An experimental study of the reactivity of the hydroxide anion in the gas phase at room temperature, and its perturbation by hydration

SCOTT D. TANNER, GERVASE I. MACKAY, AND DIETHARD K. BOHME

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

Received August 11, 1980

SCOTT D. TANNER, GERVASE I. MACKAY, and DIETHARD K. BOHME. Can. J. Chem. **59**, 1615 (1981).

Flowing afterglow measurements are reported which provide rate constants and product identifications at 298 ± 2 K for the gas-phase reactions of OH^- with CH_3OH, C_2H_5OH, CH_3OCH_3, CH_2O, CH_3CHO, CH_3COCH_3, CH_2CO, HCOOH, $HCOOCH_3$, $CH_2{=}C{=}CH_2$, $CH_3{-}C{\equiv}CH$, and $C_6H_5CH_3$. The main channels observed were proton transfer and solvation of the OH^-. Hydration with one molecule of H_2O was observed either to reduce the rate slightly and lead to products which are the hydrated analogues of the "nude" reaction, or to stop the reaction completely, $k \leq 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The reaction of $OH^-{\cdot}H_2O$ with $CH_3{-}C{\equiv}CH$ showed an uncertain intermediate behaviour.

SCOTT D. TANNER, GERVASE I. MACKAY et DIETHARD K. BOHME. Can. J. Chem. **59**, 1615 (1981).

On rapporte des mesures avec la technique de la lueur d'écoulement qui permettent d'obtenir les constantes de vitesse et d'identifier les produits des réactions en phase gazeuse à 298 ± 2 K de l'ion OH^- avec CH_3OH, C_2H_5OH, CH_3OCH_3, CH_2O, CH_3CHO, CH_3COCH_3, CH_2CO, HCOOH, CH_3COOH, $CH_2{=}C{=}CH_2$, $CH_3{-}C{\equiv}CH$ et $C_6H_5CH_3$. Les principales voies observées sont celles du transfert du proton et de la solvatation du OH^-. On a observé que l'hydratation par une molécule d'eau provoque soit l'arrêt complet de la réaction, $k \leq 10^{-12}$ cm^3 molécule^{-1} s^{-1}, soit une légère réduction de la vitesse avec la formation de produits qui sont les analogues hydratés de la réaction "nue". La réaction entre $OH^-{\cdot}H_2O$ et $CH_3{-}C{\equiv}CH$ présente un comportement incertain de l'intermédiaire.

[Traduit par le journal]

Introduction

The hydroxide anion is a relatively strong base in the gas phase where it can be readily generated in a variety of ways. Consequently it is often implicated in the chemical evolution of negative ions in electronegative plasmas such as hydrocarbon flames (1) and planetary ionospheres (2). One important practical consequence of the reactivity and ease of production of OH^- has been its use in negative chemical ionization mass spectrometry (3). While certain qualitative aspects of the gas-phase reactivity of OH^- have been well documented in the literature, only a few quantitative studies have been reported so far. Here we present an extensive flowing afterglow study of the kinetics and mechanisms of reactions of OH^- with a variety of oxygen-containing hydrocarbons, allene, propyne, and toluene. The results complement our earlier flowing afterglow studies of reactions of OH^- with olefins (4, 5), acetylene (6), simple cyanides (7), nitromethane (8), silane (9), and halogenated methanes (10), and therefore serve to extend our understanding of the intrinsic reactivity patterns of this ion. As such they also provide a benchmark for the reactivity of OH^- in solution where its basicity is much depressed as a result of solvation. An attempt is also made in this study to begin to explore the influence of hydration on the intrinsic reactivity of this ion.

Experimental

The measurements were carried out in a conventional flowing plasma mass spectrometer (flowing afterglow) system which has been described previously (11). The OH^- and $OH^-{\cdot}H_2O$ ions were established by introducing water vapor past the electron gun in either a flowing helium or hydrogen plasma. In certain instances, to avoid the presence of water vapor, OH^- was produced by the reaction of O^- with CH_4 with O_2 serving as the source gas for O^-.

The reactant neutrals were added into the reaction region either in their pure form or diluted with helium. The determination of their flows required separate viscosity measurements as has been described (12). The sources of most of the neutral reactants and their purities have also been given previously (13). The allene, propyne, and toluene were of normal research grade. Rate constants were determined in the usual manner from measurements of the $m/e = 17$ and $m/e = 35$ signals as a function of added reactant. The contribution due to $^{35}Cl^-$ was subtracted to arrive at the true $OH^-{\cdot}H_2O$ signal. The magnitude of $^{35}Cl^-$ was derived from the 37 isotope which was monitored concomitantly with product ions. The operating conditions in these experiments encompassed total gas pressures, P, in the range 0.20 to 0.53 Torr, average gas velocities, $\bar{v}$, from 7.3 to 8.0 × 10^3 cm s^{-1}, effective reaction lengths, L, between 45 and 125 cm, and a gas temperature, T, of 298 ± 2 K.

Results and Discussion

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 (11). Initial measurements of the charge transfer reaction:

$$[1] \quad OH^- + NO_2 \rightarrow NO_2^- + OH$$

0008-4042/81/111615-07$01.00/0

TABLE 1. Rate constants measured in this study for reactions of the bare hydroxide ion at 298 ± 2 K

Reaction	k^a
$OH^- + NO_2 \rightarrow NO_2^- + OH$	1.1 ± 0.4
$OH^- + CH_3OH \rightarrow CH_3O^- + H_2O$	2.2 ± 0.6
$OH^- + C_2H_5OH \rightarrow C_2H_5O^- + H_2O$	2.7 ± 0.8
$OH^- + CH_3OCH_3 \rightarrow$ products	$\lesssim 0.001$
$OH^- + CH_2O + He \rightarrow HOCH_2O^- + He$	$(2 \pm 1) \times 10^{-26\,b}$
$OH^- + CH_3CHO \rightarrow {}^-CH_2CHO + H_2O$	3.1 ± 0.8
$OH^- + CH_3COCH_3 \rightarrow CH_3COCH_2^- + H_2O$	3.7 ± 0.9
$OH^- + CH_2CO \rightarrow {}^-CHCO + H_2O$	2.2 ± 0.5
$OH^- + HCOOH \rightarrow HCO_2^- + H_2O$	2.2 ± 0.7
$\rightarrow OH^- \cdot H_2O + CO$	
$OH^- + HCOOCH_3 \rightarrow HCO_2^- + CH_3OH$	1.9 ± 0.5
$\rightarrow CH_3O^- \cdot H_2O + CO$	
$OH^- + CH_2{=}C{=}CH_2 \rightarrow CH_2{=}C{=}CH^- + H_2O$	1.7 ± 0.4
$OH^- + CH_3{-}C{\equiv}CH \rightarrow {}^-CH_2{-}C{\equiv}CH + H_2O$	1.7 ± 0.3
$\rightarrow CH_3{-}C{\equiv}C^- + H_2O$	
$OH^- + C_6H_5CH_5 \rightarrow C_6H_5CH_2^- + H_2O$	2.6 ± 0.6
$OH^- + C_6H_5CH_2D \rightarrow C_6H_5CHD^- + H_2O$	2.8 ± 0.7
$\rightarrow C_6H_5CH_2^- + HOD$	

[a] The measured rate constant along with the estimated uncertainty in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.
[b] Termolecular rate constant measured at a total pressure of 0.26 Torr.

TABLE 2. Rate constants measured in this study for reactions of the singly-hydrated hydroxide ion at 298 ± 2 K

Reaction	k^a
$OH^- \cdot H_2O + C_2H_5OH \rightarrow C_2H_5O^- \cdot H_2O + H_2O$	2.1 ± 0.5
$OH^- \cdot H_2O + CH_3CHO \rightarrow {}^-CH_2CHO \cdot H_2O + H_2O$	3 ± 1
$OH^- \cdot H_2O + CH_3COCH_3 \rightarrow CH_3COCH_2^- \cdot H_2O + H_2O$	3 ± 1
$OH^- \cdot H_2O + HCOOCH_3 \rightarrow CH_3O^- \cdot 2H_2O + CO$	1.6 ± 0.5
$\rightarrow (HCO_2^- \cdot H_2O + CH_3OH)$	
$OH^- \cdot H_2O + CH_2{=}C{=}CH_2 \rightarrow$ products	$\lesssim 0.001$
$OH^- \cdot H_2O + CH_3{-}C{\equiv}CH \rightarrow C_2H_3O^- + CH_3OH$	0.058 ± 0.023
$OH^- \cdot H_2O + C_6H_5CH_3 \rightarrow$ products	$\lesssim 0.001$

[a] The measured rate constant along with the estimated uncertainty in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.

provided a rate constant of $(1.1 \pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} in exact agreement with the accepted value (14). The following section provides a more detailed account of the observed hydroxide ion chemistry.

CH_3OH, C_2H_5OH, CH_3OCH_3

The reaction with CH_3OH was investigated over a wide range in total gas pressure (0.307 to 0.52 Torr) and effective reaction length (59, 85, and 120 cm). Also the flow of H_2O was varied over a large range from 7.8×10^{16} to 9.3×10^{19} molecules^{-1} s^{-1} in an attempt to drive reaction [2] to equilibrium:

$$[2] \quad OH^- + CH_3OH \rightleftharpoons CH_3O^- + H_2O$$

Proton transfer was the only observed reaction channel and k_2 was determined to be $(2.2 \pm 0.6) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Significant amounts of reverse reaction, as manifested by curvature in the decay of OH^-, became apparent only at the highest additions of H_2O ($>10^{19}$ molecules s^{-1}) and the long reaction lengths ($L > 85$ cm). However, under these relatively extreme conditions, a variety of competing and secondary reactions came into play as both the OH^- and CH_3O^- were observed to cluster with H_2O (up to $OH^- \cdot 3H_2O$) and CH_3OH (up to $CH_3O^- \cdot CH_3OH$), respectively. Also, the observation of mixed cluster ions of the type $CH_3O^- \cdot nH_2O$ ($n = 1$ to 3) and $CH_3O^- \cdot H_2O \cdot CH_3OH$ was indicative of some interconversion between cluster ions. These complicating reactions apparently prevented the establishment of equilibrium for the unsolvated reaction [2]. The ratio of the rate constants, k_2/k_{-2}, determined from our usual fitting procedure (11) was strongly dependent on the H_2O concentration as were the mass discrimination plots which exhibited strong curvature. Also, the ratio plots were observed to be curved for all additions of CH_3OH. Such a behaviour is expected for a reaction with a large equilibrium constant proceeding in the presence of secondary reactions. Indeed, available thermochemical information indicates a very large value for K_2 of $(2.2 \pm 0.4) \times 10^7$

(15). Equilibrium did appear to be established between several of the cluster ions as we have recently reported in a study which followed the transition in the relative acidity of water and methanol, viz. the magnitude of K_2, from the completely unsolvated behaviour in the gas phase to that in solution.

The proton-transfer reaction of OH^- with ethanol was also observed to proceed rapidly at room temperature.

[3] $OH^- + C_2H_5OH \rightarrow C_2H_5O^- + H_2O$

with $k_3 = (2.7 \pm 0.8) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Equilibrium could again not be achieved under the available operating conditions. Solvation with one molecule of water reduced the reactivity of the hydroxide ion only slightly. The rate constant for the hydrated proton transfer [4] was

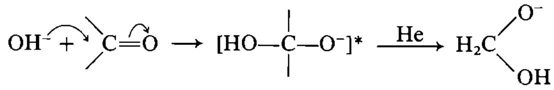
[4] $OH^- \cdot H_2O + C_2H_5OH \rightarrow C_2H_5O^- \cdot H_2O + H_2O$

measured to be $(2.1 \pm 0.5) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. The hydrated product ion was readily observed. Formation of "nude" $C_2H_5O^-$ is endothermic since the 25 kcal mol^{-1} of hydration energy for OH^- (16) exceeds the 10 kcal mol^{-1} of exothermicity for reaction [4] (17).

Dimethyl ether failed to react with OH^-, $k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The failure to observe proton transfer in this case is a manifestation of the low gas-phase acidity of dimethyl ether.

CH_2O, CH_3CHO, CH_3COCH_3

Formaldehyde was observed to react quite rapidly with OH^-, but not by proton transfer; an ion with mass 47 was produced instead. Apparently an association reaction was taking place but with an unexpectedly large rate. At the total pressure of the measurements (0.56 Torr) the observed OH^- decay was equivalent to a three-body rate constant of $(2 \pm 1) \times 10^{-26}$ cm^6 molecule^{-2} s^{-1}. This value is much larger than those expected for association reactions involving a similar number of atoms in which a "loose" adduct is formed through electrostatic interaction or proton bonding. Therefore it has been taken as a manifestation of the formation of a "tight" adduct through chemical bonding to a tetrahedrally coordinated carbon atom (18):

[5] 

$$OH^- + {>}C{=}O \longrightarrow [HO{-}\overset{|}{\underset{|}{C}}{-}O^-]^* \xrightarrow{He} H_2C\begin{smallmatrix} O^- \\ OH \end{smallmatrix}$$

Formation of the conjugate base of methyl peroxide, $CH_3O_2^-$, would require extensive chemical redisposition and so is not expected to occur efficiently. We have observed a similar addition of hydride and methoxide to formaldehyde (18).

Acetaldehyde and acetone were both observed to react rapidly with OH^- by proton transfer (see Table 1). Deuterium-labeling experiments have established previously that acetaldehyde loses the proton from the methyl position (19). Figure 1 shows a representative result obtained with acetaldehyde. Solvation with a single water molecule was seen to leave the reactivity of OH^- essentially unchanged. Since the singly-hydrated product ions were observed, we may write:

[6] $OH^- \cdot H_2O + CH_3CHO \rightarrow {}^-CH_2CHO \cdot H_2O + H_2O$

[7] $OH^- \cdot H_2O + CH_3COCH_3 \rightarrow CH_3COCH_2^- \cdot H_2O + H_2O$

Both of these reactions were measured to proceed with a rate constant of $(3 \pm 1) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

CH_2CO

Ketene was observed to react rapidly with the hydroxide ion with $k = (2.2 \pm 0.5) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} to form a mass 41 ion for which the following resonance structure may be written

[8] $H{-}\bar{C}{=}C{=}O \leftrightarrow H{-}C{\equiv}C{-}O^-$

Figure 2 shows the formation of a secondary product ion with mass 39. The HC_2O^- apparently was being consumed further by reaction with ketene to produce $C_3H_3^-$ for which the following

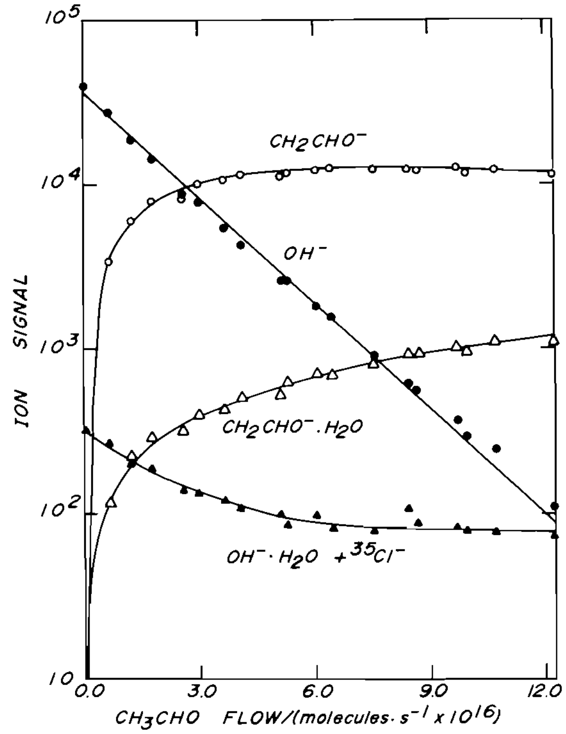


FIG. 1. The observed variation in the dominant ion signals recorded upon the addition of acetaldehyde into a flowing H_2/H_2O plasma; $T = 298$ K, $P = 0.312$ Torr, $\bar{v} = 7.8 \times 10^3$ cm s^{-1}, and $L = 84$ cm.

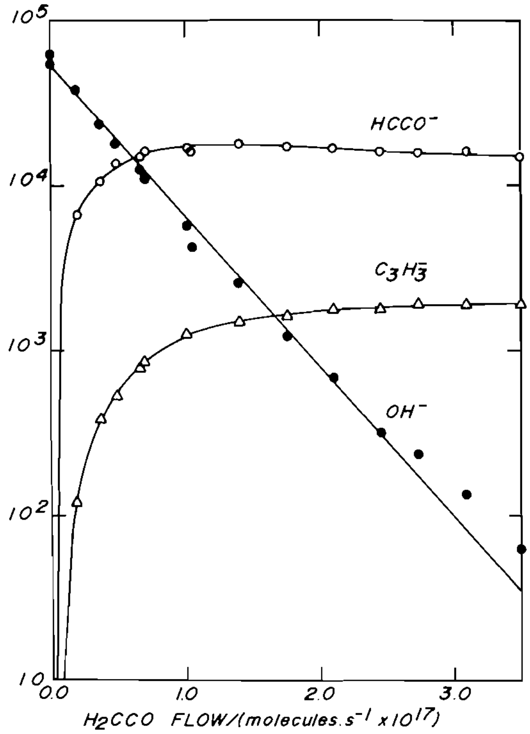
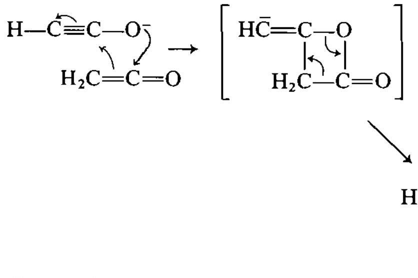


FIG. 2. The observed variation in the dominant ion signals recorded upon the addition of ketene into a flowing H_2/H_2O plasma; $T = 298\,K$, $P = 0.301$ Torr, $\bar{v} = 7.9 \times 10^3\ cm\ s^{-1}$, and $L = 59\,cm$.

resonance structures may be written:

[9] $H{-}\bar{C}{=}C{=}CH_2 \leftrightarrow H{-}C{\equiv}C{-}\bar{C}H_2$

The mechanism of this latter reaction presumably involves the formation of a four-centered intermediate which fragments to eliminate CO_2:

[10] 

The $C_3H_3^-$ in turn appeared to react further with ketene to regenerate the HC_2O^- by proton transfer,

[11] $C_3H_3^- + H_2C_2O \rightarrow HC_2O^- + C_3H_4$

This reaction, together with the previous reaction which produces $C_3H_3^-$, represents an ion-catalyzed reaction scheme for the conversion of ketene into CO_2 and C_3H_4,

[12] $H_2C_2O + H_2C_2O \rightarrow CO_2 + C_3H_4$

The overall exothermicity of reaction [12] is 18.9 kcal mol^{-1} for the formation of allene. An analysis of the steady-state ion abundance ratio for $HC_2O^-/C_3H_3^-$ indicated a value for the ratio of rate constants k_{11}/k_{10} approximately = 10.

HCOOH

The analysis of the formic acid data also indicated a high rate, $k = (2.2 \pm 0.7) \times 10^{-9}\ cm^3\ molecule^{-1}\ s^{-1}$, but with only 0.75 ± 0.05 of the reactive collisions leading to the proton-transfer product, HCO_2^-. The remaining 0.25 ± 0.05 of the collisions gave rise directly (in a bimolecular fashion) to singly-hydrated OH^-,

[13*a*] $OH^- + HCOOH \rightarrow HCO_2^- + H_2O$

[13*b*] $\rightarrow OH^-{\cdot}H_2O + CO$

For the experimental results shown in Fig. 3, the reactant OH^- was produced by the reaction of O^- with CH_4 to eliminate all but impurity H_2O and so to minimize the direct association of OH^- with H_2O. The initial signal at mass 35 was entirely accounted for under these conditions by the chlorine isotope, $^{35}Cl^-$. The change in this signal with

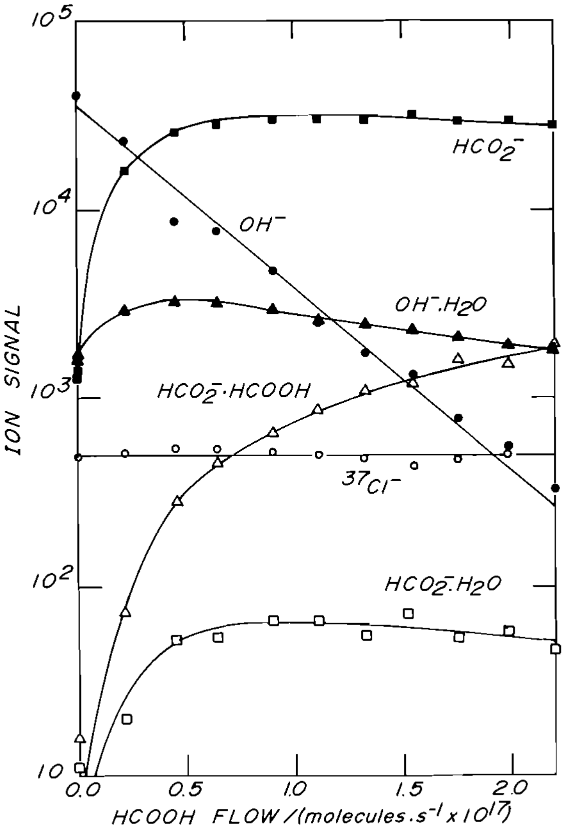
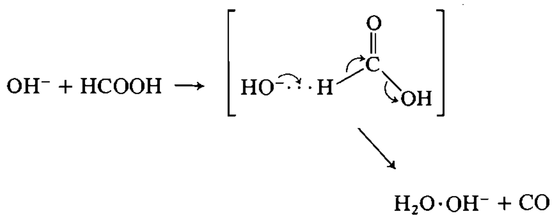


FIG. 3. The observed variation in the dominant ion signals recorded upon the addition of formic acid into a flowing $He/O_2/CH_4$ plasma; $T = 301\,K$, $P = 0.450$ Torr, $\bar{v} = 8.4 \times 10^3\ cm\ s^{-1}$, and $L = 47\,cm$.

addition of formic acid could then be attributed entirely to the bimolecular formation of $OH^-{\cdot}H_2O$ and its subsequent reaction. The channel leading to the formation of the cluster ion is rendered exothermic by the hydration energy of OH^-, 25 kcal mol^{-1} (16), without which it would be endothermic by 6 kcal mol^{-1} (16). Its mechanism may involve a nearly concerted loss of CO and capture of the water molecule by the OH^-:

[14]



The products of the reaction of the cluster ion were not established with certainty. They may include the following:

[15*a*] $OH^-{\cdot}H_2O + HCOOH \rightarrow HCO_2^- + 2H_2O$

[15*b*] $\rightarrow HCO_2^-{\cdot}H_2O + H_2O$

[15*c*] $\rightarrow OH^-{\cdot}2H_2O + CO$

Channel [15*a*] was masked by the production of HCO_2^- from "nude" OH^-. Channel [15*c*] is the analogue of channel [13*b*]. The $OH^-{\cdot}2H_2O$ was observed above the background only in those experiments in which the initial OH^- was produced from H_2O and higher signals of $OH^-{\cdot}H_2O$ were present initially. Channel [15*b*] was observed only in depressed amounts due to a secondary "solvent switching" reaction with HCOOH:

[16] $HCO_2^-{\cdot}H_2O + HCOOH \rightarrow HCO_2^-{\cdot}HCOOH + H_2O$

The reactivity of the nude hydroxide ion is reminiscent of the behaviour reported previously by Isolani and Riveros (20) in their ICR study of analogous reactions of negative ions with esters of formic acid. In the next section we report a study of the reaction of OH^- with the first member of this homologous series, methyl formate.

HCOOCH₃

Two main products were observed in the ICR studies of the reaction on OH^- with methyl formate at water pressures of 5×10^{-5} Torr (21):

[17*a*] $OH^- + HCOOCH_3 \rightarrow HCO_2^- + CH_3OH$

[17*b*] $\rightarrow CH_3O^-{\cdot}H_2O + CO$

The rate constant k_{17} and branching ratio [17*a*]/[17*b*] were reported to be 1.5×10^{-9} cm^3 $molecule^{-1}$ s^{-1} and 0.80, respectively. The results of the flowing afterglow measurements for this reaction are virtually identical: $k_{17} = 1.9 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} and [17*a*]/[17*b*] = 1.0 ± 0.2 for the measurements carried out with and without added water vapour. The $CH_3O^-{\cdot}H_2O$ product rapidly reacted further, $k > 9 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, apparently to produce an ion at $m/e = 63$, presumably $CH_3O^-{\cdot}CH_3OH$, which is known to be formed from the "nude" CH_3O^- (22). The mechanism of reaction [17] has been reviewed by Nibbering (23).

The singly-hydrated OH^- appeared to react in a fashion analogous to the bare ion. The reaction was rapid, $k = (1.6 \pm 0.5) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}, and ions were observed to be produced which correspond to the singly-hydrated counterparts of the products of reaction [17]:

[18*a*] $OH^-{\cdot}H_2O + HCOOCH_3 \rightarrow CH_3O^-{\cdot}2H_2O + CO$

[18*b*] $\rightarrow HCO_2^-{\cdot}H_2O + CH_3OH$

The assignment of the latter product ion was ambiguous since it has the same mass as the $CH_3O^-{\cdot}CH_3OH$ believed to be produced by $CH_3O^-{\cdot}H_2O$. In contrast, the second hydrate, $OH^-{\cdot}2H_2O$, reacted in a much slower fashion, $k < 3 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

C₃H₄

Both allene and propyne were observed to lose a proton to OH^-. The rate constant measured for the reaction with allene

[19] $OH^- + CH_2{=}C{=}CH_2 \rightarrow CH_2{=}C{=}CH^- + H_2O$

was $(1.7 \pm 0.4) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}, which exceeds an earlier value of $(7.5 \pm 2.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (4). The reaction with propyne

[20*a*] $OH^- + CH_3{-}C{\equiv}CH \rightarrow {}^-CH_2{-}C{\equiv}CH + H_2O$

[20*b*] $\rightarrow CH_3{-}C{\equiv}C^- + H_2O$

was observed to be equally rapid with $k = (1.7 \pm 0.3) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}. Previous deuterium-labelling experiments (19) have shown that ≥ 60% of the deprotonation of propyne initially produces ${}^-CH_2{-}C{\equiv}CH$ which may relax to the more stable allenyl anion, $CH_2{=}C{=}CH^-$ (24). The allenyl anion is computed to be less stable than $CH_3{-}C{\equiv}C^-$ but the profile for this interconversion shows a high energy barrier (25). We have probed the relative reactivity of the $C_3H_3^-$ ions produced from allene and propyne in a separate study (25). The observed relative reactivity with methyl formate suggested that only 10 ± 5% of the deprotonation of propyne in fact occurs at the $C{\equiv}CH$ position. Nonempirical molecular orbital calculations predict that the acetylenic proton is slightly more acidic than the proton at the methyl position (26). Such an order of acidity would imply that the deprotonation observed experimentally is controlled kinetically rather than thermodynamically. Indeed, on the basis of the electrostatic interaction during a collision of OH^- with polar propyne, deprotonation by OH^- can be expected to proceed preferentially at the positive methyl end of propyne.

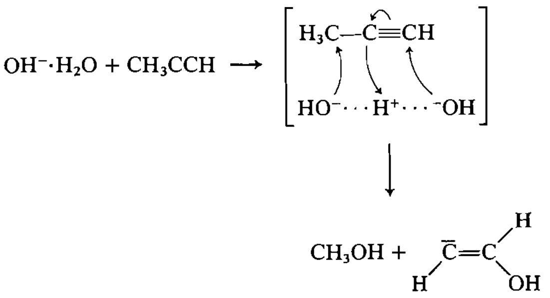
Hydration of OH^- stops the reaction with allene, $k \leq 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Apparently the exothermicity of the bare reaction, together with the hydration energy of the $C_3H_3^-$, is insufficient to compensate for the 25 kcal mol^{-1} of hydration energy of OH^-. The reaction of $OH^-\cdot H_2O$ with propyne showed the more surprising result given in Fig. 4. A slow decay is observed with addition of propyne which corresponds to a rate constant of $(5.8 \pm 2.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. An ion with $m/e = 43$ rises concomitantly, in part due to the association of C_2H^- with H_2O. A number of options are allowed by stoichiometry, for example:

[21*a*] $OH^-\cdot H_2O + CH_3CCH \rightarrow C_3H_7^- + O_2$

[21*b*] $\rightarrow C_2H^-\cdot H_2O + CH_3OH$

[21*c*] $\rightarrow {}^-CH_2CHO + CH_3OH$

Channel [21*a*] is unattractive on both energetic and mechanistic grounds. Channel [21*b*] corresponds to a hydrated nucleophilic displacement reaction which is probably endothermic because of the endothermicity of the bare reaction and the high hydration energy of OH^-. However, separate experiments have shown that C_2H^- hydrates with a three-body association rate constant similar in magnitude to that for the hydration of OH^-. This result suggests that the two hydration energies may be similar, at least to the extent that these rate constants correlate with the stability of the associated species (18). The slow reaction observed would be consistent with a hydrated nucleophilic displacement reaction endothermic by 2 kcal mol^{-1}. Channel [21*c*] is exothermic but would require an unlikely reaction mechanism. A fourth option might involve the formation of an enol type ion such as $HOCHCH^-$ which is isomeric with the $C_2H^-\cdot H_2O$ cluster ion and $^-CH_2CHO$, the conjugate base of acetaldehyde. The enol anion might result from a 1,3 nucleophilic attack in the following manner:

[22] 
$$OH^-\cdot H_2O + CH_3CCH \longrightarrow \left[\begin{array}{c} H_3C{-}C{\equiv}CH \\ HO^-\cdots H^+\cdots {}^-OH \end{array}\right] \longrightarrow CH_3OH + H\bar{C}{=}C(H)OH$$

The stability of this ion is likely to fall in between the lower stability of $C_2H^-\cdot H_2O$ and the higher stability of $^-CH_2CHO$. Consequently its formation may well be exothermic.

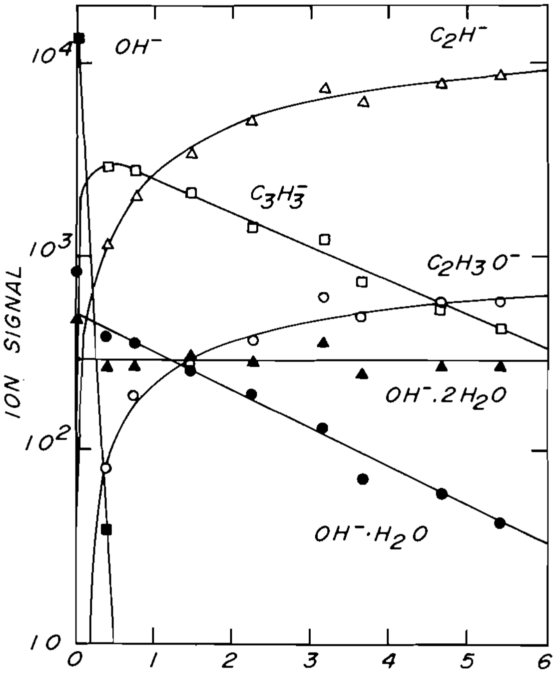


FIG. 4. The observed variation in the dominant ion signals recorded upon the addition of propyne into a flowing H_2/H_2O plasma; $T = 296$ K, $P = 0.354$ Torr, $\bar{v} = 7.6 \times 10^3$ cm s^{-1}, and $L = 46$ cm.

$C_6H_5CH_3$, $C_6H_5CH_2D$

The proton transfer from toluene to the bare hydroxide ion was also observed to be rapid, $k = (2.6 \pm 0.6) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Deuteration at one of the methyl positions failed to reveal an isotope effect; the new rate constant was measured to be $(2.8 \pm 0.7) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Furthermore, in those experiments in which OH^- was produced from O^- and CH_4 in the absence of added water vapour in helium buffer, the branching ratio [23*a*]/[23*b*] was observed to be 0.5 ± 0.1:

[23*a*] $OH^- + C_6H_5CH_2D \rightarrow C_6H_5CH_2^- + HOD$

[23*b*] $\rightarrow C_6H_5CHD^- + HOH$

The implication of this result is that the proton transfer proceeds in a direct fashion rather than through a long-lived complex for which complete scrambling would produce a branching ratio of 1.0 rather than 0.5. In those experiments in which OH^- was derived from water vapour the observed product ion ratio $[C_6H_5CH_2^-]/[C_6H_5CHD^-]$ was a function of the added water vapour, becoming as large as 11 at the highest additions. This was interpreted to reflect a rapid H/D exchange between H_2O and $C_6H_5CHD^-$. Stewart *et al.* have previously reported that $C_6H_5CH_2^-$ will exchange two hydrogen atoms in the presence of D_2O (19).

Several unsuccessful attempts were made with additions of water vapour as large as 4.2×10^{19} molecules s^{-1} at a reaction length of 125 cm to drive to equilibrium the reaction

$$[24] \quad OH^- + C_6H_5CH_3 \rightarrow C_6H_5CH_2^- + H_2O$$

We can report only a limit to the equilibrium constant of $K \geq 3 \times 10^5$.

Summary

The bare hydroxide ion has been observed to react rapidly, $k > 10^{-9}$ cm^3 molecule^{-1} s^{-1}, by proton transfer, with a variety of oxygen and carbon acids stronger than H_2O in the gas phase. With formic acid and methyl formate the proton transfer competes with the formation of a solvated hydroxide ion.

Hydration of the bare ion with one molecule of water was observed to result in either a slightly or a considerably reduced reactivity depending on the nature of the acid and the exothermicity of the bare reaction. The reactivity remains high when the hydration energy of the conjugate base produced is comparable to that of OH^-, or the exothermicity of the "nude" reaction is correspondingly high. The products are then also analogous to those observed for the "nude" reaction. Such was the case with the observed reactions of OH^- with C_2H_5OH, CH_3CHO, HCOOH, and $HCOOCH_3$. For the reactions with allene, propyne, and toluene, proton transfer was closed to the hydrated OH^- in the gas phase. Apparently the hydration energy of the carbanions produced in these cases is not sufficient to compensate for the high hydration energy of OH^- so that the acidity of the conjugate acids relative to that of H_2O has been reversed. The reaction with propyne showed an uncertain intermediate behaviour. The reduced reactivity in this case may be associated with a change in mechanism with solvation from proton transfer to hydrated displacement.

Acknowledgement

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

1. D. K. Bohme. *In* Kinetics of ion–molecule reactions. *Edited by* P. Ausloos. Plenum Press, New York, NY. 1979. p. 323.
2. F. C. Fehsenfeld and E. E. Ferguson. J. Chem. Phys. **61**, 3181 (1974).
3. A. L. C. Smit and F. H. Field. J. Am. Chem. Soc. **99**, 6471 (1977).
4. D. K. Bohme and L. B. Young. J. Am. Chem. Soc. **92**, 3301 (1970).
5. G. I. Mackay, M. H. Lien, A. C. Hopkinson, and D. K. Bohme. Can. J. Chem. **56**, 131 (1978).
6. D. K. Bohme, G. I. Mackay, H. I. Schiff, and R. S. Hemsworth. J. Chem. Phys. **61**, 2175 (1974).
7. G. I. Mackay, L. D. Betowski, J. D. Payzant, H. I. Schiff, and D. K. Bohme. J. Phys. Chem. **80**, 2919 (1976).
8. G. I. Mackay and D. K. Bohme. Int. J. Mass Spectrom. Ion Phys. **26**, 327 (1978).
9. J. D. Payzant, K. Tanaka, L. D. Betowski, and D. K. Bohme. J. Am. Chem. Soc. **98**, 894 (1976).
10. K. Tanaka, G. I. Mackay, J. D. Payzant, and D. K. Bohme. Can. J. Chem. **54**, 1643 (1976).
11. D. K. Bohme, R. S. Hemsworth, H. W. Rundle, and H. I. Schiff. J. Chem. Phys. **58**, 3504 (1973).
12. G. I. Mackay, R. S. Hemsworth, and D. K. Bohme. Can. J. Chem. **54**, 1624 (1976).
13. G. I. Mackay, S. D. Tanner, A. C. Hopkinson, and D. K. Bohme. Can. J. Chem. **57**, 1518 (1979).
14. D. L. Albritton. At. Data Nucl. Data Tables, **22**, 1 (1978).
15. G. I. Mackay and D. K. Bohme. J. Am. Chem. Soc. **100**, 327 (1978).
16. P. Kebarle. Ann. Rev. Phys. Chem. **28**, 445 (1977).
17. J. E. Bartmess, J. A. Scott, and R. T. McIver. J. Am. Chem. Soc. **101**, 6046 (1979).
18. D. K. Bohme, G. I. Mackay, and S. D. Tanner. J. Am. Chem. Soc. **102**, 407 (1980).
19. J. H. Stewart, R. H. Shapiro, C. H. DePuy, and V. M. Bierbaum. J. Am. Chem. Soc. **99**, 7650 (1977).
20. P. C. Isolani and J. M. Riveros. Chem. Phys. Lett. **33**, 362 (1975).
21. J. F. G. Faigle, P. C. Isolani, and J. M. Riveros. J. Am. Chem. Soc. **98**, 2049 (1976).
22. J. M. Riveros. Adv. Mass Spectrom. **6**, 277 (1974).
23. N. M. M. Nibbering. *In* Kinetics of ion–molecule reactions. *Edited by* P. Ausloos. Plenum Press, New York, NY. 1979. p. 165.
24. A. C. Hopkinson. Prog. Theor. Org. Chem. **2**, 194 (1977).
25. G. I. Mackay and D. K. Bohme. Org. Mass Spectrom. **15**, 593 (1980).
26. A. C. Hopkinson, M. H. Lien, K. Yates, P. G. Mezey, and I. G. Csizmadia. J. Chem. Phys. **67**, 517 (1977).