Calculated Effects of Formaldehyde Substituents on Proton Transfer in $(H_2CO{-}H{-}OCX_2)^+$

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Abstract: In quantum-chemical calculations with full geometry optimization of the energetics of proton-bridged complexes $(H_2CO{-}H{-}OCX_2)^+$, in which X = H, F, Cl, and CH_3, we used a polarized split-valence basis set 4-31G* with fourth-order Moller−Plesset perturbation theory (MP4) treatment for electron correlation. The presence of a fluorine substituent decreases the proton affinity of oxygen; formyl fluoride is more acidic than formaldehyde by 13−15 kcal/mol. In contrast, the methyl group in acetaldehyde increases the proton affinity of oxygen; acetaldehyde is more basic than formaldehyde by about 12 kcal/mol. The proton-transfer potentials for halogen-substituted complexes contain a single minimum corresponding to $(H_2COH^+\cdots OCHX)$, whereas an asymmetric double-well potential was found in methyl-substituted complexes; the global minimum energy corresponds to the conformation $(H_2CO\cdots{}^+HOCHCH_3)$. Proton transfer proceeds with greater difficulty in fluoro-substituted complexes than in the nonsubstituted complex, whereas with much greater ease in methyl-substituted counterparts. Substituted complexes are less stable than nonsubstituted ones; the binding energies are smaller by about 3−5 kcal/mol, regardless of the nature of the substituents. The structures of the complexes vary greatly with the substituents and their positions. They are further analyzed in regard to the direction of the dipole moment of the subunit in the complexes. The transition structures in the proton-transfer potentials all have the central proton on the O−O axis, but the location depends on the type of substituent.

Introduction

Proton transfer in fundamental chemical and biological systems has been extensively investigated.[1−16] In early experimental work, proton transfer occurred in solution such that properties of the transfer process were intertwined with solvent effects. With recent technical advances, solvation and ion pairing can be isolated in the gaseous phase and insight into intrinsic proton transfer is thereby derivable.[17,18]

Calculations of molecular electronic structure successfully supplement experimental work. The structure of transient complexes that are not amenable to experiment can be investigated theoretically.[19] Quantum-chemical calculations have been applied intensively to properties such as proton affinity, activation energy, and potential-energy surface involved in the process of proton transfer. Scheiner et al. systematically investigated proton transfer between groups of varied complexity in small systems, such as $(H_2O{-}H{-}OH_2)^+$ [7] and $(H_2O{-}H{-}OCH_2)^+$,[20] and in more complicated systems involving transfer between oxygen and another atom, such as $(H_2O{-}H{-}SH_2)^+$,[21] $(H_2O{-}H{-}NH_3)^+$,[10,11] $(H_2O{-}H{-}NH_2CHO)^+$,[14] $(NH_3{-}H{-}NH_3)^+$,[7] $(H_2CCH{-}H{-}CHCH_2)^+$,[22] etc. Gronert presented the results of the computations on proton transfer of first- and second-row non-metal hydrides with their conjugate bases.[23] Although several systems have been investigated by means of ab initio calculations, little work has been reported on systems with hydrogens replaced by substituents.[8]

In recent experiments,[24] many protonated aldehyde cluster ions $(RCHO)_nH^+$, n = 1−11, were observed. The structures of these ion clusters remain mysteries. We reported[25] equilibrium structures of the protonated formaldehyde dimer and proton-transfer energy barriers in the potential-energy hypersurfaces. In the present work, we examined systems of protonated formaldehyde derivatives, with the substituents being F, Cl, and CH_3 groups. We sought information about how the transfer potentials are influenced by the electron-withdrawing or -releasing substituent in the complex. The results indicate

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Table 1. Protonation Energy of HXCO (kcal/mol)[a]

	SCF (4-31G*)		MP4 (4-31G*)		
substituent	uncorr	corr	uncorr	corr	expt[b]
none	182.68	181.71	176.74	174.30	184.0 (177.2)[c]
t = F	167.84	167.19	162.91	160.95	
c = F	169.70	168.89	164.79	162.59	
t = CH_3	195.16	194.26	189.66	187.25	195.3 (188.9)[c]
c = CH_3	194.80	193.67	189.41	186.84	

[a] X represents the substituent of H, F, or CH_3. See Figure 1 for the definition of substitutional position. [b] Experimental proton affinity corrected for computed zero-point vibrational energy and contributions from translational and rotational terms. Values in parentheses lack these corrections. [c] See ref 32.

Table 2. Binding Energies of $(H_2CO{-}H{-}OCHX)^+$ (kcal/mol)[a]

	SCF (4-31G*)		MP4 (4-31G*)	
substituent	uncorr	corr	uncorr	corr
none	29.13	27.48	31.84	28.16
t = F	23.39	22.10	24.94	22.35
c = F	24.64	23.36	26.89	24.34
t = CH_3	26.04	24.52	28.15	25.06
c = CH_3	25.73	24.07	28.16	24.82

[a] X represents the substituent of H, F, or CH_3. See Figure 1 for the definition of substitutional position. Binding energy[14] (BE) for X = H, BE: $(H_2CO{-}H{-}OCHX)^+ \leftarrow H_2COH^+ + OCH_2$. For X = F, BE: $(H_2CO{-}H{-}OCHX)^+ \leftarrow H_2COH^+ + OCHF$. For X = CH_3, BE: $(H_2CO{-}H{-}OCHX)^+ \leftarrow H_2CO + HOCHCH_3{}^+$.

that the proton affinities and dipole moments are strongly affected by the position of the substitutions and the character of the substituents. The barriers to proton transfer, the structures and energetics of species on the potential-energy surfaces, are necessary for proper characterization of these systems.

Methods of Calculation

The Gaussian-92 set of ab initio computer codes[26] was employed for all calculations. The polarized split-valence 4-31G* basis set[27] was used with geometry optimization at the Hartree–Fock level. Advantages of this basis set are that it has been demonstrated to yield satisfactory results compared with experimental results[28,29] and that a convenient comparison of our calculated results exists as this set is widely used for calculation of energy barriers for proton transfer in similar systems.[7–11] To take into account the effect of electron correlation, we employed fourth-order Moller–Plesset perturbation theory (MP4).[30] The basis set superposition error (BSSE) inherent in the computation of molecular interaction energies was corrected via the Boys–Bernardi counterpoise technique.[31] These calculated data are listed in Tables 1 and 2.

In order to consider the polarization forces between the two entities, we also tried the calculation using polarization orbitals on H atoms, 4-31G** basis set. In addition, geometry optimization (at the MP2 level) in the calculation of proton affinity and binding energy was performed. These results for relative proton affinities are not better. Nevertheless, a time-consuming trial calculation using a more-extended basis set and an MP4 correction (MP4/4-31G**) for proton affinities of the systems yields satisfactory results as good as those of SCF (4-31G*).

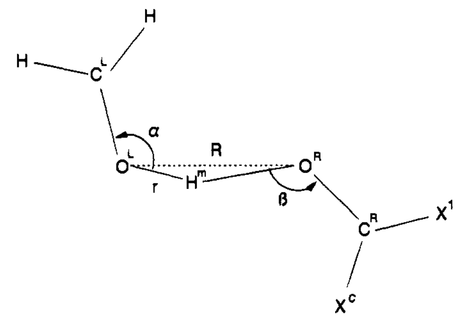

Figure 1. General geometry of fully optimized complexes $(H_2CO{-}H{-}OCX_2)^+$. It is obtained without any prior assumption concerning its symmetry, and all parameters were fully optimized. The left subunit is tagged L, the right R, and the middle proton m. The X atom represents the substituent for the hydrogen atom, and the letters c and t denote substitution on the same (cis) and opposite (trans) sides of the proton H^m, respectively, with respect to the $C^R{-}O^R$ axis.

In the investigation of proton transfer in $(H_2CO{-}H{-}OCX_2)^+$, X = H, F, Cl, and CH_3, the first step was full geometry optimization of these complexes and their isolated subsystems. The positions (c and t) of the substituents and some parameters are explained in Figure 1 (the left subunit is tagged L, the right R, and the middle m). The parameter R denotes the inter-oxygen separation, and α and β denote the angles ($C^LO^LH^m$) and ($C^RO^RH^m$), respectively; c and t represent the substituent (X) located on the same (cis) and opposite (trans) sides of the central proton (H^m), respectively, with respect to the $C^R{-}O^R$ axis. The subunits (formaldehyde monomer and its derivatives) of the complexes were investigated first, followed by calculations of optimized structures of protonated derivatives (with c or t position of substitution). The results appear in Figure 2 with energies computed at the SCF and MP4 levels. When the fully optimized equilibrium structure of each complex $(H_2CO{-}H{-}OCX_2)^+$ was determined, the second step of the calculation of the potential-energy surface for proton transfer was undertaken. The potential-energy profile was obtained by calculating the energy of the system as a function of r (the distance between the carbonyl oxygen O^L and the central proton H^m). The different R values, which were far from equilibrium, were also employed to investigate the energy barriers over a wide range of lengths.

Results and Discussion

This section has three parts to describe the subunits of the complexes, the structural variation of the complexes, and the energetics of the complexes on the potential-energy surfaces of proton transfer.

Subunits. In the lower part of Figure 2A, the energy of trans-protonated acetaldehyde is less than that of the cis one; a smaller steric effect in the trans structure is a reasonable explanation. Cis protonation of formyl fluoride is more favorable by about 2 kcal/mol in Figure 2C, possibly due to the strongly electron-withdrawing character of the F atom that is much nearer the proton (H^m) in the cis form, such that the attraction between these two atoms decreases the energy. Relative to the structure of protonated formaldehyde in Figure 2B, the bond distance $r(H^mO)$ decreases from 0.966 to 0.963 Å (cis) and 0.962 Å (trans) when methyl replaces hydrogen and r(CO) increases from 1.230 to 1.242 Å (cis) and 1.243 Å (trans). In contrast, $r(H^mO)$ increases and the r(CO) decreases when fluorine replaces hydrogen.

The energy required to extract the proton from each of the protonated monomers $(HXCO)H^+$, X = H, CH_3, and F, is given in Table 1, with and without BSSE corrections calculated at SCF and MP4 levels. These corrections are about 1 kcal/mol at the SCF level and about 2 kcal/mol at the MP4 level but have no effect on the relative energetics at both levels. These results are similar to those for the amides system found by Scheiner et al.[14] The fact that protonation of the oxygen atom of formaldehyde is energetically more stable with a CH_3

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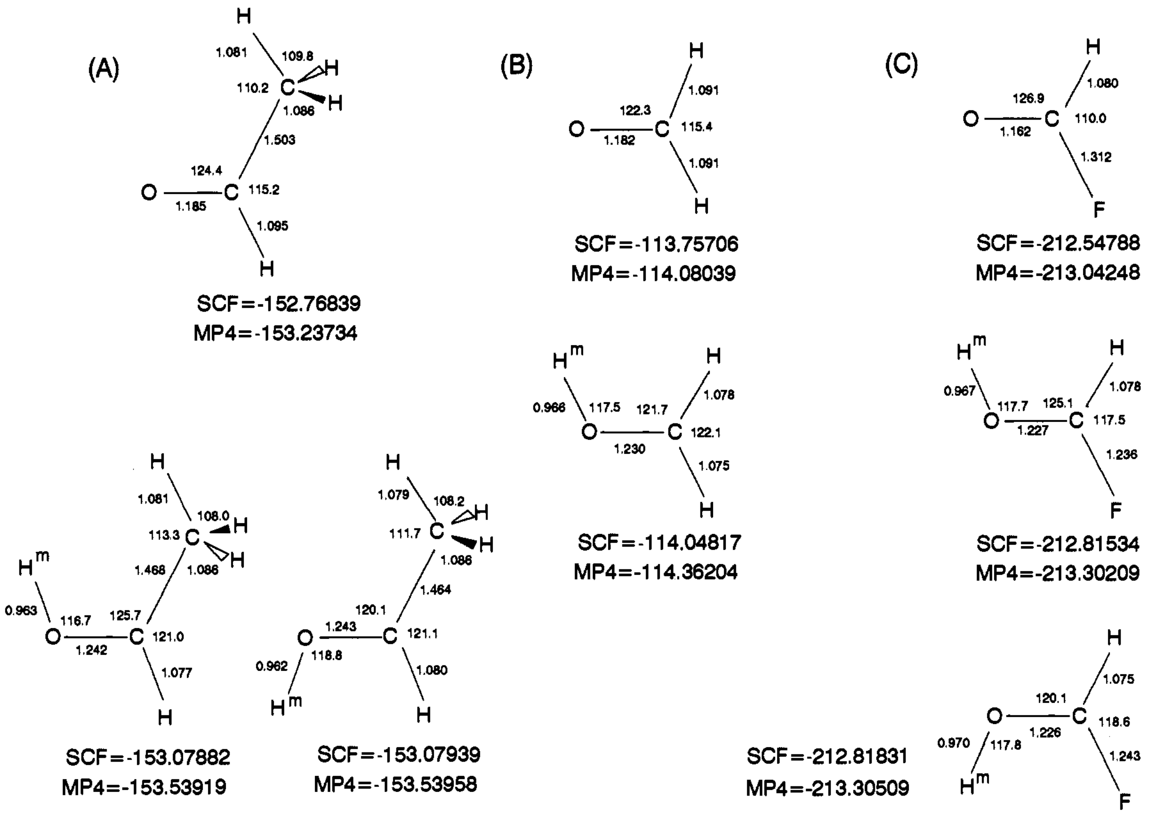

Figure 2. Optimized structures of the subunits (formaldehyde monomer and its derivatives) together with their protonated counterparts at the c and t positions (A) for acetaldehyde, (B) for formaldehyde, and (C) for formyl fluoride (bond lengths in angstroms and angles in degrees).

substituent than the fluoro-substituted counterpart can be rationalized on the basis of greater basicity induced by the electron-releasing methyl group. The experimental proton affinities,[32] corrected with computed zero-point vibrational energies and by translational and rotational contributions, are listed in the last column of Table 1. There is satisfactory agreement, especially with the SCF values uncorrected for BSSE, but MP4 values are slightly underestimated. The relative values of experimental data are in good accord with the calculated ones. Such agreement is evidence that enables us to employ these theoretical procedures to examine properly the energetics of proton transfer in the current systems.

Structural Variation. The fully optimized equilibrium structure of each protonated formaldehyde complex and its substituted (cis and trans) analogue is given in Figure 3, with energies calculated at SCF and MP4 levels. In parts A and B of Figure 3, the two stable structures of the protonated formaldehyde dimer are symmetric; the left portion of part A has exactly the same structure as the right portion in part B, and vice versa. Hence, there exists a double-well potential with parts A and B located at the two minima in the process of proton transfer.[25] When fluorine replaces hydrogen (either cis or trans), as shown in parts C and D, there is only one minimum with the proton shifted between the two oxygen extremes (O^R and O^L) at their equilibrium length; the central proton (H^m) remains nearer the left unsubstituted subunit in the structure of minimum energy, $r(O^LH^m) < r(O^RH^m)$, and no proton transfer occurs in these complexes. Energetically, the cis-substituted fluoro complex is more stable than the trans analogue, in agreement with the energies of the protonated monomers in Figure 2C. When methyl replaces hydrogen (either cis or trans), two local-minimum structures are found at their equilibrium lengths in each position of substitution. The one at the global minimum has the central proton (H^m) situated near the right substituted subunit; that is, $r(O^LH^m) > r(O^RH^m)$ as shown in Figure 3E,F. The energy of the global minimum is lower by about 5 kcal/mol relative to the energy of the other minimum, in which the proton is closer to the left unsubstituted formaldehyde.

According to the results in Table 2, the binding energies[14] of the substituted complexes (with either F or CH_3) all decrease by 3−5 kcal/mol at both levels of calculations. Hence, the substituted complexes are less stable than the protonated formaldehyde dimer, probably due to the asymmetric configurations in the substituted complexes, which increase the bond lengths of $R(O^L{-}O^R)$ and make the systems unstable. This calculated result is in good agreement with that found by Mautner[39] in his experiments where the strongest H bonds were formed between species with similar proton affinities. The counterpoise corrections amount to about 1.5 kcal/mol at the SCF level and up to 3 kcal/mol at the MP4 level; these values exceed those in Table 1, as more basis functions were employed in the calculations on complexes.

The equilibrium structures of substituted protonated complexes vary greatly relative to the unsubstituted $(H_2CO{-}H{-}OCH_2)^+$ complex. In Table 3, the distance $R(O^L{-}O^R)$ in each substituted complx, with either an electron-donating or -withdrawing substituent, is greater by at least 0.05 Å and more enhanced for disubstituted complexes. As shown in Table 3, $R(O^L{-}O^R)$ of the difluoro derivative increases by 0.10 Å from

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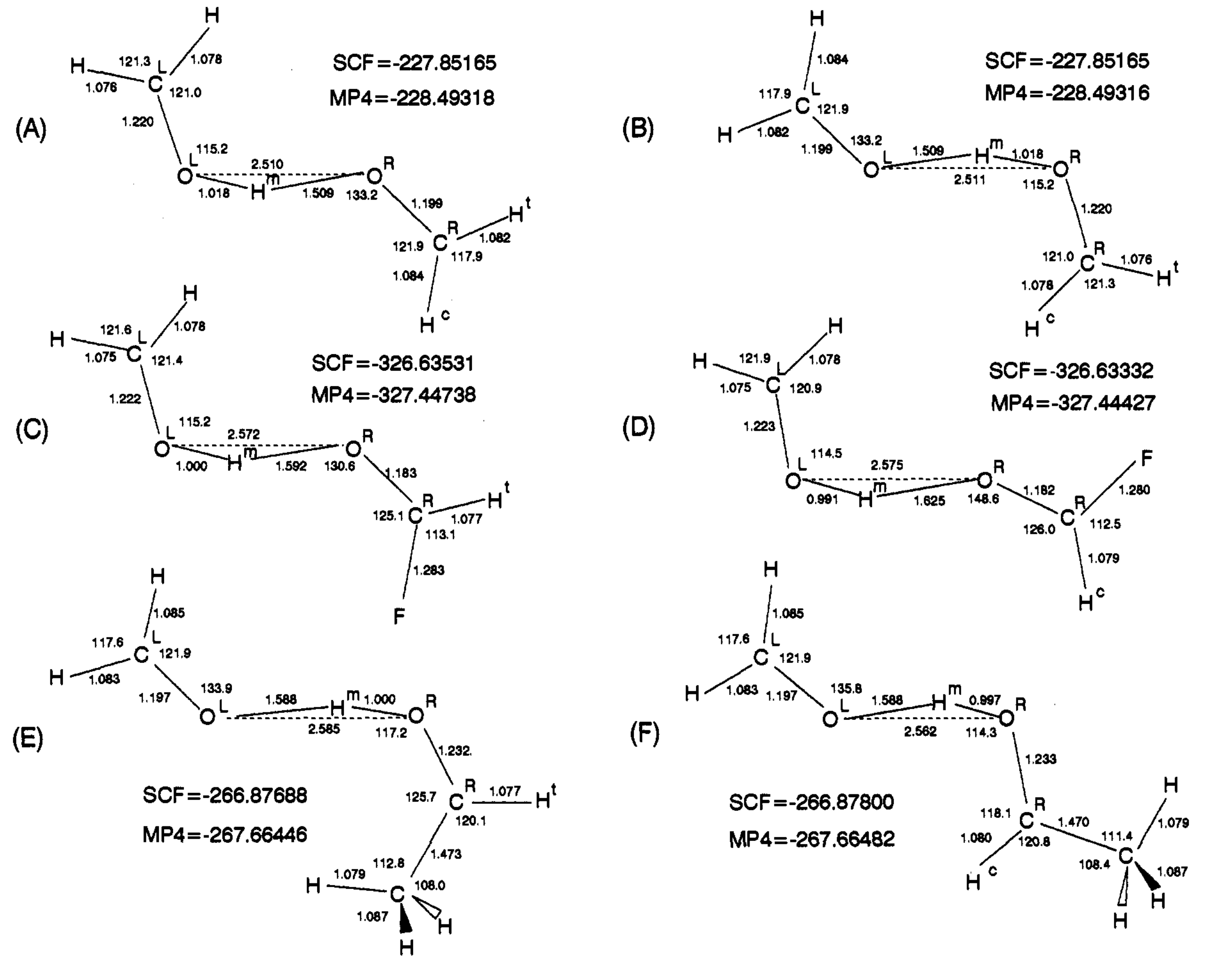

Figure 3. Optimized equilibrium structures of protonated formaldehyde complexes and their counterparts at the c and t positions. (A) and (B) are two stable symmetric structures of protonated formaldehyde complexes, (C) and (D) are for *cis*- and *trans*-fluoro-substituted complexes, and (E) and (F) are for *cis*- and *trans*-methyl-substituted complexes (bond lengths in angstroms and angles in degrees).

Table 3. Fully Optimized Geometry[a,b] of $(H_2CO-H-OCX_2)^+$, X = H, F, Cl, and CH_3

substituent	R (O^L-O^R)	r (O^LH^m)	r (O^RH^m)	α	β	r (O^LC^L)	r (O^RC^R)
none	2.509	1.018	1.509	115.2	133.2	1.220	1.198
t = F	2.575	0.991	1.625	114.5	148.6	1.223	1.182
c = F	2.572	1.000	1.592	115.2	130.6	1.222	1.183
c,t = F	2.608	0.988	1.653	115.1	143.9	1.224	1.177
t = Cl	2.561	0.997	1.600	114.6	142.5	1.223	1.189
c = Cl	2.561	1.003	1.579	115.1	131.5	1.221	1.189
c,t = Cl	2.581	0.994	1.618	114.8	137.0	1.223	1.184
t = CH_3	2.562	1.589	0.997	135.8	114.2	1.197	1.232
c = CH_3	2.585	1.588	1.000	133.9	117.2	1.197	1.232
c,t = CH_3	2.625	1.637	0.989	135.0	117.1	1.195	1.244

[a] The conformation for F and Cl substituents is $(H_2COH\cdots OCX_2)^+$ and for CH_3 is $(H_2CO\cdots HOCX_2)^+$. [b] See Figure 1 for the definition of parameters. All distances in angstroms and angles in degrees calculated by using 4-31G* basis set.

2.51 to 2.61 Å, whereas $R(O^L-O^R)$ of the dichloro analogue increases by about 0.07 Å from 2.51 to 2.58 Å. The more strongly electron-withdrawing character of the fluorine atom accounts for this result. In methyl-substituted complexes, the effect of the electron-releasing nature of the methyl group in the right subunit increases the electron density of the oxygen atom, which consequently attracts the middle proton rightward to strengthen the O^R-H^m bond and, simultaneously, to weaken the O^L-H^m bond. This effect is promoted in the dimethyl-substituted complex in which the distance $R(O^L-O^R)$ is 2.63 Å, increased by 0.12 Å compared with 2.51 Å for the nonsubstituted complex.

Other interesting properties of the substituted complexes are the α and β angles, which are strongly affected by the dipole moment of the right substituted subunit. The explanation of the large transformation of the conformations in the substituted complexes in terms of dipole moment follows that found by Scheiner and Hillenbrand[20] in the system involving carbonyl and hydroxyl oxygens. In the present paper, we employ the description given in our previous work,[25] based on the change of dipole moment to explain the alteration of these angles. In the conformation in Figure 3A, the angle (COH) of the left portion α equals 115.2°, near the ideal angle (120°) if we consider only the directionality of lone-pair orbitals (assuming sp^2 hybridization) on the oxygen atom of OCH_2. When a much smaller distance $r(O^LH^m)$ (0.65 Å) was tried, α was calculated to be 119.3°. The angle β at the right portion of the complex appears to be 133.2°, mostly determined by the direction of the dipole moment with a longer bond. At a much longer bond with $r(O^RH^m)$ equal to about 4.0 Å, this angle is calculated to be 180°, predominantly controlled by the direction of the dipole moment of the OCH_2 molecule (Figure 4A).

On the basis of these arguments on the nonsubstituted protonated formaldehyde dimer, we rationalize the variation of α and β angles in the substituted analogues. In *trans*-$(H_2COH-OCHF)^+$, the calculated angle β increased to 148.6° (Table 3). In justification, firstly, as the bond O^RH^m in the substituted complex lengthens by 0.116 Å (from 1.509 to 1.625 Å), the

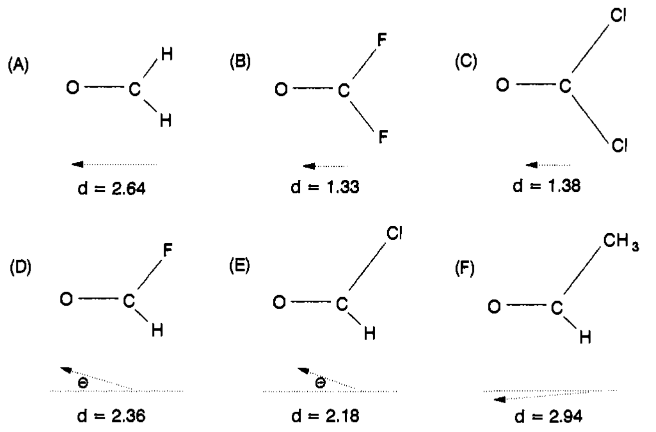

Figure 4. Directions and magnitudes of calculated dipole moments of formaldehyde and its substituted counterparts. The unit is D (debye).

influence of the dipole moment on the β angle becomes enhanced with this large increment of bond distance; secondly, the direction of the dipole moment of the OCHF subunit (Figure 4D) shifts upward with a positive angle θ with respect to the C^R-O^R axis. For these reasons, the left subunit H_2COH^+ has to turn some angle upward, and the consequence is a β angle greatly increased from 133.2 to 148.6°, whereas α diminishes only 0.7°, as the bond distance $r(O^LH^m)$ deviates by only 0.03 Å and causes no apparent alteration of the α angle. For *trans*-$(H_2COH-OCHCl)^+$, the major effects are similar; the dipole moment of OCHCl (in Figure 4E) is smaller, 2.18 D, comparable with that of OCHF, 2.36 D, and the increment of $r(O^RH^m)$ (0.091 Å) is less by 0.025 Å than the case of the trans-substituted fluorine complex. Therefore, it results in a less increased β angle (from 133.2 to 142.5°). Unlike the trans substitution, the direction of the dipole moment of OCHF in the *cis*-$(H_2COH-OCHF)^+$ complex turns counterclockwise $(-\theta)$ with respect to the C^R-O^R axis, which has the effect of forcing the left subunit to rotate downward compared with the nonsubstituted complex and results in β decreasing from 133.2 to 130.6°. Similar arguments apply to the slightly decreased β angle (from 133.2 to 131.5°) in the *cis*-$(H_2COH-OCHCl)^+$ complex.

In the difluoro-substituted complex, the direction of the dipole moment of OCF_2 is the same as that of OCH_2 in $(H_2COH-OCH_2)^+$, parallel to the C^R-O^R axis, but the magnitude decreases to 1.33 D (Figure 4B). This decreased dipole moment would reduce the β angle. However, the much longer bond distance of $r(O^RH^m)$, 1.653 Å, overturns the case. As a result, the β angle increases to 143.9°, the second largest in Table 3. Similar arguments apply to β (137.0°) calculated for the dichloro-substituted complex. In this system, the bond $r(O^RH^m)$ is shorter, owing to the smaller electron-withdrawing character of chlorine, and the effect induced by the dipole moment is thus less apparent than in the preceding difluorine case.

Energetics. The methods of calculating potential surfaces have been fully described.[25] In a small modification in the calculation of the energetics of the transition structures in this work, the constraint of fixed $R(O^L-O^R)$ was removed in the process of structure optimization of the $(H_2COH-OCH_2)^+$ complex. The optimized $R(O^L-O^R)$ value for the transition structure is considerably smaller than for the structure at equilibrium. The energy barrier for proton transfer in $(H_2CO-H-OCH_2)^+$ calculated according to this modification is much lower, 1.43 kcal/mol relative to 3.49 kcal/mol in the previous work, subject to a fixed $R(O^L-O^R)$ of the transition structure equal to that of $R(O^L-O^R)$ in the equilibrium structure. This difference of energy barriers indicates that the right OCH_2 moiety of the complex is energetically favored in moving toward the central proton when the proton begins to transfer from the left. This phenomenon can be seen for only the nonsubstituted $(H_2COH-OCH_2)^+$ complex, as there is no double-well transfer potential for other species (except methyl-substituted complexes) at their equilibrium $R(O^L-O^R)$ distances. Therefore, it is not possible to perform similar work (to release the constraint of $R(O^L-O^R)$) for other species at their elongated structures for which a double-well potential might exist. We present work related to the energy and $R(O^L-O^R)$ distance of the $(H_2COH-OCH_2)^+$ complex. The transition structure has the smallest $R(O^L-L^R)$ value (2.38 Å) when the proton transfer takes place from the equilibrium conformation (in which $R(O^L-O^R) = 2.509$ Å and $r(O^LH^m) = 1.018$ Å). For the methyl-substituted $(H_2CO-HOCHCH_3)^+$ complex, an asymmetric double-well potential exists. The search of the transition structure without the constraint of $R(O^L-O^R)$ was undertaken, and we had difficulties locating the transition structure on the potential hypersurface when the motion of H^m was restricted to the O^L-O^R coordinate. Probably, the potential-energy surface near the transition structure is too smooth (the energy barrier has been greatly reduced, and the transition structure is nearer the left well), or a more complicated topology might exist, resulting in a separate reaction path. This phenomenon observed in several systems was described as chemical hysteresis,[34] or branching points,[35] at which the reaction coordinate deviates to another blind valley.[36-38] However, the character of a decreased $R(O^L-O^R)$ with increasing energy of the complex in the process of proton transfer is definitely observed in our calculations.

For most substituted complexes, the path of proton transfer in elongated structures is similar to that in $(H_2CO-H-OCH_2)^+$,[25] in which the central proton moves from beneath the O−O axis to above it. However, they have distinct transition structures. As shown in Figure 5, all structures have the central proton H^m situated on the O−O axis, but the point of location is strongly connected to the substituents. The nonsubstituted complex in Figure 5A has the proton H^m bisecting the O−O axis, as the two subunits are equivalent to each other. However, other species all follow the Hammett principle,[33] which holds that the transition structure shifts its position toward the greater of the two minima. For example, the *cis*- and *trans*-fluoro-substituted complexes position H^m near O^R as shown in parts B and C of Figure 5, whereas the methyl-substituted analogues place H^m near O^L as given in parts D and E of the same figure.

When proton transfer proceeds from the left subunit, other features are worthy of mention. In all complexes, the length of the C^L-O^L bond decreases, but that of C^R-O^R increases. These properties can be understood as the central H^m starting to shift from O^L and the C^L-O^L bond regaining some electron density from the weakened O^L-H^m bond and thus shortening. Moreover, when H^m approaches O^R, the gradually forming H^m-O^R bond decreases the electron density between the O^R and C^R atoms; therefore, the bond length $r(C^RO^R)$ increases. Bond lengths $r(C^RH^c$ or $C^RH^t)$ in the nonsubstituted complex and $r(C^RF)$ and $r(C^RC)$ decrease moderately as the proton H^m advances. These strengthening bonds obtain some electron densities from the gradual stretching of the C^R-O^R bond.

The barriers calculated for the transfer of the proton from the left H_2CO to the right subunit are presented as E_f, and those of the transfer in the reverse direction as E_r. The barriers are calculated at three elongated $R(O^L-O^R)$ values, $R = 2.71$ Å, $R = R_{eq} + 0.15R_{eq}$, and $R = R_{eq} + 0.6$ Å (Table 4). Also listed are the energy differences both at the SCF and at the MP4 levels between the two minima in each transfer potential, defined as $\Delta E = E(H_2CO-HOCHX)^+ - E(H_2COH-OCHX)^+$ at these extended R values. In all complexes, the barriers increase

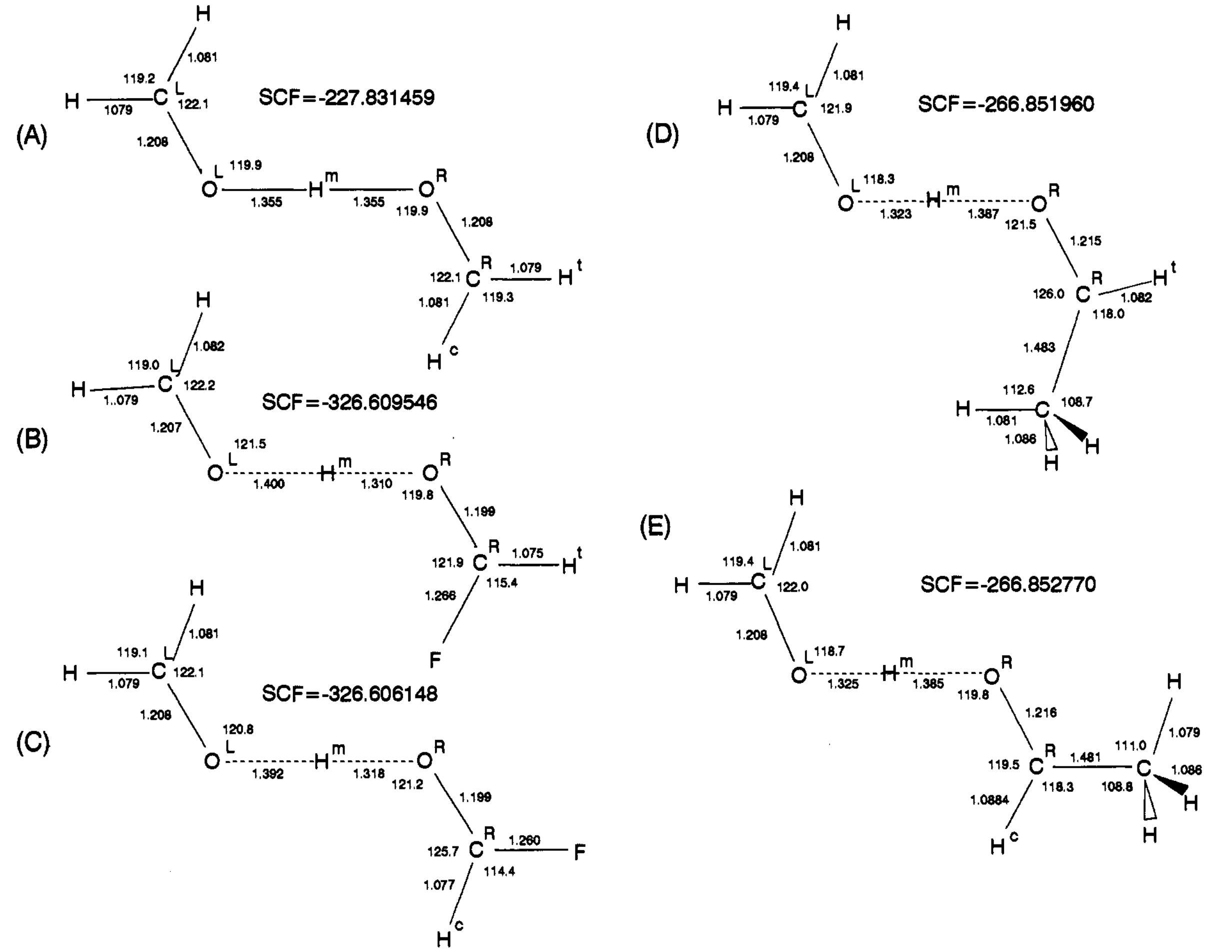

Figure 5. Optimized transition structures of $(H_2CO{-}H{-}OCH_2)^+$ and $(H_2CO{-}H{-}OCHX)^+$ during proton transfer at an elongated distance $R(O^L{-}O^R) = 2.71$ Å; X = F and CH_3 at either cis, (B) and (D), or trans, (C) and (E), position of substitution (bond lengths in angstroms and angles in degrees).

Table 4. Energy Barrier and Well Depth Difference (kcal/mol) for Proton Transfer in $(H_2CO{-}H{-}OCHX)^+$, X = F, CH_3, and H

	$R = 2.710$ Å			$R = R_{eq} + 0.15R_{eq}$[a]				$R = R_{eq} + 0.6$ Å[b]			
substituent	E_f[c]	E_r[d]	ΔE	E_f	E_r	ΔE	R	E_f	E_r	ΔE	R
none (SCF)	11.3	11.3	0.0	20.3	20.3	0.0	2.887	33.3	33.3	0.0	3.110
t = F	16.5	8.3	8.1	30.6	21.0	9.5	2.961	44.3	34.5	9.8	3.175
c = F	15.5	6.8	8.8	28.7	18.7	10.0	2.958	41.4	30.7	10.7	3.172
t = CH_3	8.6	15.1	−6.5	20.4	28.2	−7.7	2.946	33.3	41.7	−8.4	3.162
c = CH_3	8.8	15.2	−6.3	22.0	30.1	−8.1	2.973	35.1	43.6	−8.5	3.185
none (MP4)	4.0	4.0	0.0	10.1	10.1	0.0	2.887	19.4	19.4	0.0	3.110
t = F	8.7	1.9	6.7	19.0	10.7	8.3	2.961	30.1	21.0	9.1	3.175
c = F	8.4	0.9	7.5	17.9	9.0	9.0	2.958	27.8	18.2	9.6	3.172
t = CH_3	1.6	7.5	−5.9	9.4	16.8	−7.4	2.946	18.5	27.0	−8.4	3.162
c = CH_3	1.5	7.9	−6.5	10.0	18.8	−8.8	2.973	19.4	29.3	−9.9	3.185

[a] The $O^L{-}O^R$ distances of equilibrium structures plus 15% elongation. [b] The $O^L{-}O^R$ distances of equilibrium structures plus 0.6 Å. [c] Transfer from formaldehyde to the subunit having the substituent. [d] Transfer from the subunit having the substituent to formaldehyde.

rapidly as the two subunits draw away from one another, in accord with previous calculations of related transfer in other systems.[14,25,31] The two wells in the potential surface at elongated $R(O^L{-}O^R)$ distances are still symmetric with each other in the complex $(H_2CO{-}H{-}OCH_2)^+$. In substituted complexes, however, an asymmetric double-well character of the potential surface appears. With an F substituent at either the t or the c position at $R = 2.71$ Å, the left well is deeper by about 8 kcal/mol. The conformation $(H_2COH{-}OCHF)^+$ is more thermodynamically stable than that of $(H_2CO{-}HOCHF)^+$. In methyl-substituted complexes, the right well is lower by about 6 kcal/mol; the conformation $(H_2COH{-}OCHCH_3)^+$ is less stable than that of $(H_2CO{-}HOCHCH_3)^+$. According to the E_f values in Table 4, the barriers for proton transfer from protonated formaldehyde H_2COH^+ to the other subunit of the complex are altered by the substituents at the other end. One conclusion is that the more electron-donating the character of the substituent at the other end is, the easier the transfer of the proton can proceed; the opposite trend applies to an electron-withdrawing substituent.

In most complexes, the difference of the values of ΔE with respect to the values of R is small and approaches the difference of protonation energies of the two monomers, if the two subunits are further stretched. The variations of the E_f and E_r values are sensitive to intersubunit separations greater than 10 kcal/mol for every 0.2 Å extension. The value of E_f in the *trans*-

fluoro-substituted complex is greater than that in the cis counterpart, and the differences of the E_f values between the two complexes increase gradually with the elongation of R distances. A similar trend is found for the differences of the E_r values. These findings are consistent with the existing interaction between F and H^m atoms in the transition structure of the cis conformation, which lowers the energy at the transition structure and, therefore, decreases the barrier for the transfer of the proton in the *cis*-fluoro-substituted complex. This similar effect is not seen in the transition structure of the trans counterpart because of the larger separation of H^m and F atoms in the trans conformation. This feature is more evident with an increase of R, as H^m is nearer F in a more elongated transition structure, and more interaction energy is contributed to the system, which increases the differences between the two E_f and two E_r values of *cis*- and *trans*-fluoro complexes, in a more stretched $R(O^L-O^R)$ distance. The opposite trend of the E_f values holds in methyl-substituted complexes; that is, the trans one has a smaller E_f value. A reasonable explanation is that the right subunits are nearer the central proton H^m in the transition structure, which induces the steric effect (methyl group and H^m atom), more evident in the cis conformation; therefore, it increases the energy in the cis transition structure relative to the trans counterpart. The E_f value is thus greater in the *cis*-methyl complex.

The barriers computed with the inclusion of correlation (MP4) (second part of Table 4) are significantly lower than the corresponding SCF values. This pattern conforms to behavior described in the works of Scheiner et al.[14,15,22] However, the difference in energy between the two wells of the potential (ΔE) is less sensitive to intersubunit separation in either level of calculations. It is very interesting to find in the calculated MP4 data that the E_f values of the methyl-substituted complex and the E_r values of the fluoro-substituted complex reduce greatly and approach zero as R decreases. In fact, we are able to find, with electron correlation added in the calculations, that the calculated double well potentials all collapse to single-well potentials when the R values are further reduced to their equilibrium distances.

Summary

As the proton affinity of formaldehyde exceeds that of formyl fluoride by some 14 kcal/mol, it is not surprising to find a single-well potential for proton transfer between the two. However, an asymmetric double-well potential occurs in the system of methyl-substituted complexes at equilibrium, although the proton affinity of acetaldehyde surpasses that of formaldehyde by some 12 kcal/mol. Despite the two opposite effects on the proton affinity of the oxygen atom in HXCO when X is replaced by a F atom or a CH_3 group, the binding energies of the corresponding complexes $(H_2CO-H-OCHX)^+$ all decline by 3−5 kcal/mol from 29.13 kcal/mol, the binding energy of the nonsubstituted complex. As a result, the substituted complexes are less stable, regardless of the type of substituent. Moreover, according to the corresponding protonation energies of the monomers, it is not difficult to determine the products of the substituted complexes undergoing unimolecular decomposition. The complexes with electron-withdrawing substituents decompose to H_2COH^+ and OCHX, but the complexes with electron-releasing substituents decompose to H_2CO and ^+HOCHX.

When proton transfer proceeds, the central H^m moves from beneath the O−O axis to above it. In a complex like $(H_2CO-H-OCHX)^+$ in which there exits a double-well potential of proton transfer at the equilibrium structure, $R(O^L-O^R)$ is shorter in the transition structure than in the equilibrium structure, indicating the preferred mutual motions of the proton H^m and the two subunits in the process of transfer. The energy barriers for transfer of the proton in both directions increase rapidly as the two subunits of the complexes are drawn further apart.[20] However, the energy differences between the two minima in each transfer potential are less sensitive to intersubunit separations.

Our calculations have revealed the most stable structures of the derivatives of the protonated formaldehyde dimer. The type of substituents and the position of substitutions related to the energy barriers of proton transfer can provide valuable information for spectral investigation of proton transfer in cluster ions.

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