Semiempirical SCF–LCAO–MO Calculations of Carbonyl Donor Basicities and Carbonyl Adduct Structures. Protonated Formaldehyde and Acetaldehyde[1a]

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Received June 23, 1969

Abstract: Calculations of the CNDO variety have been performed for acetaldehyde and formaldehyde and for various structures of the protonated forms of these carbonyl donors. *cis* and *trans* isomers of protonated aldehydes and asymmetric ketones are known and the CNDO results are in generally excellent agreement with experiment. Theoretical confirmations of the relative stabilities of the *cis* and *trans* isomers of $CH_3CHO \cdot H^+$ and of the various J_{H-H} are presented. Bent's isovalent hybridization arguments, as applied to these carbonyl donors, are found to be consistent with basic SCF theory. Trindle's method of analysis of zero differential overlap functions is useful in interpreting donor molecule electron density changes (atom directed-orbital changes, decomposition of LCAO–MO functions into VB resonance contributions, and CH_3 "hyperconjugation"). The calculations reveal very explicitly, without recourse to a localized orbital description, the role of oxygen nonbonding electron density in determining the adduct structure.

The carbonyl group, RR′CO, as an electron pair donor, has been extensively studied. Many Lewis adducts are known and X-ray diffraction studies of many of these adducts have established the structures to be nonlinear.[2] No LCAO–MO studies have been reported which analyze the cause for the nonlinear $CO \cdot X$ arrangement.

Nmr evidence[3] has indicated that inversion at the oxygen atom in protonated aldehydes and ketones occurs, and that, in asymmetric ketones RR′CO, structural isomers are possible.

The present calculations were undertaken to examine (1) the mechanisms for substituent effects on oxygen basicity, (2) intradonor electron reorganization on adduct formation, and (3) the feasibility of intramolecular exchange (oxygen inversion) as a suitable pathway for high-temperature averaging of the Lewis acid magnetic resonance signals of $RR'CO \cdot H^+$.

As this work was nearing completion, a report[4] of similar studies with limited basis gaussian type orbitals appeared in the literature. We find basic agreement with those calculations, but disagreement is encountered regarding the relative stabilities of *cis* and *trans* adduct structures.

Calculations

The calculations are of the CNDO/2 variety.[5] Discussion of the formalism and parameterization has been given previously and will not be repeated.[6] The molecular structures of acetaldehyde and formaldehyde are well known.[7]

Results and Discussion

The variation of *total* molecular energy of H_2COH^+ as a function of OH^+ distance and COH^+ angle is shown in Figure 1. These results were obtained for an undistorted H_2CO molecule, the oxygen atom lies at the origin, and H^+ motion is confined to the molecular plane. The results are quite similar for CH_3CHO, and both H_2CO and CH_3CHO, in which the CO bond distance is increased by 0.04 Å. The minimum in total energy occurs at close to $COH^+ = 120°$, in agreement with structures of other Lewis acid adducts of carbonyl donors. There is a saddle point in the energy surface for the linear $C–O–H^+$ structure at ~20 kcal/mole above the angular structure. Combined with experimental estimates[3] of the barrier to inversion (>17 kcal/mole), these results suggest that in-plane wagging of the H^+ could be an acceptable reaction coordinate for the inversion. It might also be noted that there is a fair amount of mechanical anharmonicity to be associated with this motion.

Quantitatively (see Table I), the activation energy for $H_2CO \cdot H^+$ inversion is computed to be +23 kcal/mole for the in-plane motion, while that for $CH_3CHO \cdot H^+$ is nearly the same, +24 kcal/mole (starting from the *cis* H, H^+ structure). Another possible reaction coordinate for inversion involves rotation of the $O–H^+$ vector about the C–O axis (out-of-plane motion). For both $H_2CO \cdot H^+$ and $CH_3CHO \cdot H^+$ this motion is computed to have a lower $\Delta E^{\ddagger}$ than the in-plane motion. The values cited in Table I for this energy are really upper limits, since energy minimization with respect to ROH^+ and COH^+ in this transition state was not performed. The difference in linear and rotated transition state energies is most pronounced for acetaldehyde and can be related to hyperconjugative effects of the methyl group. Because of the approximations inherent to the CNDO/2 formalism, it would be injudicious to attach too much

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[1] (a) Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; (b) National Science Foundation Undergraduate Research Participant.

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[5] Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

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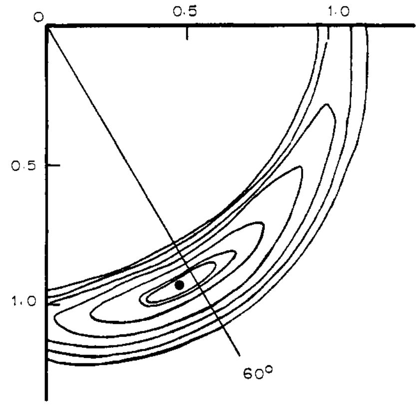

Figure 1. Energy contour map for H^+ motion in the molecular plane of H_2CO. The oxygen atom is centered at the origin; axis units are Å. Contours are drawn for the following energies (au): −27.200, −27.210, −27.220, −27.230, −27.240, −27.245, and −27.246.

significance to the difference in $\Delta E^{\ddagger}$ for the in-plane and out-of-plane reaction coordinates. It is apparent, however, that both are energetically very similar, and both mechanisms are likely to play a significant role in oxygen inversion. Similar results were found in the studies[4] with GTO's, although the rotated transition state was found to be of higher energy.

Table I. Relative Energies of Isomers of $RR'CO \cdot H^+$

	E, kcal/mole
$H_2CO \cdot H^+$ (angular)	0.0
(linear)	+23
(rotated)[a]	+22
$CH_3CHO \cdot H^+$ (*cis*)	0.0
(*trans*)	+3
(linear)	+24
(rotated)[a]	+17

[a] The rotated structures have the same R_{OH^+} and COH^+ angle as the minimum energy planar configuration; H^+ lies in the plane bisecting the HCH angle.

A point of departure of the results of these calculations from the GTO analysis concerns the relative stabilities of the *cis* and *trans* structures of acetaldehyde. The CNDO/2 results predict the *cis* structure to be more stable than the *trans* by 3.0 kcal/mole. Calculations for $CH_3CHO \cdot H^+$ with the CO distance increased by 0.04 Å retain the stability order *cis* > *trans;* ΔE is, however, slightly smaller (+1.6 kcal/mole). The more extensive GTO calculations, with the CO distance increased 0.04 Å, predict the opposite order with ΔE = 1.4 kcal/mole. The experimental nmr studies[3b] of protonated acetaldehyde suggest that the *cis* form is indeed the more stable, with $K = 5$.[3c] The experimental result is, however, subject to the assumption that *trans* proton coupling in CH_3CHOH^+ is greater than *cis.* The analogy between protonated[5] acetaldehyde and propene is obvious, and is the basis for identification of the *cis* configuration as the more stable. Certainly, the energy difference *cis* → *trans* is very small, and the CH_3 group exerts only a small directing influence on the position of the acid H^+.

Table II lists the ratios of various J_{H-H}, both experimental and computed. The J_{H-H} values (calcd) were assumed proportional to the bond index values[8] for the appropriate proton pair. Others[9] have achieved good agreement with experiment using a similar scheme. The agreement between computed and theoretical (*trans*/*cis*) ratios is remarkable and includes not only ethylenic coupling but allylic as well. Thus, *cis* allylic coupling is known[3b] to be greater than *trans*, and in *trans* $CH_3CHO \cdot H^+$ the (*cis*) CH_3–H^+ coupling is computed to be larger than the (*trans*) CH_3–H^+ coupling in the *cis* $CH_3CHO \cdot H^+$ by a factor of 3.

Table II. Ratios of $J_{H \cdot H}(trans):J_{H \cdot H}(cis)^a$

	Atom pair	Calcd	Exptl[b]
$H_2CO \cdot H^+$	CH, H^+	2.4	2.4
$CH_3CH \cdot OH^+$	CH, H^+	2.5	2.2
	CH_3, H^+	2.9	>4.0
	CH_3, H	0.8	~1.0

[a] For $H_2CO \cdot H^+$, *trans* and *cis* refer to the spatial location of the coupled nuclei; for $CH_3CHO \cdot H^+$, *trans* and *cis* refer to the molecular isomers. [b] Reference 3b.

Of considerable interest to both inorganic and organic chemists is the charge redistribution in the donor molecule on adduct formation and the effect of a carbon substituent on donor basicity. Detailed analysis of the charge redistribution, from several different points of view, is underway and will be reported. The protonation energies of H_2CO and CH_3CHO are computed to be −268 and −305 kcal/mole, respectively. These values are in line with those expected for substitution of H by CH_3. However, the value of −268 for H_2CO must be compared with the experimental[10] value of −161 kcal/mole. The agreement is rather poor and may be attributed principally to the parameterization of the CNDO formalism.[11] (Interestingly, a minimum basis set GTO calculation[12] gives a value for the protonation energy of formaldehyde of −294 kcal/mole.)

The reorganization of electron density within the donor molecule to accommodate the presence of the proton may be examined from several points of view. The atom charge densities of the free donors and proton adducts are given in Figure 2. For both donors, charge transfer to the proton is extensive throughout the molecule. The increase in positive charge at the carbonyl carbon is striking and in keeping with the enhanced electrophilicity of the carbonyl group in the presence of Lewis acids. There appears to be no pronounced difference in charge release by the formaldehyde protons, *cis* or *trans*, although slightly more charge is released by the CH proton *trans* to the acid proton.

It is very interesting to compare acetaldehyde with formaldehyde with regard to the "electron sink" properties of H and CH_3. The composite CH_3 group charge in acetaldehyde is +0.04 compared to −0.01 for the corresponding proton in formaldehyde, which reflects the electron donor character of CH_3 relative to H. The computed H and O atom densities of acetaldehyde are larger than those of formaldehyde, although replace-

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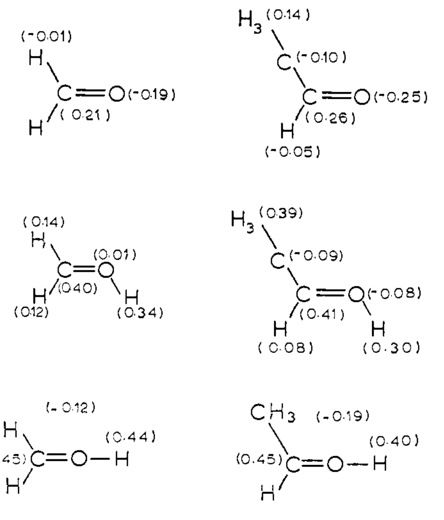

Figure 2. Atomic charges for H_2CO, CH_3CHO, and the corresponding linear and bent H^+ adducts.

ment of H by CH_3 results in a more complex charge redistribution than simple delocalization of an extra 0.05 electron; this is evidenced by the greater positive charge on the carbonyl carbon of CH_3CHO. The increased O charge could be linked with the enhanced basicity of the oxygen atom in CH_3CHO. The electron releasing character of the methyl group is not so manifest in the free donor as it is in the adduct. The methyl group charge becomes more positive by 0.26 electron, whereas that of the corresponding hydrogen of formaldehyde increases by only 0.15 electron. Slightly greater charge donation to the acid proton occurs for CH_3CHO than for H_2CO, as expected. Similarly, the oxygen charge density is greater in protonated CH_3CHO.

By making use of the technique recently published by Trindle,[13] we have decomposed the π molecular orbitals of formaldehyde and acetaldehyde into what are probably the most important valence bond structures. These are shown in Figure 3. In both formaldehyde and acetaldehyde, the C=O covalent structure makes the dominant contribution, with the C^+–O^- structure next most important, followed by C^-–O^+. As expected, both the covalent, C=O, and ionic, C^-–O^+, forms are markedly reduced in importance on adduct formation, while the ionic form, C^+–O^-, makes a greatly enhanced contribution. Trindle's technique also allows us to evaluate the importance of CH_3 hyperconjugation in acetaldehyde. It is this additional mechanism for charge release for the methyl group which facilitates greater charge donation to H^+ by acetaldehyde. In comparing protonated acetaldehyde with protonated formaldehyde, this resonance structure contributes 8% and compensates for the 6% difference in covalent, C=O, structure. Since the hyperconjugation structure places more electron density (2 e) on oxygen than does the covalent structure (1 e), the net oxygen density in $CH_3CHO \cdot H^+$ is greater than in $H_2CO \cdot H^+$.

In a further application[9] of the bond index method, we found it interesting to examine the changes in carbonyl carbon and oxygen hybridizations on adduct formation. The results are all the more interesting in view of Bent's useful isovalent hybridization concept.[14]

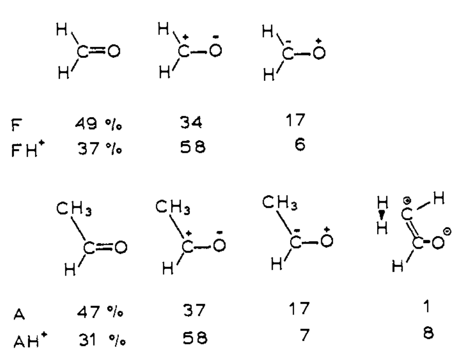

Figure 3. Decomposition of the π MO's of H_2CO, $H_2CO \cdot H^+$, CH_3CHO, and $CH_3CHO \cdot H^+$ into covalent and ionic resonance structures.

An interesting situation arises for the oxygen atom which has two lone pairs of electrons in the free donor and one in the adduct.

The per cent of p character in bonds to neighbor atoms are given in Table III. In formaldehyde and acetaldehyde, the oxygen atom is formally sp hybridized. Owing to the large axial perturbation by the carbon core, however, considerably greater oxygen p character is found in electron density shared with the carbon than in the lone pair. Correspondingly, the "axial" lone pair at oxygen contains a high degree of s character.

Table III. Distribution of Atomic p Character (%)

	H_2CO	$H_2CO \cdot H^+$	CH_3CHO	CH_3-$CHO \cdot H^+$
O → C	70.8	68.5	70.7	68.1
O → lp	29.2 (64.6)[a] 100.0 (64.6)[a]	52.7	29.3 (64.6)[a] 100.0 (64.6)[a]	51.7
O → H^+		78.8		80.2
C → O	67.8	71.2	67.4	7.12
C → H	65.0	*t*-65.5 *c*-63.3	68.2	68.2
C → C			64.4	

[a] Values in parentheses refer to the hypothetical, two equivalent lone pair (lp) alternative discussed in the text.

The carbonyl carbon in both donors is very nearly sp^2, as qualitatively expected. In formaldehyde, the greater electronegativity of oxygen than hydrogen results in greater carbon p character in density shared with oxygen than with hydrogen. In acetaldehyde, interestingly enough, the methyl carbon seems to be the least electron attracting of the three carbon neighbors. The apparent lower electron attracting propensity of oxygen than hydrogen may be a result of the greater oxygen density in this compound (Figure 2). The greater density arises primarily from the π MO *via* CH_3 hyperconjugation. This situation is analogous to synergic effects often invoked by the inorganic chemist in discussions of ligational phenomena.

Adduct formation at the oxygen atom causes only a slight reduction in oxygen p character toward carbon. The high p character in the O–H^+ bond comes primarily from the second "lone pair" (often identified as π_n) of p character in the undisturbed donor. By difference, the sole remaining lone pair has increased p character relative to the axial pair in the free donor. This inter-

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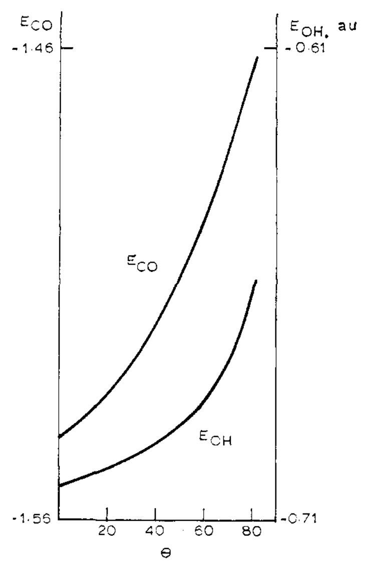

Figure 4. CO and OH+ diatom energy terms *vs.* the angle which the OH+ vector makes with the CO axis of $H_2CO \cdot H^+$.

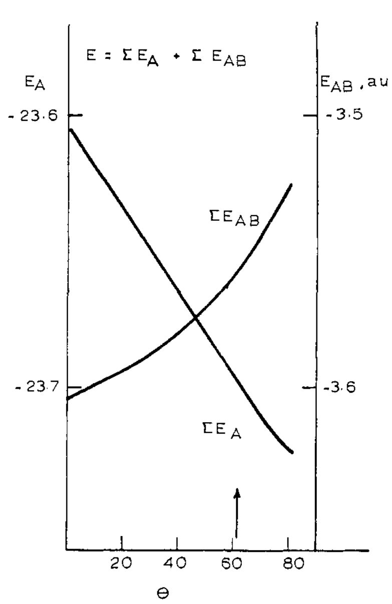

Figure 5. Total one and two center terms *vs.* the OH+, CO angle for $H_2CO \cdot H^+$.

pretation of the redistribution of oxygen lone pair p character is less satisfying (not easily accommodated in the isovalent Bent scheme) than the following alternative. Consider the two lone pairs at oxygen in the free donor (a pure p orbital and an sp hybrid) together, each with 64.6% p character (=(100 + 29.2)/2). The oxygen may be considered to be basically sp² hybridized. One of these electron pairs serves to bind the acid proton, and consequently increases in p character (64.7–78.8%) primarily at the expense of the other (64.7–52.7%). This method of interpretation is very similar to that used to rationalize the T_d structure of CH_4 from the electronic structure of a ground configuration carbon atom, and produces a result in agreement with the prediction one would make from Bent's postulates. It is interesting that the proton is viewed by oxygen as a more electronegative neighbor than the carbonyl carbon. Finally, the carbonyl carbon sees the protonated oxygen as more electronegative than in the free donor and consequently utilizes greater p character in binding the oxygen. Very much the same conclusions apply for acetaldehyde.

A final facet of these calculations which may be considered is that of driving force for the energy minimum angular rather than the linear structure. In fact, there are several terms (core repulsion + electronic) contributing to the in-plane $\Delta E^{\ddagger}$. That the computed and experimental $\Delta E^{\ddagger}$ appear to be in good agreement suggests that the CNDO formalism adequately accounts at least for the *relative* importance or magnitude of these terms. The formaldehyde case will be discussed in detail.

As discussed elsewhere,[6] the *total* molecular energy E, in the CNDO scheme, can be partitioned into chemically useful terms

$$E = \sum^{A} E_A + \sum^{B>A} E_{AB}$$

where

$$E_A = \sum_{\mu}^{A} P_{\mu\mu} U_{\mu\mu} + {}^1/_2 \sum_{\mu}^{A} \sum_{\nu}^{A} (P_{\mu\mu} P_{\nu\nu} - {}^1/_2 P_{\mu\nu}^2) \gamma_{AA}$$

The $P_{\mu\mu}$'s in this expression are the diagonal elements of the density matrix appropriate to atom A. $U_{\mu\mu}$ is defined as the one electron, one center kinetic plus core potential energy integral, $\langle \phi_\mu | -{}^1/_2 \nabla^2 - V_A | \phi_\nu \rangle$; γ_{AA} is the two electron, one center electron repulsion integral, $\langle \phi_\mu(1) \phi_\nu(2) | r_{12}^{-1} | \phi_\mu(1) \phi_\nu(2) \rangle$.

E_{AB} is the contribution to the total energy from all two center integrals involving centers A and B, and can be partitioned into covalent binding, core repulsion, and ionic terms.[6b]

In comparing the energies of the linear and bent structures of protonated formaldehyde, the energy difference is 23 kcal/mole. As shown in Table IV, the change in all two center terms is destabilizing by +27.5 kcal/mole. The positive energy contributions to the two center terms arise in $E_{C=O}$ (+28.5) and E_{OH^+} (+10.8). The sum of all other atom pair energy changes (ten of them) is stabilizing by −11.8 kcal/mole. The driving force for the bent *vs.* linear structure is, therefore, to be found principally in the one center terms. See Figures 4 and 5 for a graphical summary of the two center and one center energies, and the CO and OH two center energies as a function of θ, the angle the O–H+ vector makes with the CO internuclear axis (the ordinate units in these graphs are au's).

Table IV. Electron Redistribution and Energy Changes

	$H_2CO \cdot H^+$ (linear → bent), kcal/mole	$CH_3CHO \cdot H^+$ (linear → bent), kcal/mole
$\Delta\Sigma E_A$	−50.7	−56.6
$\Delta\Sigma E_{AB}$	+27.5	+33.1
ΔE_{CO}	+28.5	+77.4
ΔE_{OH^+}	+10.8	−1.3
ΔE_C	−15.6	−16.7
ΔE_O	−16.6	−22.2
ΔE_{H^+}	−25.1	−25.8
Oxygen AO densities	$s^{1.49}p^{4.68} \rightarrow s^{1.60}p^{4.41}$,	$s^{1.48}p^{4.71} \rightarrow s^{1.60}p^{4.48}$

Of the five one center energy changes, those for oxygen (−16.6 kcal/mole), carbon (−15.6 kcal/mole), and hydrogen (−25.1 kcal/mole) are negative. Each of these one center energy changes may be further dissected into electron–nuclear and electron–electron interactions—attractive in the former instance and repulsive in the latter. The atom charges in Figure 2 show that acid proton motion off the CO axis to the energy minimum position results in charge flow from the oxygen to the proton and from the aldehyde hydrogens to the carbon. This charge flow results in the energy changes, broken down into electron–nuclear and electron–electron changes, given in Table V. Charge removal from the oxygen has the expected effect of increasing the total energy while charge donation to carbon and H^+ has stabilizing effects. The net change in electron–nuclear energy, however, is a positive quantity (+177 kcal/mole) because of charge loss by the oxygen. Simple charge donation by oxygen (0.10 of the 0.13 electron density decrease at oxygen goes to H^+) actually destabilizes the bent structure. The third column of Table V shows a major contribution to the driving force for the structure change; the oxygen atom is stabilized by a marked decrease in electron–electron repulsion. Charge flow onto H^+ and the carbon atom results in increased electon–electron repulsion at those centers. The net change in repulsion energy for the three atoms involved is −235 kcal/mole. Thus, the major energetic consequences of the structure change are due to the oxygen density, and the decrease in oxygen electron repulsion more than offsets the effect of "ionization" of oxygen.

Table V. ΔE(e,c) and ΔE(e,e) for Linear $H_2CO \cdot H^+ \rightarrow$ Angular $H_2CO \cdot H^+$

Atom	ΔE(e,c),[a] kcal/mole	ΔE(e,e),[b] kcal/mole	ΔE_A, kcal/mole
C	−58	+42	−16
O	+274	−291	−17
H	−39	+14	−25
	+177	−235	−58

[a] $\Delta E(\text{e,c}) = \Delta(\Sigma P_{\mu\mu} U_{\mu\mu})$. [b] $\Delta E(\text{e,e}) = \Delta[{}^1/_2 \Sigma\Sigma(P_{\mu\mu}P_{\nu\nu} - {}^1/_2 \cdot P_{\mu\nu}{}^2)\gamma_{AA}]$.

An alternate interpretation may be given by simply collecting energy change terms in a different way. Thus, the major energy changes which accompany the charge redistribution in the protonated formaldehyde molecule occur at the carbonyl carbon, the oxygen, and the acid proton. Charge transfer of an additional 0.1 electron into the H 1s orbital by the donor molecule as a whole leads to stabilization of the bent structure by 25 kcal/mole, an amount nearly the same as $-\Delta E^{\ddagger}$. One point of view, and for predictive and correlative purposes, perhaps the simplest, is that enhanced charge transfer or donor–acceptor interaction occurs (recall the presence of the high energy, π_n orbital) in the bent structure relative to the linear, and this factor is responsible for the observed structural preference (all other electron reorganization effects essentially cancel one another as far as energy is concerned).

This latter view, while useful, is unnecessarily naive and masks some very important consequences of electron reorganization in the donor molecule. Large energy changes have been seen to arise from redistribution of density at the donor atom. The electron redistribution at the oxygen is very important, and the structural change, linear → bent, is, in a sense, permitted only because the oxygen atom repulsion energy can be so markedly reduced to offset the destabilizing effects of charge loss by oxygen. By examination of the oxygen atom electron–electron repulsion on an AO basis (the second term in the expression for E_A), it is apparent that the great reduction in electron repulsion stems from charge loss in the lone pair (π_n) p orbital density; that is, both the intra- and interatomic orbital repulsion energies with this orbital are reduced. The contributions of the other oxygen AO densities to the second term in the E_A expression are such that those electron–electron repulsions change in a destabilizing manner (increase) on passing from the linear to bent structures. The large repulsion associated with the π_n orbital, and between the π_n density and the other oxygen density in the linear molecule stems from the large occupation (2 e) of this AO, while the others have computed densities less than 1.5 electrons. These repulsion forces at the donor may be drastically reduced by transfer of some of the π_n orbital density to the proton, and this can only occur when the acid takes a nonaxial position. Transfer of electron density into the H 1s orbital is, on the whole, exothermic, and is greater when the oxygen p orbital pair (π_n) (of higher energy than the sp pair) can become involved in the binding of the acid. Oxygen rehybridization arises naturally from the nonaxial H^+ position.

A useful compromise view of the bent structure preference, therefore, is that not only does the electron poor acid achieve adduct stabilization through charge transfer, but also electron–electron repulsion "pressure" at the donor atom assists this charge transfer. Similar comments, on a larger scale, apply to the more energetic donor–acceptor process: donor + $H^+ \rightarrow$ donor·H^+.

There is, therefore, nothing inherent in oxygen atom hybridization (sp^2 *vs.* sp) *per se* which leads to lower energy for the bent adduct structure. Rather this is an inescapable consequence of electron–electron repulsions on the donor atom and the correspondingly high energy of the π_n orbital. The electron–electron repulsion energy arises mainly in the O π_n lone pair orbital, and between this orbital and the remaining oxygen AO density. Thus, electron–electron repulsion energies are seen to play an instrumental role in determining the structures of carbonyl adducts.[15]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[15] NOTE ADDED IN PROOF. Analysis of these molecules by the energy-localized orbital technique has been completed and many of the points discussed above are dramatically evident in terms of the localized orbitals. A manuscript which considers these points and others is in preparation.