Rate Constants at 297 K for Proton-Transfer Reactions with HCN and CH_3CN. Comparisons with Classical Theories and Exothermicity

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Rate constants for proton-transfer reactions of the type $XH^+ + HCN\ (CH_3CN) \rightarrow H_2CN^+\ (CH_3CNH^+) + X$ where X = H_2, N_2, CO, H_2O, and CO_2 and of the type $HCN\ (CH_3CN) + X^- \rightarrow CN^-\ (CH_2CN^-) + XH$ where X = H, D, OH, SH, NH_2, C_2H, and CH_3O have been measured at 297 ± 2 K using the flowing afterglow technique. These reactions for which the measured rate constants span a range from 0.15 to 1.5×10^{-8} cm^3 molecule^{-1} s^{-1} represent some of the fastest ion–molecule reactions observed to date. The rate constants are compared with the predictions of Langevin, average-dipole-orientation and locked-dipole theories of ion–molecule collisions. The average-dipole-orientation theory provides the most realistic collision rates for these reactions although these appear to be underestimated by ~10 to ~40%. The observed dependence of the efficiency for proton transfer on exothermicity indicates that the assumption of unit reaction probability resident in such comparisons may break down at low exothermicities.

Introduction

Proton-transfer reactions involving simple molecular systems constitute a large class of ion–molecule reactions which have proven to be most suitable for the testing of the rate predictions of classical theories of ion–molecule collisions. This suitability arises from the expectation that the exothermic transfer of a proton proceeds on essentially every collision. When coupled with this expectation, collision rate theories amount to reaction rate theories so that a comparison of measured reaction rates with calculated collision rates can provide an experimental assessment of the latter.[4] The flowing afterglow measurements previously reported from this laboratory for the transfer of a proton to nonpolar molecules (Xe, N_2, CH_4, CO_2, and C_2H_6), slightly polar molecules (NO, CO, N_2O: $\mu_D < 0.2$ D), and moderately polar molecules (NH_3: $\mu_D = 1.47$ D, H_2O: $\mu_D = 1.84$ D) have indicated that the Langevin[5] and average-dipole-orientation[6-8] theories predict capture rates for collisions of ions with nonpolar and polar molecules, respectively, which often agree, within experimental error, with the measured reaction rates at room temperature.[9,10] In this paper we report further measurements of proton transfer rates and their comparison with the predictions of the various collision theories. The reactions investigated involve highly polar molecules, viz. HCN ($\mu_D = 2.98$ D) and CH_3CN ($\mu_D = 3.92$ D), which may either accept a proton from an ion

$$XH^+ + HCN \rightarrow H_2CN^+ + X \qquad (1a)$$

$$XH^+ + CH_3CN \rightarrow CH_3CNH^+ + X \qquad (1b)$$

where X = H_2, N_2, CO, H_2O, N_2O, and CO_2, or transfer a proton to an ion

$$HCN + X^- \rightarrow XH + CN^- \qquad (2a)$$

$$CH_3CN + X^- \rightarrow XH + CH_2CN^- \qquad (2b)$$

where X = H, D, SH, OH, NH_2, C_2H and CH_3O.

This study also provided another opportunity to explore the effect of excess energy in the form of reaction exothermicity upon the magnitude of the efficiency for a series of homologous ion–molecule reactions. Our previous investigations of proton transfer reactions indicated no substantial dependence of the efficiency on the heat of reaction.

Experimental Section

Rate constants were measured in the usual manner in a flowing afterglow apparatus in which the ions were permitted to thermalize by collisions with a helium or hydrogen buffer gas to the ambient room temperature of 297 ± 2 K before entering the reaction region.[11] Typical operating conditions encompassed total gas pressures, P, in the range 0.25 to 0.45 Torr and gas velocities, $\bar{v}$, in the range 8.0 to 8.5×10^3 cm s^{-1}. The reaction length, L, was 60 cm. The accuracy of the rate constant measurements is estimated to be ±20 and ±25% for the HCN and CH_3CN reactions, respectively, and the precision was observed to be ±10%.

The ions XH^+, where X = N_2, CO, CO_2, N_2O, and H_2O, were generated according to the proton transfer reaction

$$H_3^+ + X \rightarrow XH^+ + H_2 \qquad (3)$$

simply by adding the appropriate gas, X, upstream of the reaction region into a pure hydrogen afterglow in which H_3^+ is the dominant ion.

The negative ions were generated in a helium carrier gas by the impact of electrons (~75 eV) and helium metastables on the appropriate neutral gas: H^- (NH_3 or CH_4), D^- (CD_4), OH^- (H_2O), C_2H^- (C_2H_2), NH_2^- (NH_3), CH_3O^- (CH_3OH). H^- and D^- were also produced by the proton-transfer reaction of NH_2^- with H_2 and D_2, respectively.

The gases used were helium (Linde, Prepurified Grade, 99.995% He), hydrogen (Linde, Very Dry Grade, 99.95% H_2), nitrogen (Matheson, Prepurified Grade, 99.998% N_2), carbon monoxide (Matheson, CP Grade, 99.5% CO), carbon dioxide (Matheson Coleman Grade, 99.99% CO_2), nitrous oxide (Matheson, 98.0% N_2O), acetylene (Matheson, Purified Grade, 99.6% C_2H_2), methane (Matheson, Ultra High Purify, 99.97% CH_4), ammonia (Matheson, anhydrous, 99.99% NH_3), distilled water, methanol (BDH Chemicals, Analytical Reagent Grade), and methyl cyanide (Matheson Coleman and Bell, Spectroquality Grade). The HCN was prepared by the action of sul-

TABLE I: Rate Constants (in units of 10^{-9} cm^3 molecule^{-1} s^{-1}) at 297 ± 2 K for Reactions of the Type $XH^+ + Y \rightarrow YH^+ + X$

XH^+	Y	k_{expt}[a]	k_L[b]	k_{LD}[c]	k_{ADO}[d]	k_{expt}/k_{ADO}	$-\Delta H°_{298}$,[e] kcal mol^{-1}
H_3^+	HCN	7.4 ± 0.5 (5)	2.29	18.9	6.48	1.1	69 ± 4
H_3O^+	HCN	3.5 ± 0.5 (7)	1.13	9.35	3.20	1.1	5 ± 2
N_2H^+	HCN	3.2 ± 0.2 (5)	1.01	8.35	2.86	1.1	53 ± 4
HCO^+	HCN	3.0 ± 0.2 (3)	1.01	8.35	2.86	1.0	27 ± 4
H_3^+	CH_3CN	10 ± 1 (9)	2.98	24.5	8.40	1.2	85 ± 2
H_3O^+	CH_3CN	4.7 ± 0.7 (18)	1.39	11.4	3.91	1.2	21 ± 4
N_2H^+	CH_3CN	4.1 ± 0.1 (2)	1.21	9.98	3.42	1.2	69 ± 3
HCO^+	CH_3CN	4.1 ± 0.4 (8)	1.21	9.98	3.42	1.2	43 ± 3
N_2OH^+	CH_3CN	3.8 ± 0.2 (5)	1.08	8.88	3.05	1.2	48 ± 3
CO_2H^+	CH_3CN	4.1 ± 0.7 (5)	1.08	8.88	3.05	1.3	57 ± 3

[a] The mean value and the precision of the measurements. The number of measurements is given in parentheses. The accuracy is estimated to be better than ±20% (HCN) and ±25% (CH_3CN). [b] Langevin theory. [c] Locked-dipole theory. [d] Average-dipole-orientation theory (the $\cos\theta$ model), $C = 0.252$. [e] Proton affinities adopted for the determination of $\Delta H°_{298}$ are given in Table III.

TABLE II: Rate Constants (in units of 10^{-9} cm^3 molecule^{-1} s^{-1}) at 297 ± 2 K for Reactions of the Type $YH + X^- \rightarrow XH + Y^-$

YH	X^-	k_{expt}[a]	k_L[b]	k_{LD}[c]	k_{ADO}[d]	k_{expt}/k_{ADO}	$-\Delta H°_{298}$,[e] kcal mol^{-1}
HCN	H^-	15 ± 2 (13)	3.82	31.7	10.8	1.4	50 ± 2
HCN	D^-	9.9 ± 0.3 (2)	2.76	22.9	7.8	1.3	50 ± 2
HCN	NH_2^-	4.8 ± 0.5 (8)	1.19	9.85	3.37	1.4	54 ± 2
HCN	OH^-	4.1 ± 0.3 (9)	1.17	9.67	3.31	1.2	41 ± 1
HCN	C_2H^-	3.9 ± 0.2 (5)	1.05	8.67	2.97	1.3	29 ± 4
HCN	SH^-	2.9 ± 0.3 (2)	0.978	8.10	2.77	1.0	1.0 ± 0.2[f]
CH_3CN	H^-	13 ± 2 (8)	5.04	41.5	14.2	0.92	25 ± 4
CH_3CN	D^-	9.9 ± 1.6 (5)	3.62	29.8	10.2	0.97	25 ± 4
CH_3CN	NH_2^-	5.1 ± 0.2 (6)	1.47	12.1	4.16	1.2	29 ± 4
CH_3CN	OH^-	4.4 ± 0.2 (7)	1.44	11.8	4.07	1.1	16 ± 4
CH_3CN	C_2H^-	1.5 ± 0.2 (9)	1.27	10.4	3.58	0.42	4.1 ± 0.9[f]
CH_3CN	CH_3O^-	3.5 ± 0.3 (5)	1.19	9.79	3.36	1.0	6.3 ± 1.6[f]

[a] The mean value and the precision of the measurements. The number of measurements is given in parentheses. The accuracy is estimated to be better than ±20% (HCN) and ±25% (CH_3CN). [b] Langevin theory. [c] Locked-dipole theory. [d] Average-dipole-orientation theory (the $\cos\theta$ model), $C = 0.252$. [e] Proton affinities adopted for the determination of $\Delta H°_{298}$ are given in Table III. [f] Based on measurements of the equilibrium constant for the proton transfer reaction, ref 13, and unpublished results from this laboratory.

furic acid on an aqueous solution of KCN,[12] dried by passing it over anhydrous $CaCl_2$, and further purified by distillation in vacuo.

Results and Discussion

The rate constants measured for reactions of type 1 are summarized in Table I. Their determination from the decay of the primary ion, XH^+, was straightforward. Proton transfer was observed to be the dominant (>90%) channel in each case. There were no other obvious primary reaction channels. For several of the reactions with CH_3CN other channels of the type

$$XH^+ + CH_3CN \rightarrow CH_3X^+ + HCN \quad (4a)$$

$$\rightarrow H_2CN^+ + CH_2X \quad (4b)$$

are exothermic but apparently do not compete effectively at room temperature with proton transfer. Secondary reactions of H_2CN^+ and CH_3CNH^+ were observed to occur at large additions of HCN and CH_3CN and result in the formation of the cluster ions $H^+(HCN)_2$ and $H^+(CH_3CN)_2$, respectively.

The results of the measurements of the rate constants for reactions of type 2 are included in Table II. Proton transfer was again observed to be the dominant reactions channel. For the reactions with HCN and CH_3CN the only product ions observed were CN^- and CH_2CN^-, respectively, and there was no evidence for the formation of reactive intermediates. For the reactions of X^- with CH_3CN these observations imply that proton transfer dominates at room temperature over nucleophilic displacement of the type

$$X^- + CH_3CN \rightarrow CH_3X + CN^- \quad (5a)$$

$$\rightarrow CH_2XCN + H^- \quad (5b)$$

TABLE III: Proton Affinities Adopted in the Determination of $\Delta H°_{298}$

X	PA, kcal mol^{-1}	Ref	X^-	PA, kcal mol^{-1}	Ref
H_2	101 ± 1	22	NH_2^-	404 ± 1	27
N_2	117 ± 1	23	H^-, D^-	400 ± 1	28
CO_2	129 ± 2	23	OH^-	391	28
N_2O	138 ± 2	23	C_2H^-	379 ± 3	23
CO	143 ± 1	24	$^-CH_2CN$	375 ± 3	23
H_2O	165 ± 3	25	SH^-	351 ± 1	13
HCN	170 ± 3	26	CN^-	350 ± 1	13
CH_3CN	186 ± 1	26			

CN^- was monitored but there was no evidence for its production via reaction 5a which is exothermic for all of the anions investigated. This contrasts the behavior previously observed in this laboratory for the reactions of these anions with halogenated methanes for which displacement was found to be the dominant channel in most instances.[14] Also there was no evidence for the production of H^- via channel 5b. This channel is athermal for X = H and could not be identified in this case since the mass spectrometer cannot distinguish between reactant and product H^- ions. However, the experiments with D^- in which H^- was monitored showed no evidence for the occurrence of channel 5b.

The proton-transfer reactions of both types 1 and 2 investigated in this study represent some of the fastest ion–molecule reactions observed to date. The rate constants, which have to our knowledge not been determined previously, are generally quite large, spanning the range 0.15 to 1.5×10^{-8} cm^3 $molecule^{-1}$ s^{-1}. Only the proton transfer reactions between CH_3CN and N_2H^+ and OH^- were observed previously by Gray[15] in an ion cyclotron resonance spectrometer although their rate constants were not reported.

Included in Tables I and II are the capture rate constants calculated according to three classical models of ion–molecule collisions involving polar and nonpolar molecules. The average-dipole-orientation (ADO) theory of Su and Bowers[6–8] predicts capture rate constants determined by the expression

$$k_{ADO} = (2\Pi q/\mu^{1/2})[\alpha^{1/2} + C\mu_D(2/\Pi kT)^{1/2}] \qquad (6)$$

where q is the charge on the ion, μ is the reduced mass of the reactants, α is the polarizability, and μ_D the permanent dipole moment of the neutral. C has been parameterized by Su and Bowers[8] to have a value between 0 and 1. Expression 6 reduces to the locked-dipole (LD) limit, k_{LD}, when $C = 1$.[16,17] The Langevin (L) expression, k_L, results when $\mu_D = 0$.[5] The three classical theories define straight lines on a plot of k vs. $\mu^{-1/2}$ for series of homologous reactions of types 1 and 2 for which the neutral substrate remains unchanged. This is illustrated for the reactions with HCN and CH_3CN in Figures 1 and 2 in which the measured reaction rate constants are compared with the capture rate constants predicted by the three theories. The values for the permanent dipole moments for HCN (μ_D = 2.98 D) and CH_3CN (μ_D = 3.92 D) were taken from the compilation of Nelson et al.[18] The experimental value of α = 2.59 Å^3 was adopted for HCN.[19] The average polarizability of CH_3CN, α = 4.56 Å^3, was determined from the average polarizability of its bonds.[19] The appropriate value of C = 0.252 for both HCN and CH_3CN was determined from the table given by Bass et al.[8] (the $\overline{\cos\theta}$ model).

It is evident from the comparisons between reaction and collision rate constants shown in Figures 1 and 2 that the high values of the thermal energy proton-transfer rate constants measured in this study are most adequately accounted for by the average-dipole-orientation theory which attributes 65% of the collision rate for these reactions to ion–permanent dipole interaction. The Langevin theory which ignores ion–permanent dipole interaction clearly underestimates the collision rate whereas the locked-dipole theory appears to overestimate the collision rate. These results reinforce the general observation that ADO theory usually provides the most realistic collision rate for proton transfers.[4]

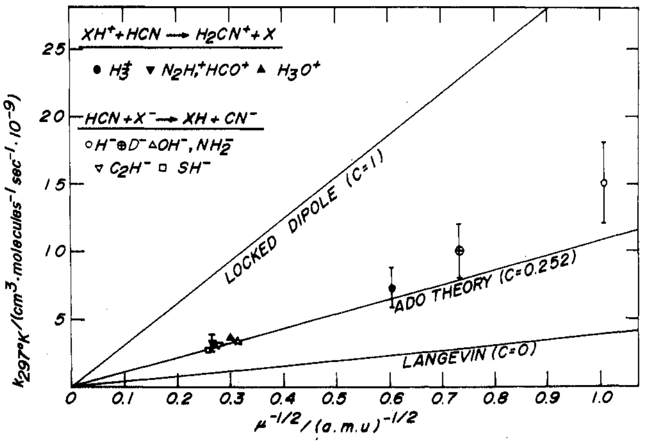

Figure 1. A comparison of measured rate constants with capture rate constants predicted by recent classical theories for proton transfer reactions with HCN (α = 2.59 Å^3, μ_D = 2.98 D) at 297 ± 2 K. The solid bars represent the estimated accuracy (±20%) of the measurements.

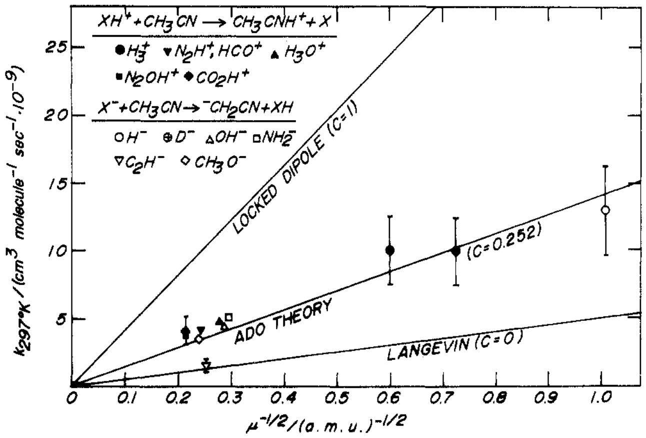

Figure 2. A comparison of measured rate constants with capture rate constants predicted by recent classical theories for proton-transfer reactions with CH_3CN (α = 4.56 Å^3, μ_D = 3.92 D) at 297 ± 2 K. The solid bars represent the estimated accuracy (±25%) of the measurements.

Notwithstanding the uncertainty in the rate constant measurements, a closer inspection of the values for k_{expt}/k_{ADO} obtained in this study suggests that the ADO theory itself may slightly underestimate the collision rate. 16 of the 22 rate constants measured exceed k_{ADO} by at least 10% and as much as 40%. These small differences appear to be significant. A similar disparity has recently been reported by Mackenzie Peers and Muller[20] for positive ion–molecule reactions with dimethyl sulfoxide (α = 7.96 Å^3, μ_D = 3.96 D). The rate constants for these reactions measured with a single-source "medium pressure" mass spectrometer were found to exceed the ADO values by ~30%. Bowers and Su[21] have recently commented on possible shortcomings in their theory and have indicated that more refined calculations will soon be forthcoming. For example, the theoretical model is being extended to include the induced dipole–induced dipole interaction arising from the polarizability of the ion which would lead to an enhanced collision rate. This enhancement is likely to be larger for negative ions. Indeed we observe the largest positive deviations from the ADO predictions for the reactions of anions with HCN, viz. type 2a. An explanation for the smaller deviations observed for the reactions of anions with CH_3CN, viz. type 2b, can be found in the discussion given below.

Earlier studies of homologous series of proton-transfer reactions have indicated that the assumption of unit reaction efficiency may break down at low reaction exothermicities.[9,10] When this is the case, the measured reaction rate constant will

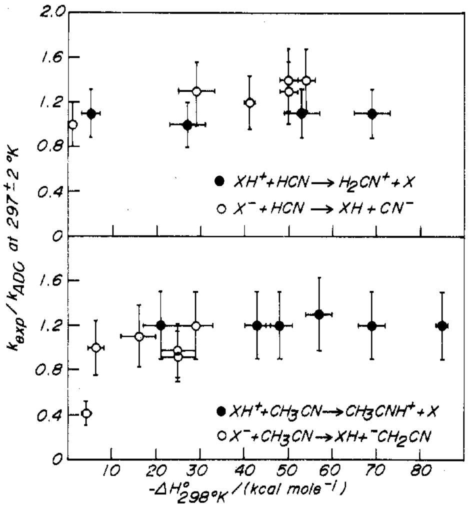

Figure 3. A plot of the ratio of the measured proton-transfer rate constant to the calculated capture (ADO) rate constant as a function of the heat of reaction, $-\Delta H^\circ_{298}$.

provide a less meaningful test of collision theory in that it indicates only a lower limit to the collision rate. Comparisons with collision theory should therefore, be confined to those reactions of a homologous series for which $k_{\mathrm{expt}}/k_{\mathrm{ADO}}$ has been demonstrated to be independent of ΔH°_{298}. 15 of the 16 reactions alluded to above fall into this category. Figure 3 explores the variation of reaction efficiency with exothermicity for all of the reactions investigated in this study. The homologous series of proton-transfer reactions of type 1a and 1b show no dependence of $k_{\mathrm{expt}}/k_{\mathrm{ADO}}$ on the heat of reaction. For the proton-transfer reactions of types 2a and 2b the least exothermic member of each series, viz. SH^- + HCN and C_2H^- + CH_3CN, respectively, exhibits the lowest reaction efficiency. For the reactions of type 2a $k_{\mathrm{expt}}/k_{\mathrm{ADO}}$ becomes independent of ΔH°_{298} for values ≤ -29 kcal mol^{-1} whereas $k_{\mathrm{expt}}/k_{\mathrm{ADO}}$ increases gradually for all of the reactions of type 2b for which $\Delta H^\circ_{298} \geq -29$ kcal mol^{-1}.

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References and Notes

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