The Temperature Dependences of Some Fast Ion–Polar Molecule H^+ Transfer and of Slow H^- Transfer Reactions

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Abstract: The rate constant of the reaction $N_2H^+ + CH_4 \rightarrow CH_5^+ + N_2$ was measured as $k_{320} = 1.3 \times 10^{-9}$. The rate constant for this reaction, involving a nonpolar neutral reactant, is found to be constant between 130 and 650°K. The reactions between N_2H^+ and NH_3 ($k_{320} = 2.0 \times 10^{-9}$ cm^3/molecule sec) and N_2H^+ and CH_3CHO ($k_{320} = 5.8 \times 10^{-9}$) involve significantly polar neutral reactants. These reactions, where the dipole moments of the neutral reactants have a significant effect on the reaction rate, exhibit small negative temperature dependences between 300 and 650°K. These temperature dependences are in good agreement with the theoretically predicted effects of temperature on the capture rates in these reactions, which are thought to proceed through loose (or orbiting) complexes. In contrast, the slow M^- transfer reaction $NO^+ + CH_3CHO \rightarrow CH_3CO^+ + HNO$ ($k_{320} = 0.76 \times 10^{-9}$ cm^3/molecule sec) exhibits a large negative temperature dependence of the form $k = AT^{-1}$. This temperature dependence and that of the slow H^- transfer reaction $t\text{-}C_4H_9^+ + C_5H_{12} \rightarrow t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10}$ ($k_{320} = 0.014 \times 10^{-9}$ cm^3/molecule sec)[1] indicate the formation of tightly bound transition complexes in hydride ion transfer reactions. Transition state theory considerations relate the large negative temperature dependences of these reactions to entropy changes involved in the formation of the transition complexes.

In a recent study[1] of the slow bimolecular hydride ion transfer reaction system

$$t\text{-}C_4H_9^+ + i\text{-}C_5H_{12}^+ \rightleftharpoons t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10}$$

we found that the forward, exothermic reaction proceeds significantly slower than the collision rate, and the rate constant exhibits an unprecedentedly large negative temperature dependence. The temperature dependence could be expressed as $k = AT^{-3}$ and interpreted as an entropy effect on the basis of transition state theory considerations. The question arises whether the slow rate of the reaction and its negative temperature dependence are related primarily to the nature of the particle transferred (H^-) or to special structural properties of the reactants.

As opposed to the above reaction, the majority of ion–molecule reactions involving the transfer of massive particles proceed at rates near the collision rate. The Gioumousis–Stevenson theory[2] predicts that the rates of such reactions are independent of temperature. If the reaction involves a neutral molecule with a permanent dipole moment, a small negative temperature dependence of the rate constant may be expected on the basis of the equation

$$k = \frac{2\pi q}{\mu^{1/2}}\left[\alpha^{1/2} + c\mu_D\left(\frac{2}{\pi kT}\right)^{1/2}\right] \qquad (1)$$

Here μ is the reduced mass, μ_D is the dipole moment, and α is the polarizability of the neutral molecule. The locking constant c is 1 in the locked dipole theory[3] and a quantity related to the average orientation of the dipole in the ionic electric field according to the recently developed average dipole orientation (ADO) theory.[4] There appears to be little experimental information available on the temperature dependence of fast ion–molecule reactions.

In the present study we examined the temperature dependence of the hydride-ion transfer reaction

$$NO^+ + CH_3CHO \longrightarrow HNO + CH_3CO^+$$

This reaction involves the most simple reactants which we found suitable for an experimental study of an exothermic hydride-ion transfer reaction by our methods. We also investigated the temperature dependence of the rate constants of some fast proton-transfer reactions involving nonpolar and polar neutral reactant molecules. These studies provide information on the interesting question of the nature of the reaction intermediates involved in ion–molecule transfer reactions.

In addition to the implications concerning basic reaction kinematics, the temperature dependences of ion–molecule reaction rates are also of potential significance in the chemistry of the thermally extreme planetary atmospheric and interstellar environments.

Experimental Section

In the present investigations The Rockefeller University chemical physics mass spectrometer was used in the mode of pulsed, time-resolved, high-pressure mass spectrometry.[1] In this technique the reactions are started by the bombardment of the reaction mixture with a pulse of 600-V electrons. The ionic composition of the reaction mixture is analyzed as a function of the reaction time. The reactions studied and the reaction mixtures used are summarized in Table I. The reactant ions of interest (N_2H^+, NO^+, $t\text{-}C_4H_9^+$, and H_3S^+) are produced by the major components of the reaction mixtures by fast reactions that go to conclusion in a few microseconds. The reactant ions then react more slowly with the minor components of the reaction mixture. The concentration of the neutral reactant of the reaction of interest in the reaction mixture and the total number densities were adjusted such that the reaction half-life was in the range of 25–50 μsec. The feasibility of these kinetic studies is largely dependent on the selection of appropriate reaction systems where competing transfer and association reactions of the reactant and product ions of interest with the components of the reaction mixtures and with impurities are negligible. In the present studies the ions of interest constituted at least 90% of the total ion current and the absence of possible competing reactions was carefully checked.

The materials used were Matheson Prepurified H_2 and N_2, Chemical Purity NO, H_2S, and D_2, Ultra High Purity CH_4, anhydrous NH_3, Matheson Coleman and Bell CH_3CHO and $(C_2H_5)_3N$. In order to check the reproducibility of our mixture preparations, some rate measurements were performed on at least two separate reaction mixtures. Furthermore, duplicate determinations were made of each temperature study here reported.

The temperature range of the kinetic studies was determined by instrumental limitations or by the vapor pressures of the least volatile reaction components.

The mean free path under our experimental conditions is always at least 50 times smaller than the narrowest constriction between the source and the pressure measuring device. Thermal transpiration effects are therefore always absent in our experiments.

Errors in the rate measurements result from errors in mixture composition, the finite widths of the electron and gate pulses, and random scattering in the kinetic plots. We estimate that rate constants are measured with error limits of ±20%. Reproducibility and relative rate constants are good to within 10%.

Table I. Composition of Reaction Mixtures and Total Number Densities Applied in the Reaction Systems Investigated

Reaction	Composition of the reaction mixture, %	Total no. density[a] $N \times 10^{16}$, molecules/cm^3	Physical properties of neutral reactant: Dipole moment[b] μ_D, D	Physical properties of neutral reactant: Electron polarizability $\alpha \times 10^{24}$, cm^3
$N_2H^+ + CH_4 \rightarrow CH_5^+ + N_2$	95, N_2; 5, H_2; 0.056, CH_4	1.9	0.0	2.60[c]
$t\text{-}C_4H_9^+ + (C_2H_5)_3N \rightarrow (C_2H_5)_3NH^+ + C_4H_8$	99.85, $i\text{-}C_4H_{10}$; 0.15, $(C_2H_5)_3N$	1.0	0.66	13.42[d]
$N_2H^+ + NH_3 \rightarrow NH_4^+ + N_2$	95.1, N_2; 4.84, H_2; 0.064, NH_3	1.3	1.47	2.26[c]
$N_2H^+ + CH_3CHO \rightarrow CH_3CHOH^+ + N_2$ $N_2D^+ + CH_3CHO \rightarrow CH_3CHOD^+ + N_2$	95, N_2; 5, H_2 (or D_2); 0.048, CH_3CHO	1.3	2.69	4.56[d]
$H_3S^+ + CH_3CHO \rightarrow CH_3CHOH^+ + H_2S$	95.8, N_2; 4.2, H_2S; 0.042, CH_3CHO	1.0	2.69	4.56[d]
$NO^+ + CH_3CHO \rightarrow CH_3CO^+ + HNO$	89.3, N_2; 10.5, NO; 0.2, CH_3CHO	1.0	2.69	4.56[d]

[a] The total number density in each reaction system was kept constant by appropriate adjustment of the pressure at the temperature of each kinetic study. [b] From R. D. Nelson, D. R. Lide, and A. A. Maryott, "Selected Values of Electric Dipole Moment for Molecules in the Gas Phase", *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 10 (1966). [c] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, N.Y., 1964, p 950. [d] Calculated from the refraction index.

Table II. Experimental and Theoretical Rate Constants of Some H^+ and H^- Transfer Reactions at 320 and 650°K

		10^9k_{320}			10^9k_{640}				
			Theoretical for dipole locking constants = (eq 1)			Theoretical for dipole locking constants = (eq 1)		Dipole locking constants	
Reaction No.	H^+ and D^+ transfer reactions	Exptl	$c_{ADO}{}^{300a}$	1.0	Exptl	$c_{ADO}{}^{300a}$	1.0	$c_{ADO}{}^{300}$	$c_{exptl}{}^{320b}$
1.	$N_2H^+ + CH_4 \rightarrow CH_5^+ + N_2$	1.3	1.2	1.2	1.3	1.2	1.2		
2.	$t\text{-}C_4H_9^+ + (C_2H_5)_3N \rightarrow (C_2H_5)_3NH^+ + C_4H_8$	1.6	1.5	2.1	1.6	1.5	1.9	0.05	0.09
3.	$N_2H^+ + NH_3 \rightarrow NH_4^+ + N_2$	2.0	1.9	5.1	1.7	1.6	3.9	0.21	0.23
4.	$N_2H^+ + CH_3CHO \rightarrow CH_3CHOH^+ + N_2$	5.8	2.6	6.9	4.2	2.2	5.2	0.25	0.78
5.	$N_2D^+ + CH_3CHO \rightarrow CH_3CHOD^+ + N_2$	6.2	2.6	6.9	4.2	2.2	5.2	0.25	0.82
6.	$H_3S^+ + CH_3CHO \rightarrow CH_3CHOH^+ + N_2$	5.1	2.5	6.5	4.2	2.1	4.9	0.25	0.87
	H^- transfer reactions								
7.	$NO^+ + CH_3CHO \rightarrow CH_3CO^+ + HNO$	0.76	2.6	6.9	0.34	2.2	5.2		
8.	$t\text{-}C_4H_9^+ + i\text{-}C_5H_{12} \rightarrow t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10}$	0.014	1.3	1.5	0.0017	1.3	1.5		

[a] Calculated from eq 1 with the dipole locking constant c as given for the particular collision system by the parameterized ADO theory.[4b] Note that this is not exactly the ADO value, in particular at 640°K, since c has been given only for 300°K in ref 4b. [b] Calculated from the experimental rate constants and eq 1, i.e., $k_{exptl} = [2\pi q/\mu^{1/2}]\,[\alpha^{1/2} + c_{exptl}\mu_D(2/\pi kT)^{1/2}]$. The values of c_{exptl} can be seen as the experimentally determined average locking of the dipole in the electric field of the ion.

Since the concentrations of the ions in the reaction plasmas are many orders of magnitude smaller than the concentrations of the neutrals, all reactions exhibit pseudo-first-order kinetics. Equilibrium constants can be estimated from tabulated heats of formation of ions and neutrals, since entropy changes in the reactions of interest are small. From the calculated equilibrium constants we can conclude that our reactions were sufficiently removed from equilibrium at all points of the kinetic studies that the inverse reactions may be neglected. Representative pseudo-first-order kinetic plots are shown in Figure 1. The second-order rate constants can be obtained from the slopes of the pseudo-first-order plots and the known pressures and densities of the neutrals. The second-order kinetics of the reactions was confirmed by the observation that the second-order rate constants measured at the densities quoted in Table I were found to be equal within experimental error limits to rate constants measured at twice these densities.

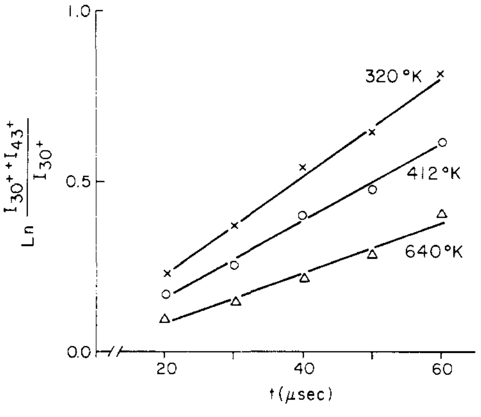


Figure 1. Representative kinetic plots for the reaction NO^+ (m/e = 30) + $CH_3CHO \rightarrow CH_3CO^+$ (m/e = 43) + HNO.

Results

(i) Fast Reactions. H^+ Transfer. The experimental rate constants and the rate constants predicted by the locked dipole and ADO theories for the proton transfer reactions studied at 320 and 640°K are shown in Table II. The detailed forms of the temperature dependences of reactions 1-5 (reactions will be referred to by their number in Table II) are shown in Figures 2-4. For reaction 1 where the neutral reactant, CH_4, is nonpolar, eq 1 reduces to the Gioumousis-Stevenson equation. The rate constant is in good agreement with the theoretical value. The rate constant for this reaction is seen to be independent of temperature within experimental accuracy between 130 and 650°K, as expected (Figure 2). Similarly the contribution of the dipole moment of the slightly polar but highly polarizable molecule $(C_2H_5)_3N$ to the rate of reaction 2 is small. The experimental rate constant of this reaction is also in good agreement with the prediction of the parameterized ADO theory and exhibits negligible temperature dependence between 320 and 650°K, as predicted (Figure 2).

The neutral reactant in reaction 3, NH_3, is a polar molecule with a small polarizability (Table I). Comparing the measured rate of this reaction with the Langevin rate (1.07

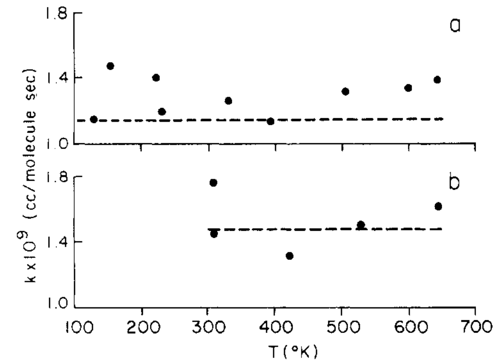


Figure 2. (a) The temperature dependence of the rate constant of the reaction $N_2H^+ + CH_4 \rightarrow CH_5^+ + N_2$ between 130 and 640°K. (b) The temperature dependence of the rate constant of the reaction $t\text{-}C_4H_9^+ + (C_2H_5)_3N \rightarrow (C_2H_5)_3NH^+ + C_4H_8$ between 310 and 640°K. Points represent experimental measurements; broken lines represent theoretical (ADO) capture rate constants.

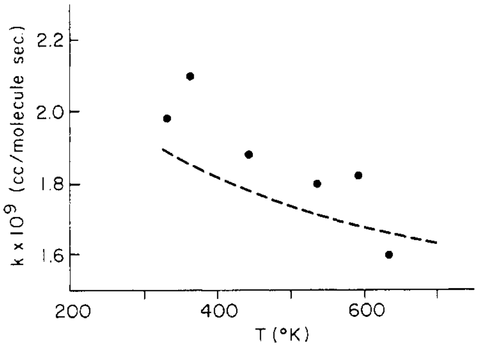


Figure 3. The temperature dependence of the rate constant of the reaction $N_2H^+ + NH_3 \rightarrow NH_4^+ + N_2$ between 320 and 640°K. The broken line represents the theoretical rate constants calculated from eq 1 with the dipole locking constant $c = 0.21 = c_{ADO}^{300}$.

$\times\ 10^{-9}$ cm^3/molecule sec), one may easily calculate that the ion–dipole interaction contributes 30% to the reaction rate at 640°K and 45% at 320°K. The experimental rate constants show that the contribution of the ion–dipole interaction to the rate constants causes a small negative temperature dependence of the rate constants, as predicted by eq 1 (Figure 3). The rate constants for this reaction are in good agreement with the predictions of the ADO theory. k_{320} is in good agreement with the experimental rate constant for this reaction published recently by Hemsworth, et al.[5]

The neutral reactant in reactions 4–6, CH_3CHO, is a highly polar molecule (μ_D = 2.67 D). Comparing the Langevin rate (1.20×10^{-9} cm^3/molecule sec) with the experimental rate constants shows that the ion–dipole interaction contributes 78% of the rate of reaction 4 at 320°K and 70% at 640°K. These results are consistent with a dipole locking constant of 0.78, rather than the ADO value of 0.25. Similar results are found in reactions 5 and 6. In light of the general success of the ADO theory,[5] the large locking of the dipole found in the reactions of this highly polar molecule is somewhat of an anomaly. We do not know the reason for this behavior.

The similarity between the rate constants of reactions 4 and 5 shows the absence of kinetic isotope effects in this reaction.

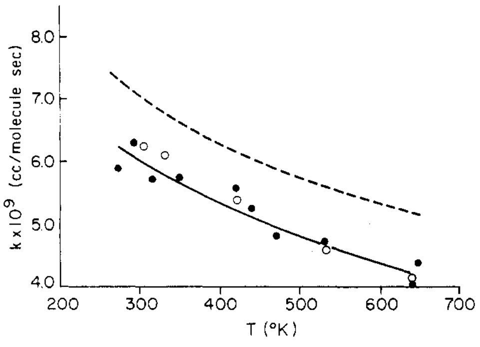


Figure 4. The temperature dependence of the rate constant of the reaction $N_2H^+ + CH_3CHO \rightarrow CH_3CHOH^+ + N_2$ between 270 and 640°K. Solid circles represent experimental values and the solid line shows the experimental temperature dependence. The broken line represents the theoretical (locked dipole) rate constants. Open circles are experimental rate constants for the reaction $N_2D^+ + CH_3CHO \rightarrow CH_3CHOD^+ + N_2$.

The temperature dependences of the rates of reactions 4 and 5 are shown in Figure 4. The experimental rate constants again show the negative temperature dependence caused by the contribution of the ion–dipole interaction to the rate constant. To the best of our knowledge, these results are the first experimental demonstrations of the effect of ion–dipole interactions on the temperature dependence of the rate constants of fast ion–molecule reactions.

(ii) Slow Reactions. H$^-$ Transfer. The experimental rate constants and the calculated collision rates of two hydride-ion transfer reactions at 320 and 640°K are shown in Table II. The experimental values may be compared with the corresponding theoretical values for each reaction. In addition the experimental values for reactions 7 and 8 may be compared with those of reactions 4 and 2, respectively, since the collision properties of the respective reaction systems involved, i.e., the reduced masses, polarizabilities, and dipole moments, are comparable. It is seen that in contrast to the proton transfer reactions, the rates of the hydride-ion transfer reactions are significantly slower than the capture rates. In the investigation of reaction 8 we found that the plot of ln k vs. ln T for that reaction was linear with a slope of -3 between 190 and 570°K.[1] This temperature dependence is significantly larger than the temperature dependence of the collisional rate of the comparable proton-transfer reaction 2 which is of the form $k = AT^0$.

We show the temperature dependence of the rate constant of reaction 7 in a plot of ln k vs. ln T in Figure 5. The rate constant of this hydride-ion transfer reaction is seen to show a temperature dependence that may be expressed as $k = AT^{-1}$. This temperature dependence is significantly larger than the temperature dependence of the capture rate of the comparable proton transfer reaction 4 (Figure 5).

Discussion and Conclusion

In the study of the reaction system $t\text{-}C_4H_9^+(i\text{-}C_5H_{12}, i\text{-}C_4H_{10})t\text{-}C_5H_{11}^+$ we found that the negative temperature dependence of the forward reaction could be interpreted on the basis of transition-state theory (TST) considerations. The temperature dependence of the rate constant may be expressed by TST equations as

$$k_r(T) = c\frac{kT}{h}\frac{Q_{tr}^{\ddagger}Q_{rot}^{\ddagger}Q_{vib}^{\ddagger}Q_{elec}^{\ddagger}}{\prod_{i=1}^{n}(Q_i)_{tr}(Q_i)_{rot}(Q_i)_{vib}(Q_i)_{elec}}e^{-E_0/RT} =$$

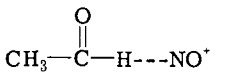
$$A\frac{(T_{tr}{}^{3/2})^{\ddagger}(T_{rot}{}^{j/2})^{\ddagger}}{\prod_{i=1}^{n}(T_{tr}{}^{3/2})_i(T_{rot}{}^{j/2})_i}T_{int\ rot}{}^{r/2}e^{-E_0/RT} \qquad (2)$$

Here Q and Q_i are the partition functions of the transition complex and the n reactants that form it. The temperature dependence of the vibrational and electronic partition functions may be neglected for the present purposes. The activation energy for exothermic ion–molecule reactions is usually assumed to be zero or negligibly small. This was shown to be true for reaction 8.[1] Our findings of zero or negative temperature coefficients found in the present study indicate that the activation energies are also negligible for exothermic ion–molecule reactions here investigated. Thus the exponential term in eq 2 is effectively unity.

Labeling the origin of the temperature dependent terms, the second expression in eq 2 is obtained. In this expression A is a constant, j is 3 for nonlinear and 2 for linear molecules, and r is the change in the number of internal rotations upon the formation of the transition complex. Applying this equation to reaction 8, for which it was found experimentally[1] that $k = AT^{-3}$, we obtained $r = -2$, i.e., two internal rotations become hindered upon the formation of the transition complex. This is a reasonable number for the molecular structures of the reactants in that reaction. For reaction 7 we obtain

$$k = AT \times \frac{(T_{tr}^{3/2})^{\ddagger}(T_{rot}^{3/2})^{\ddagger}}{(T_{tr}^{3/2})_{CH_3CHO}(T_{tr}^{3/2})_{NO^+}(T_{rot}^{3/2})_{CH_3CHO}(T_{rot}^{2/2})_{NO^+}} \times T^{r/2} = AT^{(r-3)/2} \quad (3)$$

From the slope of Figure 5 we get $(r - 3)/2 = -1$, $r = 1$. One internal rotation is created upon the formation of the transition complex. The axis of this rotation is easily seen as the H- - -NO^+ bond in the complex



$$CH_3—\overset{\overset{O}{\|}}{C}—H{-}{-}{-}NO^+$$

Thus, transition state theory accounts for hydride ion transfer reactions in a simple and satisfactory way. However, it must be recognized that these reactions may also in principle be described by RRK or quasi-equilibrium theory treatments if the reactions proceed through tightly bound complexes which permit energy redistribution in internal modes.

Turning to the H^+ transfer reactions, TST considerations applied to such reactions proceeding via tightly bound complexes would also predict generally a temperature dependence of T^{-1} or $T^{-1.5}$. This behavior is clearly not observed in our data on the fast proton transfer reactions. However, Eyring et al.[6] applied transition state theory methods to fast ion–molecule reactions which proceed through loose complexes. In this model the distance between the reactants in the activated state is determined by the position of the maximum in the potential energy surface of the reaction, and this distance is in turn determined by the difference between the rotational and ion-induced dipole interactions. In these loose complexes (for example, according to this treatment the mean distance between N_2H^+ and CH_4 in the activated state of the corresponding H^+ transfer reaction at 300°K turns out to be 3.9 Å) the reactants retain their individual rotational and vibrational degrees of freedom, and the treatment leads to an expression for the rate constant which is similar to the Langevin expression and is likewise independent of the temperature. It does not appear that the transition state theory treatment has been extended to ion–polar molecule reactions.

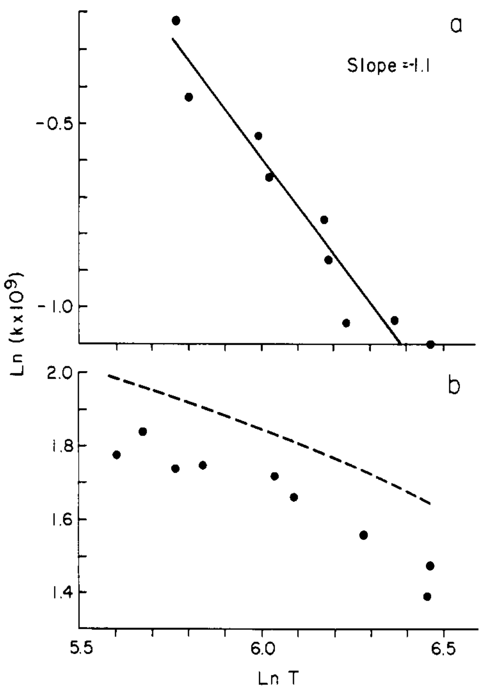


Figure 5. (a). The temperature dependence of the rate constant of the reaction $CH_3CHO + NO^+ \rightarrow CH_3CO^+ + HNO$ between 320 and 640°K. A plot of ln $k \times 10^9$ vs. ln T is shown. Solid line is the least-squares plot through experimental points. (b) For comparison the plot of ln $k \times 10^9$ vs. ln T for the comparable proton transfer reaction $N_2H^+ + CH_3CHO \rightarrow CH_3CHOH^+ + N_2$ (solid circles) and the plot of the logarithm of the theoretical capture rate ln (k locked dipole × 10^9) vs. ln T (broken line) are also shown.

In conclusion, H^- transfer reactions exhibit large negative temperature dependences which can be successfully interpreted using theoretical considerations based on the formation of tight transition complexes and cannot be accounted for satisfactorily by collisional considerations based on loose or orbiting complexes. In contrast, the absolute rates of H^+ transfer reactions, and the small negative temperature dependences thereof which we measured, can be successfully accounted for by such collisional considerations and are inconsistent with the formation of tightly bound transition complexes.

We can offer no meaningful explanation for the fundamental difference between the nature of H^+ and H^- transfer reactions, although it is obviously a matter of much interest.

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References and Notes

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