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RATE CONSTANTS AT 297 K FOR PROTON-TRANSFER REACTIONS WITH C_2H_2: AN ASSESSMENT OF THE AVERAGE QUADRUPOLE ORIENTATION THEORY *

GERVASE I. MACKAY, KENICHIRO TANAKA ** and DIETHARD K. BOHME ***

Department of Chemistry and Centre for Research in Experimental Space Science, York University, Downsview, Ontario M3J 1P3 (Canada)

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ABSTRACT

Rate constants for proton-transfer reactions of the type $XH^+ + C_2H_2 \rightarrow C_2H_3^+ + X$ (type 1) where X = H_2, D_2, CH_4, CO, N_2, CO_2 and N_2O, and the type $C_2H_2 + X^- \rightarrow XH + C_2H^-$ (type 2) where X = H, D, NH_2, CH_3NH, C_2H_5NH, $(CH_3)_2N$, OH, CH_3O, C_2H_5O and $(CH_3)_2CHO$ have been measured at 297 ± 2 K using the flowing afterglow technique. The measured rate constants are compared with the predictions of classical theories on ion—molecule collisions, viz. the Langevin and Average Quadrupole Orientation theories. The Average Quadrupole Orientation theory provides collision rates generally to within ±5% of the measured reaction rates for reactions of type (1) but underestimates by ca. 10—60% the collision rates for several of the reactions of type (2). The results for reactions of type (2) are interpreted to suggest a small contribution of induced dipole—induced dipole interaction to the collision rate. Trends in k_{expt}/k_{AQO} have been observed for homologous series of reactions involving alkoxide and amide ions. These trends have raised questions regarding the extent to which charge delocalization may affect the collision rate and the influence of reaction exothermicity on proton-transfer efficiency for these reactions.

INTRODUCTION

In their continuing efforts to extend and refine classical theories of ion—molecule capture, Su and Bowers [1] have recently developed the Average Quadrupole Orientation (AQO) theory which takes into account ion—quadrupole interaction. Empirical relationships were derived which allow the determination of the thermal energy capture rates for collisions between ions and molecules possessing a quadrupole but no dipole moment. In order to test the predictions of this theory we have extended our flowing afterglow measurements of rate constants for proton-transfer reactions to reactions

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** Present address: Institute for Molecular Science, Myodaiji, Okazaki, Aichi, Japan 444.

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involving C_2H_2, which has a moderately large quadrupole moment. The reactions studied involve both the transfer of a proton from an ion to C_2H_2

$$XH^+ + C_2H_2 \rightarrow C_2H_3^+ + X \qquad (1)$$

and the transfer of a proton from C_2H_2 to an ion

$$C_2H_2 + X^- \rightarrow C_2H^- + XH \qquad (2)$$

Previous measurements of this type have proven to be most suitable for the assessment of earlier classical theories of ion—molecule collisions involving non-polar and dipolar molecules [2—4]. This suitability arises from the expectation that the exothermic transfer of a proton to simple molecular systems proceeds on essentially every collision, in which case collision rate theories amount to reaction rate theories so that a comparison of measured reaction rate constants with predicted collision rate constants provides an assessment of the latter [5].

The X^- ions employed in this study, viz. H^-, D^-, OH^-, CH_3O^-, $C_2H_5O^-$, $(CH_3)_2CHO^-$, NH_2^-, CH_3NH^-, $C_2H_5NH^-$ and $(CH_3)_2N^-$, were chosen to encompass a wide range in physical dimension (and hence polarizability) as well as extent of charge delocalization resulting from intramolecular ion—induced dipole interaction. Since the AQO theory does not take into account induced dipole—induced dipole interaction arising from the polarizability of X^- and assumes the ion to behave as a point charge, it was expected that the comparison of measured rate constants with AQO predictions for the reactions of these ions might also allow an assessment of the extent to which such factors determine the collision rate.

EXPERIMENTAL

The experiments were performed with a flowing afterglow system in the manner described previously [6]. The proton donors $XH^+ = N_2H^+$, CO_2H^+, CH_5^+, N_2OH^+ and HCO^+ were generated in a hydrogen or helium—hydrogen plasma by proton-transfer reactions of the type

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

which proceed upon the addition of the appropriate gas X downstream of the ionizer. Sufficient X was added to ensure that reaction (3) reached completion prior to the reaction zone; H_3^+ was established by the fast reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (4)$$

D_3^+ was produced by the analogous reaction

$$D_2^+ + D_2 \rightarrow D_3^+ + D \qquad (5)$$

upon the addition of D_2 into a helium plasma. The proton acceptors $X^- = NH_2^-$, CH_3NH^-, $C_2H_5NH^-$, $(CH_3)_2N^-$ and OH^- were produced from the appropriate neutral gas XH either directly by dissociative ionization with electrons (ca. 75 eV) or indirectly by secondary ionization with He metastables. The alkoxide ions were generated by proton-transfer reactions of the type

$$OH^- + ROH \rightarrow RO^- + H_2O \quad (6)$$

Both helium and hydrogen were used as the carrier gas. H^- and D^- were generated in a helium plasma only; H^- by direct ionization of either CH_4 or NH_3 and D^- via the deuteron-transfer reaction

$$NH_2^- + D_2 \rightarrow D^- + NH_2D \quad (7)$$

The neutral reactant C_2H_2 was introduced sufficiently downstream of the ion production region to ensure that the reactant ions were thermalized by collisions with the carrier gas molecules to the ambient temperature of 297 ± 2 K prior to reaction. The total pressure in the reaction region ranged from 0.27 to 0.55 torr and the effective reaction length had values of 59 and 85 cm. The variation in the reactant ion signals as a function of C_2H_2 addition provided the raw data from which the rate constants were determined.

The gases used were helium (Linde, prepurified grade, 99.5% He), hydrogen (Linde, very dry grade, 99.95% H_2), acetylene (Matheson, prepurified grade 99.6% C_2H_2), methane (Matheson, ultra high purity, 99.97% CH_4), nitrogen (Liquid Carbonic, high purity, 99.95% N_2), carbon monoxide (Matheson, C.P. grade, 99.5% CO), carbon dioxide (Matheson, Coleman grade, 99.99% CO_2) nitrous oxide (Matheson, 98.0% N_2O), ammonia (Matheson, anhydrous, 99.99% NH_3 (liquid phase)), monomethylamine (Matheson, 98.0% minimum CH_3NH_2 (liquid phase)), monoethylamine (Matheson, 98.5% minimum $C_2H_5NH_2$ (liquid phase)), dimethylamine (Matheson, 99.0% minimum $(CH_3)_2NH$ (liquid phase)), water (boiled distilled H_2O), methanol (BDH Chemicals, analytical reagent, CH_3OH), ethanol (Consolidated Chemicals, absolute, 10% mixture of C_2H_5OH vapour in He) and isopropanol (BDH Chemicals, reagent grade, 10% mixture of $(CH_3)_2CHOH$ vapour in He). The determination of the flows of the amines and alcohol—He mixtures required a separate measurement of their viscosities [7].

RESULTS AND DISCUSSION

The measured rate constants for 7 reactions of XH^+ with C_2H_2 and 10 reactions of X^- with C_2H_2 are summarized in Tables 1 and 2 respectively. Sources of error have been described previously [6]. The absolute accuracy of the measurements is assessed at ±25%.

Proton transfer was observed to be the dominant (>90%) channel in all cases. Some typical results for reactions of type (2) are shown in Fig. 1. The ions H^- and NH_2^- are produced by electron bombardment of NH_3 in a helium carrier gas. The conversion of H^- to NH_2^- by reaction with NH_3 has been established previously to be slow [15]. The Cl^- ion is an unreactive impurity ion monitored to ensure that the sampling remains constant during

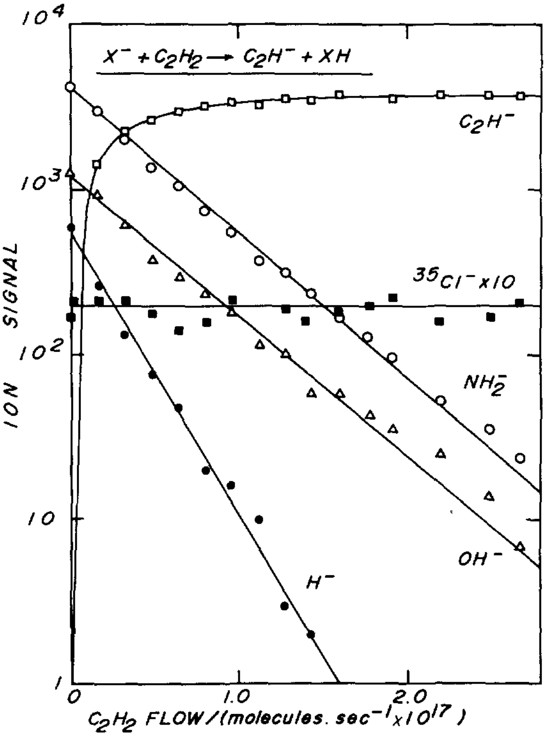

Fig. 1. The variation in the dominant ion signals recorded upon the addition of C_2H_2 into a He—NH_3 plasma in which NH_2^- is initially a major ion. $T = 297$ K, pressure = 0.48 torr, $\bar{v} = 8.9 \times 10^3$ cm^{-1}, $L = 86$ cm, and the flow of $NH_3 = 3.7 \times 10^{18}$ molecule s^{-1}.

an experiment. The OH^- ion arises from proton-transfer reactions of H^- and NH_2^- with trace amounts of H_2O present in the ammonia. The addition of C_2H_2 gives rise to a rapid decline of the H^- and NH_2^- signals and a concomitant increase in the C_2H^- signal. No additional product ions were detected in the negative ion mass spectrum so that the entire decay of the H^- and NH_2^- ions can be attributed to proton-transfer reactions of type (2). Proton transfer was also the only observable channel for reactions of type (1). The only primary product observed in the helium—hydrogen plasma was $C_2H_3^+$. When pure hydrogen was employed as the carrier gas a large fraction of the $C_2H_3^+$ was observed to convert to $C_2H_5^+$, presumably via the three-body association reaction

$$C_2H_3^+ + H_2 + M \rightarrow C_2H_5^+ + M \qquad (8)$$

Agreement of the present results with earlier flowing afterglow measurements is satisfactory. The rate constant for the proton-transfer reaction of H_3^+ with C_2H_2 had been determined previously in this laboratory [13]. We consider the present measurement to be more reliable because of improve-

TABLE 1

Rate constants in units of 10^{-9} cm^3 molecule^{-1} s^{-1} at 297 ± 2 K for reactions of the type $XH^+ + C_2H_2{}^a \rightarrow C_2H_3{}^+ + X$

XH^+	k_{expt} [b]		k_L [c]	k_{AQO} [d]	$\frac{k_{expt}}{k_{AQO}}$	$-\Delta H^0_{298}$ [e]
	this work	other work				(kcal mol^{-1})
$H_3{}^+$	2.90(3)	1.94 [f]	2.61	3.03	0.96	51 ± 3
$D_3{}^+$	2.33(3)	2.40 [g]	1.94	2.26	1.03	51 ± 3
$CH_5{}^+$	1.56(3)		1.33	1.55	1.01	25 ± 4
N_2H^+	1.41(3)		1.15	1.34	1.05	39 ± 4
HCO^+	1.36(8)		1.15	1.34	1.01	9 ± 4
CO_2H^+	1.37(5)		1.05	1.22	1.12	26 ± 6
N_2OH^+	1.21(4)		1.05	1.22	0.99	13 ± 5

[a] $\alpha = 3.33$ Å^3 [8]; $Q = 3.6 \times 10^{-26}$ e.s.u. cm^2 [9].

[b] The accuracy of the measurements is estimated to be better than ±25% and the precision is usually better than ±10%. The number of measurements is given in parentheses.

[c] Langevin theory.

[d] AQO theory.

[e] $PA(C_2H_2) = 152 \pm 2$ kcal mol^{-1} [10]; $PA(H_2) = 101 \pm 1$ kcal mol^{-1} [11]; $PA(N_2, CO_2, CH_4, N_2O, CO)$ were determined in this laboratory, ref. 12 and unpublished results.

[f] Ref. 13.

[g] Ref. 1.

ments made in both the data analysis and experimental technique. The rate constant for the reaction of $(CH_3)_2CHO^-$ with C_2H_2 represents only a lower limit to the true value since this reaction could not be studied in the flowing afterglow under non-equilibrium conditions [7]. It is likely that the result reported previously by Bohme et al. [17] is also only a lower limit for the same reason. The result for the proton-transfer reaction of $D_3{}^+$ with C_2H_2 is in excellent accord with that obtained with the ion cyclotron resonance (ICR) method [1].

Table 1 includes the capture rate constants deduced from the Langevin and AQO theories. For ion—molecule collisions involving acetylene the AQO theory predicts a collision or capture rate constant for reactions of type (1) involving positive ions given by

$$k_{AQO} = 2\pi q\left(\frac{\alpha}{\mu}\right)^{1/2} + \frac{15.88Q^{2/3}}{\mu^{1/2}}\left[\frac{Q^{2/3}}{\alpha^{1/2}} - 6.30 \times 10^{-7}\right] \qquad (9a)$$

$$k_{AQO} = 2\pi q\left(\frac{\alpha}{\mu}\right)^{1/2} + \frac{13.78Q^{2/3}}{\mu^{1/2}}\left[\frac{Q^{2/3}}{\alpha^{1/2}} - 3.98 \times 10^{-6}\right] \qquad (9b)$$

for reactions of type (2) involving negative ions [1]. These general expres-

TABLE 2

Rate constants in units of 10^{-9} cm^3 molecule^{-1} s^{-1} at 297 ± 2 K for reactions of the type $X^- + C_2H_2$[a] $\rightarrow C_2H^- + XH$

X^-	k_{expt} [b]		k_L [c]	k_{AQO} [d]	$\frac{k_{expt}}{k_{AQO}}$	$-\Delta H^0_{298}$ [e] (kcal mol^{-1})
	this work	other work				
H^-	4.42(8)		4.36	4.58	0.97	21.6 ± 3.4
D^-	3.32(4)		3.14	3.31	1.00	21.6 ± 3.4
NH_2^-	1.84(8)		1.36	1.43	1.29	24.8 ± 3.9
CH_3NH^-	1.33(3)		1.15	1.20	1.11	24.4 ± 4.6
$C_2H_5NH^-$	1.18(2)		1.06	1.11	1.06	20.6 ± 4.5
$(CH_3)_2N^-$	1.04(2)		1.06	1.11	0.94	17.6 ± 4.5
OH^-	2.18(11)	2.2 [f]	1.33	1.40	1.56	11.9 ± 3.3
CH_3O^-	1.64(4)	1.3 [g]	1.14	1.19	1.38	3.5 ± 0.7
$C_2H_5O^-$	1.41(8)	1.1 [g]	1.05	1.11	1.27	0.5 ± 0.7
$(CH_3)_2CHO^-$	$\geqslant$0.89(3)	0.52 [g]	1.01	1.06	$\geqslant$0.84	−0.6 ± 0.9

[a] $\alpha = 3.33$ Å^3 [8]; $Q = 3.6 \times 10^{-26}$ e.s.u. cm^2 [9].

[b] The accuracy of the measurements is estimated to be better than ±25% and the precision is usually better than ±10%. The number of measurements is given in parentheses.

[c] Langevin theory.

[d] AQO theory.

[e] $PA(OH^-) = 392.1 \pm 0.3$ kcal mol^{-1} and $PA(H^-) = 400.04 \pm 0.5$ kcal mol^{-1} [14]; $PA(NH_2^-$, CH_3NH^-, $C_2H_5NH^-$, $(CH_3)_2N^-$, CH_3O^-, $C_2H_5O^-$, $(CH_3)_2CHO^-$, $C_2H^-)$ were determined in this laboratory, refs. 15, 7 and unpublished results.

[f] Ref. 16.

[g] Ref. 17.

sions were derived by Su and Bowers from an empirical fit of the calculated thermal energy rate constants at 300 K to random values of the polarizability α, the rotation average quadrupole moment Q [1(b)], the reduced mass of the colliding particles μ, and the charge on the ion q. Both equations are composed of the familiar Langevin term [18] and a second term reflecting the ion—quadrupole interaction. The two expressions account for the two cases which arise: the even case (9a), for which the charge on the ion and the quadrupole moment have the same sign, and the odd case (9b) for which q and Q are of opposite sign. Acetylene has a positive quadrupole moment so that reactions with positive ions are representative of the even case while reactions involving negative ions correspond to the odd case.

For a series of reactions of types (1) and (2) for which the neutral reactant remains fixed the Langevin and AQO theories each define a straight line on a plot of k versus $\mu^{1/2}$ as illustrated in Figs. 2 and 3. In the case of the positive ion proton-transfer reactions (Fig. 2) a comparison of the measured reaction rate constants with the collision rate constants predicted by the two theories indicates that the Average Quadrupole Orientation theory, which

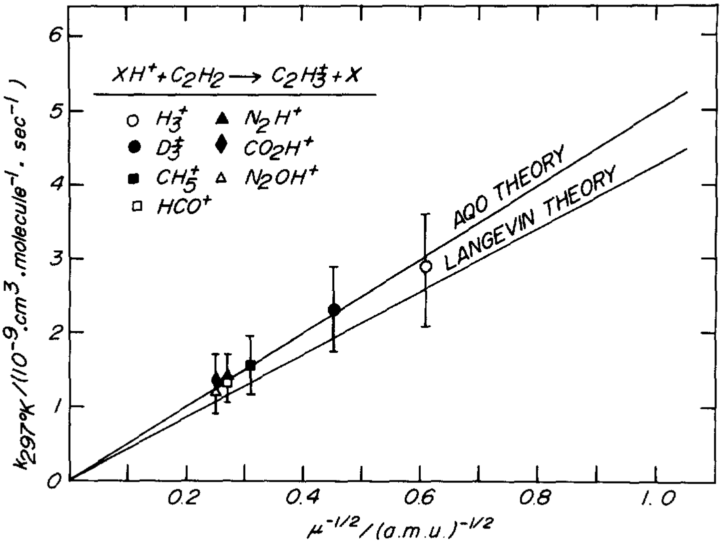

Fig. 2. A comparison of measured rate constants with capture rate constants predicted by the Langevin and Average Quadrupole Orientation theories for reactions of the type $XH^+ + C_2H_2 \rightarrow C_2H_3^+ + X$ ($\alpha = 3.33$ Å^3, $Q = 3.6 \times 10^{-26}$ e.s.u. cm^2) at 297 ± 2 K. The solid bars represent the estimated accuracy (±25%) of the measurements.

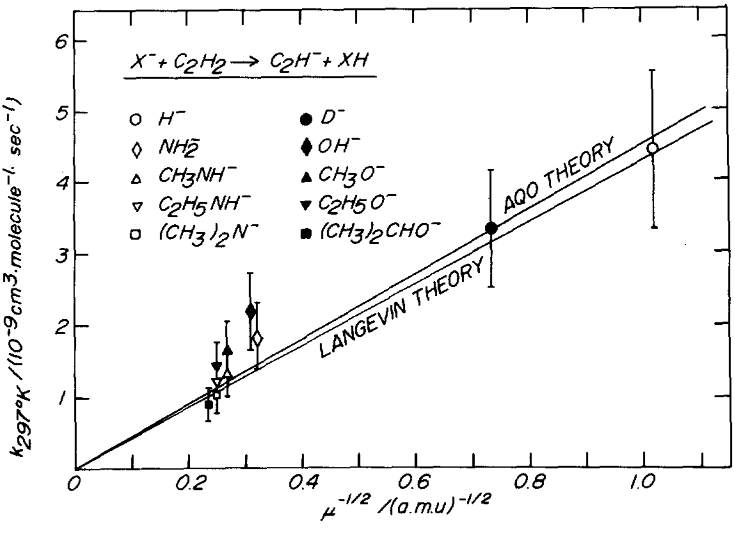

Fig. 3. A comparison of the measured rate constants with capture rate constants predicted by the Langevin and Average Quadrupole Orientation theories for reactions of the type $X^- + C_2H_2 \rightarrow XH + C_2H^-$ ($\alpha = 3.33$ Å^3, $Q = 3.6 \times 10^{-26}$ e.s.u. cm^2) at 297 ± 2 K. The solid bars represent the estimated accuracy (±25%) of the measurements.

attributes 16% of the collision rate for these reactions to the ion—quadrupole interaction, provides collision rate constants in excellent agreement with the measured reaction rate constants, generally to within ±5%. The Langevin theory, which ignores the ion—quadrupole interaction, clearly underestimates the collision rate. The agreement in the case of the negative ion proton-transfer reactions (Fig. 3) is less satisfactory. Five of the nine measured rate constants exceed the value predicted by AQO theory by at least 10% and as much as 56%. Nevertheless, the AQO theory appears to provide a more realistic collision rate than the Langevin theory.

The high values of $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ observed for the reactions of type (2) suggest that even the AQO theory underestimates the collision rate for such reactions. Su and Bowers have themselves remarked on several possible shortcomings of their theoretical treatment of ion—molecule collisions. These include (a) the neglect of net angular momentum transfer between the rotating molecule and the system as a whole [1]; (b) the treatment in an "average sense" of the angle that the molecular axis makes with the line of centres of collision [1]; (c) the use of the rotationally average polarizability of the molecule [19]; and (d) the neglect of high-order contributions to the ion—molecule interaction potential [19]. In view of the good agreement between theory and experiment observed for reactions of type (1) and the high values of $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ obtained for reactions of type (2), it would appear that shortcoming (d) is most responsible for the underestimation of the collision rate for the reactions of type (2) investigated in this study. One term in the interaction potential which may make a more substantial contribution to the collision rate of negative ion—molecule reactions is the r^{-6} term corresponding to the induced dipole—induced dipole interaction arising from the polarizability of the negative ion [19]. One might account in this manner for high values of $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ for the OH^- and NH_2^- reactions but not the trend in $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ observed for the more polarizable alkoxide and amide ions for which one would predict an increase in this ratio. As shown in Figs. 4 and 5 the values of $k_{\mathrm{expt}}/k_{\mathrm{AQO}} \equiv P$ show a definite systematic decrease with increasing size of the alkyl substituent.

If one insists on equal reaction efficiencies for these series of homologous proton-transfer reactions then the decrease in $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ must reflect a genuine decrease in the collision rate with increasing alkyl substitution. An increase in the size of the alkyl group and therefore its polarizability will lead to an increase in the extent of charge delocalization in the negative ion resulting from intramolecular ion—induced dipole interaction. Figure 6 explores the variation of $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ with the calculated net charge on the most electronegative atom (O and N in the alkoxide and amide ions respectively) for the two homologous series [20,21]. It is evident that there is a definite, almost linear correlation between $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ and charge delocalization in the anion. While the linearity may be an artifact of the limited range in charge density, the trend is undoubtedly real. One can surmise from this trend another shortcoming of the AQO theory. One of the major assump-

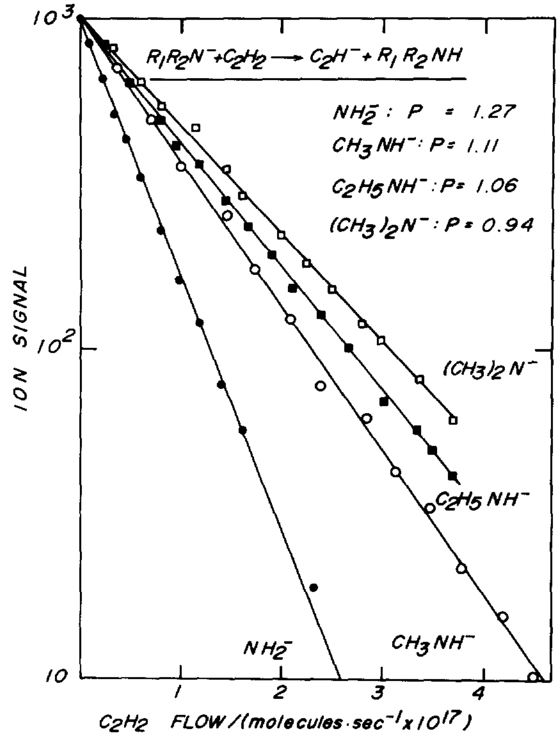

Fig. 4. Decays for the NH_2^-, CH_3NH^-, $C_2H_5NH^-$ and $(CH_3)_2N^-$ signals observed as a function of addition of C_2H_2. The decays have been normalized to the data for $NH_2^- + C_2H_2$. $P = k_{\mathrm{expt}}/k_{\mathrm{AQO}}$. $T = 297 \pm 2$ K, pressure = 0.33—0.43 torr, $\bar{v} = (7.9—9.5) \times 10^3$ cm s^{-1}, $L = 60$ cm, and the flow of $R_1R_2NH = (2.4—6.7) \times 10^{18}$ molecule s^{-1}.

tions made in the derivation of this theory is that the ion can be represented by a point charge. Realistically this assumption must break down for larger ions for which charge delocalization is likely to lead to a lower collision rate. Furthermore the observed trend in $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ for the substituted anions then implies that this latter effect overrides the enhancement in the collision rate expected from the increased intermolecular induced dipole—induced dipole interaction. For the reactions of H^- and D^- the agreement between experiment and the AQO theory is good as one might expect in terms of these arguments, since these ions should have the lowest polarizabilities and most closely resemble point charges.

Alternatively the decrease in $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ with increasing size of the alkyl substituent may reflect a genuine decrease in the efficiency of proton transfer. Recent measurements in this laboratory [4] have suggested that the assumption of constant efficiency for proton transfer may break down at low exothermicities in a given homologous series. Figure 7 explores the variation of $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ with ΔH^0_{298}. The $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ ratio is observed to decrease systematically with decreasing reaction exothermicity for both the alkoxide

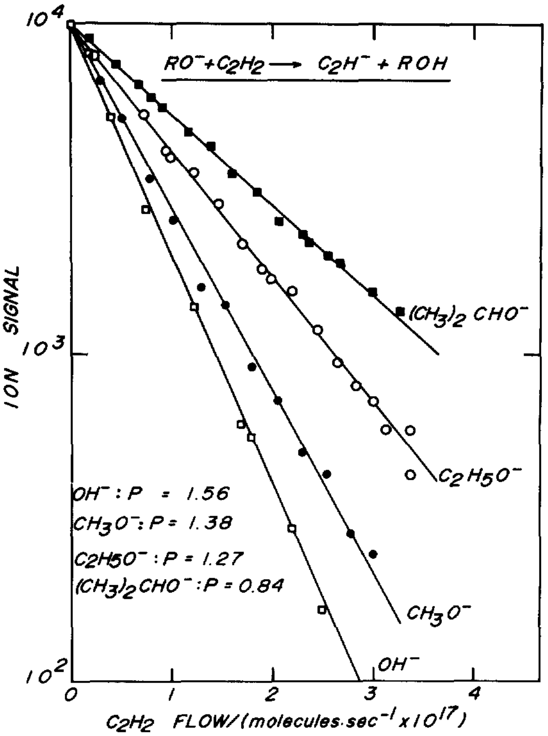

Fig. 5. Decays for the OH^-, CH_3O^-, $C_2H_5O^-$ and $(CH_3)_2CHO^-$ signals observed as a function of addition of C_2H_2. The decays have been normalized to the data for $OH^- + C_2H_2$. $P = k_{expt}/k_{AQO}$, $T = 297 \pm 2$ K, pressure = 0.33—0.47 torr, $\bar{v} = (8.7—9.5) \times 10^3$ cm s^{-1}, $L = 60$ cm, and the flow of ROH = $(0.5—1.7) \times 10^{17}$ molecule s^{-1}.

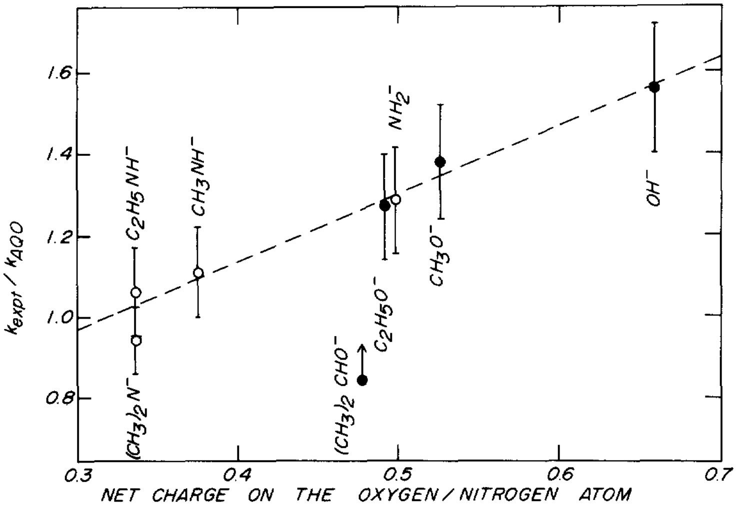

Fig. 6. A plot of the ratio of the measured proton-transfer rate constant to the calculated capture (AQO) rate constant as a function of the calculated net charge on the nitrogen or oxygen atom in the amide and alkoxide ions respectively.

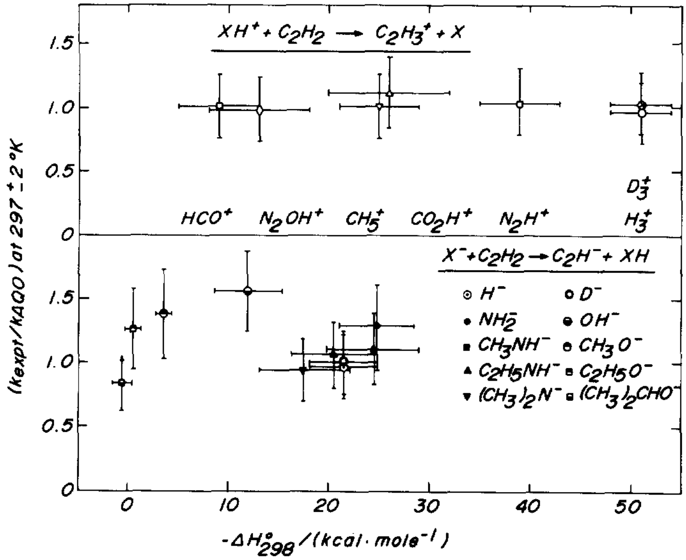

Fig. 7. A plot of the ratio of the measured proton-transfer rate constants to the calculated capture (AQO) rate constants as a function of the heat of reaction, $-\Delta H^0_{298}$.

and amide ion reactions. Theoretical aspects of the influence of exothermicity on reaction efficiency are not well understood. The recent, somewhat primitive, treatment of Kebarle [22] would suggest that the efficiency for proton transfer should become insensitive to exothermicity for $-\Delta H^0_{298} \gtrsim 10$ kcal mol^{-1}. In this case the observed variation of $K_{\mathrm{expt}}/k_{\mathrm{AQO}}$ with $-\Delta H^0_{298} \geqslant 18$ kcal mol^{-1} for the amide ion reactions would argue against an interpretation of the decrease in $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ with increasing alkyl substitution in terms of a decrease in proton-transfer efficiency.

In conclusion, our measurements of rate constants for proton-transfer reactions with C_2H_2 of both types (1) and (2) indicate that the AQO theory of Su and Bowers [1] provides to date the most realistic collision rates for such reactions. The results for reactions of type (2) are interpreted to suggest a small contribution of induced dipole—induced dipole interaction to the collision rate. Trends in $k_{\mathrm{expt}}/k_{\mathrm{AQO}}$ have been observed for homologous series of reactions involving alkoxide and amide ions. These trends have raised questions regarding the extent to which charge delocalization may effect the collision rate and the influence of reaction exothermicity on proton-transfer efficiency for these reactions.

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