# *Ab initio* SCF Calculations on the Species HO_3, HO_3^+ and HO_3^- and an Estimate of the Stability of HO_3 Relative to OH and Different States of O_2

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The geometries of the ions HO_3^+ and HO_3^-, and of the radical HO_3 have been optimized using the gradient technique within the SCF approximation. Calculated energies of different isomers have been compared. For the radical species optimization has been carried through using both medium (double zeta) and large, $(10s6p1d/5s1p)/[5s4p1d/3s1p]$, basis sets. The energy of the radical has been compared with calculated energies for the systems $OH(^2\Pi)+O_2(^3\Sigma, ^1\Delta, ^1\Sigma)$. The large basis set indicates that HO_3 is stable relative to $OH(^2\Pi)+O_2(^1\Delta)$ and to $OH(^2\Pi)+O_2(^1\Sigma)$.

The daytime production of $O_2(^1\Delta_g)$ in the upper atmosphere is based on photodissociation of ozone.[1]

$$O_3+h\nu(\lambda<3102 \text{ Å}) \rightarrow O_2(^1\Delta_g)+O(^1D) \qquad (1)$$
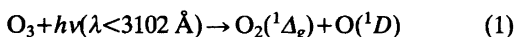
Nighttime production reactions that have been proposed are[2,3]

$$O(^3P)+O(^3P)+M \rightarrow O_2(^1\Delta_g)+M \qquad (2)$$

and

$$O(^3P)+HO_2 \rightarrow OH+O_2(^1\Delta_g) \qquad (3)$$
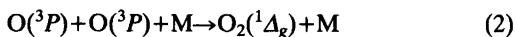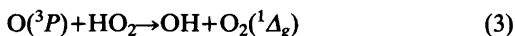
Attenuation of singlet O_2 is accomplished by radiation and collisional quenching. At altitudes above 80 km the main loss is by

$$O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-)+h\nu, \qquad (4)$$

and below 80 km, where the atmospheric density is higher, the reaction

$$O_2(^1\Delta_g)+M \rightarrow O_2(^3\Sigma_g^-)+M \qquad (5)$$

is the prevalent one.[4]

Calculated and observed density profiles for $O_2(^1\Delta_g)$ are in disagreement, especially below 60 km,[4] the calculated concentrations being higher than the observed ones.

It is possible that the radical species HO_3 might be a sink both for $O_2(^1\Delta_g)$ and OH radicals through the reaction

$$O_2(^1\Delta_g)+OH(^2\Pi) \rightarrow HO_3(^2A) \qquad (6)$$
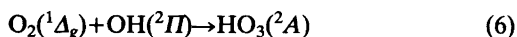
where HO_3 either appears as a reaction intermediate or as a stable product.

The possible existence of HO_3 as an intermediate has previously been alluded to.[5] However, SCF calculations with medium-sized basis sets and partial geometry optimizations have led to the conclusion that HO_3 is unstable with respect to $O_2(^3\Sigma_g^-)+OH(^2\Pi)$ by about 15 kcal/mol.[6] Very recently selected forms of the HO_3 species were studied theoretically[7] as an activated complex in a discussion of the mechanism of the reaction

$$H(^2S)+O_3(^1A_1) \rightarrow OH(^2\Pi)+O_2(^3\Sigma_g^-) \qquad (7)$$
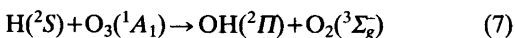
The related radical CF_3COO has been detected, and ESR data for this species are available.[8] The existence of this radical has led to the suggestion that the reaction

Table 1. Energies and optimized geometries of different structures of HO₃⁺. 4–31G basis. Bond lengths in nm, angles in degrees.

Isomer	R(OH)	$R(O_1O_2)$	$R(O_2O_3)$	$R(O_1O_3)$	∠OOH	∠OOO	α	E(au)	ΔE(kJ/mol)
I_p	0.099	0.150	0.117	—	100.7	112.2	180	−224.1594	0.0
II_p	0.100	0.150	0.117	—	105.5	119.9	0	—	36.8
III_p	0.100	0.151	0.151	0.148	110.5	58.7	66.3	—	146.7
IV_p	0.101	0.146	0.146	0.153	148.2	63.5	0	—	225.7
V_p	0.102	0.129	0.129	—	117.4	125.1	0	—	308.1
$VI_p{}^a$	0.100	0.153	0.117	—	102.4	114.5	90	—	26.8

^{a} Does not correspond to a minimum on the energy surface.

Table 2. Energies and optimized geometries of different structures of HO₃⁻. 4–31G basis. Bond lengths in nm, angles in degrees. Values in parentheses obtained by augmented basis (diffuse s- and p-functions).

Isomer	R(OH)	$R(O_1O_2)$	$R(O_2O_3)$	∠OOH	∠OOO	α	E(au)	ΔE(kJ/mol)
I_n	0.096	0.151	0.151	99.8	107.6	180	—	42.6
	(0.096)	(0.150)	(0.150)	(100.6)	(107.5)	(180)	—	(35.1)
II_n	0.097	0.149	0.151	96.8	102.7	0	−224.6360	0.0
	(0.096)	(0.149)	(0.150)	(99.1)	(103.6)	(0)	(−224.6706)	(0.0)
III_n	0.123	0.151	0.151		90.4	0	—	72.3
	(0.124)	(0.151)	(0.151)		(90.4)	(0)	—	(85.7)
IV_n	0.095	0.156	0.157	104.3	119.7	60.6	—	89.0
	(0.095)	(0.156)	(0.156)	(104.4)	(118.6)	(61.0)	—	(77.3)
V_n	0.095	0.157	0.153	112.3	135.5	0	—	111.2
	(0.095)	(0.157)	(0.157)	(112.9)	(134.3)	(0)	—	(100.3)
$VI_n{}^a$	0.096	0.149	0.151	101.5	108.4	90	—	26.3

^{a} Does not correspond to a minimum on the energy surface.

$$Me_3CO + O_2 \rightarrow Me_3COOO \qquad (8)$$

might take place.[9]

The ion HO$_3^+$, which is a protonated ozone, has been assumed to be the active species when ozone is used for oxygenation of alkenes in acid medium.[10,11] A complete analysis of the different structural forms of HO$_3^+$ has been carried through on the SCF level, and with second order Möller-Plesset calculations in selected points.[12]

A very recent experimental study indicates that the ion HO$_3^-$ might be an intermediate in the reaction [13]

$$t\text{-BuO}_2\text{H} + O_3 \rightarrow t\text{-BuO}_3\text{H} \qquad (9)$$

To our knowledge the ion HO$_3^-$ has not been studied by theoretical calculations previously.

The main purpose of the present study is to carry through a complete optimization of the geometries of the different possible forms of the radical HO$_3$. Furthermore we find it appropriate to reconsider the energy differences between this species in its optimized form and the systems OH($^2\Pi$) + O$_2$ ($^3\Sigma_g^-, ^1\Delta_g^+, ^1\Sigma_g^+$). If use of medium and large basis sets indicates moderate energy differences at the SCF level, calculations using methods accounting for electron correlation energies would probably give valuable informa-

tion on the potential surface for the reaction given by eqn. (6).

In a private communication[14] we have obtained information indicating that concentrations of OH and singlet O$_2$ in the atmosphere may be too low to make possible a significant production of HO$_3$. We find it, however, of central interest to study the energetics of the surfaces related to different states of O$_2$. A more extensive description of HO$_3$, and the possible reaction channels leading to it will give relevant information on the reaction given by eqn. (7).

We also find it appropriate to discuss the electronic and molecular structures of the ions HO$_3^+$ and HO$_3^-$ in conjunction with our study of HO$_3$. The results obtained by Kausch and Schleyer[12] in their structural studies of HO$_3^+$ are quantitatively confirmed by our calculations. In order to facilitate a comparative discussion of the radical and the ions, we have included our results on HO$_3^+$.

COMPUTATIONAL METHOD

All calculations in this study were carried out at the RHF−SCF level.

The geometry optimizations of the ions were performed by means of the program TEXAS[15] which uses a force-relaxation method.[16] As this
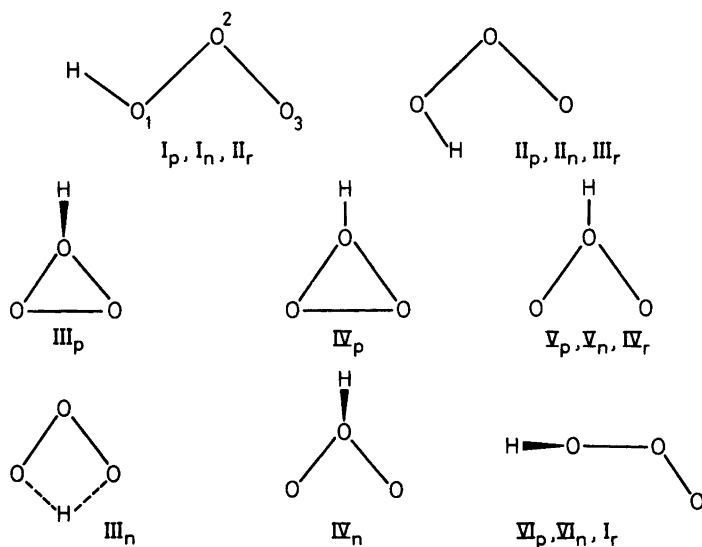

Fig. 1. Different forms of HO$_3^+$(p), HO$_3^-$(n) and HO$_3$(r) discussed in the text and referred to in the tables.

program is designed only for closed shell systems, the optimizations of the radical were undertaken by a special gradient program developed by one of us.[17] The program was based on the closed shell gradient program, MOLFORC.[18] Our program, which can handle one and two open shells, also calculates the energy gradient analytically.

The structures of the ions were optimized using a 4−31G basis set.[19] For some of the conformations this set was augmented by one diffuse s and one diffuse p orbital (exponent 0.05). The results showing the optimized geometries are displayed in Tables 1 and 2. For labelling of isomers and atoms see Fig. 1.

The basis sets used for the HO_3 radical were the $(7s3p/4s)/[4s2p/2s]$ set[20] for all isomers and the $(10s6p1d/5s1p)/[5s4p1d/3s1p]$ set[21,22] for the three isomers found to be the most stable ones using the smaller set. The exponents for the polarization functions were chosen to be 0.95 and 0.80 for the d-orbitals on O and the p-orbitals on H, respectively. The results of the optimization are given in Table 3.

The energies for the reference systems $OH(^2\Pi)+O_2(^3\Sigma,^1\Delta,^1\Sigma)$ were calculated using the larger basis set. The bond lengths were optimized using a parabola. The results are shown in Table 4.

RESULTS AND DISCUSSION

The global energy minimum was found for the isomers having the H-atom attached to the terminal oxygen atom. This was the case for the ions (structures I_p and I_n) as well as for the radical (structure I_r).

The most stable isomer of HO_3^+ is the *trans*-form (I_p). This is in accordance with results of previous calculations.[12]

The energy difference between the *cis*- and the *trans*-form of HO_3^+ (II_p and I_p) was found to be 37 kJ/mol. Both the forms have a pronounced single-bond double-bond oxygen system. Furthermore, a Mulliken population analysis, shown in Table 5, indicates a net positive charge on the free terminal oxygen atom. This charge distribution favours the *trans*-form.

As revealed by Table 1 there is one closed form (III_p) representing a local minimum on the energy surface. Energetically this form is very high above the global minimum. The closed form (IV_p) which represents the top of the barrier against a conversion from (III_p) to its equivalent

Table 3. Energies and optimized geometries of HO_3. Basis sets $(7s3p/4s)$ and $(10s6p1d/5s1p)$ (values in parentheses). Bond lengths in nm and angles in degrees.

	$R(OH)$	$R(O_1O_2)$	$R(O_2O_3)$	$\angle OOH$	$\angle OOO$	α	E (au)	ΔE (kJ/mol)
I_r	0.097 (0.095)	0.147 (0.138)	0.142 (0.128)	101.7 (102.9)	106.8 (109.5)	91.5 (90.1)	−224.6016 / −225.0252	0.0 (0.0)
II_r	0.097 (0.095)	0.149 (0.140)	0.140 (0.127)	98.8 (100.4)	104.3 (107.3)	180 (180)	—	4.6 (8.4)
III_r	0.097 (0.095)	0.149 (0.140)	0.141 (0.127)	102.4 (103.2)	107.2 (109.8)	0 (0)	—	12.1 (10.9)
IV_r	0.097	0.143	0.143	115.9	128.2	0	—	315.6

Table 4. Energies and optimized bond lengths in nm for OH($^2\Pi$) and O$_2$($^3\Sigma_g^-$, $^1\Delta_g$, $^1\Sigma_g^+$). Basis set (10s6p1d/5s1p). $\Delta E = E(\text{OH}+\text{O}_2)-E(\text{HO}_3)$. $E(\text{HO}_3) = -225.0252$ au. Relative energies[a] for different states of O$_2$.

	$R(\text{O}-\text{O})$	$R(\text{O}-\text{H})$	E(au)	ΔE(kJ/mol)
O$_2$($^3\Sigma_g^-$)	0.116		$\dot{-}149.6542$	−113.7
O$_2$($^1\Delta_g$)	0.116		−149.6073	9.2
O$_2$($^1\Sigma_g^+$)	0.116		−149.5608	131.7
OH($^2\Pi$)		0.096	−75.4143	
Exp.[a]				
O$_2$($^3\Sigma_g^-$)				0.0
O$_2$($^1\Delta_g$)				94.6
O$_2$($^1\Sigma_g^+$)				157.3

[a] Ref. 23.

Table 5. Atomic charges from gross atomic populations for HO₃⁺ and HO₃⁻. 4−31G basis. For labelling of isomers and atoms see Fig. 1.

		H	O$_1$	O$_2$	O$_3$
HO₃⁺	I$_p$	+0.56	−0.13	+0.16	+0.41
	II$_p$	+0.53	−0.09	+0.22	+0.34
HO₃⁻	I$_n$	+0.34	−0.55	−0.28	−0.51
	II$_n$	+0.38	−0.57	−0.26	−0.55

form has an energy indicating a barrier of around 79 kJ/mol.

The open form (V$_p$) having an oxygen−oxygen link disrupted, is the least stable of the isomers considered. The energy difference of 308 kJ/mol is, however, substantially reduced by inclusion of electron correlation.[12]

For the negative ion HO₃⁻ the *cis*-form (II$_n$) was found to be the most stable one. The energy difference between this form and the *trans*-form (I$_n$) is calculated to be 43 kJ/mol using the 4−31G basis (reduced to 35 kJ/mol in the augmented basis). A Mulliken population analysis, shown in Table 5, gives a charge distribution that indicates a net attraction between the H-atom and the terminal oxygen atom. This change in electrostatic interaction by going from HO₃⁺ to HO₃⁻ may explain the relative *cis-trans* energy differences for these forms.

The two electrons added to HO₃⁺ in order to make HO₃⁻ enter a π-orbital that is antibonding in the O$_2$−O$_3$ region. This induces a lengthening of this bond from 0.117 nm in HO₃⁺ to 0.151 nm in HO₃⁻, thus making the two O−O bond lengths in

HO₃⁻ virtually identical.

We did not succeed in finding any stable closed form (analogous to (III$_p$) and (IV$_p$)) for the negative ion. The two additional electrons encountered in going from HO₃⁺ enter the 5a″ orbital which is strongly antibonding in the region between the terminal oxygen atoms. As a result the ring is opened and we obtain the two open structures (IV$_n$) and (V$_n$), the former being the most stable one.

In order to detect a possible importance of diffuse functions in the basis set for the negative ion, we reoptimized the geometries for this ion using a 4−31 G basis set augmented with diffuse p-functions on oxygen and an s-function on hydrogen (exponents 0.05). As revealed by Table 2 the diffuse functions did not introduce any significant changes in the geometries, but led to a lowering of the relative energies for all isomers except one (III$_n$).

A rotation of the H−O bond around the O−O bond did not reveal any local energy minimum. The energy increased monotonically in going from (II$_n$) to (I$_n$). See Fig. 1.

The results obtained on the ions would lead us to the preliminary conclusion that in the ground state of the radical HO_3 the hydrogen atom is bonded to a terminal atom in ozone, and that the O_2-O_3 bond is slightly shorter than the O_1-O_2 bond. The results obtained by our calculations confirmed this expectation.

For the radical the global minimum was obtained for a non-planar form (I_r) with torsion angles of 91.5 and 90.2 degrees for the small and the large basis set, respectively. For definition of basis sets and torsion angle, see Table 3. The planar *trans*- and *cis*-forms were found to represent maxima on the potential curve for the rotation of $O-H$ around $O-O$. The highest energy maximum, the *cis*-barrier [represented by (III_r)], was found to be 12 kJ/mol, indicating an almost free rotation of the $O-H$ group.

Our smaller basis set is of similar quality although not identical to the $4-31G$ set used by Blint and Newton.[6] They report bond lengths of 0.144 nm and 0.137 nm for O_1-O_2 and O_2-O_3 respectively. Their calculated bond angles deviate from ours by only 1–2 degrees.

All computed bond lengths are somewhat shortened when the large basis set is used, but qualitatively the picture is the same as the one obtained with the smaller basis.

The singly occupied orbital with quasi-π symmetry is mainly localized in the O_2-O_3 region, and is strongly antibinding in this region. For the planar structures the occupation of $3a''$ is 0,1, and 2 for HO_3^+, HO_3, and HO_3^-, respectively, and the O_2-O_3 bond length increases along this series.

The calculations did not indicate an energy minimum for any closed form of the radical. We did find a minimum for a planar open form having the hydrogen atom attached to the central oxygen atom. This form (IV_r) has, however, a very high energy 316 kJ above the ground state.

As mentioned in the introduction, the main purpose of the present study is to locate HO_3 energetically relative to the systems $OH+O_2$, HO_2 being in different states. This work also has some relevance for the $H+O_3$ reaction mechanism studied by Schaefer *et al.*[7] Our SCF data presented in Table 4 show clearly that the energy of HO_3 relative to $OH(^2\Pi)$ and excited oxygen molecules is such that the reactions given by eqn. (6) are thermodynamically relevant although they may be less likely for other reasons. On the SCF-level the corresponding reaction involving O_2 in its ground state seems less likely. It is, however, conceivable that CI-effects, which are shown to be important for O_3, may significantly influence these results. Consequently, these reaction systems deserve further studies including parts of the reaction surfaces. Studies along these lines invoking methods for handling electron correlation are in progress.

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