Localized-Orbital Model for Carbonyl Donors

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Abstract: The results of INDO calculations of H_2CO and H_2COH^+ and CH_3CHO and CH_3CHOH^+ have been treated by the energy localization procedure of Edmiston and Reudenberg to describe the effect of adduct formation on the carbonyl group. Charge density analysis of the localized orbitals is used to illustrate the simplicity of the localized-orbital treatment of adduct formation in contrast with the conventional delocalized-orbital description. Concepts such as bonds formed from overlapping hybrid orbitals and distribution of atomic p character among such hybrids and the effects of adduct formation on these are discussed. The role of electron repulsions at oxygen, in making a major contribution to the oxygen inversion barrier, is discussed in terms of the four hybrid orbital bonds about the oxygen atom and localized-orbital descriptions of the oxygen inversion transition states are given. An unusual result is found for the CO bonds of CH_3CHOH^+. Finally, support from calculated proton spin coupling constants is given for the experimental and theoretical predictions that the cis structure for CH_3CHOCH^+ is more stable than the trans structure.

In a recent study[1] of the donor properties of formaldehyde and acetaldehyde by the CNDO/2 method, it was found that the inversion barrier at the carbonyl oxygen of protonated aldehydes could be attributed to *one-center* electronic energy changes as the proton passed through the linear transition state. The one-center terms which were important were those involving decreased charge donation to the proton in the transition state and greatly increased electron–electron repulsions at the oxygen. The analysis of these effects was straightforward but somewhat complex. An alternate interpretation which greatly simplifies visualization of these changes can be given if the analysis is carried out on the set of energy-localized molecular orbitals[2] for these molecules. Other aspects of interest are the description, in terms of localized orbitals, of concepts such as bond polarization, hybridization, and directed valency for the aldehydes and their proton adducts. Since the initiation of this work, several reports[3,4] of localized orbitals at various levels of theoretical sophistication have appeared for H_2CO. The general correctness of the INDO, but not CNDO/2, localized orbitals has been determined for H_2CO by comparison[5] with the results of *ab initio* calculations.[4]

Calculations

Two new programs were written in the course of these studies: a program for generation of the energy-localized molecular orbitals from the canonical orbitals, and a program for converting a set of molecular orbital functions as linear combinations of atomic (Slater) orbitals to the same set as linear combinations of parent molecular orbitals (*e.g.*, H_2COH^+ as a function of H_2CO molecular orbitals and the H 1s function). Both programs were written in Fortran IV and double-precision arithmetic for the IBM 360/50.

The energy-localized orbital program was based on the method[2] of Edmiston and Ruedenberg as adapted[6] previously by Trindle and Sinanoglu for the CNDO/2[7] set of approximations. Our program[8] will generate the localized orbitals from a set of canonical molecular orbitals which result from either the CNDO/2 or INDO[9] prescriptions. The only difference in the two options is that the latter requires special consideration of one-center electron repulsion integrals. In this report we use the INDO method.

The program begins by applying that 2 × 2 unitary transformation to the first and second of the starting molecular orbitals which maximizes their contribution to the total self-repulsion energy

$$D = \sum_i(\phi_i^2|\phi_i^2)$$

The new first orbital is then transformed with orbital three, the newly revised first orbital with orbital four, and so on. Orbital two is then successively mixed with all other orbitals and so on with each orbital in the set, each 2 × 2 transformation resulting in new forms for the orbitals just mixed. One complete pass through this process constitutes a cycle (for an n occupied orbital problem there are $n(n - 1)$ 2 × 2 transformations per cycle). The entire process is then repeated until the value of D for two successive cycles changes by less than a predetermined amount, in our studies by less than 10^{-6} (the value of the convergence limit in the INDO calculation of the canonical orbitals). Output consists of the new localized orbitals, the matrix of intra- and interorbital repulsion energies ($2J_{ij} - K_{ij}$), the transformation matrix for conversion of the starting orbitals to the final orbitals, bond index values,[10] atom charges, and active charges[11] by atoms. (The last three quantities have the same values as would be calculated from the starting orbitals, since the transformation between starting and final orbitals is unitary.)

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(1) K. F. Purcell and J. M. Collins, *J. Amer. Chem. Soc.*, **92**, 465 (1970).

(2) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963); *J. Chem. Phys.*, **43**, S97 (1965); in "Quantum Theory of Atoms, Molecules and the Solid State," by P.-O. Lowdin, Ed., Academic Press, New York, N. Y., 1966.

(3) J. del Bene, *J. Chem. Phys.*, **51**, 2290 (1969).

(4) M. D. Newton, E. Swithes, and W. N. Lipscomb, *ibid.*, **53**, 2645 (1970).

(5) W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 6864 (1969).

(6) C. Trindle and O. Sinanoglu, *J. Chem. Phys.*, **49**, 65 (1968).

(7) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

(8) T. G. M. Dolph, M. J. Schultz, and K. F. Purcell, Quantum Chemistry Program Exchange, Indiana University, Program 198.

(9) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); program available through Quantum Chemistry Program Exchange, Indiana University.

(10) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(11) C. Trindle, *J. Amer. Chem. Soc.*, **91**, 219 (1969).

If a complete set of INDO orbital functions for a molecule such as H_2COH^+ is known as a function of the atomic orbitals

$$\psi = \mathbf{C}^t\phi$$

and the complete set of INDO orbital functions for H_2CO and an isolated proton are known as a function of the same atomic orbitals

$$\chi = \mathbf{L}^t\phi$$

(χ is the set of H_2CO MO's + the hydrogen 1s orbital), then the H_2COH^+ orbitals can be written as a linear combination of the H_2CO molecular orbitals and the hydrogen 1s function by

$$\psi = \mathbf{P}^t\chi$$

where

$$\mathbf{P}^t = \mathbf{C}^t\mathbf{L}$$

A program was written to determine this latter transformation.

The orientations of the molecules on Cartesian coordinate axes are given in Table I. As before,[1] the geometries of the parent molecules have not been optimized out of uncertainty as to the reliability of this procedure by the INDO method. Our greatest concern is with bond distances. A small change in CO distance on protonation, say, will not alter the discussion of most of the results.[1] As before, we can only expect to estimate inversion barriers by these calculations, and the comparisons and conclusions given here are at a qualitative level.[1]

Table I. Atomic Coordinates[a]

	X	*Y*	*Z*
		H_2CO	
H	0.0	0.9086	−1.77594
H	0.0	−0.9086	−1.77594
C	0.0	0.0	−1.23
O	0.0	0.0	0.0
H′ (bent)	0.0	−0.93556	1.70669
H′ (linear)	0.0	0.0	2.28
H′ (out-of-plane)	−0.93556	2.0	0.47669
		CH_3CHO	
H	0.0	−0.97807	1.74876
C	0.0	0.0	1.2155
O	0.0	0.0	0.0
H′(trans)	0.0	0.934726	−0.478317
H′ (cis)	0.0	−0.934726	−0.478317
C′	0.0	1.24543	2.0524
H	0.88037	0.9956	2.63714
H	−0.88037	0.9956	2.63714
H	0.0	2.12956	1.42176

[a] In ångströms. C′ is the methyl carbon of CH_3CHO. H′ is the acid hydrogen.

Results and Discussion

Canonical *vs.* Localized Descriptions. One of the characteristic features of the molecular orbitals which result from solution of the Roothan formalism of the Hartree–Fock procedure is that the orbitals are symmetry adapted, which means that the orbitals are mathematical quantities which form bases for some or all of the irreducible representations of the molecular point group. These orbitals have come to be known as canonical orbitals. A companion characteristic is, therefore, that the orbitals are generally quite highly delocalized over the nuclear framework of the molecule. Because of the high degree of delocalization, it is often difficult to relate these orbitals and quantities calculated from them to the simpler concepts of orbitals in molecules as originally proposed by Pauling.

In the acid–base chemistry of carbonyl donors, one is interested in the changes which occur when adduct formation takes place. The most often used view of the oxygen atom is that it contains a pair of "unshared" electron pairs for coordinate bond formation. In directed orbital terms these orbitals are "sp^2" hybrids. The symmetry adapted molecular orbitals which bear most resemblance to oxygen lone pairs are one which is essentially an sp hybrid (a_1) delocalized into the CH_2 region of formaldehyde and an oxygen p orbital (b_2) delocalized into the CH_2 region. Thus neither pair is particularly well suited to a directed orbital view of the molecule. Neither are the orientations of these orbitals simply related to the bent geometry of a carbonyl adduct.

Tables II and III describe the effect of adduct formation on formaldehyde when the acid group is a simple hydrogen ion. In Table II the complexity of adduct formation is readily apparent in terms of the involvement of virtually every one of the parent base molecular orbitals (canonical) in binding the proton. It is impossible to say that any one or two of the parent molecular orbitals is responsible for binding the acid. The complexity of the response of the individual H_2CO canonical orbitals to the presence of the acid proton is demonstrated by the results given in Table III. (Major charge density changes are indicated by the circled regions of the H_2CO line figures at the bottom of each column). These atom charges also show the involvement of each parent orbital in the binding of the acid. Interestingly enough, the oxygen lone pairs exhibit charge flow into the CH_2 region while charge flows out of the CH_2 region for the CH_2 orbitals. All of the orbital changes are complex with simple inductive polarization being masked in most.

This complex pattern of individual orbital changes yields a fairly simple composite of the electron density changes for the molecule σ orbitals as a whole. The total change in atom charges due to in-plane orbitals shows (last column of Table III) the polarization of charge from the CH region toward the carbon, the polarization of charge along the CO axis away from carbon and toward oxygen, and finally polarization of oxygen density toward the proton.

This simpler picture of electron density changes in the formaldehyde molecule which result from adduct formation is more directly attainable from the set of energy localized molecular orbitals. The details are given in Table IV, where we give the changes in atomic hybrid orbital density for each localized molecular orbital. Also presented are the angles each atomic hybrid makes with the *z* axis, and the sp ratios. The localized orbital functions are given in Table V.[12]

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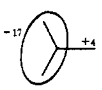
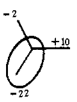
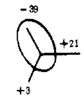
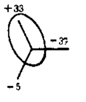
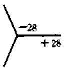
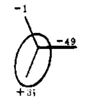
(12) (a) An anonymous referee has obtained "similar but distinctly different results" for H_2CO. The eigenvectors of Table V are those which we obtain from localization of (1) the INDO order of canonical MO's, (2) a scrambled ordering of these same MO's, and (3) a set of randomly transformed canonical orbitals. All resulted in $D = 4.320489$

Table II. H_2COH^+ Canonical Orbital Functions as Linear Combinations of H_2CO Canonical Orbitals and the H 1s Function[a]

	$H_2CO + H^+$ basis orbitals						
	H	CO σ	CH_2 (a_1)	CH_2 (b_1)	O 1p (a_1)	CO π	O 1p (b_2)
CO σ	0.24	*−0.96*	0.08	0.05	−0.04		−0.04
CH_2	0.25	0.17	*0.91*	0.20	−0.20		−0.08
CH_2	0.27	0.10	−0.33	*0.87*	−0.14		−0.16
OH	−0.21	−0.06	0.21	0.30	*0.89*		0.06
π						*0.99*	
O 1p	−0.29	−0.08	0.06	0.25	−0.24		*0.88*

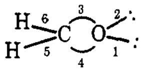
[a] Contribution from the H_2CO canonical antibonding orbitals are not listed.

Table III. Change in Atomic Charge Densities ($H_2CO \rightarrow H_2COH^+$) by Canonical Orbitals[a]

	CO σ	CH_2 (a_1)	CH_2 (b_2)	O 1p (a_1)	CO π	O 1p (b_2)	Total[b]
H_t	−0.03	−0.02	−0.27	0.18		−0.01	−0.12
H_c	−0.02	−0.16	0.03	−0.05		0.07	−0.13
C	−0.12	−0.06	−0.12	0.15	−0.28	0.26	+0.11
O	0.04	0.10	0.21	−0.37	0.28	−0.49	−0.51
H^+	0.12	0.13	0.15	0.09		0.17	+0.66
							

[a] A plus sign implies an increase and a minus sign a decrease in electron density. The units for the figures at the bottom of each column are 0.01 e. [b] For in-plane orbitals only.

Table IV. Hybrid Angles, s:p Ratios, and Changes in Hybrid Charge Density by Localized Molecular Orbitals ($H_2CO \rightarrow H_2COH^+$)



		H_2CO		H_2COH^+			
LMO		Angle[a]	sp^{x} [b]	Angle[a]	sp^{x} [b]		Δq[c]
1	O	60.3	1.86	50.7	1.74	O	0.01
2	O	60.3	1.86	61.5	3.13	O	−0.62
						H′	0.65
3	O	51.8	4.77	56.2	3.70	O	0.19
	C	50.4	4.44	45.2	4.55	C	−0.19
4	O	51.8	4.77	56.2	3.70	O	0.19
	C	50.4	4.44	45.2	4.55	C	−0.19
5	C	58.5	1.53	62.0	1.45	H	−0.11
						C	0.11
6	C	58.5	1.53	60.5	1.56	H	−0.14
						C	0.13

[a] Angles between the hybrid and the z axis in degrees. [b] The p:s ratios in the atomic hybrids. [c] The change in hybrid orbital electron density (a + sign means an increase) for each localized molecular orbital.

In this description only one of the parent (localized) orbitals strongly binds the proton. The polarization of the CH, CO, and oxygen lone-pair orbitals is readily apparent from the last column of Table IV.

Two interesting features are the effects of adduct formation on the lone pair which forms the adduct bond and on the CO bent orbitals. In accordance with Bent's isovalent hybridization rules,[13] we should expect adduct formation to increase the p character of the lone pair which forms the adduct bond. This implies a decrease in p character for the remaining 3 hybrids at oxygen. The s:p ratios illustrate this change clearly. The change in distribution of p character is interesting in that the decrease for the remaining lone pair is very slight and most of the adduct bond p character increase comes from the CO bonds.

Table V. The Localized Molecular Orbital Eigenfunctions for H_2CO and H_2COH^+ (Bent)

	CH_t[a]	CH_c[b]	CO	CO	OH^+	O
			H_2COH^+ (bent)			
C s	0.474	0.459	0.241	0.242	0.020	0.055
C p_x	0	0	−0.365	0.364	0	0
C p_y	0.504	−0.500	−0.002	−0.002	0.077	−0.077
C p_z	−0.268	−0.282	0.362	0.363	0.011	0.051
O s	0.021	0.001	0.379	0.379	−0.402	−0.599
O p_x	0	0	−0.606	0.605	0	0
O p_y	0.019	−0.001	0.015	0.015	0.625	−0.611
O p_z	−0.002	0.015	−0.406	−0.408	−0.339	−0.501
H	0.666	−0.028	−0.015	−0.015	−0.047	0.030
H	−0.030	0.676	−0.007	−0.007	0.035	−0.059
H^+	0.060	−0.023	0.006	0.006	−0.568	0.037
			H_2CO			
C s	0.438	0.438	0.277	0.277	0.038	0.038
C p_x	0	0	−0.450	0.450	0	0
C p_y	0.462	−0.462	0	0	−0.119	0.119
C p_z	−0.283	−0.283	0.372	0.372	0.015	0.015
O s	−0.008	−0.008	0.318	0.318	−0.585	−0.585
O p_x	0	0	−0.546	0.546	0	0
O p_y	−0.015	0.015	0	0	−0.692	0.692
O p_z	0.019	0.019	−0.429	−0.429	−0.395	−0.395
H	0.716	−0.040	−0.009	−0.009	0.045	−0.073
H	−0.040	0.716	−0.009	−0.009	−0.073	0.045

[a] The CH orbital trans to the OH^+. [b] The CH orbital cis to the OH^+.

Each CO bent orbital is polarized toward oxygen and experiences polarization toward the proton as a conse-

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au and all gave negative diagonal second derivatives of *D*. The source of our disagreement is unknown to us. The discrepancy is further mystifying, since he claims to have reproduced our results for H_2COH^+, CH_3CHO, and *cis*- and *trans*-CH_3CHOH^+. (b) As a measure of the success of the localization procedure, we have calculated the charge density for each localized molecular orbital which does *not* reside in atomic orbitals between atoms defining the localized pair. The extent of delocalization is generally much less than 1% for H_2CO, bent H_2COH^+, and linear H_2COH^+. For two or three of the orbitals in these three molecules, the delocalization rises to about 1.5%. For the out-of-plane molecule, however, the oxygen lone pairs exhibit delocalization of about 7% onto carbon and the OH pair of about 12% onto carbon.

(13) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

Table VI. LMO Eigenvectors for CH_3CHO, *cis*-CH_3CHOH^+, and *trans*-CH_3CHOH^+

	CH_{al}	CC	CO	CO	O_{cis}	O_{trans}	C′H	C′H	C′H
				(a) CH_3CHO					
O	0.007	−0.008	−0.318	0.319	0.584	0.581	−0.009	0.010	−0.010
	0.000	−0.000	−0.556	−0.556	0.000	−0.000	−0.000	−0.057	−0.057
	−0.019	−0.011	0.008	−0.008	−0.685	0.700	−0.004	−0.000	−0.000
	0.018	−0.019	−0.424	0.424	−0.411	−0.382	−0.015	0.016	−0.016
C	−0.409	0.450	−0.278	0.278	−0.027	−0.049	−0.009	−0.003	0.003
	0.000	−0.000	−0.433	−0.434	0.000	−0.000	0.000	0.111	0.111
	0.483	0.450	0.007	−0.007	−0.107	0.118	0.033	−0.003	0.003
	−0.259	0.288	0.373	−0.373	0.028	0.003	−0.047	0.038	−0.038
C′	0.019	0.325	0.003	−0.003	0.030	−0.021	0.405	0.355	−0.355
	0.000	−0.000	−0.016	−0.016	0.000	−0.000	0.000	0.487	0.487
	0.011	−0.485	−0.012	0.012	−0.041	0.016	0.515	−0.019	0.019
	−0.039	−0.406	0.007	−0.007	−0.024	0.021	−0.286	0.364	−0.364
H_{al}	−0.725	−0.035	0.012	−0.012	−0.051	0.082	0.040	−0.012	0.012
H	0.011	0.021	0.021	0.047	−0.005	0.001	−0.023	0.695	0.006
H	0.011	0.021	−0.047	−0.021	−0.005	0.001	−0.023	−0.006	−0.695
H	−0.039	0.010	0.015	−0.015	0.007	0.002	0.693	−0.015	0.015
				(b) CH_3CHOH^+ (cis)					
O	0.003	0.022	−0.397	−0.400	0.382	−0.585	0.014	−0.015	−0.016
	0.000	−0.001	−0.771	0.333	−0.061	0.256	−0.001	0.051	−0.048
	−0.000	−0.026	−0.124	0.036	−0.633	−0.575	−0.001	0.008	0.006
	−0.015	−0.003	−0.078	−0.603	−0.316	0.474	0.014	−0.018	−0.011
C	0.434	−0.490	−0.116	−0.318	−0.004	0.056	0.004	0.011	0.013
	0.000	−0.001	−0.410	0.178	−0.032	0.135	−0.000	−0.177	0.178
	−0.516	−0.490	−0.010	0.016	−0.075	−0.074	−0.030	0.005	0.004
	0.256	−0.269	0.194	0.476	0.005	−0.036	0.057	−0.049	−0.052
C′	−0.012	−0.289	0.005	0.005	0.020	0.013	−0.418	−0.369	−0.369
	0.000	−0.000	0.014	−0.003	0.001	−0.007	0.000	−0.498	0.498
	−0.015	0.454	−0.008	−0.016	−0.026	−0.009	−0.524	0.035	0.035
	0.027	0.384	−0.007	−0.004	−0.017	−0.014	0.302	−0.363	−0.363
H_{al}	0.688	0.028	−0.007	0.022	−0.041	−0.062	−0.043	0.013	0.012
H	−0.009	−0.018	0.033	−0.035	0.001	−0.015	0.020	−0.666	−0.006
H	−0.009	−0.018	−0.050	−0.001	−0.005	0.015	0.020	−0.006	−0.666
H	0.035	−0.006	0.008	0.020	0.001	−0.004	−0.671	0.012	0.012
H^+	−0.027	−0.066	−0.027	0.015	0.581	0.036	−0.008	0.014	0.014
				(c) CH_3CHOH^+ (trans)					
O	0.023	−0.000	0.398	0.385	0.590	−0.386	−0.019	−0.013	0.013
	0.001	0.000	0.437	−0.744	0.158	−0.049	−0.001	0.050	0.052
	0.023	−0.003	0.017	−0.073	−0.592	−0.630	−0.017	−0.002	0.004
	−0.006	0.014	0.549	0.195	−0.504	0.317	−0.011	−0.013	0.018
C	−0.449	−0.478	0.296	0.162	−0.042	0.027	−0.000	0.013	−0.012
	0.000	0.000	0.235	−0.399	0.084	−0.026	−0.000	−0.175	−0.174
	0.524	−0.488	0.002	−0.007	−0.066	0.074	0.028	0.005	−0.004
	−0.239	−0.286	−0.448	−0.252	0.055	−0.001	−0.058	−0.049	0.046
C′	0.015	−0.295	−0.003	0.001	0.022	0.017	0.415	−0.369	0.369
	0.000	0.000	−0.004	0.012	−0.004	0.001	0.000	−0.499	−0.499
	0.015	0.460	0.013	0.001	−0.032	−0.011	0.518	0.030	−0.030
	−0.029	0.386	0.001	−0.000	−0.021	−0.016	−0.304	−0.366	0.366
H_{al}	−0.676	0.026	−0.022	−0.018	−0.034	−0.051	0.038	0.010	−0.010
H	0.008	−0.019	−0.004	0.049	−0.014	−0.000	−0.021	−0.665	0.006
H	−0.034	−0.006	−0.020	−0.012	0.006	0.000	0.676	0.011	−0.011
H	0.008	−0.019	0.038	−0.029	0.004	−0.006	−0.021	−0.006	0.665
H^+	−0.069	0.021	−0.015	0.022	−0.032	−0.582	0.030	0.005	−0.005

quence of the introduction of oxygen p_y character (Table V). This increase (from zero) of oxygen p_y character in these orbitals does not violate Bent's rule because the decrease in oxygen p_z character for the CO orbitals is greater than the increase in p_y contribution (Table V). As there is an increase in the s character of the oxygen hybrids to carbon, the latter responds to adduct formation with an increase in the p character of its hybrids to oxygen. The p character of the carbon hybrids to hydrogen correspondingly decreases. The inductive polarization of the CH and CO bonds is readily apparent from the last column of Table IV.

An energy level diagram depicting the transformation from canonical H_2CO molecular orbitals to localized orbitals and the effect on the latter of adduct formation is shown in Figure 1. All these "orbital energies" were calculated from the general expression[14] $\epsilon_m = \Sigma_i\Sigma_j a_{im}\cdot a_{jm}F_{ij}$, where the a's are the LCAO coefficients (either canonical or localized) and $F_{ij} = \phi_i\hat{F}\phi_j$. $\hat{F}$ is the Hartree–Fock or self-consistent-field energy operator and the ϕ's are the atomic orbitals. The above definition of orbital energy stems from the Hartree–Fock premise that each electron in a molecule has an energy determined by its kinetic, nuclear core and *average* electron repulsion energy. While the sum of such orbital energies is invariant to the transformation from canonical to localized orbitals, the individual orbital energies are not, as is obvious from the figure. The main utility of such a diagram is to give another representation of the transformation from canonical orbitals

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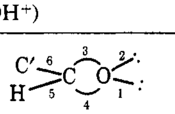
[14] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 69.

to localized orbitals. In addition, it is very easy to trace or correlate the effect of adduct formation on the orbitals of the parent base. The stabilization of all localized orbitals seen in Figure 1 is a direct consequence of the Madelung (through space) potential of the H^+ in the adduct along with the effects of bond polarization mentioned above.

As a side issue, it should be pointed out, lest the reader misunderstand, that the localized orbital energies do not have the same meaning as do those of the canonical orbitals.[15] They do not yield a diagonal Fock matrix and do not relate as closely to electronic excitation or ionization processes as do the canonical orbitals.

CH_3CHO and CH_3CHOH^+. In many respects the results for protonation of acetaldehyde are like those of formaldehyde. The localized orbital eigenvectors are given in Table VI, and a summary of atomic hybrid orbitals is given in Table VII. The one notable difference between H_2CO and CH_3CHO on protonation is the behavior of the CO bent bonds. For both cis and trans protonation the bent bonds become nonequivalent.

Table VII. Hybrid Angles, s:p Ratios, and Changes in Hybrid Charge Density by Localized Molecular Orbitals ($CH_3CHO \rightarrow$ *cis*-CH_3CHOH^+)



LMO		—CH_3CHO—		—*cis*-CH_3CHOH^+—			
		Angle[a]	sp^x [b]	Angle[a]	sp^x [b]		Δq[c]
1		59.0	1.87	63.6	3.46	O	−0.66
						H′	0.68
2		61.4	1.88	53.0	1.81	O	−0.02
3	C	49.2	4.23	64.7	15.09	C	−0.36
	O	52.7	4.84	84.3	3.90	O	0.36
4	C	49.2	4.23	20.6	2.56	C	−0.10
	O	52.7	4.81	29.0	2.97	O	0.10
5		61.8	1.80	63.6	1.76	H	−0.10
						C	0.10
6		57.4	1.41	61.2	1.30	C′	−0.14
						C	0.13

[a] Angle, in degrees, between the hybrid and the z axis. [b] The p:s ratios in the atomic hybrids. [c] The change in hybrid orbital electron density (a plus sign means an increase) for each localized molecular orbital.

The eigenvectors for *cis*-CH_3CHOH^+ in Table VI are those which resulted from localization of the canonical orbitals *after* the latter had been subjected to a randomly chosen unitary transformation. A second attempt using a different randomly chosen transformation gave LMO's virtually identical with these after reflection through the molecular plane and of only slightly smaller total intraorbital repulsion energy (5×10^{-6} au smaller). In an attempt to locate a maximum D with equivalent CO bent bonds, we tried the following. Those canonical orbitals symmetric (7) and antisymmetric (2) to reflection in the molecular plane were separately localized to give localized σ and π orbitals. These intermediate localized orbitals were then treated together to form the final localized molecular orbitals. A convergence point was quickly reached 482×10^{-6} au below the first of the random attempts. Even here, the CO orbitals are not quite equivalent (one oxygen hybrid makes an angle of 58.2° with the z axis and the other makes an angle of 56.6°). It would appear that an equivalent bent CO bond description is not possible here and that at least two relative maxima occur on the energy surface for protonated CH_3CHO. That both maxima are true maxima with respect to *pair-wise* orbital mixing was confirmed by all negative second derivatives[4,16] $D(ij, ij)$ and first derivatives less than 10^{-4} au. The repulsion energy surface curvature was smallest, in all cases, for mixing of the CO bond pairs. However, the curvature (−0.15 au) for *cis*-CH_3CHOH^+ was even greater than that for CH_3CHO (−0.06 au) which gave equivalent bent bonds.[16a]

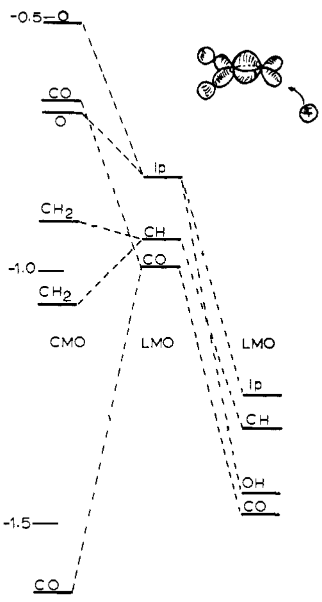


Figure 1. An orbital energy level diagram for the canonical orbitals of H_2CO, the localized orbitals of H_2CO, and the localized orbitals of H_2COH^+. Energies in atomic units.

Aside from the nonequivalent bent CO bonds, some other interesting features develop. The oxygen lone pair and the OH^+ orbitals do not lie in the molecular plane. Both are displaced to the same side of that plane by 23 and 5.5°, respectively (both angles are angles the projections of the hybrid vectors in the xy plane make with the $+y$ and $-y$ axes).

It is difficult at this point to explain the tendency for the CO bonds to *approach* a σ and π situation (Table VI). In our earlier work we found that CH_3 hyperconjugation with CO, nil in the parent base, markedly increased on protonation. This perhaps is the source of the nonequivalent CO orbital description found here (even more curious is the fact that the nonequivalent CO orbitals are 99.5% localized between carbon and oxygen).

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(15) S. R. La Paglia, "Introductory Quantum Chemistry," Harper and Row, New York, N. Y., 1971; C. C. J. Roothan, *Rev. Mod. Phys.*, 23, 69 (1951).

(16) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, 92, 3847 (1970).

(16a) NOTE ADDED IN PROOF. *Complete* second-order energy analyses[16] have been carried out for all the LMO wave functions discussed in this report. All LMO were found to correspond to true maxima on the self-repulsion surface, except those for CH_3CHOH^+ which gave a value of D some 482×10^{-6} au below the first of the random starts. Consequently we have *not* encountered two maxima on the D energy surface.

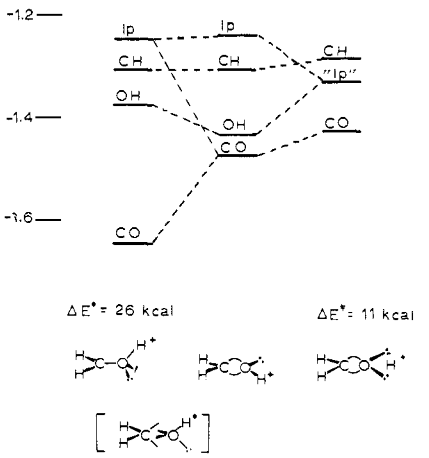


Figure 2. Localized orbital energy diagram for bent (center), linear (right), and out-of-plane (left) H_2COH^+. Energies in atomic units.

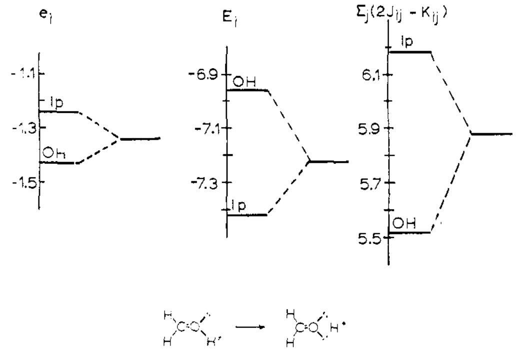


Figure 3. The lone-pair and OH bond pair orbital energies for bent H_2COH^+ in atomic units. At the center are the kinetic plus core potential energy contributions, while the electron–electron repulsion energies are at the right.

Electron Repulsion and Oxygen Inversion. In the earlier studies[1] of protonated formaldehyde, we also considered linear COH and out-of-plane COH structures for the adduct, as they represented possible transition states for inversion at the oxygen atom. The localized orbital descriptions of the transition states are quite interesting.

The striking feature for the linear geometry is that the electron-repulsion minimum criterion maintains equivalent (as opposed to sp + p) lone-pair orbitals. Each oxygen hybrid ($sp^{2.75}$) makes a 62° angle with the z axis, and each localized orbital accounts for 0.27 e on H. Thus the proton is bridging the oxygen lone pairs and, while an sp + p description is possible, it is not consistent with the requirement that interorbital electron pair repulsions be at a minimum. The second derivatives for mixing of the CO bonds are smallest (−0.11 au), with mixing of OH bonds being more sharply defined ($D = -0.24$). It is interesting that the physics of the situation yields orbitals qualitatively very similar to those of formaldehyde itself.

The essential features of the localized orbitals for the out-of-plane transition state structure are given in Figure 2. Here we find two oxygen lone pairs, a CO σ orbital, and an OH σ orbital about the oxygen atom.[12] The latter is delocalized onto the carbon ($q_C = 0.24$, $q_O = 1.20$, $q_H = 0.56$) and may be thought of as the *strongly* polarized CO π orbital from a canonical orbital treatment or in terms of an OH σ orbital which hyperconjugatively interacts with the carbon. It is initially somewhat of a surprise that the out-of-plane transition state is computed to be of not much higher energy than the linear geometry. The following point should be noted, however. With the bent geometry, the oxygen and carbon are approximately sp^4 hybridized, with two bent bonds describing the CO bonding. The simplest, but not only, relation between out-of-plane and bent geometries is the following. In the out-of-plane geometry, one of these bent bonds is replaced by a strong, "head-on" CO σ bond, while the other CO bent bond becomes an oxygen lone pair. Thus the loss of energy due to conversion of a CO bent bond to a lone pair is offset considerably by conversion of a bent bond to a strong CO σ bond. The localized orbital energy changes which correspond to this description are given in Figure 2.

Several interesting features about Figure 2 can be noted. First of all, the orbital energies, either canonical or localized, do not give an adequate description of the molecular energy change as the adduct passes through the linear and out-of-plane transition states. In fact $2\Sigma\epsilon_m$ gives the out-of-plane geometry a lower energy than the linear geometry.

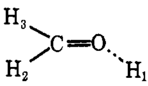
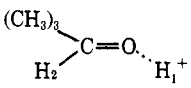
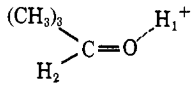
A more convenient analysis of the structure energy differences can be made in terms of the total energy expression $E = 2\Sigma E_m + \Sigma_m\Sigma_n(2J_{mn} - K_{mn}) + \Sigma_A\Sigma_B(Z_AZ_B/R_{AB})$. In this expression, E_m is the kinetic plus electron–nuclear potential of an electron in orbital m, the second term is the electron–electron repulsion energy, while the last term is the nuclear–nuclear repulsion term. The first and last terms taken together lead to the out-of-plane structure as the most stable, followed by the linear structure, followed by the bent geometry! That addition of the electron repulsion energy reverses this order shows the importance of electron repulsions in determining the relative energies of the three structures. The electron repulsion term increases by 17 kcal/mol for the linear structure and 98 kcal/mol for the out-of-plane structure and dominates the computed barriers of 11 and 26 kcal/mol, respectively.

The electron repulsions have a dramatic effect on the orbital energies as well as the total energy. Of particular interest is a comparison of the oxygen lone-pair and OH^+ pair energies, illustrated in Figure 3 for the bent and linear structures. As expected, the bonded OH^+ pair energy is lower than that of the lone pair. However, resolution of the orbital energies into kinetic plus core potential energy (center of Figure 3) shows that the lone pair would be lower in energy than the adduct bond pair as a direct consequence of the fact that the lone pair is more localized on the oxygen and has considerably greater oxygen s character. However, the electron–electron repulsion which an electron in this orbital experiences is so much greater than that of a counterpart in the OH^+ bond orbital (right side of Figure 3) that the difference in electron–electron repulsion contributions to the orbital energies dominates the difference in the kinetic plus core potential energies, and the lone-pair orbital lies higher in energy than the bond pair.

In the previous report[1] on the inversion barrier for protonated formaldehyde, it was discovered that a decrease in oxygen atom repulsions was of major importance for the stability of the bent geometry relative to the linear structure. This result is independent of the form of the molecular orbitals, as the analysis was carried out on an atomic orbital basis set and thus is the same for both canonical and localized orbitals. A major disadvantage with the canonical orbitals is the difficulty in working with molecular orbitals which are so highly delocalized and the inconsistency of that description with the concept of an oxygen lone pair and OH bond in the adduct. With the localized molecular orbitals, however, such a description is possible on the molecular level. In the earlier analysis, it was found that the electron–electron repulsions due to electron density in oxygen atomic orbitals decreased by 291 kcal/mol on passing from the linear to the bent structure. (The *total* one-center energy change for oxygen was computed to be −16 kcal/mol by the CNDO/2 method used earlier; for the INDO method used here to generate the localized orbitals, the oxygen one-center energy change is computed to be −17 kcal/mol.) Using the (four) localized *molecular* orbitals originating at the oxygen atom, the decrease in repulsion energy which can be attributed to those electrons on passing from linear to bent geometry is 50 kcal/mol. The change in total electron repulsions for the molecule turns out to be only −17 kcal/mol, and the difference in total energy is only 11 kcal/mol, so the decrease in repulsions about the oxygen is seen to be a major factor in the stability of the bent geometry.

Nmr Coupling Constants. In the previous report[1] on formaldehyde and acetaldehyde adducts with the proton, it was concluded on the basis of the CNDO/2 total molecular energies that the acetaldehyde adduct structure with the CH and OH^+ bonds cis to each other was the more stable. This was supported by the agreement of $J_{\text{cis}}/J_{\text{trans}}$ from experimental results and those ratios computed from CNDO/2 bond indices. The agreement held for the cis–trans coupling in H_2COH^+ and both the allylic and ethylenic couplings in both isomers of CH_3CHOH^+. To further confirm these results, the Fermi contact coupling constants were computed by the method for molecular orbitals as developed by Pople.[17] The INDO method was used with the results, shown in Table VIII, confirming the assignment of the *cis*-acetaldehyde adduct structure as the more stable conformer.

Table VIII. $J_{H,H}$ for H_2COH^+ and CH_3CHOH^+ [a]

		
J_{12} = 9 (9) J_{13} = 29 (21) J_{23} = 19 (22)	J_{12} = 14 (9) J_{13} = −1 (∼0)	J_{12} = 30 (20) J_{13} = 1 (1)

[a] Units are hertz. Experimental values in parentheses.

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Ground States of σ-Bonded Molecules. XV.[1] Barriers to Rotation about Carbon–Carbon Bonds[2]

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Abstract: Barriers to rotation about C—C and C═C bonds in a number of compounds have been calculated by the MINDO/2 method.

Previous papers of this series[1,3] have shown that the MINDO/2 method[3a,b] can give good estimates of the ground-state properties of molecules and for the potential surfaces for chemical reactions. One of the problems studied[3a] was the barrier to rotation about a C—C or C═C bond; estimates of the barrier heights for ethane, ethylene, and the cumulenes were in reasonable agreement with experiment.

Since this is a problem of current interest, and since the original calculations were carried out using a set of parameters that have been superceded,[3b] we have repeated them and extended them to a wide variety of additional molecules. Since the results are in reasonable agreement with the scanty evidence available and also lead to interesting predictions, we are reporting them in the hope of stimulating appropriate experimental studies.

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[1] Part XIV: M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **93**, 7201 (1971).

[2] This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121 and by the Robert A. Welch Foundation.

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