RATE CONSTANTS AT 297°K FOR PROTON TRANSFER REACTIONS WITH NH_3. COMPARISONS WITH CLASSICAL THEORIES AND EXOTHERMICITY*

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Rate constants for proton transfer reactions of the type $XH^+ + NH_3 \rightarrow NH_4^+ + X$ where $X = H_2, NH_2, CH_4, H_2O, CO, N_2, C_2H_4, C_2H_6, C_3H_6, N_2O$ and C_4H_8 have been measured at 297°K using the flowing afterglow technique. These rate constants and others measured previously in this laboratory for proton transfer reactions involving molecules of lower dipole moment than NH_3 were found to compare favourably with predictions of the average-dipole-orientation theory ($\mu_D \neq 0$) and the Langevin theory ($\mu_D = 0$). The ratio k_{exp}/k_{theor} was found to be ca. 1 and relatively independent of the exothermicity of the reaction in the range 0 to 109 kcal $mole^{-1}$.

1. Introduction

The recent formulation [1] and parameterization [2] by Su and Bowers of the average-dipole-orientation (ADO) theory for ion–polar molecule collisions prompted us to extend our own studies of the kinetics of proton transfer reactions to a measurement of the rates of a series of such reactions with NH_3. These measurements with a reactant possessing a large permanent dipole† complement earlier studies made in this laboratory of proton transfer reactions involving non-polar and slightly polar molecules and, together with these earlier results, provide an opportunity to assess the capture rate constants predicted by classical models of ion–molecule reactions, viz., the Langevin theory [4], the locked-dipole limit [5, 6], and the ADO theory [1, 2]. The systems studied encompass a wide range of mass, chemical composition and physical dimension for the ions and neutral reactants, as well as polarizability and dipole moment for the neutral species. Comparisons with the classical theories as well as empirical correlations should, therefore, lead to an appreciation of the extent to which such factors determine the rates of proton transfer reactions.

A secondary purpose of this study, prompted in part by a recent report by Solka and Harrison [7], was to appraise the effect of exothermicity on the rates of such reactions. Since NH_3 has a very high proton affinity it is a particularly good choice for studying highly exothermic proton transfer reactions. The exothermicity for these reactions which are all of the type:

$$XH^+ + Y \rightleftharpoons YH^+ + X \qquad (1)$$

can be specified from a knowledge of the difference in the proton affinity, PA, of X and Y since the exothermicity, ΔH^0_{298}, of reaction (1) is given by

$$\Delta H^0_{298} = PA(X) - PA(Y) . \qquad (2)$$

The experimental determination of the proton affinities relevant in this connection has been and continues to be the subject of a separate study in this laboratory [8–10].

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† All polarizabilities and permanent dipole moments were taken from ref. [3].

2. Experimental

The experiments were performed with a flowing afterglow system [8] in which the ions are allowed to thermalize to the ambient room temperature of 297 ± 2°K prior to their entry into the reaction region. The reactant ions XH^+ were generated in the following manner: H_3^+ is the dominant ion in a hydrogen afterglow [11]. The downstream addition of the appropriate gas X results in the rapid formation by proton transfer of the desired ions $XH^+ = CH_5^+, H_3O^+, COH^+, N_2H^+, C_2H_7^+$ and N_2OH^+. The addition of C_2H_6 also results in the formation of $C_2H_5^+$ by the H^- transfer reaction [11]

$$H_3^+ + C_2H_6 \rightarrow C_2H_5^+ + 2H_2\ . \qquad (3)$$

Large additions of C_2H_6 produce the ions $C_3H_7^+$ and $C_4H_9^+$ by the condensation reactions [11]

$$C_2H_5^+ + C_2H_6 \xrightarrow{0.9} C_4H_9^+ + H_2\ , \qquad (4a)$$

$$\xrightarrow{0.1} C_3H_7^+ + CH_4\ . \qquad (4b)$$

NH_3^+ was generated by the charge transfer reactions

$$O_2^+(O^+) + NH_3 \rightarrow NH_3^+ + O_2(O)\ . \qquad (5)$$

O_2^+ ions are produced when O_2 is added to a He–Ar afterglow [10] while both O_2^+ and O^+ are formed when O_2 is added to a pure He afterglow [12].

The rate constants were measured in the usual manner [8]. The absolute accuracy of the measurements is estimated to be ±20% and the precision was observed to be better than ±10%.

3. Results and discussion

The measured rate constants for 11 reactions of XH^+ with NH_3 are listed in table 1. The formation of NH_4^+ appeared to be the dominant (≥ 90%) channel in each case.

Agreement with previous flowing afterglow measurements is satisfactory. However, the earlier determination [12] of $k = 1.6 \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1} for the reaction of NH_3^+ with NH_3 should be regarded as a lower limit since it appears that substantial amounts of NH_3 were still being generated by O^+ and O_2^+ in the reaction region at the flows of NH_3 employed. The present value of 2.5×10^{-9} cm^3 molecule^{-1} sec^{-1} is remarkably consistent with a smooth extrapolation of recent measurements using electron impact [13,14] and photoionization [15, 16] techniques which indicate a dependence of the rate constant on the internal and translational energy of NH_3^+. A dependence on the internal energy of the ion has also recently been reported [17, 18] for the rate constant of the reaction of $C_4H_9^+$ with NH_3. Here again it appears that the rate constant increases with decreasing internal energy and that as in the case of the NH_3^+ reaction, our value represents a thermal energy limit although different geometric isomers of $C_4H_9^+$ may have been involved in the various measurements. The results for the proton transfer reactions of CH_5^+, $C_2H_5^+$ and $C_3H_7^+$ with NH_3 agree with those obtained with the ion cyclotron resonance (ICR) method although the latter technique may involve reactants with non-Boltzmann distributions [19].

Included in table 1 are capture rate constants calculated on the basis of three classical models of ion–molecule reactions involving polar and non-polar molecules. According to the ADO theory of Su and Bowers [1], the capture rate constant is given by the expression:

$$k_{\mathrm{ADO}} = (2\pi q/\mu^{1/2})[\alpha^{1/2} + C\mu_{\mathrm{D}}(2/\pi kT)^{1/2}]\ , \qquad (6)$$

where q is the charge on the ion, α is the polarizability, μ_{D} the permanent dipole moment of the neutral reactant, and μ is the reduced mass. C is a parameter which reflects the average orientation of the dipole, is a function of $\mu_{\mathrm{D}}/\alpha^{1/2}$ at constant temperature and has been parameterized by Su and Bowers [2] to have a value between 0 and 1. When $C = 1$, expression (6) reduces to the locked-dipole limit [5, 6]. The Langevin expression [4] results when $C = 0$.

Table 2 presents further comparisons between calculated capture rate constants and rate constants measured in this laboratory for proton transfer reactions involving neutral substrates of low or zero dipole moment and various polarizabilities.

Fig. 1 shows the correlation between the ratio of the experimental to the theoretical rate constant with the exothermicity, $-\Delta H^0$, of the proton transfer reactions listed in tables 1 and 2. The dotted line represents the variation observed by Solka and Harrison [7] of $k_{\mathrm{exp}}/k_{\mathrm{LD}}$ with exothermicity for proton transfer reactions of the type

Table 1
Rate constants in units of 10^{-9} cm^3 molecule^{-1} sec^{-1} at 297 ± 2°K for reactions of the type $XH^+ + NH_3$ a) → $NH_4^+ + X$

XH^+	k_{exp}		k_L b)	k_{LD} c)	k_{ADO} d)	$\frac{k_{exp}}{k_{ADO}}$	$-\Delta H^0_{298}$ e) (kcal mole^{-1})
	this work	other					
H_3^+	4.2	≈3.6 f)	2.16	10.6	3.98	1.1	109
NH_3^+	2.5	1.00–3.26 g)	1.18	5.79	2.18	1.1	20
CH_5^+	2.5	2.33 h)	1.18	5.79	2.18	1.1	81
H_3O^+	2.4		1.15	5.64	2.12	1.1	42
COH^+	2.4		1.05	5.16	1.94	1.2	69
N_2H^+	2.3		1.05	5.16	1.94	1.2	96
$C_2H_5^+$	2.1	2.00 h)	1.05	5.16	1.94	1.1	48
$C_2H_7^+$	2.0		1.04	5.10	1.92	1.0	68
$C_3H_7^+$	1.9	1.95 h)	0.986	4.84	1.82	1.0	25–44 i)
N_2OH^+	2.1		0.980	4.81	1.81	1.2	73
$C_4H_9^+$	1.9	0.90 j), 0.91–1.40 k)	0.951	4.67	1.75	1.1	20–52 i)

a) α = 2.16 Å^3 and μ_D = 1.47 D, ref. [3]. b) Langevin theory. c) Locked-dipole theory. d) ADO theory. e) PA(NH_3, H_2O) were taken from ref. [21]. PA(NH_2, C_2H_4, C_3H_6, C_4H_8) were derived from heats of formation in ref. [22]. PA(H_2, CH_4, CO, N_2, C_2H_6, N_2O) were determined in this laboratory, unpublished results. f) Ref. [11]. g) For a detailed compilation of previous measurements of the rate constant and its dependence on the internal energy of NH_3^+ see ref. [13]. h) Ref. [2]. i) Value depends on assumed geometry of reactants and products. j) Ref. [18]. k) Ref. [17]. $C_4H_9^+$ is generated by electron impact from a number of different sources and at various electron energies.

Table 2
Rate constants (in units of 10^{-9} cm^3 molecule^{-1} sec^{-1}) at 300°K for reactions of the type $XH^+ + Y \rightarrow YH^+ + X$

XH^+	Y	k_{exp}	k_L a)	k_{LD} b)	k_{ADO} c)	$\frac{k_{exp}}{k_L \text{ or } k_{ADO}}$	α (Å^3) d)	μ_D (D) d)	$-\Delta H^0_{298}$ e) (kcal mole^{-1})
H_3^+	NO	1.4 f)	1.85	4.27	1.88	0.74	1.70	0.16	27
	N_2	1.8 g)	1.88	–	–	0.96	1.74		13
	CO	1.4 f)	1.98	2.54	1.99	0.70	1.94	0.1	40
	CO_2	1.9 f)	2.25	–	–	0.84	2.59		27
	CH_4	1.6 f)	2.36	–	–	0.68	2.56		28
	N_2O	1.8 f)	2.39	3.32	2.41	0.75	2.92	0.17	36
CH_5^+	N_2O	0.95 h)	1.14	1.59	1.15	0.83	2.92	0.17	8
N_2H^+	CO_2	0.92 f)	0.90	–	–	1.0	2.59		15
	Xe	0.66 h)	0.96	–	–	0.69	4.02		0.3
	N_2O	0.79 f)	0.96	1.32	0.97	0.82	2.92	0.17	23
	CH_4	0.89 f)	1.17	–	–	0.76	2.56		16
CO_2H^+	CH_4	0.76 i)	1.09	–	–	0.70	2.56		1.5
N_2OH^+	CO	0.50 i)	0.79	1.01	0.79	0.63	1.94	0.1	3.5
	C_2H_6	1.06 h)	1.16	–	–	0.91	4.39		5
KrH^+	N_2	0.58 h)	0.67	–	–	0.87	1.74		12

a) Langevin theory. b) Locked-dipole theory. c) ADO theory. d) Ref. [3]. e) Calculated from differences in proton affinities determined in this laboratory, unpublished results. f) Ref. [11]. g) Ref. [8]. h) Unpublished result from this laboratory. i) Ref. [9].

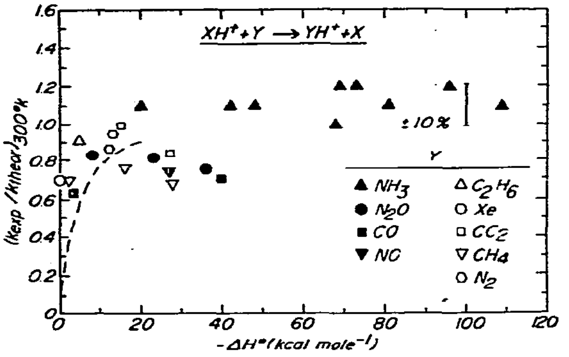

Fig. 1. A comparison at 300°K of the ratio of the experimental to the theoretical rate constant with the exothermicity, $-\Delta H^0$ for simple proton transfer reactions of the type $XH^+ + Y \rightarrow YH^+ + X$. For the nature of the ions XH^+ see tables 1 and 2. For the molecules, Y, denoted with open symbols $\mu_D = 0$ and $k_{theor} = k_L$; for the molecules denoted with solid symbols $\mu_D \neq 0$ and $k_{theor} = k_{ADO}$. The dashed curve represents the variation of k_{exp}/k_{LD} with $-\Delta H^0$ observed by Solka and Harrison [7] at ion energies = 0.43 V (lab) for reactions of the type $CH_3SH_2^+ + Y \rightarrow YH^+ + CH_3SH$ for a series of polar molecules, Y.

$$CH_3SH_2^+ + Y \rightarrow YH^+ + CH_3SH\ . \qquad (7)$$

These measurements were made with the trapped-ion technique at ion energies = 0.43 V (lab) for a series of polar molecules, Y, with permanent dipole moments in the range 1.30 to 2.88 debye.

All the proton transfer reactions listed in tables 1 and 2 are fast, spanning the range $k = 0.5$ to 4.2×10^{-9} cm^3 molecule^{-1} sec^{-1} and indicating that the physical and chemical characteristics of the reactants can at best play only a minor role in determining the magnitude of the rate constant at 300°K. A test for the effect of reduced mass is provided by the reactions with H_3^+ for which the reduced masses are essentially equal. The rate constants are considerably larger than those for the same neutral species reacting with other ions. Another test is provided by comparison of those reactions involving the same neutral (thereby ensuring a constant α and μ_D) with different ions. For the series of reactions with NH_3 only a small trend with the mass of the ion is evident. For the few examples involving N_2O and CH_4, a larger effect is seen. Inspection of reactions involving the same ion but different neutrals indicate that the physical properties (e.g., the polarizability or the permanent dipole moment) of the neutral over-ride the effect of reduced mass. A comparison of the rate constants for the sequences of identical mass ions COH^+, N_2H^+, $C_2H_5^+$ and CH_5^+, NH_3^+ reacting with NH_3 shows little if any effect of the chemical composition or physical dimension of the ion. The largest effect appears to be attributable to the permanent dipole moment: the reactions with NH_3 are at least twice as fast as reactions with a comparable reduced mass but with neutrals of zero or small dipole moments.

The measured rate constants of the proton transfer reactions involving non-polar molecules are, on the average, ca. 20% lower than the Langevin capture rate constants whereas for reactions involving NH_3, the experimental values are roughly twice the Langevin value. For all the reactions involving polar molecules, k_{exp} is substantially smaller than the locked-dipole limit, k_{LD}. Consequently, it appears that in this series of reactions the rotation of the molecules at 300°K is sufficient to prevent a total alignment of the dipole in the electric field of the ion.

The rate constants of the reactions involving polar molecules measured in the flowing afterglow are in reasonable accord with the predictions of the ADO theory. Some specific trends are evident. The experimental values for the reactions with NH_3 (μ_D = 2.16 debye) appear to be consistently higher than the ADO values by ca. 10%. This trend is also evident in the measurements reported by Su and Bowers [20] for proton transfer reactions of CH_5^+ with alkyl chlorides (μ_D ca. 2 debye). In contrast to the observations of Su and Bowers [17] and Hellner and Sieck [18], the reaction of $C_4H_9^+$ [produced by reaction (4a)] with NH_3 is not anomalous. For the reactions involving molecules with small permanent dipoles (viz., NO, CO and N_2O for which μ_D is ca. 0.2 debye) the ADO and Langevin theories predict similar results. The experimental values, therefore, are smaller than those predicted by either theory by ca. 25%.

The experimental rate constants are quite insensitive to the exothermicity of the proton transfer reaction and no marked trend at low exothermicities is observed.

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