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An ab initio investigation of possible intermediates in the

reaction of the hydroxyl and hydroperoxyl radicals.

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ABSTRACT

Ab initio quantum chemical techniques have been used
to investigate covalently-bonded and hydrogen-bonded
species that may be important intermediates in the
reaction of hydroxyl and hydroperoxyl radicals.
Stable structures of both types were identified.
Basis sets of polarized double zeta quality and large
scale configuration interaction wave functions have
been utilized. Based upon electronic energies, the
covalently bonded HOOOH species is found to be 26.4
kcal/mol more stable than the OH and HO_2 radicals.
Similarly, the hydrogen bonded HO---HO_2 species is
found to have an electronic energy 4.7 kcal/mol below
that of the component radicals, after correction is
made for the basis set superposition error. The
hydrogen bonded form is found to be planar, to
possess one relatively "normal" hydrogen bond, and to
have lowest energy $^3A'$ and $^1A'$ states that are
essentially degenerate. The $^1A''$ and $^3A''$ excited
states produced by rotation of the unpaired OH
electron into the molecular plane are found to be
very slightly bound.

I. INTRODUCTION

Radical-radical gas phase reactions have received considerable experimental and theoretical attention in recent years. In large part this has been motivated by their importance in atmospheric and combustion chemistry. In the past, it often proved attractive to view those reactions that resulted in simple atom transfer (metathesis) as proceeding _via_ direct abstraction mechanisms. However, as detailed kinetics studies have become available, it is now clear that a significant number of these "simple" reactions actually display complicated kinetic behavior,[1] such as pressure dependence of their rate constants and negative activation energies. This is frequently rationalized in terms of mechanisms that proceed through stabilizable intermediate species.

The hydroxyl and hydroperoxyl radicals play important roles in the chemistry of both the lower and upper atmospheres.[2] The OH radical is an important initiator of atmospheric hydrocarbon oxidation. Both the generation and destruction of ozone in the troposphere are partially accounted for by chemistry involving the HO_x species, and the coupling of HO and HO_2 to the NO_x and Cl_x cycles is very important in determining the loss rate of stratospheric ozone. The concentrations of the OH and HO_2 radicals are controlled to a significant degree by radical-radical recombination reactions.

The reaction between the hydroxyl and hydroperoxyl radicals

$$HO + HO_2 \longrightarrow H_2O + O_2 \qquad (1)$$

has received a great deal of attention because of its importance in atmospheric HO_x chemistry.[3] There are now several direct measurements[4-6] of the bimolecular rate constant k_1 in the low pressure regime that are in agreement, giving values in the range $(6.4-7.5) \times 10^{-11}$ cm^3s^{-1} at total pressures of a few torr. At pressures of about one atmosphere, there is general agreement among several experiments[7-11] that k_1 is in the range $(1.0-1.2) \times 10^{-10}$ cm^3s^{-1}. This apparent pressure dependence is included in the value of k_1 currently recommended by the NASA panel for use in atmospheric modeling.[12] Regardless of its detailed pressure dependence, the rate of Reaction (1) is unusually fast. The superficially similar self-recombination reactions of OH and HO_2 are both much slower, with rate constants[12] in the range $(1-2) \times 10^{-12}$ cm^3s^{-1}. Finally, a recent study[13] shows that k_1 has a negative temperature dependence that can be described by an E_a/R of -416 in the range 250-420 K.

The data discussed above has led several authors to suggest that Reaction (1) may proceed _via_ formation of an intermediate species. It is also possible that multiple mechanisms, both direct and indirect, are important. Thus far, there have been no direct observations of an intermediate, and such an experiment promises to be difficult. The goal of the present project is to apply _ab initio_ quantum chemical methods to the study of possible intermediates for Reaction (1). The structures of these intermediate species will be elucidated and their stabilities will be estimated. These stabilities are calculated as the energy of the formation reaction

$$OH + HO_2 \longrightarrow H_2O_3, \tag{2}$$

in which H_2O_3 represents any proposed intermediate species.

In determining which of the H_2O_3 intermediates are possible, it is necessary to consider the electronic states of the reactants and products. The reactant ground states, $^2\Pi(OH)$ and $^2A''(HO_2)$, can correlate with either singlet or triplet intermediates. The products have $^3\Sigma_g^-(O_2)$ and $^1A_1(H_2O)$ ground states, correlating only with triplet intermediates. However, the reaction is exothermic, and it is necessary to consider product excited states as the initially formed species. Using standard heats of formation,[14] the enthalpy change for Reaction (1) at 298 K is calculated to be -69.6 kcal/mol. This energy is sufficient to open channels leading to the $^1\Delta_g$ and $^1\Sigma_g^+$ excited states of O_2. These excited state products can be correlated with a singlet intermediate, making possible both singlet and triplet spin-allowed mechanisms. Restrictions on the spatial symmetry of the intermediate exist only if the reaction is constrained to proceed _via_ a path with high symmetry.

It should also be noted that there are two studies[15,16] in the literature that have questioned whether the pressure dependence of Reaction (1) is real and, therefore, whether there is any need to invoke a mechanism with an intermediate species. In fact, if the isotope study of Reference 16 could be verified by other experiments, it would appear to place a serious limitation on the acceptable nature of any proposed intermediate.

While an intermediate in Reaction (1) has not been studied directly and no species of the formula H_2O_3 has been observed in

the gas phase, such a species has been generated and studied in condensed phase experiments.[17-19] The vibrational spectra of both H_2O_3 and D_2O_3 have been observed and bands have been assigned to the oxygen framework modes, assuming an open-chain HOOOH structure.[18c] The ultraviolet spectrum of H_2O_3 is reported to be similar to, but more intense than, that of H_2O_2.[17b]

Early theoretical studies of the HOOOH molecule included SCF calculations using both minimal and extended basis sets with partial geometry optimization.[20-22] A recent SCF study[23] employing minimal and split valence basis sets treated the HOOOH isomer and three possible hydrogen-bonded forms of H_2O_3. These workers reported that only the HOOOH isomer is stable relative to the HO and HO_2 fragments. This is in disagreement with the results of the present study and will be further discussed in the conclusion section of this paper. The only previous study to include a treatment of electron correlation is that of Cremer.[24] This work employed basis sets ranging from minimal to polarized double zeta and accounted for the effects of electron correlation with second order many-body perturbation theory. In addition to the minimum-energy geometry of HOOOH, an extensive characterization of the potential surface as a function of the OH rotational angles was reported.

The stability of the HOOOH intermediate relative to the OH and HO_2 radicals, i.e. the energy of Reaction (2), has not been accurately calculated from _ab initio_ methods or measured directly. From group additivity principles Benson[25] has estimated the heat of formation of the H_2O_3 open chain form to be

-17.7 kcal/mol. Combined with tabulated[14] heats of formation for HO (9.3 kcal/mol) and HO_2 (2.5 kcal/mol), this yields an enthalpy change at 298 K for Reaction (2) of -29.5 kcal/mol.

II. COMPUTATIONAL METHOD

A. SCF method and basis sets

The molecular geometries were optimized by SCF gradient calculations that were carried out using the method and computer program due to Komornicki[26]. These programs use the unrestricted Hartree Fock method for open shell systems. As a measure of the UHF spin contamination, we note that the expectation value of the S^2 operator was no greater than 0.76 for the doublet cases and 2.02 for the triplet case. The basis set used in these SCF gradient calculations was the standard $6\text{-}31G^{**}$ polarized split valence set,[27] except that the polarization functions were chosen to have exponents of 0.85 on oxygen and 1.0 on hydrogen.

In all phases of this study except the gradient calculations, a polarized double-zeta (DZP) quality Cartesian Gaussian basis set was used. In particular, all energies reported in this paper were calculated using the DZP basis set, which consisted of Dunning's [4s2p|2s] contraction[28] of Huzinaga's[29] (9s5p|4s) set. A scale factor of $\zeta = 1.2$ was chosen for the hydrogen s-functions, and polarization was provided by sets of d functions on oxygen ($\alpha = 0.85$) and p functions on hydrogen ($\alpha = 1.0$). Except for the gradient calculations, the open-shell SCF solutions were obtained in the spin restricted form (RHF), and the molecular orbitals were constrained within D_{2h} subgroups to reflect the symmetry of the nuclear framework.

B. Configuration interaction calculations

Conventional CI techniques[30] with configuration selection and extrapolation were used. The master configuration list in

each case consisted of all single and double excitations relative
to either a single- or multi-configuration reference set such
that the oxygen 1s-core orbitals remained doubly occupied.
Generally, all single excitations were retained and the A_k
perturbation theory technique of Gershgorn and Shavitt[31] was used
to select the most important double excitations. The selection
procedure accepted or rejected a particular space configuration,
with its entire set of spin couplings, based upon the sum of the
A_k contributions for that set. Beginning with the least
important one, configurations were rejected in sequence until the
sum of the energy contributions for the rejected configurations
was equal to τ, the cumulative selection threshold.[32] CI
energies $E(\tau)$ were obtained at three values of τ, fit to a
straight line, and extrapolated[33] to zero threshold. The
resulting energies are denoted as "CI(SD)" or "extrap CI(SD)".

   To obtain improved CI convergence. approximate natural
orbitals (ANO's) were used throughout. At each conformation,
preliminary CI calculations in the SCF orbital basis were
performed to define the ANO's. Configuration selection was used
to reject all configurations with estimated energy contributions
less than 10^{-4} hartree. After freezing[34] those orbitals that
were occupied in the SCF wave function, the natural orbitals[35] of
these small CI expansions (1000-2500 terms) were obtained. The
ANO's consisted of the occupied SCF orbitals plus the set of
"lightly occupied" natural orbitals. The three ANO's with
smallest occupation numbers, generally equal to zero, were core

correlation orbitals and were discarded, since the 1s core orbitals remained fully occupied throughout this work.

The most important effects of quadruple excitations were accounted for in an approximate way using Davidson's[36] correction formula,

$$\Delta E_q = (1 - C_o^2)\Delta E_d, \qquad (3)$$

where ΔE_d is the correlation energy due to the entire set of double excitations, ΔE_q is the analogous quantity due to quadruple excitations, and C_o is the coefficient of Φ_{SCF} in the "all doubles" CI. In this work, the quantity ΔE_d was estimated to be equal to the extrapolated "singles plus doubles" correlation energy, and C_o was taken from the CI calculation at the smallest of the selection thresholds. Where a multi-configuration reference state was used, C_o^2 was taken as the sum of the squares of the coefficients corresponding to the reference configurations.[37] These CI energies that include the Davidson correction are denoted as "CI(SDQ)".

C. Computer programs

In the course of this work several computer programs were used. These include the SCF gradient program of A. Komornicki, the MOLECULE integral program due to J. Almlof, the NASA Langley SCF-CI package due largely to C. W. Bauschlicher and B. H. Lengsfield, and the MELD package developed by E. R. Davidson and coworkers.

III. RESULTS AND DISCUSSION

A. HO and HO$_2$ radicals

A primary goal of this study is the calculation of relative stabilities of possible intermediates for Reaction (1). In practice this is accomplished by calculating the energy change for Reaction (2), in which H_2O_3 represents the particular intermediate being considered. Care must be taken to ensure a well balanced treatment of the reactants and products so that the calculated energy difference will be an accurate estimate of the reaction energy. To this end, the energies of the OH and HO$_2$ radicals have been obtained using the same basis set and CI procedures that are used for the H_2O_3 complexes.

The literature[38,39] contains geometry optimization studies of both HO and HO$_2$ using basis sets and CI procedures that are very similar to the ones used here. Since the theoretical geometries for these species have been found to be in good agreement with experiment, reoptimization was considered unnecessary. Except as noted otherwise, the experimental HO$_2$ and HO geometries are used in this work. For the OH radical the bond length[40] is 0.971 Å, and for HO$_2$ the parameters are[41] 0.977 Å (R_{OH}), 1.334 Å (R_{OO}), and 104.2° (bond angle). The reference (SCF) configurations for the ground states are

OH: $\quad 1\sigma^2 \; 2\sigma^2 \; 3\sigma^2 \; 1\pi^3 \qquad\qquad\qquad {}^2\Pi \qquad$ (4)

HO$_2$: $1a'^2 \; 2a'^2 \; 3a'^2 \; 4a'^2 \; 5a'^2 \; 6a'^2 \; 1a''^2 \; 7a'^2 \; 2a''^1 \qquad {}^2A'' \quad$ (5)

Equivalence restrictions were not imposed on the π_x and π_y orbitals of OH.

The energies obtained at three levels of theory for the OH and HO_2 radicals and their sums are entered on the first three lines of Table I. As is well known[42], truncated CI expansions are generally not size extensive. In the present case, this is manifest in the fact that the sum of CI energies for OH and HO_2 at a particular excitation level will not be equal to the corresponding energy obtained for them as a supermolecule. On line four of Table I results are given for the supermolecule treatment of the HO_2 and OH radicals at a separation of 500 a_o. This calculation was carried out for the $^1A'$ (in C_s symmetry) coupling of configurations (4) and (5). Comparison of the third and fourth rows of Table I shows that the SCF energies are size extensive as expected, but at the extrapolated CI(SD) level there is an error of 25.2 mh. Since the presence of a nonnegligible size extensivity error means that higher excitations are important, it is expected that the Davidson correction for quadruple excitations will reduce this error. As the last column of the table shows, the error is reduced considerably at the CI(SDQ) level, but is still significant, with a value of 11.1 mh.

It is somewhat difficult to estimate a priori the accuracy of the Davidson correction for a particular problem. One approach is to repeat the calculation using multi-configuration reference states (MREF), thus including many of the most important quadruple excitations explicitly. This should leave a smaller correction to be made with the multi-reference analogue of Eq (3)[37]. In this spirit, MREF calculations were carried out using four-configuration reference states for both OH and HO_2 and

a three-configuration reference state for the supermolecule calculation. The supplementary reference configurations were those that had been found to be the most important in the single-reference (SREF) calculations. The ANO's were not redefined at the MREF level. If the Davidson correction is reasonably accurate, the SREF and MREF results should compare favorably at the CI(SDQ) level. In fact, the MREF value of $E(OH)$ + $E(HO_2)$ was only 0.5 mh below the SREF result, and the MREF supermolecule energy was 1.3 mh lower than its SREF counterpart. These results suggest that the Davidson correction yields reasonably well-converged CI(SDQ) energies at the SREF level.

In the limit of very large reference sets, the size extensivity error should vanish. However, it was reduced only slightly from 11.1 to 10.3 mh by the present procedure, indicating that the supermolecule approach is still required at this limited MREF level. For this particular electronic state of the separated fragments the MREF and SREF results agree closely, and the MREF description does not seem to be required for "chemical accuracy". That, of course, would not necessarily be true for other choices of geometries and electronic states. It is concluded that CI(SD) with the Davidson correction yields results for this system that are converged to approximately 1 mh. and that the supermolecule treatment of the separated fragments should be used to account for the size extensivity error inherent in the CI approach.

B. Covalently-bonded HOOOH intermediate

1. Equilibrium geometry

One possible intermediate in Reaction (1) results from formation of a covalent bond between the HO_2 and OH radicals and is represented here by the formula HOOOH. The equilibrium conformation of this covalent molecule has not been determined experimentally, but has been predicted by the theoretical study of Cremer.[24] This previous work employed a 6-31G** basis set that is of similar quality to the DZP basis used here and treated electron correlation via many-body perturbation theory. It was expected a priori that the difference between Cremer's H_2O_3 structure and one determined by the present CI methods would be small. Since these structures would both correspond to the same minimum in the potential surface, the energy difference between them should also be quite small. This consideration could have led us to directly employ Cremer's structure in these calculations. However, in order to make sure that there was no inconsistency between his approach[24] and our own, a partial geometry optimization of the H_2O_3 molecule was carried out.

The SCF gradient procedure converged to a conformation similar to the expected one, with the hydrogens above and below the OOO plane in an arrangement with C_2 symmetry. The electronic ground state is of ^1A symmetry, and the SCF configuration is given by

$$1a^2\ 2a^2\ 1b^2\ 3a^2\ 2b^2\ 4a^2\ 3b^2\ 5a^2\ 4b^2\ 6a^2\ 5b^2\ 7a^2\ 6b^2 \quad (^1A) \quad (6)$$

A sketch is shown below:
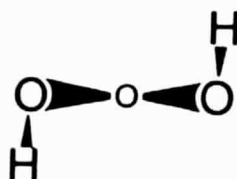
The bond lengths and angles at the SCF level differed from the previous results[24] in a way that is consistent with the use of an uncorrelated wave function, with the following differences being noted: R_{OH}(-.026 Å), R_{OO}(-0.067 Å), OOO angle(+0.9°), HOO angle(+2.6°), and dihedral angle(+8.0°).

Using the DZP basis set and CI wave functions, these molecular parameters were optimized sequentially. For this purpose we employed a cumulative CI selection threshold of 75 mh without any extrapolation. After one complete cycle of optimization, the discrepancies with Cremer's results had been reduced to: R_{OH}(-0.004 Å), R_{OO}(-0.03 Å), OOO angle (+0.9°), HOO angle(+2.2°), and dihedral angle(+5.8°). At this point it was clear that the geometry eventually obtained with the CI method would be rather close to the published result;[24] certainly, the two methods appear to be consistent. From the magnitudes of the energy changes during the optimization cycle, it was estimated that further refinement would result in an energy drop of no more than 1.5 mh. Therefore, further optimization cycles were not carried out, and Cremer's geometry was used for the remaining calculations: R_{OH}(0.972 Å), R_{OO}(1.439 Å), OOO angle(106.3°), HOO angle(100.2°), and dihedral angle(78.1°).

2. Wave function and molecular properties

The electronic structure and bonding in HOOOH has previously been discussed by Cremer.[24] We have examined the natural orbitals and find that they generally support his analysis. The rationalization of the OH bond orientation at the equilibrium geometry was given both in terms of dipole-dipole repulsion and in terms of the electronic anomeric effect.[43]. This latter argument is usually presented in a way that requires the lone pair on the terminal oxygen atom to be coplanar with the nonadjacent O-O bond, such that the lone pair may interact favorably with the O-O antibonding orbital. Examination of the contour plots for the lone pair orbitals on the terminal oxygen atoms showed that they are oriented within 5-10 degrees of the OOO plane, making that explanation plausible.

The Mulliken populations[44] for the largest CI wave function show a considerable transfer of charge from the hydrogen atoms to the terminal oxygens, with only a little charge accumulating on the central oxygen. The electronic populations are 8.31 on terminal oxygen atoms, 8.07 on central oxygen, and 0.65 on each hydrogen atom. The electric dipole moment is constrained by symmetry to lie along the C_2 axis and points from the central oxygen atom (negative end) toward the plane of the hydrogen atoms. The OH bond moments are situated such that there is considerable cancellation, giving a relatively small net moment of 1.26 Debye at the CI level.

3. Energies

In Table I are presented HOOOH total energies and the binding energies for dissociation into the OH and HO_2 radicals. The geometry of the HOOOH molecule was that given above, and the extrapolated CI energy was obtained using selection thresholds of 100, 75, and 50 mh. At the 50 mh threshold the CI expansion consisted of approximately 15 600 terms, and yielded a variational energy (before extrapolation) of -226.0752 hartree. The binding energy of HOOOH is calculated at each level of theory as the difference between Lines 4 and 5 of Table I. From the CI(SDQ) data this binding energy is +42.1 mh, or +26.4 kcal/mol. At the CI(SD) level this quantity is only +32.4 mh and at the SCF level it is -16.5 mh (unbound). Thus, some treatment of electron correlation is essential in order to obtain the correct sign for the binding energy, and a careful treatment of its contribution is necessary for an accurate value.

The CI(SDQ) electronic binding energies (Table I) are the "best" purely theoretical results presented here, in the sense that no experimental data or _ad_ _hoc_ corrections have been included. However, to facilitate comparison with experiment, it is desirable to include the zero point energy correction and the effects of temperature, as well as to estimate the inherent error due to basis set limitations. This resulting series of "derived" energies is discussed in subsequent paragraphs and presented in Table II.

The thermodynamic energy change of Reaction (2) at 0 K, ΔE_o can be calculated as the negative of the electronic binding energy plus a contribution from the zero point vibrational

energy. For this purpose all vibrational modes were treated as harmonic, and experimental values of the vibrational frequencies were used where available. Otherwise, the necessary frequencies were estimated by analogy to hydrogen peroxide. The vibrational frequencies of OH (3735 cm^{-1})[40] and HO$_2$ (3436, 1392, and 1098 cm^{-1})[45] were available in the literature. Of the nine vibrational modes in H$_2$O$_3$, the stretching and bending modes of the oxygen framework were taken from the matrix study[18c] (855, 755, and 500 cm^{-1}), while the remaining modes were estimated from the H$_2$O$_2$ spectrum.[46] The OH stretches were both taken as equal to 3607 cm^{-1}, the corresponding value in H$_2$O$_2$. Similarly, the O-O-H bending frequencies were set equal to 1330 cm^{-1}, the average of the H$_2$O$_2$ values, and the hindered rotations were both taken equal to the 317 cm^{-1} mode of hydrogen peroxide. Using these wave numbers, the difference in zero point energies of the product and reactants in Reaction (2) is 1478 cm^{-1}, or 4.23 kcal/mol. Inclusion of this correction results in a calculated energy (ΔE_o) of Reaction (2) at 0 K of -22.2 kcal/mol.

The calculated energy of Reaction (2) includes the effects of higher order CI excitations in an approximate way and represents a reasonably thorough treatment of the correlation energy contribution. The largest source of error remaining is probably due to the limitations of the basis set. In general, basis sets of medium quality such as the present one (DZP) describe the atomic situation more adequately than the molecular one. Consequently, bond dissociation energies calculated with such basis sets are usually too small if the computational

procedure is otherwise well balanced. When, as in the present case, the dissociation process goes to fragment molecules rather than atoms, the error may be somewhat smaller, but still significant. It was not feasible to repeat these calculations with a larger basis set. However, the literature contains several studies with basis sets of similar quality in which calculated binding energies are compared to experimental dissociation energies. These results have been employed to obtain an approximate correction to the binding energy.

In the recent literature there are several reports based on MBPT or the closely related CCD approaches that attempt to calculate dissociation energies with basis sets of roughly the same quality as the present one. Since the treatment of electron correlation in the present CI approach and that of the MBPT or CCD methods are quite comparable, it is expected that the conclusions about basis set deficiencies drawn from those studies will be applicable to this work. Bartlett and coworkers[47] have studied several systems with DZP basis and found the calculated binding energies to be too small by 1-6%. Adams et al.[47b] state that for this same quality basis set, one can expect calculated dissociation energies for single bonds to be 1-3 kcal/mol too small. Using the 6-311G** basis set, Pople and coworkers[48] find dissociation and atomization energies to be in the range 4-15% too small if directly calculated for cases such as the present one, in which the number of unpaired electrons is not conserved. Using both 6-31G** and DZP basis sets, dissociation energies of several first row diatomics have been calculated[49] accurately to

within 5-15%. The general experience is that calculated

dissociation energies are almost always too small and are

somewhat worse for the cases that involve breaking of multiple

bonds or dissociation into atoms rather than into fragment

molecules.

The error estimates given above have broad ranges and

exceptions can easily be found. However, it is clear that the

calculated energy change for Reaction (2) is almost certainly too

small in magnitude because of basis set limitations. We do not

anticipate an exceptionally large error because Reaction (2)

represents the breaking of a single bond. However, the error

will probably be somewhat larger than in the very best cases,

which seem to be the breaking of a bond involving hydrogen.[47b]

Accordingly, we have elected to make an _ad hoc_ correction of 6%,

or 1.3 kcal/mol. This gives a corrected value for the energy of

Reaction (2), $\Delta E'_o$ of -23.5 kcal/mol. In this discussion the

prime on the thermodynamic quantities indicates that this

correction has been included.

For comparison purposes it is useful to derive an estimate

of the room temperature enthalpy of Reaction (2) from our

results. To convert $\Delta E'_o$ to $\Delta E'_{298}$, it is noted that Reaction

(2) represents the loss of three translational and two rotational

degrees of freedom. Treating them classically, they contribute

-2.5 RT (-1.48 kcal/mol at 298 K) to $\Delta E'$. The vibrations are

treated as harmonic oscillators and the internal energy above the

zero point is given by the usual formula for an oscillator of

frequency ν

$$E_{vib} = Nk\theta/[\exp(\theta/T)-1]$$

where θ is $h\nu/k$. Using the product and reactant wave numbers chosen for the zero point energy calculations, the vibrational contribution to $\Delta E'_{298}$ is calculated to be +0.73 kcal/mol. Including the vibrational (+0.73 kcal/mol) and rotational-translational (-1.48 kcal/mol) contributions at 298 K yields an energy of reaction $\Delta E'_{298}$ of -24.3 kcal/mol. To convert this to an enthalpy change, the work term (ΔPV) is estimated as -RT (-0.59 kcal/mol), giving $\Delta H'_{298} = -24.8$ kcal/mol.

As stated in the introduction, Benson's estimate[25] of ΔH_f^{298} of H_2O_3 implies a room temperature change for Reaction (2) of -29.5 kcal/mol. The disagreement between that value and the present one is a little less than 5 kcal/mol, a number that possesses at least marginal significance. Many of the uncertainties in the present work, such as the CI extrapolation error, accuracy of the quadruple excitation correction, and errors in choice of unknown vibrational frequencies are essentially random and should combine with some cancellation. The estimate made of the error in reaction energy due to basis set limitations could easily be too small by as much as 2 kcal/mol, but is unlikely to be more than 0.5 kcal/mol too large. If it were 2 kcal/mol larger, the present estimate and Benson's would be in reasonable agreement. Rather than saying that these two numbers are in disagreement, it is more realistic to say that our results suggest that the correct enthaply change of Reaction

(2) may lie between the present value and that derived from Benson's[25] result.

C. Hydrogen-bonded H_2O_3 Complex

1. Minimum-energy conformation

In addition to the covalently bonded HOOOH species, the various hydrogen bonded forms should also be considered as possible intermediates for Reaction (1). In this section we report the results of a potential energy surface study of the hydrogen-bonded form of H_2O_3 and a theoretical estimate of the energy of reaction for its formation

$$HO_2 + OH \longrightarrow HO----HOO \qquad (7)$$
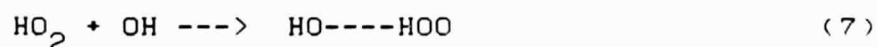
Since hydrogen bonding does not involve large scale reorganization of the fragments' electronic distributions, it is expected that the SCF description will be reasonably correct. Accordingly, the geometry optimization was carried out at only the SCF level, but the final energies were determined by both the SCF and CI procedures.

The minimum-energy conformation for the complex was located with the open shell (UHF) variant of the SCF gradient program. The electronic configuration used represents the triplet spin pairing of the OH and HO_2 radicals. The minimum energy conformation was found to be planar and to possess a single hydrogen bond with the HO_2 radical serving as proton donor. The electronic wave function possessed C_s symmetry and is represented by the configuration

$$1a'^2 \; 2a'^2 \; 3a'^2 \; 4a'^2 \; 5a'^2 \; 6a'^2 \; 7a'^2$$

$$8a'^2 \; 9a'^2 \; 1a''^2 \; 10a'^2 \; 11a'^2 \; 2a''^1 \; 3a''^1 \qquad (^3A') \qquad (8)$$

The unpaired electrons on both radicals are in oxygen p-type orbitals situated perpendicular to the molecular plane (a"). The

3a" MO, which represents the HO_2 unpaired electron, is mostly localized on the terminal oxygen atom. A drawing of the complex is given in Fig. 1 along with the structural parameters.

The structure in Fig. 1 strongly resembles unperturbed OH and HO_2 fragments held together by one fairly "normal", albeit bent, hydrogen bond. Since the structure of the complex was determined at the UHF level, it should be compared to structures of the free radicals that were also calculated at that level. Therefore, UHF gradient calculations were carried out for the HO and HO_2 radicals. When compared with these structures, it is seen that the bond lengths and angles within the fragments have undergone the following distortions upon complex formation:

OH: R_{OH}(+0.002 Å)

HO_2: R_{OH}(+0.003 Å), R_{OO}(-0.002 Å), HOO Angle(+1.4°).

The effects of including electron correlation should be almost identical for the parameters of the isolated radicals and their complexed counterparts. Therefore, the distortions upon complex formation that are given above would be expected to carry over almost unchanged to geometries determined at the CI level.

2. Energy of the complex

The binding energy of the hydrogen-bonded complex has been determined at the various levels of theory and the results are presented in Table III. CI calculations were carried out for the separate OH and HO_2 radicals and for their supermolecule using the UHF conformations. The size extensivity error as calculated from Lines 4-5 of Table III differs by only 0.2 mh from that found using experimental conformations (Table I). From Table III

it is seen that the SCF calculations predict the complex to be stable with a binding energy of 7.4 mh or 4.6 kcal/mol. At the CI(SDQ) level this quantity increases to 8.5 mh or 5.3 kcal/mol. Although the correlation energy contribution to binding is only about 1-2 mh, it is significant because the binding energy itself is quite small. The use of either the supermolecule approach or an explicit size extensivity correction is essential in this situation, because otherwise, the CI results would predict the complex to be unbound.

In theoretical treatments of weak hydrogen bonds, such as in the case of the water dimer, some correction is often made for the basis set superposition error (BSSE). This error results from basis set deficiencies and manifests itself in binding energies that are too large. If the basis set is inadequate, an improvement in the description of each _fragment_ may be obtained upon complex formation by making use of the orbitals of the other fragment. This improvement is an artifact of the basis set and has nothing to do with the real binding energy of the complex. The counterpoise correction,[50] a common method of estimating this effect, is determined by recalculating the fragment energies in the presence of the basis functions of the other fragment. Any improvement in energy is considered an estimate of the BSSE. This error can be very large when small basis sets are used.

In the present case the BSSE at the SCF level was found to be 0.7 mh for OH and 0.3 mh for HO_2, giving a total error of 1.0 mh (0.6 kcal/mol). At the CI(SD) and CI(SDQ) levels the error was reduced by about 50%. This reduction was unexpected

and may be due to fortuitous cancellation by the CI extrapolation error, which is also on the order of 1 mh. Even allowing for such a cancellation, this result can be taken as evidence that the CI BSSE in this case is not very much larger than that at the SCF level. Accordingly, we assume a BSSE correction of +0.6 kcal/mol, giving corrected binding energies of 4.0 and 4.7 kcal/mol, respectively, at the SCF and CI(SDQ) levels.

The relatively small BSSE calculated in this case, especially at the CI level, should not be taken as a measure of the completeness of this modest basis set. The magnitude of these errors depends strongly on the particular nature of the basis set being used and on the molecular conformation being considered. For example, the basis set used by Clementi and Habitz[51] in their water dimer calculation was certainly more complete than the present one, and their BSSE was smaller at the SCF level. However, at the CI level the apparent error grew significantly. The reader is referred to Ref. 51 for a careful discussion of the CI superposition error and the difficulty and ambiguities involved in correcting for it. Also, Bauschlicher[52] has pointed out that a large BSSE can arise with DZP quality basis sets when they are augmented with bond functions.

3. Wave function and molecular properties

In hydrogen bond formation the electrostatic interaction is generally very important,[53] and between polar neutral species the dipole-dipole interaction is its leading component. Therefore, the ability of a particular class of wave function to accurately reproduce the electric dipole moments of the fragments may be

some indication of its ability to predict their interaction energy. In Table IV are given theoretical and experimental values of the dipole moments of OH, HO_2, and the $HO---HO_2$ complex. The calculated moments for OH and HO_2 are too large by approximately 9 and 3%, respectively. If the interaction between the radicals was purely dipolar, the binding energy would be overestimated by about 12%. This serves as an indication that the interaction energy may be slightly overestimated, but should not be greatly in error.

It has been our observation that well-correlated wave functions frequently have less charge separation and smaller dipole moments than their uncorrelated (SCF) counterparts. This observation is consistent with the results for two of the species in Table IV, but is the opposite of that for HO_2. The HO_2 wave function indicates a considerable charge transfer from the hydrogen to the central oxygen atom, as is shown in the table by the Mulliken populations[44]. In the CI wave function the charge has been somewhat more evenly distributed over the two oxygen atoms than at the SCF level. Contributing to this redistribution is an important configuration (c=0.088) that is generated from configuration (5) by the single excitation 1a" -> 2a". This excitation moves an electron from a π-type orbital that is mostly on the central oxygen to one that is primarily on the terminal oxygen atom. The use of a well-correlated wave function has resulted in a more even charge distribution between the oxygen atoms in HO_2, but it is accomplished in a way that moves electron density to the terminal oxygen atom, increasing the overall

charge separation and dipole moment. The SCF dipole moment of
HO_2 actually agrees rather well with the experimental value.
That situation appears to be the result of a fortuitous
cancellation between the error due to the use of a limited (DZP)
basis set and that due to use of an uncorrelated (SCF) wave
function.

Comparison of the electron populations for the complex and
isolated radicals supports our earlier observation that the
radicals change little upon binding. Table IV shows a net
transfer of only 0.03 electrons from OH to HO_2 upon complexation.
A one to one comparison was made of the heavily occupied natural
orbitals belonging to the isolated and complexed species. All
except two of the $HO---HO_2$ natural orbitals have a very close
resemblance to either an OH or HO_2 orbital. However, two of the
NO's, both with populations of about 1.98, showed considerable
change. In Fig. 2 are shown contour plots of the NOs that
primarily represent the σ_{HO} bond of HO_2 for the isolated radical
and the hydrogen bonded complex. It is easily seen from the
figure that the negative end of the hydroxyl dipole has caused
some of the charge density to push from the H-O bonding region
back onto the terminal oxygen atom. The population analysis for
this orbital shows a transfer of about 0.4 electron from hydrogen
and the central oxygen in HO_2 to the terminal oxvgen. The nodal
structure of this orbital is such that this introduces some O-O
π-type antibonding character. A quite different situation is
found if the NO corresponding to the p-type lone pair on the
terminal oxygen atom of HO_2 is examined (Fig.2). In this case

complexation with the OH radical causes this electron pair to
delocalize significantly, transferring approximately 0.35
electron onto the central oxygen and hydrogen atoms. The nodal
pattern of this orbital causes this transfer to introduce π-type
O-O bonding character. Thus, while individual natural orbitals
undergo significant changes upon formation of the hydrogen bonded
complex, they compensate in such a way that the total description
changes only a little. It should be noted that, since this pair
of natural orbitals is nearly degenerate with respect to
occupation numbers, a more complete CI description could result
in their further mixing.

The electric dipole moment calculated for the $HO---HO_2$
complex at the CI level is 2.17 Debye. It is oriented to point
roughly from the central oxygen atom in HO_2 (negative end) toward
the midpoint of the hydroxyl bond (positive end). This vector
makes an angle of 72.1° with the O-O bond in HO_2.

4. Comparison with H_2O and HO_2 dimers.

The hydrogen bond in the water dimer has received a great
deal of experimental and theoretical attention in recent years
and is quite well characterized. Although this bond is weak when
compared to the entire range of hydrogen bonds, it is an
appropriate subject for comparison to the present system because
both species involve bonding with the OH moiety. In Table V are
shown experimental[54] and theoretical[51,55] values of the water
dimer electronic binding energy as well as those that we have
calculated for the $HO---HO_2$ system. These latter values include
the BSSE correction described above. The data in Table V suggest

that the hydrogen bond in HO---HO$_2$ is about 80% as strong as that in the water dimer. The numbers reported for HO---HO$_2$ might decrease a few tenths of a kcal/mol if the DZP basis set were to be expanded considerably. This expectation is based on the observation that the present basis set yields dipole moments for the fragments that are a few percent too large.

The experimental value[56] of the oxygen-oxygen distance in $(H_2O)_2$ is 2.98 Å and the geometry of the hydrogen bond (O-H---O) is linear to within 1-2 degrees. The equilibrium HO distance in water (0.9572 Å) was used for the monomer in the above analysis[56], yielding an experimental H---O distance of 2.02 Å. In the present case, the H---O distance is only 0.02 Å shorter than this value, although the O-O distance (2.85 Å) is 0.13 Å shorter than R_{OO} in the water dimer. This decrease is mostly the result of the hydrogen bond being bent in HO----HO$_2$, rather than there being a large decrease in the H---O or O-H distances. The principal difference between the hydrogen bond in the present case and that in the water dimer is the significant deviation from linearity. It is noted, however, that the difference in SCF energy between the minimum energy structure (Fig. 1) and one formed by straightening the O-H---O linkage is only about 0.5 kcal/mol.

It is interesting to compare the hydrogen bonded HO---HO$_2$ system with the HO$_2$ dimer that has recently been studied theoretically.[57] The HO$_2$ dimer is considered a possible intermediate in the self recombination of HO$_2$ radicals, a reaction that also shows complex kinetic behavior. The

theoretical study[57], carried out at the SCF-DZP level, found a minimum energy conformation that was planar and cyclic with two equivalent hydrogen bonds. The total binding energy of the dimer was predicted to be about 4.9 kcal/mol. Although this is about the same stabilization energy as in the water dimer, there are two hydrogen bonds formed, and individually they must be considered very weak. Consistent with this interpretation, the H---O bond lengths were found[57] to be 2.19 Å, or over 8% longer than in the water dimer.

When compared with the HO_2 dimer structure, that of $HO---HO_2$ is seen to be quite different. Although the general shape of the $HO---HO_2$ complex is suggestive of a quasi-cyclic nature, the H---O distances do not support such an interpretation. The shorter H----O distance is nearly the same as found in the water dimer, and the other one that would correspond to a second hydrogen bond is much too long, at 2.77 . Also, the $HO---HO_2$ potential surface is quite flat and very little energy (~ 0.5 kcal/mol) is required to distort the complex away from the "cyclic" form. This is easily provided by thermal collisions at room temperature.

Although the experimentalist is most likely to measure the room temperature enthalpy change of Reaction (7), it is not possible to estimate it quantitatively because some of the vibrational frequencies of the complex are unknown. This becomes especially critical when computing the room temperature energy of the low frequency inter-radical vibrations and hindered rotations. However, because the hydrogen-bond is similar to that

in the water dimer, it may be useful to treat these frequencies as approximately equal in the two species. Both Curtiss et al.[54] and DelBene et al.[55] have recently converted the enthalpy change for water dimer formation to the electronic energy change in order to compare experimental and theoretical results. In this context, the main differences between water dimer formation and Reaction (7) are that in the present case two degrees of rotational freedom are lost instead of three and there is one less low frequency vibrational mode gained. At room temperature these two effects are largely offsetting, allowing us to use the published water dimer result as a rough estimate. A correction of +1.7 kcal/mol was found for the water dimer at 298 K.[55] Applying this correction to the CI(SDQ) data in Table V yields an estimated enthalpy change for Reaction (7) at 298 K of -2.9 kcal/mol.

5. Other electronic states and isomers

Calculations were carried out at the conformation of Fig. 1 for three other electronic states of the complex. A $^1A'$ state can be made from configuration (8) by recoupling the two unpaired spins to yield a singlet state. The unpaired electrons are heavily localized in p -type orbitals that are centered approximately 3 Å apart, and their coupling energy is expected to be small. In fact, the $^1A'$ state was found to be 0.2 mh below the $^3A'$ state at the CI(SDQ) level. This small energy difference is beyond the precision of the computational procedure, and the two states should be considered degenerate. There is also a pair of $^1A''$ and $^3A''$ states that can be represented by the excitation

11a' ---> 2a" relative to configuration (8). Physically, these states correspond to placing the unpaired electron of the OH radical in an in-plane molecular orbital. The $^1A"$ and $^3A"$ states were found to lie 6-8 mh above the $^3A'$ ground state. It is emphasized that these energy gaps were calculated using the $^3A'$ minimum energy geometry, and no attempt has been made to explore the potential energy surfaces of the excited states.

SCF calculations were performed for the $^3A'$ state at conformations that would be reasonable choices for hydrogen bonded complexes with the hydroxyl radical acting as proton donor to either the central or terminal oxygen atom of the hydroperoxyl radical. Such conformations had already been rejected as energy minima by the gradient search procedure, and the energies at these conformations were found to be 4-5 mh above that for the structure in Fig. 1. No attempt was made to determine the correlation energy contribution to these numbers, but a large differential effect would not be expected. Our conclusion is that the other conformations are probably not thermally accessible to a complex that has been stabilized at the low energy structure. It is clear, however, that there are large parts of the potential surface at relatively low energies and that, until stabilized, a hydrogen bonded complex will have a relatively large amount of phase space available to it.

IV. CONCLUSIONS

This study has investigated possible intermediates in the reaction between hydroxyl and hydroperoxyl radicals. Two forms of the proposed intermediate were investigated. A covalently bonded form with the structure HOOOH is calculated to have an electronic binding energy of approximately 26 kcal/mol. Reasonable correction for basis set incompleteness would increase that energy by 1-2 kcal/mol. This value yields a predicted room temperature enthalpy change for Reaction (2) of -24.8 kcal/mol, which is approximately 5 kcal/mol less negative than a prediction made using group additivity considerations to estimate the heat of formation[25] of the complex. In addition, this study has identified a hydrogen bonded complex that has a binding energy of about 4.7 kcal/mol. There is no direct experimental or theoretical data for comparison, but we note that the bonding is similar to that found in the water dimer and considerably different than predicted[57] for the HO_2 dimer.

The covalently bonded intermediate has C_2 symmetry and is in a ^1A electronic state, which cannot be correlated to ground state products [H_2O ($^1A_1$) and O_2($^3\Sigma_g^-$)] via a spin allowed mechanism. However, the initial product states in Reaction (1) are unknown. Both of the excited-state oxygen channels ($^1\Delta_g$ and $^1\Sigma_g^+$) are energetically accessible, and cannot be ruled out as the primary reaction paths. The HOOOH ^1A state could be correlated with these asymptotes.

The lowest energy form of the hydrogen-bonded intermediate is found to be planar with $^3A'$ and $^1A'$ states that are

essentially degenerate. If the reaction were constrained to
proceed along a planar path, these states would have incorrect
symmetry for correlation with the ground state products ($^3A''$).
The $^1A'$ state could be correlated with the low-lying singlet
excited states of the products, but the $^3A'$ state must be
correlated with excited triplet channels that are not
energetically accessible. There is no a priori reason, however,
for requiring the reaction to proceed with C_s symmetry. If,
during the course of the reactive event the molecule distorted
away from planarity, the ground state triplet could mix with
other states of the correct symmetry ($^3A''$) to yield ground state
products.   Although geometry optimization was only carried out
for the $^3A'$ state, these calculations indicate that there is a
low lying set of $^1A''$ and $^3A''$ states that are very slightly bound
with respect to the reactant radicals.

As stated in the introduction, our results are not
consistent with the theoretical results of Rao et al.[23] These
authors have calculated the stability of various H_2O_3 forms
relative to OH + HO_2 using smaller basis sets (STO-3G, 4-31G) at
the SCF level. They conclude that the hydrogen bonded form is
not stable and that the covalent HOOOH intermediate has a
stability of 6.3 kcal/mol. While our best CI calculations
clearly show HOOOH to be stable, the SCF results would predict
that it is unbound by about 10 kcal/mol. To explore this
disagreement further, we repeated the SCF calculations using the
basis set (4-31G) and conformations given in Ref. 23. At this
level our results would have predicted HOOOH to be even more

unstable than with the larger basis set. The energies we

obtained for the OH and HO_2 fragments were about 3 mh higher than

reported in Ref. 23. Since we employed RHF calculations, this

small discrepancy would be expected if the previous results were

obtained with a UHF procedure. For HOOOH, however, our 4-31G

energy is -225.2123 hartree, about 48 mh above that of Ref. 23.

There is no obvious explanation of this large discrepancy. It

should be noted that several previously published reports[20,22,24]

include SCF(4-31G) treatments of HOOOH, and that all of these

results are in disagreement with that of Rao et al.[23].

It is equally difficult to understand the prediction of Ref.

23 that the hydrogen bonded form of H_2O_3 would not be stable. It

is common for unpolarized basis sets such as the 4-31G to give

dipole moments that are too large for the unbound fragments. In

a hydrogen-bonding situation, this defect usually leads to

binding energies that are much too large. For example, the 4-31G

set has been shown[58] to yield an SCF stabilization energy for the

water dimer of 8.2 kcal/mol without correction for BSSE. Some of

our preliminary SCF gradient calculations on HO---HO_2 were

carried out with a 4-31G basis set. While the geometry was never

completely optimized, energies were obtained that were lower than

the fragment energies published in Ref. 23 and would have

indicated binding. The only simple explanation for this

discrepancy is that the geometry search procedures of Ref. 23 did

not sample regions of the potential surface sufficiently close to

the energy minimum.

One other possibility that comes to mind is that the authors of Ref. 23 have simply misidentified their calculated values for the covalent and hydrogen bonded forms. The energy they have published for the covalent form (-225.260 au) would not be an unreasonable 4-31G UHF value for the hydrogen bonded complex. If this change in identification were made, their results would be in qualitative agreement with the present ones.

Of the two intermediates studied here, the hydrogen bonded form is not as stable as is usually suggested in proposed mechanisms[13] for Reaction (1). However, we note that the hydrogen bonded part of the potential surface is rather flat and that a large amount of phase space would appear to be accessible to the reactant radicals during complex formation. In addition to the nearly degenerate singlet and triplet A' states, the low lying singlet and triplet A" states have energies below that of the reactants and can be expected to contribute to the dynamics. The stability of the covalently bonded intermediate is in the usual range. The test of whether or not either of these species can serve as intermediates in a mechanism that explains the experimental data is in the application of kinetics models to the problem. In order to do this, we must know the barriers to product formation for each of these intermediates as well as the vibrational frequencies in the complexes and their transition states. Work in both of these directions is proceeding in these laboratories.

ACKNOWLEDGMENTS

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TABLE I. Total and binding energies (in hartrees) of the HOOOH molecule.

	SCF	CI(SD)	C_0	CI(SDQ)
E(OH)	-75.4063	-75.5630	0.9775	-75.5700
E(HO$_2$)	-150.2121	-150.5377	0.9525	-150.5678
E(OH) + E(HO$_2$)[a]	-225.6184	-226.1007	...	-226.1378
E(OH + HO$_2$)[b]	-225.6184	-226.0755	0.9424	-226.1267
E(HOOOH)	-225.6019	-226.1079	0.9380	-226.1688
Binding Energy[c]	-0.0165	+0.0324	...	+0.0421

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a. Calculated separately for each radical.

b. Calculated as supermolecule with radicals separated by 500 a_0.

c. Calculated as Line 5 - Line 4.

Table II. Reaction energies for formation of HOOOH.

	Energy(kcal/mol)	Description[a]
ΔE_e	-26.4	Electronic energies only
ΔE_o	-22.2	Vibrational zero pt. energy
ΔE_o.[b]	-23.5	ad hoc correction for basis set incompleteness.
$\Delta E'_{298}$	-24.3	Vib, rot, and trans energy at 298 K.
$\Delta H'_{298}$	-24.8	ΔPV work term (-RT).

a. Indicates what contribution has been included to obtain entry from previous one.

b. The prime indicates that the basis set correction is included.

TABLE III. Total and binding energies (in hartrees) for the HO----HO$_2$ complex.[a]

	SCF	CI(SD)	C_o	CI(SDQ)
E(OH)	-75.4065	-75.5627	0.9778	-75.5696
E(HO$_2$)	-150.2133	-150.5365	0.9538	-150.5657
E(OH) + E(HO$_2$)[b]	-225.6198	-226.0992	...	-226.1353
E(OH + HO$_2$)[c]	-225.6198	-226.0742	0.9435	-226.1240
E(HO----HO$_2$)	-225.6272	-226.0842	0.9457	-226.1325
Binding Energy[d]	0.0074	0.0100	...	0.0085

a. Calculated using UHF gradient conformations.

b. Calculated separately for each radical.

c. Calculated as supermolecule with radical separated by 500 a$_o$.

d. Calculated as Line 5 - Line 4.

TABLE IV. Electric dipole moment and Mulliken populations for the HO, HO_2, and HO---HO_2 species.

	Dipole Moment	Populations[a]				
	(Debye)	H1	O1	O2	H2	O3
HO_2						
SCF	2.08	0.64	8.30	8.06	...	...
CI	2.16	0.65	8.24	8.10	...	...
EXP	2.09[b]	...	...	...	...	...
HO						
SCF	1.91	...	...	...	0.66	8.34
CI	1.82	...	...	...	0.68	8.32
EXP	1.67[c]	...	...	...	...	...
HO---HO_2						
SCF	2.28	0.63	8.29	8.10	0.63	8.35
CI	2.17	0.64	8.25	8.14	0.64	8.33

a. HO_2 and OH are labelled as follows: H1-O1-O2 and H2-O3.

b. Reference 59.

c. Reference 60.

Table V. Electronic binding energies for three hydrogen
bonded species.

	E(kcal/mol)	Method	Reference
$(H_2O)_2$			
	5.44	Exptl	55
	3.6	SCF	51
	5.5	CI	51
	4.3	SCF	56
	5.4	MBPT	56
$(HO_2)_2$			
	4.9	SCF	57
$HO---HO_2$			
	4.0	SCF	This study
	4.7	CI(SDQ)	This study

FIGURE CAPTIONS

1. Minimum energy conformation of hydrogen bonded HO---HO$_2$ complex, determined at the UHF level.

2. The H-O sigma bonding natural orbital in isolated HO$_2$ (top) and in the hydrogen bonded complex (bottom). Contour intervals are 10% of the function's range.

3. The in-plane lone pair natural orbital in isolated HO$_2$ (top) and in the hydrogen bonded complex (bottom). Contour intervals are 10% of the function's range.