(40) W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960); also see ref 39, p 268.
(41) (a) A. J. Parker, *Q. Rev., Chem. Soc.*, **16**, 163 (1962); (b) A. J. Parker et al., *J. Am. Chem. Soc.*, **88**, 1911 (1966).
(42) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).
(43) Reference 39, p 266.
(44) (a) For a review, see R. F. W. Bader and R. A. Gangi, *Spec. Period. Rep.: Theor. Chem.*, **2**, 1 (1975); (b) H. B. Schlegel and K. Mislow, *Theor. Chim. Acta*, **44**, 245 (1977).
(45) O. I. Asubiojo, H. L. McPeters, W. N. Olmstead, and J. I. Brauman, *Chem. Phys. Lett.*, **48**, 127 (1977).
(46) R. C. Dougherty and J. D. Roberts, *Org. Mass Spectrom.*, **8**, 81 (1974).
(47) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.
(48) From group additivity, ΔH_f° of tetrahedral CH_3CCl_2OH was estimated as −80 kcal/mol. From this value, the O–H dissociation energy of an alcohol (104 kcal/mol), and ΔH_f° of H (+52 kcal/mol), ΔH_f° of tetrahedral CH_3CCl_2O radical was estimated.
(49) B. S. Freiser and J. L. Beauchamp, unpublished results referred to in ref 28b.
(50) These values were obtained from the reversible transfer of Cl^- between $CH_3COCl_2^-$ and CH_3Br on the one hand, and $CF_3COCl_2^-$ and $CHCl_3$ on the other. O. I. Asubiojo, Ph.D. Thesis, Stanford University, 1977, p 35.
(51) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **93**, 7139 (1971).
(52) (a) W. Forst, "Theory of Unimolecular Reactions", Academic Press, New York, 1973; (b) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley-Interscience, New York, 1972.
(53) E. V. Waage and B. S. Rabinovitch, *Chem. Rev.*, **70**, 377 (1970).
(54) Reference 52b, p 89.
(55) Reference 52a, Chapter 9.
(56) W. L. Hase and D. L. Bunker, Quantum Chemistry Program Exchange No. 234, Indiana University. The subroutine in this RRKM program was used intact except for the addition of the capability to handle two-dimensional rotors.
(57) (a) E. Gorin, *Acta Physiochim. URSS*, **9**, 691 (1938); (b) E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, 7, 633 (1939).
(58) W. N. Olmstead, M. Lev-On, D. M. Golden, and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 992 (1977).
(59) JANAF Thermochemical Tables, 1974 Supplement, *J. Phys. Chem. Ref. Data*, **3**, 311 (1974).
(60) This value was obtained using Benson's group additivity method.
(61) Heat of formation of Cl^- is obtained from K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, **56**, 1516 (1974); heat of formation of CH_3COCl from ref 47.
(62) (a) B. K. Janousek, A. H. Zimmerman, K. J. Reed, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 6142 (1978); (b) J. E. Bartmess and R. T. McIver, Jr., *ibid.*, **99**, 4163 (1977).
(63) (a) E. A. C. Lucken, *J. Chem. Soc.*, 2954 (1959); (b) also see ref 28.
(64) A. H. Zimmerman, K. J. Reed, and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 7203 (1977).
(65) M. J. S. Dewar, "Electronic Theory of Organic Chemistry", Oxford University Press, London, 1949, p 117.

An Experimental Study of the Gas-Phase Kinetics of Reactions with Hydrated H_3O^+ Ions (n = 1–3) at 298 K

D. K. Bohme,* G. I. Mackay, and S. D. Tanner

Contribution from the Department of Chemistry, York University, Downsview, Ontario M3J 1P3, Canada. *Received October 13, 1978*

Abstract: Flowing afterglow experiments are reported which follow the influence of stepwise hydration on the kinetics of proton transfer from the hydronium ion to H_2S, CH_2O, HCOOH, CH_3OH, CH_3CHO, C_2H_5OH, CH_3COOH, $HCOOCH_3$, $(CH_3)_2O$, $(CH_3)_2CO$, and NH_3 at 298 ± 2 K. Rate constants have been measured for the reactions of these molecules with $H_3O^+\cdot H_2O$, $H_3O^+\cdot(H_2O)_2$, and $H_3O^+\cdot(H_2O)_3$. The reactions were observed to proceed according to the general equation $H_3O^+\cdot(H_2O)_n + B \rightarrow BH^+\cdot(H_2O)_m + (n - m + 1)H_2O$ with $0 \leqslant m \leqslant n$, albeit product distributions could not be unraveled. Comparisons are made with the rate constants for the "nude" reactions involving H_3O^+. The reversal in the relative basicity of H_2O and H_2S upon hydration which can be deduced from known energetics of solvation is manifested by a sharp drop (by $\gtrsim 10^3$) in the observed reaction rate constant for n = 1, 2, and 3. For B = CH_2O, equilibrium-constant measurements are reported which indicate a trend toward the equalization of the basicities of H_2O and CH_2O upon hydration with up to three water molecules. All of the hydrated H_3O^+ ions are observed to react rapidly and irreversibly with the remaining, somewhat stronger, oxygen bases with $k \geqslant 10^{-9}$ cm^3 molecule^{-1} s^{-1} and decreasing slightly and monotonically with increasing hydration. Comparisons with calculated capture rate constants indicate that these reactions proceed with approximately unit probability. The intriguing possibility of generating polymeric water molecules from the reactions investigated is discussed briefly.

Introduction

Hydrated H_3O^+ ions containing large numbers of water molecules can be generated in the gas phase through the sequential action of termolecular association or "clustering" reactions of the type

$$H_3O^+\cdot(H_2O)_n + H_2O + M \rightarrow H_3O^+\cdot(H_2O)_{n+1} + M \quad (1)$$

where M is an inert third body which serves to deactivate the hydrated H_3O^+ ion. For example, Kebarle and co-workers[1] were able to observe hydrates up to n = 7 in irradiated water vapor at pressures from 0.1 to 6 Torr and temperatures from 288 to 873 K, and also to measure the equilibrium constant for each of the steps involved in the buildup of $H_3O^+\cdot(H_2O)_7$ from H_3O^+. Indeed, gas-phase observations have been reported of cluster ions with water contents as large as n = 27, from which it has been inferred that hydrated H_3O^+ ions may grow directly and continually in the gas phase from the "nude" hydronium ion to charged droplets.[2] The availability of these ions in the gas phase has led to the exciting prospect of actually monitoring their reactions as a function of stepwise hydration and in the absence of interference from the bulk solvent effects present when such species react in solution. Concomitant information about the reaction of H_3O^+ then allows the extrapolation of the fine structure effect of hydration from the extreme of the intrinsic reaction to extents of hydration at which the distinction between the gas phase and solution begins to dissolve. We have recently reported such a study for reactions involving the isoelectronic counterparts associated with OH^-, vis., $OH^-\cdot(H_2O)_n$, and methanol, in which we followed the transition in the relative acidity of water and methanol from the gas phase to solution.[3]

The present study is concerned with the influence of the stepwise hydration on the kinetics of proton transfer from H_3O^+ to a variety of molecules, i.e., with reactions which may be represented by the general equation

$$H_3O^+\cdot(H_2O)_n + B \rightarrow BH^+\cdot(H_2O)_m + (n - m + 1)H_2O \quad (2)$$

where m may conceivably have any value between 0 and n with the water being produced as individual molecules, dimers, or

0002-7863/79/1501-3724$01.00/0

even polymers of H_2O. Hydrated H_3O^+ ions (n = 1-3) are established experimentally in a flowing H_2O-hydrogen or H_2O-helium plasma at low pressures, ca. 0.4 Torr, and room temperature. They are reacted with ammonia and a variety of oxygen bases including alcohols, aldehydes, carboxylic acids, methyl formate, dimethyl ether, and acetone. We have previously characterized the kinetics and energetics of the corresponding unsolvated reactions (n = 0) under similar operating conditions.[4] The studies reported here are not the first of their kind. The gas-phase kinetics of reactions of hydrated H_3O^+ ions first received serious attention from Fehsenfeld, Ferguson, and co-workers in their investigations of the ion chemistry of the earth's troposphere and stratosphere.[5,6] Of specific interest to them was the conversion of $H_3O^+\cdot(H_2O)_n$ to $NH_4^+\cdot(H_2O)_n$ due to the presence of NH_3 in the atmosphere and the possible role of reactions of $H_3O^+\cdot(H_2O)_n$ as sinks for $CFCl_3$ (fluorocarbon 11) and CF_2Cl_2 (fluorocarbon 12) in the troposphere.[5] These authors have also very recently investigated the reactions of hydrated H_3O^+ ions with formaldehyde and methanol in an attempt to understand the results of the first rocket mass spectrometric measurements of positive ions in the stratosphere.[6]

Experimental Section

The measurements were carried out in a conventional flowing plasma mass spectrometer (flowing afterglow) system which has been described previously.[7] The hydrated H_3O^+ ions were established by introducing distilled water vapor into either a flowing helium or hydrogen plasma. In the helium buffer the ions H_2O^+, OH^+, and H^+ are produced first, either directly by electron impact or indirectly by reactions of helium ions or excited atoms with the water vapor. These ions then react further with H_2O to eventually establish H_3O^+. In the flowing hydrogen plasma H_3O^+ is partly established by reactions of H_2^+ and H_3^+ with the water vapor. In either case the H_3O^+ reacts still further with H_2O to yield the hydrated H_3O^+ ions according to clustering reactions of type (1). The relative amount of the cluster ions was adjusted by varying the addition of water vapor over a range of at least a decade.

The reactant neutrals were added into the reaction region as vapors either in their pure form or diluted with helium. The determination of their flows required separate viscosity measurements as has been described.[8] Rate constants were determined in the usual manner from measurements of the hydrated H_3O^+ ion signal as a function of addition of reactant vapor into the reaction region.[7] The measurements were repeated at several different additions of water vapor. Product ion signals with values of m/e up to at most 115 were measured concomitantly. The operating conditions in these experiments encompassed total gas pressures, P, in the range 0.258-0.509 Torr, average gas velocities, $\bar{v}$, in the range 6.7-8.2 × 10^3 cm s^{-1}, effective reaction lengths, L, of the order of 60 and 85 cm, and a gas temperature, T, of 298 ± 2 K.

The vapors were derived from the following liquids: CH_3OH, $HCOOH$, and $(CH_3)_2CO$ (BDH Chemicals, analytical reagent grade), C_2H_5OH (Consolidated Alcohols, absolute), CH_3CHO (BDH Chemicals, laboratory reagent grade, 99.0% minimum), $HCOOCH_3$ (BDH Chemicals, 98%), CH_3COOH (Anachemia Chemicals, glacial, 99.7%), and $(CH_3)_2O$ (Matheson, 99.8% (typical)). CH_2O was prepared by the low-pressure distillation of paraformaldehyde (Fisher Scientific, purified grade) by an adaptation of the method of Spence and Wild.[9]

The flows of formic acid and acetic acid were corrected for dimerization using the disssociation equilibrium constants K_p (Torr) = 2.704 and 0.5458, respectively, at 299 K.[10,11] This correction was based on the reasonable assumption that the dimers were present in their equilibrium amounts in the storage bulbs and prior to their entry into the reaction region at which point essentially complete dissociation of the dimers will occur (mol % dimer <0.01%).

Results and Discussion

Energetics of Solvation. Rate and equilibrium constant measurements for the hydration of H_3O^+ via association reactions of type (1) have now been reported from several laboratories.[12,13] These measurements indicate that the three-body rate constant of association and the standard free energy of hydration, $\Delta G^\circ_{n,n+1}$, decrease smoothly in absolute value up to and beyond $H_3O^+\cdot(H_2O)_3$ so that no special stability need be associated with any of these hydrated species, at least not in the gas phase. The standard free energies of hydration of H_3O^+ are given in Table I along with those of other ions, $BH^+\cdot(H_2O)_n$, for which appropriate experimental support data were available. The standard free energies of hydration of the latter ions were deduced from suitable thermodynamic cycles which combined available standard free energy changes for the appropriate unsolvated proton transfer, solvent association, and solvent exchange processes. The hydration energies are required to describe the overall energetics of reactions of type (2) and thus to follow the trends in energetics with solvation. The standard free-energy changes for the reactions of the nude H_3O^+ with the molecules investigated in this study span a range from −3.8 to −34 kcal mol^{-1}, the two extremes involving H_2S and NH_3, respectively.

Table I. Energetics[a] of Hydration for Ions of the Type $BH^+\cdot(H_2O)_n$

n	H_3O^+	H_3S^+	CH_2OH^+	NH_4^+
1	23.6[b]	12.7[c]	19.2[d]	11.4[e]
2	14.1[b]	14.9[c]	13.2[d]	9.3[e]
3	9.6[b]		9.5[d]	5.4[e]

[a] The negative of the standard free energy charge in kcal mol^{-1} for the hydration $BH^+\cdot(H_2O)_{n-1} + H_2O \rightleftharpoons BH^+\cdot(H_2O)_n$ at 300 K. [b] Arithmetic mean of the values reported by Cunningham et al.[12] and Moet-Ner and Field[13] which generally agree within 2 kcal mol^{-1}. [c] Deduced from the standard free energies reported for the proton transfer from H_3O^+ to H_2S by Tanaka et al.[14] and the exchange reactions involving $H_3S^+\cdot H_2O$ and $H_3S^+\cdot(H_2O)_2$ reported by Hiraoka and Kebarle.[15] [d] Arithmetic mean deduced from the equilibrium studies reported here and by Fehsenfeld et al.[6] which generally agree within 0.6 kcal mol^{-1}. [e] Arithmetic mean deduced from the standard free energy changes reported by Fehsenfeld and Ferguson[16] and Payzant et al.[17] (which generally agree within 1.7 kcal mol^{-1}) for the formation of cluster ions of the type $NH_4^+\cdot(NH_3)_n$ and their hydration by solvent exchange reactions.

Reactions with H_2S. It is clear from the energetics given in Table I that hydration may shift the equilibrium position of reactions of type (2) with $m = n$ from right to left in favor of the hydrated H_3O^+ ions to a degree which may in fact change the sign of ΔG°. Indeed this appears to be the case for the reactions of the hydrated H_3O^+ ions with H_2S given in Table II. The standard free-energy changes at 300 K for the reactions

$$H_3O^+ + H_2S \rightleftharpoons H_3S^+ + H_2O \quad (3)$$

$$H_3O^+\cdot H_2O + H_2S \rightleftharpoons H_3S^+\cdot H_2O + H_2O \quad (3a)$$

$$H_3O^+\cdot(H_2O)_2 + H_2S \rightleftharpoons H_3S^+\cdot(H_2O)_2 + H_2O \quad (3b)$$

are −3.8 ± 0.2, +7.1 ± 0.5, and +6.3 ± 0.6 kcal mol^{-1}, respectively.[14,15] Hydration has therefore led to a change in ΔG° of ~10 kcal mol^{-1} with a change in sign resulting already with one molecule of hydration. Our observations indicate a concomitant decrease in the value of the rate constant by more than 10^3 from $(1.9 \pm 0.4) \times 10^{-9}$ for the unhydrated reaction (3) to $< 1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for the reactions of $H_3O^+\cdot(H_2O)_n$ with n = 1-3.

Reactions with CH_2O. The reactions of the hydrated H_3O^+ ions with CH_2O apparently represent an intermediate case. Figure 1 shows their observation in a fairly wet flowing H_2 plasma. The H_3O^+ reacts rapidly with CH_2O to produce CH_2OH^+ which then associates with CH_2O to cause the observed increase in the $CH_2OH^+\cdot CH_2O$ ion signal. Our previous measurements[14] of the equilibrium constants for the reaction

Table II. Rate Constants[a] at 298 ± 2 K (10^{-9} cm^3 molecule^{-1} s^{-1}) for Reactions of $H_3O^+ \cdot (H_2O)_n$ (n = 0–3) with Molecules, B

B	$PA°_{298}(B)$[b]	H_3O^+	$H_3O^+ \cdot H_2O$	$H_3O^+ \cdot 2H_2O$	$H_3O^+ \cdot 3H_2O$
H_2S	170.2 ± 1.8	1.9 ± 0.4 (13)	<0.001	<0.001	<0.001
		1.89 (1.0)	1.57 (<0.001)	1.44 (<0.001)	1.37 (<0.001)
CH_2O	170.9 ± 1.2	3.4 ± 0.9 (14)	3.0 ± 2.0 (3)	≳0.1	≳0.1
		2.77 (1.23)	2.32 (1.29)	2.14 (≳0.05)	2.05 (≳0.05)
HCOOH	178.1 ± 2	2.7 ± 0.8 (12)	2.4 ± 0.7 (6)	1.5 ± 0.5 (3)	>1
		1.95 (1.38)	1.58 (1.52)	1.43 (1.05)	1.34 (>0.7)
CH_3OH	181 ± 3	2.8 ± 0.7 (7)	2.4 ± 0.6 (3)	2.0 ± 0.5 (3)	1.9 ± 0.5 (3)
		2.31 (1.21)	1.93 (1.24)	1.78 (1.12)	1.69 (1.12)
CH_3CHO	185.4 ± 2	3.6 ± 0.9 (12)	3.1 ± 0.8 (2)	2.6 ± 0.7 (2)	2.3 ± 0.6 (2)
		3.08 (1.17)	2.51 (1.24)	2.27 (1.15)	2.14 (1.07)
C_2H_5OH	186.8 ± 2	2.8 ± 0.7 (4)	2.5 ± 0.6 (3)	2.0 ± 0.5 (3)	1.7 ± 0.4 (3)
		2.42 (1.15)	1.96 (1.28)	1.78 (1.12)	1.67 (1.02)
CH_3COOH	187.4 ± 2	3.0 ± 0.9 (6)	2.7 ± 0.8 (5)	2.4 ± 0.7 (5)	2.2 ± 0.7 (3)
		2.36 (1.27)	1.87 (1.44)	1.67 (1.44)	1.56 (1.41)
$HCOOCH_3$	187.8 ± 2	3.3 ± 0.8 (3)	2.8 ± 0.7 (3)	2.5 ± 0.8 (2)	2.2 ± 0.5 (2)
		2.48 (1.33)	1.97 (1.42)	1.76 (1.42)	1.64 (1.34)
$(CH_3)_2O$	190.1 ± 2	2.7 ± 0.7 (5)	2.2 ± 0.6 (2)	2.0 ± 0.5 (2)	1.8 ± 0.5 (2)
		2.25 (1.20)	1.82 (1.21)	1.65 (1.21)	1.55 (1.16)
$(CH_3)_2CO$	193.6 ± 1	3.9 ± 1.0 (7)	3.5 ± 0.9 (3)	3.0 ± 0.8 (2)	2.9 ± 0.7 (2)
		3.29 (1.19)	2.62 (1.34)	2.34 (1.28)	2.19 (1.32)
NH_3	200.4 ± 2	2.4 ± 0.5 (3)	2.0 ± 0.4 (2)	1.9 ± 0.4 (2)	1.8 ± 0.4 (2)
		2.25 (1.07)	1.97 (1.02)	1.87 (1.02)	1.81 (1.00)

[a] The measured reaction rate constant, k, is given first along with its estimated accuracy and the number of measurements which is given in parentheses. The collision rate constant, k_c, calculated from the ADO theory[18] is given underneath with k/k_c in parentheses. [b] The proton affinity of molecule B in kcal mol^{-1}. Values for PA(H_2S, CH_2O) were taken from ref 14, PA(HCOOH, CH_3CHO, C_2H_5OH, CH_3COOH, $HCOOCH_3$, $(CH_3)_2O$, NH_3) from ref 19, PA(CH_3OH) from ref 20, and PA($(CH_3)_2CO$) from ref 21. We have taken $PA°_{298}(H_2O)$ = 166.4 ± 2.4 kcal mol^{-1}.[14]

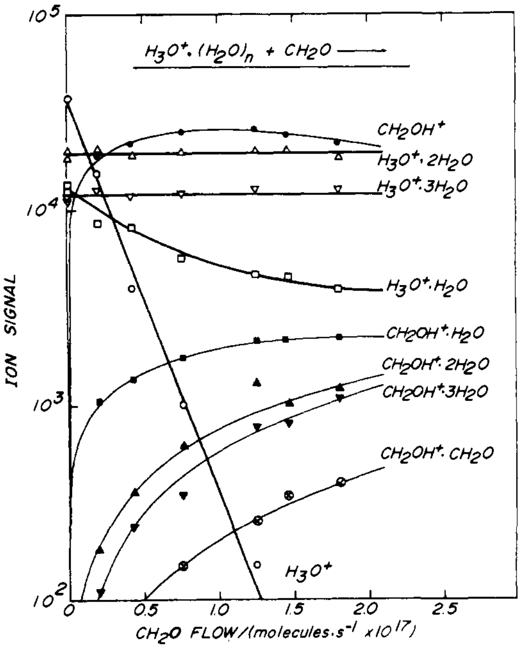

Figure 1. Variation in ion signals recorded upon the addition of formaldehyde into a flowing H_2O–H_2 plasma containing hydrated H_3O^+ ions. H_2O flow = 1.7 × 10^{18} molecules s^{-1}, P = 0.315 Torr, L = 84 cm, $\bar{v}$ = 7.7 × 10^3 cm s^{-1}, and T = 299 K. The decay of the H_3O^+ signal provides a rate constant of 3.28 × 10^{-9} cm^3 molecule^{-1} s^{-1}.

pairs

$$H_3O^+ + HCN \rightleftharpoons HCNH^+ + H_2O \quad (4)$$

$$HCNH^+ + CH_2O \rightleftharpoons CH_2OH^+ + HCN \quad (5)$$

and

$$H_3O^+ + H_2S \rightleftharpoons H_3S^+ + H_2O \quad (6)$$

$$H_3S^+ + CH_2O \rightleftharpoons CH_2OH^+ + H_2S \quad (7)$$

provide a value of (6.1 ± 1.7) × 10^3 at 296 ± 2 K for the equilibrium constant of the reaction

$$H_3O^+ + CH_2O \rightleftharpoons CH_2OH^+ + H_2O \quad (8)$$

which is too large to introduce significant curvature into the H_3O^+ decay from the occurrence of reaction (−8). In contrast, the curved decay of the $H_3O^+ \cdot H_2O$ signal is a manifestation of the approach to and attainment of equilibrium for the reaction

$$H_3O^+ \cdot H_2O + CH_2O \rightleftharpoons CH_2OH^+ \cdot H_2O + H_2O \quad (8a)$$

This was verified by the application of our usual fitting procedure and ion signal ratio plot analysis[9] to observations made at several additions of H_2O in the range from 7.6 × 10^{16} to 1.7 × 10^{18} molecules s^{-1}, which yielded values for K_{8a} = 5.7 ± 1.6 and k_{8a} = (3.0 ± 2.0) × 10^{-9} cm^3 molecule^{-1} s^{-1}. Furthermore, a ratio plot analysis of the $CH_2OH^+ \cdot (H_2O)_2/H_3O^+ \cdot (H_2O)_2$ and $CH_2OH^+ \cdot (H_2O)_3/H_3O^+ \cdot (H_2O)_3$ ion signal ratios indicated that the reactions

$$H_3O^+ \cdot (H_2O)_2 + CH_2O \rightleftharpoons CH_2OH^+ \cdot (H_2O)_2 + H_2O \quad (8b)$$

$$H_3O^+ \cdot (H_2O)_3 + CH_2O \rightleftharpoons CH_2OH^+ \cdot (H_2O)_3 + H_2O \quad (8c)$$

were at equilibrium under our experimental operating conditions with equilibrium constants having values of 0.6 ± 0.3 and 0.8 ± 0.4, respectively. These observations are generally in agreement with the results reported very recently by Fehsenfeld et al.[6] in their study of the stratospheric positive ion chemistry of CH_2O. From the thermochemical constants which they determined from measurements made at temperatures from 325 to 470 K, we have deduced the following equilibrium constants at 300 K: K_8 = (1.7 ± 0.9) × 10^4, K_{8a} = 7.2 ± 3.6, and $K_{8b,c}$ = 1.2 ± 0.6. Figure 2 compares these values with our own flowing afterglow measurements and illustrates the shift in the equilibrium positive with increasing hydration. $\Delta G°$ changes by about 5.5 kcal mol^{-1} (to approximately 0 kcal mol^{-1}) as a result of hydration with the three water molecules but apparently with no change in sign and no sharp drop in the rate constant.

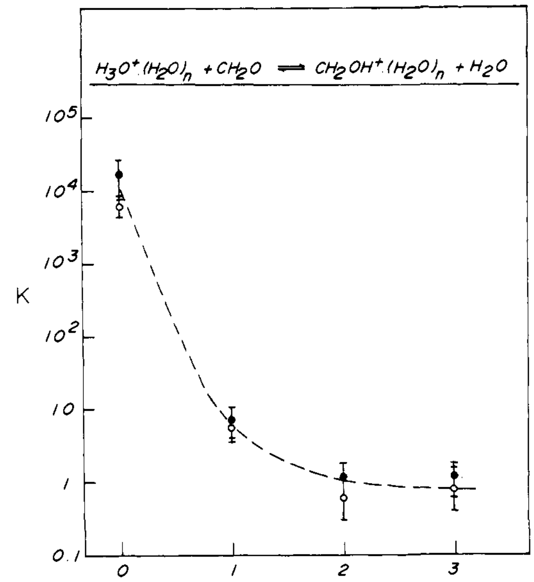

Figure 2. The shift in the relative basicity of H_2O and CH_2O with hydration at 300 K. The solid circles represent values deduced from the thermochemical constants reported in ref 6. The open circles represent values determined in the present study.

Reactions with NH_3. The situation is more extreme with NH_3, which has the highest proton affinity of the reagent molecules employed in this study. The unsolvated reaction

$$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O \qquad (9)$$

has a relatively large standard free energy change of −34 ± 5 kcal mol^{-1} at 300 K.[4] The hydrated reactions remain highly exoergic, in fact exoergic enough to "boil off" additional waters of hydration as has been discussed by Fehsenfeld and Ferguson.[16] The free energies of hydration given in Table I result in the following exoergicities (in kcal mol^{-1}):

$$\begin{aligned} H_3O^+\cdot H_2O + NH_3 &\rightarrow NH_4^+\cdot H_2O + H_2O + 22 \quad (9a)\\ &\rightarrow NH_4^+ + 2H_2O + 11\\ H_3O^+\cdot(H_2O)_2 + NH_3 &\rightarrow NH_4^+\cdot(H_2O)_2 + H_2O + 17 \quad (9b)\\ &\rightarrow NH_4^+\cdot H_2O + 2H_2O + 8\\ &\rightarrow NH_4^+ + 3H_2O - 3\\ H_3O^+\cdot(H_2O)_3 + NH_3 &\rightarrow NH_4^+\cdot(H_2O)_3 + H_2O + 13 \quad (9c)\\ &\rightarrow NH_4^+\cdot(H_2O)_2 + 2H_2O + 8\\ &\rightarrow NH_4^+\cdot H_2O + 3H_2O - 2\\ &\rightarrow NH_4^+ + 4H_2O - 13 \end{aligned}$$

Here it has been assumed that the water molecules are boiled off as monomers, although it is conceivable that these appear as dimers or polymers. The reactions of the hydrated H_3O^+ ions with NH_3 have been studied extensively by Fehsenfeld and Ferguson[16] in a flowing afterglow with O_2 or CO_2 as a buffer gas. They have reported rate constants of 2.1 ± 0.6, 2.6 ± 0.8, 1.6 ± 0.5, and 2.1 ± 0.6 × 10^{-9} cm^3 $molecule^{-1}$ s^{-1} for n = 0, 1, 2, and 3, respectively. They also drew attention to the difficulty in unraveling the product ion spectrum which arises from the simultaneous presence of similar amounts of more than one hydrate and in part is due to distortion by secondary reactions. This is certainly apparent in Figure 3, which shows results obtained in this laboratory with H_2 as the buffer gas. The observations do not permit an identification of the products which are to be associated with the individual hydrated H_3O^+ ions. Also, the observed maxima in the $NH_4^+\cdot H_2O$ and $NH_4^+\cdot NH_3\cdot H_2O$ ion signals provides an indication of the occurrence of complicating secondary reactions of the type

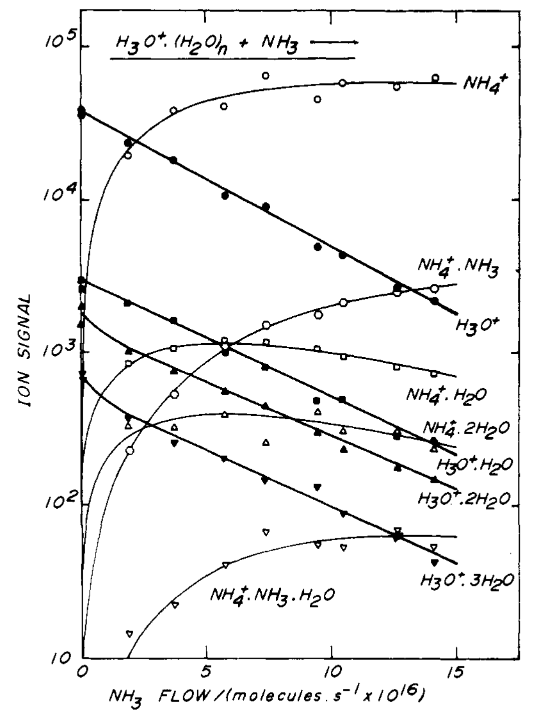

Figure 3. Variation in ion signals recorded upon the addition of ammonia into a flowing H_2O–H_2 plasma containing hydrated H_3O^+ ions. H_2O flow ~5 × 10^{-17} molecules s^{-1}, P = 0.359 Torr, L = 59 cm, $\bar{v}$ = 8.1 × 10^3 cm s^{-1}, and T = 299 K. The decays provide rate constants of 2.26, 1.94, 1.80, and 1.87 × 10^{-9} cm^3 $molecule^{-1}$ s^{-1} for the reactions of H_3O^+, $H_3O^+\cdot H_2O$, $H_3O^+\cdot(H_2O)_2$, and $H_3O^+\cdot(H_2O)_3$, respectively.

$$NH_4^+\cdot H_2O + NH_3 \rightleftharpoons NH_4^+\cdot NH_3 + H_2O \qquad (10a)$$

$$NH_4^+\cdot(H_2O)_2 + NH_3 \rightleftharpoons NH_4^+\cdot NH_3\cdot H_2O + H_2O \qquad (10b)$$

both of which have been observed to be rapid, $k > 9 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, by Fehsenfeld and Ferguson.[16] Nevertheless, rate constants could be determined for the total loss of the individual hydrated H_3O^+ ions: k = 2.4 ± 0.5, 2.0 ± 0.4, 1.9 ± 0.4, and 1.8 ± 0.4 × 10^{-9} cm^3 $molecule^{-1}$ s^{-1} for n = 0, 1, 2, and 3, respectively. These values agree within experimental error with those reported by Fehsenfeld and Ferguson but indicate a monotonic decrease in the rate constant with hydration, in contrast to the alternating pattern reported by these authors.[16]

Reactions with Oxygen Bases Having Intermediate Proton Affinities. A similar situation appeared to prevail for the reactions of the hydrated H_3O^+ ions with the other eight molecules investigated in this study, all of which are oxygen bases with proton affinities intermediate between those of CH_2O and NH_3. However, no thermochemical information appears to be available at this time for the hydration of the conjugate acids of these bases, and thus for the hydrated reactions of type (2) involving these eight molecules.

Results obtained in this study for the reactions of hydrated H_3O^+ ions with ethanol and acetic acid are shown in Figures 4 and 5, respectively. The products which are to be associated with the individual hydrated H_3O^+ ions again could not be unraveled from the observed product ion spectrum. Also, there was again evidence for secondary reactions of the hydrated product ions as these ions strive to acquire their most stable solvent composition. The reactions are of types analogous to those observed with ammonia. For example, the results shown

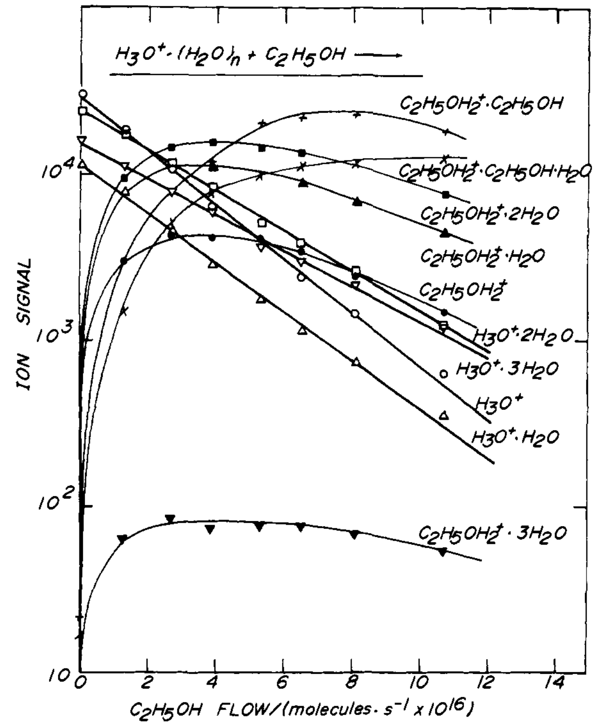

Figure 4. Variation in the ion signals recorded upon the addition of ethanol into a flowing H_2O–H_2 plasma containing hydrated H_3O^+ ions. $P = 0.316$ Torr, $L = 84$ cm, $\bar{v} = 7.7 \times 10^3$ cm s^{-1}, and $T = 298$ K. The decays provide rate constants of 2.80, 2.63, 1.96, and 1.64×10^{-9} cm^3 molecule^{-1} s^{-1} for the reactions of H_3O^+, $H_3O^+\cdot H_2O$, $H_3O^+\cdot(H_2O)_2$, $H_3O^+\cdot(H_2O)_3$, respectively.

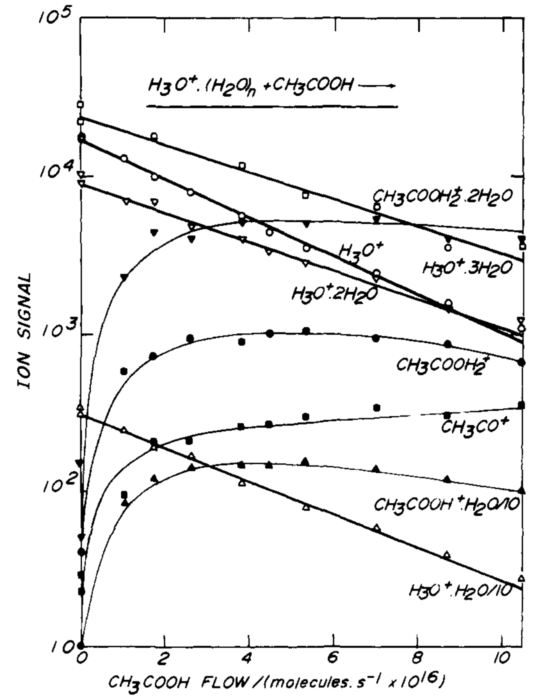

Figure 5. Variation in the ion signals recorded upon the addition of acetic acid into a flowing H_2O–He plasma containing hydrated H_3O^+ ions. $P = 0.364$ Torr, $L = 59$ cm, $\bar{v} = 7.7 \times 10^3$ cm s^{-1}, and $T = 298$ K. The decays provide rate constants of 3.35, 2.92, 2.45, and 2.29×10^{-9} cm^3 molecule^{-1} s^{-1} for the reactions of H_3O^+, $H_3O^+\cdot H_2O$, $H_3O^+\cdot(H_2O)_2$, and $H_3O^+\cdot(H_2O)_3$, respectively.

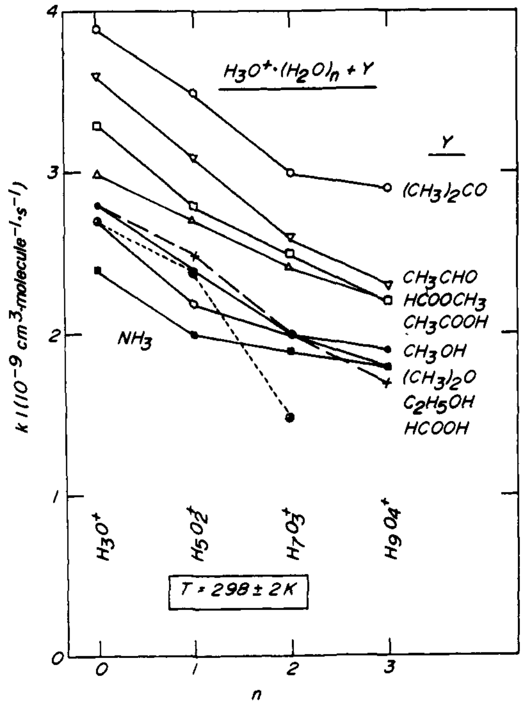

Figure 6. Variation in the rate constant with extent of hydration for reactions of the hydrated H_3O^+ ion with oxygen bases and NH_3 at 298 ± 2 K.

for ethanol suggest the occurrence of the solvent switching reactions

$$C_2H_5OH_2^+\cdot H_2O + C_2H_5OH \rightleftharpoons C_2H_5OH_2^+\cdot C_2H_5OH + H_2O \quad (11a)$$

$$C_2H_5OH_2^+\cdot(H_2O)_2 + C_2H_5OH \rightleftharpoons C_2H_5OH_2^+\cdot C_2H_5OH\cdot H_2O + H_2O \quad (11b)$$

with some contribution to the rise in the $C_2H_5OH_2^+\cdot C_2H_5OH$ from association of $C_2H_5OH_2^+$ with C_2H_5OH. We have shown previously that the extra product ion CH_3CO^+ observed with acetic acid arises from the dissociative proton-transfer reaction of this molecule with the nude H_3O^+ ion.[22] The extent to which the analogous reaction proceeds with the hydrated H_3O^+ ions is uncertain. For example, $H_3O^+\cdot H_2O$ could conceivably react as follows:

$$H_3O^+\cdot H_2O + CH_3COOH \rightarrow [CH_3COOH_2^+\cdot H_2O]^* + H_2O \quad (12)$$

$$\downarrow$$

$$CH_3CO^+\cdot H_2O + H_2O \quad (12a)$$

However, the $CH_3CO^+\cdot H_2O$ could not be distinguished from $CH_3COOH_2^+$, which itself can conceivably be produced from this reaction by the elimination of the solvent H_2O molecule. The elimination of H_2O according to reaction 12a would involve $A_{Ac}1$ fission with the solvent H_2O molecule remaining attached to the resulting acetyl cation.[22]

The rate constants determined for the reactions of the individual hydrated species with each of the eight oxygen bases are included in Table II. All of these reactions were observed to be rapid with $k \geqslant 10^{-9}$ cm^3 molecule^{-1} s^{-1} at room temperature. As is the case with NH_3, the rate constants decrease only slightly but systematically with increasing hydration. This is displayed graphically in Figure 6. In the case of CH_3OH the values determined in this study are in agreement, within experimental error, with the slightly lower values of 2.2 ± 0.9, 1.9 ± 0.8, 1.7 ± 0.7, and $1.5 \pm 0.6 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} reported recently by Fehsenfeld et al.[6]

Reactivities of the Hydrated H_3O^+ Ions. The magnitudes of the measured rate constants may be compared with those

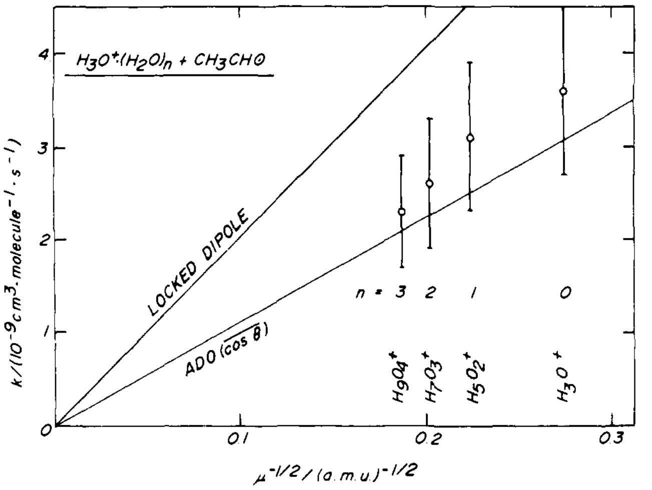

Figure 7. A comparison of the measured rate constants with rate constants predicted by collision theories for the reactions of hydrated H_3O^+ ions with acetaldehyde ($\alpha = 4.40$ Å^3, $\mu_D = 2.69$ D) at 298 ± 2 K. The solid bars represent the estimated accuracy of the measurements.

of the capture rate constants predicted by various ion-molecule collision theories as is done in Figure 7 for the reactions of hydrated H_3O^+ ions and H_3O^+ with acetaldehyde. The measured rate constants are found to have values intermediate between the locked dipole limit[23] and the average dipole orientation (ADO) theory (the $\overline{\cos\theta}$ model)[18] exceeding the latter by 10-50%. Table II includes the actual values calculated for the predictions of the ADO theory together with the ratio of the measured over the calculated rate constant which should provide a measure of reactivity. Evidently the hydrated H_3O^+ ions react with approximately unit probability with only a slight hint of a decrease in reactivity with increasing hydration ($n \geq 1$). The permanent dipole moments required for the calculations were taken from the compilation of Nelson et al.[24] The polarizabilities for H_2S, CH_2O, CH_3OH, $(CH_3)_2CO$, and NH_3 were taken from existing compilations.[25] The mean polarizabilities of the remaining molecules were calculated from bond and group polarizabilities to be 3.09, 4.40, 5.17, 5.03, 5.90, and 6.04 Å^3 for HCOOH, CH_3CHO, C_2H_5OH, CH_3COOH, $HCOOCH_3$, and $(CH_3)_2O$, respectively.[26]

Possible Mechanism. As written, reaction 2 is meant to be viewed to proceed by the following steps: (1) the incorporation of the proton acceptor molecule, B, into the hydration "shell" of the hydrated H_3O^+ ion, (2) the protonation of B, and (3) the partial or even complete displacement of water molecules perhaps accompanied by reorganization of the remaining hydration "shell" with the protonated acceptor molecule, BH^+, becoming the new "center" of hydration. To what extent such a simplified picture provides a reasonable account of the mechanism of these reactions remains uncertain. However, some insight may be gained from theoretical studies such as the ab initio molecular orbital calculations of Newton and Ehrenson[27] and Newton[28] in which changes in structure and energy which accompany the successive addition of water molecules to H_3O^+ are followed systematically. These recent calculations clearly show that the equilibrium geometries of the hydrated H_3O^+ ions in the gas phase correspond roughly to a central hydronium ion surrounded by water molecules, as depicted in Figure 8, held to the central ion by strong O---H---O bonds which become increasingly weaker and asymmetric as successive water molecules are added.[29] The bonding arises from charge-dipole interactions perturbed by polarization charge transfer, and covalent bonding involving the bridge proton.[27] The incorporation of an oxygen base such as those investigated in this study into such a hydration "shell" may be viewed, as a very rough first approximation of course, to proceed in the manner of the addition of a water molecule. The structures shown in Figure 8 (with the last H_2O added in each structure replaced by B) might in consequence provide a reasonable indication of the geometry to be associated with the initial incorporation of B into the hydration shell. Ensuing changes in charge distribution and H-O bond lengths may then leave the proton in the newly formed O---H---O bond in an asymmetric position associated preferentially with the proton acceptor molecule B. Elimination of an H_2O molecule at another extreme end of the hydration shell will then readily produce clusters of the type $BH^+ \cdot (H_2O)_n$, however, with BH^+ in a terminal rather than central position so that a rearrangement would be required to leave BH^+ as the new "center" of hydration, e.g., a rearrangement of the type

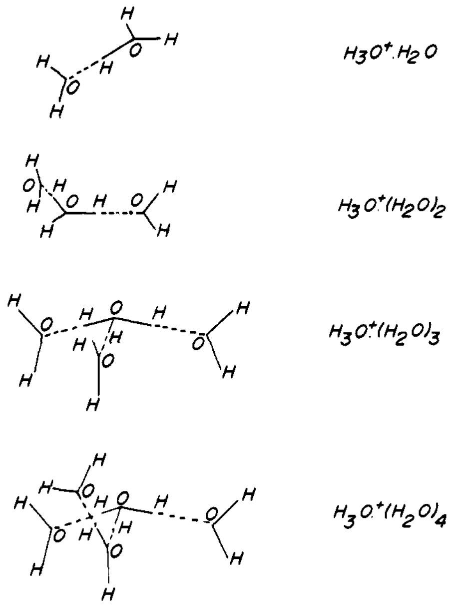

Figure 8. Structures of hydrated H_3O^+ ions adopted from the results of ab initio molecular orbital calculations reported by Newton and Ehrenson[26] and Newton.[27]

$$BH^+ \cdot H_2O \cdot H_2O \rightarrow H_2O \cdot BH^+ \cdot H_2O \qquad (13)$$

Such a rearrangement has been shown by Newton and Ehrenson to be ~13 kcal exothermic for B = H_2O.[27] Alternatively, elimination of more than one water molecule may be preferred. Elimination of $(H_2O)_2$ from $BH^+ \cdot (H_2O)_2$ could leave the dimer with a structure very near to its equilibrium configuration.[30] Also, elimination of water from $BH^+ \cdot (H_2O)_3$ and $BH^+ \cdot (H_2O)_4$ could produce a trimer in the "double donor" configuration[31] whereas the latter cluster ion could also eliminate a branched tetramer of water by simple scission of the H-O bond adjacent to the terminal BH^+. These considerations point toward the intriguing possibility of generating polymeric water molecules through an ion-molecule reaction scheme involving the buildup of hydrated H_3O^+ ions by three-body association reactions of type (1) followed by the two-body reaction of these ions with a molecule of high proton affinity according to reaction 2. The occurrence of such a scheme has of course not been established by the experiments reported in this study. Further experimental insight into its possibility must await measurements in which the reactions of hydrated H_3O^+ ions of a specific degree of hydration are followed essentially in isolation so that the distribution among the products allowed by reaction 2 can be identified for each degree of hydration.

Acknowledgment. We thank the National Research Council of Canada for financial support.

References and Notes

(1) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Am. Chem. Soc.*, **89**, 6393 (1967).
(2) J. Q. Searcy and J. B. Fenn, *J. Chem. Phys.*, **61**, 5282 (1974).
(3) G. I. Mackay and D. K. Bohme, *J. Am. Chem. Soc.*, **100**, 327 (1978).
(4) G. I. Mackay, S. D. Tanner, A. C. Hopkinson, and D. K. Bohme, *Can. J. Chem.*, accepted for publication.
(5) F. C. Fehsenfeld, P. J. Crutzen, A. L. Schmeltekopf, C. J. Howard, D. L. Albritton, E. E. Ferguson, J. A. Davidson, and H. I. Schiff, *J. Geophys. Res.*, **81**, 4454 (1976).
(6) F. C. Fehsenfeld, I. Dotan, D. L. Albritton, C. J. Howard, and E. E. Ferguson, *J. Geophys. Res.*, **83**, C3, 1333 (1978).
(7) D. K. Bohme, R. S. Hemsworth, H. W. Rundle, and H. I. Schiff, *J. Chem. Phys.*, **58**, 3504 (1973).
(8) G. I. Mackay, R. S. Hemsworth, and D. K. Bohme, *Can. J. Chem.*, **54**, 1624 (1976).
(9) R. Spence and W. Wild, *J. Chem. Soc.*, 338 (1935).
(10) M. D. Taylor and J. Burton, *J. Am. Chem. Soc.*, **74**, 4151 (1952).
(11) M. D. Taylor, *J. Am. Chem. Soc.*, **73**, 315 (1951).
(12) A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Am. Chem. Soc.*, **94**, 7627 (1972).
(13) M. Moet-Ner and F. H. Field, *J. Am. Chem. Soc.*, **99**, 998 (1977).
(14) K. Tanaka, G. I. Mackay, and D. K. Bohme, *Can. J. Chem.*, **56**, 193 (1978).
(15) K. Hiraoka and P. Kebarle, *Can. J. Chem.*, **55**, 24 (1977).
(16) F. C. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.*, **59**, 6272 (1973).
(17) J. D. Payzant, A. J. Cunningham, and P. Kebarle, *Can. J. Chem.*, **51**, 3242 (1973).
(18) L. Bass, T. Su, W. J. Chesnavich, and M. T. Bowers, *Chem. Phys. Lett.*, **34**, 119 (1975); T. Su, E. C. F. Su, and M. T. Bowers, *J. Chem. Phys.*, **69**, 2243 (1978).
(19) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976).
(20) G. I. Mackay and D. K. Bohme, *Int. J. Mass Spectrom. Ion Phys.*, **26**, 327 (1978).
(21) P. Ausloos and S. G. Lias, *Chem. Phys. Lett.*, **51**, 53 (1977).
(22) G. I. Mackay, A. C. Hopkinson, and D. K. Bohme, *J. Am. Chem. Soc.*, **100**, 7460 (1978).
(23) S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967).
(24) R. D. Nelson, D. R. Lide, and A. A. Maryott, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 10** (1967).
(25) E. W. Rothe and R. B. Bernstein, *J. Chem. Phys.*, **31**, 1619 (1959).
(26) E. R. Lippincott and J. M. Stutman, *J. Phys. Chem.*, **68**, 2926 (1964).
(27) M. D. Newton and S. Ehrenson, *J. Am. Chem. Soc.*, **93**, 4971 (1971).
(28) M. D. Newton, *J. Chem. Phys.*, **67**, 5535 (1977).
(29) A complete picture of the equilibrium population of hydrated hydronium ions at room temperature should include other structural isomers.[26]
(30) For the equilibrium structure of the water dimer see, for example, D. Hankins and J. W. Moskowitz, *J. Chem. Phys.*, **53**, 4544 (1970).
(31) See, for example, ref 29.

An Electron-Diffraction Investigation of the Molecular Structure of Gaseous 2,3-Butanedione (Biacetyl) at 228 and 525 °C

Donald D. Danielson and Kenneth Hedberg*

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received January 8, 1979*

Abstract: An earlier electron-diffraction investigation of biacetyl at a nozzle-tip temperature of 228 °C revealed only a trans conformer, in contrast to certain similar conjugated systems which have substantial amounts of gauche forms as well. New experiments at 525 °C have been carried out with the same result: there is no evidence for the presence of any but the trans conformer in gaseous biacetyl. The important distance (r_a) and angle values for the molecule at 228 (older data reanalyzed in terms of the present, more sophisticated model including shrinkages) and 525 °C are respectively $r(\mathrm{C{=}O}) = 1.215\ (2), 1.216\ (2)$ Å; $\langle r(\mathrm{C{-}C})\rangle = 1.524\ (2), 1.522\ (2)$ Å; $r(\mathrm{C{-}C})_{\mathrm{conj}} - r(\mathrm{C{-}C})_{\mathrm{Me}} = -0.014\ (21), -0.028\ (26)$ Å; $r(\mathrm{C{-}H}) = 1.108\ (4), 1.101\ (4)$ Å; $\angle\mathrm{CCO} = 119.5\ (6), 118.7\ (8)°$; $\angle\mathrm{CCC} = 116.2\ (2), 117.1\ (4)°$; $\angle\mathrm{CCH} = 109.6\ (12), 110.4\ (13)°$; δ (root mean square amplitude of $\mathrm{C{-}C_{conj}}$ torsion) = 24.1 (34), 30.5 (69)°. The absence of any but the trans form, remarkable in view of the long $\mathrm{C{-}C_{conj}}$ bond which is suggestive of a very little conjugation stabilization, is discussed.

I. Introduction

An early electron-diffraction investigation[1] of gaseous 2,3-butanedione (biacetyl) at room temperature as well as spectroscopic studies[2-5] of the gaseous, liquid, and solid material gave evidence of the presence of only one conformer, the s-trans form of molecular symmetry C_{2h} shown in Figure 1. This result is surprising inasmuch as oxalyl chloride[6a] and bromide[6b] with the same type of conjugated chain have substantial amounts of a gauche form of symmetry C_2 as well as the lower energy trans conformer. A recent electron-diffraction study[7] was carried out at 228 °C with the hope that the elevated temperature would generate enough of a second form for detection, but again only the trans form was found.

We have recently designed a nozzle for diffraction experiments which permits heating sample gases to very high temperatures, and we decided to look again for evidence of internal rotation in biacetyl. We report here the results of a study at a nozzle-tip temperature of 525 °C. Because the model for this study is somewhat more elaborate than that used before, we have also reanalyzed the earlier data for comparison. In neither case have we found any evidence for the presence of a second form.

II. Experimental Section

A. Diffraction Experiments. The 2,3-butanedione sample (99.5 wt % pure) was obtained from the Aldrich Chemical Co. A glass sample bulb was attached to the nozzle via a Monel Swagelok fitting having a Nylon front ferrule, and the bulb temperature was maintained at temperatures between 0 and 9 °C during the diffraction experiments.

Diffraction photographs were made in the Oregon State apparatus with an r^3 sector at a temperature of 525 °C using 8 × 10 in. Kodak projector slide plates (medium contrast) developed for 10 min in D-19 developer diluted 1:1. Exposures were made for 35–210 s with pressures in the apparatus of 5.0×10^{-6} to 1.2×10^{-5} Torr at nozzle-to-plate distances of 75.146 (long camera) and 30.115 cm (middle camera). Undiffracted beam currents were 0.40–0.43 μA with wavelengths of 0.056 67–0.056 78 Å calibrated in separate experiments from CO_2 diffraction patterns (r_a(CO) = 1.1646 Å, r_a(OO) = 2.3244 Å). Six plates were selected for structure analysis.

The conditions for the 228 °C experiments have been reported.[7] In our reanalysis, only long-camera and middle-camera data were used for more direct comparison with the higher temperature results.

B. Experimental Intensity Curves. The scattered intensity distributions s^4I_t were obtained by procedures previously described.[8] Experimental backgrounds were calculated[9] and subtracted yielding molecular intensity data in the form given by

0002-7863/79/1501-3730$01.00/0