Analysis of the Principles Governing Proton-Transfer Reactions. Carboxyl Group

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Abstract: The participation of the –COOH group in proton-transfer processes is investigated by ab initio calculations with a 4-31G* basis set. Of particular interest is the influence of the –OH group upon the attached C=O functionality, extracted by comparison with the simpler H_2CO molecule. The primary effect of the –OH is to increase the proton affinity of C=O, raising the barrier for proton transfer to an acceptor molecule for any given H bond length. As in the case of H_2CO, displacement of the proton acceptor away from an O lone pair and toward the C=O axis provides an impetus for the proton to be transferred away from HCOOH. The strength of this impetus, however, is found to depend upon the specific orientation of the OH group of HCOOH. This added level of complexity, absent in H_2CO, can be simply explained on the basis of two factors: (i) electrostatic interactions between the subunits involved in the H bond and (ii) removal of a proton from $HC(OH)_2^+$ to leave behind two possible conformers of HCOOH (cis or trans) which differ in intrinsic stability. Proton-transfer energetics of HCOOH are found to be less sensitive than H_2CO to H-bond deformations out of the molecular plane. With regard to the OH portion of the carboxyl group, its proton affinity is lowered relative to HOH, making it a much less likely proton acceptor, especially if the proton is positioned trans to the C–H bond.

Because of their importance and widespread occurrence, proton-transfer reactions have been the subject of a great deal of attention.[1-7] Experimental studies carried out over the last decade or so have established an absolute scale of proton affinities for a wide range of molecules in the gas phase, free of solvent effects.[3-7] This work has also indicated that exothermic transfers take place extremely rapidly, the entire process being limited only by the rate of diffusion of the proton donor and acceptor molecules. Theoretical calculations[8,9] have shed light on certain aspects of the reaction which are not amenable to experimental inquiry, e.g., the structure of transient intermediates.

Recent work in this laboratory[10-15] has been aimed at an elucidation of the fundamental physical principles which control the energetics of proton transfer through a systematic theoretical treatment of various different systems. Our earlier work has illustrated the extreme sensitivity of the transfer barrier height to the distance between the proton donor and acceptor groups. This dependence, as well as the different barriers for various pairs of groups, was explained quantitatively on the basis of fundamental properties of each group such as its proton affinity and equilibrium X–H bond length.

Our most recent calculations[11] have explored the distinctions in proton-transfer properties between oxygen atoms in a single- and double-bonded situation, using the hydroxyl group of HOH as a model for the first and the carbonyl group of H_2CO for the second. The results were traced back to the different proton affinities, intrinsic flexibilities, multipole moments, and dispositions of the lone pairs of the two groups. Similar principles were shown to be operating in analogous comparisons between the amine and imine N atoms. One important conclusion arising from this work is that the equilibrium position of the proton can be shifted from one group of the H bond to the other by geometrical rearrangements that reorient the two groups even without affecting their separation. This effect was attributed to the electrostatic interaction between the charge of one subunit and the dipole moment of the other.

We turn our attention now to the carboxyl group, a component of a large number of organic systems. It is also of the utmost importance in proteins, occurring widely as the terminus of the side chains of the Glu and Asp residues. Proton transfers to this group appear to be an integral component of the catalytic mechanism of a wide variety of enzymes[16] and to be directly involved in bacteriorhodopsin's pumping of protons across biomembranes.[17] The observation that the proton-translocating activity of the F_0 segment of H^+-ATPase is inactivated by the blockage or removal of a carboxyl group[18] further underscores its importance to bioenergetic phenomena. From a more fundamental perspective,

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Principles Governing Proton-Transfer Reactions

J. Am. Chem. Soc., Vol. 108, No. 23, 1986 7179

Table I. Optimized Geometries of HCOOH and Its Protonated Derivatives (Distances in Å, Angles in Deg)

	$r(CH)$	$r(CO^t)$	$r(CO^c)$	$r(O^tH^t)$	$r(O^cH^c)$	$\theta(HCO^t)$	$\theta(HCO^c)$	$\theta(COH^t)$	$\theta(COH^c)$	E, kcal/mol
					HCOOH					
T	1.083	1.322	1.179	0.954		110.3	124.7	108.7		0[a]
C	1.090	1.173	1.327		0.949	123.2	113.8		111.6	6.2
					HC(OH)$_2^+$					
CT	1.076	1.245	1.254	0.965	0.961	116.6	122.7	115.9	116.6	0[b]
CC	1.078		1.248		0.960		121.6		116.4	3.2
TT	1.073	1.251		0.962		116.3		119.7		4.7

|	$r(CH)$	$r(CO'')$	$r(CO')$	$r(OH^t)$	$r(OH^c)$	$\theta(HCO'')$	$\theta(HCO')$	$\theta(CO'H^t)$	$\theta(CO'H^c)$	E, kcal/mol
					HCO(OH$_2$)$^+$					
	1.076	1.129	1.569	0.966	0.968	139.2	105.3	116.8	123.9	28.5[d]

[a] $E^{SCF} = -188.583\,19$ au. [b] $E^{SCF} = -188.883\,67$ au. [c] H^c refers to hydroxyl H cis to C–H bond; the O to which it is bonded is designated O^c. The t superscript has a similar meaning for the trans OH group. [d] Relative to CT geometry of HC(OH)$_2^+$; O'' refers to carbonyl O while two hydrogens are bonded to O'; nonplanar molecule: dihedral angles $\phi(O''CO'H^t) = 7.2°$, $\phi(O''CO'H^c) = 158.5°$.

it is well-known that the chemical properties of –COOH are substantially different from those of the individual C=O and –OH moieties of which it is composed. Now that we have identified the essential principles governing the proton transfers involving the OH and C=O groups within their simple HOH and H$_2$CO prototypes, it would be particularly interesting to investigate how these groups influence the proton-transfer properties of one another when placed in direct contact on the same molecule. Analysis of these mutual perturbations is crucial in efforts to understand the behavior of large systems on the basis of properties of smaller model molecules.

In this work, we take formic acid HCOOH as our model carboxyl-containing group. The paper is divided into two primary sections. The first examines the influence of the OH upon the properties of the double-bonded oxygen via comparison with H$_2$CO. We take the converse perspective of the perturbation of OH by C=O in the second section by contrasting the hydroxyl O of HCOOH with that of HOH.

Methods

For purposes of consistency with our past calculations[11] of (H$_2$O–H–OH$_2$)$^+$ and (H$_2$CO–H–OH$_2$)$^+$, we again take OH$_2$ as the proton-acceptor molecule, pairing it here with formic acid in a H bond containing an additional proton. Our previous comparisons have made use of the 4-31G* basis set[19] for a number of reasons, most important of which has been its accurate re-

Scheme I. Pathways for Protonation and Subsequent Hydration of Formic Acid and the Resulting Geometries. Energies of Each Reaction (kcal/mol) Are Indicated along Arrows
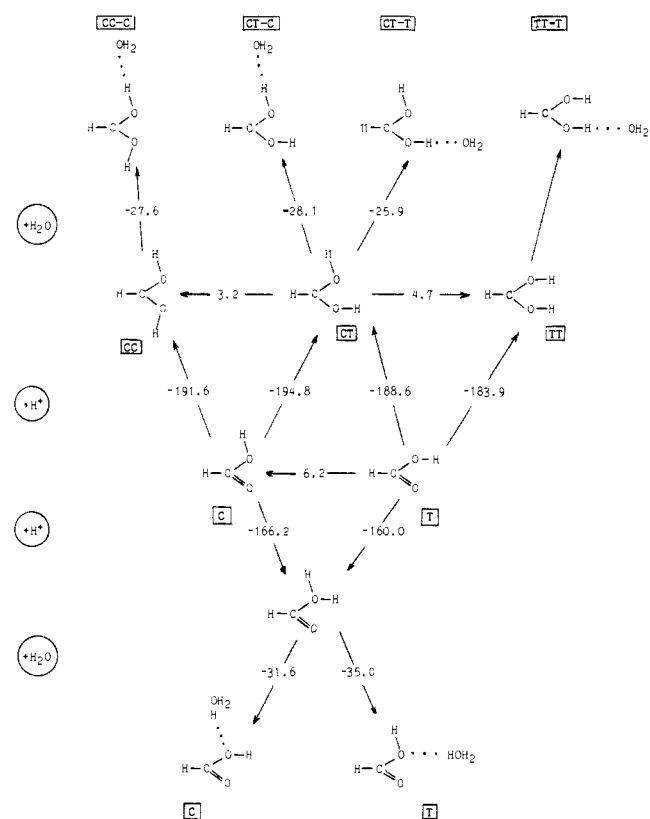
production of the relative proton affinities of the species involved in the transfers. In the case of formic acid and water, their gas-phase proton affinities have been measured[5] to be 178.8 and 166.5 kcal/mol, respectively, a difference of 12.3 kcal/mol. Corrections for zero-point vibrational energies[20] lead to a difference in protonation energies between the two molecules of 12.6 kcal/mol. The 4-31G* basis set yields protonation energies of 188.6 and 175.8 kcal/mol, respectively; the calculated difference of 12.8 kcal/mol is in excellent agreement with the experimental value. It is hence the 4-31G* basis set which we apply here.

This basis set offers the advantage of direct comparison with past work. In addition, the split-valence character of 4-31G* and the polarization functions contained within it should furnish a satisfactory framework for electronic redistributions accompanying

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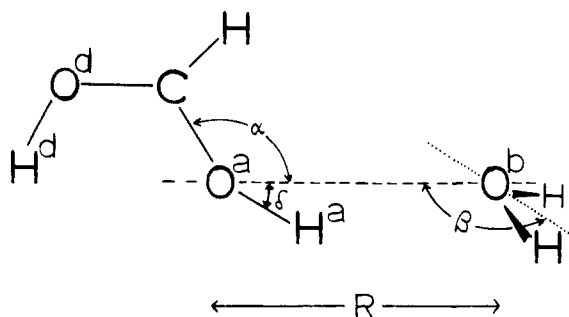
Figure 1. CT-C geometry of $(HC(OH)OH-OH_2)^+$. R represents the distance between O atoms and β measures the angle between the O--O axis and the HOH bisector. H^a is below the O--O axis for positive values of δ. Switching the H atom bonded to C with the O^dH^d group (H^d away from O^b) yields the CT-T geometry while CC-C may be obtained by a 180° rotation of H^d about the $C-O^d$ bond.

the transfer. Moreover, our prior calculations[10,11] have indicated that energetics of proton transfer computed with this basis set are rather accurate, compared to calculations with larger sets and including electron correlation. The relative energies of the ionic H bonds contained in $(AH{\cdot\cdot}B)^+$ and $(A{\cdot\cdot}HB)^+$ are very little affected by correlation since (i) they are dominated by electrostatic interactions and (ii) any correlation effects are similar in the two configurations and hence tend to cancel one another in the energy difference. It is therefore the proton affinity difference between A and B (HCOOH and H_2O) which is of primary concern and motivates our use of 4-31G*.

All calculations were carried out within the framework of the GAUSSIAN-80 series of ab initio programs.[21] Geometry optimizations made use of the gradient algorithms contained therein.

Transfers Involving C=O Oxygen

Before detailing the results for the $(HC(OH)O-H-OH_2)^+$ system, it is necessary to consider the most relevant configurations of both formic acid and its protonated derivatives. It was found that all species preferred a fully planar arrangement to which we restrict our attention. Formic acid may have its hydroxyl proton either cis or trans to the C-H bond, for which we use the designations C and T, respectively.[22] The T rotamer was found to be 6.2 kcal/mol more stable than C after full geometry optimizations of both, in good agreement with prior calculations[23] as well as experiment.[24] As indicated in Scheme I, there are three possibilities for $HC(OH)_2^+$. The most stable has one hydroxyl proton cis to C-H and the other trans, indicated as CT. CC, with both hydrogens cis to C-H, is 3.2 kcal/mol higher in energy, while TT is 1.5 kcal/mol higher still. The optimized geometries of all these species, along with their energies, are displayed in Table I.

We now turn our attention to the full $(HC(OH)O-H-OH_2)^+$ illustrated in Figure 1. The specific configuration pictured there contains the CT structure of $HC(OH)_2^+$. Since the water is H-bonded to the hydrogen which is cis to C-H, the entire geometry is designated as CT-C. In keeping with our earlier conventions,[11] R represents the length of the H bond and δ the deviation of the connecting proton from the H-bond axis. α and β refer to the orientations of the two subunits. There are several alternate possibilities for hydration of $HC(OH)_2^+$, as indicated in the upper portion of Scheme I. A full geometry optimization was carried

Table II. Optimized Geometries (Å and Deg) and Energetics of $(HC(OH)OH-OH_2)^+$ Complexes[a]

	CT-C	CT-T	CC-C
$R(O{\cdot\cdot}O)$	2.546	2.543	2.566
$r(O^aH^a)$	1.006	1.016	1.003
$r(O^dH^d)$	0.963	0.960	0.957
$r(CO^a)$	1.239	1.231	1.233
$r(CO^d)$	1.255	1.263	1.258
$r(CH)$	1.076	1.076	1.079
$r(O^bH)$	0.954	0.958	0.959
δ	5.6	-0.7	5.1
α	110.0	118.8	109.8
β	152.2	149.4	148.9
$\theta(HCO^a)$	122.4	117.5	121.1
$\theta(HCO^d)$	115.8	121.1	120.7
$\theta(CO^dH^d)$	114.5	115.5	115.6
$\theta(HO^bH)$	106.8	107.1	106.5
E, kcal/mol	0.0^b	2.2	3.7
E^D, kcal/mol[c]	28.1	25.9	27.6

[a] "a" superscript refers to H-bonding OH group of protonated formic acid and "d" to the other OH. See Figure 1 for definition of "b" superscript. [b] $E^{SCF} = -264.86743$. [c] Energy of dissociation to $HC(OH)_2^+$ + HOH where protonated formic acid remains in same form (viz. CT for first two columns and CC for third).

out as well for CT-T which is similar to CT-C except that the water H-bonds to the hydrogen trans to C-H. Likewise, the geometry of CC-C, involving the CC configuration of $HC(OH)_2^+$, was also optimized. The geometries of all three fully optimized structures are listed in Table II. (A final possibility, indicated in the upper right corner of Scheme I, is TT-T.) In all cases, the "a" superscript is used to indicate the OH group involved in the H bond, while the other OH is designated by a "d".

The H-bond length lies between 2.54 and 2.57 Å for all three complexes, only slightly longer than the value of 2.52 Å obtained earlier[11b] for $(H_2COH-OH_2)^+$. In all cases the OH bond involving the H-bonding proton is significantly longer than O^dH^d, as would be expected. O^aH^a stretches by 0.04 to 0.05 Å, as compared to its length in the isolated $HC(OH)_2^+$. This stretch results in a 0.015-Å contraction of the associated CO^a bond, whereas the CO^d bond stretches by about 0.010 Å.

In both geometries in which the water H-bonds to the cis OH group (CT-C and CC-C), H^a lies 5° below the O--O axis and α is 110°. These angles are essentially identical with the values obtained previously for the $(H_2COH-OH_2)^+$ complex.[11b] In contrast, α is 9° larger for CT-T and H^a lies within 1° of the H-bond axis. The larger value of α may be attributed to the electrostatic repulsion between the partial negative charges on the O^b and O^d atoms in the CT-T geometry (the positions of O^dH^d and the H bonded to C are reversed in CT-T relative to Figure 1 which illustrates CT-C). This repulsion is of course absent in $(H_2COH-OH_2)^+$ and in the other two geometries of (HC-$(OH)OH-OH_2)^+$ where the O^d atom is trans to O^b. The $O^b{\cdot\cdot}O^d$ repulsion in CT-T rotates the $HC(OH)_2^+$ subunit, pulling H^a up closer to the O--O axis; hence δ is closer to 0°.

As may be seen in the penultimate row of Table II, the geometry of lowest energy is CT-C. Its dissociation to the CT conformer of $HC(OH)_2^+$ and H_2O requires 28.1 kcal/mol, indicated in the last row, while CT-T requires only 25.9 kcal/mol. The 2.2-kcal/mol higher energy of CT-T may be ascribed to the aforementioned $O^d{\cdot\cdot}O^b$ repulsion. CC-C is 3.7 kcal/mol less stable than CT-C and dissociates not to CT but to CC and water, requiring 27.6 kcal/mol. The lesser stability of this complex is due primarily to the CC structure of $HC(OH)_2^+$ which is intrinsically 3.2 kcal/mol higher in energy than CT (see Table I). For purposes of comparison, the dissociation energy of $(H_2COH-OH_2)^+$ was calculated to be 30.0 kcal/mol.[11b] The stronger binding energy of the latter complex (as well as its shorter O--O distance) is related to the smaller proton affinity of H_2CO, closer to that of water.[14a]

In all three cases discussed above, the H-bonding proton H^a remains on the formic acid subunit, stretching toward the water by only 0.05 Å or less. Attempts were made in each case to locate

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(22) The C and T geometries correspond respectively to the anti and syn designations frequently used for formic acid. C and T are applied here so as to have a consistent reference point (the C-H bond) for use with this molecule as well as other species throughout this paper for which syn and anti nomenclature would be ambiguous and cumbersome.

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Table III. Geometries (Å and deg) During Proton Transfer from C=O of HCOOH to OH$_2$ for $R(OO)$ = 2.75 Å[a]

|	CT–C			CT–T		
	OCOH--O	OCO–H–O	OCO--HO	OCOH--O	OCO–H–O	OCO--HO
$r(O^aH^a)$	0.992	1.417	1.734	1.001	1.414	1.730
$r(O^dH^d)$	0.963	0.960	0.957	0.959	0.955	0.953
$r(CO^a)$	1.244	1.219	1.203	1.235	1.211	1.196
$r(CO^d)$	1.252	1.273	1.288	1.260	1.282	1.299
$r(CH)$	1.075	1.077	1.079	1.076	1.079	1.082
$r(O^bH)$	0.952	0.959	0.965	0.952	0.958	0.965
δ	8.4	−0.3	−2.0	0.7	−0.7	−2.0
α	105.6	121.7	138.0	116.1	119.8	127.7
β	156.9	132.3	128.0	154.5	132.0	127.9
$\theta(HCO^a)$	122.3	123.7	123.9	117.1	119.4	121.5
$\theta(HCO^d)$	116.2	113.3	111.8	121.6	119.0	117.0
$\theta(COH^d)$	115.0	113.0	111.8	115.7	114.6	113.8
$\theta(HO^bH)$	106.4	109.0	111.3	106.6	109.1	111.3
E, kcal/mol	0.0[b]	17.0	9.2	2.2	17.4	9.8

[a] See Figure 1 for definition of a–d superscripts. [b] E^{SCF} = −264.865 24.

a second minimum corresponding to (HC(OH)O–HOH$_2$)$^+$ in which the proton has been transferred over to the water. Failure to identify a minimum of this type is consistent with our previous findings for H$_2$CO and H$_2$O and is not surprising in view of the 13-kcal/mol higher proton affinity of HCOOH as compared to H$_2$O. We would conclude that formation of the (HC(OH)OH–OH$_2$)$^+$ complex in the gas phase from HC(OH)$_2$$^+$ and H$_2$O is exothermic by the amounts listed in the last row of Table II for each conformation of the former subunit, with the CT–C route being preferred.[25] Decomposition to HCOOH and H$_3$O$^+$ would occur directly without passing through (HC(OH)O–HOH$_2$)$^+$ as an intermediate.

Dependence upon Length of H Bond. In the case of intramolecular H bonds, the distance between the two groups is controlled in part by overall structural constraints external to the bond itself which would not allow the two groups to reach their otherwise preferred separation. We have in the past modeled this situation by calculating proton-transfer potentials for a series of different H-bond lengths.[10-13] A value of $R(O$--$O)$ is chosen and held fixed throughout the transfer, with all other geometrical parameters fully optimized at each stage. For O--O distances greater than approximately 2.5 Å, in addition to the (HC(OH)OH–OH$_2$)$^+$ configuration, the potential energy curve contains a second (and less stable) minimum corresponding to (HC(OH)O–HOH$_2$)$^+$ in which the proton has been transferred to the OH$_2$ subunit. Geometry optimization of these two minima and the transition state separating them (again with R held fixed) determines the energy barriers to transfer in both the forward and reverse directions.

These optimized geometries are reported for $R(OO)$ = 2.75 Å in Table III for the CT–C and CT–T structures. OCOH--O refers to the left well in the potential (HC(OH)OH–OH$_2$)$^+$, OCO--HO to the right well (HC(OH)O–HOH$_2$)$^+$, and OCO–H–O to the top of the barrier separating them. The changes occurring in the CT–C geometry as the proton is transferred across to the water very closely parallel the trends observed previously for th (H$_2$CO–H–OH$_2$)$^+$ system.[11b] Specifically, the CO^a bond gets shorter, acquiring more double-bond character, as the water subunit resembles more closely H$_3$O$^+$. In the specific case of formic acid, the CO^d bond not involved in the H bond elongates. The central proton crosses the O--O axis as δ changes sign and α increases by some 33°. The decrease in β corresponds to the pyramidalization of the H$_3$O$^+$ subunit. The geometry variations in the CT–T structure are by and large quite similar with one key exception: α changes by only 11° as compared to the 33° increase in CT–C. The larger value of α in the OCOH--O configuration of CT–T has already been attributed to electrostatic repulsion between O^d and O^b. After the proton has been transferred, the positive charge of the H$_3$O$^+$ subunit now *attracts* O^d and α is consequently smaller in the OCO--HO configuration of CT–T as compared to CT–C.
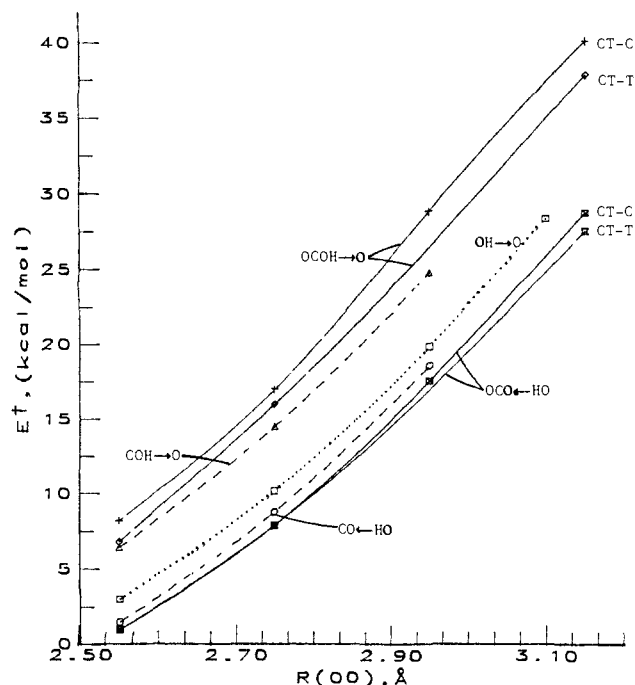
Figure 2. Computed energy barriers to proton transfer in (H$_2$O–H–OH$_2$)$^+$, dotted curve; (H$_2$CO–H–OH$_2$)$^+$, dashed curves; (HC(OH)O–H–OH$_2$)$^+$, solid curves. Labels on each curve omit H atoms not involved in H bond and arrow indicates direction of transfer.

The energy barriers to proton transfer are presented in Figure 2 as a function of the various values of R chosen. For purposes of comparison, the interhydroxyl transfer barriers in (H$_2$O–H–OH$_2$)$^+$ are indicated by the dotted curve. Immediately above and below this curve are the dashed curves representing our previous results for the (H$_2$CO–H–OH$_2$)$^+$ system. The COH→O notation indicates transfer from carbonyl to hydroxyl while the lower barriers for the reverse direction are represented by CO←HO. Our barriers for the formic acid–water pair are included as the solid curves, labeled OCOH→O and OCO←HO.

The most obvious trend apparent in Figure 2 is the rapid rise of barrier height with increasing R for all systems. The various curves are more or less parallel and obey the principle that the barriers are directly related to the difference in proton affinity between the proton donor and acceptor subunits.[14a] For example, the greater proton affinity of H$_2$CO as compared to H$_2$O makes it harder to pull a proton off the carbonyl; hence, the COH→O barriers are higher than OH→O. The even greater proton affinity of HCOOH produces a further barrier increase, as indicated by the two highest curves in Figure 2. Progressive barrier lowerings are observed for the reverse directions of transfer for similar reasons. The greater spacing between the curves toward the top of the figure can be easily explained by a simple variant of Marcus

7182 *J. Am. Chem. Soc., Vol. 108, No. 23, 1986*

Hillenbrand and Scheiner

theory.[14a] The projected intercepts of the curves with the horizontal axis indicate that the barriers disappear and the double-well potentials of $(H_2CO-H-OH_2)^+$ and $(HC(OH)O-H-OH_2)^+$ collapse into an asymmetric single well when the O--O distance diminishes below about 2.50 Å.

One last point concerns the fact that the OCOH→O barriers are somewhat lower for the CT-T geometry than for CT-C. This difference is due chiefly to the higher energy of the OCOH--O configuration of the former geometry, as listed in the last row of Table III, while the OCO-H-O configurations of the two geometries are nearly equal in energy. The O^d--O^b repulsion is responsible for the higher energy of CT-T when the proton is near the formic acid subunit. As the proton moves toward the water, the charge on O^b gets progressively less negative and its repulsion with O^d diminishes accordingly. Hence, α in the OCO-H-O configuration of CT-T is nearly equal to its value in CT-C where there is no possibility of O^d--O^b interaction.

Effects of Intermolecular Orientation

Since many H bonds are prevented from achieving their preferred fully linear geometry by the overall structural constraints imposed upon them,[26] we have investigated the influence of angular characteristics of the H bond upon the proton transfer taking place within it. In our earlier work, it was demonstrated that these angles affect not only the transfer barrier but also the equilibrium position of the central proton, consistent with experimental findings of a strong dependence of proton transfer upon the specific geometry of the H bond.[27] For example, whereas the proton prefers association with the H_2CO subunit when the proton acceptor water molecule lies along the direction of a carbonyl oxygen lone pair, displacement of the water toward the C=O axis pushes the proton across the H bond to the water instead.[11] We were able to trace this behavior to fundamental principles involving charge-dipole interactions and bending force constants of the pertinent subunits. It would be particularly interesting to determine whether these same principles, perhaps in some modified form, apply to the more complicated carboxyl group.

In order to investigate this question, proton-transfer potentials were calculated for each of several values of the CO^a--O^b angle, α. Other than this angle, and the O^a--O^b distance R which was held at 2.75 Å, all other geometrical parameters were fully optimized at each stage of proton transfer. The proton H^a was not restricted to the O^a--O^b axis but was free to follow its lowest energy path between these two atoms. The difference in energy between the two wells in the potential is defined as $\Delta E = E(\text{OCO--HO}) - E(\text{OCOH--O})$. A positive value of ΔE corresponds to the situation where the proton is associated with the carboxyl group in the lowest energy configuration, while a preference for the water is expressed by a negative ΔE.

Let us first focus our attention on the computed values of ΔE, represented by the lower group of curves in Figure 3. The broken curve illustrates the trend found in our previous study of the simple carbonyl of H_2CO toward more negative ΔE as α tends toward 180°. That is, the proton is shifted from the carbonyl group toward the water as the latter group approaches the C=O axis. The results computed here for the carboxyl group are represented by the solid curves, the first of which we discuss is the CT-C geometry. We note that this curve is almost exactly parallel to the dashed curve, indicating very similar principles are in action as for the simple carbonyl. The upward displacement of the CT-C curve relative to H_2CO is a simple result of the higher proton affinity of HCOOH which makes ΔE intrinsically more positive. For the $(H_2CO-H-OH_2)^+$ system, the transfer potential becomes symmetric ($\Delta E = 0$) at about $\alpha = 150°$. This transition from

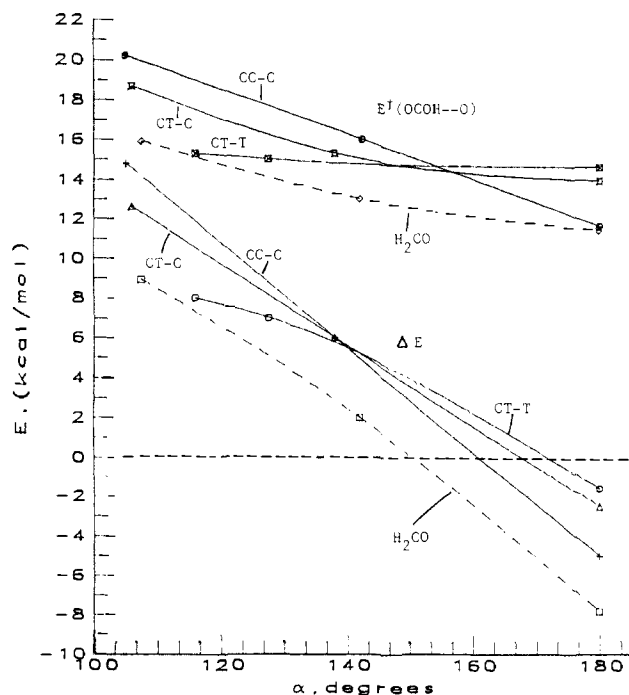**Figure 3.** Energetic properties of proton transfer from C=O oxygen to water as a function of α, with R fixed at 2.75 Å. The broken curves refer to replacement of HCOOH by H_2CO.

positive to negative ΔE is shifted by about 18° toward higher angles in the CT-C geometry of $(HC(OH)O-H-OH_2)^+$, consistent with the expectation that removal of the proton from the more basic HCOOH requires a greater angular deformation. We have thus arrived at the potentially very useful conclusion that the CT-C carboxyl geometry is quite similar in qualitative behavior to the much simpler carbonyl group. However, there are additional geometrical possibilities for carboxyl that are not available to carbonyl because of the more complicated nature of the former group. We now explore these other geometries using CT-C as a convenient point of reference.

From Figure 3 it may be seen that the CT-T curve is less steep than that for CT-C, the two curves crossing at about $\alpha = 140°$. Let us analyze this lesser slope by focusing on two extreme values of α: 110° for which ΔE of CT-T is less positive and 180° for which CT-T is less negative. For each angle α, we present in Figure 4 the relative energies of the two minima in each potential, corresponding to the $(HC(OH)OH--OH_2)^+$ and $(HC(OH)O--HOH_2)^+$ configurations, abbreviated once again as OCOH--O and OCO--HO, respectively. Beginning with $\alpha = 110°$ in the left half of the figure, it may be seen that the CT-T OCOH--O is 2.2 kcal/mol higher in energy than CT-C, while the order of stabilities reverses for the OCO--HO configuration with CT-T being more stable by 0.4 kcal/mol.[28] Since ΔE represents the difference in energy between OCO--HO and OCOH--O, this energy reversal leads to a smaller value of ΔE for CT-T at $\alpha = 110°$. The situation is the opposite of this for $\alpha = 180°$ where both configurations of CT-T are higher in energy than CT-C and, in fact, the energy difference *increases* (from 0.8 to 1.7) on going from OCOH--O to OCO--HO; hence, ΔE is more positive for CT-T.

Our understanding of the different behavior of the CT-T and CT-C geometries is thus rooted in the relative energies of the individual configurations. Let us compare the OCOH--O structures for $\alpha = 110°$. As pointed out before, the 2.2-kcal/mol higher energy of CT-T is due principally to the electrostatic repulsion between the partial negative charges of the O^d and O^b atoms. Raising α to 180° lessens this repulsion by rotating O^d away from O^b, thus reducing the energy difference between CT-T

(26) Vedani, A.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 7653. Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320. Taylor, R.; Kennard, O.; Versichel, W. *J. Am. Chem. Soc.* **1984**, *106*, 244; **1983**, *105*, 5761. Murray-Rust, P.; Glusker, J. P. *Ibid.* **1984**, *106*, 1018.

(27) Houriet, R.; Rüfenacht, H.; Carrupt, P.-A.; Vogel, P.; Tichy, M. *J. Am. Chem. Soc.* **1983**, *105*, 3417. Manring, L. E.; Peters, K. S. *Ibid.* **1985**, *107*, 6452. Menger, F. M.; Chow, J. F.; Kaiserman, H.; Vasquez, P. C. *Ibid.* **1983**, *105*, 4996. Menger, F. M. *Tetrahedron* **1983**, *39*, 1013.
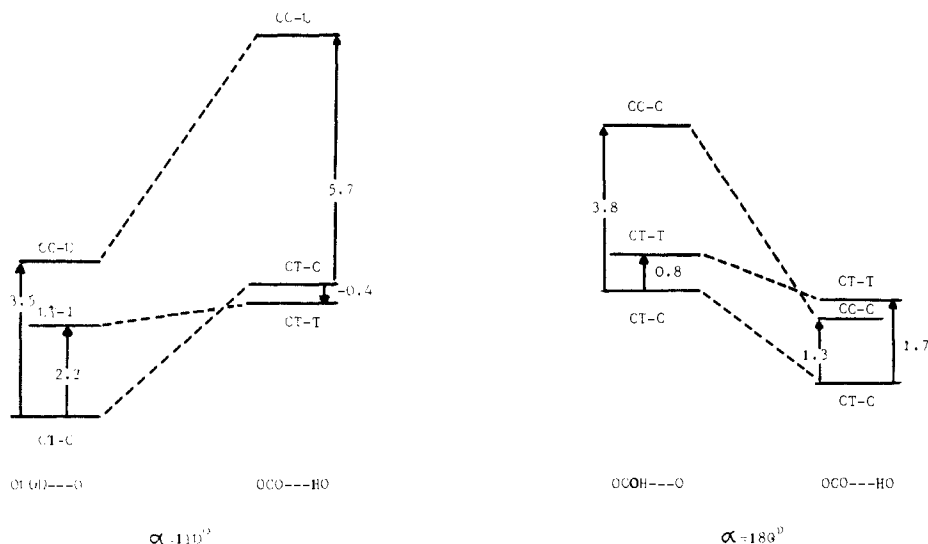
(28) Energy differences of less than ca. 1 kcal/mol should be treated as indicating approximate equality rather than as an absolute ordering.

Principles Governing Proton-Transfer Reactions

J. Am. Chem. Soc., Vol. 108, No. 23, 1986 7183

Figure 4. Relative energies (in kcal/mol) of various configurations of $(HCO(OH)-H-OH_2)^+$.

and CT–C to only 0.8 kcal/mol.

In the case of the OCO--HO configurations, there are two important points to consider. First, transfer of H^a from the protonated formic acid to the water in CT–C leaves behind a trans geometry of HCOOH which is intrinsically 6.2 kcal/mol more stable than the C geometry (see Table I) resulting from the same transfer in CT–T. There is thus a natural predisposition for the CT–C OCO--HO configuration to be lower in energy than CT–T by up to this amount.[29] On the other hand, the dipole moment of cis HCOOH is nearly three times larger than that of the trans geometry.[30] The electrostatic attraction between the positive charge of H_3O^+ and the dipole moment of the neutral cis HCOOH in CT–T is therefore potentially much greater than in CT–C. These two opposing forces approximately cancel one another when $\alpha = 110°$, as evidenced by the nearly equal energies of the CT–C and CT–T OCO--HO configurations in Figure 4. The rotation of HCOOH to $\alpha = 180°$ weakens the charge-dipole interaction, making it less capable of stabilizing CT–T, and this geometry is hence higher by 1.7 kcal/mol than is CT–C. (This rationale involving the dipole moment is equivalent to a description which considers the attraction between H_3O^+ and the partial negative charge on O^d.)

Similar reasoning may be applied to a comparison of CT–C with CC–C. We note first that these two geometries differ only in the orientation of the nonbonding proton H^d of the formic acid subunit, remote from the water, and any substantial differences may appear at first sight surprising. Nonetheless, inspection of Figure 3 reveals that ΔE in CC–C is notably more sensitive to α than is CT–C. One important distinction between the two structures is that the CT geometry of $HC(OH)_2^+$ is 3.2 kcal/mol more stable than CC (see Table I). It is therefore not surprising that the OCOH--O configuration of CC–C is 3.5 kcal/mol higher in energy than CT–C for $\alpha = 110°$, and a similar difference of 3.8 kcal/mol is found for $\alpha = 180°$, as reported in Figure 4. As in our previous comparison of CT–C with CT–T, transfer of a proton to water leaves behind T formic acid for CT–C but the less stable C arrangement in CC–C, raising the energy of the latter by up to 6.2 kcal/mol. It is here that a second consequence of the 180° rotation of H^d on going from CT–C to CC–C enters our argument. This rotation reorients the dipole moment of formic acid away from the positive charge of H_3O^+ when $\alpha = 110°$,

raising the energy of the CC–C configuration. In contrast, when $\alpha = 180°$, the reoriented dipole moment in CC–C is *more* favorably disposed toward H_3O^+ than in CT–C, thus lowering the energy difference to only 1.3 kcal/mol. The net result is that the value of ΔE is more positive for CC–C than for CT–C at 110° but more negative at 180°, leading to the greater angular sensitivity noted above.

Still more sensitive to α is the TT–T geometry for which ΔE decreases by 24.2 kcal/mol when α changes from 110 to 180° (not shown in Figure 3). Comparison will be made with CT–T which differs only in the orientation of H^d (see Scheme I). Since the TT geometry of $HCO(OH_2)^+$ is less stable than CT by 4.7 kcal/mol (Table I), it is not surprising to find a similar higher energy for the TT–T OCOH--O configuration as compared to CT–T when $\alpha = 180°$. However, reduction of α to 110° for TT–T brings H^d much closer to O^b, permitting their strong electrostatic attraction to lower the energy below that of CT–T, which contains a repulsion between the partial negative charges of O^b and O^d. Turning now to the OCO--HO configuration, removal of the proton from $HC(OH)_2^+$ to water in the TT–T case leaves behind a T geometry of HCOOH, more stable by 6.2 kcal/mol than the C structure remaining for CT–T. Therefore, OCO--HO is more stable for TT–T when $\alpha = 180°$. At the lower value of α, however, electrostatic effects again come into play. The interaction of H^d with the other subunit is now *destabilizing* in TT–T since $(HOH_2)^+$ bears a positive charge; hence, TT–T is very much higher in energy (7 kcal/mol) than CT–T where H^d is out of the way, allowing a stabilizing interaction between O^d and $(HOH_2)^+$. In summary, the OCOH--O configuration of TT–T is stabilized relative to CT–T when α is decreased from 180 to 110°, while the opposite occurs for OCO--HO. The net result is the substantially greater steepness of ΔE vs. α for TT–T.

The principles used above to understand the trends in ΔE may be extended to explain the behavior of the energy barriers to proton transfer, E^+. The barriers for transfer from the carboxyl (or carbonyl) group to the water subunit are illustrated as a function of α by the upper group of curves in Figure 3. We note first that the CT–C barriers run parallel to the carbonyl data, consistent with the aforementioned pattern for ΔE, further underscoring the similar behavior of the carbonyl and carboxyl groups. The higher barriers for the carboxyl group (ca. 2.5 kcal/mol) may again be ascribed to its greater proton affinity. The relationships between the CT–C, CT–T, and CC–C barriers resemble the ΔE patterns and similar arguments offer an explanation. Specifically, as pointed out in Figure 4, at small values of α there is a preferential destabilization of the left side of the potential of CT–T as compared to CT–C which might be expected to diminish the barrier for transfer from left to right. This is indeed the case, with the CT–T barrier being lower than CT–C for $\alpha = 110°$. At $\alpha = 180°$, the trend exhibited in Figure 4 is for a greater destabilization of

(29) This difference in energy between the two conformations of HCOOH has been incorporated into a proposed model of catalytic efficiency of the –COO⁻ group: Gandour, R. D. *Bioorg. Chem.* **1981**, *10*, 169.

(30) The dipole moment of C HCOOH is calculated with the 4-31G* basis set to be 4.33 D, as compared with 1.57 D for T. The ratio of 2.76 compares quite favorably with the experimentally determined ratio[24] of (3.79/1.42) = 2.67. Both dipoles are oriented more or less along the C=O bond; negative end of C dipole vector deviates by 16° from C=O axis (away from C–H) while T dipole is turned 24° toward C–H.

7184 *J. Am. Chem. Soc., Vol. 108, No. 23, 1986*

Hillenbrand and Scheiner

Table IV. Changes in Energetics of Proton Transfer (kcal/mol) Caused by 40° Out-of-Plane Distortion

	(HC(OH)O–H–OH₂)⁺		(H₂CO–H–OH₂)⁺	
	CT–C	CT–T		
δE(OCOH--O)	0.3	0.4	δE(COH--O)	0.4
δE(OCO–H–O)	-1.6	-1.3	δE(CO–H–O)	1.2
δE(OCO--HO)	1.2	1.3	δE(CO--HO)	1.9
$\delta(\Delta E)$	0.9	0.9	$\delta(\Delta E)$	1.6
$\delta E^\dagger$(OCOH→O)	-1.9	-1.7	$\delta E^\dagger$(COH→O)	0.8
$\delta E^\dagger$(OCO←HO)	-2.8	-2.6	$\delta E^\dagger$(CO←HO)	-0.8

the *right* side of the CT–T potential. The expected higher transfer barrier for CT–T at $\alpha = 180°$ is confirmed by the calculations. Just as the trends for the CC–C geometry with respect to ΔE are opposite to those of CT–T (Figures 3 and 4), so too is this true with respect to the energy barriers.

Out-of-Plane Distortions. Our previous work has shown that the carbonyl and hydroxyl oxygens differ dramatically with respect to displacements of the proton-acceptor molecule out of the plane of the O lone pairs. Whereas such H-bond distortions markedly increase the transfer barriers for the hydroxyl, the barriers in the carbonyl case change very little. Nor are the energies of the minima in the transfer potentials of the carbonyl very sensitive to the out-of-plane deformation, in contrast to the hydroxyl case where these energies change a great deal.

For purposes of comparison, the effects of out-of-plane distortions were investigated here for the carboxyl group. As in our previous work,[11b] the proton-accepting water subunit was placed directly along the C=O axis ($\alpha = 180°$) and then displaced by various angles ϕ out of the HCOOH plane. Other than this relative orientation and a fixed R(OO) distance of 2.75 Å, the geometries of the relevant configurations were completely optimized and the proton was free to follow its lowest energy path between the two subunits.

The results of a 40° deformation are presented in Table IV for the CT–C and CT–T geometries of the (HC(OH)O–H–OH₂)⁺ system as well as for the carbonyl analogue in the last column. The first three rows list the changes in energy of individual configurations caused by increasing ϕ from 0 to 40°, followed by the effects on the energetics of transfer. We note first that the CT–C and CT–T geometries behave nearly identically with one another. In both cases, the energy of the OCOH--O configuration increases very little, i.e., 0.4 kcal/mol or less, consistent with the value listed in the last column for the carbonyl analogue (H₂COH--OH₂)⁺. The energy of the OCO--HO configuration is somewhat more sensitive to ϕ, rising by about 1.2 kcal/mol for the same distortion of 40°. A slightly higher energy increase of 1.9 kcal/mol was noted for CO--HO in the carbonyl case.

This lesser sensitivity of (HC(OH)O--HOH₂)⁺ to ϕ can be related to the electron density distribution of HCOOH as compared to that of H₂CO. Since the stability of the OCO--HO configuration rests in part on a H bond with the Oᵃ oxygen, let us focus our attention on the region near this atom with which the central proton must interact. Substitution of one H of H₂CO by a OH group was found to increase the electron density above and below the HCOOH plane. This greater density, as compared to H₂CO, makes it energetically less costly to displace the HOH₂⁺ subunit out of the plane, since it may maintain a stronger H bond in the former case. This distinction between carbonyl and carboxyl is even more dramatic for the transition states representing the proton-transfer midpoint (second row of Table IV). In contrast to the carbonyl case where the displacement of water out of the plane raises the energy of this CO–H–O configuration, the transfer midpoint structure is stabilized for carboxyl owing to the buildup of density out of the plane which maintains a stronger covalent attachment between the oxygen and the departing proton.

In sum, the out-of-plane distortion slightly destabilizes the OCOH--O configuration while OCO--HO is raised in energy by a greater amount (larger for carbonyl than carboxyl). The net result is that raising ϕ from 0 to 40° increases ΔE (i.e., less negative) by 0.9 kcal/mol in (HC(OH)O–H–OH₂)⁺ as compared to a somewhat greater increase of 1.6 kcal/mol in the carbonyl
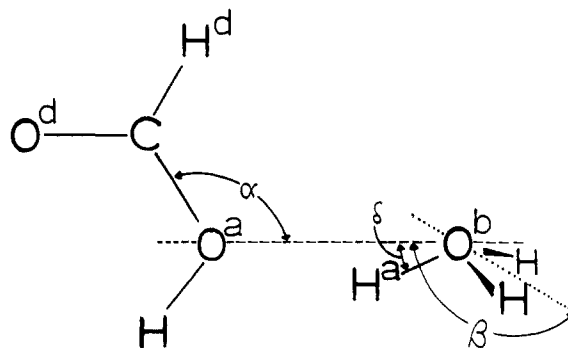
Figure 5. Geometrical parameters defined for transfer of a proton to –OH group of HCOOH. Conformation illustrated is denoted C because transferring proton is cis to C–H bond. T structure is identical except for reversal of positions of Hᵈ and Oᵈ.

analogue. The stabilization of the transfer midpoints lowers the barriers in the carboxyl systems unlike H₂CO where the COH→O barrier is raised owing to the destabilization of the midpoint configuration.

Transfers Involving –OH Group

As indicated earlier, we are interested not only in transfer to the C=O segment of the carboxyl group but to the OH portion as well. Such a transfer yields the HCO(OH₂)⁺ species in Scheme I, the optimized geometry of which is described in the last row of Table I. We note first that addition of a second proton to the hydroxyl group of formic acid drastically elongates the bond between the central carbon and the oxygen to which it becomes attached from 1.33 to 1.57 Å. At the same time, the C=O bond contracts by 0.05 Å. The OH bonds are somewhat longer in HCO(OH₂)⁺ than they are in HC(OH)₂⁺ where one proton is bonded to each O atom. Whereas the latter species is planar, the arrangement about the OH₂ group in the former is pyramidal.

Transfer of a proton to the OH group of HCOOH is much less favorable energetically than transfer to C=O, in conformity with recent spectroscopic measurements by Patten and Andrews.[31] Protonation of OH is calculated to be exothermic by 160.0 kcal/mol, as compared to 188.6 kcal/mol for protonation of the carbonyl oxygen (assuming the most stable geometry of all species involved). It was noted above that the OH group enhances the basicity of C=O; i.e., the proton affinity of HCOOH is higher by 12.8 kcal/mol than that of H₂CO. From the opposite perspective, the C=O acts to make the OH group of HCOOH *less* basic. Specifically, the proton affinity of this group is 15.8 kcal/mol smaller than that of HOH.

As a consequence of this reduced proton affinity, the proton prefers association with the water subunit in the system depicted in Figure 5. This figure illustrates an H bond to the side of Oᵃ cis to the C–H bond and the complex is hence denoted as C.[32] When the internal structure of HCOOH is cis, it is possible for H₃O⁺ to form a H bond on the trans side of Oᵃ. This T structure for the complex is similar to the C geometry in Figure 5 except that the positions of Oᵈ and Hᵈ are reversed. The C and T geometries are illustrated in the lower portion of Scheme I.

Table V contains the optimized geometries of both the T and C structures of the (HCOOH--HOH₂)⁺ complex. As may be seen in the penultimate row, the T structure is 1.5 kcal/mol more stable than C. This observation is surprising in view of the fact that the T complex contains the cis internal geometry of HCOOH[32] which is intrinsically less stable than trans by 6.2 kcal/mol (see Table I). The greater stability of the T complex is a consequence of the electrostatic attraction between the Oᵈ atom, with

(31) Patten, K. O., Jr.; Andrews, L. *J. Phys. Chem.* **1986**, *90*, 1073.
(32) Protonation of the hydroxyl group yields only one geometry for HCO(OH₂)⁺ in which one hydrogen is cis to the C–H bond and the other trans. Because of this lack of ambiguity, the CT prefix is omitted from the nomenclature of the relevant complexes. It should be emphasized, however, that transfer of the proton from HCO(OH₂)⁺ to OH₂ in the C configuration leaves behind HCOOH in its internal trans geometry (and vice versa for T).

Principles Governing Proton-Transfer Reactions

J. Am. Chem. Soc., Vol. 108, No. 23, 1986 7185

Table V. Optimized Geometries (Å and deg) and Energetics of $(HCOOH--HOH_2)^+$ Complexes[a]

	T	C
$R(O--O)$	2.574	2.524
$r(O^bH^a)$	1.011	1.029
$r(O^aH)$	0.955	0.960
$r(CO^a)$	1.368	1.380
$r(CO^d)$	1.165	1.161
$r(CH^d)$	1.082	1.080
$r(O^bH)$	0.963	0.964
δ	1.8	1.2
α	110.7	129.4
β	140.3	138.6
$\theta(H^dCO^a)$	113.8	110.4
$\theta(H^dCO^d)$	127.4	128.1
$\theta(CO^aH)$	114.8	108.4
$\theta(HO^bH)$	112.6	111.7
E, kcal/mol	0.0^b	1.5
E^D, kcal/mol[c]	25.5	17.8

[a] See Figure 5 for definitions of a, b, and d superscripts. [b] E^{SCF} = -264.83301. [c] Energy of dissociation to HCOOH and H_3O^+ with former molecule remaining in same internal conformation as in complex (cis for first and trans for second).

its partial negative charge, and the positive HOH_2^+ subunit. This force pulls the O^d atom closer to O^b; hence, α is only 110.7° in the T structure, as compared to 129.4° in C where the position of O^d is taken by H^d.

The last row of the table reports the dissociation energy of the T and C complexes to H_3O^+ and the appropriate conformation of HCOOH. The much greater value of E^D for the T complex may also be attributed to the aforementioned attraction. It may appear surprising at first sight that despite the stronger total interaction between subunits in T, its $R(O--O)$ distance is longer and the stretch of the O^b-H^a bond is smaller, both normally taken as evidence of a *weaker* H bond. The answer rests again in the $O^d..O^b$ interaction in T which substantially reduces α, rotating the HCOOH subunit to the point where the lone pairs of O^a are turned away from H^a, thus reducing the "covalent" portion of the interaction. It is this covalent part which is responsible for the stretch of O^b-H^a and hence entirely reasonable that the geometry of the T complex indicate a "weaker" interaction.

A search was conducted in the potential energy surface of both the T and C geometries for a second minimum corresponding to $(HCO(OH_2)--OH_2)^+$ in which the central proton resides on the formic acid rather than on the water. There was no evidence for such a minimum for T while one was located for C. However, the barrier for decay of the latter local minimum to $(HCO(OH)--HOH_2)^+$ is so small (less than 0.1 kcal/mol) that the potential may be treated for all intents and purposes as containing but a single minimum with the proton bonded to the more basic HOH subunit.

In comparison, the potential energy surface of $(H_2O-H-OH_2)^+$ is also of single-minimum type, although in this case the symmetry of the system leads to a structure in which the central proton is midway between the two O centers.[10,11] The $R(O--O)$ distance is 2.39 Å for the proton-bound water dimer, as compared to the longer values of 2.57 and 2.52 Å for the complexes in Table V. Thus, replacement of one H_2O subunit of $(H_2O-H-OH_2)^+$ by the OH group within HCOOH weakens the interaction, consistent with the reduction in OH proton affinity caused by the attached C=O.[14a]

Let us consider now the likely properties of the proton-bound complex of HCOOH and H_2O in the gas phase. Whereas the OH of HCOOH is not capable of removing a proton from H_3O^+, the results outlined in the earlier sections suggest spontaneous transfer of a proton to the C=O oxygen. Hence, the OH group of HCOOH would not be likely to participate in the proton-transfer process. Should a proton be located on the -OH group of HCOOH, it could be pulled off by a H_2O with no energy barrier. After appropriate repositioning of H_3O^+, a proton could be extracted by the C=O oxygen, again without an energy barrier. The only impediment to the full process would be the energy
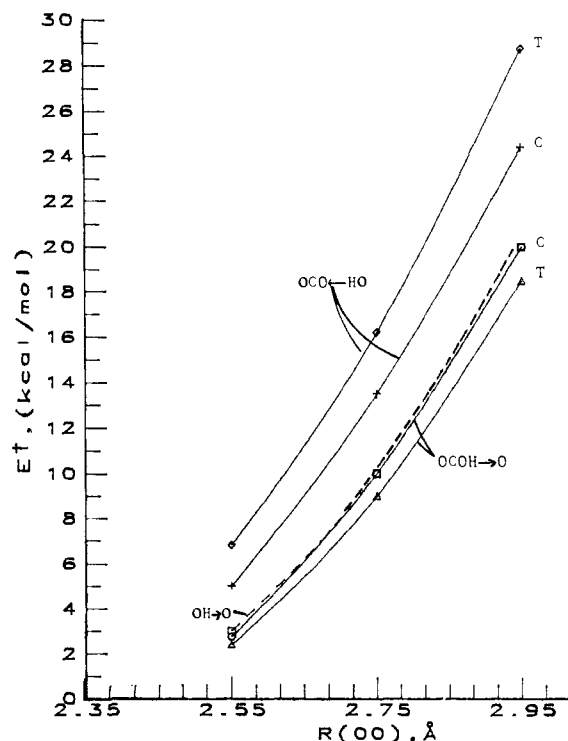
Figure 6. Energy barriers for proton transfer between H_2O and -OH group of HCOOH (solid curves) and HOH (broken curve). C and T respectively refer to positioning of the OH_2 subunit cis or trans to the C-H of HCOOH.

needed to move the H_3O^+ away from the OH group and toward the C=O. This energy would be somewhat less than the 18 kcal/mol corresponding to complete dissociation of the two subunits. In contrast, the internal transfer of a proton from the OH to C=O oxygen in the unimolecular rearrangement reaction $HCO(OH_2)^+ \rightarrow HC(OH)_2^+$, without the intervention of a water molecule, is exothermic by 28.5 kcal/mol but passes through a transition state 40 kcal/mol above the reactant.

Dependence upon H Bond Length. Analogous to the previous case of transfer from the carbonyl group, we consider the transfer between the hydroxyl group and water at a series of fixed $R(O--O)$ distances. The results are presented in Figure 6 where OCO$\leftarrow$HO again refers to transfer to the carboxyl group from water, but in this case the proton is added to the OH rather than to the C=O oxygen as in Figure 2. The broken curve illustrates the barriers in $(H_2O-H-OH_2)^+$ with which the current results are to be compared. We note first that the barriers for transfer to the -OH group of carboxyl are considerably higher than for transfer to HOH, because replacement of a H atom of HOH by the HC=O moiety lowers the proton affinity, thus making it more difficult for the OH to extract a proton from the other subunit.

This diminished proton affinity raises the energy of the $(HCO(OH_2)--OH_2)^+$ configuration relative to $(HCO(OH)--HOH_2)^+$, leading to negative values of ΔE. For either the C or T geometry, the numerical value of ΔE at any value of R is equal to the vertical separation between the two curves in Figure 6 representing the barriers for the forward and reverse directions of proton transfer. The greater separation between the two T curves and the associated more negative ΔE involves both a destabilization of the $(HCO(OH_2)--OH_2)^+$ configuration and a stabilization of $(HCO(OH)--HOH_2)^+$, relative to C. This pattern may be simply explained on the basis of electrostatic arguments similar to those used above as follows.

For purposes of illustration, let us consider a fixed $R(O--O)$ distance of 2.75 Å. The geometries of both wells in the proton-transfer potential, as well as the transition-state configuration, are reported in Table VI for both the C and T geometries. As expected, transfer from $HCO(OH_2)^+$ to OH_2 shortens the CO^a bond while elongating CO^d. The most revealing insights are gleaned from examination of the angles, however. Note that α

Table VI. Geometries (Å and deg) during Proton Transfer between -OH Group of HCOOH and Water for $R(OO)$ = 2.75 Å[a]

	C			T		
	OCOH--O	OCO-H-O	OCO--HO	OCOH--O	OCO-H-O	OCO--HO
$r(O^aH^a)$	1.010	1.354	1.744	1.018	1.339	1.758
$r(CO^a)$	1.470	1.409	1.368	1.468	1.407	1.359
$r(CO^d)$	1.142	1.154	1.164	1.142	1.153	1.170
$r(CH^d)$	1.077	1.078	1.081	1.077	1.080	1.082
$r(O^aH)$	0.966	0.963	0.959	0.963	0.959	0.955
$r(O^bH)$	0.952	0.958	0.965	0.952	0.956	0.964
δ	1.6	0.3	0.3	-0.8	0.6	-3.0
α	121.7	128.5	130.7	121.3	118.4	103.4
β	164.8	140.1	135.4	199.2	144.2	133.1
$\theta(H^dCO^a)$	107.7	109.7	110.6	108.5	111.2	114.9
$\theta(O^dCO^a)$	117.7	119.8	122.1	117.5	118.6	118.4
$\theta(CO^aH)$	118.0	112.2	107.7	123.3	118.8	115.1
$\theta(HO^bH)$	107.0	109.6	112.2	107.1	109.9	112.7
E, kcal/mol	0.0[b]	10.1	-3.5	1.0	10.0	-6.1

[a] Parameters defined in Figure 5.   [b] E^{SCF} = -264.822 73.

is equal to 121° in the OCOH--O configuration of both C and T. Proton transfer to the water increases α for C whereas this angle is markedly reduced in the T case. The increasing value of α for C is readily explained by the partial positive charge of H^d. This atom is attracted toward the negative end of the OH_2 dipole moment in the OCOH--O configuration. As H^a moves toward the OH_2 subunit, this attraction turns to a repulsion away from the positively charged H_3O^+ subunit; hence α rises. The replacement of H^d by the negatively charged O^d in the T geometry reverses the above pattern and accounts for the rapid reduction in α as the proton is transferred to the water. The negative charge of O^d and its repulsion with the OH_2 dipole in the OCOH--O T configuration also causes the OH_2 subunit to rotate so as to turn its dipole down away from O^d; i.e., β becomes greater than 180°.

These same principles help explain the energetics in the last row of Table VI. With regard to the OCOH--O configurations, the higher energy of T than that of C is due to the repulsion between the O^d atom and the dipole moment of OH_2. The conversion of this interaction to an attraction with the positive H_3O^+ subunit in OCO--HO is responsible for the lower energy of T following the proton transfer, particularly notable in view of the intrinsically higher energy of the cis HCOOH subunit involved in that structure.

One final point concerns the near coincidence of the OCOH→O curve in Figure 6 and the broken curve representing the transfer barrier in $(H_2O-H-OH_2)^+$. Owing to the smaller proton affinity of the OH group of HCOOH than that of HOH, one would normally expect lesser difficulty in removing a proton from the former molecule and hence a lower barrier at any given value of $R(O--O)$. However, the $(HCO(OH_2)--OH_2)^+$ configuration is stabilized by the aforementioned attraction between the partial positive charge of H^d and the dipole of the OH_2 subunit whereas no such stabilizing force is present in $(H_2OH--OH_2)^+$. The depression of the left well in the potential of the formic acid system raises the barrier to the point where it is nearly equal to that of $(H_2O-H-OH_2)^+$.

Conclusions

The proton-transfer properties of the C=O within carboxyl are very much like those of the carbonyl within H_2CO, despite the greater complexity of the former group. The primary effect of the neighboring OH is to increase the proton affinity of C=O, making it more difficult for a proton to be extracted. Secondary effects arise from the various possible orientations of the OH, leading to differing intrinsic stabilities of the formic acid subunit and to variations in electrostatic interactions with the partner subunit.

The lowest energy complex of protonated HCOOH with water has the latter molecule H-bonded to the proton cis to the C-H group; there is no second minimum in the potential energy surface corresponding to $(HC(OH)O-HOH_2)^+$ in which the proton resides on the water. In situations where the H-bond length is frozen at some value longer than the equilibrium separation, the proton-transfer potential acquires double-well character. It requires more energy to pull a proton from protonated HCOOH than from the H_2CO analogue, again because of the greater proton affinity of the C=O group in HCOOH. Somewhat higher barriers are associated with removal of the proton cis to C-H as compared to the trans H.

Just as in the case of H_2CO, motion of the proton acceptor toward the C=O axis tends to lower ΔE, pulling the proton away from HCOOH. The primary difference is that the higher proton affinity of HCOOH shifts ΔE to more positive values overall. The rate at which ΔE decreases is affected somewhat by the orientation of the OH group of the carboxyl, because of a number of factors. First are the electrostatic interactions between the OH_2 subunit and the most proximate atoms of HCOOH. A second factor is the intrinsic relative stability of the particular HCOOH or HC-$(OH)_2^+$ conformer within the complex. With regard to out-of-plane distortions, HCOOH manifests somewhat different behavior than does H_2CO. Whereas these distortions raise the transfer barrier for the latter molecule, the barrier is lowered for HCOOH. This discrepancy is attributed to the greater electron density located out of the HCOOH plane as compared to H_2CO.

With regard to the OH group, its proton affinity is lowered by its association with C=O in HCOOH. It is for this reason that the hydroxyl group of HCOOH is not capable of removing a proton from H_3O^+. For any fixed intermolecular separation, it is most difficult (high barrier) to pull a proton from H_3O^+ to a position trans to the C-H bond of HCOOH and to keep it there (low barrier for its removal). The distinction with the cis position is again due to electrostatic interactions between the two subunits.

It thus appears possible to understand the behavior of the COOH group on the basis of the principles developed earlier for the simpler C=O and OH groups within the context of smaller molecules. The additional factors which must be included in the analysis are relatively straightforward and augur well for application of these principles to larger systems for which ab initio calculations may not be feasible.