A Molecular Orbital Study of Protonation. 3. Equilibrium Structures and Energies of Ions RCHOH+

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Abstract: Ab initio SCF calculations with the STO-3G and 4-31G basis sets have been performed to determine the equilibrium structures of protonated monosubstituted carbonyl compounds, and the proton affinities of the corresponding bases. Protonation of these bases leads to significant structural changes in the relaxed ions, including an increase in the carbonyl C–O bond length, a decrease in the length of the bond from the carbonyl carbon to the substituent in particular cases, and changes in the bond angles about the carbonyl carbon. The rigid monomer restriction when applied to these protonated carbonyl bases is therefore a severe restriction, since it neglects these changes in the ions. In addition, this approximation introduces an error into the computed proton affinities of these bases, the magnitude of which depends on the substituent. As a result, relaxation of this restriction may lead to changes in the calculated relative proton affinities of carbonyl bases. Protonation of carbonyl compounds results in electron transfer to the proton, and a further polarization of the π electron density toward and within the carbonyl group, which leaves the carbonyl oxygen negatively charged in these ions. The ease of this π electron polarization appears to be an important factor in determining the relative proton affinities of carbonyl bases.

Introduction

Recent developments in chemical ionization mass spectrometry and ion cyclotron resonance have led to the determination of gas-phase equilibrium constants for proton transfer reactions

$$B_1H^+ + B_2 \rightleftarrows B_1 + B_2H^+$$

yielding the relative proton affinities of B_1 and B_2 to a precision of ±0.2 kcal/mol.[1,2] The importance of these measurements in the gas phase derives from the fact that they have been obtained in the absence of a solvent, and are therefore a direct reflection of the intrinsic basicity of molecules toward a proton. When combined with data on the proton affinities of the same molecules in solution, they assume increased significance as a reference for evaluating the effect of the solvent on molecular basicity.[3]

Although the experimental gas-phase data provide accurate proton affinities, they do not provide direct information concerning the equilibrium structures of the protonated compounds. Nor is information available concerning the electron distribution in these ions, except through inference based on the reactions which these ions undergo. Providing such data and interpreting the gas-phase results are functions well suited to molecular orbital studies.

In part 1 of this series,[4] a study was made of the relative proton affinities of substituted carbonyl compounds. In that study, the rigid monomer approximation was applied to the base, and the protonated carbonyl compounds were geometry optimized in two protonation coordinates: R, the H^+–O distance, and θ the H^+–O–C angle. This restriction was investigated in protonated formaldehyde, where it was shown to neglect significant structural changes in the base, and to introduce a rather small (2%) error into the computed proton affinity. It was noted at that time that since this restriction might be more severe both structurally and energetically in more complex bases, a more thorough investigation of the rigid monomer approximation was a problem for future study. Such an investigation comprises part of the present study, in which the equilibrium structures of relaxed protonated monosubstituted carbonyl compounds $RCHOH^+$ have been determined. The substituents R consist of the isoelectronic saturated groups CH_3, NH_2, OH, and F and the unsaturated groups CHO and C_2H_3. The purpose of this study is threefold: (1) to determine the equilibrium structures of these relaxed ions and the proton affinities of the bases RCHO; (2) to examine the effect of protonation on the structures of ions $RCHOH^+$ and on the electron distribution in these ions, and (3) to evaluate the severity of the rigid monomer restriction by comparing both specific results and general conclusions from this work and from part 1.

Method of Calculation

Wave functions for the bases RCHO and the corresponding ions $RCHOH^+$ have been expressed as single Slater determinants Ψ

$$\Psi = |\psi_1(1)\bar{\psi}_1(2)\cdots\psi_n(2n-1)\bar{\psi}_n(2n)|/\sqrt{(2n)!}$$

consisting of doubly occupied molecular orbitals (MOs). The MOs ψ_i are expressed as linear combinations of atomic basis functions ϕ_μ (the LCAO approximation)

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu$$

with the coefficients $c_{\mu i}$ determined by solving the Roothaan equations.[5] Two atomic orbital basis sets have been used in this investigation. The first, the minimal STO-3G basis set with standard scale factors,[6] has been employed in the determination of the equilibrium structures of the series of ions $RCHOH^+$. Although this basis set leads to proton affinities which are significantly larger than experimental values, it has been shown in part 1 that some general features of protonated ions are evident even at this level. However, since the basis set influences the computed properties of these ions, the larger 4-31G basis set,[7] which yields proton affinities in much better agreement with experimental data,[8] has also been used to investigate the bases H_2CO, $(CH_3)CHO$, and FCHO and the corresponding ions H_2COH^+, $(CH_3)CHOH^+$, and $FCHOH^+$. By comparing the STO-3G and 4-31G results, general trends independent of these two basis sets may be identified, and the rigid monomer restriction may be evaluated at two different levels of theoretical treatment.

Protonation of the monosubstituted carbonyl compounds RCHO, which are shown in Figure 1, may occur at the carbonyl oxygen on either side of the carbonyl group. As a result, two sets of ions $RCHOH^+$ exist, as illustrated in Figure 2. Ions in set A are those in which protonation occurs trans to the substituent R, while ions in set B are those in which cis protonation occurs. For ions in both sets, bond distances and bond angles have been optimized cyclicly and independently with both the STO-3G and 4-31G basis sets to ±0.01 Å and ±1°,

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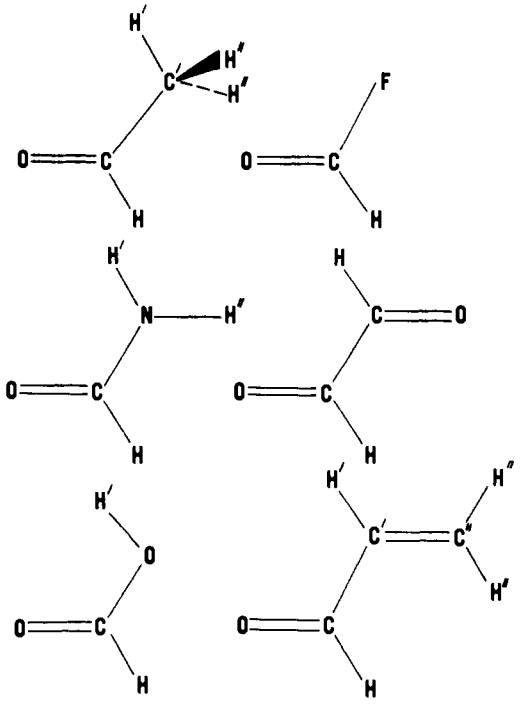


Figure 1. The monosubstituted carbonyl compounds.

respectively, subject to C_s symmetry and the constraints noted in Table I. Parabolic interpolation has been employed to estimate bond distances to 0.001 Å and bond angles to 0.1°. The same optimization procedure has been used to determine the 4-31G equilibrium structures of the bases $(CH_3)CHO$ and FCHO, which have not been determined previously. The 4-31G structure of H_2CO has been reported,[7] and was used in this study.

The proton affinity of the base RCHO is the negative ΔE for the exothermic reaction

$$B + H^+ \rightarrow BH^+$$

The proton affinities of the substituted carbonyl compounds relative to H_2CO are then given by the quantity $-\delta\Delta E$, which is the energy of the proton transfer reaction

$$H_2COH^+ + RCHO \rightleftharpoons H_2CO + RCHOH^+$$

A positive value of $-\delta\Delta E$ indicates that the proton affinity of RCHO is greater than that of H_2CO. All calculations reported in this work have been performed in double precision on IBM 370/145 and 370/148 computers.

Results and Discussion

STO-3G Results. The relative proton affinities ($-\delta\Delta E$) of the bases RCHO determined from the fully optimized ions $RCHOH^+$ are reported in Table II. The effect of the rigid monomer restriction on calculated relative proton affinities can be evaluated by comparing these data with the proton affinities obtained in part 1, which are also reported in Table II. Relaxing the rigid monomer restriction necessarily leads to a larger proton affinity. Relaxation of this restriction increases the calculated proton affinity of acetaldehyde and glyoxal by approximately 5 kcal/mol (a 2% change), similar to the 4 kcal/mol increase determined for formaldehyde. The increase in the calculated proton affinity upon ion relaxation is about 8 kcal/mol (4%) for formyl fluoride and acrolein. A larger increase of about 12 kcal/mol (5%) is found for formic acid, where a significant increase in the C-O-H angle is coupled to a decrease in the C-O single bond distance in the ions. The largest increase in proton affinity upon ion relaxation occurs

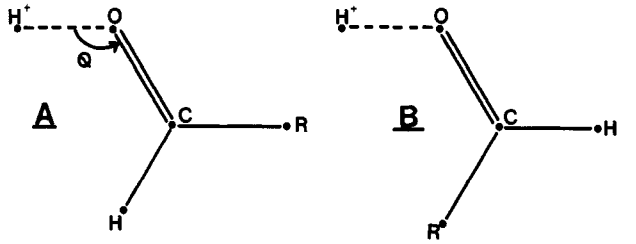


Figure 2. The ions $RCHOH^+$, A and B.

for formamide, the base which has the highest proton affinity, where relaxation increases the stabilities of the trans and cis protonated structures by 15 and 20 kcal/mol, respectively.

Figure 3 shows graphically the effect of the rigid monomer restriction on the proton affinities of substituted carbonyl bases relative to formaldehyde. In Figure 3, $-\delta\Delta E$ for the fully optimized ions $RCHOH^+$ is plotted against $-\delta\Delta E$ for the rigid monomer ions. The line through the point (0,0) with a slope of 1 is a reference on which all points would lie if geometry optimization increased all of the proton affinities by the same amount, so that the rigid monomer restriction on proton affinities would be independent of the substituent. The distance along the ordinate from any point to the reference line measures the severity of the rigid monomer restriction for a given base relative to formaldehyde. It is significant that all of the points for ions in both sets A and B lie above this line. Therefore, the rigid monomer restriction is more severe in the protonated substituted carbonyl compounds than it is in protonated formaldehyde, even when the proton affinity of the base is lower than that of formaldehyde.

The data of Table II and Figure 3 indicate that the severity of the rigid monomer restriction on the computed proton affinities of bases RCHO has a greater dependence on the nature of the substituent than on the position of the proton cis or trans to the substituent. The only significant change in the relative stabilities of corresponding ions in sets A and B resulting from ion relaxation is found in the protonated formamides, where relaxation of the rigid monomer restriction stabilizes the cis structure 5.2 kcal/mol more than the trans. Despite the errors introduced by the rigid monomer restriction, some general observations made in part 1, namely, that for $(CH_3)CHO$ and $(C_2H_3)CHO$ cis and trans protonated ions have similar stabilities, and that trans protonation is more favorable than cis in all other cases except FCHO, are supported by the results of this study in which the rigid monomer restriction has been relaxed. Similarly, the prediction of part 1 that all of the bases RCHO except FCHO have higher proton affinities than H_2CO is consistent with the data for the fully optimized ions. However, it is apparent that since the severity of the rigid monomer restriction does depend to some extent on the nature of the substituent, changes in the relative proton affinities of bases RCHO can occur when this restriction is relaxed. In particular, the data for the fully optimized ions indicate that FCHO and H_2CO have similar proton affinities, and that (HO)CHO has a greater proton affinity than $(CH_3)CHO$, contrary to experimental data.[2] It should be noted, however, that the proton affinities of FCHO and (HO)CHO computed with the STO-3G basis set are probably too high relative to H_2CO, owing to an underestimation of the electronegativity of the substituents F and OH by this minimal basis set.

The equilibrium structures of the fully optimized ions $RCHOH^+$ A and B are reported in Table I. Also reported are the equilibrium structures of the bases RCHO[9] and the optimized values of the protonation coordinates R and θ obtained subject to the rigid monomer restriction.[4] The effect of protonation on the structures of the ions $RCHOH^+$ may be determined by comparing these two sets of data.

Table I. Structures of Ions RCHOH⁺ (STO-3G)[a]

RCHOH⁺		Rigid monomer[b]	Optimized A[c]	Optimized B[c]	RCHOH⁺		Rigid monomer[b]	Optimized A[c]	Optimized B[c]
R = H[d]	CO	1.217	1.271			OCH	125.9	124.4	115.9
	CH_a[e]	1.101	1.114			COH′	104.8	111.0	114.2
	CH_b[e]	1.101	1.114			θ	117 (119)	111.9	114.2
	R	1.00	1.003		F	CO	1.210	1.289	1.285
	OCH_a[e]	122.8	116.4			CH	1.108	1.123	1.121
	OCH_b[e]	122.8	123.0			CF	1.351	1.294	1.297
	θ	117.	114.7			R	1.00 (1.00)	0.999	1.002
CH_3	CO	1.218	1.282	1.280		OCF	122.1	116.1	121.0
	CH	1.104	1.113	1.113		OCH	125.6	125.0	118.3
	CC′	1.534	1.515	1.518		θ	117 (117)	113.2	113.6
	C′H′[f]	1.087	1.092	1.092	CHO	CO	1.220	1.279	1.279
	R	1.00 (1.00)	0.999	1.000		CH	1.102	1.114	1.114
	OCC′	124.8	119.2	126.2		CC	1.542	1.545	1.546
	OCH	121.4	120.1	113.4		CO	1.220	1.221	1.221
	CC′H′	111.9	110.6	111.6		CH	1.102	1.099	1.100
	H′CH″[f]	108.5	110.1	109.8		R	1.00 (1.00)	1.001	1.001
	θ	117 (116)	114.0	113.5		OCC	122.4	118.3	125.2
NH_2	CO	1.218	1.323	1.319		OCH	122.8	121.3	112.0
	CH	1.105	1.108	1.108		CCO	122.4	117.7	117.8
	CN	1.403	1.317	1.321		OCH	122.8	127.6	126.5
	NH′	1.014	1.031	1.030		θ	117 (116)	114.4	113.9
	NH″	1.013	1.029	1.029	C_2H_3	CO	1.221	1.300	1.298
	R	0.99 (0.99)	0.992	0.995		CH	1.104	1.108	1.107
	OCN	124.3	118.3	126.1		CC′	1.510	1.440	1.442
	OCH	124.3	123.0	115.0		C′C″	1.312	1.343	1.343
	CNH′	120.1	120.5	123.1		C′H′[h]	1.083	1.090	1.090
	CNH″	121.6	120.9	120.1		R	1.00 (1.00)	0.995	0.997
	θ	115 (116)	110.2	111.3		OCC′	123.9	119.5	126.2
OH[g]	CO	1.214	1.308	1.305		OCH	121.8	119.7	113.1
	CH	1.104	1.114	1.115		CC′C″	122.7	119.3	119.3
	CO	1.386	1.299	1.305		C″C′H	121.2	123.4	122.4
	OH′	0.991	0.999	0.997		C′C″H″[h]	122.0	121.8	121.8
	R	0.99 (1.00)	0.994	0.997		θ	116 (115)	112.1	111.8
	OCO	123.7	119.1	128.2					

[a] Bond lengths in Å, bond angles in degrees. See Figure 1 for labeling of atoms. [b] Structures of bases RCHO taken from ref 9. Protonation coordinates R and θ taken from ref 4. Values of ions in set B given in parentheses. [c] In this and subsequent tables, A denotes ions in set A in which the proton is trans to the substituent, while B denotes ions in set B in which the proton is cis to the substituent. See Figure 2. [d] Structures of H_2CO and H_2COH^+ reported in W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974). [e] In H_2COH^+, H_a is the C-H proton trans to H^+, H_b is cis to H^+. [f] Methyl CH bonds and HCH angles assumed equal. [g] Optimized ion in set B has C_{2v} symmetry. [h] C′H′ and C″H″ bond lengths and both C′C″H″ bond angles assumed equal.

Table II. Relative Proton Affinities of Substituted Carbonyl Compounds (STO-3G)[a]

RCHO	Rigid monomer restriction[b] $-\delta\Delta E$(A)	Rigid monomer restriction[b] $-\delta\Delta E$(B)	Optimized ions[c] $-\delta\Delta E$(A)	Optimized ions[c] $-\delta\Delta E$(B)
R = H	0.0	0.0	0.0	0.0
CH_3	14.0	13.8	15.3	15.3
NH_2	31.2	23.0	41.9	38.9
OH	9.5	2.7	17.7	11.4
F	−6.7	−4.8	−2.1	−0.8
CHO	2.3	0.6	3.2	1.9
C_2H_3	21.7	21.8	26.2	26.5

[a] In kcal/mol. [b] Data taken from ref 4, based on a computed proton affinity of 217.2 kcal/mol for H_2CO. [c] Based on a computed proton affinity of 221.3 kcal/mol for H_2CO.

A major effect of protonation of carbonyl compounds is a lengthening of the carbonyl C-O bond, which shows an increase ranging from 0.05 Å in protonated formaldehyde to 0.10 Å in protonated formamide. Also, protonation of the bases RCHO produces a greater variation in the C-O bond length (1.27 to 1.32 Å) in the ions RCHOH⁺ than is found in the corresponding bases RCHO (1.21 to 1.22 Å). For a given substituent, the change in the C-O bond length upon protonation is insensitive to the position of the proton trans or cis to the substituent. The C-X bond length (X is the first-row atom

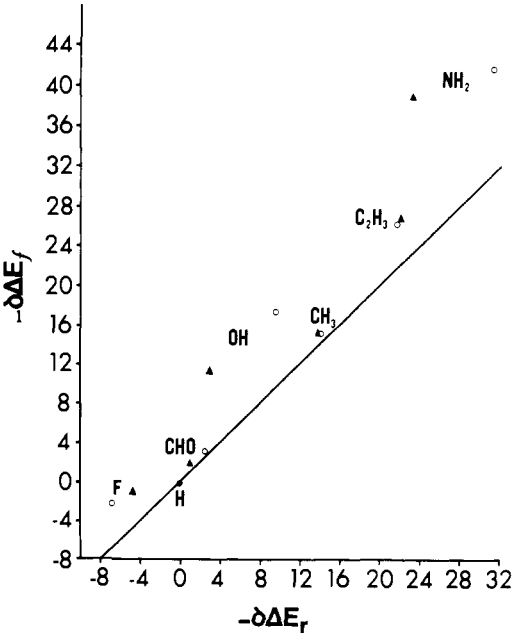


Figure 3. The relative proton affinities of carbonyl bases computed from the fully optimized ions ($-\delta\Delta E_f$) vs. the relative proton affinities computed subject to the rigid monomer restriction ($-\delta\Delta E_r$). Data taken from Table II. ○, ions in set A with the proton trans to the substituent; ▲, ions in set B with the proton cis to the substituent.

Table III. Mulliken Population Data for Ions $RCHOH^+$ (STO-3G)[a]

$RCHOH^+$		Oxygen electron population	Electron transfer to H^+	Electron loss by CO	π electron gain by CO
R = H		8.117 (8.127)	0.617 (0.598)	0.280 (0.272)	0.0 (0.0)
CH_3	A	8.146 (8.155)	0.640 (0.617)	0.253 (0.247)	0.044 (0.035)
	B	8.141 (8.151)	0.644 (0.621)	0.254 (0.249)	0.042 (0.033)
NH_2	A	8.197 (8.205)	0.673 (0.628)	0.190 (0.211)	0.285 (0.185)
	B	8.180 (8.195)	0.688 (0.641)	0.214 (0.227)	0.259 (0.170)
OH	A	8.194 (8.198)	0.647 (0.607)	0.237 (0.233)	0.221 (0.120)
	B	8.169 (8.180)	0.669 (0.627)	0.267 (0.259)	0.196 (0.112)
F	A	8.150 (8.161)	0.622 (0.590)	0.287 (0.272)	0.122 (0.073)
	B	8.145 (8.157)	0.627 (0.596)	0.291 (0.275)	0.108 (0.069)
CHO	A	8.140 (8.147)	0.631 (0.610)	0.235 (0.234)	0.059 (0.055)
	B	8.133 (8.141)	0.640 (0.618)	0.240 (0.241)	0.058 (0.053)
C_2H_3	A	8.168 (8.169)	0.664 (0.631)	0.189 (0.212)	0.208 (0.126)
	B	8.162 (8.166)	0.669 (0.634)	0.194 (0.214)	0.196 (0.119)

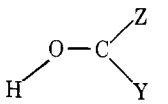
[a] Data in parentheses obtained subject to the rigid monomer restriction, taken from ref 4.

of the substituent bonded to the carbonyl carbon) may also change upon protonation, depending on the substituent. In protonated formamide and protonated formic acid, this bond decreases by about 0.09 Å relative to the corresponding bases. In protonated formyl fluoride and protonated acrolein, the decrease ranges from 0.05 to 0.07 Å. Only an 0.02 Å decrease in the C-C bond length is found in protonated acetaldehyde, while the C-C bond length in protonated glyoxal remains unchanged. The C-X bond length in the ions shows little dependence on the position of the proton relative to the substituent. There appears to be a correlation between the extent of the decrease in the C-X bond length in the ions $RCHOH^+$ and the severity of the rigid monomer restriction on the computed relative proton affinities of the bases RCHO.

The increase in the carbonyl C-O bond length in these ions suggests that protonation weakens the C-O bond. Likewise, a decrease of the C-X bond length is suggestive of a strengthening of this bond. These conclusions are supported by the results of Mulliken population analyses[10] which show that the total and π C-O overlap populations decrease in ions A and B relative to the corresponding base, whereas the C-X total and π overlap populations increase in the ions $RCHOH^+$ relative to the corresponding base RCHO, except for glyoxal, where the total C-C overlap population decreases slightly in the ions.

In part 1 it was noted that the protonation coordinate R is essentially independent of the nature of the substituent, and of its position relative to the proton. As evident from the data of Table I, geometry optimization of the ions $RCHOH^+$ does not change the H^+-O distances to any significant extent. Hence, the rigid monomer restriction does not affect the value of this coordinate. Likewise, the C-H bond length increases only slightly in the fully optimized ions, and is essentially the same in corresponding ions in sets A and B. Thus, it may be concluded from the above data that protonation leads to a significant increase in the carbonyl C-O bond length. In addition, there may or may not be a large decrease in the C-X bond length upon protonation, depending on the substituent. Bond lengths in protonated ions are essentially independent of the position of the proton relative to the substituent.

In contrast to changes in bond distances, changes in bond angles in the ions $RCHOH^+$ do show a dependence on the proton position relative to the substituent. Thus, the data of Table I indicate that the O-C-X bond angle decreases from 4 to 6° in an ion when the C-X bond is trans to the proton as in set A, whereas no more than a 3° change occurs in this angle for an ion in set B, except in protonated formic acid, which turns out to have C_{2v} symmetry. In all cases except protonated $FCHOH^+$, protonation increases the O-C-X angle of ions in set B. Similarly, the O-C-H angle decreases by 8-11° in ions in set B, but only by 2° or less in ions in set A. Thus, it appears that in an ion the O-C-Y angle changes only slightly upon



protonation, while the O-C-Z angle decreases significantly. Therefore, a net result of protonation is to increase the Y-C-Z angle from 6 to 8° in going from RCHO to $RCHOH^+$.

A decrease of 2-5° is found in the protonation coordinate θ, the H^+-O-C angle, upon relaxation of the rigid monomer restriction. In the fully optimized ions, there is little variation in the value of this coordinate in corresponding ions in sets A and B, except for protonated formic acid ion B, which has C_{2v} symmetry. In addition, there is only a 4.5° variation in this angle in the entire series of ions $RCHOH^+$. Thus, the conclusion stated in part 1 that the protonation coordinates R and θ show little dependence on the nature of the substituent, and on its position relative to the proton, is reinforced by the results of this present study. The near constancy of the protonation coordinates R and θ indicates that the bond between the proton and the proton acceptor carbonyl oxygen has the structural characteristics generally associated with typical intramolecular covalent bonds.

An interesting comparison can be made between the effect of ion relaxation on the C-C single bond and the C-C and C-O double bonds in protonated acrolein and glyoxal, respectively. In protonated acrolein, the C-C single bond distance decreases by 0.07 Å, while the C-C double bond distance increases by 0.03 Å. This suggests that protonation strengths the bond between the carbonyl carbon and the substituent, but weakens the C-C double bond within the substituent. In contrast, both the C-C single and the substituent C-O double bond lengths remain essentially unchanged upon protonation of glyoxal. As evident from the Mulliken population data of Table III, π electron donation to the protonated carbonyl group is significantly larger in protonated acrolein than in protonated glyoxal. Thus, the manifest differences in the equilibrium structures of these ions and the proton affinities of the bases may be attributed to the well-known differences in the π electron donating abilities of the unsaturated groups CHO and C_2H_3.

In the study of the protonated carbonyl compounds reported in part 1, Mulliken gross populations were employed to describe the effect of protonation on the electron redistribution in these ions. It was noted that, although the amount of electron transfer to the proton is overestimated by the STO-3G basis set, a trend of increasing charge transfer to the proton with increasing proton affinity of the base was evident. This charge transfer to the proton occurs through the σ electron system in the symmetry plane of the ion, and is accompanied by an in-

Table IV. Relative Proton Affinities of H_2CO, $(CH_3)CHO$, and FCHO (4-31G)[a]

	Rigid monomer restriction[b]		Optimized ions[c]	
	$-\delta\Delta E$(A)	$-\delta\Delta E$(B)	$-\delta\Delta E$(A)	$-\delta\Delta E$(B)
H_2CO	0.0	0.0	0.0	0.0
$(CH_3)CHO$	11.8	11.1	13.1	12.6
FCHO	−27.3	−23.9	−22.6	−20.1

[a] In kcal/mol. [b] Based on a computed proton affinity of 178.9 kcal/mol for H_2CO. [c] Based on a computed proton affinity of 181.1 kcal/mol for H_2CO.

creased polarization of the π electron cloud of the base toward and within the carbonyl group. It is through this π electron polarization that the oxygen atom remains negatively charged in these ions. It was also observed in part 1 that ions having high proton affinities are those in which electron density loss by the carbonyl group of the base is minimized by donation of π electron density by the substituent into the carbonyl group. It is apparent from comparing the data of Table III for the fully optimized ions to the data from part 1 that the trends in population changes identified earlier are found in this study of these same ions with optimized geometries. Upon relaxation of the ions, electron transfer to the proton increases, the carbonyl group experiences a further increase in π electron density, and the protonated oxygen atom still remains negatively charged. It is interesting to note that those ions in which relaxation has the greatest effect on the proton affinity of the base (formamide and formic acid) are those in which the largest increase of π electron density is experienced by the carbonyl group as the bond length between the carbonyl group and the substituent decreases. Those in which ion relaxation has a smaller effect (glyoxal and acetaldehyde) show only small increases in the carbonyl π electron density as the C–C bond lengths in these ions change only slightly upon protonation. These observations lend further support to the conclusion of part 1 that the ease with which an already polarized π electron cloud in the base may be further polarized in the ion is an important factor in determining the relative proton affinities of the bases RCHO.

It has been noted from experimental data that molecules with high proton affinities often have low ionization potentials.[11] The results of these calculations suggest that the particular factor which may be responsible for this correlation is the ease of electron polarization, provided that the ionization potential reflects the energy required to remove an n electron from a single center which is also the site of protonation.[12] Vertical ionization of an n electron from a base leaves the atom at the basic site electron deficient through complete removal of the electron, while protonation leaves the same atom electron deficient through electron transfer to the proton. In both cases, stabilization of the resulting positively charged ions through relaxation involves electron redistribution which polarizes the electron density toward the basic site. This is most readily accomplished in systems such as substituted carbonyls which have mobile π electron systems through a further polarization of the π electron cloud in these ions.

4-31G Results. The relative proton affinities of the bases H_2CO, $(CH_3)CHO$, and FCHO computed with the 4-31 G basis set in the rigid monomer approximation and from the fully optimized ions are reported in Table IV. Like the STO-3G results, the 4-31G results also indicate that the severity of the rigid monomer restriction is greater in the substituted carbonyl compounds than in formaldehyde, and that it is strongly dependent on the nature of the substituent but only slightly dependent on its position relative to the proton. Thus, relaxation of the rigid monomer restriction at the 4-31G level has the smallest effect on the computed proton affinity of H_2CO, which increases by 2.2 kcal/mol (a 1% change). The effect is greater in $(CH_3)CHO$, where the proton affinity of the base increases by about 4 kcal/mol (a 2% change). The largest effect is found in FCHO, where increases of 7 (5%) and 6 kcal/mol (4%) are found in the stabilization energies of the trans and cis protonated ions, respectively, even though the proton affinity of FCHO is less than that of H_2CO. The 4-31G results of Table IV also suggest that cis and trans protonation of acetaldehyde produces ions with similar stabilization energies, while cis protonation of FCHO is more favorable than trans. These predictions are unaffected by relaxation of the rigid monomer restriction, and are also evident from both the STO-3G and 4-31G studies. It should be noted, however, that there is a significant basis set dependence of the relative proton affinities of FCHO and H_2CO. While the STO-3G results predict that the proton affinities of these two bases are similar, the 4-31G results suggest that the proton affinity of H_2CO is about 20 kcal/mol greater than that of FCHO. On the other hand, the computed relative proton affinities of $(CH_3)CHO$ and H_2CO are in fairly good agreement at the STO-3G and 4-31G levels. Both the STO-3G value of 15.3 kcal/mol and the 4-31G value of 13.1 kcal/mol for the proton affinity of acetaldehyde relative to formaldehyde are larger than the experimental gas-phase value of 10.4 kcal/mol ($-\delta\Delta H$).[2]

Protonation of the carbonyl bases H_2CO, $(CH_3)CHO$, and FCHO results in a significant lengthening of the C–O bond, as illustrated by the 4-31G structural data of Table V. In each case, the increase in the C–O bond length is predicted to be slightly smaller than that found in the corresponding relaxed ions with the STO-3G basis set. A small decrease of 0.03 Å in the C–C bond length of acetaldehyde is found in the protonated ions, while larger decreases of 0.08 and 0.07 Å are found for the C–F bond length in the trans and cis protonated ions $FCHOH^+$, respectively. The changes which occur in the O–C–H and O–C–X bond angles in the relaxed 4-31G ions are

Table V. Ion Structures (4-31G)[a]

RCHOH⁺		Rigid monomer	Optimized A	Optimized B
R = H[b]	CO	1.206	1.247	
	CH_a[c]	1.081	1.071	
	CH_b[c]	1.081	1.075	
	R	0.97	0.967	
	OCH_a[c]	121.8	116.0	
	OCH_b[c]	121.8	121.9	
	θ	126.	124.5	
CH_3	CO	1.209	1.261	1.260
	CH	1.085	1.077	1.073
	CC′	1.495	1.459	1.466
	C′H′[d]	1.083	1.084	1.084
	R	0.96 (0.97)[e]	0.964	0.965
	OCC′	124.2	120.0	125.8
	OCH	119.8	118.9	113.0
	CC′H′	109.9	111.6	113.1
	H′CH″[d]	108.7	108.8	108.6
	θ	125. (125.)[e]	123.4	123.4
F	CO	1.179	1.235	1.236
	CH	1.070	1.074	1.071
	CF	1.357	1.279	1.288
	R	0.97 (0.97)[e]	0.968	0.973
	OCF	122.1	117.3	120.8
	OCH	127.9	126.2	120.7
	θ	131. (130.)[e]	127.1	126.4

[a] Bond lengths in Å, bond angles in degrees. See Figure 1 for labeling of atoms. [b] Equilibrium structure of H_2CO taken from ref 7. [c] In H_2COH^+, H_a is the C–H proton "trans" to H^+, H_b is "cis" to H^+. [d] Methyl CH bonds and HCH angles assumed equal. [e] Protonation coordinates for ions in set B given in parentheses.

Table VI. Mulliken Population Data (4-31G)[a]

	Oxygen electron population	Electron transfer to H^+	Electron loss by CO	π electron gain by CO
H_2COH^+	8.538 (8.521)	0.457 (0.447)	0.099 (0.106)	0.0 (0.0)
$(CH_3)CHOH^+$ A	8.585 (8.560)	0.474 (0.466)	0.070 (0.077)	0.057 (0.041)
B	8.586 (8.568)	0.478 (0.465)	0.078 (0.085)	0.049 (0.034)
$FCHOH^+$ A	8.566 (8.536)	0.434 (0.413)	0.121 (0.136)	0.069 (0.039)
B	8.561 (8.532)	0.435 (0.418)	0.123 (0.134)	0.059 (0.036)

[a] Data in parentheses obtained subject to the rigid monomer restriction.

also similar to those found in the STO-3G structures. These changes lead to a net increase of 5.7° in the H-C-H angle of protonated formaldehyde, 5.0 and 5.2° in the H-C-C angle of protonated acetaldehyde ions A and B, respectively, and 6.5 and 8.5° in the H-C-F angle of protonated formyl fluoride, ions A and B, respectively. While changes in the C-X bond length exhibit a strong dependence on the substituent but only a slight dependence on its position relative to the proton, changes in the O-C-H and O-C-X bond angles are dependent on whether protonation occurs cis or trans to the substituent. It is also apparent from the data of Table V that the protonation coordinate R, the H^+-O distance, does not change in the ions when the rigid monomer restriction is relaxed, while the angle θ, the H^+-O-C angle, decreases. Changes which occur in this angle upon ion relaxation are essentially independent of the position of the proton relative to the substituent. In the relaxed ions, there is little variation in the values of the coordinates R and θ. Thus, it is apparent from the 4-31G results that protonation of H_2CO, $(CH_3)CHO$, and FCHO leads to significant changes in the intramolecular coordinates of carbonyl bases, and that the same general features of these changes are evident from both the STO-3G and 4-31G relaxed ions.

Mulliken population data for the ions H_2COH^+, $(CH_3)CHOH^+$, and $FCHOH^+$ are reported in Table VI. Trends in electron population changes upon protonation which can be identified in the rigid ions are evident and slightly enhanced in the relaxed ions. Electron transfer to the proton, π electron density gain by the carbonyl group, and the negative charge on the oxygen atom increase upon ion relaxation, while electron loss by the carbonyl group decreases slightly. As noted in part 1, basis set dependencies are evident in population changes of carbonyl bases upon protonation, and in addition, relaxation of the rigid monomer restriction has different effects on the oxygen electron populations and on the electron density loss by the carbonyl group, when determined from the STO-3G and 4-31G results. However, the general observations that the oxygen atoms in these ions remain negatively charged, and that increasing proton affinity shows some correlation with an increased electron transfer to the proton and a further polarization of π electron density toward and within the carbonyl group, are supported by both the STO-3G and 4-31G results. It is significant that the 4-31G results also suggest that π electron donation to the carbonyl group, which is enhanced by a shortening of the bond between the carbonyl carbon and the substituent, is a critical factor in the error introduced into the calculated relative proton affinities of substituted carbonyl compounds by the rigid monomer restriction.

Conclusions

The following conclusions concerning the structures of the ions $RCHOH^+$ and the effect of protonation on the electron distribution in these ions are supported by the results of the STO-3G and 4-31G calculations.

1. Protonation of monosubstituted carbonyl bases results in a weakening of the carbonyl C-O bond, which lengthens significantly in the relaxed ions.

2. Depending on the nature of the substituent, protonation may also lead to a strengthening and shortening of the bond from the carbonyl carbon to the substituent (the C-X bond). The change in the C-X bond in the ion is dependent on the substituent and essentially independent of the position of the proton relative to the substituent.

3. Changes in the O-C-H and O-C-X bond angles occur upon protonation of monosubstituted carbonyl bases, the nature of these changes being dependent on whether protonation occurs cis or trans to the substituent. As a result of protonation, the H-C-X angle is larger in the relaxed ion than in the corresponding base.

4. The H^+-O bond length and the H^+-O-C angle in these ions exhibit a small dependence on the nature of the substituent and on its position cis or trans to the proton. Thus, the bond between the proton and the carbonyl oxygen has the structural characteristics of a normal intramolecular covalent bond.

5. Protonation of carbonyl bases results in electron transfer to the proton, and a further polarization of the π electron density toward and within the carbonyl group, which leaves the carbonyl oxygen negatively charged in the ions. These calculations suggest that it is the ease of polarization of the π electron density which appears to be a critical factor in determining the relative proton affinities of carbonyl bases, and which may be the particular factor responsible for the correlation between low ionization potential and high proton affinity of related bases.

The results of these calculations demonstrate a significant basis set dependence of proton affinities, which are overestimated when computed with the STO-3G basis set, but in reasonable agreement with experimental data when computed with the 4-31G basis set. Even more significantly, the relative proton affinities of these bases are also basis set dependent. Finally, it is apparent from both the STO-3G and 4-31G calculations that the rigid monomer restriction is a severe approximation when applied to protonated carbonyl bases, since it neglects the significant structural changes which occur in the relaxed ions. In addition, it also introduces an error into the computed relative proton affinities of these bases, the magnitude of which depends on the nature of the substituent and appears to be related to the change in the C-X bond length in the ion. As a result, the calculated relative proton affinities of substituted carbonyl compounds may change upon relaxation of this restriction.

Acknowledgments. This work was supported by NIH Research Grant GM 19032 from the National Institute of General Medical Sciences. The support of NIH and of a Camille and Henry Dreyfus Foundation Teacher-Scholar Grant (1974-1979) is gratefully acknowledged. Thanks are also due to Dr. Ronald Jonas and the Youngstown State University Computer Center for continued support and assistance. The author is also very grateful to Professors Robert W. Taft and Jack L. Beauchamp for providing their experimental data on gas-phase proton affinities prior to publication.

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The Effect of Micellar Phase on the State and Dynamics of Some Excited State Charge Transfer Complexes

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Received July 26, 1977

Abstract: The effect of micellar phase on kinetic processes of electron transfer reactions of exciplexes formed by pyrene (P) and *N,N*-dimethylaniline (DMA) has been studied. Transitory species are produced by a 10-ns pulse of 347.1-nm light from a Q-switched ruby laser and detected by rapid spectrophotometric or conduction techniques. Singlet excited pyrene (P*) readily accepts an electron from DMA to form an ion pair (P^- and DMA^+), and the fate of the ion pairs depends critically on the micellar environment. In the case of cationic micelles, DMA^+ is quickly expelled from the micellar surface while P^- is retained, leading to a long anion lifetime (~500 μs). On the other hand, an anionic micellar surface traps DMA^+ ions and enhances the geminate ion recombination process with P^-. Several pyrene derivatives such as pyrenebutyric acid, pyrenesulfonic acid, pyrenetetrasulfonic acid, pyrenedodecanoic acid, and pyrenecarboxaldehyde which are solubilized at different sites in micelles are also selected as e^- acceptors to investigate the effect of separation between P* and DMA on the forward and back e^- transfer processes. Similar studies were carried out with the molecule $P-(CH_2)_3-DMA$ which forms intramolecular exciplexes. Here neither ion can escape from the exciplex owing to the restraint of the propyl chain. The physical and chemical properties of excited states of this molecule-micellar system are dramatically different from those of intermolecular complexes. Micellar systems suggest the constituent ions of exciplexes. This has implications for conversion of light energy into ionic fragments which can be subsequently utilized.

Introduction

Since Weller[2a] first identified exciplexes or excited charge transfer complexes, these systems have received detailed attention and are now comparatively well characterized. The formation of a charge transfer complex between any two molecules depends on the overall energetics of the processes leading to the transfer of an electron from one molecule of the pair to the other. Excitation of the partners often provides sufficient incentive for this process to take place. The polarity of the surrounding medium also sharply affects the nature of and extent of formation of the exciplex. The formation of an exciplex results in a diminution of the natural spectroscopic properties of the excited but separated partners of the pairs, and in the formation of new properties which are specific to the exciplex. In polar media such as alcohols or acetonitrile the exciplex dissociates into ions of the molecular pair. The dynamics of these varied processes have been extensively studied in simple solvents.[2b,3-7]

An intriguing extension of exciplex studies is provided by molecules of configuration $A-(CH_2)_n-D$ where the electron acceptor A and donor D are linked by a number of methylene groups. Intra- rather than intermolecular exciplexes are then found on excitation. Diffusion of A and D is no longer a parameter of the system, and the ability of the electron to jump from D to A under different geometrical orientations of D and A is now of prime importance.

The present paper describes the effect of the micellar phase on formation and subsequent reactions of exciplexes. Micelles possess a lipid or hydrocarbon-like core bounded by a polar water-lipid interface, which, consisting of the head group of the surfactant, may be anionic, cationic, or neutral in nature. Molecules may be absorbed in the surface of the micelle or be incorporated into the lipid structure. Such events lead to quite dramatic modifications of radiation induced reactions of these solubilized species.[8] The solvent-dependent nature of exciplexes and their highly polar nature suggest that charged micellar surfaces should have some influence on these species.

Laser photolysis and time-resolved fluorescent techniques were used to investigate various pathways of the exciplex in micellar systems. Photoconduction experiments where the currents are observed subsequent to the excitation of the exciplex by the laser light were carried out to elucidate directly the formation of the dissociated ion radicals. Both the intermolecular exciplex (pyrene and *N,N*-dimethylaniline) and intramolecular exciplex pyrene-$(CH_2)_3$-*N,N*-dimethylaniline were investigated in cationic, anionic, as well as nonionic micelles. A comparison of the fates of exciplexes in micelles and simple solvents is documented and discussed. Several pyrene derivatives such as pyrenesulfonic acid (PSA), pyrenebutyric acid (PBA), pyrenetetrasulfonic acid (PTSA), pyrenedodecanoic acid (PDA), and pyrenecarboxyaldehyde (PCHO)

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0002-7863/78/1500-1679$01.00/0