An experimental study of the influence of hydration on the reactivity of the hydroxide anion in the gas phase at room temperature

ASIT B. RAKSIT and DIETHARD K. BOHME

Department of Chemistry and Centre for Research in Experimental Space Science, York University, Downsview, Ont., Canada M3J 1P3

Received November 15, 1982

ASIT B. RAKSIT and DIETHARD K. BOHME. Can. J. Chem. **61**, 1683 (1983).

Flowing afterglow measurements of rate constants and ionic products are reported which explore the influence of step-wise hydration on the reactivity of the hydroxide anion in the gas phase at 296 ± 2 K. Rate constants have been measured for the reactions of $OH^-.(H_2O)_n$ and/or $OD^-.(D_2O)_n$ with CO_2, SO_2, CH_3OH, C_2H_5OH, C_2H_2, CH_3COCH_3, CH_3NO_2, and HCN, in most instances for values of n from 0 to 3. The reactions with CO_2 and SO_2 involve ligand addition or exchange and the results of their study corroborate earlier measurements. The remaining reactions proceed by proton transfer. For these reactions the results establish trends in reactivity as a function of step-wise hydration when relative acidity is preserved and when a reversal occurs in the relative acidity upon hydration. The fast hydrated acid–base reactions were observed to establish interesting hydrated product ions many of which underwent secondary reactions involving the exchange of H_2O or D_2O for the reagent molecule.

ASIT B. RAKSIT et DIETHARD K. BOHME. Can. J. Chem. **61**, 1683 (1983).

On rapporte les mesures de phosphorescence d'écoulement des constantes de vitesse et des produits ioniques. Ces mesures permettent d'étudier l'influence d'une hydratation par étape sur la réactivité de l'anion hydroxyde en phase gazeuse à 296 ± 2 K. On a mesuré les constantes de vitesse des réactions de $OH^-.(H_2O)_n$ et/ou de $OD^-.(D_2O)_n$ avec les molécules suivantes: CO_2, SO_2, CH_3OH, C_2H_5OH, C_2H_2, CH_3COCH_3, CH_3NO_2 et HCN et ceci pour des valeurs de n allant de 0 à 3 dans la plupart des cas. Les réactions avec CO_2 et SO_2 impliquent l'addition ou l'échange de ligand et les résultats de leur étude corroborent les mesures antérieures. Les réactions avec les autres substances se font par transfert de proton. Dans le cas de ces réactions, les résultats établissent la tendance de la réactivité en fonction de l'hydratation par étape lorsqu'on protège l'acidité relative et lorsqu'il se produit une inversion de l'acidité relative durant l'hydratation. On a observé des réactions rapides acide–base hydraté afin d'identifier les ions hydratés intéressants dont plusieurs subissent des réactions secondaires qui impliquent, dans le cas du réactif, un échange de H_2O ou de D_2O.

[Traduit par le journal]

Introduction

The hydroxide ion is an important base in solution chemistry and has become so as well in gas-phase ion chemistry. In the gas phase the bare hydroxide ion has a high basicity and a high reactivity which are now both well established (1) and much is known of the reactivity of the hydrated species in solution. In this study we explore the influence of step-wise hydration on the intrinsic reactivity of the hydroxide ion in the gas phase, primarily with measurements of the specific rates and ionic products of reactions of type [1]

$$[1] \quad OH^-.(H_2O)_n + AH \rightarrow A^-.(H_2O)_m + (n - m + 1)H_2O$$

for values of $n = 1$ to 3. The measurements were carried out using a flowing plasma mass spectrometer (flowing afterglow) system (2, 3) which allows the hydrated species to be produced in an inert atmosphere in thermalized and controlled amounts and to be identified and monitored with a mass spectrometer. The reagent acids, AH, were chosen to span a range in overall energetics sufficient to establish the pattern of reactivity which emerged from these studies. The observed trends in reactivity begin to bridge the gap between the gas phase and solution. For a number of acids reaction [1] was observed to be followed by further ion chemistry which exhibits a clear tendency of the solvent aggregate of the solvated ions to evolve to a state of maximum stability by solvent exchange and solvent addition reactions.

Experimental

The experiments were carried out in a flowing plasma mass spectrometer (flowing afterglow) system. Details of the instrument together with the method of operation and data analysis have been reported elsewhere (2, 3). The hydrated hydroxide ions were established by introducing water vapour, either H_2O or D_2O, past the electron gun in either a flowing helium or hydrogen plasma. Ions were hydrated upstream by reactions of type [2] at total pressures of ca.

$$[2] \quad OH^-.(H_2O)_n + H_2O + He(H_2) \rightarrow OH^-.(H_2O)_{n+1} + He(H_2)$$

0.4 Torr and thermalized by collisions with the buffer gas molecules prior to the reaction region. The reacting mixture was sampled through a small orifice mounted at the tip of a nose cone situated at the end of the reaction region and mass analysed with a quadrupole mass spectrometer. The observed variations of the reactant ion signals as a function of neutral reagent addition provided the raw data from which the rate constants were derived.

The partial pressure of the added water vapour was varied from ca. 0.005 to 2 mTorr in order to achieve a wide range in the initial relative population of the hydrated hydroxide ions. The hydroxide ion was observed to add up to three water molecules at the operating conditions of the experiments reported here. In deriving rate constants from the observed decays of $OH^-.(H_2O)_n$ account was taken of the initial decay which could arise due to the depletion of the precursor ion $OH^-.(H_2O)_{n-1}$. The magnitude of the depletion could be assessed in those studies in which the daughter ion $OH^-.(H_2O)_n$ did not react with the added neutral reagent. In many experiments D_2O was used in place of H_2O to avoid overlap of ion signals, particularly of $OH^-.(H_2O)_n$ and $Cl^-.(H_2O)_{n-1}$ and of $OH^-.(H_2O)_2$ and $CN^-.HCN$.

Results

The results of the measurements are summarized in Tables 1 and 2. The sources of uncertainty associated with the determination of the rate constants have been described previously (2, 3). The following section describes the measurements in

TABLE 1. Rate constants[a] measured for binary reactions of $OH^-.(H_2O)_n$ with CO_2 and SO_2 at 296 ± 2 K

n	CO_2	SO_2[b]
1	≥0.4	1.0±0.3 (≥0.5)
2	0.54±0.22	1.2±0.3 (≥0.5)
3	0.56±0.22	1.2±0.4 (1.2±0.5)
2, 3, 4[c]	0.6	2

[a] In units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}.
[b] Values in parentheses apply to $OD^-.(D_2O)_n$.
[c] Reference 4.

more detail. They are presented in order of increasing acidity of the reagent acids. The reactions with CO_2 and SO_2 were investigated in part to assess the performance of the instrument. Previous flowing afterglow measurements for these two reactions carried out primarily in O_2 buffer gas were available for comparison (4).

CO_2, SO_2

The unsolvated hydroxide ion rapidly associates with CO_2 and SO_2 in the gas phase to form the anions of carbonic and sulphurous acid, respectively, via reactions [3] and [4] where M is a third body.

$$[3] \quad OH^- + CO_2 + M \rightarrow HCO_3^- + M$$

$$[4] \quad OH^- + SO_2 + M \rightarrow HSO_3^- + M$$

Reaction [3] was investigated in H_2 buffer gas at total pressures in the range 0.276 to 0.582 Torr while reaction [4] was studied in a He buffer with OH^- between 0.320 and 0.447 Torr and with OD^- between 0.317 and 0.567 Torr. Figure 1 displays the observed pressure dependencies for the apparent binary rate constants which were measured. The slopes of these plots provide ternary rate constants of (1.0 ± 0.3) and (4.2 ± 1.3) × 10^{-27} cm^6 $molecule^{-2}$ s^{-1} for reactions [3] and [4], respectively. A comparison with the previously reported measurements indicates the H_2 to be slightly more effective as a stabilizing third body for HCO_3^- than O_2 which in turn is more effective than He: rate constants of 7.6 and 2.5 × 10^{-28} cm^6 $molecule^{-2}$ s^{-1}, respectively, have been reported for the latter two buffer gases (4). Our results also indicate that the relative effectiveness of O_2 and He in stabilizing HCO_3^- is approximately the same as that in stabilizing HSO_3^-: a rate constant of 1.0 × 10^{-26} cm^6 $molecule^{-2}$ s^{-1} has been reported for reaction [4] with M = O_2 (4).

The hydrated hydroxide ions were observed to undergo the binary ligand exchange reactions [5] and [6] reported

$$[5] \quad OH^-.(H_2O)_n + CO_2 \rightarrow HCO_3^-.(H_2O)_m + (n - m)H_2O$$

$$[6] \quad OH^-.(H_2O)_n + SO_2 \rightarrow HSO_3^-.(H_2O)_m + (n - m)H_2O$$

previously by Fehsenfeld and Ferguson (4). In writing these reactions allowance has been made for the excess energy in these exothermic reactions to cause some of the H_2O to be "boiled-off" and so permit m to take on values from 0 to $n - 1$. In the present experiments in which the flowing plasma contained a mixture of $OH^-.(H_2O)_n$ ions with $n = 0$ to 3, product ions were observed for $m = 0$, 1, and 2 but the latter in only relatively trace amounts. The rate constants determined from these experiments are summarized in Table 1. They compare favourably with the values obtained previously by Fehsenfeld and Ferguson (4).

CH_3OH

We have reported previously that the bare hydroxide ion rapidly removes a proton from methanol in the gas phase, $k = (2.2 \pm 0.6) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} (5). Also hydration of the OH^- was observed to promote the reverse of reaction [7]. Measurements of the equilibrium constant for reaction [7]

$$[7] \quad OH^-.(H_2O)_n + CH_3OH \rightleftharpoons CH_3O^-.(H_2O)_n + H_2O$$

for $n = 1$, 2, and 3 provided insight into the shift of the position of equilibrium for this reaction with hydration (6). Reaction [7] is rapid, $k > 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}, for $n = 0$ to 3 and the product ions quickly undergo secondary reactions with CH_3OH which displace H_2O in the solvation shell as is indicated by reaction [8]. In this study the measurements were repeated with

$$[8] \quad CH_3O^-.(H_2O)_n + CH_3OH \rightleftharpoons CH_3O^-.(H_2O)_{n-1}.CH_3OH + H_2O$$

$OD^-.(D_2O)_n$ ions derived from heavy water and a very similar behaviour was observed. The semi-logarithmic decays recorded for these solvated ions and the formations of product ions were indicative of fast reactions of type [9] for $n = 0$ to 4. Increased curvature was apparent in the decays of

$$[9] \quad OD^-.(D_2O)_n + CH_3OH \rightarrow CH_3O^-.(D_2O)_n + HOD$$

$OD^-.(D_2O)_n$ with increasing values of n which may be attributed to reverse reactions with the source gas D_2O which was present in the reaction tube in large excess to the HOD generated by reaction [9], viz to reactions of type [10]. Plots of the ion

$$[10] \quad CH_3O^-.(D_2O)_n + D_2O \rightarrow OD^-.(D_2O)_n + CH_3OD$$

concentration ratios $[CH_3O^-.(D_2O)_n]/[OD^-.(D_2O)_n]$ against flow of CH_3OH exhibited linearity at higher flows of CH_3OH. Normally such linearity would be indicative of equilibrium but in this case the linearity is a consequence of the rate equalities [11] rather than the equilibrium equalities [12], and thus pro-

$$[11] \quad k_9[OD^-.(D_2O)_n][CH_3OH] = k_{10}[CH_3O^-.(D_2O)_n][D_2O]$$

$$[12] \quad k_9[OD^-.(D_2O)_n][CH_3OH] = k_{-9}[CH_3O^-.(D_2O)_n][HOD]$$

vides a measure of k_9/k_{10} rather than k_9/k_{-9}. Values for k_9/k_{10} of ≥ 5.3 × 10^2, ≥1.7 × 10^2, 22, and 10 were obtained for $n = 1$, 2, 3, and 4, respectively. These are close to the values of ≥1.3 × 10^3, 1.5 × 10^2, and 25 for $n = 1$, 2, and 3 which were obtained previously for k_7/k_{-7} and are thus indicative of a negligible isotope effect.

The product ions of reaction [9] were observed to rise and then fall at higher additions of methanol concomitant with the production of ions with masses corresponding to the cluster ions $CH_3O^-.(D_2O)_{n-1}.CH_3OH$ with $n = 1$, 2, and 3. These observations can be attributed to rapid solvent exchange reactions of type [13] and indicate a preference for methanol over heavy water in the solvation of CH_3O^-.

$$[13] \quad CH_3O^-.(D_2O)_n + CH_3OH \rightarrow CH_3O^-.(D_2O)_{n-1}.CH_3OH + D_2O$$

CH_2CCH_2, $C_6H_5CH_3$

Allene and toluene have equal acidities in the gas phase (7). We have reported previously that the bare hydroxide ion will abstract a proton from these two acids with essentially unit efficiency and that hydration of the bare ion with just one molecule of water lowers this efficiency by more than a factor of 10^3 (7).

TABLE 2. Rate constants[a] measured for binary reactions of $OH^-.(H_2O)_n$ and $OD^-.(D_2O)_n$ with acids, AH, at 296 ± 2 K

AH	Rate constant $n=0$	 $n=1$	 $n=2$	 $n=3$
CH_3OH	2.2±0.6	2.1±0.5		
	[2.7±0.8]	[2.3±0.7]		
CH_2CCH_2	1.7±0.4	≤0.001	≤0.001	≤0.001
$C_6H_5CH_3$	2.6±0.6	≤0.001		
C_2H_5OH	2.2±0.7	2.0±0.7	1.0±0.6	0.7±0.5
	[2.1±0.6]	[1.9±0.6]	[0.9±0.4]	[0.7±0.4]
C_2H_2	2.2±0.4	≥1	≤0.01	≤0.01
	[1.9±0.4]	[≥1]	[≤0.001]	[≤0.001]
CH_3COCH_3	3.8±0.8	3.4±0.9	≥1	≤0.01
	[3.9±0.8]	[3.2±0.8]	[≥1]	[≤0.01]
CH_3NO_2	3.5±0.7	2.8±0.7	2.2±0.6	2.0±0.6
	[3.4±0.7]	[2.5±0.6]	[2.4±0.6]	[2.2±0.6]
HCN	3.5±0.7	3±1		3±1
	[3.4±0.7]	[3.1±0.8]	[3.0±0.8]	[2.9±0.7]

[a] Rate constants and their estimated accuracies are given in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. The numbers in brackets refer to reactions with $OD^-.(D_2O)_n$.

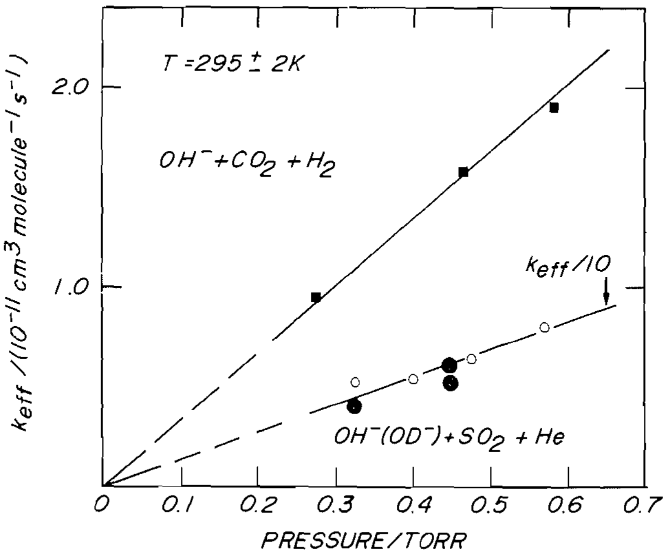

FIG. 1. Observed dependence of the effective two-body rate constant on the total pressure for the association of $OH^-(OD^-)$ with CO_2 and SO_2 at 295 ± 2 K. The open circles refer to measurements made with OD^-.

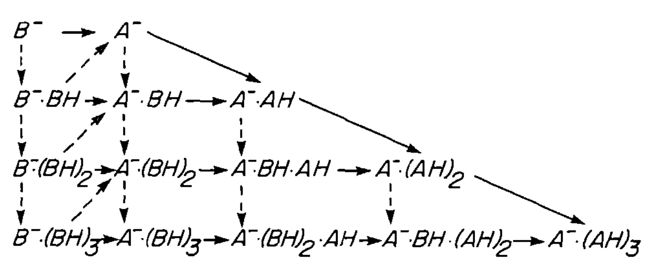

FIG. 2. A general scheme representative of the possible solvated ion chemistry proceeding under flowing afterglow conditions for the acid–base reactions investigated in this study. The solid horizontal arrows represent solvated acid–base or solvent exchange reactions with AH. The dashed vertical arrows represent possible solvent addition reactions with BH. The dashed diagonal arrows represent possible solvated acid–base reactions with a concomitant "boiling-off" of solvent BH.

C_2H_5OH

The reactivities of $OH^-.(H_2O)_n$ and $OD^-.(D_2O)_n$ observed for their reactions with ethanol were similar to those observed for methanol. Rapid proton transfer reactions of type [14] were indicated for n = 1 to 3. The measured rate constants are listed

[14] $OD^-.(D_2O)_n + C_2H_5OH \rightarrow C_2H_5O^-.(D_2O)_n + HOD$

in Table 2. Also the hydrated ethoxide ions were observed to react further by solvent exchange reactions of type [15]. At

[15] $C_2H_5O^-.(D_2O)_n + C_2H_5OH \rightarrow C_2H_5O^-.(D_2O)_{n-1}.C_2H_5OH + D_2O$

still higher flows of ethanol, ion signals were observed to rise at m/e = 137 and 157 and finally at m/e = 183. This behaviour is consistent with still further displacement of D_2O by C_2H_5OH to ultimately establish ethoxide ions solvated exclusively by ethanol as is indicated by the general scheme shown in Fig. 2. All of the ions indicated in this scheme were observed for BH = D_2O and AH = C_2H_5OH.

C_2H_2

We have reported previously that OH^- rapidly abstracts a proton from acetylene to produce C_2H^- (8). The results of the present study indicate that this reactivity is extremely sensitive to the degree of hydration. As is evident from the observations recorded in Fig. 3, the reactivity remains high with the addition of one molecule of water to OH^- but the addition of a second molecule of hydration leads to an abrupt drop in reactivity by more than two orders of magnitude. For reactions of type [16] and the heavy water analogues, our observations indicate that

[16] $OH^-.(H_2O)_n + C_2H_2 \rightarrow C_2H^-.(H_2O)_n + H_2O$

$k \geq 1 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} for n = 0 and 1 but $k \leq 1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for n = 2 and 3. An ion with a mass corresponding to the product of reaction [17] was clearly identified. The curvature in the decay of $OD^-.D_2O$ in Fig. 3 is

[17] $OD^-.D_2O + C_2H_2 \rightarrow C_2H^-.D_2O + HOD$

caused by the rapid occurrence of the reverse reaction [18] with D_2O which is in large excess over the HOD produced by

[18] $C_2H^-.D_2O + D_2O \rightarrow OD^-.D_2O + C_2HD$

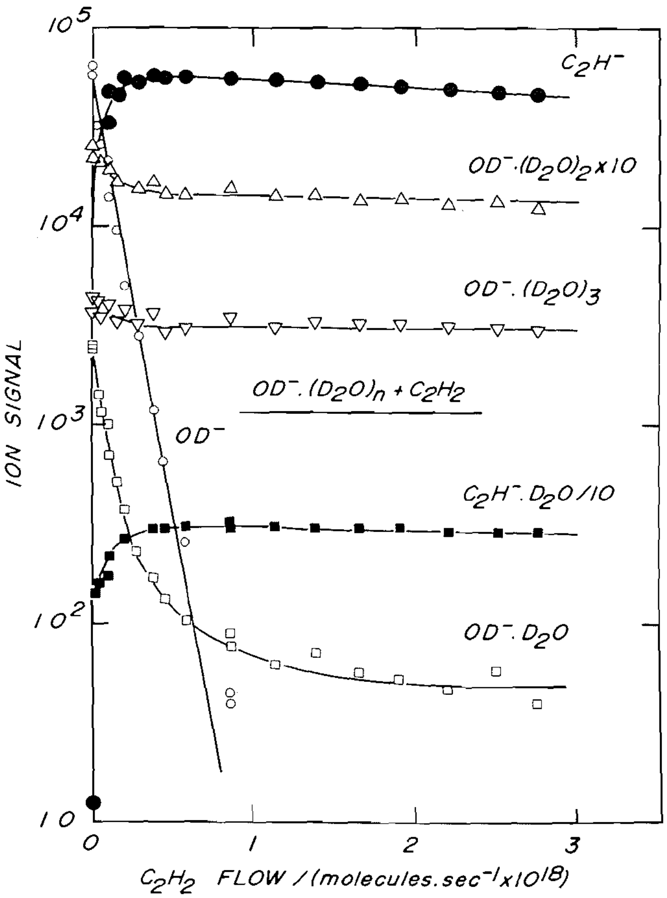

FIG. 3. Observations recorded for the reactions of $OD^-.(D_2O)_n$ with acetylene in a He buffer. $T = 296$ K, $P = 0.331$ Torr, $\bar{v} = 8.1 \times 10^3$ cm s^{-1}, $L = 46$ cm, and the flow of D_2O is approximately 2×10^{19} molecules s^{-1}.

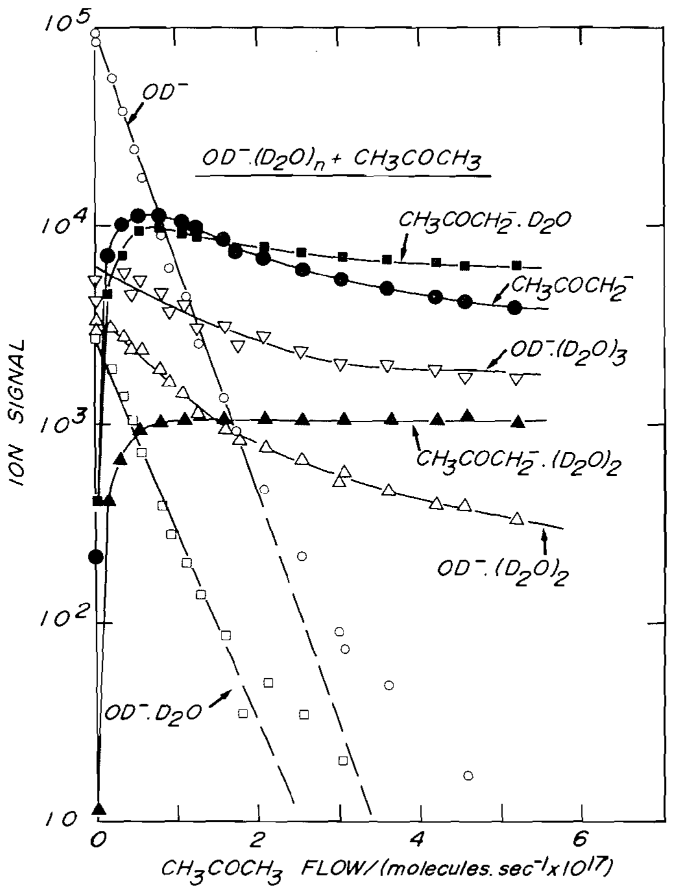

FIG. 4. Observations recorded for the reactions of $OD^-.(D_2O)_n$ with acetone in a He buffer. $T = 295$ K, $P = 0.316$ Torr, $\bar{v} = 8.0 \times 10^3$ cm s^{-1}, $L = 46$ cm, and the flow of D_2O is approximately 2×10^{19} molecules s^{-1}.

reaction [17]. A fit to this curvature provided lower limits for k_{17}/k_{18} of 8×10^2 and for k_{17} of 1×10^{-9} cm^3 molecule^{-1} s^{-1}. The slight decays observed initially in the profiles for $OD^-.(D_2O)_2$ and $OD^-.(D_2O)_3$ are attributable to the depletion in the reaction region of their precursor ions, $OD^-.D_2O$ and $OD^-.(D_2O)_2$, respectively. The $C_2H^-.D_2O$ did not react further to exchange D_2O for C_2H_2.

CH_3COCH_3

Figure 4 illustrates the reactivities of $OD^-.(D_2O)_n$ towards acetone. OD^- and $OD^-.D_2O$ are seen to react rapidly with acetone with a concomitant rise in the $CH_3COCH_2^-$ and $CH_3COCH_2^-.D_2O$ ion signals. The rate constants for both of these reactions were measured to be $\geq 3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} (see Table 2). Reaction [19] and the analogous reactions [20] and [21] with D_2O appeared to

[19] $OH^-.(H_2O)_2 + CH_3COCH_3 \rightleftharpoons CH_3COCH_2^-.(H_2O)_2 + H_2O$

[20] $OD^-.(D_2O)_2 + CH_3COCH_3 \rightarrow CH_3COCH_2^-.(D_2O)_2 + HOD$

[21] $CH_3COCH_2^-.(D_2O)_2 + D_2O \rightarrow OD^-.(D_2O)_2 + CH_3COCH_2D$

achieve equilibrium under the conditions employed in these experiments. The corresponding ion ratio plots were linear and provided values for $k_{19}/k_{-19} = 3 \times 10^2$ and for $k_{20}/k_{21} = 4 \times 10^2$. The situation for the reaction of $OD^-.(D_2O)_3$ is somewhat uncertain. There is a slight decay in the $OD^-.(D_2O)_3$ signal initially but it appears to level off at moderate flows of acetone. This behaviour was interpreted to reflect the removal of the $OD^-.(D_2O)_2$ percursor ion in the reaction region and a low reactivity for the $OD^-.(D_2O)_3$, $k \leq 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The product ion $CH_3COCH_2^-.(D_2O)_3$ did not appear to be produced. An alternative interpretation would involve a reverse reaction of the $CH_3COCH_2^-.(D_2O)_3$ with D_2O which strongly favours a net production of $OD^-.(D_2O)_3$. At the flows of D_2O and acetone employed this would still imply an equilibrium constant for reaction [22] or the analogous reactions with D_2O

[22] $OH^-.(H_2O)_3 + CH_3COCH_3 \rightleftharpoons CH_3COCH_2^-.(H_2O)_3 + H_2O$

of less than unity.

CH_3NO_2

The ions $OH^-.(H_2O)_n$ and $OD^-.(D_2O)_n$ with $n = 0$ to 3 all were observed to react rapidly with nitromethane in the manner indicated by reaction [23].

[23] $OH^-.(H_2O)_n + CH_3NO_2 \rightarrow CH_2NO_2^-.(H_2O)_m + (n - m + 1)H_2O$

All of the corresponding product ions, viz. $CH_2NO_2^-.(H_2O)_n$ and $CH_2NO_2^-.(D_2O)_n$ with $n = 0$ to 3, were observed to be produced but product distributions for the individual hydrated ions could not be ascertained. The rate constants measured for the disappearance of the reactant ions are given in Table 2. Exchange of H_2O or D_2O for CH_3NO_2 was observed at higher flows of CH_3NO_2 in secondary switching reactions such as reactions [24] and [25] but no attempt was made to follow the

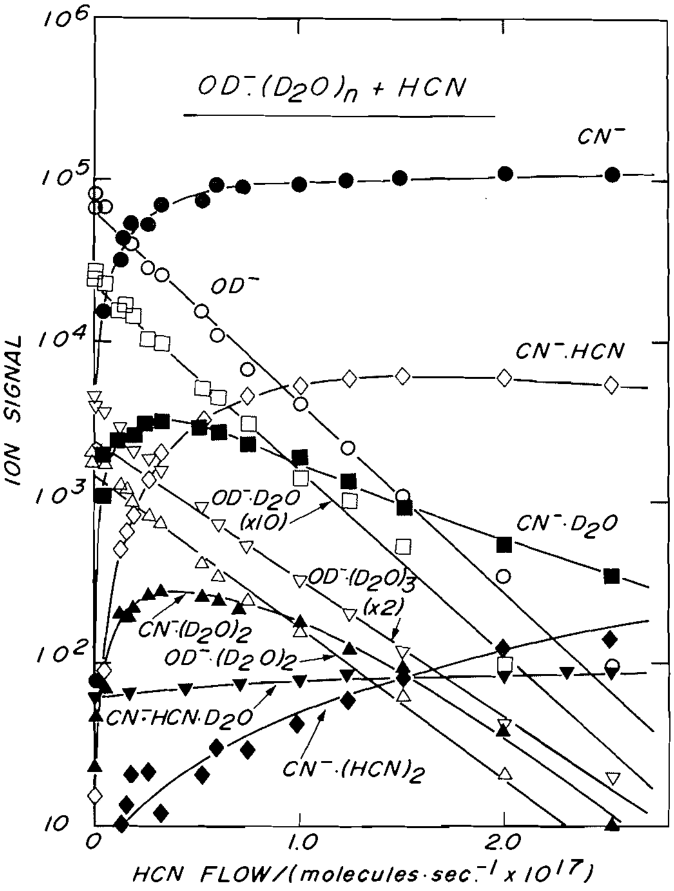

FIG. 5. Observations recorded for the reactions of $OD^-.(D_2O)_n$ with HCN in a He buffer. $T = 298$ K, $P = 0.337$ Torr, $\bar{v} = 7.3$ cm s^{-1}, $L = 46$ cm, and the flow of D_2O is approximately 3×10^{19} molecules s^{-1}.

[24] $CH_2NO_2^-.D_2O + CH_3NO_2 \rightarrow CH_2NO_2^-.CH_3NO_2 + D_2O$

[25] $CH_2NO_2^-.(D_2O)_2 + CH_3NO_2 \rightarrow CH_2NO_2^-.D_2O.CH_3NO_2 + D_2O$

kinetics of these processes in detail.

HCN

Figure 5 shows the influence of hydration on the reaction of the hydroxide ion with HCN observed under flowing afterglow conditions. The primary reactions which were observed may be interpreted in terms of eq. [26]. The ions $OD^-.(D_2O)_n$ were all observed to react very rapidly with HCN with rate constants

[26] $OD^-.(D_2O)_n + HCN \rightarrow CN^-.(D_2O)_m + (n - m)D_2O + HOD$

$\gtrsim 3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Similar results were obtained with $OH^-.(H_2O)_n$ except for $n = 2$ in which case the decay of the ion was obscured by the rise in the secondary product ion $CN^-.HCN$. Product ions for reaction [26] were observed for $m = 0$, 1, and 2. There was no evidence for the formation of $CN^-.(D_2O)_3$ to match the initial $OD^-.(D_2O)_3$ signal. Apparently the fast reaction of this latter ion leads to the "boil-off" of at least one molecule of D_2O.

Both $CN^-.D_2O$ and $CN^-.(D_2O)_2$ were observed to undergo rapid secondary reactions involving the exchange of D_2O for HCN as indicated in reactions [27] to [29].

[27] $CN^-.D_2O + HCN \rightarrow CN^-.HCN + D_2O$

[28] $CN^-.(D_2O)_2 + HCN \rightarrow CN^-.D_2O.HCN + D_2O$

[29] $CN^-.D_2O.HCN + HCN \rightarrow CN^-.(HCN)_2 + D_2O$

Discussion

Previous measurements carried out in our laboratory have clearly established the intrinsic reactivity of the bare hydroxide ion in the gas phase towards a variety of oxygen and carbon acids (5). Here we have scrutinized changes in this reactivity as a function of step-wise hydration. The bare hydroxide ion is allowed to build up a hydration shell by successive additions of water molecules upstream in a flowing He or H_2 buffer gas at low total pressures (ca. 0.3 Torr). The resulting $OH^-.(H_2O)_n$ ions then participate in hydrated ion–molecule reactions with the added neutral as they enter the reaction region downstream. The hydrated product ions have an opportunity to establish solvated ions of higher stability by solvent exchange or solvent addition reactions. The overall reaction scheme initiated by acid–base reactions is summarized in Fig. 2.

The mode of reaction of OH^- with CO_2 and SO_2 was observed to change upon hydration from three-body association to a binary switching reaction. Both three-body association reactions are relatively fast as in both instances ions of high stability are formed: the reaction with CO_2 is likely to yield the covalently bonded bicarbonate ion, $OCO(OH)^-$, and the bisulfite ion, $OSO(OH)^-$, is likely to be formed in the reaction with SO_2. The binary switching or ligand exchange reactions with the hydrated hydroxide ions proceed close to the collision limit. The higher rate constants for SO_2 can be attributed to its permanent dipole moment and also SO_2 has a slightly higher polarizability than CO_2. Application of the average-dipole-orientation (ADO) theory (9, 10) to the collisions of $OH^-.(H_2O)_n$ with SO_2 and the Langevine theory (11) to the collisions of $OH^-.(H_2O)_n$ with CO_2 yields ratios of collision rate constants for SO_2 to CO_2 which are approximately equal to 2 for $n = 1$, 2, and 3. These ratios are in accord with the ratios of the reaction rate constants determined in this study.

The product distributions associated with each specific degree of hydration were not resolved in this study, but, as in the earlier results reported by Fehsenfeld and Ferguson (4), the recorded product spectra indicated a strong bias towards formation of unsolvated HCO_3^- and HSO_3^-, and more so in the latter case. The same reactions have recently been investigated in tandem mass spectrometry studies at collision energies less than 1 eV (CM) in which the ions with a specific degree of solvation were selected with a mass spectrometer before they were allowed to react (12). The results of these studies also indicated very little retention in the product ions of the water of hydration of the reactant ions. With the exception of the reaction of $OH^-.(H_2O)_3$ with CO_2 which produced primarily $HCO_3^-.H_2O$, the reactions of $OH^-.(H_2O)_{1,2,3}$ with CO_2 and SO_2 were observed to produce predominantly the unhydrated product ions HCO_3^- and HSO_3^-, respectively. It has been suggested that the excess energy available in these reactions is sufficient to cause the water of hydration to be "boiled-off" in the course of the reaction (4).

The reaction of hydroxide ions with CO_2 makes a significant contribution to the total rate of disappearance of CO_2 in aqueous solution at pH values above about 7.5, and above pH 10 it predominates (13). The analogous reaction with SO_2 apparently does not compete to a measurable degree with the normal hydration of SO_2 by H_2O which is 100 million times as rapid as that of CO_2 (14). Reaction [30] has a reported rate constant in aqueous solution at 25°C of $6.0 \times 10^3 M^{-1} s^{-1}$ or 1.0×10^{-17}

[30] $OH^-(aq) + CO_2(aq) \rightarrow HCO_3^-(aq)$

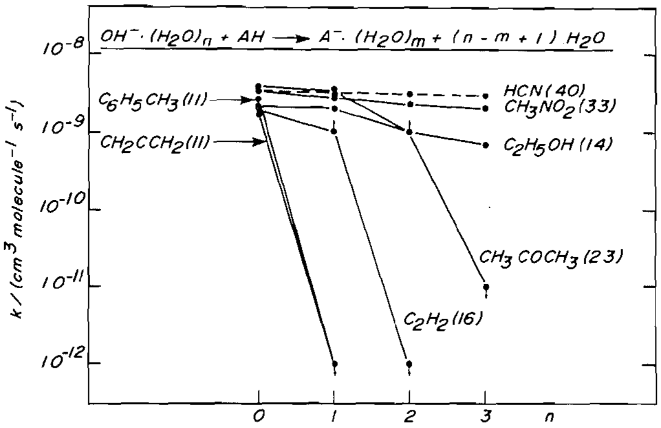

FIG. 6. Observed trends in the rate constants for reactions of hydrated hydroxide ions with acids, AH, as a function of step-wise hydration. The values indicated in parentheses correspond to the relative intrinsic acidities of the acids AH and H_2O, i.e. $-\Delta G^0$ (in kcal mol^{-1}) for the unhydrated reactions at 298 K.

cm^3 molecule^{-1} s^{-1} with an apparent Arrhenius activation energy of 13.25 kcal mol^{-1} (15). This is in contrast with the observations for reaction [5] between hydrated hydroxide ions, $OH^-.(H_2O)_n$, and CO_2 in the gas phase which indicate reaction on essentially every collision.

The rate constants measured in this study for the reactions of hydrated hydroxide ions with acids, AH, are presented graphically in Fig. 6. As this figure clearly illustrates, hydration of the highly reactive bare hydroxide ion results in either a slight or a precipitous reduction in the specific rate of reaction, the latter occurring after the addition of three, two, or even just one molecule of water. The following examination of the overall energetics of these reactions suggests that these trends in reactivity with degree of hydration are thermodynamically rather than kinetically controlled.

The intrinsic exoergicities of the acid–base reactions investigated in this study span a range from 11 to 40 kcal mol^{-1}. The differences in gas-phase acidity indicated in Fig. 6 represent average values derived from the absolute gas-phase acidities based on pulsed-ICR (16) and flowing afterglow measurements (7, 17, 18). Hydration of the hydroxide ion acts to decrease the reaction exoergicity and can render the reaction endoergic unless it is offset by the hydration energy of the conjugate base that is produced (and the hydration energy of possible hydrated neutral products). The standard enthalpies and free energies of hydration for $OH^-.(H_2O)_n$ are available from gas-phase measurements (they are reported here as positive quantities and so refer to the removal of water molecule from the hydrated ion): they are 25, 16.4, 15 and 19, 10, and 7.5 kcal mol^{-1}, for $n = 1$, 2, and 3, respectively (19). In contrast, the hydration energies of the conjugate bases produced in the reactions which were investigated are generally not known. Values of 13.8 and 7.9 kcal mol^{-1} are available for the standard enthalpy and free energy of hydration of CN^- with one water molecule (19). Also a calculated value of 18 kcal mol^{-1} is available for the binding energy (ΔE) of $C_2H^-.H_2O$ (20) which allows us to estimate the overall energetics for the reaction of $OH^-.H_2O$ with C_2H_2. But because of the sparsity of energies of hydration, we can only surmise the thermodynamic situation for the majority of the reactions investigated.

Allene and toluene are the acids closest in intrinsic acidity to that of water. The carbanions produced by their deprotonation appear to have energies of hydration insufficient to compensate for the high hydration energy of OH^- in spite of the intrinsic exoergicity of 11 kcal mol^{-1}. The weak hydration of carbanions is not unexpected (21). Our results suggest a standard free energy of hydration for $C_6H_5CH_2^-$ and $C_3H_3^-$ of less than 8 kcal mol^{-1}. The sharp drop by more than three orders of magnitude in the specific rate for deprotonation observed with the addition of just one molecule of water is therefore a manifestation of an immediate reversal in the relative acidity of these two carbon acids and water.

A similar reversal in relative acidity is apparent with acetylene but in this case two molecules of water are required to drive the proton transfer endoergic. The unhydrated reaction is exoergic by 16 kcal mol^{-1} which alone is almost enough to compensate for the free energy of hydration of OH^- and thus to render exoergic the formation of unhydrated C_2H^-. Transformation of the calculated energy of hydration, $\Delta E = 18$ kcal mol^{-1}, into an enthalpy of hydration (20) and correction for the entropy change for the association of H_2O to C_2H^- estimated to be -20 cal mol^{-1} deg^{-1} (19) yields an estimated standard free energy of hydration for C_2H^- of 9 kcal mol^{-1}. Reaction [31] is thus estimated to be exoergic by 6 kcal mol^{-1}. This is in

$$[31]\quad OH^-.H_2O + C_2H_2 \rightleftharpoons C_2H^-.H_2O + H_2O$$

reasonable accord with the value of 4 kcal mol^{-1} which may be derived from the measured ratio of rate constants of 8×10^2 obtained in this study for the similar reaction with heavy water and neglecting isotope effects. An average value of 5 kcal mol^{-1} for the exoergicity of reaction [31] yields an upper limit of 5 kcal mol^{-1} for the standard free energy for removal of H_2O from $C_2H^-.(H_2O)_2$ if the failure to observe a reaction between $OH^-.(H_2O)_2$ and C_2H_2 is attributed to endoergicity.

Figure 6 suggests that a reversal in relative acidity also occurs with acetone, delayed in this case until the addition of at least three water molecules to OH^-. This result is consistent with the early observations of a relative acidity for acetone and water in the gas-phase which is reverse to that observed in aqueous solution (22), and with a rate constant of only 4.5×10^{-22} cm^3 molecule^{-1} s^{-1} reported for the reaction of hydroxide ions with acetone in aqueous solution (23).

No reversals in relative acidity were observed with ethanol, nitromethane, and hydrogen cyanide. Ethanol is an oxygen acid whose conjugate base is expected to be strongly hydrated. This accounts for the continued high reactivity of the hydrated hydroxide ions towards ethanol in contrast to the falloff in reactivity observed for the reactions with acetylene and acetone which are intrinsically more exoergic. Nitromethane and hydrogen cyanide are intrinsically the strongest of the acids investigated. The intrinsic exoergicities of the proton-transfer reactions with these two acids are extremely high allowing for almost total "boil-off" of the water of hydration up to $n = 3$: reaction [23] is exoergic for m down to $n - 2$ and reaction [26] is exoergic for $m = 0$, viz. no retention of water. Thus, while the order of acidity between H_2O and ethanol is preserved primarily by the strong hydration of $C_2H_5O^-$, the order between H_2O and both HCN and CH_3NO_2, whose conjugate bases are expected to be more weakly hydrated, is preserved largely as a result of the much higher intrinsic exoergicities. Again these results are consistent with rate measurements made in solution and with known solution acidities. For example, the reaction between hydroxide ions and HCN is extremely rapid in aqueous solution proceeding at close to the diffusion limit, $k = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (23).

We have recently reported a parallel study of the gas-phase reactivity of methoxide ions solvated with methanol towards the same acids used in the present experiments (7). There is good correlation with the observations and interpretations reported here and, taken together, the studies of these two systems have provided new insight into the transition in the kinetics of acid–base reactions between the gas-phase and solution (24).

Acknowledgement

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

1. S. D. TANNER, G. I. MACKAY, and D. K. BOHME. Can. J. Chem. **59**, 1615 (1981).
2. D. K. BOHME, R. S. HEMSWORTH, H. W. RUNDLE, and H. I. SCHIFF. J. Chem. Phys. **58**, 3504 (1973).
3. G. I. MACKAY, R. S. HEMSWORTH, and D. K. BOHME. Can. J. Chem. **54**, 1624 (1976).
4. F. C. FEHSENFELD and E. E. FERGUSON. J. Chem. Phys. **61**, 3181 (1974).
5. S. D. TANNER, G. I. MACKAY, and D. K. BOHME. Can. J. Chem. **59**, 1615 (1981).
6. G. I. MACKAY and D. K. BOHME. J. Am. Chem. Soc. **100**, 327 (1978).
7. G. I. MACKAY, A. B. RAKSHIT, and D. K. BOHME. Can. J. Chem. **60**, 2394 (1982).
8. D. K. BOHME, G. I. MACKAY, H. I. SCHIFF, and R. S. HEMSWORTH. J. Chem. Phys. **61**, 2175 (1974).
9. L. BASS, T. SU, W. J. CHESNAVICH, and M. T. BOWERS. Chem. Phys. Lett. **34**, 119 (1975).
10. T. SU, E. C. F. SU, and M. T. BOWERS. J. Chem. Phys. **69**, 2243 (1978).
11. G. GIOUMOUSIS and D. P. STEVENSON. J. Chem. Phys. **29**, 294 (1958).
12. P. M. HIERL, M. J. HENCHMAN, and J. F. PAULSON. Paper presented at the 29th Annual Conference on Mass Spectrom. and Allied Topics, Minneapolis, MN, May 24–29 (1981).
13. Y. POCKER and D. W. BJORKQUIST. J. Am. Chem. Soc. **99**, 6537 (1977).
14. M. EIGEN, K. KUSTIN, and G. MAASS. Z. Physik. Chem. (N.F.) **30**, 130 (1961).
15. J. A. SIRS. Trans. Faraday Soc. **54**, 201 (1958).
16. J. E. BARTMESS, J. A. SCOTT, and R. T. MCIVER. J. Am. Chem. Soc. **101**, 6046 (1979).
17. G. I. MACKAY and D. K. BOHME. Int. J. Mass Spectrom. Ion Phys. **26**, 327 (1978).
18. D. BETOWSKI, G. MACKAY, J. PAYZANT, and D. BOHME. Can. J. Chem. **53**, 2365 (1975).
19. P. KEBARLE. Ann. Rev. Phys. Chem. **28**, 445 (1977).
20. R. R. SQUIRES. Private communication.
21. R. B. MCMAHON and P. KEBARLE. J. Am. Chem. Soc. **96**, 5940 (1974).
22. D. K. BOHME, E. LEE-RUFF, and L. B. YOUNG. J. Am. Chem. Soc. **94**, 5153 (1972).
23. M. EIGEN. Angew. Chem., Int. Ed. Eugl. **3**, 1 (1964).
24. D. K. BOHME, A. B. RAKSHIT, and G. I. MACKAY. J. Am. Chem. Soc. **104**, 1100 (1982).