A Molecular Orbital Study of Protonation. Substituted Carbonyl Compounds

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Abstract: Ab initio SCF calculations with minimal STO-3G and slightly extended 4-31G basis sets have been performed to determine the structures and energies of protonated carbonyl compounds, $RCHOH^+$ and R_2COH^+. The structures of the protonated ions show little dependence on the nature of the R group or on its position "cis" or "trans" to the proton with respect to the carbonyl C–O bond. However, the protonation energies show a strong dependence on the nature of the substituent and a lesser dependence on its position relative to the proton. Trends in the protonation energies and factors which influence the relative stabilities of these ions, which are evident from both the STO-3G and 4-31G calculations, have been identified. The basis set dependence of computed results and the effect of the rigid monomer restriction have also been investigated. Some comparisons are made between the structures and stabilization energies of these ions and the structures and hydrogen bond energies of dimers HOH···OCHR and $HOH\cdots OCR_2$.

In the past several years there have appeared in the literature a number of ab initio studies of carbonyl compounds as bases.[1-12] Among these are two studies carried out in this laboratory. In the first, equilibrium structures and hydrogen bond energies were obtained for a series of dimers represented by the general formula HOH···OCHR, where R may be H, one of a group of isoelectronic saturated substituents CH_3, NH_2, OH, or F, or the unsaturated substituents CHO (glyoxal) or C_2H_3 (acrolein).[11] In a subsequent study, equilibrium structures and hydrogen bond energies were determined for dimers $HOH\cdots OCR_2$, where R was restricted to the saturated substituents.[12] In these studies, emphasis was placed on the effect of the substituent on the proton accepting ability of the carbonyl group for the formation of a hydrogen bond.

A parallel study has now been completed, in which the effect of the substituent on the proton affinities of these same bases has been investigated. In this study, energies of the exothermic reactions

$$RCHO + H^+ \rightarrow RCHOH^+$$

$$R_2CO + H^+ \rightarrow R_2COH^+$$

have been computed, with R defined as above. Emphasis has again been placed on the effect of the substituent on the relative proton affinities (protonation energies for the above reactions) of carbonyl bases, on the equilibrium structures of the protonated ions, and on the charge redistribution which occurs upon protonation of these bases. In addition to the information gained about protonation, some interesting results are obtained concerning the relationship between protonation and hydrogen bond formation through a comparison of these carbonyl compounds as bases toward H^+ and H_2O. The purpose of this paper is to present the results of this study.

Method

The closed shell ground state wave functions for the carbonyl compounds and the protonated ions are described by single Slater determinants Ψ

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

in which each molecular orbital is doubly occupied. The molecular orbitals 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 expansion coefficients obtained by solving the Roothaan equations.[13] Two basis sets have been used extensively in this study. The first is the minimal STO-3G basis set, with standard scale factors.[14] This basis set was also used in the study of substituted carbonyl compounds as proton acceptors in the dimers HOH···OCHR and $HOH\cdots OCR_2$, thereby making possible some direct comparisons between protonation and hydrogen bond formation. In this study of protonation, certain calculations have been repeated using STO-NG basis sets, with $N = 4$, 5, and 6, in order to evaluate the effect of truncation of the Gaussian expansion on the structures and energies of protonated ions.

The second basis set used in this study is the split-valence 4-31G basis set, with standard scale factors.[15] The structures and energies of the protonated carbonyl compounds obtained with the 4-31G basis set are compared with the STO-3G results and with experimental data. A few calculations have also been performed with the slightly larger 6-31G basis,[16] so that the effect of improving the description of the inner-shell carbon and oxygen orbitals may be evaluated.

Optimized STO-3G geometries have previously been reported for the substituted carbonyl compounds.[17] Except for the study of the rigid monomer restriction, these monomer geometries have been used for all calculations and held rigid in the protonated ions. The structures of these ions have been optimized to ±0.01 Å in R, the H^+–O distance, and to ±1° in θ, defined in Figure 1 as the H^+–O–C angle. All calculations have been performed in double precision on an IBM 370/145 computer.

Results and Discussion

The Rigid Monomer Restriction. In studies of hydrogen bonding, it has been the practice to optimize the structures of hydrogen bonded dimers in an intermolecular coordinate system with the restriction that the monomers retain their optimized geometries. This approximation assumes that in the dimer any changes which may occur in intramolecular coordinates are negligibly small. That this is a reasonable approximation for open-chain dimers is evident from the structures and energies of these dimers, which are similar to the structures and energies of fully optimized dimers.[7,18] However, since the approach of the proton to the proton acceptor atom in a protonated ion is closer than the approach of the hydrogen bonded proton to the proton acceptor atom in a dimer, and since protonation energies are significantly larger than hydrogen bond energies, it is necessary to examine to what extent the rigid monomer restriction affects the computed equilibrium structures and energies of protonated ions.

The structures and energies of a number of small, fully optimized molecules and the corresponding protonated ions have been reported,[18] and some comparisons may be made between the structures and energies of these ions and the structures and energies of the same ions optimized in this study with the rigid monomer restriction. At the STO-3G level, protonation energies of 228.7 and 221.3 kcal/mol have been obtained for the fully optimized ions H_3O^+ and H_2COH^+, respectively, The same ions optimized under the rigid monomer restriction have protonation energies of 225.4 and 217.2 kcal/mol, respectively.

Of particular interest in this study is protonated formaldehyde, which is the reference for comparison of substituent effects on the protonation of carbonyl compounds. For this ion, optimization of R and θ produced values of 1.00 Å and 117°, respectively, with the STO-3G geometry of formaldehyde held rigid. In the fully optimized ion, the coordinates R and θ have similar values of 1.00 Å and 114.7°, respectively.[18] However, changes in the intramolecular coordinates of formaldehyde are found in the ion, the more notable being an increase of about 6° in the methylene H–C–H angle, and a lengthening of the C–O bond from 1.217 to 1.271 Å. Despite the neglect of these significant intramolecular coordinate changes by the rigid monomer restriction, the energy difference between the ion optimized with this restriction and the fully optimized ion is only 4.1 kcal/mol, out of a total protonation energy of 221.3 kcal/mol. Thus, in this case an energy error of approximately 2% is introduced by the rigid monomer restriction. In other specific cases, this approximation may be more severe. This is a subject for future study.

Basis Set Dependence. It has already been noted that proton affinities are significantly overestimated when computed with the STO-3G basis set.[19,20] For example, the computed STO-3G protonation energies of water and formaldehyde are 225.4 and 217.2 kcal/mol, significantly larger than the experimental values of 169[21] and 166[22] kcal/mol, respectively. That this overestimation is a characteristic of a minimal STO basis set, and not due to the truncation of the Gaussian expansion at $N = 3$, is supported by the following data. With the STO-3G optimized geometry of water held rigid, the protonation energies of water are 225.4, 223.8, and 223.6 kcal/mol, at the STO-3G, 4G, and 5G levels, respectively, In each case, these energies refer to ions optimized in the protonation coordinates R and θ. Similarly, the protonation energies of formaldehyde are 217.2, 215.8, and 215.6 kcal/mol, respectively, at the STO-3G, 4G, and 6G levels. These energies also refer to structures optimized in R and θ, with the STO-3G geometry of the base held rigid. From these data, it is evident that the truncation of the Gaussian expansion of the Slater orbitals at $N = 3$ introduces an error of a few kilocalories per mole, which is small when compared to the difference between the computed STO-3G proton affinities and experimental data. It appears that reasonable estimates of proton affinities are not obtainable with a minimal STO basis set.

A considerable improvement is found when proton affinities are computed with the split-valence 4-31G basis set. A protonation energy of 183 kcal/mol has been reported for an equilibrium H_3O^+ ion of D_{3h} symmetry.[19] It is interesting to note that the optimized STO-3G structure of H_3O^+ is pyramidal, as it is when computed with much larger basis sets including polarization functions.[23,24] However, at the 4-31G level, the energy difference between the optimized D_{3h} structure and a structure of C_{3v} symmetry (the optimized STO-3G structure) is only about 1 kcal/mol. A calculation on H_3O^+ with a larger basis set including polarization functions yielded an equilibrium structure of C_{3v} symmetry and a protonation energy of 177 kcal/mol. The authors suggested that this result for the protonation energy approaches the Hartree–Fock limit.[23]

With the optimized 4-31G geometry of formaldehyde held rigid, the optimized ion H_2COH^+ has $R = 0.97$ Å and $\theta = 126°$, with a protonation energy of 178.9 kcal/mol. If the optimized STO-3G geometry of formaldehyde is used instead, the structure of the ion H_2COH^+ is described by optimized coordinates $R = 0.97$ Å and $\theta = 125°$, with a protonation energy of 179.2 kcal/mol. Thus, the use of an optimized STO-3G geometry for this base has little effect on the computed structure of the ion or on the protonation energy obtained at the 4-31G level.

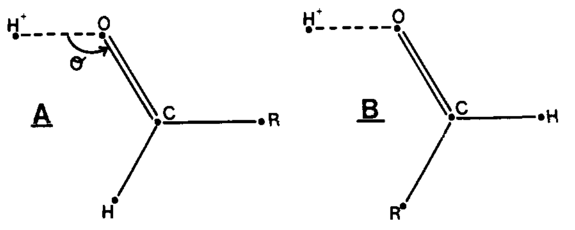

Figure 1. The ions $RCHOH^+$, A and B.

The computed proton affinity of formaldehyde with the 6-31G basis set is 178.6 kcal/mol. This result refers to an ion in which formaldehyde has its optimized STO-3G geometry, and the protonation coordinates R and θ have optimized values of 0.97 Å and 125°, respectively. Thus, the improvement of the carbon and oxygen 1s orbitals which occurs when the 4-31G basis set is replaced by the 6-31G basis set has little effect on the results of protonation studies. The 4-31G and 6-31G protonation energies are very similar and in reasonable agreement with the gas-phase proton affinity of formaldehyde.

Although the protonation energies at the 4-31G level are reasonable, they are still consistently larger than experimental proton affinities. This is due in part to the 4-31G basis set which tends to overestimate the polarity of molecules, as indicated by the computed dipole moment of formaldehyde of 3.0 D, which is larger than the experimental value of 2.2 D.[25] However, it should also be noted that before quantitative agreement with experimental data may be expected, both zero-point and correlation energy corrections must be made.

In the above analyses of studies of protonation within the Hartree–Fock framework, an attempt has been made to indicate the errors introduced by the rigid monomer restriction and those associated with the basis set. Although results in quantitative agreement with experiment cannot be expected at this level of treatment, new and important information concerning protonation can be obtained. For a related series of bases, relative proton affinities at the STO-3G level may still be meaningful, since trends in the series may be evident. Likewise, structural information can also be obtained. Therefore, in this study, the STO-3G structures and energies of ions in the series $RCHOH^+$ and R_2COH^+ will be reported and analyzed. In addition, comparisons will be made with the results of 4-31G calculations and with experimental data. In this way, it may be possible to identify and establish trends in the structures and stabilities of protonated ions, which are independent of basis set. This type of information is useful in itself and for future studies in systems whose size precludes thorough geometry searches for equilibrium structures or the use of larger basis sets. Where differences between the STO-3G and 4-31G results are found, insight into the basis set dependence of computed properties may be gained.

Equilibrium Structures of Protonated Carbonyl Compounds. The computed STO-3G equilibrium structures and energies of the protonated carbonyl compounds are reported in Table I. For ions in the series $RCHOH^+$, two sets of equilibrium structures have been obtained, set A, in which the proton is "trans" to the substituent R with respect to the C–O bond, and set B, in which the proton is "cis" to R, as shown in Figure 1.

Table I. STO-3G Structures and Energies of Protonated Carbonyl Compounds

R		R, Å	θ, deg	ΔE, kcal[a]
		$RCHOH^+$		
H		1.00	117	217.2
CH_3	A	1.00	117	231.2
	B	1.00	116	231.0
NH_2	A	0.99	115	248.4
	B	0.99	116	240.2
OH	A	0.99	117	226.7
	B	1.00	119	219.9
F	A	1.00	117	210.5
	B	1.00	117	212.4
CHO	A	1.00	117	219.5
	B	1.00	116	217.8
C_2H_3	A	1.00	116	238.9
	B	1.00	115	239.0
		R_2COH^+		
CH_3		1.00	116	242.3
NH_2		0.99	115	263.7
OH		0.99	119	226.1
F		1.00	118	204.2

[a] ΔE is the proton affinity (protonation energy for the exothermic reaction $B + H^+ \rightarrow BH^+$).

Table II. 4-31G Structures and Energies of Selected Protonated Carbonyl Compounds[a]

		R, Å	θ, deg	ΔE, kcal
H_2COH^+		0.97	125	179.2 (166[c])
CH_3CHOH^+	A	0.97	124	190.5 (183,[c] 185[d])
	B	0.97	124	189.9
$(CH_3)_2COH^+$[b]		0.97	124	198.8 (190,[c] 195[d])
$(OH)CHOH^+$	A	0.97	126	173.4 (178[d])
	B	0.97	126	166.5
$(OH)_2COH^+$		0.96	132	160.6
$FCHOH^+$	A	0.97	128	155.3
	B	0.97	128	159.1
F_2COH^+		0.98	129	137.3

[a] Optimized STO-3G geometries have been used for the carbonyl bases. [b] R and θ values are not optimized but were taken from $(CH_3)CHOH^+$ results. [c] Experimental gas-phase proton affinities reported in ref 22. [d] Experimental gas-phase proton affinities reported in ref 21.

A striking feature of the equilibrium structures of ions $RCHOH^+$ in both of these sets is the near constancy of the optimized values of the protonation coordinates R and θ. As evident from Table I, the values of these coordinates are essentially independent of the nature of the substituent and of its position "cis" or "trans" to the proton. The equilibrium structures of ions in the series R_2COH^+ are also similar to the structures of the protonated monosubstituted carbonyl compounds. Thus, the equilibrium structures of ions in both series $RCHOH^+$ and R_2COH^+ are similar to the equilibrium structure of protonated formaldehyde.

The structures and energies of selected ions in the two series $RCHOH^+$ and R_2COH^+ obtained with the 4-31G basis set are reported in Table II. The optimized values of the coordinates R and θ in these ions also indicate that the structures of protonated substituted carbonyl compounds are similar to the structure of protonated formaldehyde. Thus, the data obtained in this study with two different basis sets suggest that the bond formed between the proton and the carbonyl oxygen in these ions is strongly directional and not significantly affected by the nature of the bonding at the carbonyl carbon atom. This type of behavior is generally associated with normal intramolecular covalent bonds. It implies that protonation occurs in one of the trigonal directions with respect to the carbonyl oxygen and directly involves one of the oxygen lone pairs of electrons.

Protonation Energies. While the substituent R may have little effect on the structures of the protonated carbonyl compounds, it has a pronounced effect on the protonation energies, as evident from Table I. With the STO-3G basis set, a variation of about 60 kcal/mol is found in the computed proton affinities of substituted carbonyl compounds, which range from 204.2 kcal/mol for carbonyl fluoride to 263.7 kcal/mol for urea. While there does not appear to be a single property either of these bases or of the protonated ions which bears a one-to-one correspondence with the order of increasing proton affinity, there are certain factors, which will be identified and discussed below, that obviously influence that order.

It has already been observed that except for CHO in glyoxal, the substituents R are σ-electron withdrawing and π-electron donating groups relative to H.[17,26] σ-Electron withdrawal by the substituent reduces the electron density on the carbonyl oxygen, which tends to decrease the electrostatic interaction between the oxygen and the proton. A second effect of σ withdrawal, mediated by an increase in the effective nuclear charge on the oxygen, is to cause the n orbital to be more tightly bound relative to formaldehyde. Therefore, σ withdrawal by R tends to decrease the proton affinities of substituted carbonyl bases, relative to formaldehyde. On the other hand, π donation by the substituent increases the electron density of the carbonyl oxygen, which tends to increase the electrostatic interaction between the oxygen and the proton. In addition, since π donation tends to decrease the oxygen effective nuclear charge, a second effect is to destabilize the n orbital relative to formaldehyde. Thus, π donation by R tends to increase the proton affinities of substituted carbonyl bases compared to formaldehyde.

The relative importance of these opposing σ and π effects of the substituents is most apparent when the strongest and weakest bases toward H^+ are compared, with formaldehyde as a reference. From Table I, it is apparent that substitution of a fluorine atom lowers the proton affinity of formyl fluoride relative to formaldehyde. Substitution of two fluorine atoms lowers the proton affinity of carbonyl fluoride even further, making protonated carbonyl fluoride the least stable ion. Since fluorine is the most electronegative substituent, it is apparent that the σ effect is predominant. Dramatic evidence of the strong electron withdrawing ability of fluorine is found by comparing the n-orbital energies of formaldehyde, formyl fluoride, and carbonyl fluoride, which are −9.64, −10.45, and −11.18 eV, respectively.

From Table I, it is also apparent that formamide is the strongest base toward H^+ among the monosubstituted carbonyl compounds, while urea is the strongest base in the entire set. The strong π-donating effect of the NH_2 group is well-known and reflected in the n-orbital energies which are −9.08 and −8.66 eV in formamide and urea, respectively. In terms of the properties of the unprotonated bases, there appears to be a correlation between the n-orbital energy (the n-orbital ionization potential as approximated by Koopmans' theorem) and the proton affinity of the base. From experimental data, Beauchamp also noted that low ionization potentials correspond to high basicities through increased n-donor ability.[22] However, the nature of the n orbital is also a factor which must be considered before such a correlation can be expected in a particular case. In glyoxal, for example, the high energy n orbital is a combination of n orbitals from the two carbonyl groups and is destabilized, as reflected by an orbital energy of −8.92 eV. Although this is the least stable among the n orbitals of the monosubstituted carbonyl compounds, the computed proton affinity of glyoxal is similar to that of formaldehyde.

Table III. Mulliken Population Analysis (STO-3G)

R			Oxygen electron population	Electron transfer to H$^+$	Electron loss by CO	π electron gain by CO
			RCHO			
H	Base		8.188			
	Ion		8.127	0.598	0.272	0.0
CH$_3$	Base		8.209			
	Ion	A	8.155	0.617	0.247	0.035[a]
		B	8.151	0.621	0.249	0.033
NH$_2$	Base		8.267			
	Ion	A	8.205	0.628	0.211	0.185
		B	8.195	0.641	0.227	0.170
OH	Base		8.251			
	Ion	A	8.198	0.607	0.233	0.120
		B	8.180	0.627	0.259	0.112
F	Base		8.217			
	Ion	A	8.161	0.590	0.272	0.073
		B	8.157	0.596	0.275	0.069
CHO	Base		8.184			
	Ion	A	8.147	0.610	0.234	0.055
		B	8.141	0.618	0.241	0.053
C$_2$H$_3$	Base		8.205			
	Ion	A	8.169	0.631	0.212	0.126
		B	8.166	0.634	0.214	0.119
			R$_2$CO			
CH$_3$	Base		8.226			
	Ion		8.172	0.639	0.232	0.056[a]
NH$_2$	Base		8.319			
	Ion		8.231	0.652	0.221	0.214
OH	Base		8.300			
	Ion		8.228	0.628	0.244	0.162
F	Base		8.236			
	Ion		8.180	0.583	0.289	0.113

[a] Note that σ–π separation of electron density is not possible in the methyl-substituted compounds. Thus, π refers to the C and O atomic orbitals perpendicular to the molecular symmetry plane defined by the C–C and C–O bonds.

Thus, the destabilization of this n orbital through delocalization is not an indicator of the proton affinity of this base.

Results of Mulliken population analyses[27] for the carbonyl bases and the corresponding protonated ions are reported in Tables III and IV. Despite the known limitations of such an analysis, some enlightening information can be obtained from these data. From the STO-3G data of Table III, a trend is evident which indicates that within the series RCHOH$^+$ a correlation exists between increasing charge transfer to H$^+$ and increasing stability of the protonated ion, although a one-to-one correspondence is not found. Similarly, within the series R$_2$COH$^+$, the same type of correlation is also evident. However, a correlation is also indicated between increasing retention of electron density by the carbonyl group upon protonation and increasing stability of the resulting ion. For example, 0.583 electron is transferred to H$^+$ in protonated carbonyl fluoride as the carbonyl group loses 0.289 electron. In protonated urea, although 0.652 electron is transferred to H$^+$, the carbonyl group loses only 0.221 electron relative to the unprotonated molecule. Similar results are found and even further emphasized in the 4-31G data reported in Table IV. Thus, increasing ion stability appears to correlate with increasing electron transfer to H$^+$ (and therefore increasing electron density loss by the base) and decreasing electron density loss by the carbonyl group. These results may be understood in terms of the mechanism of charge transfer to the proton. It is evident that the presence of the proton polarizes the electron distribution in the base. Charge transfer to the proton occurs through the sigma electron system and is accompanied by a further polarization toward and within the carbonyl group of an already polarized π cloud. The ease with which the π electron density may be further polarized in the ion appears to be a factor in determining the relative stabilities of ions in these series.

Table IV. Mulliken Population Analysis (4-31G)

		Oxygen electron population	Electron transfer to H$^+$	Electron loss by CO	π electron gain by CO
H$_2$CO		8.484			
H$_2$COH$^+$		8.521	0.447	0.106	0.0
CH$_3$CHO		8.528			
CH$_3$CHOH$^+$	A	8.565	0.463	0.066	0.038[a]
	B	8.570	0.466	0.076	0.032
(CH$_3$)$_2$CO		8.560			
(CH$_3$)$_2$COH$^+$		8.608	0.476	0.044	0.054[a]
(OH)CHO		8.555			
(OH)CHOH$^+$	A	8.597	0.438	0.103	0.081
	B	8.578	0.457	0.128	0.069
(OH)$_2$CO		8.573			
(OH)$_2$COH$^+$		8.628	0.436	0.100	0.112
FCHO		8.489			
FCHOH$^+$	A	8.547	0.422	0.144	0.041
	B	8.546	0.426	0.140	0.037
F$_2$CO		8.466			
F$_2$COH$^+$		8.542	0.399	0.154	0.066

[a] See footnote *a* of Table III.

It is also apparent from these data that while the strong π donating ability of the NH$_2$ group is reflected in the Mulliken gross atomic populations for the oxygens in formamide and urea, the strong σ-withdrawing effect of F is not evident from the oxygen electron populations in formyl fluoride and carbonyl fluoride. The data of Tables III and IV suggest that there is little correlation between charges on the oxygen atoms and the proton affinities of the carbonyl bases.

In the monosubstituted carbonyl compounds, protonation may occur "trans" or "cis" to the substituent R, giving rise to equilibrium structures A and B. It appears that except for formyl fluoride, the protonation energies for "trans" protonation are larger than those for "cis" protonation. The difference between the "cis" and "trans" protonation energies may be insignificantly small, as in protonated acetaldehyde and acrolein, or substantial, as in protonated formic acid and formamide. Because of the large error in the absolute protonation energies found in these STO-3G calculations, it may be questionable whether these distinctions have any real significance. Therefore, it is important to note that the data of Table II obtained from 4-31G calculations also show a slight preference for "trans" protonation in acetaldehyde, a greater preference for "trans" protonation in formic acid, and a preference for "cis" protonation in formyl fluoride. It is interesting to note that the position of the proton "trans" to the substituent tends to produce a greater polarization of the π electron density. As noted above, the ease of polarization of the π electron density appears to be a factor in determining the relative stabilities of these ions. Therefore, it may be expected that, in general, facilitation of this polarization should enhance ion stability. Of course, polarization of the π electron density occurs at the expense of the substituent. Perhaps the facilitation of polarization by the "trans" approach of the proton is unfavorable only in formyl fluoride, where it leads to an increased electron density loss by the fluorine atom. The destabilization of the base which results may not be compensated by the formation of a stronger H^+–O bond. Therefore, in this case "cis" protonation, in which the fluorine atom retains a greater electron density, is more favorable.

The STO-3G and 4-31G results of Tables I and II suggest that successive substitution of methyl groups increases the proton affinities of carbonyl bases, in agreement with experimental data.[21,22] Similarly, both basis sets predict that successive substitution of fluorine atoms lowers the proton affinities of the resulting carbonyl compounds relative to formaldehyde. However, it is interesting to note that the degree to which these proton affinities change relative to formaldehyde may be different when computed with the two basis sets. At the STO-3G level, the proton affinity of acetone is predicted to be approximately 25 kcal/mol greater than that of formaldehyde, while at the 4-31G level, the difference is 20 kcal/mol. On the other hand, the difference between the proton affinities of carbonyl fluoride and formaldehyde is only 13 kcal/mol at the STO-3G level but 42 kcal/mol at the 4-31G level. The data of Tables I and II also suggest that the proton affinities of formic acid and formaldehyde are similar. However, the STO-3G results indicate that formic acid is a better proton acceptor than formaldehyde by 3 or 10 kcal/mol, depending on whether protonation occurs "cis" or "trans" to the OH group. The 4-31G results predict that the proton affinity of formic acid is either 6 or 12 kcal/mol less than that of formaldehyde. Discrepancies such as these can be understood if characteristics of these basis sets are considered. It is known that minimal basis sets tend to underestimate the electronegativities of the more electronegative elements, while basis sets such as 4-31G tend to overestimate these electronegativities. These characteristics are reflected in the relative proton affinities of the substituted carbonyl compounds. The proton affinity of carbonyl fluoride is probably too great relative to formaldehyde at the STO-3G level and too small at the 4-31G level. Basis set characteristics are also evident in the results of the Mulliken population analyses. Thus, the STO-3G results indicate that the carbonyl oxygen becomes slightly less negatively charged in a protonated ion compared to the corresponding base, as significant electron density is transferred to the proton. The 4-31G results suggest that when the base is polarized by the proton, the oxygen actually gains a little electron density. Again, the fluorine atom in protonated formyl fluoride is predicted to be approximately uncharged at the STO-3G level, while the 4-31G results indicate that the fluorine retains a significant amount of electron density and remains negatively charged in the ion.

Protonation vs. Hydrogen Bonding. It is appropiate at this time to make some comparisons between the substituted carbonyl compounds as bases toward the strong acid H^+ and toward the weak acid H_2O. The STO-3G results from ref 11 and 12 will be used for comparison. In those studies of hydrogen bonded dimers HOH···OCHR and HOH···OCR_2, equilibrium structures were analyzed in terms of the General Hybridization Model (GHM) for the hydrogen bond. Qualitatively, this model suggests that there should exist a directional character for hydrogen bonds, which arise as a lone pair of electrons takes part in the formation of a linear hydrogen bond. The gas-phase structures of $(H_2O)_2$[28] and $(HF)_2$[29] support this model. However, it has also been noted that some distortions of these dimer structures may easily occur, as intermolecular force constants are relatively small.[30] Therefore, it is important to distinguish between the directed lone pair and the linear hydrogen bond, which are the primary factors which determine the structures of equilibrium dimers, and secondary factors, which have been associated with secondary structural features of these dimers or which are responsible for variations in equilibrium dimer structures away from idealized GHM structures. The secondary factors have been identified as the orientation of the dipole moments of the proton donor and proton acceptor molecules and long-range interactions.[11]

An example of the structural influence of secondary factors is found in the water–formamide dimers A and B. Structures of A- and B-type dimers are illustrated in Figure 2. In dimer A, the substituent R is "trans" to the water molecule with respect to the C–O bond, while in dimer B, the substituent R is "cis" to water with respect to the C–O bond. In the water–formamide dimer A, the angle θ_2 is 117°, a value consistent with the directed lone pair of GHM. However, in dimer B, in which the NH_2 group is "cis" to water, the angle θ_2 is reduced to 95° as a cyclic dimer is formed. This dimer is stabilized by the formation of two nonlinear O–H···O and N–H···O hydrogen bonds, and by a favorable alignment of the dipole moments of water and formamide. In the study of ref 11, no equilibrium B-type structure for a water–formic acid dimer was reported which had formic acid as the proton acceptor molecule. When the OH group of formic acid is "cis" to water, the equilibrium dimer structure is one in which formic acid is the proton donor. Therefore, while the structures of dimers in the series HOH···OCHR are generally consistent with structures anticipated from GHM, strong interaction between the substituent R in the "cis" position to the proton donor molecule may result in significant structural differences between A- and B-type dimers. Thus, substituent effects on dimers structures are more directly related to secondary effects. As noted above, the structures of the protonated ions $RCHOH^+$ A and B are similar, being essentially independent of R, and of its position "cis" or "trans" to the proton. This is a structural indication of one significant difference between hydrogen bonding, a weak acid–base interaction which results in a hydrogen bonded complex, and protonation, a strong interaction between a proton and a base which results in the formation of a protonated ion.

An even more dramatic difference exists between substituent effects on hydrogen bond energies and substituent effects on protonation energies. In the study of the dimers HOH···OCHR, it was observed that except for the water–formamide dimers the hydrogen bond energies of dimers in this series are within 0.5 kcal/mol of the 3.3 kcal/mol stabilization energy of the water–formaldehyde dimer. This small variation in dimer stabilities was attributed to a counterbalancing of opposing σ and π effects of the substituents. Thus, it is apparent that the substituent effect on hydrogen bond energies is a rather small effect on a weak acid–base interaction energy in this series.

The increased stability of the water–formamide dimers relative to other dimers in the series was also noted in ref 11. In dimer A, the hydrogen bond energy is 5.1 kcal/mol, compared to the 3.3 kcal/mol stabilization energy of the water–formaldehyde dimer. The increased stability of the water–formamide dimer A was attributed to the strong π-donating effect of the NH_2 group. The stability of the cyclic water–formamide dimer B is even greater, at 6.4 kcal/mol. Its increased stability is directly attributable to secondary effects.

The importance of secondary effects in dimer stabilization is also illustrated by comparing the stabilities of two water–formaldehyde dimers, both having planar C_s symmetry.[3] In the first, the external O–H bond of water is "trans" to the C–O bond of formaldehyde with respect to the O–O line. The structures A and B of Figure 2, with R = H, correspond to this structure, which is an equilibrium structure on the intermolecular surface. The "trans" arrangement of O–H and C–O occurs when the ϕ coordinate is 180°. The second dimer, which is not an equilibrium structure on the surface, has $\phi = 0°$. In this dimer, there is a "cis" arrangement of the O–H and C–O bonds with respect to the O–O line. Although both structures can provide for a directed lone pair of electrons and a linear hydrogen bond, the structure with $\phi = 0°$ is 1.1 kcal/mol less stable than the equilibrium "trans" structure, a reflection of an unfavorable alignment of molecular dipole moments in the "cis" form. Thus, these data suggest that in many dimers, secondary factors may have as great an influence on hydrogen bond energies as the more direct substituent effects which alter the electron distribution of the base. This, of course, is in dramatic contrast to the substituent effect on protonation energies.

Conclusions

In this study, the structures and stabilization energies of ions $RCHOH^+$ and R_2COH^+ have been determined from ab initio SCF calculations. The structures of the protonated substituted carbonyl compounds are similar to the structure of protonated formaldehyde, when computed with both the STO-3G and 431-G basis sets. This suggests that the bond formed between the proton and the carbonyl oxygen has little dependence on the bonding at the carbonyl carbon, as is typical of normal intramolecular covalent bonds. The protonation energies, however, show a strong dependence on the nature of the substituent bonded to the carbonyl carbon and a somewhat lesser dependence on its position "cis" or "trans" to the proton with respect to the C–O bond. Trends in protonation energies for ions in the series $RCHOH^+$ and R_2COH^+ are apparent in the results of these calculations at both the STO-3G and 4-31G levels. Thus, increasing ion stability shows some correlation with increasing charge transfer to H^+, decreasing electron density loss by the carbonyl group through increasing π electron polarization in the ion, and increasing n-orbital energy of the base. Where differences between the STO-3G and 4-31G results for relative ion stabilities are found, characteristics of these basis sets are evident.

In studies at this level, quantitative agreement with experimental data cannot be expected. Studies with large basis sets including polarization functions, in which some account is also made of zero-point and correlation energy corrections, and in which the rigid monomer restriction is not invoked, are necessary. In particular, investigations of ion relaxation would be most informative in providing insights into changes in molecular geometry which result as a consequence of the significant electron redistribution which occurs upon protonation.

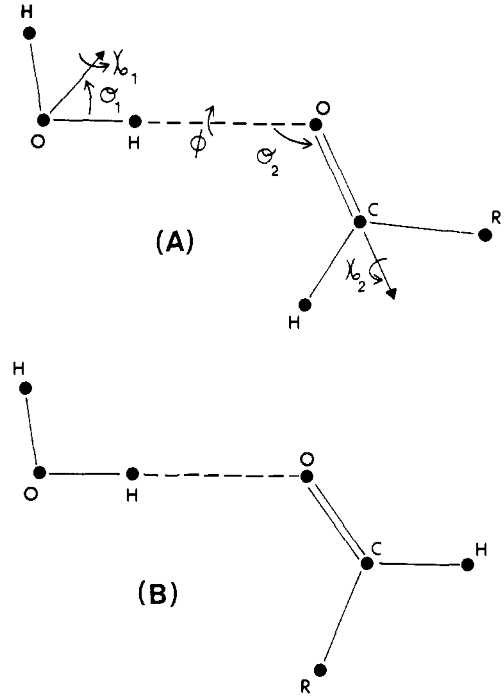

Figure 2. The dimers HOH···OCHR, A and B.

At the conclusion of an investigation such as this, it is appropriate to ask the question, "What is basicity?". It is apparent from theoretical studies of hydrogen bonding that the ability of a base to form a hydrogen bond depends not only on the proton acceptor molecule but also on the proton donor–proton acceptor combination as well.[31,32] Recent studies have noted that differences also exist between basicities measured in terms of hydrogen bond energies and basicities measured from proton affinities.[33] That basicity depends not only on some intrinsic ability of a base to donate a pair of electrons but also on the ability of an acid to accept that electron pair was fundamental to the concepts of hard and soft acids and bases[34] and charge and frontier controlled chemical reactions.[35] Essential to an understanding of basicity is the recognition that the interaction energy in any acid–base reaction is influenced by several factors, which may be weighted differently depending on the acid and the base. In a recent paper, Arnett noted differences between hydrogen bond energies and proton affinities of various bases and suggested that the gas-phase proton affinity of a molecule be used as the standard measure of basicity.[36] This suggestion could be quite beneficial if adopted. Gas-phase proton affinities are least complicated by other factors and are becoming more readily available through such experimental techniques as chemical ionization mass spectrometry and ion-cyclotron resonance and through molecular orbital calculations. However, even the basicity toward H^+ is not a measure of some intrinsic molecular property called basicity, for undoubtedly, basicity toward any acid also depends upon the properties of that acid.

Acknowledgments. This investigation was supported by NIH Research Grant No. 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, is gratefully acknowledged. Thanks are also due to Dr. Ronald Jonas and the staff of the Youngstown State University Computer Center for their continued support and assistance.

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Π and Σ States of the *N*-Formamido Radical: An ab Initio Molecular Orbital Study[1]

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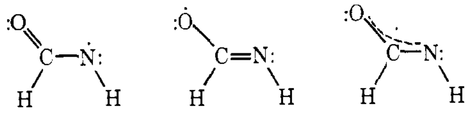
Received November 18, 1975

Abstract: Ab initio molecular orbital calculations are reported for the *N*-formamido free radical in its low-lying states. Geometry searches using an STO-3G basis set predict that both Σ and Π states each have at least two potential minima in their planar conformations, corresponding to localization of the unpaired electron at oxygen and at nitrogen. The energies of the different minima in the two states are all rather similar according to 4-31G basis set calculations. Both "allylic" and "twisted" geometries for the lowest Π state were also considered. Unpaired spin densities calculated by the restricted Roothaan open-shell method are reported for the various potential minima.

There has been considerable discussion in the literature with regard to the electronic structure of simple amido radicals.[2] For the planar *N*-formamido radical, two types of low-lying states should exist (as in the $NH_2\cdot$ free radical): so-called Π states in which the odd electron occupies a molecular orbital which is antisymmetric with respect to reflection in the molecular plane and Σ states in which the electron occupies a symmetrical orbital. The lowest-energy Π state could possess a carbon–oxygen double bond and a "single" carbon–nitrogen linkage (Π_N) as in formamide, or a carbon–nitrogen double bond and a carbon–oxygen single bond (Π_O), or exist with intermediate CN and CO bond lengths in an "allylic" form (Π_a). (Scheme I. The π electrons are indicated by dots *above* the atom symbols, whereas lone-pair electrons in the σ system are denoted by dots to the *side* of the symbol. The C, N, O, or a subscript on the state designation indicates the atom on which the unpaired electron principally is localized.)

Scheme I. Π State


Π_N Π_O Π_a

The unpaired electron in the lowest-energy Σ state of the formamide radical could be localized on the nitrogen (Σ_N), giving rise to a π-bonding stiuation similar to that in formamide itself, or localized in an in-plane 2p orbital on oxygen (Σ_O), thereby yielding a carbon–nitrogen double bond (Scheme II).

Scheme II. Σ State


Σ_N Σ_O

Since the interpretation of the ESR spectra of amido radicals has proved somewhat controversial[2] and since only semiempirical calculations regarding the energetics of the Π and Σ states have been reported,[2,3] we thought it worthwhile to reconsider the problem using ab initio calculations. Here we report the results of these computations, which used the Roothaan restricted open-shell MO method[4] together with the