TEMPERATURE DEPENDENCE OF RATE COEFFICIENTS FOR REACTIONS OF IONS WITH DIPOLAR MOLECULES

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We present a comparison of theoretical and experimental rate coefficients for the reactions of H_3^+ , HCO^+ , H^- , C^+ and O^+ with HCN, and H_3^+ with HCl, over the temperature range 205-540 K. The theoretical results are obtained using an adiabatic capture theory which is selective in the initial rotational states of the reacting dipolar molecules. The experiments were performed using a variable-temperature SIFT apparatus. For the H_3^+ and HCO^+ proton transfer reactions in particular, there is excellent agreement between theory and experiment, with the rate coefficients increasing sharply with decreasing temperature

1. Introduction

There has been considerable recent interest in the theoretical and experimental determination of rate coefficients for the reactions of ions with dipolar molecules in the gas phase. One reason for this is that these reactions are thought to play an important role in the synthesis of molecules in interstellar clouds Given the difficulties in measuring rate coefficients for these reactions at very low temperatures, the theoretical results have great value.

Of the theoretical techniques that have been proposed for ion--dipole reactions, the average dipole orientation (ADO) approximation [1,2] and its extension to include approximately the conservation of angular momentum [3] (the AADO method), have been most widely employed and often given encouraging agreement with room-temperature experimental rate coefficient data. Other theories used in this area include classical trajectory theories [4,5], transition-state theories of various types [6] and the semiclassical perturbed rotational states (PRS) approximation [7]. All of these calculations assume that the reaction is dominated by long-range intermolecular forces, and a capture approximation is used such that once a certain distance from the ion to the molecule is reached, which is beyond the centrifugal barrier, the collision always proceeds to reaction.

One of us [8] has recently been examining a practical procedure for computing rate coefficients for ion-molecule reactions dominated by long-range intermolecular forces. The method is based on the quantum-mechanical theory of non-reactive energy transfer. It involves a combined rotationally adiabatic capture and centrifugal sudden approximation (ACCSA) which, for brevity, will be called the AC method in this paper. The method gives reaction cross sections and rate coefficients which are stateselected in the initial rotational states (i) of the reacting molecule. The AC approximation has been tested against experimental data, and more accurate calculations, for a range of neutral reactions dominated by long-range intermolecular forces, and all the evidence suggests that the method is accurate for strongly exothermic reactions with no barrier in the potential energy surfaces [9,10].

For ion-dipole reactions, the AC theory gives

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rate coefficients similar to those obtained with the ADO theories at room temperature, but the AC rate coefficients increase much more sharply with decreasing temperature [8]. This is because the AC rate coefficients, k_i , selected with respect to initial j_i , increase considerably with decreasing *j* for a given temperature and, as the temperature is decreased, the k, with j small give an increasingly more dominant contribution to the Maxwell-Boltzmann averaged rate coefficient k. The ADO theory is not stateselective in j, and thus cannot describe this effect accurately. The physical reason behind this rotational effect is obvious. The minimum potential energy path for ion-dipole reactions is collinear, and hence any mitial rotational excitation will hinder the attacking ion from taking up this minimum energy path.

A major problem that has arisen in determining the theories that are most reliable in predicting rate coefficients for ion-dipole reactions is the scarcity of appropriate experimental data, particularly for the temperature range below 300 K. One reason for this is that molecules with large dipole moments have a propensity for forming dimers and clusters at lower temperatures and this presents a severe technical challenge to the experimental determination of rate coefficients for reactions involving monomers of such gases (see section 2)

In this paper, we go some way to clarifying this situation by reporting experimental rate coefficients, obtained with a SIFT apparatus [11], for the reactins of H_3^+ , HCO⁺, H^+ , C⁺ and O⁺ with HCN, and H_3^+ with HCl, over the temperature range 205–540 K. Significantly, all of the reactions (except for the H^+ reaction with HCN) are very exothermic (see section 4). These experimental results are used to examine the relative reliabilities of the ADO and AC methods for predicting the temperature dependence of ion-dipole reaction rate coefficients. Previous comparisons of predicted AC rate coefficients with experimental values have been made for the reactions of H^- , D^- , and H_3^+ with HCN at room temperature [8].

Section 2 gives a brief description of the measurements made with the SIFT apparatus and refers to the special problems met in dealing with dipolar molecules. Section 3 presents details of the AC computations of the rate coefficients for the reactions studied and alludes to the features of the ADO theory. Section 4 gives a comparison of the experimental, AC and ADO results. Conclusions are in section 5 in which we mention the relevance of our findings to interstellar chemistry.

2. Experimental determinations of rate coefficients

The measurements were made using our variabletemperature selected ion flow tube (SIFT) apparatus which has been described in detail elsewhere [11]. Reactant ions were generated in a high-pressure electron impact ion source containing an appropriate gas, i.e. H₂ for H⁺ and H₃⁺ production, a H₂/CO mixture for HCO⁺ production and CO for C⁺ and O⁺ production. High source gas pressures ensured that sufficient ion-parent molecule collisions occurred in the source to relax any internal excitation of the ions. For example, $H_3(v > 0)$ is efficiently relaxed in proton transfer collisions with H₂ thus generating $H_3^+(v=0)$ [12]. The ions were then injected into pure helium carrier gas, reactant gases were added downstream of the ion injection aperture and the rate coefficients for the ion-molecule reactions were determined in the usual manner [11].

The lowest temperature at which we were able to measure rate coefficients for the HCN and HCl reactions was 205 K for the following reasons. At the lowest temperature attainable with our SIFT apparatus (80 K), these gases condensed onto the cold surfaces of the gas entry ports and the flow tube. At 160 K, reactant gas did enter the flow tube but clear evidence was obtained that the gas comprised appreciable fractions of dimer molecules (especially severe for HCN). No such problems were encountered at 205 K at which temperature the HCN and HCl were pure monomers at the required partial pressures in the helium carrier gas. The maximum temperature used in these studies was 540 K.

Because the major objective of this study was to critically compare our measured rate coefficients with theoretical predictions we paid special attention to the careful measurement of the critical parameters of the experiment, i.e. temperature, reactant gas and carrier gas flow rates, etc. Also we made several measurements of each rate coefficient at each temperature in order to obtain mean values and statistical error figures.

3. Theory

Our theoretical approach has been described in detail elsewhere [8]. Here the salient aspects of the AC method are described in simple terms. For an ion linear dipole collision, the potential of interaction is

$$V(R,\theta) = -\alpha q^2/2R^4 - q\mu_{\rm D} \cos\theta/R^2 , \qquad (1)$$

where α is the isotropic polarisability of the molecule, *q* is the charge on the ion, *R* is the distance between the ion and the centre of mass of the molecule, μ_D is the dipole moment of the molecule and θ is the angle of orientation of the center of mass vector with the dipole.

The rotational energy levels of the molecule are found for a grid of values in ion-molecule distance R. This is done by finding the eigenvalues of a Hamiltonian to which the "centrifugal sudden approximation" [13] has been applied It is assumed that, as the ion moves into the molecule, each initial rotational state j stays on its own adiabatic potential energy curve. Then, for each j and initial collisional energy, the maximum impact parameter (in classical language) or total angular momentum (in quantum language) is determined such that reaction will occur with no tunnelling through the centrifugal barrier. This gives directly reaction "capture" cross sections which are state-selected in *j*. After Maxwell-Boltzmann averaging these cross sections over collision energy, the rotationally selected rate coefficients (k_i) are obtaoned. These can then be Maxwell-Boltzmann averaged to give k.

It should be stressed that this method, along with all others that use the capture approximation, will be reliable only for strongly exothermic reactions for which back reflection of reactive flux through the centrifugal barrier is unlikely. Furthermore, the reaction must occur on a single electronic potential energy surface which must contain no barriers. Exothermic proton transfers are good examples of such reactions (see section 4).

The parameters used in the calculations of the rate coefficients for reactions involving HCN were $\alpha \approx 2.56 \text{ Å}^3$, $\mu_D = 2.98 \text{ D}$ and $B = 1.478 \text{ cm}^{-1}$ [2]. For HCl, the parameters were $\alpha = 2.63 \text{ Å}^3$, $\mu_D = 1.08 \text{ D}$ and $B = 10.59 \text{ cm}^{-1}$ [14,15] The numerical parameters defining the convergence of the cross sections and rate coefficients are as described in ref. [8].

The ADO theory uses classical arguments to obtain an average value of $\cos \theta$ for a given temperature [2]. The standard classical capture theory is then used to obtain the formula

$$k = (2\pi |q|/\mu^{1/2}) [A + C\mu_{\rm D} (2\pi k_{\rm B} T)^{1/2}]$$
⁽²⁾

for the rate coefficient, where $k_{\rm B}$ is the Boltzmann constant, $A = \alpha^{1/2}$ and C is a "dipole locking" constant that depends on $\mu_{\rm D}/\alpha^{1/2}$ and temperature. For the systems and temperature range considered here, C is hardly sensitive to temperature [16].

In the AC theory, the ADO formula (2) is found to be accurate for each k_j [8], but with A and C differing for each j state and with C decreasing as j increases. Thus the small j rate coefficients will show a steeper temperature dependence than the large j rate coefficients, and this will be reflected in the temperature dependence of the Maxwell-Boltzmann averaged rate coefficient k.

4. Results and discussion

Table 1 presents the measured rate coefficients at 205, 300, 440 and 540 K for the reactions included in this study, together with the AC and ADO (300 K) predicted values. In this section, we first discuss in 4.1 the proton transfer reactions of H_3^+ with HCN and HCl, and HCO⁺ with HCN. Then, in 4.2 we discuss the reactions of H^+ , C⁺ and O⁺ with HCN.

4.1. Proton transfer reactions

Since the proton affinities of HCN and HCl greatly exceed the proton affinity of H_2 , the reactions of H_3^+ with HCN and HCl are very exothermic. Similarly, the HCO⁺ + HCN reaction is appreciably exothermic. The actual exothermicities (calculated using the data in ref. [17]) are

$$H_3^+ + HCN \rightarrow H_2CN^+ + H_2 + 70.1 \text{ kcal mol}^{-1}$$
, (3)

$$H_3^+ + HCl \rightarrow H_2Cl^+ + H_2 + 33.5 \text{ kcal mol}^{-1}$$
, (4)

 $HCO^+ + HCN \rightarrow H_2CN^+ + CO + 29.5 \text{ kcal mol}^{-1}$. (5)

These reactions are therefore good tests of the AC theory. Fig. 1 shows graphically the comparison between the experimental AC and ADO rate coefficients

Table 1

Rate coefficients for the reactions indicated at the temperatures indicated. The first row for each reaction (a) gives the measured values and the second row (b) gives the Boltzmann-averaged values calculated using the AC theory. Also given in the last column are the 300 K values calculated using the ADO theory [2]. Units are cm³ s⁻¹ and numbers in parentheses are powers of ten

Reaction		Temperature (K)				ADO (300 K)	
		205	300	440	540		
$H_3^+ + HCN \rightarrow$	(a)	9_5(_9)	8.1(-9)	7.1(-9)	6.7(-9)	6.6(–9)	
$H_2CN^+ + H_2$	(b)	9.6(–9)	8.3(-9)	7.3(–9)	6.9(9)		
H₃ ⁺ + HCL →		4.2(-9)	3.8(-9)	3 5(9)	3 4(–9)	3 4(-9)	
$H_2Cl^+ + H_2$		4.1(–9)	3.6(-9)	3.3(–9)	3.2(-9)		
HCO ⁺ + HCN →		3.7(-9)	3.1(-9)	2.9(-9)	2.8(-9)	2.2(-9)	
$H_2CN^+ + CO$		4.2(-9)	3 5(-9)	31(-9)	2.9(-9)		
H ⁺ + HCN →		1.1(-8)	1.1(-8)	1.0(-8)	9.7(-9)	1.1(-8)	
HCN ⁺ + H		1.6(-8)	1 3(-8)	11(-8)	1.1(-8)		
$C^+ + HCN \rightarrow$		3.4(–9)	3.1(-9)	3.0(-9)	2.9(-9)	3.7(9)	
$C_2 N^+ + H$		5 5(–9)	4.6(-9)	4.0(-9)	3.7(-9)		
$O^+ + HCN \rightarrow$		3.7(-9)	3.5(-9)	3 3(9)	3.1(-9)	3.4(9)	
$CO^+ + NH a$) $HCO^+ + N a$)		5.0(–9)	4.2(-9)	3.6(-9)	3_4(-9)		

a) Approximately equal product channels.



Fig. 1. Comparison of the experimental, AC and ADO rate coefficients for the reactions of H_3^+ with HCN and HCl Note the excellent agreement between the experimental values (0, ∇ symbols) and the AC predicted Boltzmann-averaged values (continuous lines). The ADO theory clearly greatly underestimates the rate coefficients at low temperatures.

for the H⁺ reactions It can be seen from this figure and the results presented in table 1 for the HCO+ reaction with HCN and the agreement between the AC and experimental rate coefficients is excellent, with a definite increase in the experimental rate coefficient, with a definite increase in the experimental rate coefficient as the temperature is decreased. The ADO rate coefficients are relatively insensitive to temperature over the range 150-600 K and hance do not give good agreement with the experimental findings for these reactions. Since the agreement between the AC and experimental rate coefficients is so good, it is very likely that the AC predictions will be accurate for temperatures below the lowest temperature of our experiments, 250 K. Table 2 presents our AC predictions of Boltzmann-averaged rate coefficients for the proton transfer reactions, H_3^+ + HCN and HCl, and HCO+ + HCN, over the temperature range 5 to 205 K. Note the enormous value of $1.1 (-7) \text{ cm}^3$

Table	2
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Boltzmann-averaged rate coefficients calculated using the AC theory for the proton transfer reactions at the temperatures indicated. Units are $\text{cm}^3 \text{ s}^{-1}$ and numbers in parentheses are powers of ten

	Reaction	Temperature (K)								
		5	10	15	50	150	300	600		
	H_3^+ + HCN	1.1(-7)	7 0(-8)	5 4(-8)	2.4(-8)	1.2(-8)	8.3(–9)	6 8(-9)		
	Н ⁺ + НСІ	3 0(-8)	2.1(-8)	1.6(-8)	7.6(9)	4 5(-9)	3 6(-9)	3.1(-9)		
	HCO ⁺ + HCN	4.6(-8)	3.1 (-8)	2 4(-8)	1.0(-8)	5.1(-9)	3.5(-9)	2.8(-9)		

 s^{-1} for the H_3^+ + HCN reaction at 5 K! Clearly an even more stringent test of the AC theory would be to measure the rate coefficients over this very-low-temperature range.

During the writing of this paper, we heard the exciting news that the reactions of the dipolar molecules H_2O and NH_3 with He^+ , C^+ and N^+ had been studied at 27 K [18] Preliminary indications are that the rate coefficients at this very low temperature are much greater than the room-temperature values and are consistent with the AC predictions.

The reason behind the strong sensitivity of the AC rate coefficients to temperature, and particularly at low temperatures, is that the k_j are much more sensitive to temperature for low *j* than high *j*. This is illustrated in figs. 2 and 3, where the AC calculations of k_j for a range of different *j* values are presented. At 540 K, however, the AC, ADO, and experimental rate coefficients are all in good agreement. At this tem-



Fig. 2. The AC theoretical rate coefficients for the reactions of H_3^+ with HCN in the j = 0 and j = 9 rotational states, illustrating the very rapid increase in the rate coefficients at low temperatures.



Fig. 3. The AC theoretical rate coefficients for the reactions of H_3^+ with HCl in the j = 0, 1 and 2 rotational states, illustrating the important general feature that the rate of increase in the rate coefficient with temperature decrease is greater the smaller the j value.

perature, a very large number of *j* states contribute to the Maxwell-Boltzmann average and the stateselectivity is not so crucial.

4.2. Reactions of H^+ , C^+ and O^+ with HCN

(1) The reaction

$$H^+$$
 + HCN → HCN⁺ + H + 0.18 ± 0.23 kcal mol⁻¹
(6)

is a charge transfer reaction which is nearly thermoneutral (the thermicity of this reaction and of the D^+ reaction below has been calculated using the critical data in ref. [19]). As such it is not considered to be a good test of the AC theory. Nevertheless, the experimental and AC predicted rate coefficients are in reasonable agreement above room temperature (see table 1). However, at 250 K, the experimental value Volume 119, number 4

is significantly smaller than the AC prediction. This could be a manifestation of a slight endothermicity in the reaction (this is not inconsistent with the available thermodynamic data). In the hope of gaining further insight into this, we looked at the reacuon of D^+ with HCN at 300 and 540 K. Charge transfer in this reaction is probably slightly exothermic,

$$D^+$$
 + HCN → HCN⁺ + D + 0.28 ± 0.23 kcal mol⁻¹.
(7a)

Also isotope exchange is possible thus:

$$D^+ + HCN \rightarrow DCN^+ + H, \qquad (7b)$$

$$\rightarrow DCN + H^{+} . \tag{7c}$$

We estimate these reactions to be slightly exothermic $(\approx 1 \text{ kcal mol}^{-1})$ by virtue of the stronger C-D relauve to C-H bond. At both temperatures the isotope exchange and the charge transfer channels were clearly evident and the experimental rate coefficients were in reasonable agreement with the AC predictions. Thus at 300 K, $k(expt_{.}) = 9.0(-9)$, k(AC) = 9.8(-9) and at 540 K. k(expt.) = 7.1(-9). k(AC) = 82(-9) all in units of cm³ s⁻¹. The relative k(expt.) to k(AC) values for this D⁺ reaction are not significantly different than those for the H⁺ + HCN reaction, in spite of the additional isotope exchange channel in the D⁺ reaction. That both are somewhat close to thermoneutral (the AC theory is expected to be applicable only to appreciably exothermic reactions).

(ii) The reaction

$$C^+ + HCN \rightarrow C_2N^+ + H + 32.2 \text{ kcal mol}^{-1}$$
 (8)

is an exothermic ion—atom interchange reaction. Such reactions are often observed experimentally to proceed somewhat slower than the collisional rate [20] presumably due to minor barriers on the reactive potential surface. However, the increase of the rate coefficient with decreasing temperature (table 1) indicates that the inhibiting effect of the barrier is counteracted and overcome at low temperatures. It must be noted that the exothermicity of this reaction given above was calculated on the basis that the structure of the product ion is (CNC)⁺ since production of the structural isomer (CCN)⁺ is slightly endothermic [21].

(iii) The reaction

exhibits the three products shown and thus involves concerted rearrangement within the reaction complex. All product channels are appreciably exothermic. Again, the experimental rate coefficient falls short of the AC predictions but increases with decreasing temperature and exceeds the ADO prediction at 205 K. It seems likely that, for both the C⁺ and O⁺ reactions with HCN, potential energy surfaces more complicated than eq. (1) are needed to explain fully the experimental results.

5. Summary and conclusions

The central objective of this paper is to illustrate that the collision rate coefficients for ion-molecule reactions involving molecules with large permanent dipole moments increase sharply at temperatures below room temperature. The AC theory which predicts this phenomenon has been outlined, and some experimental data have been presented which support the theoretical predictions, particularly for proton transfer reactions. A far reaching consequence is in the area of interstellar ion chemistry via which interstellar molecules are synthesized [22]. This chemistry proceeds under conditions of very low pressures and at temperatures which can be as low as 5 K. The significance of this is that reactant molecules are predominantly in very low rotational states and molecules with appreciable or large permanent dipole moments are essentially in their ground rotational states. Hence, according to the AC theory, the collisional rate coefficients will be very large, greatly exceeding the 10^{-9} cm³ s⁻¹ commonly adopted for interstellar models and in some cases about a factor of 100 greater than this value. This has a profound influence on the rate of the ion chemistry and hence on the rate of evolution of interstellar molecules, a subject which will be discussed in another paper [23].

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