A QUANTUM-MECHANICAL STUDY OF THE STRUCTURE OF INORGANIC DERIVATIVES OF HYDROGEN PEROXIDE

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Peroxymono- and peroxydi-sulfuric acids may be considered as derivatives of hydrogen peroxide in which one or two of the hydrogen atoms have been replaced by acid residues. The clarification of the effect of the substituents on the behavior of the peroxy group in chemical reactions is undoubtedly important in the comparison of the reactivity of hydrogen peroxide derivatives. It has been shown in [1-3], taking hydrogen peroxide as the example, that a quantum-mechanical approach may be used to explain the structure, chemical nature and, consequently, the reactivity of peroxy compounds. The results of a quantum-mechanical calculation of the electronic strucutre of the H_2SO_5 and $H_2S_2O_8$ molecules are presented in the present communication together with similar results for H_2O_2 and its particles HO_2^- and $HO_2^{\cdot}$. The calculations were carried out using the extended Hückel method.*

The modified extended Hückel program, described in [5-7], was used to execute the calculations. The off-diagonal elements in the matrix for the effective Hamiltonian were computed using Cusachs' formula [8]. The ground state of the oxygen atoms was represented by 2s and 2p Slater atomic orbitals. In the case of the sulfur atoms the 3s and 3p orbitals were also taken into account while 1s orbitals were used for the hydrogen atoms. The effective charges were calculated using Slater's rules [9, 10]. The diagonal matrix elements of H were taken as being equal to the negative magnitudes of the ionization potentials of the atomic AO's in their valence states [11].

The coordinate system and the method used for enumerating the atoms in the H_2O_2 calculation are shown in Fig. 1. We first carried out calculations in order to estimate the dihedral angle φ since there is no data in the literature for this quantity in the case of peroxymonosulfuric and peroxydisulfuric acids. The optimum value for the dihedral angle was determined from the minimum of the total energy of the molecule.† The following parameter values were used in the calculations on hydrogen peroxide and its particles: R(O—O) = 1.49 Å, R(O—H) = 0.97 Å, OOH = θ = 100°. The total energy of the H_2O_2 molecule was determined for various different (from 0 to 180°) values of the dihedral angle φ. The minimum energy, corresponding to the most stable state of the H_2O_2 molecule, was attained when φ = 140° which is somewhat higher than the value obtianed by other authors.

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*In the literature [1, 2, 4] there is data obtained from quantum-mechanical calculations on the hydrogen peroxide molecule using various different methods. We have carried through the calculation on this molecule with the aim of achieving a valid comparison of the data obtained for all of the above-mentioned molecules by the one and the same method.

†The total energy was obtained by summing the one-electron energies, since in the extended Hückel method, as in a single-electron method, the interelectronic repulsions are not explicitly taken into account. It is implicitly taken account of by the choice of parameters.

‡Since a dihedral angle φ = 120° was obtained by the more accurate methods, we consider this value to be preferable and we shall use this value of φ in the further treatment of the electronic structure of H_2O_2, HO_2^-, and $HO_2^{\cdot}$.

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TABLE 1. Atomic Charges in the Hydrogen Peroxide Molecule and the Perhydroxyl Ion

Particle	H^1	O^2	O^3	H^4
H_2O_2	+0,65	—0,65	—0,65	+0,65
HO_2^-	+0,65	—0,64	—1,01	—

TABLE 2. Atomic Populations in the Hydrogen Peroxide Molecule and the Perhydroxyl Ion

Atomic orbitals \ Atom	H^1	O^2	O^3	H^4
		H_2O_2		
ns	0,3476	1,8759	1,8759	0,3476
$2p_x$	—	1,7891	1,9993	—
$2p_y$	—	1,0596	1,0596	—
$2p_z$	—	1,9278	1,7175	—
Total atomic population	0,3476	6,6524	6,6524	0,3476
		HO_2^-		
ns	0,3480	1,8745	1,9135	—
$2p_x$	—	1,7907	1,9993	—
$2p_y$	—	1,0473	1,0995	—
$2p_z$	—	1,9302	1,9998	—
Total atomic population	0,3480	6,6427	7,0121	—

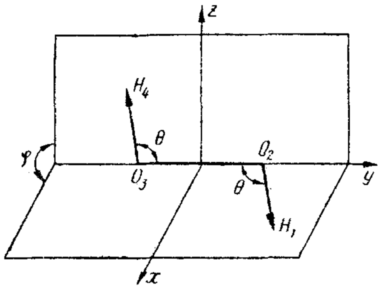

Fig. 1. The Cartesian coordinate system and the method used for numbering the atoms in the calculations on H_2O_2, HO_2^-, and $HO_2^{\cdot}$ (in the two latter calculations the H^4 atom was missing).

As the result of the computation, the following components of the populations of the molecular orbitals of the peroxy bond were obtained for the hydrogen peroxide molecule.

$$p_\sigma(O^2 - O^3) = 2s(O^2)[-0.031 \cdot 2s(O^3) + 0.067 \cdot 2p_y(O^3)] +$$
$$+ 2p_y(O^2)[0.067 \cdot 2s(O^3) + 0.329 \cdot 2p_y(O^3)] = 0.432;$$
$$p_\pi(O^2 - O^3) = 2p_x(O^2)(-0.02) \cdot 2p_x(O^3) + 2p_z(O^2)(-0.024) \cdot 2p_z(O^3) = -0.44;$$
$$p(O^2 - O^3)_{H_2O_2} = p_\sigma + p_\pi = 0.432 + (-0.044) = 0.388.$$

It can be seen from this data that the peroxy bond in H_2O_2 is formed as the result of the overlapping of hybridized spy AO's and is a (σ) bond.* In the case of the perhydroxyl ion, the population of the MO's in the peroxy bond is equal to:

$$p(O^2 - O^3)_{HO_2^-} = p\sigma + p\pi = 0.406 + (-0.039) = 0.367.$$

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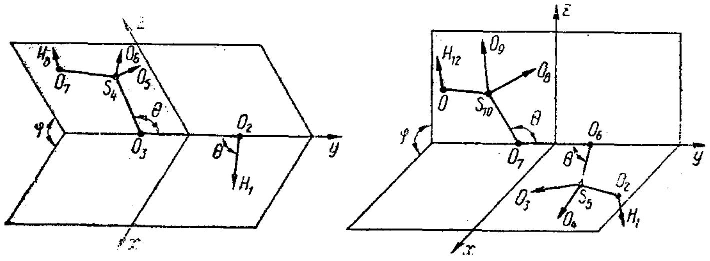
*Here and in what follows the notions of σ and π bonds are used by us conventionally with allowance for the local symmetry of the O—O bond and are denoted (σ) and (π).



a b

Fig. 2. The Cartesian coordinate system and numbering of the atoms for the calculations on the H_2SO_5 (a) and $H_2S_2O_8$ (b) molecules.

Consequently, the dissociation of hydrogen peroxide to form the HO_2^- ion is accompanied by a decrease in the electron density in the peroxy bond. In the perhydroxyl radical, the participation of the unpaired electron in the formation of the peroxy bond leads to an increase in its population with respect to $p(O^2{-}O^3)$ in H_2O_2:

$$p(O^2{-}O^3)_{HO_2^{\cdot}} = P_\sigma + P_\pi = 0.407 + 0.067 = 0.474.$$

The calculated distribution of the atomic charges in the H_2O_2 molecule and the perhydroxyl ion is shown in Table 1 where it can be seen that the O — H bond in the investigated particles is significantly polarized. The dipole moment of the H_2O_2 molecule, calculated using the values for the atomic populations (see Table 2) was found to be equal to 2.26 D which is in satisfactory agreement with the experimental magnitude of 2.19 D [1].

The oxidizing properties of peroxides are realized by an electron undergoing a transition into an unoccupied molecular orbital (LUMO) while the reducing properties are attributable to the departure of an electron from the highest occupied molecular orbital (HOMO) into the vacant orbital of the acceptor [2]. The energies of the LUMO and HOMO have the following values of eV:

	H_2O_2	HO_2^-	$HO_2^{\cdot}$
HOMO	— 14.93	— 14.787	— 15.061
LUMO	— 9.050	— 8.988	— 14.787

It can be seen from the data presented above that the perhydroxyl ion has the highest level with respect to its HOMO. This is in agreement with the experimental data in so far as the HO_2^- ion possesses reducing donor properties to the greatest extent.

The coordinate system and the method of numbering the atoms in the calculations on the H_2SO_5 and $H_2S_2O_8$ molecules is shown in Fig. 2. The internuclear O—O distance in the peroxymonosulfuric acid molecule was taken as being equal to 1.46 Å in analogy with the $H_2S_2O_8$ molecule [12, 13]. The bond lengths R(S—O) were taken as being equal to 1.5 Å as in the $S_2O_8^{2-}$ ion [12, 13]. The $\widehat{OSO}$ angles are 109° 28', since the sulfate groups in these substances are right tetrahedra. R(O—H) = 0.97 Å for H_2SO_5 as in H_2O_2 [3], $\widehat{HOS}$ = 105° in analogy with the water molecule [10]. The $\widehat{OOS}$ angles for $H_2S_2O_8$ were taken as being equal to 122° [12, 13] while, for H_2SO_5, they were put equal to 100° in analogy with the hydrogen peroxide molecule.

In order to select the equilibrium dihedral angle φ in the peroxymono- and peroxydisulfuric acids, their total energy was also calculated for various different values of this angle The total energy of the H_2SO_5 molecule was computed for φ values lying between 0 and 150° with an allowance for the possible existence of an intramolecular hydrogen bond in analogy with the peroxymonoacetic and peroxymonocarbonic acids [14, 15]. There is little likelihood of an

TABLE 3. Charges on the Atoms in the Peroxide Group in H_2SO_5 for Various Different Values of φ.

φ°	Oxygen atoms of the peroxide group	Charge on atoms O^2 and O^3	Oxygen atoms of the SO_4^2 group	Charge on atoms O^5 and O^6
40	O^2	—0,6902	O^5	—1,4303
	O^3	—0,4465	O^6	—1,4623
90	O^2	—0,6618	O^5	—1,4576
	O^3	—0,4452	O^6	—1,4635
120	O^2	—0,6586	O^5	—1,4628
	O^3	—0,4451	O^6	—1,4636

TABLE 4. Bond Populations in the Peroxymonosulfuric Acid Molecule for Various Different Values of φ.

Bond	40°	90°	120°
H^1—O^2	0,3296	0,3504	0,3530
O^2—O^3	0,3901	0,3860	0,3831
O^3—O^4	0,4578	0,4551	0,4540
S^4—O^5	0,4388	0,4404	0,4407
S^4—O^6	0,4407	0,4407	0,4408
S^4—O^7	0,4664	0,4463	0,4663
O^7—H^8	0,3561	0,3561	0,3561
H^1—O^5	0,0438	0,0088	0,0015

intramolecular hydrogen bond in the $H_2S_2O_8$ molecule and hence the total energy of this molecule was determined for values of φ lying between 60 and 180°. The peroxydisulfuric acid molecule was found to be most stable at $\varphi = 120°$. In the case of the peroxymonosulfuric acid the value of φ corresponding to a minimum energy was equal to about 40°. As in the case of the hydrogen peroxide molecule, the quantitative values for the angle φ are apparently of somewhat different magnitude owing to the approximations involved in the method and the failure to take into account the change in the mutual interaction of the cores as a function of the change in this angle.

The results of the calculations (Table 3) show that, in the case of peroxymonosulfuric acid, a reduction in the dihedral angle favors the transfer of electron density from oxygen atoms O^5 and O^6 of the sulfate group onto the peroxide oxygen atom O^2 due to the formation of a H^1—O^5 hydrogen bond. This leads to an increase in the negative charge on the O^2 and O^3 atoms of the peroxide bond. The formation of an intramolecular hydrogen bond is also confirmed by the increase in the electron density between the peroxide hydrogen atom H^1 and atom O^5 of the sulfate group as the angle is reduced (Table 4). It can be seen from this table that the population of the O^2—O^3, O^3—S^4, and H^1—O^5 bonds falls off as the angle φ increases while the population of the H^1—O^2 and S^4—O^5 bonds gets larger. The populations of the S^4—O^6, S^4—O^7, and O^7—H^8 bonds remain unchanged as the angle is varied.

The hydrogen bond energy, obtained as the difference between the energy of the H_2SO_5 molecule with $\varphi = 40°$, the dihedral angle of the molecule in its most stable state, and the energy of the molecule for $\varphi = 120°$, which corresponds to the practically complete rupture of the H^1—O^5 bond, is about 4 kcal/mole according to our calculations. This is close to the heat of formation of a O—H...O [16] hydrogen bond and is found to be in agreement with the magnitude for the hydrogen bond in peroxymonocarbonic acid [15].

The computed electronic populations of the peroxy bond for the H_2SO_5 and $H_2S_2O_8$ molecules are equal to:

TABLE 5. Atomic Populations in the Peroxymonosulfuric Acid Molecule (φ = 40°)

Atomic orbital \ Atom	H^1	O^2	O^3	S^4	O^5	O^6	O^7	H^8
$ns(\sigma)$	0,344	1,875	1,836	0,978	1,914	1,924	1,887	0,352
$np_x(\pi)$	—	1,895	1,984	0,391	1,709	1,709	1,985	—
$np_y(\sigma)$	—	1,069	1,054	0,401	1,899	1,916	1,554	—
$np_z(\pi)$	—	1,851	1,572	0,408	1,908	1,914	1,669	—
Total atomic population	0,344	6,690	6,446	2,178	7,430	7,463	7,095	0,352

TABLE 6. Atomic Populations in the Peroxydisulfuric Acid Molecule (φ = 120°)

Atomic orbital \ Atom	H^1	O^2	O^3	O^4	S^5	O^6	O^7	O^8	O^9	S^{10}	O^{11}	H^{12}
$ns(\sigma)$	0,352	1,887	1,911	1,933	0,961	1,811	1,811	1,924	1,924	0,968	1,887	0,352
$np_x(\pi)$	—	1,824	1,666	1,986	0,395	1,761	1,981	1,710	1,710	0,391	1,985	—
$np_y(\sigma)$	—	1,451	1,958	1,968	0,415	0,999	0,999	1,965	1,965	0,415	1,450	—
$np_z(\pi)$	—	1,929	1,900	1,610	0,385	1,899	1,679	1,868	1,868	0,385	1,766	—
Total atomic population	0,352	7,091	7,435	7,497	2,156	6,470	6,470	7,467	7,467	2,159	7,088	0,352

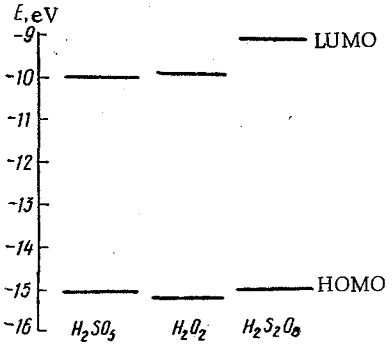


Fig. 3. Energy level diagram showing the HOMO and LUMO for H_2SO_5, H_2O_2, and $H_2S_2O_8$.

$$p(O^2-O^3)_{H_2SO_5} = p_\sigma + p = 0.415 + (-0.025) = 0,390$$
$$(\text{for } \varphi = 40^\circ);$$
$$p(O^6-O^7)_{H_2S_2O_8} = p_\sigma + p = 0.405 + (-0.023) = 0.382$$
$$(\text{for } \varphi = 120^\circ).$$

It can be seen from these results that the peroxy bond in peroxymono- and peroxydisulfuric acids was formed due to the same orbitals as in hydrogen peroxide and is a (σ) bond. The total electron population of the O–O bond is highest in the case of peroxymonosulfuric acid and decreases along the series

$$H_2SO_5 > H_2O_2 > H_2S_2O_8.$$

From a comparison of the O–O bond populations and the corresponding bond strengths [17], it may be concluded that the peroxy bond is the strongest in peroxymonosulfuric acid. Hydrogen peroxide occupies an intermediate position followed by peroxydisulfuric acid. It is well-known from the literature that the O–O bond energy in hydrogen peroxide (38 to 52 kcal/mole [1]) is greater than that for $S_2O_8^{2-}$ (33 kcal/mole [18]). The energy of the peroxy bond in peroxymonosulfuric acid has not been determined.

The populations on the atoms in peroxymono- and peroxydisulfuric acids are shown in Tables 5 and 6. It can be seen from the data in Table 6 that the atomic populations on the O^6—O^7 peroxy bond in peroxydisulfuric acid are lower in comparison with the populations of the O^2—O^3 atoms in hydrogen peroxide (see Table 2). In peroxymonosulfuric acid (Table 5), a reduction in the electron density in comparison with H_2O_2 is only observed on the second peroxide oxygen atom O^3 due to the electron-accepting action of the sulfuric acid residue. This leads to a polarization of the peroxide bond which has an effect on the reactivity of the O—O group in peroxy compounds.

The energy level diagram in Fig. 3 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the H_2SO_5, H_2O_2, and $H_2S_2O_8$ molecules. According to their HOMO's their oxidants are arranged in the series

$$H_2O_2 < H_2SO_5 < H_2S_2O_8,$$

and, according to their LUMO's

$$H_2SO_5 < H_2O_2 < H_2S_2O_8.$$

In fact, among the peroxides which have been studied, hydrogen peroxide manifests donor-reducing properties, which are determined by the HOMO level, to the greatest extent. Peroxymonosulfuric acid is a more energetic reagent in reactions with nucleophilic substances. Apparently, this is associated with the presence of a polarized peroxide bond in monoperoxy acids with a relatively low energy for their LUMO's.

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