double bond character in the HOMO accounts only in part for further changes of R_{PC} and k_{PC}. Other significant contributions come from the complete d set on carbon and the remaining d functions on phosphorus. It is of course possible to calculate bond orders in a formal sense from force constants and bond distances.[8,9,39] But, as it was shown in this work, the situation is much too complicated in the case of methylenephosphorane (and certainly also in other cases of similar types of bonding) to allow the interpretation of such bond orders in the simple scheme of d_π–p_π bonding according to structure **1b.**

Acknowledgment. The calculations were performed on the CDC CYBER 73/74 of the computer centers of the University and the Technical University of Vienna. We are grateful for sufficient supply of computer time and thank the staff of both centers for their cooperation. The computer program for plotting the orbital contour diagrams has been written by F. Keil, Karlsruhe/F.R.G.

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Condensation Reactions Involving Carbonium Ions and Lewis Bases in the Gas Phase. Hydration of the *tert*-Butyl Cation

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Abstract: The gas-phase reactions $R^+ + OH_2 = ROH_2^+$ where $R = s\text{-}C_3H_7^+$ and $t\text{-}C_4H_9^+$ lead to protonated 2-propanol and protonated *tert*-butyl alcohol. Proof for this is given by comparing the heats of formation of the ROH_2^+ species obtained as above with those obtained by protonation of the corresponding alcohols. The reactions of alkyl carbocations with n-donor bases like OH_2, CH_3OH, NH_3, CH_3NH_2, etc., probably lead to the corresponding protonated alcohols, ethers, primary amines, secondary amines, etc., and represent a general class of ion–molecule condensation reactions. Condensation reactions of this type and other oligo condensation reactions occur readily in methane containing CO, H_2O, and NH_3 and must be considered, if the importance of ion–molecule reactions to prebiotic synthesis is to be assessed. The energies released in the hydration of the *tert*-butyl$^+$ and protonated *tert*-butyl alcohol, obtained by measurement of the corresponding equilibria, show an interesting pattern: $C_4H_9^+ + OH_2 = C_4H_9OH_2^+$, $-\Delta H = 11.2$ kcal/mol; $C_4H_9(OH_2)_2^+ + OH_2 = C_4H_9(OH_2)_3^+$, $-\Delta H = 17.7$ kcal/mol; $C_4H_9(OH_2)_3 + OH_2 = C_4H_9(OH_2)_4^+$, $-\Delta H = 14.0$ kcal/mol. The low exothermicity of the first reaction is considered to be due to a shift of positive charge from the methyl groups to the OH_2 group which makes the stabilization due to the methyl substituents much less important for the protonated butanol. The conversion of the $C_4H_9OH_2^+$ hydrates to isobutene by the reaction $C_4H_9(OH_2)_n^+ + OH_2 = i\text{-}C_4H_8 + H^+(H_2O)_{n+1}$ was also observed. This reaction is analogous to acid-catalyzed dehydration of alcohols in solution. Thermochemical information for some of the observed reactions is provided.

The present work deals with experimental studies of gas-phase condensation reactions involving alkyl carbocations R^+ and Lewis bases. The reactions occur in a "high pressure" ion source using electron pulses for ionization and operating at a few Torr of pressure. The reactions are followed by mass spectrometric detection of the ions. Equations 1–4 illustrate the reaction type considered where R^+ is $C_2H_5^+$ and $t\text{-}C_4H_9^+$ and the n-donor bases B are: OH_2, CH_3OH, NH_3, and CH_3NH_2.

$$t\text{-}C_4H_9^+ + OH_2 = t\text{-}C_4H_9OH_2^+ \tag{1}$$

$$s\text{-}C_3H_7^+ + CH_3OH = C_3H_7OHCH_3^+ \tag{2}$$

$$C_2H_5^+ + NH_3 = C_2H_5NH_3^+ \tag{3}$$

$$C_2H_5^+ + CH_3NH_2 = C_2H_5NH_2CH_3^+ \tag{4}$$

The question can be asked whether the resulting condensation products have the structure of protonated *tert*-butyl alcohol, protonated *sec*-propyl methyl ether, protonated ethylamine, and protonated methylethylamine, respectively. These of course are the expected products considering the above processes as direct reactions between the Lewis acid R^+ and the Lewis n-donor bases B. In solution, where the carbonium ions are most often created in superacid media, the above mentioned compounds are the known reaction products. However, in the gas phase these and other reactions to be disussed later have not really been recognized as a general class and the structure of the reaction products has seldom if ever been verified. In the present work we have set out to verify the nature of the condensation products for at least some of the reactions and to examine some parallels between gas phase and solution carbocation reactions.

The present work follows earlier studies from this laboratory[1-3] of condensation reactions between alkyl carbocations and H_2 and paraffins, i.e., systems in which the electrophilic attack by the carbocation occurs on a σ bond. In these systems extensive analogies with reaction mechanisms proposed in condensed phase, i.e., reactions in superacid media,[4] were found. This led us to believe that the situation with n-donor bases should be similar. The gas-phase experiments are useful not only in showing that often very much the same reactions occur in both phases but also because they often provide thermochemical data, i.e., heats of formation of the participating ions and enthalpy changes for the reactions. This information is directly applicable only to the gaseous reactions since the thermochemistry in solution is modified by the different solvation energies of the ionic reactants involved. Nevertheless the thermochemistry of the isolated species increases our understanding also of the reactions in solution.

Synthetic ionic reactions in the gas phase are of interest also from a very different point of view, namely the abiogenic synthesis of biologically important compounds. The pioneering experiments of Miller[5] showed that electrical discharges in a mixture of gases containing methane, ammonia, water, and CO could produce significant amounts of biologically important compounds such as amino acids. Since ion–molecule reactions must occur in electric discharges, these reactions may play a part in the mechanisms involved in prebiotic synthesis. Some attempts have been made to establish possible ion–molecule pathways. For example Huntress, Baldeschwieler, and Ponnamperuma[6] using results obtained with an ICR spectrometer at 10^{-5} Torr came to the conclusion that ion–molecule reactions are probably not important. However condensation reactions of the type $A^+ + B = (AB)^+$ cannot be conveniently observed at low pressure since the AB^+ condensation product is internally excited by the exothermicity of the condensation reaction and in the absence of collisions with third bodies falls apart either into the original reactants or in some other way. Yet condensation reactions of the type mentioned are very important synthetic pathways. Furthermore they occur readily at gas pressures in the Torr range and above, i.e., under conditions where the electric discharge experiments were made.

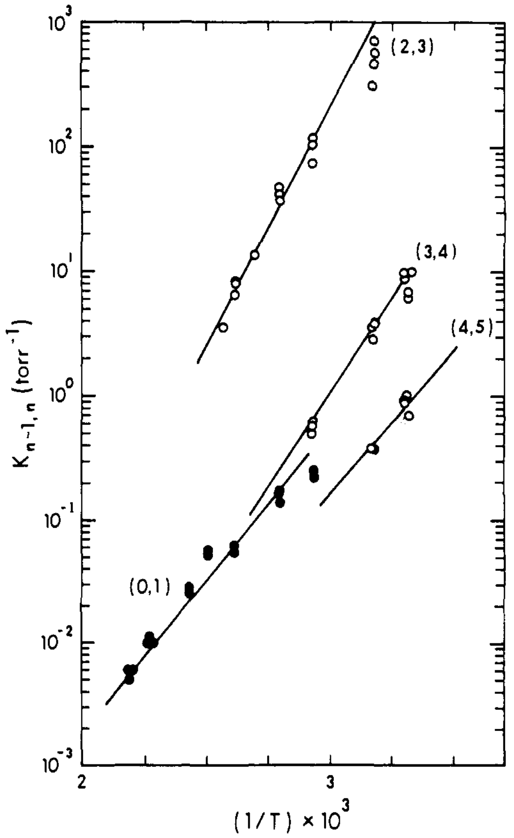


Figure 1. van't Hoff plot for hydration equilibria: $t\text{-}C_4H_9\cdot(OH_2)_{n-1}^+ + OH_2 = t\text{-}C_4H_9(OH_2)_n$ ($n - 1$, n). Equilibrium constants given for pressure in Torr. Corresponding $\Delta H°$ and $\Delta S°$ values shown in Table I.

Experimental Section

The experiments were made with a pulsed electron beam high ion source pressure mass spectrometer which has been described previously.[7]

The major gas, methane, was Linde ultrahigh purity which was further purified by passing it through a dry ice cooled, 5 Å molecular sieve, trap. The amounts of the various gaseous additives, isobutane, propane, and H_2O, were metered into the methane stream through calibrated capillaries, a procedure often used in previous work.[7]

Results and Discussion

(a) Formation of Protonated Alcohols by the Reaction $R^+ + OH_2 = ROH_2^+$. The General Reaction of R^+ with n-Donor Bases. The experiments in which the *tert*-butyl ion reacted with H_2O according to reaction 1 will be described in detail in section c.

$$t\text{-}C_4H_9^+ + OH_2 = t\text{-}C_4H_9OH_2^+ \tag{1}$$

At this place it suffices to say that conditions could be found where the $t\text{-}C_4H_9^+$ and $t\text{-}C_4H_9OH_2^+$ reached equilibrium. The equilibrium constant K_1 could be determined at different water pressures and temperatures. The van't Hoff plot of the equilibrium constant is shown in Figure 1 and the resulting $\Delta H°_1$ and $\Delta S°_1$ are given in Table I. This table contains also results for some of the higher ($n - 1$, n) hydration equilibria of *tert*-butyl which are discussed in section c. Using $\Delta H_f(t\text{-}C_4H_9^+) = 169$ kcal/mol due to Lossing, Semeluk and Tsang,[8] $\Delta H_f(H_2O, g) = -57.8$ kcal/mol, and $\Delta H_1 = -11.2$ kcal/mol (Table I) one obtains $\Delta H_f(t\text{-}C_4H_9OH_2^+) = 100.0$ kcal/mol. The proton affinity of *tert*-butyl alcohol was determined in a separate experiment using *tert*-butyl alcohol and proton transfer equilibria from known standard acids. The result obtained was PA(*tert*-butyl alcohol) = 192 kcal/mol. Combining this with $\Delta H_f(H^+) = 367.2$ and ΔH_f(*tert*-butyl alcohol)

Table I. Energetics of Condensation Reactions of Alkyl Carbocations with n-Donor Bases and Some Hydration Reactions

Reaction	$-\Delta H$, kcal/mol	Reaction	$-\Delta H$, kcal/mol
$CH_3^+ + OH_2 = CH_3OH_2^+$	66[a]	$H_3O^+ + H_2O = H^+(H_2O)_2$	31.6[c]
		$H^+(H_2O)_2 + H_2O = H^+(H_2O)_3$	19.6[c]
$s\text{-}C_3H_7^+ + OH_2 = s\text{-}C_3H_7OH_2^+$	22.8[a]	$H^+(H_2O)_3 + H_2O = H^+(H_2O)_4$	17.5[c]
$t\text{-}C_4H_9^+ + OH_2 = t\text{-}C_4H_9OH_2^+$	11.2[a,b]		
$C_2H_5^+ + OH_2 = C_2H_5OH_2^+$	37[a]	$CH_3OH_2^+ + H_2O = CH_3(OH_2)_2^+$	~25[e]
$C_2H_5^+ + C_2H_5OH = C_2H_5OHC_2H_5^+$	54[a]	$(CH_3)_2OH^+ + H_2O = (CH_3)_2OHOH_2^+$	22.6[d]
$C_2H_5^+ + NH_3 = C_2H_5NH_3^+$	65.8[a]	$t\text{-}C_4H_9OH_2^+ = i\text{-}C_4H_8 + H_3O^+$	−36[g]
		$t\text{-}C_4H_9OH_2^+ + H_2O = i\text{-}C_4H_8 + H^+(H_2O)_2$	−4[g]

Reaction	$-\Delta H°$, kcal/mol	$-\Delta S°$, eu
$t\text{-}C_4H_9^+ + OH_2 = C_4H_9OH_2^+$	11.2	22
$C_4H_9OH_2^+ + OH_2 = C_4H_9(OH_2)_2^+$	f	f
$C_4H_9(OH_2)_2^+ + OH_2 = C_4H_9(OH_2)_3^+$	17.7	29
$C_4H_9(OH_2)_3^+ + OH_2 = C_4H_9(OH_2)_4^+$	14	28.7

[a] Calculated from $\Delta H_f(R^+)$,[8] ΔH_f(base), and proton affinity PA(base).[12] [b] From present equilibria measurement. [c] From ref. 7. [d] K. Hiraoka, E. P. Grimsrud, and P. Kebarle, *J. Am. Chem. Soc.*, **96**, 3359 (1974). [e] Interpolated value from results for hydration of H_3O^+ and $(CH_3)_2OH^+$. [f] Equilibria could not be measured (see section c). [g] From $\Delta H_f(H_3O^+) = 140$ kcal/mol, $\Delta H_f(H^+(H_2O)_2) = 50$ kcal/mol based on PA(H_2O) = 169 kcal/mol[12] and $\Delta H = -31.6$ kcal/mol[7] for reaction $H_3O^+ + H_2O = H^+(H_2O)_2$.

= −74.9 kcal/mol[9] one obtains ΔH_f(*tert*-butyl alcohol H$^+$) = 100.3 kcal/mol. This value is in complete agreement with the $\Delta H_f(t\text{-}C_4H_9OH_2^+)$ obtained from ΔH_1. This means that the species formed by reaction 1 must be protonated *tert*-butyl alcohol.

Experiments were made also in order to examine for the occurrence of the analogous reactions 5 and 6 involving the ethyl and *sec*-propyl ion.

$$C_2H_5^+ + OH_2 = C_2H_5OH_2^+ \tag{5}$$

$$s\text{-}C_3H_7^+ + OH_2 = s\text{-}C_3H_7OH_2^+ \tag{6}$$

In 4.4 Torr of CH_4 containing 10 mTorr of H_2O at 30 °C the major reaction was not the condensation (eq 5) but the proton transfer (eq 7).

$$C_2H_5^+ + OH_2 = C_2H_4 + H_3O^+ \tag{7}$$

The observed rate of the condensation (eq 5) was only about 1% of the proton transfer rate. The dominance of the exothermic proton transfer (eq 7) is expected and has been observed in earlier work by Field and Munson.[10,11]

Condensation reactions like (1)–(6) can be expected to be kinetically third-order reactions at pressures in the Torr range.[7] The third-order results from the short lifetime of the condensation product which is excited by the exothermicity of the reaction and must be stabilized by third body collisions. At a given total pressure one can obtain only the pseudo-first-order rate constant (reaction frequency) ν of an ion–molecule reaction. Values for ν_5 were obtained in the present work. The determination of the order of the reaction requires determination of ν_5 with extensive variation of the total pressure and is not an easy experiment. Therefore we assumed third-order dependence $\nu_5 = k_5[H_2O][CH_4]$ and obtained using the known ν_5, $[H_2O]$ and $[CH_4]$ a value for $k_5 \approx 10^{-28}$ cm^6 molecules^{-2} s^{-1} at 30 °C. It is interesting to note that at atmospheric pressure the rate of (5) will be about 300 times higher and condensation will probably dominate over proton transfer. It is therefore to be expected that in condensed phases the reaction of the ethyl ion with H_2O should lead with high yield to protonated ethanol.

The condensation product $s\text{-}C_3H_7OH_2^+$ resulting from reaction 6 was observed in high yield in a gas-phase mixture of a few Torr of H_2 containing several mTorr of propane and H_2O. In this system *sec*-propyl ions are produced by the reaction: $H_3^+ + C_3H_8 \rightarrow H_2 + (C_3H_9^+)^* \rightarrow H_2 + s\text{-}C_3H_7^+ + H_2$. Measurements of the rate of (6) and the assumption that (6) is third order lead to an approximate value $k_6 \approx 5 \times 10^{-28}$ cm^6 molecules^{-2} s^{-1} at 30 °C. This rate constant is somewhat higher but still of the same order of magnitude as k_5, the rate constant for $C_2H_5^+$. The high yield for reaction 6 is due to the fact that the parallel proton transfer reaction $s\text{-}C_3H_7^+ + H_2O$ = *sec*-propane + H_3O is endothermic[12] and therefore too slow to be competitive.

Reactions 5 and 6 are very similar to reaction 1 where the condensation product was proven to be the protonated alcohol. Therefore we assume that the products in (5) and (6) correspond also to the protonated alcohols. This view is supported by earlier work of Beggs and Field[13] who observed and studied reaction 6.

(b) Ion–Molecule Condensation Reactions and Prebiotic Synthesis. In the preceding section we showed that the general reaction $R^+ + OH_2 = ROH_2^+$ where R^+ is an alkyl ion and ROH_2^+ the protonated alcohol, does not occur only in solution but also in the gas phase and with high yield if the pressure is above 100 Torr.

In solution the addition of CH_3OH to an alkyl carbocation leads to the protonated methyl alkyl ether:

$$R^+ + CH_3OH = (\underset{\substack{| \\ H}}{R\text{—}O}\text{—}CH_3)^+$$

Thus Hogeveen[14] obtained with $R^+ = CH_3^+$ and *tert*-butyl$^+$ the protonated dimethyl ether and methyl *tert*-butyl ether, respectively. There can be little doubt that with suitable R^+ and at higher pressures the analogous reactions should occur also in the gas phase. If methanol is replaced by ammonia or methylamine, at higher pressures where condensation will be competitive with proton transfer, the formation of the protonated primary and secondaryamines can be expected.

One may conclude that the reaction of R^+ with n-donor bases should be generally expected in the gas phase, but that it has been little reported on because most of the experimental work was done at low pressures or under otherwise unsuitable conditions.

Summarized in Table I are enthalpy changes for several reactions $R^+ + B = (RB)^+$. These values were obtained from available thermochemical data or from the present measurements. The series $R^+(CH_3^+ \rightarrow t\text{-}C_4H_9^+)$ and $B = OH_2$ illustrates the very rapid decrease of Lewis acidity from CH_3^+

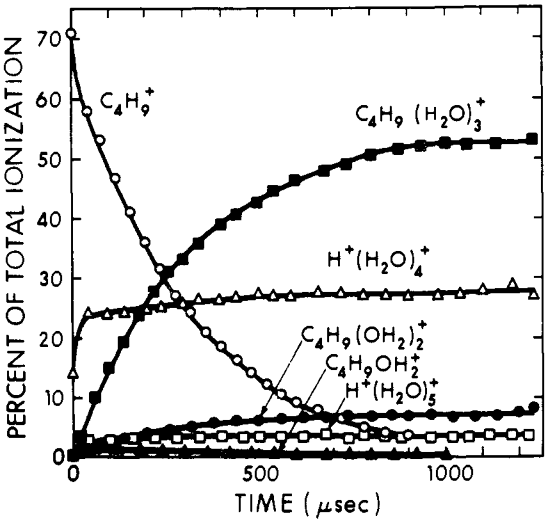


Figure 2. Normalized ion intensities as a function of time observed in 4.1 Torr of H_2 containing 0.17 Torr of H_2O and 0.12 Torr of i-C_4H_{10}, at 84 °C.

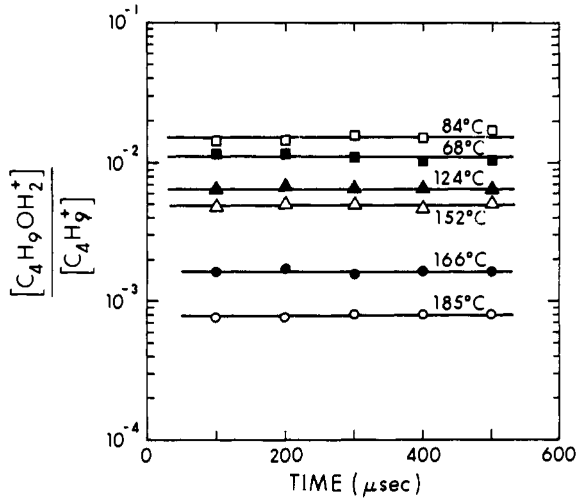


Figure 3. Time-independent ratios, $[C_4H_9OH_2^+]/[C_4H_9^+]$, observed in runs with low water concentration. P_{H_2} and $P_{C_4H_{10}}$ in all runs ~4 Torr and ~0.1 Torr, respectively. P_{H_2O} =: (○) 0.17; (●) 0.17; (▲) 0.12, (□) 0.096; (■) 0.043; (△) 0.17 Torr.

to t-$C_4H_9^+$. The 11.2 kcal/mol obtained with *tert*-butyl is indeed very small. The effect is easily understood. The very important stabilization of the *tert*-butyl ion by the methyl groups is not so important in the protonated *tert*-butyl alcohol where a lot of the positive charge is removed to the two hydroxylic hydrogen atoms (see also the discussion at end of section c).

The change of Lewis base strength is illustrated in the series $R^+ = C_2H_5^+$ and B = OH_2, CH_3OH, and NH_3. The energy is seen to increase greatly in that order corresponding to an expected increase of Lewis base strength.

In all the reactions considered above a true electron pair bond is formed. Comparing the energies released with those of the $H^+(H_2O)_n$ hydration reactions (Table I) we see that the electron pair bond formation is not necessarily a more exothermic process.

The condensation mechanism involving electrophilic attack by the positive ion is not restricted to carbocations. For example, Fehsenfeld et al.[15] on the basis of gas phase experiments have concluded that the products of reactions 8 and 9, occurring at room temperature, are the protonated nitrous and nitric acid.

$$H_2O + NO^+ = H_2ONO^+ \tag{8}$$

$$H_2O + NO_2^+ = H_2ONO_2^+ \tag{9}$$

In both cases most of the positive charge of the reactant ion is on the nitrogen. Therefore both reactions represent simple Lewis acid-base reactions of the type discussed above.

In the following paper[16] in this issue we show that the Koch-Haaf carbonylation (eq 10), which is well known in solution, occurs readily in the gas phase.

$$R^+ + CO + OH_2 = RCOOH_2^+ \tag{10}$$

Thus in methane containing some carbon monoxide and water, protonated formic acid, propionic acid, and isobutyric acid are produced from $R^+ = HCO^+$, $C_2H_5^+$, and s-$C_3H_7^+$, the three R^+ ions being themselves synthesized by spontaneous ion-molecule reactions occurring on electron irradiation of the above gas mixture. The production of protonated isobutyric acid is a spontaneous oligosynthesis by ion-molecule reactions which combines five molecules into one! Evidently, in the presence of ammonia and HCN, variation of relative concentrations and temperature, a large number of complex compounds would probably result from spontaneous ion-molecule condensation reactions in the gas phase. We intend to explore some of these possibilities in future work. Whether amino acids or precursors of amino acids can be obtained remains to be seen. Nevertheless it is clear that the role of ion-molecule reactions to prebiotic synthesis cannot be correctly assessed without a consideration of the very important class of condensation reactions.

(c) **Hydration of *tert*-Butyl$^+$ and Protonated *tert*-Butyl Alcohol. Acid-Catalyzed Dehydration of *tert*-Butyl Alcohol to Isobutene.** Some of the results for the hydration of the *tert*-butyl ion were used in section a. In the present section we will describe the experimental observations in more detail and also give an account of the acid-catalyzed dehydration of *tert*-butyl alcohol which is observed in the same experiments. Shown in Figure 2 are ion-time profiles for an experiment at an intermediate temperature of 84 °C. The gas mixture used contained H_2 at ~4 Torr with H_2O and isobutane at 0.17 and 0.12 Torr, respectively. In this system the initial ions obtained on electron impact are mostly H_2^+, which react rapidly with more H_2 to give H_3^+. The reactions of H_3^+ with isobutane and water are well known:

$$H_3^+ + H_2O = H_2 + H_3O^+ \tag{11}$$

$$H_3^+ + i\text{-}C_4H_{10} \rightarrow [C_4H_{11}^*] + H_2 \rightarrow t\text{-}C_4H_9^+ + 2H_2$$
$$\rightarrow s\text{-}C_3H_7^+ + CH_4 + H_2 \tag{12}$$

The $C_3H_7^+$ obtained in (12) is converted to *tert*-butyl$^+$ by the well known exothermic hydride abstraction

$$s\text{-}C_3H_7^+ + i\text{-}C_4H_{10} = C_3H_8 + t\text{-}C_4H_9^+ \tag{13}$$

All these reactions occur within microseconds under the experimental conditions. Therefore the major ions observed in Figure 2 are $C_4H_9^+$ produced by (12) and (13) and $H^+(H_2O)_n$ formed from H_3O^+ and its subsequent rapid clustering reactions (14). The rate constant for the third-order reaction 14 where $n = 2$, measured previously,[7] is $k_{14} = 3 \times 10^{-27}$ cm^6 molecules^{-2} s^{-1}.

$$H^+(H_2O)_{n-1} + H_2O = H^+(H_2O)_n \tag{14}$$

For the conditions of the experiment shown in Figure 2 this value leads to a half-life of the forward reaction of only about 1 μs. The rapid buildup of $H^+(H_2O)_4$ clusters observed in Figure 2 is thus to be expected. The observation in Figure 2 also shows that equilibrium 14 is reached for $n = 5$.

The decrease of *tert*-butyl$^+$ (Figure 3) should be due to reaction 1 and subsequent hydrations of the protonated *tert*-butyl alcohol.

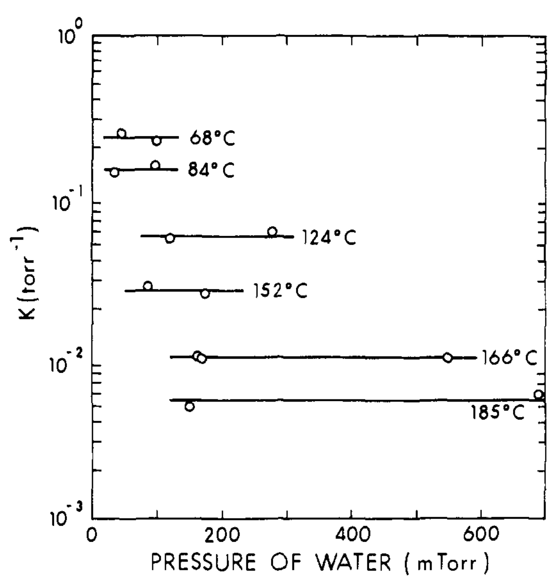


Figure 4. Some of the determinations of the temperature and pressure dependence of the equilibrium constant for reaction 1: $t\text{-}C_4H_9^+ + OH_2 = t\text{-}C_4H_9OH_2^+$. At lower temperatures constant ion ratios with time as in Figure 3 could be obtained only at progressively lower water concentrations.

$$t\text{-}C_4H_9^+ + OH_2 = t\text{-}C_4H_9OH_2^+ \qquad (1)$$

The very slow decrease of $t\text{-}C_4H_9^+$ is in contrast with the rapid hydrations of the H_3O^+ in the sequence of (14), yet third body dependent condensation reactions are involved in both cases. The protonated butanol is observed in only low abundance as an intermediate in a reaction sequence (15)–(17) leading to the hydrates of protonated *tert*-butyl alcohol

$$C_4H_9OH_2^+ + OH_2 = C_4H_9(OH_2)_2^+ \qquad (15)$$

$$C_4H_9(OH_2)_2^+ + OH_2 = C_4H_9(OH_2)_3^+ \qquad (16)$$

$$C_4H_9(OH_2)_3^+ + OH_2 = C_4H_9(OH_2)_4^+ \qquad (17)$$

with equilibrium being approached at reaction 16.

Analysis of a large number of runs done at different temperatures and different water and isobutene concentrations showed that there was a range of conditions where after some 100 μs, $C_4H_9^+$ and $C_4H_9OH_2^+$ were observed to decrease while maintaining a constant concentration ratio, i.e., where $[C_4H_9^+]/C_4H_9OH_2^+] = R =$ constant. Such constant concentration ratios are shown in Figure 3. These runs where characterized by the low water concentrations used (see Figure 3). The decrease of the $C_4H_9^+$ and $C_4H_9OH_2^+$ ions was due to the further hydrations of (15)–(17). No conditions could be found for which the normalized intensities of $C_4H_9^+$ and $C_4H_9OH_2^+$ ions did not decrease with time. We assumed that the constant concentration ratio R was due to equilibrium occurring between $C_4H_9^+$ and $C_4H_9OH_2^+$, i.e., in reaction 1. It should be noted that equilibrium 1 can occur, even when both ions decrease, if the forward and reverse steps of (1) are faster than the ion removed by the subsequent hydration (15).

In all previous studies of hydration and clustering we were always able to find conditions where two ions, engaged in a given hydration equilibrium, had normalized intensities which became constant with time. Therefore the situation observed with reaction 1 and the higher hydrates is unusual. In all the previous studies the binding energies of successive water molecules, i.e., $\Delta H°_{n,n-1}$ and $\Delta G°_{n,n-1}$, decreased continuously with n, a situation that is natural for clusters like $H^+(H_2O)_n$, $Cl^-(H_2O)_n$, etc. As will be seen below, examination of the change of energies with n shows that the present situation is different and that reaction 1 does not provide the maximum energy as is normally the case.

The constant ratios R obtained in runs like those in Figure 3 were used to evaluate the equilibrium constant K_1 (for the 0.1 hydration of the butyl cation). Some of these equilibrium constants are shown in Figure 4 as a function of water pressure. The corresponding van't Hoff plot in Figure 1 was already discussed in section a. The ΔH_1 obtained was in agreement with that expected for reaction 1 leading to protonated *tert*-butyl alcohol. Shown in Figure 1 are also van't Hoff plots for the higher hydration equilibria of the protonated butanol, i.e., reactions 16 and 17 observed for a variety of water pressures and reaction temperatures. No conditions were found for which the equilibrium 15 involving the $C_4H_9OH_2^+$ and $C_4H_9(OH_2)_2^+$ could be measured. In all runs tried the protonated butanol was always going down with time as its first hydrate was going up. The enthalpy and entropy changes obtained from the van't Hoff plots are summarized in Table I.

The enthalpy changes of Table I provide the clue for the peculiar clustering kinetics that were encountered. We see that the energy released on putting one water molecule and *tert*-butyl$^+$ together, i.e., reaction 1, is only 11.2 kcal/mol while the energy released on putting one water molecule on the monohydrate of protonated *tert*-butyl alcohol, i.e., reaction 16, is much larger at 17.7 kcal/mol. The addition of one more molecule as in (17) leads to an energy release of 14 kcal/mol. The van't Hoff plots (Figure 1) demonstrate most directly that the higher hydrates are more stable toward dissociation of one water molecule than the "hydrate" of *tert*-butyl$^+$. This means that if sufficient time is given to the reaction system the position of true thermodynamic equilibrium will move toward the protonated butanol hydrates. We understand now why the equilibrium 1 could be measured only in a kinetic experiment where both participating ions were decreasing continuously.

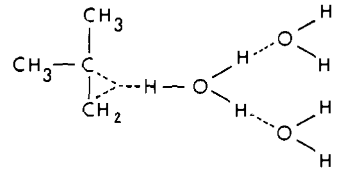
One can ask the question "what are the chemical reasons for the unusual changes in hydrate bond energies, i.e., why is the bond energy of $C_4H_9^+\text{-}OH_2$ smaller than that for the higher hydrates?" Comparing (16) with the proton clustering reaction 18 we note that $-\Delta H_{16} = 17.7$ kcal/mol is only some 2 kcal/mol smaller than the $-\Delta H_{18} = 19.6$ kcal/mol.[7]

$$C_4H_9(OH_2)_2^+ + OH_2 = C_4H_9(OH_2)_3^+ \qquad (16)$$

$$H^+(H_2O)_2 + H_2O = H^+(H_2O)_3 \qquad (18)$$

This result suggests that as far as hydrations go, the $C_4H_9(OH_2)_2^+$ species is very similar to the $H^+(H_2O)_2$ species.

The reasons for the low value of $-\Delta H_1 = 11.2$ kcal/mol were considered in section b, where it was pointed out that because of the very favorable accommodation of positive charge on *tert*-butyl not much is gained by the addition of a water molecule since this removes much of the positive charge to the OH_2 group. It is not clear whether this shift of charge is sufficient to produce the high exothermicities observed in reactions 16 and 17. Additional reorganization could be involved making the water carrying end of the ion even more similar to a $H^+(H_2O)_n$ species. This would require taking nearly all the positive charge and a hydrogen away from the hydrocarbon end of the ion. The driving force for such a reorganization will be the superior accommodation of the proton by water molecules, when many water molecules are present. A possible resulting structure is shown in I. This ion corre-



I

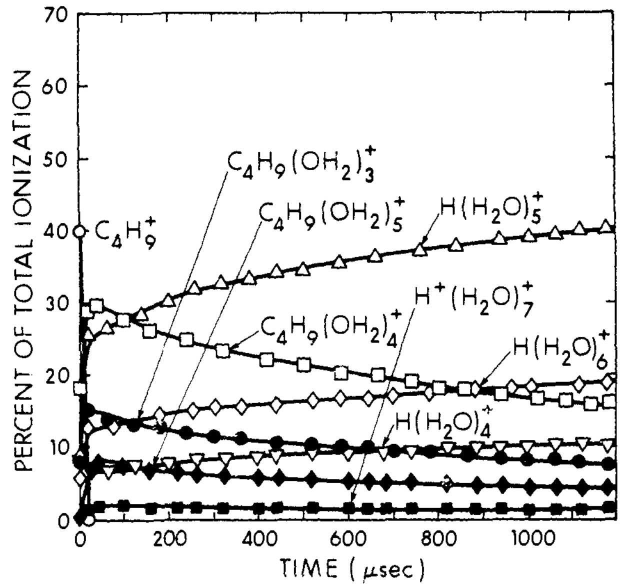


Figure 5. Normalized ion intensities observed in 4 Torr of H_2 containing 0.49 Torr of H_2O and 0.2 Torr of i-C_4H_{10} at 28 °C. Gradual decrease of $C_4H_9(OH_2)_n{}^+$, due to reaction 20: t-$C_4H_9(OH_2)_n{}^+$ = i-C_4H_8 + $H^+(H_2O)_n$.

sponds to a $H^+(H_2O)_n$ interacting with the π bond of isobutene via one partially positive hydrogen atom.

The ion of structure I is the probable intermediate in the conversion of protonated *tert*-butyl alcohol hydrate to isobutene. This reaction was indeed observed to occur in the present experiments. The ion intensities observed in two runs, one at near room temperature and the other at 116 °C, are shown in Figures 5 and 6. Characteristic to both runs are the relatively high water concentration used. Examining the low-temperature run of Figure 5 we observe that the disappearance of $C_4H_9{}^+$ and the formation of the $C_4H_9OH_2{}^+$ hydrates is very rapid. What is more important is to note that the hydrates, at longer reaction times, decrease while a corresponding increase occurs for the $H^+(H_2O)_n$ ions. The same process is observed also in Figure 6 taken at a higher temperature where at long reaction times the butanol hydrates are also seen to decrease while a corresponding increase is observed for the proton hydrates. The transfer from protonated butanol to protonated water was observed in all runs with higher water concentration and is attributed to reactions 19 or 20 which are analogous to the acid-catalyzed dehydration of alcohols occurring in solution and used for the preparation of olefins.

$$t\text{-}C_4H_9(OH_2)_n{}^+ + H_2O = i\text{-}C_4H_8 + H^+(H_2O)_{n+1} \qquad (19)$$

$$t\text{-}C_4H_9(OH_2)_n{}^+ = i\text{-}C_4H_8 + H^+(H_2O)_n \qquad (20)$$

The enthalpy changes for the reactions where $n = 1$, i.e., where protonated butanol is the reactant, are $\Delta H_{19} = +4$ and $\Delta H_{20} = +36$ kcal/mol (see Table I). Both (19) and (20) will become less endothermic as n increases. The highest hydrate observed in the near-room-temperature run of Figure 5 is $C_4H_9(OH_2)_5{}^+$. The disappearance of the butyl hydrates is quite slow indicating an endothermic reaction, yet reaction 19 for this high n should certainly be exothermic. In fact already reaction 19 for $n = 1$ can be expected to occur with observable rate since it has an endothermicity of only 4 kcal/mol! The most likely reason for the nonoccurrence of reaction 19 for low n is the presence of a free energy activation barrier. For n = 1 and reaction 19 the activation barrier may be due to the rearrangement from the protonated butanol hydrate to the structure I type complex $C_4H_8{\cdot}H^+(H_2O)_2$. The fact that the $C_4H_9(OH_2)_2{}^+$ ions also do not react rapidly via reaction 19 argues that also in this case a barrier is present. The presence of such an activation barrier for an ion with the already rearranged structure I is unlikely. This argues that the $C_4H_9(OH_2)_2{}^+$ ion is the hydrate of protonated butanol and not $C_4H_8{\cdot}H^+(OH_2)_2{}^+$. The same argument can be applied also for the $C_4H_9(OH_2)_3{}^+$ ion.

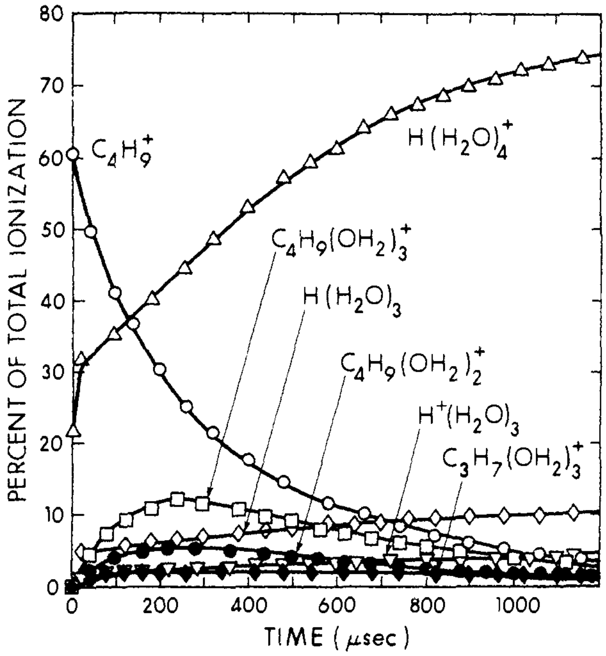


Figure 6. Normalized ion intensities observed in 5 Torr of H_2 containing 0.7 Torr of H_2O and 0.17 Torr of i-C_4H_{10}. Conversion of protonated butanol hydrates to proton hydrates leads to decrease of $C_4H_9(OH_2)_n{}^+$ and increase of $H^+(H_2O)_n$ at 116.4 °C.

From the considerations given above it follows that the relatively high exothermicities of the hydration reactions 16 and 17 cannot be explained as being due to hydration of structure I type ions. We conclude that the high exothermicity is due to the special charge distribution, i.e., that the positive charge in the butanol hydrates $C_4H_9(OH_2)_2{}^+$ and $C_4H_9{}^+(OH_2)_3{}^+$ is located largely on the hydroxy hydrogens with little use being made of the *tert*-butyl group. The experimentally observed enthalpies ΔH_{16} and ΔH_{17} can be shown to be compatible with the protonated butanol structures t-$C_4H_9(OH_2)_n$ by the following argument. The exothermicities resulting from hydrating protonated methanol and dimethyl ether (i.e., the water affinities) are given in Table I. We notice that the water affinity of the protonated ether is over 22 kcal/mol. Unfortunately, the water affinity for protonated ethanol is not available; however, a general correlation shows that it will be higher than that for the protonated ether and thus over 22 kcal/mol.[18] No water affinity is available also for protonated 2-propanol. However, the changes of proton affinities for the alcohols are available and can be used as a guide for the effect of methyl substitution in the stabilization of positive charge. In the series ROH with R = CH_3, C_2H_5, i-C_3H_7, and t-C_3H_9, the proton affinities are:[17] 182, 187, 190, and 192 kcal/mol. We see that there is relatively little increase of proton affinity from ethanol to *tert*-butyl alcohol. This means that the stabilizing effect of methyl substitution is very much decreased at this stage. Therefore we may expect that the water affinity of *tert*-butyl alcohol H^+ will not be much lower than that of ethanol H^+ and in the range of 20 kcal/mol. In the light of the above considerations the values for the subsequent hydrations $-\Delta H_{16}$ = 17.7 and $-\Delta H_{17}$ = 14 kcal/mol while somewhat high are still in the right range, to be compatible with the structures t-$C_4H_9(OH_2)_n{}^+$. This means that a rearrangement to $C_4H_8{\cdot}H^+(H_2O)_n$ of structure I does not have to be invoked to explain the enthalpy changes.

Acknowledgment. The proton affinities of 2-propanol and *tert*-butyl alcohol were determined by Mr. Yan Lau in our laboratory. The present work was supported by grants from the Canadian National Research Council. Encouragement to undertake the hydration studies of carbocations was received by one of us (P.K) in a conversation with C. D. Ritchie.

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(18) NOTE ADDED IN PROOF. A recent measurement of the equilibrium $C_2H_5OH_2^+ + OH_2 = C_2H_5OH_2OH_2^+$ by D. K. Sen Sharma in our laboratory leads to $\Delta H = -24$ kcal/mol for this reaction.

Condensation Reactions Involving Carbonium Ions in the Gas Phase. Synthesis of Protonated Acids in Gaseous Methane Containing Carbon Monoxide and Water Vapor

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Abstract: In methane gas containing small amounts of CO and H_2O vapor one can observe the carbonylation and subsequent hydration of the carbonium ions $R^+ = C_2H_5^+$ and $s\text{-}C_3H_7^+$ by the Koch–Haaf reaction: $R^+ + CO = RCO^+$ and $RCO^+ + OH_2 = RCOOH_2^+$. The $C_2H_5COOH_2^+$ ion produced with $R^+ = C_2H_5^+$ was shown to be protonated propionic acid by proving that the hydrates of this ion had identical thermochemistry to the hydrates obtained when in a separate experiment propionic acid was protonated and hydrated. The Koch–Haaf reaction forming protonated formic acid was also observed. Protonated formic acid did not hydrate but decarbonylated by the reaction $HCOOH_2^+ + H_2O = H^+(H_2O)_2 + CO$. It is suggested that the decarbonylation of formic acid in acid solution follows a similar mechanism. Analogies with the Koch–Haaf reaction of HCO^+ with H_2O led to a reexamination of the reaction $HCO^+ + H_2 = H_3CO^+$ observed in earlier work. It is concluded that the H_3CO^+ formed is the methoxy carbocation. The heat of formation of the H_3CO^+ is 197.8 kcal/mol. The ion is unstable at room temperature since the dissociation to $HCO^+ + H_2$ requires only 3.9 kcal/mol. The Lewis acidity of the RCO^+ ions is briefly discussed. Thermochemical information for some hydration reactions of protonated propionic acid is also given.

The parallels between gas-phase ion–molecule condensation reactions of carbocations with reactions observed in solution described in the preceding paper[1] in this issue encouraged us to examine the two-step gas-phase synthesis of an acid as represented in the equations below. This carbonylation reaction is well known in organic synthesis in solution as the Koch–Haaf synthesis.[2]

$$R^+ + CO = RCO^+$$

$$RCO^+ + OH_2 = RCOOH_2^+$$

The idea to examine the Koch–Haaf reaction in the gas phase came to us after reading a report by Hogeveen[3] describing the production of propionic acid by carbonylation of $R^+ = C_2H_5^+$ in a condensed phase containing SbF_5, plus methane and CO dissolved under pressure.

In the present work we thought it important to provide proof that the condensation product is indeed a protonated acid. The experiments led to additional observations concerning the hydration of the protonated acids. By measuring ion equilibria involved in some of the reaction steps and by using available literature data, fairly complete thermochemical description could be obtained for the processes involved. The results should be of interest to gas-phase and solution chemists working with carbonium ions.

Experimental Section

The experiments were made in the pulsed electron beam high pressure mass spectrometer. The general experimental procedures were very similar to those described in the preceding paper.[1]