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RATE COEFFICIENTS AT 297 K FOR PROTON TRANSFER REACTIONS WITH H_2O. COMPARISONS WITH CLASSICAL THEORIES AND EXOTHERMICITY*

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Rate coefficients for proton transfer reactions of the type $XH^+ + H_2O \rightarrow H_3O^+ + X$ where X = H_2, CH_4, CO, N_2, CO_2 and N_2O and the type $H_2O + X^- \rightarrow XH + OH^-$ where X = H, NH_2 and C_2H_5NH have been measured at 297 K using the flowing afterglow technique. The results compare favourably with the predictions of the average-dipole-orientation theory. A trend is observed with exothermicity on a plot of $(k_{exp}/k_{ADO})_{298\,K}$ versus $-\Delta H^0_{298\,K}$. The question is raised whether the relatively low probability observed for slightly exothermic proton transfer reactions is a consequence of reaction mechanism or results from the presence of a small activation energy barrier.

1. Introduction

As part of a continuing program directed towards the systematic assessment of current theories of ion–molecule reactions [1,2] we have extended our measurements of reaction rate coefficients for proton transfer to a series of reactions with H_2O involving both the transfer of a proton from an ion to H_2O:

$$XH^+ + H_2O \rightarrow H_3O^+ + X \tag{1}$$

and the transfer of a proton from H_2O to an ion:

$$H_2O + X^- \rightarrow XH + OH^- . \tag{2}$$

Comparisons of measured reaction rate coefficients with capture (collision) rate coefficients predicted by classical models of ion–molecule collisions, viz. the Langevin theory [3], the locked-dipole theory [4,5], and the average-dipole-orientation (ADO) theory [6,7], provide insight into any natural limitations of these models. Upon the assumption that these models adequately predict the collision rate such comparisons also allow the identification of the possible presence of energies or entropies of activation.

Proton transfer reactions in general also provide a unique opportunity to explore the effect of excess energy in the form of reaction exothermicity upon the rates for a series of ion–molecule reactions different in exothermicity but otherwise quite similar and generally not subject to restrictive activation energy or entropy barriers. For reactions (1) and (2) the choice available in practice affords control of reaction exothermicity from 7 to 64 kcal mole^{-1}.

Especially intriguing is the proton transfer reaction

$$H_2O + H^- \rightarrow H_2 + OH^- , \tag{3}$$

which was the first example reported of a negative ion–molecule reaction [8]. Stockdale et al. [9,10] studied this reaction in a pulsed source time-of-flight mass spectrometer and reported an unusually large value for the rate coefficient of $(5.1 \pm 1.6) \times 10^{-7}$ cm^3 molecule^{-1} s^{-1} ($E_{lab}(H^-) \approx 0$ eV) whereas the conventional ion source experiments and double mass spectrometer experiments (at 0.6 eV) of Paulson [11] led to values of 4.6×10^{-9} and 1.5×10^{-9} cm^3 molecule^{-1} s^{-1}, respectively, for the rate coefficient of the isotopic analogue

$$D_2O + D^- \rightarrow D_2 + OD^- . \tag{4}$$

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2. Experimental

The experiments were performed with a flowing afterglow system [12] in which the ions are allowed to thermalize by collision with the carrier gas molecules to the ambient temperature of 297 ± 2 K prior to their entry into the reaction region. In the studies of reactions of type (1) and (2) hydrogen and helium were used as the carrier gas, respectively. Total gas pressures were in the range 0.24 to 0.67 torr. The effective length of the reaction region had values of 59 and 85 cm. The proton donors $XH^+ = CH_5^+$, HCO^+, N_2H^+, N_2OH^+ and CO_2H^+ were generated by proton transfer reactions of the type

$$H_3^+ + X \rightarrow XH^+ + H_2 \qquad (5)$$

as a result of the downstream addition of the appropriate gas X into a hydrogen plasma in which H_3^+ was initially the dominant ion. H_3^+ is formed by the fast reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H\,. \qquad (6)$$

The proton acceptors X^- were generated by dissociative ionization with ca. 35 eV electrons: H^- from CH_4, NH_2^- from NH_3, and $C_2H_5NH^-$ from $C_2H_5NH_2$.

H_2O was added into the reaction region as a ca. 10% mixture of H_2O vapor in helium. The mixtures were prepared by allowing the H_2O vapor to equilibrate in the gas inlet system to the ambient room temperature (at a pressure $\lesssim 0.8$ of the vapor pressure) and subsequently adding the helium. The viscosity of the mixture was determined by comparing its flow through a capillary with the flow of pure helium.

The gases used were helium (Linde, Prepurified Grade, 99.995% He), hydrogen (Linde, 99.95% H_2), methane (Matheson, Ultra High Purity, 99.97% CH_4), nitrogen (Liquid Carbonic, High Purity, 99.995% N_2), carbon monoxide (Matheson, C.P. grade, 99.5% CO), ammonia (Matheson, anhydrous, 99.99% NH_3), monoethyl amine (Matheson, 98.5% $C_2H_5NH_2$), nitrous oxide (Matheson, 98.0% N_2O), and carbon dioxide (Matheson, Coleman Grade, 99.99% CO_2).

The rate coefficients were measured in the usual manner [12]. The absolute accuracy is estimated to be ±25% and the precision was observed to be better than ±10%.

Table 1.
Rate constants in units of 10^{-9} cm^3 molecule^{-1} s^{-1} at 297 ± 2 K for reactions of the type $XH^+ + H_2O$ a) $\rightarrow H_3O^+ + X$ and $H_2O + X^- \rightarrow OH^- + XH$

XH^+ or X^-	k_{exp}		k_L c)	k_{LD} d)	k_{ADO} e)	$\frac{k_{exp}}{k_{ADO}}$	$-\Delta H^0_{298\,K}$ f) (kcal mole^{-1})
	this work b)	others					
H_3^+	4.3 (2)		1.76	12.4	4.39	0.98	64
CH_5^+	3.7 (3)		0.954	6.71	2.38	1.6	37
HCO^+	3.2 (9)		0.846	5.95	2.11	1.5	26
N_2H^+	2.6 (4)	8 g) 2.5 ± 0.7 h)	0.846	5.95	2.11	1.2	51
N_2OH^+	2.8 (5)		0.789	5.53	1.96	1.4	29
CO_2H^+	3.0 (3)		0.789	5.53	1.96	1.5	38
H^-	3.7 (4)	$\geqslant 0.05$ i) $(5.4 \pm 1.6) \times 10^2$ j)	2.90	20.4	7.23	0.51	8
NH_2^-	2.6 (2)	$\geqslant 0.05$ i)	0.969	6.81	2.42	1.1	12
$C_2H_5NH^-$	2.4 (2)		0.789	5.55	1.97	1.2	8

a) $\alpha = 1.45$ Å^3, $\mu_D = 1.84$D, ref. [13].
b) The accuracy of the measurements is estimated to be better than ±25%. The number of measurements is given in parentheses.
c) Langevin theory.
d) Locked-dipole theory.
e) ADO theory, $C = 0.248$.
f) The values of ΔH^0_{295} are believed to be reliable to within approximately ±5 kcal mole^{-1}. PA(H_2O) = 165 ± 3 kcal mole^{-1}, ref. [14]. PA(H_2) = 101 kcal mole^{-1}, ref. [15]. PA(CH_4, CO, N_2, N_2O, CO_2) were determined in this laboratory, ref. [2] and unpublished results. PA(OH^-) = 392.1 ± 0.3 kcal mole^{-1}. PA(H^-) = 400.4 ± 0.5 kcal mole^{-1}. PA(NH_2^-, $C_2H_5NH^-$) were determined in this laboratory, ref. [16] and unpublished results.
g) Ref. [17]. h) Ref. [18]. i) Ref. [19]. j) Refs. [9,10].

3. Results and discussion

The measured rate coefficients for 6 reactions of XH^+ with H_2O and 3 reactions of H_2O with X^- are summarized in table 1. Proton transfer was observed to be the dominant ($\geqslant 90\%$) channel in each case. The rate coefficient for the reaction of N_2H^+ with H_2O is in excellent agreement with the value determined recently by Bolden et al. [18] with their flowing afterglow apparatus. The results for the reactions of H^- and NH_2^- with H_2O are consistent with the lower limits reported previously by Young et al. [19]. Our result for reaction (3) does not corroborate the large value reported by Stockdale et al. [9,10] which exceeds the capture rate coefficient predicted by the "locked-dipole" theory [4,5] by more than an order of magnitude. The result obtained by Paulson [11] for reaction (4) appears more plausible.

Table 1 includes the capture rate coefficients deduced from the three classical models of ion–molecule collisions according to which the capture rate coefficient can be expressed as

$$k_c = 2\pi e(\alpha/\mu)^{1/2} + C(2\pi e\mu_D/\mu)(2\mu/\pi kT)^{1/2}\,, \qquad (7)$$

where e is the charge on the ion, μ the reduced mass of the collidants, α is the polarizability and μ_D is the permanent dipole moment of the neutral molecule. Eq. (7) is composed of the familiar Langevin term [3] and a "correction" term reflecting the ion–permanent dipole interaction. In the ADO theory [6,7] C is a measure of the extent to which the dipole is orientated with respect to the direction of the approaching ion. For $C = 1$, eq. (7) reduces to the "locked-dipole" limit [4,5]. For a series of reactions of type (1) and (2) for which the neutral reactant remains fixed, the three classical theories define three straight lines on a plot of k versus $\mu^{-1/2}$ as shown in fig. 1. A comparison of the measured reaction rate coefficients with the capture rate coefficients predicted by the three theories indicates that the ADO model is the most realistic whereas the "locked-dipole" model clearly overestimates the effect of the dipole. The low experimental value of the rate coefficients for reaction (3) may reflect the presence of a small activation energy barrier for this reaction which should manifest itself in measurements of the rate coefficient as a function of temperature or translational energy of H^- at low energies ($E_{lab} < 1$ eV). The low reactivity of H^- could, however, be rationalized in another manner.

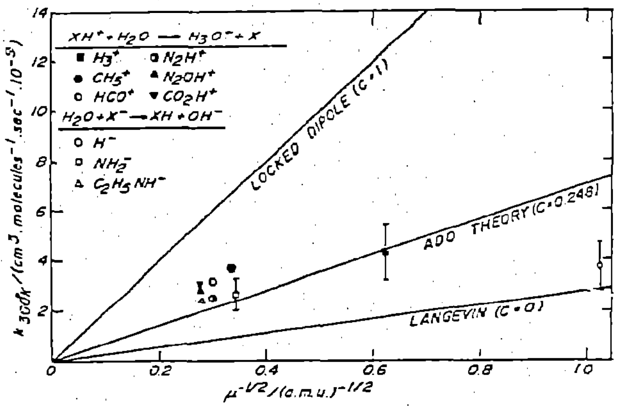

Fig. 1. A comparison of experimental reaction rate coefficients for proton transfer with H_2O with collision rate coefficients predicted by recent classical theories of ion–molecule collision. The solid bars represent the estimated accuracy (±25%) of the measurements.

Fig. 2 shows the variation of the measured rate coefficients normalized to the capture rate coefficients as calculated from the ADO theory with the exothermicity, $\Delta H^0_{298\,K}$, of the proton transfer reaction. The probability of proton transfer is seen to increase from the low value for reaction (3) as the exothermicity increases to ca. 40 kcal mole^{-1}, and to decrease slightly at larger exothermicities. The initial trend may be in-

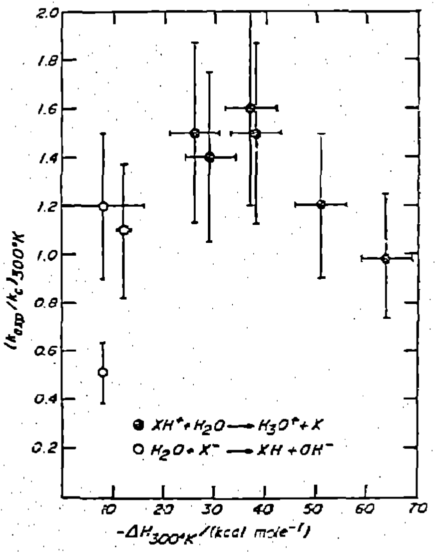

Fig. 2. A comparison at 300 K of the ratio of the experimental to the theoretical (ADO) capture rate coefficient with the exothermicity, ΔH^0_{298}, for proton transfer reactions with H_2O.

terpreted in terms of a reaction mechanism which proceeds through a proton-bound intermediate of the type $(X...H^+...H_2O)$ or $(OH^-...H^+...X^-)$ which may undergo unimolecular decay to products, the proton associating with H_2O or X^- respectively, or decay back to reactants, the proton remaining associated with X or OH^- respectively. Decay into the product channel is increasingly favoured over decay back to reactants as the overall exothermicity of the proton transfer increases. Such a model was invoked by Solka and Harrison [20] who observed a similar trend with exothermicity for reactions of the type

$$CH_3SH_2 + Y \rightarrow YH^+ + CH_3SH \qquad (8)$$

for a series of polar molecules, Y, with permanent dipole moments in the range 1.30 to 2.88 D. The low probability of reaction (3) which is only 8 kcal $mole^{-1}$ exothermic may, therefore, be a consequence of reaction mechanism rather than result from the presence of an activation energy barrier.

The trend with exothermicity observed for reactions (1) and (2) contrasts the lack of dependence on exothermicity of the rate coefficients at 297 K observed previously in this laboratory [1] for proton transfer reactions with NH_3. Similar studies are now in progress in this laboratory for proton transfer reactions involving other molecules of large dipole moment, e.g., HCN, CH_3CN.

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