.*7) measured the rate constants of the proton transfer reactions of several ions with NH_3 as a function of the relative kinetic energy. They found that the rate constants are generally in good agreement with those predicted by the ADO (average-dipole-orientation) theory in the thermal energy range.

In the present study, the photoionization technique has been applied to the study of the effects of the translational and internal energies on the probabilities of the proton transfer reactions:

$$C_3H_4^+ + NH_3 \rightarrow C_3H_3 + NH_4^+. \tag{1}$$

As the sources of $C_3H_4^+$, three structural isomers of C_3H_4 (propyne, allene, and cyclopropene) were used. These systems constitute a favorable case for investigating the factors which govern the reaction probability, since, in these systems, the reduced masses and the polarizability and permanent dipole moment of the neutral reactant are identical.

Experimental

The experiments were carried out using a photoionization apparatus which has been described previously in considerable detail.8) Briefly, it consists of a continuum light source, a Seya-Namioka-type vacuum monochromator, an ionization chamber, and a quadrupole mass spectrometer, these being combined together *via* a five-stage differential pumping system. Radiation from a Hinteregger-type hydrogen discharge lamp passed through the monochromator and irradiated the sample gas in the ionization chamber to produce reactant ions. Since the ionization potentials of allene and cyclopropene are 9.61 eV (corresponding to 129.0 nm) and 9.63 eV (corresponding to 128.3 nm) respectively, the radiation of wavelengths shorter than the respective IP, but longer than 121.7 nm (corresponding to the ionization potential of ammonia), produced only $C_3H_4^+$ ions as reactants in the mixture of C_3H_4 and NH_3, thus enabling one to study Reaction 1 by the single-source method. In the case of the propyne–ammonia system, however, the photons which can ionize propyne ($IP = 10.35$ eV) always ionize ammonia in the mixture; thus there is a possibility that the secondary NH_4^+ ions were produced also by Reaction 3. This problem will be discussed in a later section.

Five or more wavelengths were used for each system to produce $C_3H_4^+$ ions in various vibrational states. Pressure studies were carried out at each wavelength, λ then to determine the phenomenological cross section, Q_λ. The results were this analyzed in terms of the "maximum excess internal energy," E, which is given by equation: E = (photon energy) − (ionization potential). The actual internal energy E_i, of the reactant ions produced by irradiation at λ ranges from 0 to E. The effect of the translational energy was studied by changing the ion-exit energy E_t, between 0.5 and 5.6 eV. The ions were detected by means of a pulse-counting technique using a 20-stage electron multiplier. The pressures of the 1 : 1 mixtures of C_3H_4 and NH_3 in the ionization chamber were typically less than 1×10^{-3} Torr, and the resolution width (FWHM) of the ionizing radiation was 0.23 nm.

Commercial pure propyne, allene, and ammonia were used without further purification. The cyclopropene was synthesized from allyl chloride and sodium amide by the method of Closs and Klantz;9) it was then purified by bulb-to-bulb distillation.

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Results and Discussion

General. In all the C_3H_4+NH_3 systems, the $C_3H_4^+$ ions react with C_3H_4 in addition to undergoing Reaction 1. These reactions have been studied by Myher and Harrison[10] in both pure propyne and pure allene. They found that Reactions 4 and 5 are dominant for propyne, while only Reaction 5 is dominant for allene:

$$C_3H_4^+ + C_3H_4 \rightarrow C_3H_5^+ + C_3H_3 \tag{4}$$

$$\rightarrow C_6H_7^+ + H. \tag{5}$$

In the present study, these results have been confirmed in runs with pure propyne and allene; in addition, similar reactions in pure cyclopropene have been examined. In the latter systems, it was found that the reaction

$$C_3H_4^+ + C_3H_4 \rightarrow C_3H_3^+ + C_3H_5, \tag{6}$$

is the dominant one, with the reaction

$$C_3H_4^+ + C_3H_4 \rightarrow C_6H_5^+ + H_2 + H, \tag{7}$$

occuring to a moderate extent and Reactions 4 and 5, to only a minor extent.[11] All these reactions were taken into account in all systems as the loss processes of the reactant $C_3H_4^+$ ion, in obtaining the relative cross sections for Reaction 1. That is, they were calculated by means of the equation

$$Q_j \cdot p_s \cdot d = I_{sj}/(I_p + \sum_i I_{si}),$$

where I_p, I_{si}, p_s, and d are the intensity of the primary ion, the intensity of the secondary ion, the sample pressure, and the distance between the origin of the primary ion and the exit slit respectively.

Internal Energy Dependence. The experimental results for the cyclopropene–ammonia and allene–ammonia systems are shown in Figs. 1 and 2. In these figures, the relative cross sections (Q) at three ion-exit energies are plotted *vs.* the maximum excess internal energy. It may be seen from these figures that the reaction cross section decreases with an increase in the excess energy at all translational energies. This can be explained qualitatively in terms of the complex formation mechanism, as has been done in other reactions.[1,3,6] In the complex mechanism, the decrease in the reaction cross section with an increase in the internal energy can be predicted from the phase space theory of Light[12] if the cross section for complex formation is independent of the internal energy. According to this theory, the collision complex decomposes along all energetically available channels, including the backward reaction, the relative probabilities for the different decomposition channels depending on the energy content of the collision complex. When the vibrational energy of a reactant is low (*e.g.*, when all vibrational modes are in the ground state), only one backward decay channel (forming reactants with all modes in the ground state) would be energetically available for the collision complex. This channel is thermoneutral and would correspond to a very small volume of the phase space, resulting in a negligibly small probability for this channel compared with that for the exothermic forward channels. As the excess energy of the reactant (and, accordingly, the energy content of the complex) increases, the exothermic backward decay channels, *i.e.*, the channels going back to the reactants which have lower vibrational quantum numbers than they had initially, become increasingly available. With complex molecular ions such as those used in the present study, the channels going back to the reactants which are excited in a different mode from the original one also become available at high excess energies. All these channels cause substantial increases in the relative volume of the phase space for the back reaction; thus, the reaction cross section decreases with an increase in the excess energy of the reactant ion.

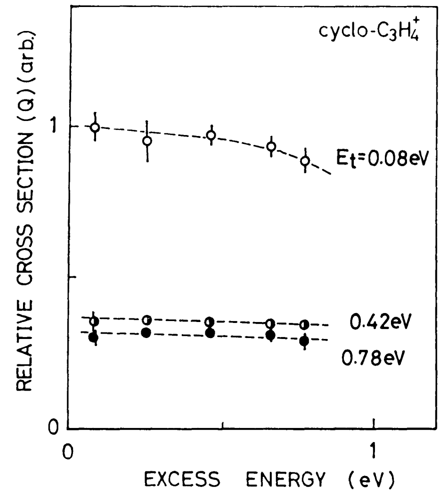

Fig. 1. Dependence of the cross section for the reaction $C_3H_4^+$(cyclopropene) + $NH_3 \rightarrow NH_4^+ + C_3H_3$ on the excess internal energy of $C_3H_4^+$. E_t indicates relative kinetic energies.

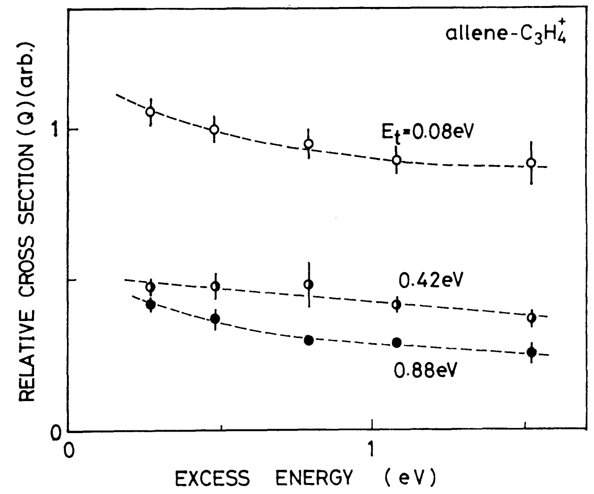

Fig. 2. Dependence of the cross section for the reaction $C_3H_4^+$(allene) + $NH_3 \rightarrow NH_4^+ + C_3H_3$ on the excess internal energy of $C_3H_4^+$. E_t indicates relative kinetic energies.

Recently we have studied the translational and vibrational energy dependence of the cross section for the reaction:[1]

$$NO^+ + i\text{-}C_4H_{10} \rightarrow HNO + C_4H_9^+, \qquad (8)$$

and have concluded that this reaction proceeds *via* complex formation at low translational energies, but the mechanism changes to a stripping type as the ionic translational energy increases. A similar mechanistic change has also been proposed by Chupka *et al.*[3] for the reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H. \qquad (9)$$

These conclusions are based on the different vibrational energy dependence of the cross section at low and high translational energies. In contrast, all the present reactions show the same vibrational energy dependence at all the translational energies studied. The highest relative kinetic energy used here is much higher than the energy at which the mechanism change was observed in the previous system ($NO^+ + C_4H_{10}$). Thus, the above results indicate that the complex formation in the present system persists up to much higher energies than in Reactions 8 and 9. One of the origins of this difference might be the presence of a permanent dipole moment in the neutral reactant, NH_3. Because of the long-range interaction between the charge on the ion and the permanent dipole moment, the collisons in the present system are expected to be more "sticky" than those in Reactions 8 and 9. In this connection, it is to be noted that Reaction 3, which involves NH_3 as a neutral reactant, also shows a single-complex-type behavior at all the energies studied.[6]

Translational Energy Dependences. The translational energy dependences of Reaction 1 for the two $C_3H_4^+$ isomers with NH_3 are shown in Fig. 3. The solid and broken lines indicate the $E^{-1/2}$ and E^{-1} dependences respectively. In the ADO theory, the cross section for reaction between an ion and a polar molecule is given by

$$\sigma = \pi e[(2\alpha)^{1/2}E^{-1/2} + c\mu_D E^{-1}],$$

where E is the collision energy, α and μ_D, the polarizability and permanent dipole moment of the neutral molecule respectively, and c, a parameter characteristic of the neutral reactant. Thus, the cross-sections might be expected to show energy-dependence curves which lie between the solid and broken lines in Fig. 3. However the results were that the cross sections almost obey the $E^{-1/2}$ dependence.

The rate constants for several exothermic proton transfer reactions have recently been studied by Lindinger *et al.*[7] using a flow-drift tube. Their results show that the thermal-energy rate constants were given reasonably well by the Langevin (nonpolar) or the ADO(polar) collision rate constants in most cases. However, the translational-energy dependence of the reaction-rate constants was not that predicted by these theories; *i.e.*, the rate constants of all proton transfer reactions to NH_3, except that for the reaction $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$, decline with the relative kinetic energy less steeply than would be predicted from the ADO theory. These rate constants even show a Langevin-like behavior in a certain kinetic energy region above the thermal region. Thus, although no generalized conclusion can be drawn from this limited number of studies, the $E^{-1/2}$ dependence of the cross section observed in the present study is in line with the general trend observed by Lindinger *et al.* for the proton transfer reactions with NH_3.

Propyne–Ammonia System. In the propyne–ammonia system, the determination of the relative

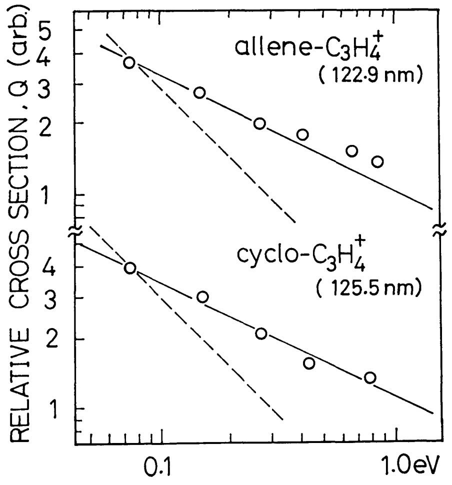

Fig. 3. Kinetic energy dependence of the cross sections for the reactions $C_3H_4^+ + NH_3 \rightarrow NH_4^+ + C_3H_3$. Allene and cyclopropene were ionized to produce $C_3H_4^+$ at 122.9 and 125.5 nm radiation, respectively. Solid and broken lines indicate the $E^{-1/2}$ and E^{-1} dependence, respectively.

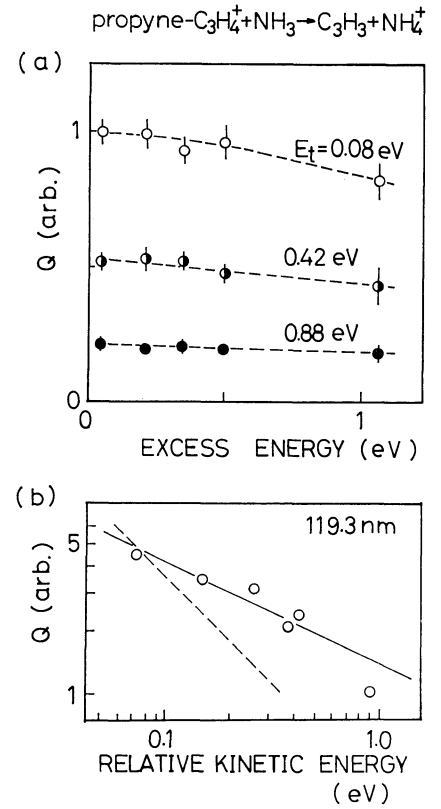

Fig. 4. Dependence of the cross section for the reaction $C_3H_4^+$(propyne) + $NH_3 \rightarrow NH_4^+ + C_3H_3$ on the excess internal energy of $C_3H_4^+$ at 119.3 nm radiation. Solid and broken lines indicate the $E^{-1/2}$ and E^{-1} dependence, respectively.

cross section of Reaction 1 is not as straightforward as in the above two systems, since, as was mentioned earlier, ammonia is always ionized by the radiation which ionizes propyne. That is, the following reactions must also be taken into consideration:

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2, \qquad (10)$$

$$C_3H_4^+ + NH_3 \rightarrow NH_3^+ + C_3H_4, \qquad (11)$$

$$NH_3^+ + C_3H_4 \rightarrow NH_4^+ + C_3H_3. \qquad (12)$$

The extent to which Reaction 10 contributes to the formation of NH_4^+ could easily be estimated from the study with pure ammonia, thus, the NH_4^+ intensities obtained in the mixtures have been corrected for this contribution. However, it is difficult to assess the importance of Reactions 11 and 12 by the use of the present technique. We have examined the variation in the NH_3^+ intensity as a function of the pressure of the added C_3H_4, keeping the NH_3 pressure constant; no significant change was observed within the experimental error at any wavelength. The implication of this result may be either that both Reactions, 11 and 12, are negligible compared, respectively, with Reactions 1 and 10, or that both reactions are fast but proceed, fortuitously, at almost the same rate, leading to no net change in the NH_3^+ intensity. Although the latter possibility can not be ruled out completely, we dared to assume that both Reactions, 11 and 12, are negligible under the present experimental conditions and analyzed the data in the same way as in the allene–ammonia and cyclopropane–ammonia systems. The resulting relative cross sections for Reaction 1 are presented in Fig. 4 as a function of both the excess internal energy (Fig. 4a) and the relative kinetic energy (for the 119.3 nm irradiation). It is interesting to see that the cross sections obtained for the propyne-ammonia system with the above assumption show the same excess energy and translational energy dependence as those in the other two systems.

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