1876 *J. Am. Chem. Soc.* **1998,** *120,* 1876−1882

Acid−Base Catalyzed Reactions in Ionic Water Clusters

Uwe Achatz, Stefan Joos, Christian Berg, Thomas Schindler, Martin Beyer, Gerhard Albert, Gereon Niedner-Schatteburg, and Vladimir E. Bondybey*

Contribution from the Institut für Physikalische und Theoretische Chemie, Technische Universität München, 85747 Garching, Germany

Received June 6, 1997

Abstract: Fourier Transform-Ion Cyclotron Resonance (FT-ICR) mass spectrometric studies of both cationic water clusters $H^+(H_2O)_n$, $n = 1-70$, and anionic water clusters $X^-(H_2O)_n$, $n = 1-30$, X = OH, O, with acetone and acetaldehyde are reported. For the cations a sequence of ligand exchange and fragmentation reactions results in "solvated proton" complex ion final products. In the anionic $OH^-(H_2O)_n$ clusters, on the other hand, an OH^- catalyzed aldol addition of the carbonyl compounds with a true covalent bond formation is observed. The anionic and cationic water clusters thus behave similar to basic and acidic aqueous solutions.

I. Introduction

The rate or outcome of a condensed phase chemical reaction can be strongly affected by the solvent. Many important chemical reactions, including numerous industrially relevant processes, take place in solutions. The most important solvent for the processes in earth's troposphere is water, and the chemistry on which life itself is based takes place in aqueous solutions. Many organic and inorganic compounds are ionized in the polar water solvent, and the course of the reactions often can be altered by changing the composition of the solution and the ions present. Particularly important are the concentrations of the H^+ and OH^- ions, which are usually described by the pH value of the solution. Numerous "acid catalyzed" or "base catalyzed" reactions depend sensitively on their concentrations.[1−4]

We have recently initiated studies of hydrated H^+ and OH^- ions in the gas phase and shown that they can be used as simple model systems for investigating charge-transfer processes and solution chemistry.[5,6] We have constructed a supersonic expansion discharge source and interfaced it to our FT-ICR mass spectrometer, an arrangement that permits us to produce, store, and mass-select ions solvated with up to about 100 water molecules. We have also been able to show that such ion clusters, once prepared, gradually lose the solvent ligands one by one due to the absorption of the ambient temperature infrared background radiation.[7] This provides us with a gentle way of removing the water ligands one at a time, and observing the effect of the removal of the stabilizing solvent upon the system properties and stability.

In the present paper we wish to address the question if and to what extent the solvated H^+ and OH^- ions can "catalyze" chemical reactions. Specifically, we investigate reactions of simple carbonyl compounds, acetaldehyde and acetone, with water clusters. Several related previous studies of similar organic species are available in the literature.[8−10] The dissociation energies of water molecules with organic compounds (e.g., CH_3CN, CH_3OH) have been investigated by high-pressure mass spectrometry by Meot-Ner,[11−14] while the stability, structure, and unimolecular decomposition of protonated organic clusters were the subject of study by Castleman et al.[15−17] Several interesting theoretical as well as experimental studies of reactions of proton bound organic clusters with small organic molecules originated in the group of Ch. Lifshitz.[18−20] Adsorption of organic molecules on large water clusters was investigated by Ahmed et al.[21,22] A prior investigation of chemical ionization of acetaldehyde revealed some evidence for acid-catalyzed aldol addition in the gas phase but remained somewhat inconclusive with respect to the mechanism.[23]

---

(1) Hattori, H.; Mison, M.; Ono, Y., Eds.; *Acid−Base Catalysis*; Kodansha Ltd.: Tokyo, 1994.

(2) Imelik, B.; Nacchache, C.; Coudurier, G.; Ben Taarit, Y.; Vedrine, J. C., Eds. *Studies in Surface Science and Catalysis*; Vol. 20: Catalysis by Acids and Bases; Elsevier: Amsterdam, 1985.

(3) vanOss, C. J. *Colloids Surf. A* **1993**, *78*, 1−49.

(4) Stewart, R.; Srinivasan, R. *Can. J. Chem.* **1981**, *59*, 957−963.

(5) Schindler, T.; Berg, C.; Niedner-Schatteburg, G.; Bondybey, V. E. *Chem. Phys. Lett.* **1994**, *229*, 57−64.

(6) Schindler, T.; Berg, C.; Niedner-Schatteburg, G.; Bondybey, V. E. *J. Phys. Chem.* **1995**, *99*, 12434−12443.

(7) Schindler, T.; Berg, C.; Niedner-Schatteburg, G.; Bondybey, V. E. *Chem. Phys. Lett.* **1996**, *250*, 301−308.

(8) Daly, G. M.; Gao, J.; El-Shall, M. S. *Chem. Phys. Lett.* **1993**, *206*, 500−508.

(9) El-Shall, M. S.; Olafsdottir, S. R.; Meot-Ner (Mautner), M.; Sieck, L. W. *Chem. Phys. Lett.* **1991**, *185*, 193−198.

(10) El-Shall, M. S.; Daly, G. M.; Gao, J.; Meot-Ner (Mautner), M.; Sieck, L. W. *J. Phys. Chem.* **1992**, *96*, 507−510.

(11) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1988**, *110*, 3858−3862.

(12) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1986**, *108*, 6189−6197.

(13) Deakyne, C. A.; Meot-Ner (Mautner), M.; Campell, C. L.; Hughes, M. G.; Murphy, S. P. *J. Chem. Phys.* **1986**, *84* (9), 4958−4969.

(14) El-Shall, M. S.; Marks, C.; Sieck, L. W.; Meot-Ner (Mautner), M. *J. Phys. Chem.* **1992**, *96*, 2045−2051.

(15) Tzeng, W. B.; Wei, S.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1990**, *168*, 30−36.

(16) Tzeng, W. B.; Wei, S.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1990**, *166*, 343−352.

(17) Zhang, X.; Yang, X.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1991**, *185*, 298−302.

(18) Feng, W. Y.; Goldenberg, M.; Lifshitz, C. *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 695−703.

(19) Martin, J. M. L.; Aviyente, V.; Lifshitz, C. *J. Phys. Chem. A* **1997**, *101*, 2597−2606.

(20) Feng, W. Y.; Lifshitz, Ch. *Int. J. Mass Spectrom. Ion Proc.* **1995**, *149/150*, 13−25.

(21) Ahmed, M.; Apps, C. J.; Hughes, C.; Watt, N. E.; Whitehead, J. C. *J. Phys. Chem. A* **1997**, *101*, 1250−1253.

(22) Ahmed, M.; Apps, C. J.; Hughes, C.; Whitehead, J. C. *Chem. Phys. Lett.* **1995**, *240*, 216−223.

(23) Wesedemiotis, C.; McLafferty, F. W. *Org. Mass Spectrom.* **1981**, *16*, 381−382.

S0002-7863(97)01869-6 CCC: $15.00

A first step of a base- or acid-catalyzed reaction is assumed to be addition of the H^+ or OH^- ion onto one of the reactants. It is easily seen that an $H^+(H_2O)_n$ cluster with n around 55 will have the same relative H^+ "concentration" as a strongly acid solution with pH ≈ 0, and a similarly sized $OH^-(H_2O)_n$ ion can be compared with a pH ≈ 14 basic medium. The specific purpose of the present study is to investigate to what extent one can view such solvated H^+ ions as "acid" and solvated OH^- ions as "basic" medium, and if and how the presence of in this case a single H^+ or OH^- ion will influence the chemistry taking place in the water cluster.

II. Experimental Section

All experiments were performed in a modified Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer Spectrospin CMS47X[24] equipped with a superconducting 4.7 T magnet, an ASPECT 3000 data station, and a cylindrical 60 × 60 mm "infinity" cell.[25] A fourth differential pumping stage was added to the original instrument to permit the use of external molecular beam cluster ion sources. In the source used in the present work, an argon−water mixture (200:1) was partially ionized by a low current corona discharge (1−3 kV, 1−4 mA).[26,27] A subsequent adiabatic expansion through a 150 μm orifice leads to formation of both protonated water clusters $H^+(H_2O)_n$, $n = 1-70$,[5] and hydrated anions $X(H_2O)_n$, $n = 1-30$, X = OH^-, O^-, O_2H^-, O_2^-.[6] The initial distribution of the clusters depends somewhat on source conditions. Switching between anions and cations is accomplished by changing the polarity of the ion transfer optics. The temperature of the cluster ions is determined by a balance between evaporative cooling and radiative heating by the ambient temperature background and is estimated to be around $\lesssim 150$ K.[7]

Downstream of the source the molecular beam is skimmed (400 μm) and the cluster ions are transferred into the ICR cell by a system of electrostatic lenses. After accumulation of a sufficient number of ions (typically after $\approx$ 300 ms), the molecular beam is blocked by a mechanical shutter to prevent collisions of the stored ions with the background gas from the molecular beam. Typical pressures with the cluster source in operation are 5×10^{-3} mbar in the source chamber and 6×10^{-10} mbar in the cell region with a closed shutter.

The water cluster distribution $Y(H_2O)_n$, Y = H^+ or OH^- and O^-, was allowed to react with acetone and acetaldehyde admitted through a leak valve at a pressure inside the cell of 7×10^{-8} mbar. The reaction and fragmentation processes occurring in the cell were followed by recording mass spectra after variable reaction delays.

III. Results and Discussion

(a) Reactions of Cationic Water Clusters with Acetone and Acetaldehyde. When cationic water clusters $H^+(H_2O)_n$, $n = 2-80$, are reacted with acetone at a pressure of about 7×10^{-8} mbar, which corresponds to about five collisions per second, basically two processes are observed, fragmentation and ligand exchange. The former process is not caused only by collisions, but as we have been able to demonstrate previously, it is in part due to absorption of infrared blackbody radiation.[7] The ligand exchange efficiently replaces water molecules with acetone, and after some 300 ms, clusters containing one acetone already prevail over pure water clusters.

The reactions do not stop there, and solvated ions of the type $H^+(H_2O)_n(C_3H_6O)_k$ with two and eventually up to 8 acetone ligands form. The spectra at longer times get significantly simplified, due to the preferential stability of $H^+(H_2O)_n(C_3H_6O)_k$ ions with $k = n + 2$. The same stability pattern was previously observed in reactions of water clusters with ethers and other organic ligands.[28−34] These stable structures correspond to a hydrophilic, hydrogen bonded $H^+(H_2O)_n$ "core", completely terminated by a hydrophobic shell of the organic ligands, with an oxygen (or nitrogen) of the organic molecules bound to each of the $k = n + 2$ peripheral hydrogens. Even these particularly stable cluster ions fragment further, losing both acetone and water ligands. After a sufficiently long time (40 s), all water ligands are lost and a proton solvated with two acetone molecules, $H^+(C_3H_6O)_2$, remains as an essentially unique "final" product ion.

The reactions of the cationic $H^+(H_2O)_n$ clusters with acetaldehyde follow a very similar pattern as the reactions of acetone, but with a few important differences. While the protonated water clusters of all sizes studied (up to $n = 80$) efficiently ligand exchange with acetone (Figure 1a), in the case of acetaldehyde ligand exchange only for smaller clusters is observed. For $n > 25$ the rates decrease drastically, and essentially only fragmentation is noticeable for clusters with $n > 48$ (Figure 1b). The probable conclusion that one can draw from this observation is that acetone exchanges ligands with the "neutral" water surface, while acetaldehyde interacts efficiently only with smaller clusters, where the surface is activated by the proximity of the positively charged ionic core. This behavior may be the result of the higher polarity and a somewhat larger dipole moment of the acetone carbonyl group (2.88 D) compared with acetaldehyde (2.75 D). A consequence of this reluctance of larger clusters to ligand exchange with acetaldehyde is that the clusters $H^+(H_2O)_n(C_2H_4O)_k$ with $n > 2$ form to a much lesser extent than in acetone, and only trace quantities of $n > 4$ clusters are detected.

The differences in the carbonyl properties, and the higher proton affinities of acetone compared with acetaldehyde also result in some interesting differences in the stability of their clusters. This can be exemplified by the fragmentation of the size selected $(n, k) = (1, 3)$ clusters of both species. The $H^+(H_2O)(C_3H_6O)_3$ loses a water molecule in the first step, resulting in a proton solvated by three acetones, with the final product then being formed by a loss of one of the acetone ligands. The order of fragmentation for the acetaldehyde species is reversed as shown by the first-order kinetics fit of the data (Figure 2), and the $(H_3O)^+(C_2H_4O)_3$ ion first loses an acetaldehyde ligand. The resulting (1, 2) cluster then loses water, forming proton solvated by two acetaldehydes, again an $n = 0$, $k = 2$ final product, with the $n = 0$, $k = 3$ cluster hardly appearing at all.

(b) Reactions of Water Anion Clusters with Acetone and Acetaldehyde. The anion reactions are somewhat complicated by the fact that the initial distribution contains not only "hydrated hydroxyl anion" species $OH^-(H_2O)_n$, but also ions of the solvated O^-, O_2^-, O_2H^- types, and for larger values of n also "solvated electrons", $e^-(H_2O)_n$, are present. Fortunately, the anions of the $OH^-(H_2O)_n$ type are dominant, and only the $O^-(H_2O)_n$ species represent a significant impurity. Although a

---

[24] Kruppa, G. H.; Caravatti, P.; Radloff, C.; Zuercher, S.; Laukien, F.; Watson, C.; Wronka, J. FT-ICR/MS: Analytical applications of Fourier Transform ion cyclotron resonance spectrometry; Asamoto, B., Ed.; VCH: Weinheim, 1991.

[25] Caravatti, P.; Allemann, M. *Org. Mass Spectrom.* **1991**, *26*, 514−518. Caravatti, P. US.-Patent Nr. 4 924 089, dated 8.5.1990.

[26] Searcy, J. Q.; Fenn, J. B. *J. Chem. Phys.* **1974**, *61*, 5282−5288.

[27] Engelking, P. C. *Rev. Sci. Instrum.* **1986**, *57*, 2274−2277.

[28] Hiraoka, K.; Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1974**, *96*, 3359−3364.

[29] Veenstra, B. R.; Meijers, H. C.; de Lange, P. J.; Kommandeur, J. *Chem. Phys.* **1991**, *156*, 157−162.

[30] Schindler T.; Berg C.; Niedner-Schatteburg G.; Bondybey V. E. Chem. Phys. **1995**, *201*, 491−496.

[31] Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1992**, *114*, 3312−3322.

[32] Stace, A. J.; Moore, C. *J. Am. Chem. Soc.* **1983**, *105*, 1814−1819.

[33] Stace, A. J.; Shukla, A. K. *J. Phys. Chem.* **1982**, *86*, 865−867.

[34] Stace, A. J.; Shukla, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 5314−5318.

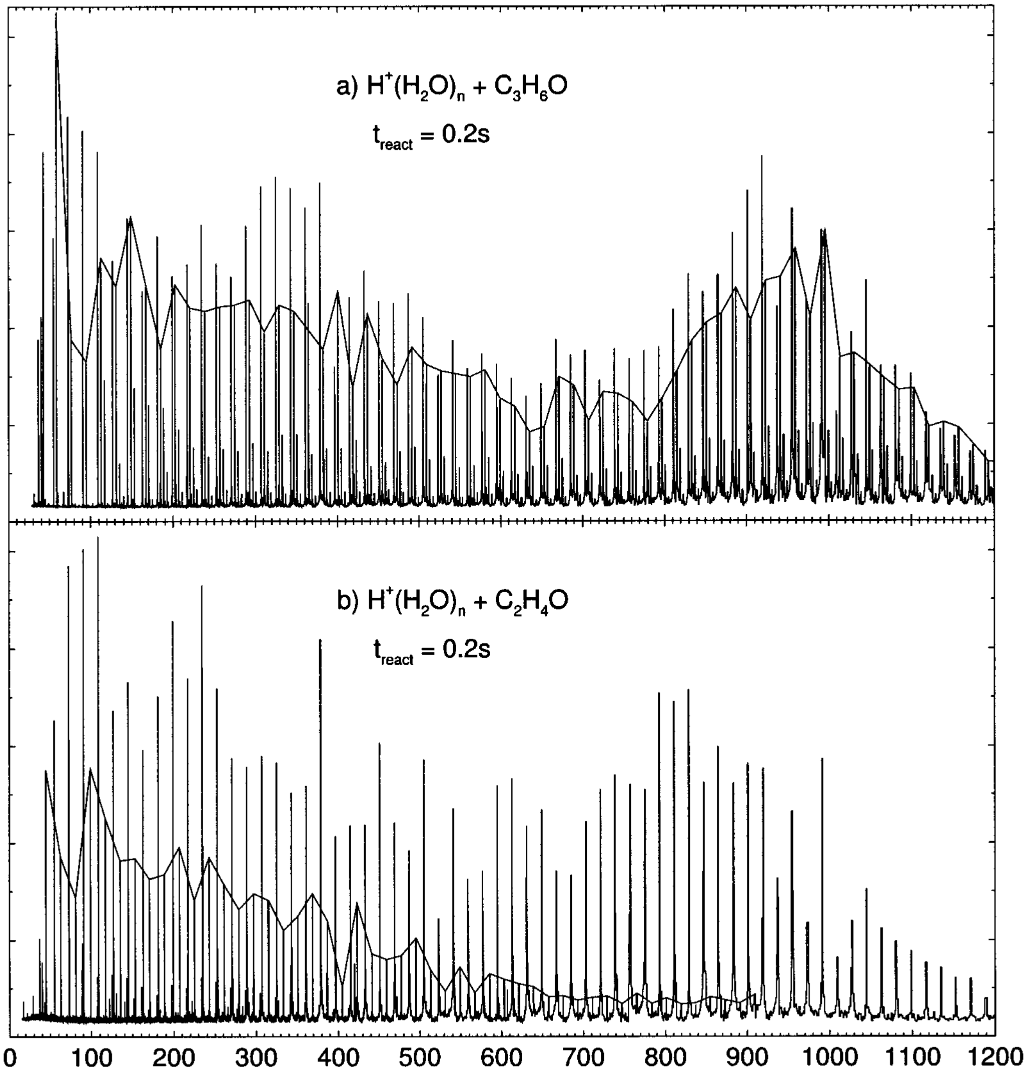

Figure 1. Reactions of protonated water clusters $H^+(H_2O)_n$, $n = 2-80$, with acetone (a) and acetaldehyde (b) after a reaction delay of 0.2 s ($p = 7 \times 10^{-8}$ mbar). The solid lines link clusters of the type $H^+(H_2O)_m(C_3H_6O)$ and $H^+(H_2O)_n(C_2H_4O)$. While the protonated water clusters ligand exchange over the entire mass range with acetone, only the smaller cluster sizes react with acetaldehyde.

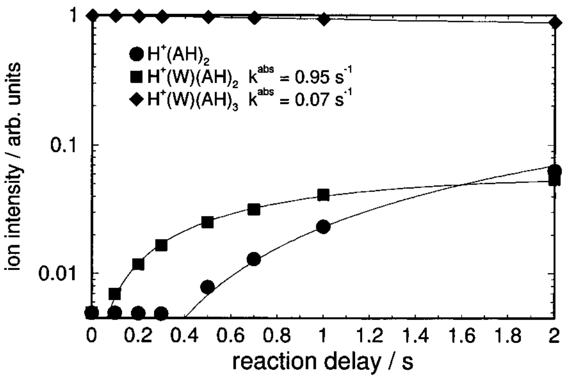

Figure 2. Time-resolved kinetics of the fragmentation of $H^+(W)(AH)_3$. The solid lines represent a first-order reaction kinetics fit to the data points. $W_n = (H_2O)_n$ and $(AH)_n = (CH_3CHO)_n$.

full separation of the different groups of ions was not practicable, the solvated OH^- and O^- ions differed substantially in their reaction rates, so that their products could easily be distinguished from each other. The other types of ions which are present only in trace amounts simply exchange water for the organic ligands, and their overall contribution to the observed reaction products is very minor.

The hydrated O^- ions react nearly an order of magnitude faster than the other anionic clusters, so that already after about 3 s they are basically absent from the reaction mixture (Figure 3a, denoted by a downward pointing arrow). At the same time, product ions corresponding to the formula $(CH_3COO)^-(H_2O)_n$ grow rapidly in intensity. We conclude that the oxygen anion oxidizes the aldehyde to the acetate anion, as described in ref 35 for the naked O^-, with a concomitant loss of a hydrogen atom:

$$O^-(H_2O)_n + CH_3CHO \rightarrow (CH_3COO)^-(H_2O)_{n-x} + H + xH_2O \quad (1)$$

The rate of reaction 1 is surprisingly high for all cluster sizes over the whole mass range. One can argue that in contrast to $OH^-(H_2O)_n$, where the hydroxide ion is positioned inside the cluster, the ion O^- may be located near the surface of the cluster, so it is able to react faster with the acetaldehyde molecules. This first step is followed by the uptake of a second acetaldehyde and further fragmentation and loss of the water ligands. Interestingly the last water molecule is not lost even at the longest time studied and remains in the cluster, resulting formally in a $(CH_3COO)^-(CH_3CHO)(H_2O)$ final product (121 amu).

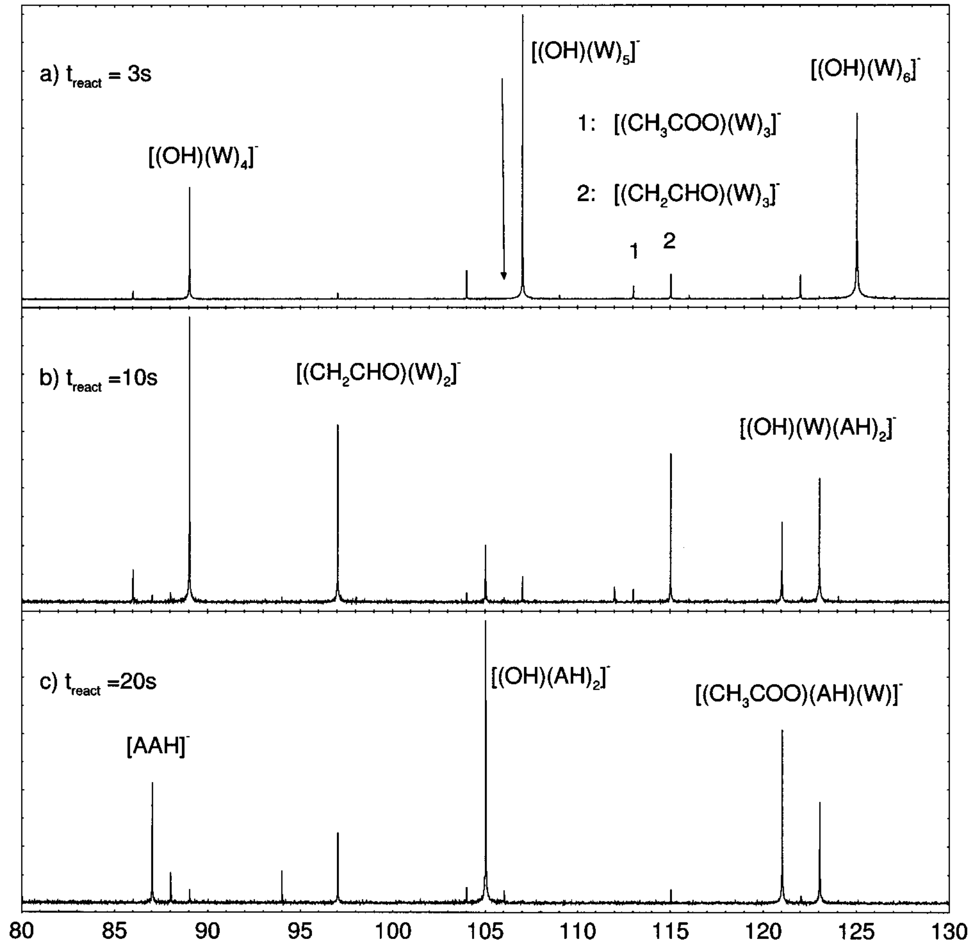

Figure 3. Reaction of anionic water clusters with acetaldehyde ($p = 7 \times 10^{-8}$ mbar) as a function of reaction delay. $O^-(H_2O)_n$ clusters react with acetaldehyde an order of magnitude faster than the $OH^-(H_2O)_n$ species yielding hydrated acetate ions. The $OH^-(H_2O)_n$ react via ligand exchange and proton transfer (a, see text). In a secondary step condensation and aldol formation can take place (b, c). $W_n = (H_2O)_n$, $(AH)_n = (CH_3CHO)_n$, AAH = $(CH_3CHO^-CH_2CHO)$ − aldolate adduct.

Most interesting for the purpose of the present study are the most abundant cluster anions, of the type $OH^-(H_2O)_n$. These react considerably more slowly, and as in the case of cations, the first reaction step formally appears to be a ligand exchange, and formation of ions containing one aldehyde ligand, $OH^-(H_2O)_n(C_2H_4O)$. In the second reaction step ions containing two ligands, that is corresponding to an overall formula $OH^-(H_2O)_n(C_2H_4O)_2$, are formed, but in contrast to the cation reactions, there is little evidence of formation of ions containing three or more organic ligands (Figure 3b). This may partially be due to the fact that the initial cluster anion distribution was narrower than that for the cations, with only species up to about $n = 30$ being efficiently produced.

In subsequent reactions, the clusters fragment and gradually lose their water ligands, forming smaller $OH^-(H_2O)_n(C_2H_4O)_2$, and the process is essentially complete after about 20 s (Figure 3c). Interestingly, the major product is not only an ion with 105 amu, corresponding to $n = 0$, but also a peak at 87 amu, 18 mass units lower, which would formally correspond to $n = -1$. This dominant product, a $(C_4H_7O_2)^-$ anion, indicates that the reactions occurring in this case are not simple exchange and loss of water ligands. Since at least one hydrogen atom from the acetaldehyde molecules is also lost, a more complex chemistry must be taking place, with covalent bonds being broken and perhaps also formed, and acetaldehyde losing its chemical identity. Furthermore, even though the mass 87 corresponds formally to a water molecule loss from the 105 amu species, the two ions are clearly not purely sequential fragmentation products. Their time evolution indicates that they grow in more or less in parallel, and even though already after about 10 s appreciable mass 87 ion signal is present, further fragmentation of the remaining mass 105 amu ions is quite inefficient. This can be seen in Figure 4a, where after 60 s the 105 amu peak remains quite prominent, comparable to the mass 87, and it persists with comparable intensity even after 150 s, the longest time investigated. It is rather clear that the two persistent peaks at 105 and 87 amu are two independent, structurally different products.

To gain more insight into the reactions occurring in the clusters, and to identify the source of the hydrogen atom being lost from the cluster, we have examined the reactions of isotopically substituted, deuterated acetaldehydes. The product spectrum resulting from reactions of acetaldehyde-d_1, CH_3CDO, is shown in Figure 4b. All three major final products are shifted by two units to higher masses, indicating that both deuterium atoms are being retained, and that the hydrogen atom lost from the 87 amu product originates from the methyl, and not from the aldehydic group.

The conclusion that the mass peaks 105 and 87 are two chemically different species and not just sequential fragmentation products is confirmed by experiment with perdeuterated acetaldehyde-d_4, exemplified by spectrum c in Figure 4. Here the mass peak at 105 amu in Figure 4a shifts to 113 amu confirming that all eight deuterium atoms are retained in this

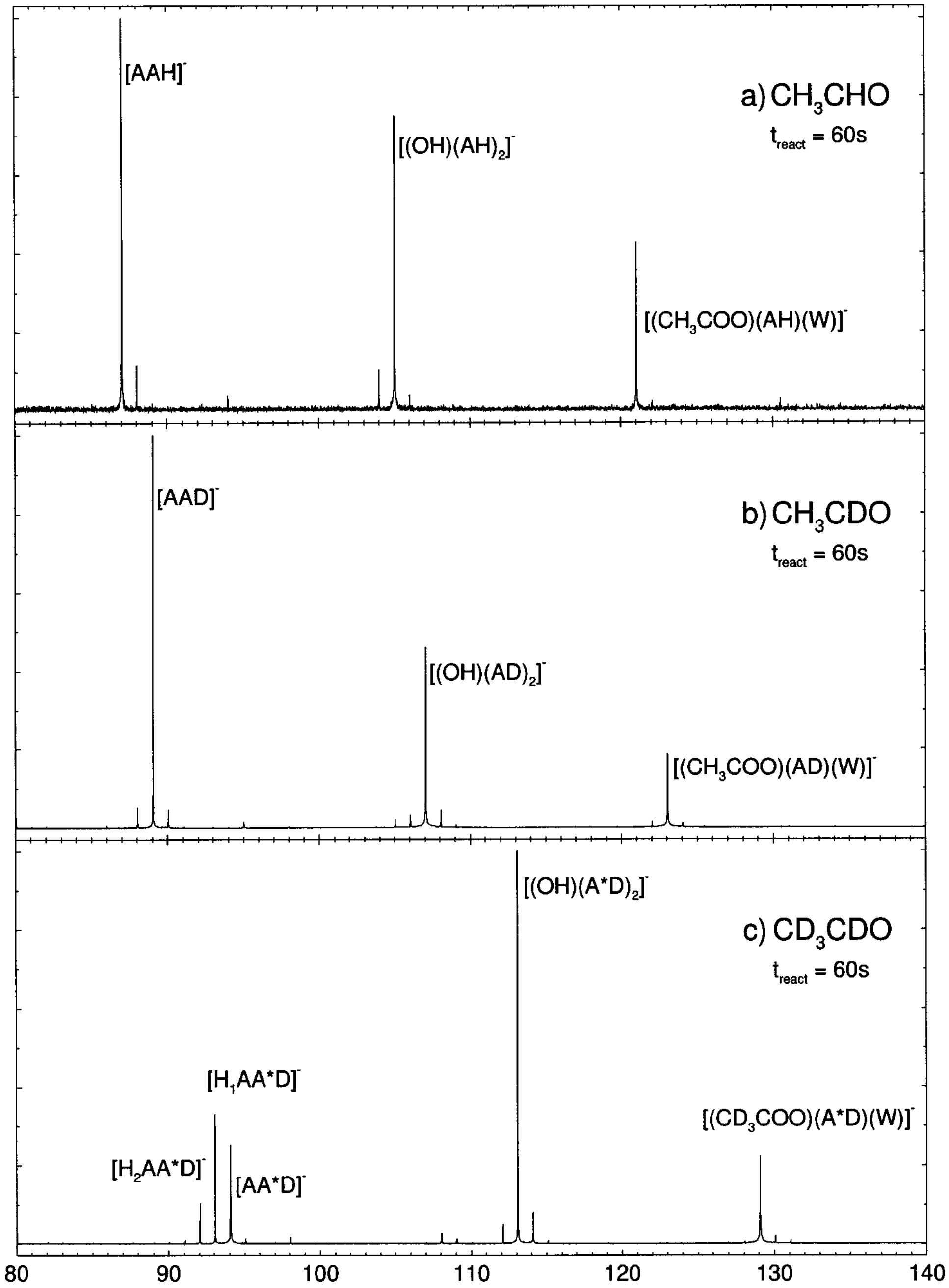

Figure 4. Reaction of $OH^-(H_2O)_n$ and $O^-(H_2O)_n$ with (a) acetaldehyde (CH_3CHO), (b) CH_3CDO, and (c) CD_3CDO (delay 60 s; $p = 7 \times 10^{-8}$mbar); W = H_2O; AH = CH_3CHO; AD = CH_3CDO; A*D = CD_3CDO; AAH = $CH_3CHO^-CH_2CHO$ aldol; AAD = $CH_3CDO^-CH_2CDO$ (note that both D atoms remain in the product); AA*D = $CD_3CDO^-CD_2CDO$. Note peaks resulting from isotopic exchange 1, 2, and 3 amu below the fully deuterated product—see text.

product and no isotopic exchange with the water solvent has taken place. Similarly also the 121 amu signal shifts by eight mass units to 129 amu, indicating no deuterium loss. A quite different story is told by the third, 87 amu, product peak, which is replaced by strong signals at 94, 93, and 92 amu, with weak signals appearing also at mass 91 and 90. It is apparent that, in addition to the loss of one deuterium atom from the methyl group, in many of the product ions also one, two, or possibly even three or four additional deuterium atoms have been exchanged for hydrogens from the water "solvent".

One can understand the results if one recalls the basic properties of carbonyl compounds, and reactions of aldehydes and ketones in basic solutions. In the first reaction step the acetaldehyde molecule apparently interacts with the "surface" of the hydrated hydroxide cluster, with a proton being transferred to the OH^- group, and a hydrated CH_2CHO^- anion being formed.

$$OH^-(H_2O)_n + CH_3CHO \rightarrow CH_2CHO^-(H_2O)_{n-x} + (x+1)H_2O \quad (2)$$

The above reaction is postulated to occur in basic aqueous solutions, and for the specific $n = 1$, $x = 1$ case, that is for OH^- bound to one molecule of water, it was in fact previously studied in the gas phase by Tanner et al.[36] They determined the absolute rate constant of the reaction of $OH^-(H_2O)$ with

---

(35) Lee, J.; Grabowski, J. J. *Chem. Rev.* **1992**, *92*, 1611−1645.

(36) Tanner, S. D.; Mackay, G. I.; Bohme, D. K. *Can. J. Chem.* **1981**, *59*, 1615−1621.

acetaldehyde to be $(3 \pm 1) \times 10^{-9}$ cm^3 molecules^{-1} s^{-1}, nearly equal to the rate constant of the reaction of naked OH^- ($k^{abs} = (3.1 \pm 0.8) \times 10^{-9}$ cm^3 molecules^{-1} s^{-1}). With the help of deuterated measurements Stewart et al. and the group of Bohme[37,38] were able to show that the proton transferred to the OH^- originates from the methyl group. The resulting CH_2CHO^- ion can be formally written as an equilibrium between two ionic forms, aldehydic and enolate:

$$CH_2{=}CHO^- \rightleftarrows {}^-CH_2{-}CH{=}O \qquad (3)$$

In the presence of a second acetaldehyde (or another molecule containing a carbonyl bond), a nucleophilic addition of the anion to the carbonyl group of the nonionized molecule can take place, forming an anion of dimer containing both alcoholic and aldehydic groups, "aldol". This sequence of steps, that is reaction of the OH^- "catalyst" with a molecule of acetaldehyde (reaction 2), and the subsequent nucleophilic addition of the resulting enolate anion to a carbonyl group of a second molecule (reaction 4) is known in organic chemistry as the "aldol addition reaction":[39]

$$CH_3CHO + {}^-CH_2{-}CH{=}O(H_2O)_n \rightarrow CH_3CHO^-CH_2CHO(H_2O)_{n-x} + xH_2O \qquad (4)$$

In the finite size cluster, the reaction enthalpy will heat the cluster, and may result in evaporating one or more water molecules from the cluster ion. Due to the competition of blackbody heating and collisional fragmentation, we can make no definitive statement as to how many water molecules are lost in this process. In subsequent reaction steps further fragmentation and loss of complexed water molecules take place. A final, unique product of the reaction sequence at very long times is the aldolate dimer anion, $C_4H_7O_2^-$ at 87 amu. The presence of the hydroxyl anion in the cluster thus catalyzes dimerization of the acetaldehyde, the same way it does in strongly basic aqueous solutions.

Examination of reaction sequence 2 and 4 reveals that the aldehydic hydrogen is not involved. This is consistent with the results of experiments with CH_3CDO, that is acetaldehyde deuterated in the aldehydic group. The aldehydic hydrogens cannot exchange with the water solvent, and accordingly both deuterium atoms are retained with the final aldolate product, $CH_3CDO^-CH_2CDO$, which occurs at mass 89. In the perdeuterioacetaldehyde experiment, where the methyl group is also deuterated, the situation is different. In the course of the proton-transfer reaction 2, one of the deuterium atoms from the methyl group is lost to the water solvent. Since the proton transfer is reversible and can repeatedly proceed back and forth, more than one deuterium may be exchanged and lost from the final products. Accordingly, besides a fully deuterated aldolate at 94 amu, also products at masses 93, 92, and even 91 are detected, corresponding to an exchange of 1, 2, or even 3 deuterium atoms, in addition to the one lost in the condensation.

Interesting is the presence of the persistent product at mass 105 in Figure 4a. This signal after long reaction times is apparently not due to the condensed aldolate ion with one molecule of water, but is the result of "failed" aldol addition, which can perhaps be seen structurally as an OH^- anion "solvated" by two acetaldehyde molecules. Consistent with this picture are the results of the isotopic experiments. Both deuterium atoms are retained in the CH_3CDO experiment with the product appearing at 107 amu, and the product shifts to mass 113 in the perdeuterio study, again indicating all eight deuterium atoms are retained, and none have been exchanged and lost with the evaporating water solvent.

We have noted above that a cluster with one OH^- and 55 water molecules can be compared with a strongly basic solution with pH = 14. Extending this argument, one could predict that by further loss of water ligands the cluster will become increasingly "basic", further increasing the rate of base-catalyzed reactions. The presence of the mass 105 complex indicates that this is not the case. The aldol addition does not occur in the complete absence of water, and a minimum number of solvent molecules is apparently required for an efficient condensation to take place. If too many solvent molecules were lost before the condensation took place, only a complex ion, rather than the aldolate, will form as a final product. Unfortunately, competition of cluster fragmentation with their reactions makes it difficult to determine this minimum amount of solvent needed. Such an experiment could, however, easily be done in an instrument with cooled walls, where the blackbody fragmentation would be suppressed.

A further support for this interpretation and the presence of two independent, structurally different products can be found by observing the time evolution of the individual mass signals. It is clear that one cannot explain the 93, 92, or 91 amu signals in the perdeuterioacetaldehyde experiment (Figure 4c) as "dehydration" products of the prominent 113 amu ion. Loss of H_2O or HDO could only produce masses 95 and 94, respectively. The formation of the lighter, deuterium-depleted products must proceed via deuterium-depleted hydrated ions at mass 112 or 111. This can be verified by comparing the time evolution of the fully deuterated d_8 complex at mass 113 with, for instance, the 112 amu peak. While the 113 mass signal continuously grows during the experiment, as is appropriate for a final product, the 112 amu peak goes through a maximum at much earlier times, and is nearly absent in the final spectrum (Figure 4c). It disappears almost completely by losing ligand water, and contributes to the 93 and 92 amu aldolate anion final products.

As mentioned previously, the third rather strong peak appearing in the spectrum in Figure 4a, mass 121, is the final product of the $O^-(H_2O)_n$ reactions, and corresponds at least formally to an acetate anion, CH_3COO^-, solvated with one water molecule and one additional acetaldehyde ligand, $(CH_3COO)^-(CH_3CHO)(H_2O)$. Interesting and somewhat puzzling is the retention of all eight deuterium atoms in this product, which as noted above shifts from 121 to 123 amu in the acetaldehyde-d_1 and to 129 amu in the perdeuterio experiment, indicating no deuterium exchange and loss. Perhaps the final product is an acetate ion bound over the water molecule and strong hydrogen bonds to the second aldehyde. The strong bonds to the bridging water molecule might perhaps explain the observed lack of deuterium loss and isotopic exchange.

The aldol addition is not a property of aldehydes alone, but can also take place in other compounds containing carbonyl groups, in particular ketones. In the present work, we have also examined, although in somewhat less detail, the reactions of anionic water clusters with acetone. As in the aldehyde case, we observe also for acetone an efficient aldol condensation. A similar OH^- catalyzed sequence of reactions, as described for the aldehydes, takes place in the hydrated hydroxyl anions, $OH^-(H_2O)_n$. In the case of acetone it leads efficiently to a

---

[37] Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650−7653.

[38] Raksit, A. B.; Bohme, D. K. *Can. J. Chem.* **1983**, *61*, 1683−1689.

[39] Streitwieser, A.; Heathcock, C. H. *Organische Chemie*; VCH: Weinheim, 1986.

$C_6H_{11}O_2$-condensation product. This ion, the anion of 4-hydroxy-4-methyl-2-pentanone, is a well-known product of the aldol addition of acetone. The aldol condensation in solutions is an equilibrium process whose equilibrium constants are in the case of ketones often fairly unfavorable, leading to small yields. In the present case, the two acetone molecules are trapped in the same cluster. Evaporation of the water solvent prevents the reverse process from occurring once the addition has taken place, and the reaction proceeds almost completely to the addition product.

IV. Summary

In this paper we examine and compare the reactions of the simple organic compounds acetone and acetaldehyde with ionic water clusters. The results indicate that both acetone and acetaldehyde react quite differently in hydrated proton, $H^+(H_2O)_n$, and hydrated hydroxyl, $OH^-(H_2O)_n$ clusters. While in the former, "acid" clusters only ligand exchange is observed, in the latter case OH^- catalyzed addition of two molecules of the carbonyl compound takes place, and a true covalent bond between them is formed. The reactions thus parallel the behavior of carbonyl compounds in strongly basic solutions, and in the hydrated hydroxyl anions an efficient OH^- catalyzed aldol addition takes place.

Acknowledgment. Financial support of the Deutsche Forschungsgemeinschaft through the Schwerpunktprogramm Molekulare Cluster and by the Fonds der Chemischen Industrie is gratefully acknowledged.

JA971869T