formation. The results for the σ model show that total charge densities on the F and C atoms increase and s–s and p–σ bond order between C add F atoms decreases. This indicates that in the above complex formation halomethane accepts the electron into the antibonding orbital of the C–X bond, causing the weakening of the C–X bond. In fact, when DTBN was added to the solution of CHI_3, they reacted immediately and no esr signal was observed. For CH_2I_2 solution, this reaction was slow and the esr signal gradually disappeared. These results appear to correspond with the above interpretation of the charge-transfer interaction.

Finally we briefly comment on the charge-transfer interaction between free radical and halomethane in light of the mechanism of the halogen abstraction reaction. Recently it has been suggested[23] that the transition state of the halogen abstraction reaction process produces anionic character on the carbon from which the iodine is being removed.

$$\text{R–I} + \cdot\text{Rad} \longrightarrow [\overset{\delta-}{\text{R}}\cdots\text{I}\cdots\overset{\delta+}{\text{Rad}}] \longrightarrow \cdot\text{R} + \text{I–Rad}$$

The above scheme corresponds to the abovementioned charge-transfer model of the transition state in which an odd electron transfers to the antibonding orbital of the R–X bond, causing the release of the C–X bond.[24] The anionic character and release of the C–X bond was well reproduced by INDO–MO calculations for the model molecule, CH_3F. The failure to observe the esr spectrum and the ^{13}C contact shift of the CHI_3 + DTBN system may result from the strong CT interaction, leading to the iodine abstraction reaction. It has been shown by Fukui, *et al.*,[25] that the polarographic reduction potential of haloalkanes is connected with the energy of their lowest unoccupied σ level. The parallel relation between the DTBN-induced ^{13}C contact shift and reduction potential ($E_{1/2}$) [$CHBr_3$ ($E_{1/2} = -0.64$) > $CHCl_3$ (-1.67), CH_2I_2 (-1.12) > CH_2Br_2 (-1.48) > CH_2Cl_2 (-2.33)][25] also shows that the lowest unoccupied orbital is important in the DTBN–halomethane interaction.

Acknowledgment. We are greatly indebted to Professor H. Kato and Mr. K. Okada for helpful discussions. Technical assistance of Mr. T. Matsui in the ^{13}C nmr measurements is also gratefully acknowledged.

---

(23) W. C. Danen and D. G. Saunders, *J. Amer. Chem. Soc.*, **91**, 5924 (1969); W. C. Danen and R. L. Winter, *ibid.*, **93**, 716 (1971).

(24) A similar discussion along with the CT interaction has been made on the photochemical halogen abstraction reaction of halomethanes in the presence of amines using as the electron donor (see ref 4).

(25) K. Fukui, K. Morokuma, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, **36**, 217 (1963).

Localized Charge Distributions. II. An Interpretation of the Barriers to Internal Rotation in H_2O_2[1]

Walter England* and Mark S. Gordon

Contribution from the Department of Chemistry and Institute for Atomic Research, Iowa State University, Ames, Iowa 50010.

Received June 18, 1971

Abstract: The INDO geometry optimized H_2O_2 barriers are analyzed with localized molecular orbitals and findings from an earlier study of C_2H_6. Emphasis is placed on the slight delocalization of an orbital onto bonds coplanar with its largest amplitude and accompanying nodal properties. The cis barrier is found to arise from HH interferences in the OH orbitals. The trans barrier is found to arise from OO interferences in lone pairs roughly trans to OH bonds in the equilibrium molecule. An explanation for the incorrect INDO H_2O_2 frozen frame barrier is also offered.

Many theoretical studies[2–8] have been stimulated by the barriers to internal rotation in H_2O_2. The *ab initio* calculations[3–8] have undoubtedly been motivated by the fact that barriers and geometries were usually obtained that agreed poorly with experiment.[9,10] In fact, until the recent work of Veillard,[8] it was not clear that the barriers and conformation could be understood in the molecular orbital (MO) theory.[3–7] This, as pointed out by Veillard,[8] is surprising in the sense that H_2O_2 is the simplest molecule to exhibit an internal rotation barrier. However, Lowe[11] has shown that the high symmetry of a methyl rotor may force a great deal of error cancellation, and this would not occur in H_2O_2.

It is known[12,13] that both CNDO/2[14] and INDO[15]-SCF theory predict barriers and *optimized* geometries in

---

(1) Work performed in the Ames Laboratory of the Atomic Energy Commission, Contribution No. 3001.

(2) W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, 2, 492 (1934).

(3) U. Kaldor and I. Shavitt, *ibid.*, 44, 1823 (1966).

(4) W. H. Fink and L. C. Allen, *ibid.*, **46**, 2261, 2276 (1967).

(5) L. Pedersen and K. Morokuma, *ibid.*, 46, 3941 (1967).

(6) W. Palke and R. M. Pitzer, *ibid.*, 46, 3948 (1967).

(7) R. M. Stevens, *ibid.*, 52, 1397 (1970).

(8) A. Veillard, *Chem. Phys. Lett.*, 4, 51 (1969); *Theor. Chim. Acta*, 18, 21 (1970).

(9) R. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, **36**, 1311 (1962).

(10) R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *ibid.*, 42, 1931 (1965).

(11) J. P. Lowe, *Progr. Phys. Org. Chem.*, 6, 23 (1968).

(12) M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, 49, 4643 (1968).

(13) M. S. Gordon, *J. Amer. Chem. Soc.*, 91, 3122 (1969).

(14) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 44, 3289 (1966).

(15) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, 47, 2026 (1967).

semiquantitative agreement with experiment. Frozen frame CNDO/2 calculations, however, fail to predict the trans barrier.[13] Reasons for this are not clear since both theories contain purely empirical parameters as well as parameters partly obtained by reference to minimal basis *ab initio* results. Combined with the fact that both neglect inner shells, it is, therefore, not really appropriate to regard them as approximations to minimal basis *ab initio* theory which, according to Stevens,[7] does not predict a trans barrier. We take the viewpoint that CNDO/2 and INDO are semiempirical MO theories with a minimal basis of valence atomic orbitals. In this way we expect that they may include effects that are omitted or differently emphasized by *ab initio* minimal basis theory.

Our present study will extend ideas obtained from the previous understanding of the ethane barrier.[16] The method employs localized charge distributions[16] and the interference concept originally introduced to theoretical chemistry by Ruedenberg.[17] The subsequent interpretation will be seen to be similar to C_2H_6, but with the involvement of lone pairs of electrons. These last results were the motivation for our study of H_2O_2, for it is our hope that "complex" barriers can be at least semiquantitatively interpreted with techniques which are similar to those discovered for "simple" barriers.

Methods and Results

Geometries and Barriers. The INDO geometries[12] are given with the experimental geometry[9,10] in Table I.

Table I. Comparison of INDO and Experimental Geometries[a]

	ω[b]	R_{OO}	R_{OH}	ϕ[c]
Skewed	83.5	1.22	1.04	108.8
Trans	180	1.23	1.04	104.5
Cis	0	1.23	1.04	111.1
Exptl[d]	111.5, 120	1.475	0.95	94.8

[a] Bond lengths in ångströms, angles in degrees. [b] ω is the dihedral angle between the OH bonds. [c] ϕ is the OOH angle. [d] See ref 9 and 10 of text.

The calculated equilibrium geometry is essentially that predicted by CNDO/2 calculations.[13] Later, it will become clear why we use the INDO results. Since experimental geometries are not known for the planar isomers, we shall briefly compare our results with those of Veillard's successful *ab initio* calculation.[8]

We find the OOH angle largest in the cis isomer and smallest in the trans isomer. Although the values predicted by INDO are larger, the relative agreement with Veillard's angles is good.[8] The OH bond length is seen to be unaffected by the internal rotation, as he assumed *a priori*. There is different behavior, however, in the case of the OO bond length. We find it shortest in the equilibrium isomer and equal in both planar forms, while the *ab initio* value is longest in the cis isomer by 0.025 Å, and equal to 1.475 Å in both the trans and equilibrium configurations. This overestimation of the trans OO bond length by INDO is not totally unexpected in view of the energies involved. That is, Veillard finds one "substantial" torsional barrier (see Table II), and with it the longest OO bond, whereas we find two major barriers and, correspondingly, two equal OO bonds. Our dihedral angle is rather small, but in view of the past difficulties[3-7] associated with the calculation of this quantity, we regard it as acceptable. Again, one might expect the high trans barrier to be associated with a smaller minimum energy torsional angle.

Table II. H_2O_2 Barriers[a,b]

	Veillard[c]	Stevens[d]	INDO	Exptl[e]
Trans	0.6	0	4.15	1.1
Cis	10.9	9.4	4.95	7.0

[a] Energy (planar form)–energy (skewed). [b] Units are kilocalories per mole. [c] Reference 8 of text. [d] Reference 7 of text. [e] References 9 and 10 of text.

Similar remarks apply to the INDO energy quantities. It is evident from Table II that the trans barrier is overemphasized while the cis barrier is in better agreement with experiment. To be consistent with this, we feel that an interpretation of the INDO barriers which makes use of an approximation to them should provide barriers accordingly, *i.e.*, the approximate barriers should be close to those of INDO rather than, say, the experimental barriers. It will be seen later that our interference interpretation is consistent in this sense. In view of the near equality of the cis and trans barriers, we shall not compare the two planar forms with each other, but ask only why both are less stable than the skewed form.

Finally, the fact that INDO neglects inner shells may be responsible for some of the disparity with experiment. However, based on our experience with *ab initio* C_2H_6,[16] we would not expect this to greatly influence the analysis we shall give.

Energy Localization and INDO Localized Orbitals. The concept of energy localization was first suggested by Lennard-Jones and Pople[18] in an effort to obtain molecular orbitals which conform to chemical intuition and are quantum mechanically *completely equivalent* to the usual, or canonical, solutions of the SCF equations.[19] Until the advent of modern computers and the work of Edmiston and Ruedenberg,[20,21] these localized orbitals were difficult to calculate. Now, as we have pointed out elsewhere,[22] they are becoming routinely available. For this reason, we shall not review their properties here but refer the reader to earlier works.[18,20-22]

It is our feeling that localized orbitals for any approximate orbital theory should agree with existing *ab initio* orbitals (LMO's) before they can be considered as approximations to LMO's. This is particularly true, we feel, when concepts such as hybridization are analyzed. We have shown previously[23] that the CNDO/2

---

(16) W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **93**, 4649 (1971).

(17) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

(18) J. E. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc., Ser. A*, **202**, 166 (1950).

(19) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(20) C. Edmiston and K. Ruedenberg, *ibid.*, **35**, 457 (1963).

(21) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43**, S97 (1965).

(22) W. England, L. S. Salmon, and K. Ruedenberg, *Fortschr. Chem. Forsch.*, **23**, 31 (1971).

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

Table III. Localized Orbitals for H_2O_2[a]

Atoms	AO	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7
				Skewed				
O_1	2s	0.5883	0.5848	0.0086	−0.0272	0.3204	−0.0018	0.2852
	$2p_x$	−0.3300	−0.3104	0.0310	−0.0627	0.6639	−0.0009	0.0442
	$2p_y$	0.6901	−0.7139	0.0000	−0.0002	0.0019	0.0004	0.0261
	$2p_z$	−0.2559	−0.2006	−0.0169	0.0097	−0.1692	−0.0027	0.6448
O_2	2s	0.0086	−0.0272	0.5883	0.5848	−0.0018	0.3204	0.2852
	$2p_x$	0.0035	−0.0073	0.6483	−0.7445	0.0003	0.0770	0.0309
	$2p_y$	0.0308	−0.0623	−0.4060	−0.2276	−0.0009	0.6595	0.0409
	$2p_z$	0.0169	−0.0097	0.2559	0.2006	0.0027	0.1692	−0.6448
H_3	1s	−0.0213	−0.0215	−0.0403	0.0803	0.6541	0.0011	−0.0143
H_4	1s	−0.0403	0.0803	−0.0213	−0.0215	0.0011	0.6541	−0.0143
				Trans				
O_1	2s	0.5887	0.5887	0.0001	0.0001	0.3218	−0.0187	0.2803
	$2p_x$	−0.3089	−0.3089	0.0090	0.0090	0.6725	−0.0473	0.0117
	$2p_y$	0.7071	−0.7071	−0.0000	−0.0000	−0.0000	−0.0000	−0.0000
	$2p_z$	−0.2392	−0.2392	−0.0103	−0.0103	−0.1380	0.0086	0.6490
O_2	2s	0.0001	0.0001	0.5887	0.5887	−0.0187	0.3218	0.2803
	$2p_x$	−0.0090	−0.0090	0.3089	0.3089	0.0473	−0.6725	−0.0117
	$2p_y$	0.0000	0.0000	0.7071	−0.7071	0.0000	−0.0000	−0.0000
	$2p_z$	0.0103	0.0103	0.2392	0.2392	−0.0086	0.1380	−0.6490
H_3	1s	−0.0207	−0.0207	−0.0121	−0.0121	0.6472	0.0602	−0.0117
H_4	1s	−0.0121	−0.0121	−0.0207	−0.0207	0.0602	0.6472	−0.0117
				Cis				
O_1	2s	0.5854	0.5854	−0.0170	−0.0170	0.3235	0.0108	0.2823
	$2p_x$	−0.3292	−0.3292	−0.0352	−0.0352	0.6562	0.0327	0.0718
	$2p_y$	0.7071	−0.7071	0.0000	0.0000	−0.0000	0.0000	0.0000
	$2p_z$	−0.2120	−0.2120	0.0042	0.0042	−0.1924	−0.0152	0.6441
O_2	2s	−0.0170	−0.0170	0.5854	0.5854	0.0108	0.3235	0.2824
	$2p_x$	−0.0352	−0.0352	−0.3292	−0.3292	0.0327	0.6562	0.0718
	$2p_y$	0.0000	0.0000	0.7071	−0.7071	0.0000	0.0000	0.0000
	$2p_z$	−0.0042	−0.0042	0.2120	0.2120	0.0152	0.1924	−0.6441
H_3	1s	−0.0165	−0.0165	0.0458	0.0458	0.6516	−0.0428	−0.0166
H_4	1s	0.0458	0.0458	−0.0165	−0.0165	−0.0428	0.6516	−0.0166

[a] Units are $(\mathrm{Bohr})^{-3/2}$.

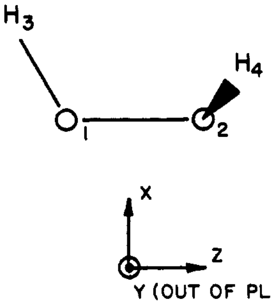

Figure 1. Numbering of atoms and coordinate axes in H_2O_2.

approximations to the two-electron integrals do not lead to such approximate LMO's, while those of INDO do.

We shall now explicitly discuss the INDO LMO's obtained from the energy localization process. These, labeled by λ_i, are given in Table III. The numbering of the atoms and the coordinate system are shown on Figure 1 for the skewed isomer, being the same for all rotamers.

λ_1–λ_4 correspond to lone pairs of electrons. Note that all are equivalent in the planar forms, but only λ_1,λ_3, and λ_2,λ_4 are equivalent in the equilibrium isomer. The orbitals are not really "lone" since there is some delocalization onto all centers. It is significant that λ_2 and λ_4 are substantially more delocalized onto the geminal oxygen and farthest hydrogen in the skewed isomer than are any of the other lone pairs, for since these orbitals here are roughly trans to OH bonds (the angle between λ_2 and the O_2H_4 bond is 164°), this is the trans effect we observed for the CH bonds in C_2H_6. In analogy with the C_2H_6 barrier, we shall find this to be very important for the H_2O_2 barriers.

λ_5 and λ_6 are the LMO representation of the *electronic contribution* to the OH bonds and are equivalent in all cases. Again we see that there is slight delocalization and, by looking at the trans isomer, we again see the trans effect.

The electronic contribution to the OO bond is represented by λ_7 and is similar in all isomers.

It is natural to wonder if the LMO's could be more perfectly localized than they are at present. We can partially answer this question in terms of MO bond orders. If

$$\lambda_n = \sum_{A}^{\text{atoms}} \sum_{\mu}^{A} C_{\mu n} X_{\mu} \tag{1}$$

with X_μ an atomic orbital (AO) on atom A, then the bond order between atoms A and B is

$$P(\mathrm{A,B}) = \sum_{n}^{\text{occ}} P_n(\mathrm{A,B}) \tag{2}$$

where

$$P_n(\mathrm{A,B}) = 2\sum_{\mu}^{\mathrm{A}}\sum_{\gamma}^{\mathrm{B}} C_{\mu n} C_{\gamma n} \tag{3}$$

represents the contribution of each occupied orbital. We see from the invariance of (2) to unitary transformations in the space of occupied MO's that the existence of long-range bond orders (those involving "nonbonded" atoms) implies the inherent delocalization of any set of MO's. Since it can easily be verified that long-range bond orders presently occur, a perfectly localized set of orthogonal MO's cannot exist. In this way the slight delocalization of our LMO's is a characteristic of the present solutions of the LCAO–SCF equations.[19]

Analysis of the Barriers

Interference Partitioning and C_2H_6 Results. The interference concept is part of a bonding theory put forth by Ruedenberg.[17] It can be simply understood in terms of the wave properties of electrons. Consider two atoms A and B. If the electrons on each were governed by the Poisson's equation[24] of classical electrostatics, then to obtain densities for the molecule AB one could superpose those determined for the isolated atoms. In this way the molecular density would be a sum of contributions from the atoms. The Schrödinger equation, however, requires that one superpose wave functions for the atoms to obtain a molecular wave function, and thus the density is *not* a sum of contributions from individual atoms. Nevertheless, one can partition the actual density $\rho(x)$ according to

$$\rho(x) = \rho^{\mathrm{CL}}(x) + \rho^{\mathrm{I}}(x) \tag{4}$$

and require that ρ^{CL} correspond to the densities of classical electrostatics, *i.e.*, be a sum of atomic contributions and conserve the number of electrons

$$\int \mathrm{d}V\rho(x) = \int \mathrm{d}V\rho^{\mathrm{CL}}(x) \tag{5}$$

The quantity $\rho^{\mathrm{I}}(x)$ is the interference density, *which displaces charge from one region to another*, but does not contribute to the total population

$$\int \mathrm{d}V\rho^{\mathrm{I}}(x) = 0 \tag{6}$$

Because of these properties it is of primary importance with regard to the origin of covalent binding.[17] Whenever $\rho^{\mathrm{I}} > 0$, the interference is constructive, which leads to covalent bonding, while destructive interference ($\rho^{\mathrm{I}} < 0$) leads to anticovalent bonding.[17] In general, one must also examine the "pair density" as well as ρ,[17] but we do not need this for what follows.

The one-electron, two-center interference energy associated with λ_n in the INDO theory is[16]

$$\beta_n = \sum\sum_{\mathrm{A}\neq\mathrm{B}}^{\mathrm{atoms}} \beta_n(\mathrm{A,B}) \tag{7}$$

where

$$\beta_n(\mathrm{A,B}) = 2\sum_{\mu}^{\mathrm{A}}\sum_{\gamma}^{\mathrm{B}} C_{\mu n}C_{\gamma n}\int \mathrm{d}V_1 \mathrm{X}_\mu(1)\{-{}^1/_2\nabla_1{}^2 - Q_{\mathrm{A}}/R_{\mathrm{A}_1} - Q_{\mathrm{B}}/R_{\mathrm{B}_1}\}\mathrm{X}_\gamma(1) = 2\sum_{\mu}^{\mathrm{A}}\sum_{\gamma}^{\mathrm{B}} C_{\mu n}C_{\gamma n}\beta_{\mu\gamma} \tag{8}$$

is the contribution from the interference between atoms A and B, having core charges Q_{A}, Q_{B} (since inner shells are neglected in INDO). The matrix elements $\beta_{\mu\gamma}$ are explicitly parameterized[15] so the kinetic and attractive potential contributions are separately inaccessible. Reference to eq 3 for the bond orders $P_n(\mathrm{A,B})$ shows that they are related to the $\beta_n(\mathrm{A,B})$ and, in general, when the bond order between two atoms is nonzero, the interference energy between the two will also be nonzero. In this way the bond orders provide some indication of what to expect in an interference energy analysis.

Paper I[16] of this series presented an interpretation of the ethane barrier using localized distributions. We found that *the preference for the staggered isomer is due to the change from constructive to destructive interference between the portion of the CH orbital localized near the bond hydrogen and the tail near the H of the coplanar, vicinal CH bond.* We were able to arrive at this conclusion in spite of the fact that many of the one-electron interference energies were of the same magnitude (see Table V of ref 16). The latter situation obtains in H_2O_2 also, but there are even more terms involved because of the lower symmetry and the more pronounced geometry changes. Our tactic will therefore be to examine the interference energies in H_2O_2 which correspond to those we found responsible for the C_2H_6 barrier and see if we can account for the H_2O_2 barriers.

Cis Barrier. We discuss this barrier first because we find it to involve the same interactions discovered in C_2H_6,[16] *i.e.*, repulsive HH interferences in the OH orbital between the positive lobe localized near the bonding hydrogen and the tail on the cis atom. In H_2O_2 these give rise to the energy

$$\Delta\beta_{\mathrm{OH}}(\mathrm{HH}) = \sum_{i=5,6}[\beta_i(\mathrm{HH,cis}) - \beta_i(\mathrm{HH,skewed})] = 6.45 \text{ kcal/mol} \tag{9}$$

which exceeds the INDO cis barrier by only 1.5 kcal/mol. Moreover, it can be determined from Table III that there is very little interference between the H's in the skewed OH bonds since they delocalize negligibly onto the vicinal hydrogens. *We therefore attribute the cis barrier to the repulsive, or destructive, interferences between the H atoms in the cis isomer's OH orbitals.*

Trans Barrier. This barrier must, in contrast to the cis barrier, involve interactions which do not occur or are differently emphasized in C_2H_6. Hence, we must consider some aspects of the differences between H_2O_2 and C_2H_6 before we can account for it. A simple way of doing this follows.

In the skewed molecule there are two lone pairs (λ_2 and λ_4) which are almost "trans" to OH bonds as well as a substantial π bond order (0.121) between the oxygens (which is zero in the trans geometry).[13] We can infer from our C_2H_6 study[16] and the work of Pople and Santry[25] that localized orbitals which are trans to bonds give rise to important interferences, so it is reasonable to compare the OO and HH interference energies in the OH orbitals (since they are trans to OH bonds in the trans isomer) with those of the lone pairs λ_2 and λ_4 (since they are "trans" to OH bonds in the skewed isomer). We include the OO interferences because we would expect them to be important for the delocalization of the lone pairs and because of the marked change in the π bond order mentioned above.

---

[24] J. D. Jackson, "Classical Electrodynamics," Wiley, New York, N. Y., 1962, p 13.

[25] J. A. Pople and D. P. Santry [*Mol. Phys.*, 7, 269 (1963); **9**, 301 (1965)] have predicted this effect within the framework of a Hückel-like perturbation theory of localized bonds.

The interference energies for the OH orbitals are

$$\Delta\beta_{\mathrm{OH}}(\mathrm{OO}) = \sum_{i=5,6} [\beta_i(\mathrm{OO,trans}) - \beta_i(\mathrm{OO,skewed})] = -24.02 \text{ kcal/mol} \quad (10)$$

and

$$\Delta\beta_{\mathrm{OH}}(\mathrm{HH}) = \sum_{i=5,6} [\beta_i(\mathrm{HH,trans}) - \beta_i(\mathrm{HH,\ skewed})] = -2.84 \text{ kcal/mol} \quad (11)$$

while for the lone pairs, we have

$$\Delta\beta_{\mathrm{LP}}(\mathrm{OO}) = \sum_{i=2,4} [\beta_i(\mathrm{OO,trans}) - \beta_i(\mathrm{OO,skewed})] = 33.21 \text{ kcal/mol} \quad (12)$$

and

$$\Delta\beta_{\mathrm{LP}}(\mathrm{HH}) = \sum_{i=2,4} [\beta_i(\mathrm{HH,trans}) - \beta_i(\mathrm{HH,skewed})] = -0.26 \text{ kcal/mol} \quad (13)$$

We approximate the trans barrier as the sum of these interference energies to obtain

$$\Delta\beta = \Delta\beta_{\mathrm{OH}}(\mathrm{OO}) + \Delta\beta_{\mathrm{OH}}(\mathrm{HH}) + \Delta\beta_{\mathrm{LP}}(\mathrm{OO}) + \Delta\beta_{\mathrm{LP}}(\mathrm{HH}) = 6.09 \text{ kcal/mol} \quad (14)$$

which is only 1.94 kcal/mol greater than the INDO result. Also, the INDO cis barrier is 0.80 kcal/mol larger than the trans, while the corresponding difference between our interference barriers is 0.36 kcal/mol, in rather good agreement.

We are in a position to further understand the barrier with our interference analysis because all terms in (14) except $\Delta\beta_{\mathrm{LP}}(\mathrm{OO})$ stabilize the trans isomer. Thus, the deciding factor for this barrier must be *the constructive OO interferences occurring in the lone pairs roughly trans to OH bonds in the skewed isomer.* They involve the large positive lobe on one oxygen and the slight tail on the other. We point out that interactions like these also occur in C_2H_6 (see Table V of ref 16) but are much smaller.

Earlier, we mentioned that frozen frame CNDO/2 rotations fail to produce a trans barrier. To see if we could account for this, we decided to apply our approximation to the similar frozen frame INDO rotations. We used the experimental geometry and assigned values to the dihedral angle of 83.5, 90, 111.5, and 120° (to include dihedral angles near both the INDO and experimental values). The trans isomer is predicted most stable by about 1–1.5 kcal/mol. Our approximation also predicts trans stability by (correspondingly) 0.7–1.0 kcal/mol, so we feel that it can be used to analyze the frozen frame failure.

Direct examination of the approximation revealed the failure to be due to the virtual cancellation of the OO interferences in λ_2 and λ_4 by the OO interferences in the OH orbitals. We can rationalize this by defining hybrids on O the same way as done for carbon in paper I[16] and then allowing the HOO angles to relax. Our method will be to approximate the positive lobes and "tails" of the LMO's.

The positive lobe of a lone pair is approximated as a hybrid. To approximate the lobe of an OH orbital, we add a weighted contribution from a hydrogen 1s orbital to the appropriate hybrid and normalize the sum for consistency. The precise values of the resulting coefficients are unimportant for our purposes, so we can obtain bonding lobes which satisfy this and are close to the observed polarity of OH LMO's by weighting the hybrid with about 0.8 and the 1s orbital with about 0.6. We assume that these coefficients are independent of conformation.

We will only need to consider the delocalized portion of the LMO on the vicinal oxygen and then only when the positive lobe and the vicinal OH bond are "trans." We shall use the same "tail" for both of the orbital types we consider and assume that it is unaffected by distortions in the HOO angle. The tail is oriented so that constructive OO interferences occur between it and the "trans" positive lobe.

The INDO and *ab initio* geometries both predict the trans HOO angle to be a few degrees smaller than the skewed. Thus, we assume that a decrease in the HOO angle accompanies the rotation (from skewed to trans). If the hybrids at least partially follow it, we can use the analysis in paper I to deduce that there will be a decrease in the 2s character of those directed away from the OO bond. Similarly, we deduce an increase in the 2p character of these hybrids.

In this way the changes in the OO interferences which accompany the relaxation can be attributed to the changed 2s and 2p contributions to the positive lobes. We have held the OO bond length constant, but this is not essential. There are integral formulas[25] which show that, of the energies which arise from these interferences, those from the 2s are negligible. If we assume that the lobes follow the distortions equally, then the resulting enhancement of the 2p lobe-tail interferences in the "trans" position will be smaller by about 0.8 for OH orbitals because they are bonding. Hence, *we expect to find lone pairs "trans" to the OH bonds,* which is approximately the equilibrium INDO situation.

It is also interesting from this viewpoint that the cis H_2O_2 barrier is nearly unchanged by the frame relaxation.[18] That is, the cis barrier arises from HH interactions and we would not expect these to be greatly affected by distortions because they do not involve oxygen hybrids.

Delocalization of Localized Orbitals

It is apparent from paper I[16] and the present work that our results emphasize the slight but (we feel) nonnegligible extensions and nodal properties of LMO's outside the "bond" region. We recognize that this approach differs from some authors,[26,27] who consider localized orbitals as bond functions, *i.e.*, as confined to the bond region only. As was first mentioned by Pople and Santry,[25] and as we discussed earlier,[16] the existence of long-range bond orders in an MO calculation implies the *inherent* delocalization of any set of MO's. Again, as we have mentioned before,[16] we feel that this slight delocalization is physically important and gave some evidence that it does not arise from orthogonality requirements. Furthermore, unpublished results obtained in this laboratory indicate that LMO's (including their delocalized portions) are highly transferable among similar molecular fragments. The great reg-

---

[26] O. Sovers and M. Karplus, *J. Chem. Phys.*, 44, 3033 (1966).

[27] V. Magnasco and G. Musso, *Chem. Phys. Lett.*, 9, 433 (1971); *J. Chem. Phys.*, 54, 2925 (1971).

ularity of our results, and the comparisons we have been able to make with *ab initio* LMO's,[23] suggests to us that this is not peculiar to the INDO approximation.

Finally, recent work performed here[22,28] on π electron systems with the Hückel approximation also supports the importance of the delocalization of LMO's. We found, for example, that the slight extension of the localized π orbitals over more centers than the perfectly two-center ethylene π orbital can be used to explicitly account for the theoretical resonance energy.[22,28] Moreover, we found a great deal of regularity among the LMO's of the cata- and pericondensed hydrocarbons we considered. These results show that the LMO formalism clearly has advantages, even in systems traditionally considered as "delocalized."

Connection with Previous Studies

Early Work. A valence bond study of H_2O_2 by Penney and Sutherland[2] employing the s orbital on each hydrogen and the p orbitals on each oxygen also dealt with interactions between lone pairs of electrons. These were assumed to be 2p orbitals on the oxygen atoms and they concluded that interactions between them were largely responsible for a dihedral angle between 90 and 100°. In his book,[29] Pauling gives the same argument but uses sp hybrids on the oxygen atoms for the lone pairs. While qualitatively similar conclusions emerge, there is an important difference between our conclusions and theirs. Namely, *our results arose from the delocalization of the lone pairs while they assumed perfectly localized lone pairs.* As we have pointed out, this delocalization is inherent to the present solutions of the SCF equations.

Hyperconjugation. In paper I,[16] we demonstrated that the hyperconjugation arguments used by Lowe[30] and the present approach are basically equivalent, except that we use the LMO's and he uses the canonical orbitals.[30] Arguments similar to those given by him for C_2H_6 and other molecules could therefore be given for H_2O_2 also. These may be deduced from his work[30] in a manner similar to paper I.

Attractive–Repulsive Dominant Theory. This is a theory due to Fink and Allen[4,31] which rests upon the energy partitioning

$$E = (T + V_{\mathrm{nn}} + V_{\mathrm{ee}}) + (V_{\mathrm{ne}}) = (V_{\mathrm{repulsive}}) + (V_{\mathrm{attractive}}) \quad (15)$$

where T is the kinetic energy, V_{nn} is the nucleus–nucleus repulsion energy, V_{ee} is the electron–electron repulsion energy, and V_{ne} is the electron–nucleus attraction energy. When applied to H_2O_2, this theory predicts the cis barrier to be attractive dominant ($\Delta V_{\mathrm{attractive}} > \Delta V_{\mathrm{repulsive}}$)[31] and the trans barrier to be repulsive dominant ($\Delta V_{\mathrm{repulsive}} > \Delta V_{\mathrm{attractive}}$).[31] Veillard,[8] however, finds that this interpretation changes if the geometry relaxes and/or the basis is varied.

We cannot directly compare our conclusions with these for two reasons. First, the definitions (15) combine the interference and quasiclassical energies, while our analysis separates them. Second, it follows from eq 8 that in INDO we cannot make the partition (15). We can, however, compare our physical interpretations. Theirs makes use of tails also, but *considers only the portion near the heavy atom and how it is influenced by the changing position of the neighboring protons.*[4] On the other hand, *we consider the entire tail and how its interferences with the large lobe of the orbital are affected by the rotation.* To exemplify the difference, we recall that our analysis gives the same interpretation for relaxed and frozen frame C_2H_6,[16] while Epstein and Lipscomb[32] point out that the attractive–repulsive dominant theory does not.

CNDO/2 Results. The CNDO/2 study[13] attributed the trans barrier to π bonding between the oxygens in the nonplanar configuration and the cis barrier to increased antibonding between the hydrogens. These, as can be expected, are interactions similar to what we find. However, with our partition and LMO representation, we are able to give a more detailed account and can say *which parts of localized orbitals contribute to the interactions.* Finally, whereas the partitioning we use can be applied to any MO wave function,[16] the one used in the CNDO/2 study[13] applies only when the total energy has a form (one- and two-atom terms) similar to the CNDO/2 energy.

Acknowledgments. We are indebted to a skeptical referee whose challenges greatly improved our effort. We also thank Professor Klaus Ruedenberg for supporting the research.

---

(28) W. England and K. Ruedenberg, *Theor. Chim. Acta,* **22**, 196 (1971).

(29) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 134.

(30) J. P. Lowe, *J. Amer. Chem. Soc.*, **92**, 3799 (1970).

(31) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968).

(32) I. R. Epstein and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **92**, 6094 (1970).