

- N.Y., 1973, 1975; (b) W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, N.Y., 1971.
- (3) P. J. Stang, *Chem. Rev.*, **78**, 383 (1978). This comprehensive review is devoted exclusively to the chemistry of unsaturated carbenes.
 - (4) P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.*, **98**, 3731 (1976).
 - (5) M. L. Halberstadt and J. R. McNesby, *J. Am. Chem. Soc.*, **89**, 3417 (1967).
 - (6) R. W. Carr, Jr., T. W. Elder, and M. G. Topor, *J. Chem. Phys.*, **53**, 4716 (1970).
 - (7) H. M. Frey, *J. Chem. Soc., Chem. Commun.*, 1024 (1972).
 - (8) R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932).
 - (9) J. F. Harrison and L. C. Allen, *J. Am. Chem. Soc.*, **91**, 807 (1969). This paper includes a detailed summary of the earlier semiempirical, ab initio, and experimental studies on methylene.
 - (10) J. F. Harrison, *Acc. Chem. Res.*, **7**, 378 (1974). References cited in this paper provide a comprehensive overview of experimental and theoretical results on methylene prior to 1974.
 - (11) S. V. O'Neil, H. F. Schaefer, III, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971).
 - (12) P. J. Hay, W. J. Hunt, and W. A. Goddard, III, *Chem. Phys. Lett.*, **13**, 30 (1972).
 - (13) C. F. Bender, H. F. Schaefer, III, D. R. Franceschetti, and L. C. Allen, *J. Am. Chem. Soc.*, **94**, 6888 (1972).
 - (14) D. R. McLaughlin, H. F. Schaefer, III, and C. F. Bender, *Theor. Chim. Acta*, **25**, 352 (1972).
 - (15) V. Staemmler, *Theor. Chim. Acta*, **31**, 49 (1973).
 - (16) J. A. Altmann, I. G. Csizmadia, and K. Yates, *J. Am. Chem. Soc.*, **96**, 4196 (1974).
 - (17) C. P. Baskin, C. F. Bender, C. W. Bauschlicher, Jr., and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **96**, 2709 (1974).
 - (18) V. Staemmler, *Theor. Chim. Acta*, **35**, 309 (1974).
 - (19) U. Lamanna and M. Maestro, *Theor. Chim. Acta*, **36**, 103 (1974).
 - (20) J. F. Harrison and D. A. Wernette, *J. Chem. Phys.*, **62**, 2918 (1975).
 - (21) J. S. Altmann, I. G. Csizmadia, and K. Yates, *J. Am. Chem. Soc.*, **97**, 5216 (1975).
 - (22) A. H. Pakiari and N. C. Handy, *Theor. Chim. Acta*, **40**, 17 (1975).
 - (23) C. W. Bauschlicher, Jr., H. F. Schaefer, III, and C. F. Bender, *J. Am. Chem. Soc.*, **98**, 1653 (1976).
 - (24) C. W. Bauschlicher, Jr., C. F. Bender, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **98**, 3072 (1976).
 - (25) J. H. Meadows and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **98**, 4383 (1976).
 - (26) C. W. Bauschlicher, Jr., H. F. Schaefer, III, and P. S. Bagus, *J. Am. Chem. Soc.*, **99**, 7106 (1977).
 - (27) L. B. Harding and W. A. Goddard, III, *J. Chem. Phys.*, **67**, 1777 (1977).
 - (28) D. Gervy and G. Verhaegen, *Int. J. Quantum Chem.*, **7**, 115 (1977).
 - (29) C. W. Bauschlicher, Jr., and I. Shavitt, *J. Am. Chem. Soc.*, **100**, 739 (1978).
 - (30) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968).
 - (31) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Am. Chem. Soc.*, **94**, 9095 (1972).
 - (32) A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **55**, 3835 (1971).
 - (33) J. H. Davis, W. A. Goddard, III, and L. B. Harding, *J. Am. Chem. Soc.*, **99**, 2919 (1977).
 - (34) C. E. Dykstra and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **100**, 1378 (1978).
 - (35) W. J. Hehre, J. A. Pople, W. A. Lathan, L. Radom, E. Wasserman, and Z. R. Wasserman, *J. Am. Chem. Soc.*, **98**, 4378 (1976).
 - (36) G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand-Reinhold, Princeton, N.J., 1966.
 - (37) D. C. Moule and A. D. Walsh, *Chem. Rev.*, **75**, 67 (1975).
 - (38) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).
 - (39) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
 - (40) J. Almlöf, University of Stockholm Institute of Physics Report 74-29, Dec 1974; Proceedings of the Second Seminar on Computational Problems in Quantum Chemistry, Strasbourg, France, 1972.
 - (41) R. J. Bartlett and I. Shavitt, *Chem. Phys. Lett.*, **50**, 190 (1977); *Int. J. Quantum Chem.*, **S11**, 165 (1977).
 - (42) R. J. Bartlett and D. M. Silver, *J. Chem. Phys.*, **62**, 3258 (1975); **64**, 1260, 4578 (1976); *Phys. Rev. Sect. A*, **10**, 1927 (1974); *Chem. Phys. Lett.*, **29**, 199 (1974); **37**, 198 (1976); *Int. J. Quantum Chem.*, **S8**, 271 (1974); in "Quantum Science", J. L. Calais, O. Goscinski, J. Linderberg, and Y. Öhrn, Ed., Plenum Press, New York, N.Y., 1976, p 393.
 - (43) R. J. Bartlett, S. Wilson, and D. M. Silver, *Int. J. Quantum Chem.*, **12**, 737 (1977); S. Wilson, D. M. Silver, and R. J. Bartlett, *Mol. Phys.*, **33**, 1177 (1977).
 - (44) G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.*, **68**, 2114 (1978).
 - (45) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem.*, **S10**, 1 (1976).
 - (46) A. Meunier, B. Levy, and G. Berthier, *Int. J. Quantum Chem.*, **10**, 1061 (1976).
 - (47) J. A. Pople, R. Seeger, and R. Krishnan, *Int. J. Quantum Chem.*, **S11**, 149 (1977).
 - (48) E. R. Davidson in "The World of Quantum Chemistry", R. Daudel and B. Pullman, Ed., Reidel, Dordrecht, Holland, 1974, p 17; S. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, **8**, 61 (1974).
 - (49) G. A. Baker, Jr., *Adv. Theor. Phys.*, **1**, 1 (1965); in "The Padé Approximant in Theoretical Physics", G. A. Baker, Jr., and J. L. Gammel, Ed., Academic Press, New York, N.Y., 1970, p 1.
 - (50) O. Goscinski, *Int. J. Quantum Chem.*, **1**, 769 (1967).
 - (51) E. Brändas and O. Goscinski, *Phys. Rev. Sect. A*, **1**, 552 (1970).
 - (52) R. J. Bartlett and E. J. Brändas, *J. Chem. Phys.*, **56**, 5467 (1972); **59**, 2032 (1973).
 - (53) J. L. Whitten and M. Hackmeyer, *J. Chem. Phys.*, **51**, 5584 (1969).
 - (54) H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4997 (1961).

A Molecular Orbital Study of Protonation. 5. Equilibrium Structures and Energies of Ions R_2COH^+

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Abstract: Ab initio SCF calculations have been performed to determine the relative proton affinities of the carbonyl bases R_2CO and the structures of the ions R_2COH^+ , with R one of the isoelectronic saturated groups CH_3 , NH_2 , OH , and F . The predicted order of proton affinity with respect to R is $NH_2 > CH_3 > OH > H > F$, which is the same order predicted for the monosubstituted carbonyl bases $RCHO$. Replacement of the hydrogen atom in $RCHO$ by a second R group causes a further change in the proton affinity of the base in the same direction as observed upon substitution of the first R group, although the effect of two substituents is less than additive except in F_2CO . Protonation of carbonyl bases leads to an increase in the C-O bond distance and a decrease in the bond distance between the carbonyl carbon and the substituent, the magnitude of which depends on the substituent. Protonation also causes changes in the bond angles about the carbonyl carbon which are essentially independent of the nature of the substituent, but strongly dependent on the position of the proton relative to the two substituents. Changes in bond lengths and bond angles and in the electron distribution upon protonation of the bases R_2CO are similar to the changes which occur upon protonation of the bases $RCHO$. From the computed results, a model for the protonation of carbonyl bases is proposed.

Introduction

In part 3 of this series,¹ the relative proton affinities of the bases $RCHO$ were computed, and an analysis was made of substituent effects on proton affinities. In that study, the equilibrium structures of the relaxed ions $RCHOH^+$ were

determined, and comparisons between the structures of these ions and the structures of the corresponding bases $RCHO$ provided insight into the geometry changes due to protonation. That study has now been extended to the disubstituted carbonyls R_2CO , with R comprising the isoelectronic saturated

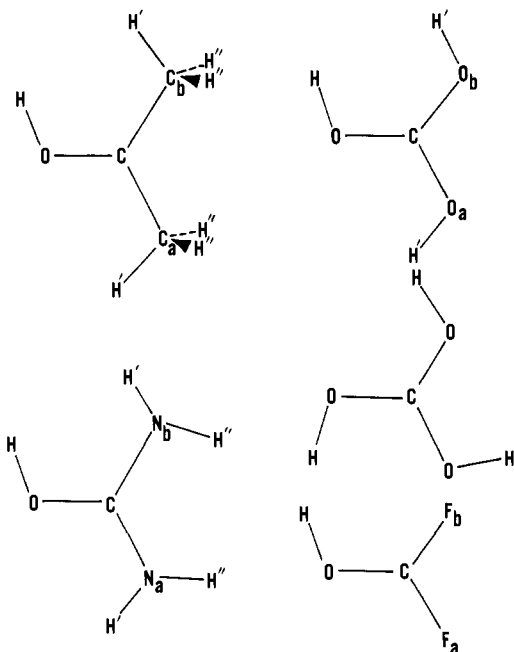


Figure 1. The ions R_2COH^+ .

groups CH_3 , NH_2 , OH , and F . The purpose of the present study is sixfold: (1) to determine the relative proton affinities of the bases R_2CO ; (2) to investigate the effect of varying the R group and the effect of mono- vs. disubstitution on the proton affinities of carbonyl bases; (3) to determine the equilibrium structures of the ions R_2COH^+ ; (4) to compare the structures of these ions with each other and with the structures of the corresponding ions $RCHOH^+$; (5) to investigate the electron redistribution which occurs upon protonation of these bases, and to compare these data with trends in the electron redistribution observed upon protonation of the bases $RCHO$; and (6) to formulate a model for the protonation of carbonyl compounds.

Method of Calculation

Wave functions for the closed-shell ground states of the ions R_2COH^+ have been expressed as single Slater determinants constructed from doubly occupied molecular orbitals. The orbitals ψ_i have been 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 $c_{\mu i}$ determined by solving the Roothaan equations.² Two atomic orbital basis sets have been employed for these calculations. The first is the minimal STO-3G basis set with standard scale factors.³ The second is the extended split-valence 4-31G basis set.⁴

In part 3 of this series,¹ it was demonstrated that although the STO-3G basis set severely overestimates the proton affinities of carbonyl bases, the STO-3G structures of ions $RCHOH^+$ are similar to the structures obtained from 4-31G calculations. More significantly, similar trends in changes in bond lengths and bond angles upon protonation of bases $RCHO$ are evident at both the STO-3G and 4-31G levels. Therefore, in the present study, the structures of the relaxed ions R_2COH^+ have also been computed using the STO-3G basis set. For these ions, C_s symmetry has been assumed, and bond distances and bond angles have been optimized cyclicly and independently to $\pm 0.01 \text{ \AA}$ and $\pm 1^\circ$, respectively. Parabolic interpolation has then been employed to estimate bond distances to 0.001 \AA and bond angles to 0.1° . For protonated

Table I. Relative Proton Affinities of Substituted Carbonyl Compounds (STO-3G)^a

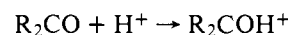
	R_2CO $-\delta\Delta E$	$RCHO$ ^b	
		$-\delta\Delta E(A)$ ^c	$-\delta\Delta E(B)$ ^c
$R = H$	0.0	0.0	0.0
CH_3	27.9	15.3	15.3
NH_2	61.3	41.9	38.9
OH	21.1 (30.1) ^d	17.7	11.4
F	-6.4	-2.1	-0.8

^a In kcal/mol. Based on a computed proton affinity of 221.3 kcal/mol for H_2CO . ^b Data for $RCHO$ taken from ref 1. ^c Ions in set A have the proton trans to R with respect to the CO bond. Those in set B have the proton cis to R . ^d Proton affinity of $(OH)_2CO$ determined from the ion of C_{3h} symmetry.

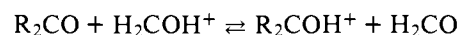
acetone and protonated carbonic acid, the conformations of the methyl and hydroxyl groups, respectively, have been constrained to be those found in the lowest energy structures of the bases,⁵ and are shown in Figure 1. However, since this conformation of hydroxyl groups does not lead to the lowest energy structure for protonated carbonic acid, a second conformation which leads to an ion structure having C_{3h} symmetry has also been optimized. The equilibrium structures of the bases R_2CO have been reported previously.⁶

In addition to the STO-3G calculations, 4-31G calculations have been performed to determine the relative proton affinities of acetone and carbonic acid. To this end, the structures of acetone, protonated acetone, carbonic acid, and protonated carbonic acid (C_{3h}) have also been optimized using the 4-31G basis set, and the same optimization procedure as employed for the STO-3G studies. All calculations have been performed in double precision on an IBM 370/148 computer.

The proton affinity of a base R_2CO is the negative energy ($-\Delta E$) for the exothermic reaction



computed as the difference between the energies of the geometry-optimized ion R_2COH^+ and the corresponding base R_2CO . The proton affinity of a disubstituted carbonyl base relative to H_2CO is expressed as $-\delta\Delta E$, which is the energy of the proton transfer reaction



A positive value of $-\delta\Delta E$ indicates that the proton affinity of R_2CO is greater than that of H_2CO .

Results and Discussion

Proton Affinities. The computed STO-3G relative proton affinities of the bases R_2CO are reported in Table I. These data indicate that substitution of two NH_2 groups has the most dramatic effect on the proton affinity of a carbonyl base, as the computed proton affinity of urea is 61.3 kcal/mol greater than that of formaldehyde, and more than 30 kcal/mol greater than that of the other disubstituted carbonyl bases. While substitution of two CH_3 , NH_2 , or OH groups increases the proton affinities of carbonyl bases relative to H_2CO , substitution of two F atoms lowers the proton affinity of F_2CO relative to H_2CO .

As evident from Table I, the computed STO-3G proton affinities of acetone and carbonic acid differ by only 2.2 kcal/mol, with carbonic acid predicted to have the higher proton affinity. However, this prediction is suspect since the computed STO-3G proton affinity of formic acid is also greater than that of acetaldehyde, a prediction which is contrary to experimental data⁷ and to the results of 4-31G calculations.⁸ As noted previously, the minimal STO-3G basis set may be too inflexible to provide generally reliable estimates even of relative proton affinities of related bases,^{8,9} since it appears to over-

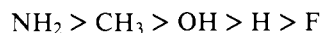
Table II. Relative Proton Affinities and Ionization Potentials of H₂CO, CH₃CHO, and (CH₃)₂CO

	$-\delta\Delta E^a$	$-\delta\Delta E^a$	$-\delta\Delta H^a$	ionization potentials ^b		
	(STO-3G)	(4-31G)	(exptl) ^c	(STO-3G)	(4-31G)	(exptl) ^d
H ₂ CO	0.0	0.0	0.0	9.64	12.00	10.88
CH ₃ CHO	15.3	13.1	10.4	9.17	11.54	10.23
(CH ₃) ₂ CO	27.9	23.1	19.3	8.76	11.16	9.70

^a In kcal/mol. ^b In eV. ^c Experimental data taken from ref 7. ^d G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1967.

estimate electron transfer to the proton^{8,10} and underestimate the electronegativities of the substituents OH and F in protonated carbonyl bases.^{1,8} Therefore, the proton affinities of acetone and carbonic acid have been recomputed with the larger 4-31G basis set.

As anticipated, there is a reversal in the computed relative proton affinities of these bases at the 4-31G level, with acetone predicted to have the higher proton affinity by 13.2 kcal/mol. The 4-31G relative proton affinities ($-\delta\Delta E$) for formaldehyde, carbonic acid, and acetone are 0.0, 9.9, and 23.1 kcal/mol, respectively. These 4-31G results and those of part 1¹¹ combined with the STO-3G relative proton affinities lead to a predicted order of proton affinity for the bases R₂CO with respect to R of



which is the same order predicted for the bases RCHO.

The effect of mono- vs. disubstitution on the proton affinities of carbonyl bases may be analyzed by comparing the relative proton affinities of the bases R₂CO with the relative proton affinities of the corresponding bases RCHO, which are also reported in Table I. To make this comparison for carbonic acid, it is appropriate to use the proton affinity computed from the energy of the ion of C_s symmetry, since the relative hydrogen atom positions are the same in this ion as in cis and trans protonated formic acid. It is apparent from the data of Table I that replacement of the H atom in RCHO by a second R group further changes the proton affinity of the base in the same direction as observed upon substitution of the first R group. For the bases RCHO, only F substitution lowers the proton affinity relative to H₂CO. Substitution of the second F atom further reduces the proton affinity of F₂CO, and only in this case is the effect of two substituents more than additive. This may be due to the fact that in FCHOH⁺, electron transfer to the proton through the σ electron system occurs to a significant extent at the expense of the H atom, owing to the greater electronegativity of F. Since electron transfer to the proton has a stabilizing effect on protonated bases, and since replacement of the H atom by a second F atom tends to decrease the amount of electron transfer, the relative proton affinity of F₂CO is significantly lower than that of FCHO. In contrast, for those substituents CH₃, NH₂, and OH which increase the proton affinity of the bases relative to H₂CO, substitution of a second R group further increases the proton affinity, although the effect of the two R groups is less than additive in these cases.

The effect of mono- vs. disubstitution of methyl groups on computed relative proton affinities of carbonyl bases may be compared with experimental gas-phase data. As evident from Table II, the theoretical STO-3G and 4-31G results and the experimental data indicate that methyl substitution in carbonyl bases increases proton affinities, but that the effect of two methyl groups is less than additive. The relative proton affinities of these bases computed with the 4-31G basis set are in better agreement with experimental data than the STO-3G values.

The first ionization potentials as approximated by Koopmans' theorem for the same bases H₂CO, CH₃CHO, and

Table III. Mulliken Population Data for R₂COH⁺ (STO-3G)

R ₂ COH ⁺	oxygen electron population ^a	electron transfer to H ⁺	electron loss by CO	π -electron gain by CO
R = H	8.117 (8.188)	0.617	0.280	0.0
CH ₃	8.164 (8.226)	0.662	0.233	0.072
NH ₂	8.212 (8.319)	0.706	0.208	0.322
OH ^b	8.211 (8.300)	0.678	0.265	0.277
F	8.160 (8.236)	0.623	0.313	0.176

^a Data in parentheses are oxygen electron populations in the bases.

^b Data for protonated carbonic acid are for the C_s structure.

(CH₃)₂CO are *n* electron ionizations from the carbonyl oxygens. Although these ionization potentials are underestimated by the STO-3G basis set and overestimated by the 4-31G basis, the decrease in the computed ionization potentials upon successive methyl substitution does parallel the experimental data, as evident from Table II. Thus, both theory and experiment indicate a correlation between increasing proton affinity and decreasing ionization potential for this series of bases. This type of correlation is expected in a related series of molecules in which *n* electron ionization is essentially localized at a single atom which is also the site of protonation. As noted previously,¹ the correlation between decreasing ionization potential and increasing proton affinity may arise from the common mechanism of stabilizing the resulting ions, which involves a polarization of electron density toward the basic site.

The electron redistribution in the ions R₂COH⁺ has the same general characteristics found in the ions RCHOH⁺, and is a consequence of the strong interaction between the proton and the electrons of the carbonyl base. As evident from the Mulliken populations¹² of Table III, protonation results in a loss of electron density by the base through electron transfer to the proton. Increasing electron transfer to the proton tends to correlate with increasing stability of the ion, and therefore with increasing proton affinity of the base, except that charge transfer in F₂COH⁺ is slightly greater than in H₂COH⁺ even though H₂CO has the higher proton affinity. The larger charge transfer in F₂COH⁺ is most probably due to the underestimation of the electronegativity of F by the minimal STO-3G basis set.

Protonation leads to a further polarization of electron density toward and within the carbonyl group. As a result of this polarization, the carbonyl oxygen remains negatively charged in the ions, and the carbon atom and atoms in the substituents lose electron density. In ions which have separable π electron systems, electron polarization occurs in both σ and π systems. A correlation exists between the order of increasing proton affinity of the bases F₂CO, (OH)₂CO, and (NH₂)₂CO and the order of increasing π -donating ability of the substituents F, OH, and NH₂. In the protonated bases, π electron polarization tends to compensate for σ electron density loss by the carbonyl group. As a result, even though charge transfer to the proton increases in these ions as the proton affinity increases, the electron density lost by the carbonyl group decreases with increasing proton affinity. Thus, these data suggest that the ability of substituents to donate electrons is an important factor

in stabilizing these ions, and therefore in determining the relative proton affinities of these carbonyl bases.

Structures. The structures of the relaxed ions R_2COH^+ and of the corresponding bases R_2CO are reported in Table IV, and the ion structures are shown in Figure 1. As evident from these data, dramatic structural changes occur upon protonation of carbonyl bases. In the ions, there is a significant lengthening of the carbonyl C–O bond, the increase varying with the substituent, and ranging from 0.072 Å in protonated acetone to 0.126 Å in protonated urea. Protonation thus produces a much greater variation in the C–O bond length in the ions R_2COH^+ than occurs in the bases R_2CO . Moreover, protonation lengthens the C–O bond in R_2COH^+ to a greater extent than in the corresponding ions $RCHOH^+$. The longer C–O bonds and the reduced Mulliken total and π C–O overlap populations in R_2COH^+ relative to R_2CO suggest that protonation weakens the C–O bond in these ions. This is consistent with experimental data which show that complexation of carbonyl compounds with Lewis acids lowers the C–O stretching frequency.¹³

Protonation of the bases R_2CO also leads to a decrease in the bond distance between the carbonyl carbon and the substituent (the C–X bond, where X is the first-row atom of the R group bonded to the carbon), the magnitude of which depends on the nature of the substituent. Significant decreases in C–X bond lengths are found upon protonation of the bases $(NH_2)_2CO$, $(OH)_2CO$, and F_2CO , which have separable π systems and π -donating substituents. The largest decreases are found in protonated urea, the base with the strongest π -donating groups, where the C–N bonds trans and cis to the proton (C–N_a and C–N_b, see Figure 1) shorten by 0.069 and 0.062 Å, respectively, thereby facilitating π donation. The shorter C–X bonds and the increased total and π C–X overlap populations suggest that protonation strengthens the C–X bonds in these ions.

In contrast to the large changes in the C–X bond lengths which occur upon protonation of $(NH_2)_2CO$, $(OH)_2CO$, and F_2CO , protonation of $(CH_3)_2CO$ leads to only small decreases of 0.017 and 0.019 Å in the C–C_a and C–C_b bond distances, respectively. In addition, only slight increases in the C–C Mulliken overlap populations are found, and the C–O π overlap population does not increase significantly. These data suggest a different mechanism for electron donation from the substituents. In protonated acetone, electron donation from the methyl groups results in electron density loss almost exclusively by the methyl hydrogens which, combined, bear an increased positive charge of 0.424 e. Therefore, it appears that methyl groups stabilize the positive charge in protonated acetone by through-bond electron transfer to the carbonyl group rather than by a hyperconjugative effect.

As evident from Table IV, the two C–X bond lengths in R_2COH^+ are nearly equal, and therefore essentially independent of the position of the proton. A similar observation was made concerning the C–X bond length in $RCHOH^+$, which was found to be essentially independent of whether protonation occurs cis or trans to the C–X bond. However, protonation does lead to a larger decrease in the C–X bond length in $RCHOH^+$ than in the corresponding ion R_2COH^+ , presumably because stabilization of the ion through electron donation by the substituents is limited to one R group in the former and divided between two in the latter.

Unlike changes in bond lengths, changes in the O–C–X bond angles about the carbonyl carbon exhibit a strong dependence on the proton position, and only a slight dependence on the nature of the substituent. In the ions of C_s symmetry, protonation results in a significant decrease in the O–C–X angle trans to the proton (O–C–X_a), ranging from 6.4° in protonated acetone to 8.9° in protonated urea. On the other hand, protonation leads to only small changes in the O–C–X angle cis

Table IV. Structures of Ions R_2COH^+ (STO-3G)^a

R_2COH^+	base ^b	ion		
R = H ^c	CO	1.217	1.271	
	CH _a	1.101	1.114	
	CH _b	1.101	1.114	
	R		1.003	
	OCH _a	122.8	116.4	
	OCH _b	122.8	123.0	
	θ		114.7	
	CH ₃	CO	1.219	1.291
		CC _a	1.543	1.526
		C _a H ^d	1.086	1.090
CC _b		1.543	1.524	
C _b H ^e		1.086	1.090	
R			0.997	
OCC _a		122.3	115.9	
CC _a H ^f		109.9	110.1	
H'C _a H'' ^d		108.8	110.1	
OCC _b		122.3	122.3	
CC _b H ^f	109.9	112.1		
H'C _b H'' ^e	108.8	109.4		
θ		113.0		
NH ₂	CO	1.222	1.348	
	CN _a	1.412	1.343	
	N _a H'	1.013	1.024	
	N _a H''	1.012	1.022	
	CN _b	1.412	1.350	
	N _b H'	1.013	1.023	
	N _b H''	1.012	1.022	
	R		0.991	
	OCN _a	123.7	114.8	
	CN _a H'	119.0	119.0	
CN _a H''	122.6	122.1		
OCN _b	123.7	123.0		
CN _b H'	119.0	121.6		
CN _b H''	122.6	120.7		
θ		109.3		
OH ^f	CO	1.216	1.331 (1.322)	
	CO _a	1.385	1.320	
	O _a H'	0.990	0.996 (0.995)	
	CO _b	1.385	1.327	
	O _b H'	0.990	0.994	
	R		0.993	
	OCO _a	125.8	117.8	
	CO _a H'	104.2	109.2 (110.0)	
	OCO _b	125.8	128.2	
	CO _b H'	104.2	111.8	
θ		112.8		
F	CO	1.209	1.299	
	CF _a	1.347	1.300	
	CF _b	1.347	1.306	
	R		1.001	
	OCF _a	125.0	118.2	
	OCF _b	125.0	123.6	
	θ		112.8	

^a Bond lengths in Å, bond angles in degrees. See Figure 1 for labeling of atoms. ^b Structures of bases R_2CO taken from ref 6. ^c Data for H_2CO and H_2COH^+ taken from ref 1. ^d Methyl C_aH bonds and HC_aH angles assumed equal. ^e Methyl C_bH bonds and HC_bH angles assumed equal. ^f Data in parentheses are for the ion of C_{3h} symmetry.

to the proton (O–C–X_b). The largest change in the O–C–X_b angle, which is only 2.4°, occurs in the C_s structure of protonated carbonic acid, and is the only case in which this angle increases upon protonation. This increase most probably occurs to reduce the repulsion between nearby hydrogen atoms (see Figure 1). The net result of changes in the O–C–X angles upon protonation of carbonyl bases is an increase in the X–C–X angle in the ions from 6 to 10° relative to the corresponding bases. It appears that the X–C–X angle increases to reduce the increased repulsion between the substituents, which is a con-

sequence of the electron redistribution in the ion. Since the $X-C-X$ angle increases if one or both of the $O-C-X$ angles decrease, and since a reduction in the $O-C-X_b$ angle would result in a closer approach of the cis R group to the proton, the $O-C-X_b$ angle remains relatively constant while the $O-C-X_a$ angle decreases significantly. The angular changes which occur in the ions R_2COH^+ are similar to those found in the ions $RCHOH^+$, where protonation also leads to a significant decrease in the $O-C-X$ and $O-C-H$ angles when they are trans to the proton, and only a slight change in these angles when they are cis to the proton, with the net result being an increase in the $X-C-H$ angle.

The position of the proton relative to the carbonyl group, described by the protonation coordinates R , the $O-H$ distance, and θ , the $H-O-C$ angle, is only slightly dependent on the nature of the substituent. In the combined series of ions R_2COH^+ and $RCHOH^+$, the $O-H$ distance varies only from 0.991 Å in protonated urea to 1.003 Å in protonated formaldehyde, while the $H-O-C$ angle varies from 109.3° in protonated urea to 114.7° in protonated formaldehyde. The variations in the values of these protonation coordinates are within the limits suggested by categorizing the bond between the proton and the carbonyl oxygen as a polar covalent bond.

As noted above, the major structural changes caused by protonation of the bases R_2CO have been analyzed in the ions of C_s symmetry, in which the conformations of the R groups are the same as in the corresponding bases. However, for protonated carbonic acid, the ion of C_s symmetry is not the most stable structure. Rather, the equilibrium structure is an ion of C_{3h} symmetry which has three equivalent $C-O$ and $O-H$ bonds, as shown in Figure 1. The $C-O$ and $O-H$ bond lengths and the $C-O-H$ bond angles in this ion are similar to the $C-O$ and $O-H$ bond lengths and the $C-O-H$ bond angles in the ion of C_s symmetry, as evident from the data of Table IV. Of course, the $O-C-O$ angles in the C_{3h} structure are fixed by symmetry at 120° .

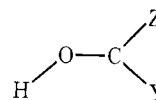
A Model for the Protonation of Carbonyl Bases. The following theoretical model, which includes major energetic, electronic, and structural features, has emerged from the STO-3G and 4-31G studies of the protonation of mono- and disubstituted carbonyl bases reported in this paper and in part 3.¹

Protonation of a carbonyl base at the carbonyl oxygen occurs in a region of high electron density associated with one of the oxygen lone pairs of electrons, and leads to the formation of a polar covalent bond between the oxygen atom and the proton. The formation of this bond is accompanied by electron transfer from the base to the proton, which tends to increase with increasing proton affinity, and by a further polarization of the electrons in the base both toward and within the carbonyl group. As a result, the electron population of the oxygen atom in the ion changes to only a small extent, the overlap population in the $C-O$ bond decreases, and the carbonyl carbon and the atoms or groups of atoms bonded to it (the substituents) lose electron density. This electronic reorganization leaves the oxygen atom negatively charged in the ion, weakens and lengthens the $C-O$ bond, and disperses the positive charge onto the carbonyl carbon and the substituents. Thus, the electron density transferred to the proton comes primarily from the carbonyl carbon and the substituents rather than the oxygen atom.

In ions with separable σ and π systems, the proton polarizes both the σ and the π electrons. There is a correlation between increasing π -donating ability of the substituent and increasing proton affinity of the base. Donation of π electrons is accompanied by a shortening of the bond between the carbon and the substituent, the magnitude depending on the substituent but not on its position cis or trans to the proton with respect to the

carbonyl $C-O$ bond. When a methyl group is the substituent, in which case there is no $\sigma-\pi$ separability, electron donation occurs almost exclusively from the hydrogen atoms in a through-bond rather than hyperconjugative interaction, and the length of the $C-C$ bond to the substituent decreases only slightly. In all ions, the ability of substituents to donate electrons to the carbonyl group is an important factor in determining the relative proton affinities of carbonyl bases.

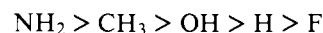
The loss of electron density by the carbonyl substituents affects the interaction between them in two ways. First, it increases the repulsion between the atomic cores (nuclei and inner-shell electrons) of the two substituents, and second, it reduces the unfavorable electronic interaction indicated by negative Mulliken overlap populations. The first effect appears to be the more important one, as the angle defined by the carbonyl carbon and the atoms bonded to it (the $Y-C-Z$ angle)



always increases upon protonation of carbonyl bases. An increase in the $Y-C-Z$ angle requires a reduction in either or both the $O-C-Y$ and $O-C-Z$ angles. Since a reduction in the $O-C-Y$ angle is restricted by the presence of the proton, this angle remains relatively constant, while the $O-C-Z$ angle which is trans to the proton decreases significantly relative to the base.¹⁴

Conclusions

Ab initio SCF calculations have been performed in this study to determine the relative proton affinities of the carbonyl bases R_2CO , and the structures of the relaxed ions R_2COH^+ , with R one of the isoelectronic saturated groups CH_3 , NH_2 , OH , and F . These calculations predict that the order of proton affinity of the bases R_2CO with respect to R is



which is the same order predicted for the bases $RCHO$. A comparison of the relative proton affinities of the bases $RCHO$ with the corresponding bases R_2CO indicates that substitution of a second R group causes a further change in the proton affinity of the base in the same direction as observed upon substitution of the first R group. Only when R is F does substitution lead to a decrease in the proton affinity of the carbonyl base, and only in F_2CO is the effect of two substituents more than additive.

Protonation results in a significant electron redistribution in the protonated bases due to the strong interaction between the proton and the electrons of the base. Upon protonation, electron density is lost by the base through electron transfer to the proton. This is accompanied by a further polarization of electron density toward and within the carbonyl group. It appears that the ability of substituents to donate electrons to stabilize the positive charge is an important factor in determining the relative proton affinities of carbonyl bases.

Protonation also leads to dramatic structural changes in the ions. These include an increase in the carbonyl $C-O$ bond length and a decrease in the bond length between the carbonyl carbon and the substituent (the $C-X$ bond), the magnitude of which is strongly dependent on the substituent but only slightly dependent on the position of the proton relative to the two $C-X$ bonds. In contrast, changes in the $O-C-X$ bond angles about the carbonyl carbon are essentially independent of the substituent, but strongly dependent on the proton position. While the $O-C-X$ bond angle trans to the proton decreases significantly in these ions, the $O-C-X$ bond angle cis to the proton changes very little. The net result of these angular changes is an increase in the $X-C-X$ bond angle. The values of the pro-

tonation coordinates which include the O-H distance and the H-O-C angle are relatively constant, which suggests that the bond between the carbonyl oxygen and the proton may be classified as a polar covalent bond. Structural changes which occur upon protonation of the bases R_2CO are similar to the changes which occur upon protonation of the bases $RCHO$. From the computed results, a model for the protonation of carbonyl bases has been proposed.

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References and Notes

- (1) J. E. Del Bene, *J. Am. Chem. Soc.*, **100**, 1673 (1978).
- (2) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

- (3) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (4) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
- (5) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *Aust. J. Chem.*, **25**, 1601 (1972).
- (6) J. E. Del Bene, G. T. Worth, F. T. Marchese, and M. E. Conrad, *Theor. Chim. Acta*, **36**, 195 (1975).
- (7) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).
- (8) J. E. Del Bene, *Chem. Phys. Lett.*, **55**, 235 (1978).
- (9) J. E. Del Bene, *J. Am. Chem. Soc.*, **99**, 3617 (1977).
- (10) H. Uneyama and K. Morokuma, *J. Am. Chem. Soc.*, **98**, 4400 (1976).
- (11) J. E. Del Bene and A. Vaccaro, *J. Am. Chem. Soc.*, **98**, 7526 (1976).
- (12) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
- (13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Chapman and Hall, London, 1975; "Advances in Infrared Group Frequencies", Chapman and Hall, London, 1975.
- (14) Implicit in this model is the assumption that the H-Y interaction is generally not a stabilizing one. This had been proposed by other investigators [A. C. Hopkinson and I. G. Csizmadia, *Can. J. Chem.*, **52**, 546 (1974)], who suggested that the H-F interaction in cis protonated $FCHOH^+$ is stabilizing due to the formation of an $O-H \cdots F$ hydrogen bond. Neither the small but negative H-F Mulliken overlap populations nor the changes in the cis O-C-F angles in $FCHOH^+$ and F_2COH^+ support this suggestion.

Theoretical Study of Some Ethylene-Halogen Molecule (Cl_2 , Br_2 , I_2) Complexes at Large and Intermediate Distances from ab Initio Calculations

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Abstract: Ab initio calculations have been carried out on several configurations of the $C_2H_4 \cdots Cl_2$ complex, adding the dispersion energy to the SCF supermolecule energy. It is found that the most stable configuration is the axial model. Similar calculations have been performed for the axial geometry of the $C_2H_4 \cdots Br_2$ and $C_2H_4 \cdots I_2$ complexes. The three axial complexes exhibit the same qualitative behavior for each intermolecular energy contribution: the charge transfer and induction energy are important but not able to give a really significant minimum depth; it is essential to take account of the dispersion energy, as in the case of van der Waals molecules. The depths of the minima and the corresponding intermolecular distances are evaluated. The nature of the binding is discussed.

I. Introduction

The special importance of ethylene-halogen molecules complexes is largely due to their possible role in the trans addition of halogen molecules to ethylene. It is most generally admitted that the first step of this reaction may begin by the formation of such complexes.¹⁻⁵

The origin of the stability of these complexes is not clear and experimental data may support different interpretations.⁶ Some authors⁴ describe them as three-center covalently linked Dewar's π complexes.^{7,8} This idea initiated the first theoretical work,³ based on the use of an extended Hückel molecular orbital approach. Other authors⁵ rather consider them as charge-transfer complexes, by analogy with the class of complexes described by Mulliken.⁹ The difference between these two categories of complexes has been underlined by Bantorpe.¹⁰ In particular, the possible role of van der Waals forces is discussed in the case of the second class of complexes.^{9,10}

Clearly, theoretical information is necessary to understand the origin of the binding of these complexes since experimental data are not able to give a definitive answer. Unfortunately, difficulties are also encountered in theoretical treatments and we must be aware that artificial results are easily obtained. For

instance, some approximations lead to a systematic overestimation of the binding energy with a too short intermolecular equilibrium distance. This happened with the two SCF calculations^{11,12} based on the CNDO approximation which treated some geometrical configurations of the $C_2H_4 \cdots Cl_2$ or $C_2H_4 \cdots F_2$ systems. For the axial configuration of $C_2H_4 \cdots Cl_2$, both calculations give a very large SCF minimum depth (-6.2 ,¹¹ -2.38 ¹² kcal/mol) and a very short intermolecular distance (2.259 ,¹¹ 2.210 Å¹²) while our ab initio SCF calculations^{13,14} give a stabilization energy of -0.64 kcal/mol and an intermolecular distance of 3.704 Å. In the latter paper,¹⁴ we also showed that the dispersion energy contribution, not taken into account in a SCF treatment, is larger than the induction and charge transfer energy. Thus a correct minimum depth cannot be obtained from SCF calculations and it is absolutely necessary to take the dispersion energy contribution into account.

Experimental data¹⁵ show that the ethylene chlorine complex has a C_{2v} symmetry. As discussed by Fredin and Nelander,¹⁵ two models—the axial and the resting configurations—may be of particular interest. These two configurations are studied in the present work, along with an "X" configura-