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]

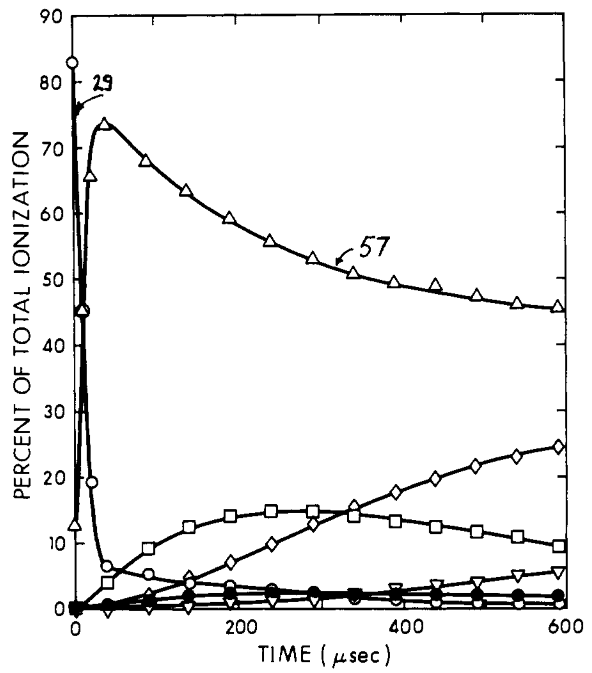


Figure 1. Ions observed after electron pulse ionization in a gas mixture containing 4.2 Torr of CH_4, 0.42 Torr of CO, and traces of H_2O at 30 °C: (○) mass 29 due to $C_2H_5^+$ and HCO^+, (△) mass 57 due to $C_2H_5CO^+$ and $H(CO)_2^+$, (□) $HCOOH_2^+$, (◇) $H^+(H_2O)_2$, (▽) $H^+(H_2O)_3$, (●) $C_2H_5COOH_2^+$.

Results and Discussion

(a) The Koch–Haaf Carbonylation of Carbocations in Electron-Irradiated Methane. One may expect to be able to observe the Koch–Haaf reaction for $R^+ = C_2H_5^+$ if one takes methane as the major gas and adds to it small amounts of CO and H_2O. Electron irradiation of methane creates two major primary ions CH_4^+ and CH_3^+ in roughly 1:1 ratio. These two ions are known to react rapidly with more methane by the gas-phase ion–molecule reactions 1 and 2.

$$CH_4^+ + CH_4 = CH_5^+ + CH_3 \qquad (1)$$

$$CH_3^+ + CH_4 = C_2H_5^+ + H_2 \qquad (2)$$

The resulting CH_5^+ does not react further with methane; however, the $C_2H_5^+$ can react very slowly by the recently described[4] reaction

$$C_2H_5^+ + CH_4 = s\text{-}C_3H_7^+ + H_2 \qquad (3)$$

Addition of suitable amounts of CO and lesser amounts of water may be expected to lead to the carbonylation reactions 5a and 6a:

$$CH_5^+ + CO = CH_4 + HCO^+ \qquad (4)$$

$$C_2H_5^+ + CO = C_2H_5CO^+ \qquad (5a)$$

$$C_2H_5CO^+ + H_2O = C_2H_5COOH_2^+ \qquad (5b)$$

$$s\text{-}C_3H_7^+ + CO = s\text{-}C_3H_7CO^+ \qquad (6a)$$

$$C_3H_7CO^+ + H_2O = C_3H_7COOH_2^+ \qquad (6b)$$

In the presence of CO an additional exothermic[5] reaction may be expected, namely the proton transfer from CH_5^+ to CO as shown in (4). The ratio of (5) to (6) can be increased by increasing the CO concentration.

The observed ion intensities for a suitably selected gas mixture are shown in Figure 1. Reactions 1 and 2 are very fast and have occurred to completion within microseconds, i.e., in a time short compared to that displayed in Figure 1. The major ion observed initially is of mass 29 which corresponds to $C_2H_5^+$ produced by (2) and HCO^+ produced by (4). Mass 29 is observed to decrease rapidly with time being replaced by mass 57 which must be due to the formation of $C_2H_5CO^+$ (mass 57) by (5a) and $H(CO)_2^+$ by reaction 7.

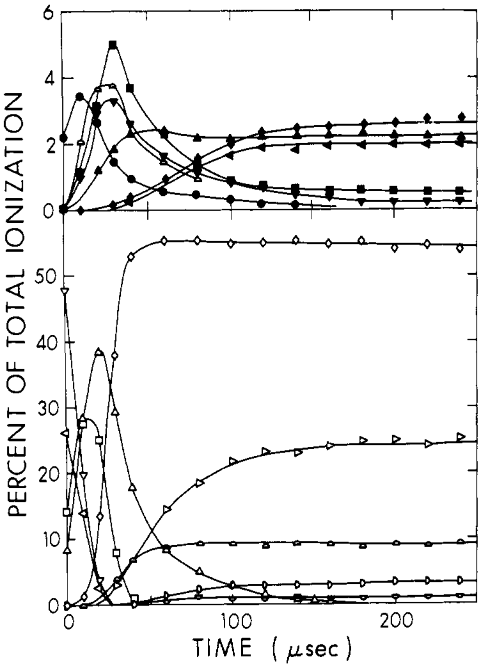


Figure 2. Ions observed after electron pulse ionization in a gas mixture containing 4.2 Torr of CH_4, 0.4 Torr of CO, and 0.01 Torr of H_2O. Lower figure, major ions: (▽) H_3O^+, (△) $C_2H_5^+$, (□) $H^+(H_2O)_2$, (△) $C_2H_5CO^+$ and $H(CO)_2^+$, (◇) $H^+(H_2O)_4$, (△) $C_2H_5CO(OH_2)_3^+$, (○) $H^+(H_2O)_5$, (○) $C_2H_5CO(OH_2)_4^+$, (○) $C_2H_5CO(OH_2)_2$. Upper figure, minor ions: (●) $C_3H_7^+$, (▼) $C_3H_7CO^+$, (■) $C_2H_5COOH_2^+$, (○) $C_3H_5CO^+$, (◆) $C_3H_7CO(OH_2)_3^+$, (◀) $C_3H_5CO(OH_2)_3$, (▲) $H^+(H_2O)_3$.

$$HCO^+ + CO = H(CO)_2^+ \qquad (7)$$

The formation of $H(CO)_2^+$ by (7) and higher clusters $H^+(CO)_n$ in hydrogen gas containing CO was the subject of an earlier study[6] in our laboratory. The mass 57 ion is seen to decrease on its own turn (Figure 1) reaching a final concentration of approximately 50% of the ion total. The new ions appearing are $HCOOH_2^+$ and later $H^+(H_2O)_2$. These two ions must originate from the reaction sequence (8), (9).

$$H^+(CO)_2 + H_2O = HCOOH_2^+ + CO \qquad (8)$$

$$HCOOH_2^+ + H_2O = H^+(H_2O)_2 + CO \qquad (9)$$

$$H^+(H_2O)_2 + H_2O = H^+(H_2O)_3 \qquad (10)$$

Only small amounts of $C_2H_5COOH_2^+$ by reaction 5b and $H^+(H_2O)_3$ by reaction 10 are formed at the low water concentrations used in the experiment of Figure 1. The formation of $C_2H_5COOH_2^+$ ion by (5b) and $H^+(H_2O)_3$ by (10) involves third body dependent reactions which at the total pressure used are slower than the two body displacement reactions 8 and 9. The 57^+ ion observed at 600 μs should be pure $C_2H_5CO^+$ which is expected to continue to decrease slowly at longer reaction times because of removal by reaction 5b. The development of the reaction when more water vapor is present is shown in Figure 2. With more water the hydration of the acyl cation (eq 5b) and the protonated water clustering (eq 10) can proceed faster. Not only $C_2H_5COOH_2^+$ and $H^+(H_2O)_3$ are formed but additional water molecules are taken up until the hydrates reach equilibrium as represented by reactions 11 and 12.

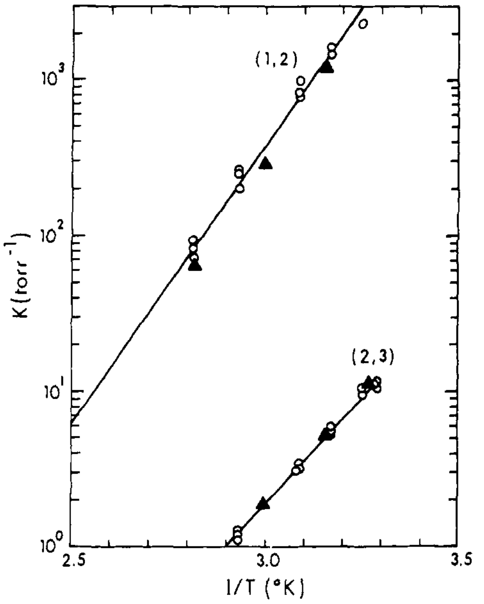


Figure 3. van't Hoff plots for hydration reactions $C_2H_5COOH_2(OH_2)_{n-1}^+ + OH_2 = C_2H_5COOH_2(OH_2)_n$ ($n-1$, n): (○) $C_2H_5COOH_2^+$ obtained by carbonylation of $C_2H_5^+$; (▲) $C_2H_5COOH_2^+$ obtained by protonation of propionic acid. Numbers beside van't Hoff lines correspond to ($n-1$, n).

$$C_2H_5COOH_2^+(OH_2)_{n-1} + H_2O = C_2H_5COOH_2^+(OH_2)_n \qquad (11)$$

$$H^+(H_2O)_{n-1} + H_2O = H^+(H_2O)_n \qquad (12)$$

The presence of more water also leads to some modification of the initial stages of the reaction (Figure 2). Thus H_3O^+ is formed early by the exothermic proton transfer reactions 13-15.

$$CH_5^+ + H_2O = CH_4 + H_3O^+ \qquad (13)$$

$$HCO^+ + H_2O = CO + H_3O^+ \qquad (14)$$

$$C_2H_5^+ + H_2O = C_2H_4 + H_3O^+ \qquad (15)$$

Reaction 15 proceeds only to a minor extent since, in the presence of a large excess of CO, $C_2H_5^+$ reacts mostly via carbonylation (eq 5a).

The products from reaction 5 were proven to be protonated propionic acid by showing that the hydrates $C_2H_5CO_2H^+(OH_2)_n$ observed in the carbonylation runs, like that shown in Figure 2, were identical with hydrates obtained when in separate experiments propionic acid vapor was admitted in the ion source, protonated, and then hydrated. Shown in Figure 3 are van't Hoff plots of the hydration equilibria 11 as observed in carbonylation systems like that of Figure 2. The van't Hoff plots for the $(C_2H_5CO_2H)^+(OH_2)_n$ hydrates observed with pure CH_4 to which some propionic acid and a known amount of water vapor were added are shown in the same figure. In this system protonated propionic acid results from protonation of propionic acid by CH_5^+ and $C_2H_5^+$. As can be seen from Figure 3 the van't Hoff plots of the hydrates obtained by the carbonylation reaction and the propionic acid protonation are identical. This means that the species formed in the carbonylation-hydration reaction 5 is protonated propionic acid and not some isomeric ion.

The confirmation of the Koch-Haaf mechanism for the ethyl ion allows us to assume that the species formed by reaction 8 is protonated formic acid. Reaction 8 is not completely analogous to the Koch-Haaf mechanism since it involves $H(CO)_2^+$ and not HCO^+ as precursor and is thus a displacement and not a condensation reaction.

Earlier studies[6] have shown that the $H(CO)_2^+$ species is fairly weakly bonded $HCO^+(CO)$ with $D(HCO^+\text{-}CO) = 12.8$ kcal/mol.[6] This value permits one to evaluate $\Delta H_8 = -32.5$ kcal/mol since the heats of formation of all other compounds are available.

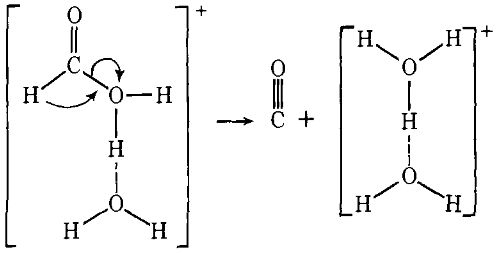
Protonated formic acid does not form hydrates but decarbonylates by reaction 9 (see Figure 1).

$$HCOOH_2^+ + H_2O = H^+(H_2O)_2 + CO \qquad (9)$$

Reaction 9 is a close analogue to the acid-catalyzed decarbonylation of formic acid observed in solution as for example when formic acid is dissolved in sulfuric acid. The solution decarbonylation is commonly[7] written in two steps as shown in (16).

$$HCOOH_2^+ \rightarrow HCO^+ + OH_2 \rightarrow CO + H_3O^+ \qquad (16)$$

The heats of formation of the reactants of the gas-phase decarbonylation (eq 9) are available so that the enthalpy change $\Delta H_9 = -16.3$ kcal/mol can be calculated.[8] The considerable exothermicity is due to the strong hydrogen bond formed in $H_3O^+\text{-}H_2O$ which is 31.4 kcal/mol.[9] The possible intermediate of reaction 9 is shown below.



Decarbonylation in solution by a similar, concerted step is more likely than the creation of an HCO^+ intermediate envisaged in (16). A dehydrated HCO^+ in aqueous solution does not make physical sense. Furthermore the creation of HCO^+ is strongly endothermic (see Table I).

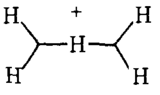
The formation of $s\text{-}C_3H_7CO^+$ and $C_3H_7COOH_2^+$ by the Koch-Haaf reaction involving $s\text{-}C_3H_7^+$ ion can be observed as a side reaction in Figure 2.

The hydration energies of the protonated propionic acid obtained from the van't Hoff plots in Figure 3 are of considerable interest. These data will be discussed in section c.

(b) The Methoxy Carbocation H_3CO^+. In earlier work[10] we studied the gas-phase equilibrium (eq 17) at low temperatures (−107 to −162 °C).

$$HCO^+ + H_2 = H_3CO^+ \qquad (17)$$

Combination of ΔH_{17} with available thermochemical information led to $\Delta H_f(H_3CO^+) = 197.8$ kcal/mol.[10] This was much higher than the heat of formation of protonated formaldehyde $\Delta H_f(H_2COH^+) = 169.8$ kcal/mol so that the species formed by (17) could not be protonated formaldehyde. The small enthalpy obtained $\Delta H_{17} = -3.9$ kcal/mol showed that the H_3CO^+ can be considered as a loose complex of H_2 and HCO^+. At the time we had just completed a study of three-center bonded hydrogen clusters like H_5^+ (see structure I) and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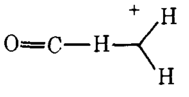
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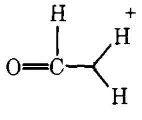
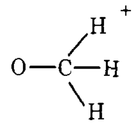

III


IV

the influence of that work[11] led us to suggest structure II for the species formed in (17). However, considering the Koch-Haaf reaction mechanism discussed in the previous section, it is much more likely that reaction 17 proceeds similarly, i.e.,

Table I. Summary of Thermochemical Information for Observed and Related Reactions

Reaction	ΔH,[a] kcal/mol	Reaction	ΔH,[a] kcal/mol	ΔS, eu
$H_5^+ = H_3^+ + H_2$	9.6[b]	$C_2H_5COOH_2^+ = CH_3CO^+ + OH_2$	19[h]	
$H_3CO^+ = HCO^+ + H_2$	3.9[c]	$C_2H_5COOH_2^+ = C_2H_5CO^+ + OH_2$	17.4[k]	
$HCOOH_2^+ = HCO^+ + OH_2$	45.3[d]	$C_2H_5COOH_2OH_2^+ = C_2H_5COOH_2^+ + OH_2$	[l]	
$HCOOH_2^+ + CO = H(CO)_2^+ + OH_2$	32.5[e]	$C_2H_5COOH_2(OH_2)_2^+ = C_2H_5COOH_2OH_2^+ + OH_2$	16.4[m]	24[m]
$HCOOH_2^+ + OH_2 = H^+(H_2O)_2 + CO$	−16.3[f]	$C_2H_5COOH_2(OH_2)_3^+ = C_2H_5COOH_2(OH_2)_2^+ + OH_2$	12.7[m]	24[m]
$CH_3OH_2^+ = CH_3^+ + OH_2$	66[g]	$H^+(H_2O)_3 = H^+(H_2O)_2 + H_2O$	19.5[n]	
$C_2H_5OH_2^+ = C_2H_5^+ + OH_2$	37[g]			

[a] The enthalpies of formation of all neutral species were taken from ref 14. [b] From ref 11. [c] From ref 10. [d] From $\Delta H_f(HCOOH_2^+) = 98.6$ kcal/mol based on PA(HCOOH) = 178 kcal/mol[13] and $\Delta H_f(HCO^+) = 201.7$ kcal/mol based on PA(CO) = 139 kcal/mol, D. K. Bohme, private communication. [e] Based on data given under footnote *d* and $\Delta H_f(H(CO)_2^+) = 162.5$ kcal/mol. Heat of formation of $H(CO)_2^+$ from $\Delta H_f(HCO^+)$ and $\Delta H = -12.8$ kcal/mol for reaction $HCO^+ + CO = H(CO)_2^+$ (see ref 6). [f] From $\Delta H_f(HCOOH_2^+) = 98.6$ kcal/mol (see footnote *d*) and $\Delta H_f(H^+(H_2O)_2) = 50.9$ kcal/mol based on $\Delta H_f(H_3O^+) = 140.3$ kcal/mol from PA(H_2O) = 169 kcal/mol[13] and $\Delta H = -31.6$ kcal/mol for reaction $H_3O^+ + H_2O = H^+(H_2O)_2$ (see ref 9). [g] See preceding paper in this issue. [h] From $\Delta H_f(CH_3COOH_2^+) = 75.3$ kcal/mol based on PA(CH_3COOH) = 187.4 kcal/mol[13] and $\Delta H_f(CH_3CO^+) = 152$ kcal/mol.[14] ΔH value obtained is considered only approximate since $\Delta H_f(CH_3CO^+)$ was based on appearance potential measurements. [k] From $\Delta H_f(C_2H_5COOH_2^+) = 67.8$ kcal/mol based on PA(C_2H_5COOH) = 189.5 kcal/mol[13] and $\Delta H_f(C_2H_5CO^+) = 143$ kcal/mol[14] which is an approximate value. [l] Value could not be obtained by equilibria measurements. [m] Present equilibria measurements.

by an electrophilic attack by the carbon atom. The only difference between the Koch–Haaf reaction and (17) is that the attack is not on the lone pair of water but on the H–H bond. The expected product of this reaction should be the three-center bonded species of structure III. Evidently structure III is very similar to IV which is the classical methoxy carbocation, where all three hydrogens are equivalent. The question whether III or IV describes the methoxy carbocation better can be answered only by theoretical calculations. If all hydrogen atoms are equivalent as in IV one may expect that the C–H bonds will show considerable electron deficiency since a large part of the positive charge of the ion may be residing on this part of the molecule and not on the oxygen atom.

Since the species formed by (17) is most likely identical with the methoxy carbocation, it is important to note that this ion is unstable at room temperature and dissociates to $HCO^+ + H_2$.

Considerable effort was expended in the past to determine the heats of formation of the protonated formaldehyde H_2COH^+ and the methoxy ion H_3CO^+ by mass spectrometric appearance potential measurements. (See Munson and Franklin[12] and references therein.) The great tendency of H_3CO^+ to dissociate to $H_2 + HCO^+$ must have contributed to the difficulties in these measurements. The values selected by Munson and Franklin[12] were $\Delta H_f(H_2COH^+) = 174$ kcal/mol and $\Delta H_f(H_3CO^+) = 202$ kcal/mol which give a stability difference of 28 kcal/mol between the two species. The heats of formation discussed above were $\Delta H_f(H_2COH^+) = 169.8$ kcal/mol and $\Delta H_f(H_3CO^+) = 197.8$ kcal/mol also with a difference of 28 kcal/mol between them. The data thus are in essential agreement.

The earlier work[10] showed that the H_3CO^+ species when reacting with H_2 at temperatures below −100 °C, the only temperatures at which the H_3CO^+ itself is stable, formed a $H_3COH_2^+$ complex in which the binding energy to H_2 was only about 2 kcal/mol. This extremely weak bonding made the species dissociate to H_3CO^+ and H_2 already above −150 °C. This $H_3COH_2^+$ cannot be protonated methanol since this compound is stable well above 300 °C. On the other hand, the formation of protonated methanol could have been considered as a possible product of an electrophilic attack by the oxygen atom on the H–H bond. Evidently an energy barrier exists for this reaction. The barrier must be caused by the charge distribution in the methoxy cation, i.e., the concentration of positive charge on the methyl group and specifically the methyl hydrogens.

(c) Lewis Acidity of Acyl Carbocations. Hydration of Protonated Propionic Acid. The thermochemical data for the reactions observed in the present work are summarized in Table I. Also included in the table are calculated energies for some related reactions which allow a comparison to be made for the Lewis acidities of several carbocations to the Lewis base water. In the series HCO^+, CH_3CO^+, and $C_2H_5CO^+$ we notice that the energy changes from 45.3 to 17.4 kcal/mol with by far the biggest change occurring between HCO^+ and CH_3CO^+. The alkyl ions as represented by CH_3^+ and $C_2H_5^+$ are seen to be considerably stronger Lewis acids than the corresponding acyl carbocations HCO^+ and CH_3CO^+.

Also shown in Table I are the hydration energies of the protonated propionic acid obtained by equilibria measurements done in the present work. No conditions could be found under which equilibrium 18 could be observed.

$$C_2H_5COOH_2^+ + OH_2 = C_2H_5COOH_2 \cdot OH_2^+ \quad (18)$$

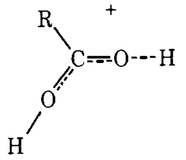
The other two higher equilibria could be easily measured. It is interesting to note that the hydration energy in reaction 19 at 16.4 kcal/mol is almost as large as the hydration of the $C_2H_5CO^+$ ion which is 17.4 kcal/mol, yet in the first case only a hydrogen bond is formed while in the second case a "true" electron pair bond is generated.

$$C_2H_5COOH_2(OH_2)^+ + OH_2 = C_2H_5COOH_2(OH_2)_2^+ \quad (19)$$

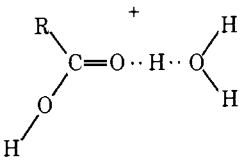
The energy release in reaction 19 is almost as large as the energy release of 19.5 kcal/mol in reaction 20.

$$H^+(H_2O)_2 + H_2O = H^+(H_2O)_3 \quad (20)$$

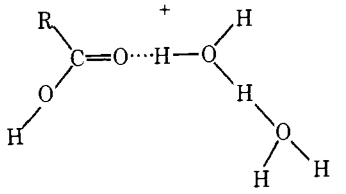
The structure of the protonated propionic acids should be as in I. After the addition of the water molecule in reaction 18 the structure should be as in II. In I most of the positive charge is evenly distributed among the two hydrogen atoms. In II most of the positive charge has shifted away from one of the original hydrogen atoms and located on the H atoms of the water molecule. This exclusion of one of the original hydroxy groups is not favorable and the exothermicity of (18) is probably lower than that for (19). This is a situation which would make the measurement of equilibrium 18 very difficult or impossible under ordinary circumstances since at all temperatures the hydration will move to higher hydrates. A similar situation was encountered in the preceding paper. With the addition of the next water molecule a structure like III could be formed. Further hydration would lead gradually more and more to



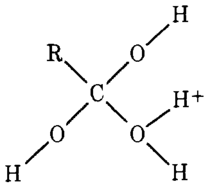
I



II



III



IV

structures which are essentially $H^+(H_2O)_n$ so that a gradual deprotonation of the acid will occur. The driving force for this change will be the superior accommodation of the proton in a water cluster, when many water molecules are available.

In analogy with the generally accepted intermediate in acid catalyzed esterification one might argue that the monohydrated, protonated propionic acid should not have the hydrogen bonded structure II but the structure IV. However one cannot be certain that structure IV is of greater stability. Structure IV offers covalent and therefore one might think better bonding. However the carbon atom is burdened by three C–O single bonds, an unusual situation and is electron density deficient to start with. As mentioned above the present results suggest that the exothermicity for the addition of the first water molecule (i.e., reaction 18) is lower than that for the second (reaction 19). This taken together with the fact that ΔH_{18} is so close to ΔH_{19} argues that at least the dihydrate has the structure III and does not correspond to a monohydrated structure IV.

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Theory of Electron Transfer Generation and Quenching of Singlet Oxygen [$^1\Sigma_g{}^+$ and $^1\Delta_g$] by Superoxide Anion. The Role of Water in the Dismutation of $O_2{}^-$

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Abstract: A critical dependence on the number of water molecules present has been found in a theoretical analysis applying the electron transfer theory of Marcus to the generation of singlet oxygen in the dismutation reaction of ion clusters of the superoxide ion $O_2{}^-$ of the form $O_2{}^-\cdot(H_2O)_n$. For the $n \geq 5$, excited oxygen is produced from the reaction. There is a narrow H_2O concentration range for the production of $O_2(^1\Delta_g)$, beyond which $O_2(^1\Sigma_g{}^+)$ becomes the dominant product. The theoretical analysis also predicts that singlet oxygen can be efficiently quenched by the $O_2{}^-$ ion in solution through electron transfer reactions.

Experimental evidence is accumulating that singlet oxygen is generated in electron transfer reactions of the superoxide anion.[1-3] Failure to improve singlet oxygen $O_2(^1\Delta)$ yields from potassium superoxide in dimethyl sulfoxide (DMSO)[1,4] solution suggests $O_2{}^-$ plays a dual role in these solutions: generating singlet oxygen in a dismutation reaction and, at higher $O_2{}^-$ concentration, quenching singlet oxygen. Moisture is necessary for the solution and gas phase dismutation reaction. We have used the theory of Marcus on adiabatic electron transfer[5-7] to study the reactions: (i) $O_2{}^-\cdot(H_2O)_n + O_2{}^-\cdot(H_2O)_n \rightarrow O_2{}^{2-}\cdot(H_2O)_n + O_2\cdot(H_2O)_n$ and (ii) $O_2{}^- + O_2(^1\Sigma_g{}^+, {}^1\Delta_g) \rightarrow O_2(^3\Sigma_g{}^-) + O_2{}^-$. The results show for reaction (i) singlet oxygen is generated from hydrated superoxide ions with $n \geq 5$ and for reaction (ii) quenching of singlet oxygen is very efficient.

To construct potential energy surfaces for the electron transfer reaction, Marcus has developed an empirical formula $G_d = m^2\lambda$, where $-1 \leq m \leq +1$ is the fraction of charge transferred. λ can be evaluated from the theoretical expression $\lambda = \Delta e^2/2(1/2a_1 + 1/2a_2 - 1/R)(1/\epsilon_{op} - 1/\epsilon_s)$ where Δe is the total electronic charge transferred; a_1 and a_2 are the ionic radii, including the inner coordination shell; R is the interionic separation; and ϵ_{op} and ϵ_s are the optical and static dielectric constants of the surrounding solvent. An $R = 10$ Å is a reasonable limiting distance. As the reaction proceeds, a crossing point is reached where spatial configurations of the nuclei, including solvent orientation, are the same for both reactants and products. This intersection represents the activation barrier $\Delta G_d{}^*$. Once $\Delta G_d{}^*$ is evaluated, the rate can be estimated from $k = Z\kappa\rho \exp(-\Delta G_d{}^*/kT)$ where Z is approximately 10^{11} l. mol^{-1} s^{-1} and κ and ρ are approximately unity.[5-7]

ΔG for reaction (i) was estimated using: (1) Mass spectro-