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Binding Energies and Structural Effects in Halide Anion–ROH and –RCOOH Complexes from Gas-Phase Equilibria Measurements

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Abstract: The equilibrium constants for the gas-phase reactions $AH + I^- = AHI^-$ were measured for compounds where AH = HOH, MeOH, EtOH, *i*-PrOH, *t*-BuOH, HCOOH, MeCOOH, EtCOOH, *i*-PrCOOH, and *t*-BuCOOH. van't Hoff plots lead to $\Delta G°_1(300)$, $\Delta H°_1$, and $\Delta S°_1$. The observed AHI^- binding energies are compared with AHF^- and $AHCl^-$ results from the literature. The changes of binding energies in $ROHF^-$ and $ROHI^-$ are quite different. For $ROHF^-$, the binding energies increase linearly with the gas-phase acidities of ROH, such that HOH < MeOH < EtOH < *i*-PrOH < *t*-BuOH. For $ROHI^-$, there is an increase only from HOH to MeOH and EtOH while EtOH ≈ *i*-PrOH ≈ *t*-BuOH. These results illustrate the diminished importance of the polarizability of the alkyl group for the large I^- ion complexes. The series $RCOOHI^-$, which has much higher binding energies than the $ROHI^-$ group, gives the order *t*-BuCOOH ≪ MeCOOH ≈ EtCOOH ≈ *i*-PrCOOH ≪ HCOOH, while the gas-phase acidity order is quite different, MeCOOH < EtCOOH < *i*-PrCOOH < HCOOH < *t*-BuCOOH. The bonding changes are explained on the basis of electrostatic considerations. The strongest bonding observed for $HCOOHI^-$ is due to closeness and alignment of the OH, C=O, and HC bond dipoles with the ion. The weakest bonding in *t*-BuCOOH results from steric interference of the methyl groups with I^-. This causes an increase of distance and misalignment of the C=O dipole; also a C–H dipole is absent. The remaining $RCOOHI^-$ interactions represent intermediate cases.

During the past several years, it has been demonstrated that important information concerning the solvation of anions and cations can be obtained from determinations of the equilibrium constants for equilibria involving gaseous ions and molecules of a given solvent vapor, using a high ion source pressure mass spectrometer.[1] Early work on halide anions and hydroxy compounds ROH and RCO_2H showed[2] that the strength of the hydrogen bond of $ROH–X^-$ and $RCOOH–X^-$ increased linearly with an increase of the gas-phase acidity of ROH and RCOOH. An extension of these studies examining the validity of the relationship for Cl^- and a wide range of compounds AH including carbon acids was published later.[3] These studies showed that the carbon acids had relatively lower AHX^- binding energies, i.e., they did not fit on the same linear relationship with the alcohols and carboxylic acids. The acidity of many carbon acids is not only due to the presence of inductively electron withdrawing groups but also to stabilization in the anion by resonance delocalization of the negative charge. Cyclopentadiene and fluorene are extreme examples of this behavior. In view of the above, the failure of carbon acids to give $AHCl^-$ binding energies corresponding to their gas-phase acidities was not considered surprising since the resonance delocalization stabilizing the carbanion A^- cannot be expected to develop to any significant extent in the complex AHX^-.

More recently Larson and McMahon[4] have reported a comprehensive study of the binding energies of a large number of AH compounds to F^-, based on measurements with an ion cyclotron resonance mass spectrometer. In particular, these authors showed that the binding energies of the $ROHF^-$ and $RCOOHF^-$ complexes increase linearly with the gas-phase acidity of ROH and RCOOH. However, the two groups of compounds did not quite fit on the same straight line. The binding energies of the $RCOOHF^-$ complexes were somewhat lower than would be predicted from the acidities correlation. The authors[4] explained this observation by pointing out that the stabilization of the carboxylate anions, which is due to resonance delocalization on to the two oxygens, cannot be expected to occur in a proportionate fashion in the $RCOOHF^-$ complexes. This situation is somewhat similar to, though less extreme than, that occurring for the carbon acid complexes.[3]

Comparing the available data for F^{-4} and Cl^-,[1-3] certain trends depending on the nature of the ion were noticed. In order to clarify the picture we decided to accentuate the ion change by making a study of the ROH and RCOOH series with I^-. Comparison of the results for F^-, Cl^-, and I^- in the present work provides interesting insights into the bonding changes and dominating structural effects caused by a large increase of the ion radius.

Results

The clustering (eq 1) and solvent exchange equilibria (eq 2)

$$AH + I^- = AHI^- \tag{1}$$

$$A'HI^- + A''H = A''HI^- + A'H \tag{2}$$

where AH denotes ROH or RCOOH were measured with a pulsed high-pressure mass spectrometer. The apparatus was the same as that used in an earlier work on the Cl^-HA adducts.[2,3] The equilibrium constants K_1 and K_2 were obtained by passing through the ion source a carrier gas (CH_4) between 1 and 5 torr, typically containing methyl iodide at 0.1–0.5 mtorr and the AH compounds at 4–20 mtorr. The equilibrium data were constant (approximately 5–10% deviation from the mean value) over the 1–5-torr pressure range. Efficient I^- production was obtained by capture of secondary electrons with MeI. Establishment of equilibrium 1 and 2 was observed some 100 μs after the short (10 μs) electron pulse, and a constant ion ratio could be observed for more than 1000 μs. Under these conditions, no peaks other than I^- and AHI^- were detected.

The equilibrium constants K_1 and K_2 were calculated from known neutral concentrations of the AH compounds admitted to the ion source and the measured ion ratio $[AHI]^-/[I]^-$ and $[A''HI]^-/[A'HI]^-$ observed after equilibriums 1 and 2 were established. To obtain accurate relative thermodynamic data, known concentrations of all alcohols (or carboxylic acids) were admitted to the ion source simultaneously and K_1 and K_2 were determined. With this procedure, the equilibrium constants were being evaluated under exactly the same temperature and total pressure conditions. This method should allow us to calculate the corresponding $\delta\Delta G°_2$ ($= -RT \ln K_2$) to better than ±0.2 kcal/mol. The absolute $\Delta G°_{1,0}$ ($= -RT \ln K_1$) are probably accurate to ±1 kcal/mol.

The van't Hoff plots for reaction 1 for the ROH and RCOOH series where R = H, Me, Et, *i*-Pr, and *t*-Bu are shown in Figure

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Table I. Thermodynamic Data[a] for the Reaction $X^-HA = X^- + HA$ (where AH = ROH and RCO_2H)

X^-AH	HOH	MeOH	EtOH	*i*-PrOH	*t*-BuOH	$MeCO_2H$	$EtCO_2H$	*i*-$PrCO_2H$	HCO_2H	*t*-$BuCO_2H$
					$-\Delta H^\circ_{1,0}$ [a]					
F^- [c]	23.3[f]	29.6	31.5	32.3	33.3	41.7			45.3	
Cl^- [d]	13.1[f]	14.2			19.2	21.6			27.4	
I^- [e]	10.1 (10.2)[f]	11.3	12.1	12.2	12.1	16.9	16.6	16.7	18.9	15.4
AH[b]	390.7	379.2	376.1	374.1	373.3	348.5	347.3	346.2[g]	345.2	344.6[g]
					$-\Delta G^\circ_{1,0}(300)$ [a]					
F^- [c]	18.1	22.8	24.0	24.6	25.5	34.0			38.0	
Cl^- [d]	8.2	9.8			11.1	15.8			20.1	
I^- [e]	5.4	6.0	6.4	6.5	6.5	10.5	10.5	10.6	12.7	8.9
AH[b]	384.1	372.6	369.5	367.5	366.7	341.5	340.3	339.2[g]	338.2	337.6[g]
					$-\Delta S^\circ_{1,0}$ [a]					
F^- [c]	17.4[f]	22.6	24.9	25.6	26.1	25.6			24.2	
Cl^- [d]	16.5[f]	14.8			27.0	19.3			24.5	
I^- [e]	15.8 (16.3)[f]	17.8	18.9	19.1	18.7	21.3	20.4	20.5	20.7	21.7

[a] All energy values are in kcal/mol except for entropy values which are in eu. Free energy values for the standard state are 1 atm. Reported $\Delta H^\circ_{1,0}$ values are probably accurate to ±1 kcal/mol and the $\Delta S^\circ_{1,0}$ values to ±4 eu. [b] Gas-phase acidity of AH. Values given are for ΔH° and $\Delta G^\circ(300)$ for the reaction $AH = A^- + H^+$. Acidity increases as ΔH° and ΔG° decrease. From Bartmess and McIver[6] and Cumming and Kebarle.[7] [c] Larson and McMahon.[4] [d] Kebarle et al.[2,3] [e] Present work. [f] Kebarle et al.[5] [g] Caldwell, G.; Renneboog R.; Kebarle, P., to be published.

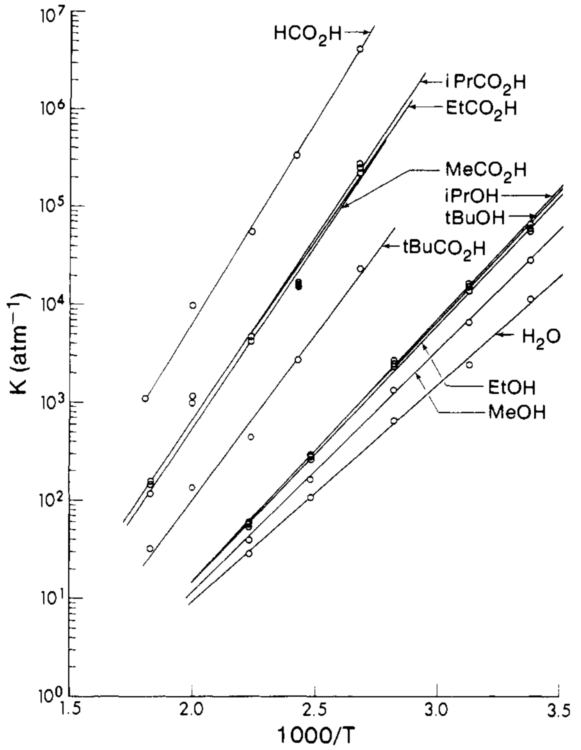

Figure 1. van't Hoff plots of equilibrium constants for the gas-phase reactions $AH + I^- = AHI^-$. Compounds AH are given in the figure.

1. The thermodynamic data derived from Figure 1 are given in Table I along with the binding energies of the fluoride and chloride complexes. The present results for $HOHI^-$ are found in good agreement with an earlier determination from this laboratory,[5] see Table I. Also shown in the table for comparison purposes are the gas-phase acidities of ROH[6] and RCOOH.[7]

Discussion

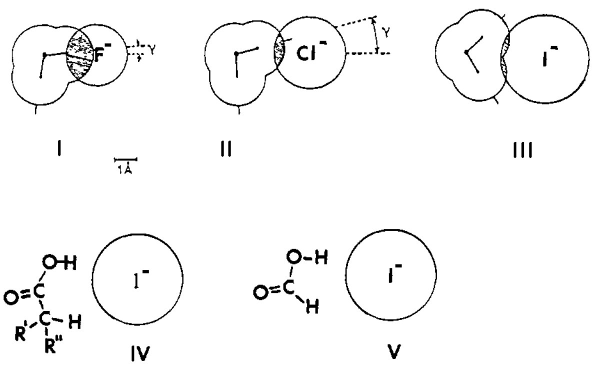

Figure 2. Predicted geometries for $HOHF^-$ (I) and $HOHCl^-$ (II) from ab initio calculations, Clementi.[10] γ° = 4.5 for I and 15 for II. The probable structure for $HOHI^-$ (III) is suggested by electrostatic calculations. Structures I to III are drawn approximately to scale using Pauling radii for ions and van der Waals radii for H_2O. Structures IV and V are proposed on the basis of present results. IV and V are based on the assumption that the $RCOOHI^-$ bonding is governed by the interaction of three bond dipoles in RCOOH with I^-. These are the OH, C═O, and CH dipoles. Structures IV and V maximize the interactions of these dipoles with the ion. The presence of a third methyl group in *t*-BuCOOH causes an increase of distance and misalignment of the C═O dipole and removes the C–H dipole; these effects lead to the weakest bonding in *t*-BuCOOH.

The van't Hoff plots for the $ROHI^-$ and $RCOOHI^-$ complexes, Figure 1, give a quick and direct overview of the results. Starting with ROH, at constant temperature one observes an increase of the ln K_1 values, which indicates an increase of $-\Delta G^\circ_1$ (the binding free energy) in the order HOH < MeOH < EtOH ≈ *i*-PrOH ≈ *t*-BuOH. The same order is observed also for the slopes of the van't Hoff lines, which gives the $-\Delta H_1$ values (the bonding enthalpies, see Table I). Comparing these results with the data for $ROHF^-$ and $ROHCl^-$, one finds first that the bond energies for $ROHI^-$ are much smaller. For example, $-\Delta H_1$ for the $ROHF^-$ series changes from 23.3 to 33.3 kcal/mol while for $ROHI^-$ the values are from 10.1 to 12.1 kcal/mol. The much weaker bond energies for $ROHI^-$ of course are caused by the large increase of ion radius from F^- to I^-. More interesting are the relative changes in the ROH series. While the bond energies for $ROHF^-$ increase substantially over the whole series, for $ROHI^-$ an increase is observed only from HOH to EtOH while the values for EtOH, *i*-PrOH, and *t*-BuOH are essentially identical. For the $ROHF^-$ series, McMahon[4] observed an increase of bond energies which was proportional to the increase of ROH acidity. Clearly for the last three members in the $ROHI^-$ series, a bond–acidity relationship does not hold. The increase of acidity and hydrogen-bonding ability in the $ROHF^-$ series is largely due to an increase of polarizability of the alkyl groups in the order H, Me, Et, *i*-Pr, *t*-Bu.[8,9] Either the complete removal of the proton (acidity) or

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the formation of a hydrogen bond to F^- increases the negative charge on the oxygen atom. The polarizability of the alkyl group represents the dominant factor in the stabilization of this change.[8,9] When F^- is replaced with the much larger I^-, we expect that the stabilization due to the polarizability of the alkyl group will be much less important due to the large increase of distance between the negative charge and ROH.

Other structural changes in the complex $ROHX^-$ can also occur as the size of X^- increases. Clementi and co-workers, using large basis set ab initio calculations, have shown that for $HOHF^-$ the most stable structure is the essentially linear hydrogen bond (strucutre I, Figure 2). However, for $HOHCl^-$ the angle changes resulting in a bent hydrogen bond, see structure II, Figure 2. Extrapolating this trend, one expects that $HOHI^-$ will have the two H atom attachment (bifurcated) structure III (C_{2v} symmetry). It is interesting to note that improved classical electrostatic calculations[11,12] in which the dipole of H_2O is represented by atomic point charges (net atomic charges) and the polarizability by atomic polarizabilities predict the bifurcated structure III to be the most stable one for all the $HOHX^-$ complexes. For the small F^- ion there is significant orbital overlap in X^----H---O and thus a true strong hydrogen bond. It is not surprising that the electrostatic calculations fail to predict the most stable structure for this case. However, for $HOHI^-$ where the overlap is minimal and the binding is essentially pure electrostatic one expects structure III predicted by the electrostatic calculations to be the true one. A more extensive discussion of the theoretical results for $HOHX^-$ can be found in Schuster.[12] For $ROHI^-$ one expects a change over from the C_{2v} structure III with HOH to a more linear H-bonded structure like I or II for R = Me to *t*-Bu. Such a structure allows the dominant O–H bond dipole to point toward the center of the ion. The dipole moments of H_2O and CH_3OH are 1.8 and 1.7 D. Assuming that most of the dipole of CH_3OH is concentrated in the OH bond, the permanent dipole contribution will lead to a somewhat weaker bond for $MeOHI^-$ than for $HOHI^-$. The experimentally observed stronger bonding for MeOH (and the other ROH) must be due to the larger polarizabilities of the alkyl groups, i.e., the induced dipole contribution due to R tips the balance in favor of these alcohols; however, since R is at a large distance from the the ion charge center, the polarizability effect is rather small.

The results for $RCOOHI^-$ follow an unusual pattern. The interaction is strongest for R = H, there is an appreciable drop to Me, Et, *i*-Pr, which have almost equally strong interactions, and then *t*-C_4H_9, which might have been expected to be in the same group, gives a much weaker interaction again (see Figure 1 and Table I). Had the $RCOOHI^-$ bonding followed the RCOOH acidities, the *t*-$BuCOOHI^-$ should have had a bonding energy even higher than that of HCOOH (see acidity changes in Table I). The one important difference between Me, Et, *i*-Pr, and *t*-Bu is that *t*-BuCOOH does not have a hydrogen atom on the carbon adjacent to the carboxylic group. Considering that the carboxylic group is strongly electron withdrawing, such hydrogens can be expected to carry a small positive charge. Suggested structures (IV and V) for $RCOOHI^-$ and $HCOOHI^-$ are given in Figure 2. These are based on a consideration of the detailed charge distribution in the acid. We assume that the interactions with the I^- ion are largely dependent on the magnitude and spatial position of three bond dipoles in the acid, the OH bond dipole—the carbonyl C=O bond dipole, and the C–H bond dipole involving the partially positive hydrogens mentioned above. Most important is the OH dipole which can come close to the ion because of the smallness of hydrogen. The C=O dipole even though substantial is less important since it cannot be brought close to the ion (see IV and V). The C–H dipoles are the smallest and vary from acid to acid but should be considered since they may be close to the ion.

The relative magnitude of the carbon–hydrogen dipoles can be very roughly estimated from relative gas-phase acidities. One can deduce[13] that H-COOH is only a little less acidic than CH_3O–H, which suggests that this CH dipole will not be very much weaker than that for the OH in CH_3OH. The acidity of $HOOCH_2$–H is expected to be considerably weaker than that of HOOC–H[13] so that the CH dipole in CH_3COOH and the other RCOOH will be considerably weaker than that for HOOC–H. The strongest bonding observed for $HCOOHI^-$ (structure V) should be due to radial alignment of the OH bond dipole to the center of the ion, simultaneous approximate alignment of the C=O dipole, and simultaneous closeness and alignment of the relatively strong C–H dipole. In contrast, the weakest bond observed for *t*-$BuCOOHI^-$ should be due to steric interference of the (third) methyl group in *t*-Bu. Space-filling models show that the presence of three methyl groups causes an increase in distance and a misalignment of the C=O dipole; also for this compound there is essentially no assistance from a CH dipole. The intermediate bonding cases, involving *R* = Me, Et, and *i*-pr (structures IV), can have good position and alignment of the OH and C=O and C—H dipoles, but the C—H dipoles involved are considerably weaker than that for formic acid.

Acknowledgment. Our interest in the $ROHI^-$ measurements was stimulated by a conversation with Professor R. W. Taft. The present work was supported by a grant from the National Science and Engineering Council of Canada.

Registry No. HOH, 7732-18-5; MeOH, 67-56-1; EtOH, 64-17-5; *i*-PrOH, 67-63-0; *t*-BuOH, 75-65-0; $MeCO_2H$, 64-19-7; $EtCO_2H$, 79-09-4; *i*-$PrCO_2H$, 79-31-2; HCO_2H, 64-18-6; I^-, 20461-54-5; *t*-$BuCO_2H$, 75-98-9.

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