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REGULAR ARTICLE

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Stationary points on the energy hypersurface of the reaction $O_3 + H^{\cdot} \rightarrow [^{\cdot}O_3H]^* \leftrightarrow O_2 + {}^{\cdot}OH$ and thermodynamic functions of $^{\cdot}O_3H$ at G3MP2B3, CCSD(T)-CBS (W1U) and MR-ACPF-CBS levels of theory

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Abstract The relative enthalpies, ΔH° (0) and ΔH° (298.15), of stationary points (four minimum and three transition structures) on the $^{\bullet}O_3H$ potential energy surface were calculated with the aid of the G3MP2B3 as well as the CCSD(T)–CBS (W1U) procedures from which we earlier found mean absolute deviations (MAD) of 3.9 kJ mol^{-1} and 2.3 kJ mol^{-1}, respectively, between experimental and calculated standard enthalpies of the formation of a set of 32 free radicals. For CCSD(T)-CBS (W1U) the well depth from $O_3 + H^{\bullet}$ to *trans*-$^{\bullet}O_3H$, $\Delta H^{\circ}_{\mathrm{well}}(298.15) = -339.1$ kJ mol^{-1}, as well as the reaction enthalpy of the overall reaction $O_3 + H^{\bullet} \rightarrow O_2 + {}^{\bullet}OH$, $\Delta_r H^{\circ}(298.15) = -333.7$ kJ mol^{-1}, and the barrier of bond dissociation of *trans*-$^{\bullet}O_3H \rightarrow O_2 + {}^{\bullet}OH$, $\Delta H^{\circ}(298.15) = 22.3$ kJ mol^{-1}, affirm the stable short-lived intermediate $^{\bullet}O_3H$. In addition, for radicals *cis*-$^{\bullet}O_3H$ and *trans*-$^{\bullet}O_3H$, the thermodynamic functions heat capacity $C^{\circ}_{p}(T)$, entropy $S^{\circ}(T)$, and thermal energy content $H^{\circ}(T) - H^{\circ}(0)$ are tabulated in the range of $100 - 3000$ K. The much debated calculated standard enthalpy of the formation of the *trans*-$^{\bullet}O_3H$ resulted to be $\Delta_f H^{\circ}(298.15) = 31.1$ kJ mol $^{-1}$ and 32.9 kJ mol $^{-1}$, at the G3MP2B3 and CCSD(T)-CBS (W1U) levels of theory, respectively. In addition, MR-ACPF-CBS calculations were applied to consider possible multiconfiguration effects and yield $\Delta_f H^{\circ}(298.15) = 21.2$ kJ mol $^{-1}$. The discrepancy between calculated values and the experimental value of -4.2 ± 21 kJ mol^{-1} is still unresolved.[1]

Keywords HOOO radical · Ab initio calculations · Thermochemistry · Anharmonic vibrations

1 Introduction

Trioxy radicals $^{\bullet}O_3R$ are assumed to play key roles in hydrocarbon oxidation, combustion, atmospheric chemistry, as well as chemical and biochemical oxidations [1–6]. Specifically, the $^{\bullet}O_3H$ radical has been postulated repeatedly in the past as an important intermediate in atmospheric processes, although it had never been detected experimentally. In particular, it was not clear whether the combination of atomic hydrogen with ozone might lead to a long-lived $^{\bullet}O_3H$ radical or if immediate dissociation into O_2 and $^{\bullet}OH$ takes place. In 1996, ion cyclotron resonance mass spectrometry was used by Speranza to estimate the enthalpy of formation of $^{\bullet}O_3H$ to -4.2 ± 21 kJ mol^{-1} [7]. This estimate implies that the reaction enthalpy of $O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}O_3H$ is -41.8 ± 21 kJ mol^{-1} [7]. In 1999, neutralization–reionization mass spectrometry (NRMS) experiments conducted by Cacace et al. [8] with mass-selected O_3H^+ ions generated from protonated ozone, proved the existence of the neutral $^{\bullet}O_3H$ radical in the μs range, thereby corroborating the need for the inclusion of this species in the modeling of the atmospheric chemistry of ozone. In 2000, Nelander et al. [9] studied the formation of the complex between $^{\bullet}O_3H$ and stable molecules in argon matrices. In the course of these studies, they have noted a set of bands in the infrared absorption spectrum, which gave evidence that these bands can be assigned to $^{\bullet}O_3H$.

In view of the importance of the $^{\bullet}O_3H$ in atmospheric chemistry numerous computational studies, reviewed by Speranza [10], had already been conducted prior to the experimental verification of $^{\bullet}O_3H$ as a stable species. Generally, agreement between experiment and computations was found to be poor. Quite disturbingly, more recent computational estimates ($\sim$17–35 kJ mol^{-1}) for the enthalpy of formation of $^{\bullet}O_3H$ [11–13] also differ substantially from the experimental value of -4.2 ± 21 kJ mol^{-1} [7]. Similar discrepancies in enthalpies of formation have been derived by Denis et al. [12] from energies calculated by Yu and Varandas [14] and Setokuchi et al. [15]. These more recent calculated enthalpies of formation of $^{\bullet}O_3H$, summarized in Table 1, have led Denis et al. [12] to question the reliability of the experimental proce-

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[1] *Note added in proof*: Yu-Ran Luo and J. Alistair Kerr, based on the discussion in reference 12, recently presented an experimental value of $\Delta_f H^{\circ}(298.15) = 29.7 \pm 8.4$ kJ mol^{-1} in the 85th edition of the CRC Handbook of Chemistry and Physics (in progress).

Table 1 Summary of more recent calculated enthalpies of formation $\Delta_f H^o(298.15)$/kJ mol^{-1} for the radical $^\bullet O_3H$

$\Delta_f H^o(298.15)$	Method
34.7	G2(RCC) [11]
25.5	CBS-QCI/APNO [11]
21.9	MR-MP2 [15]
17.5	QCISD(T)-CBS [14]
35.1	G3 [12]
22.2	CBS-QB3 [12]
26.4	CBS-APNO [12]
33.1	CCSD(T)/∞ [12]
31.1	G3MP2B3 [13]
32.9	CCSD(T)-CBS (W1U) [13]
-4.1 ± 21	Experiment [7]*

* See note added in proof in the abstract

dure used to determine $\Delta_f H^o(298.15)$ of $^\bullet O_3H$. However, the possibility cannot be completely dismissed that the "convergence" of the calculated enthalpy of formation of $^\bullet O_3H$ merely reflects the similarity of the underlying computational schemes rather than being an indication of inaccurate procedures used in the experimental estimation of $\Delta_f H^o(298.15)$ ($^\bullet O_3H$).

It is known that ozone requires a multireference treatment, owing to the singlet diradical character, to obtain the proper enthalpy of formation. One might assume similar effects to be responsible for the above-mentioned discrepancies between calculated and experimental standard enthalpies of $^\bullet O_3H$. Therefore, we will treat this radical by multireference – averaged coupled pair functionals – complete basis set (MR–ACPF–CBS).

In addition to the intermediate radical $^\bullet O_3H$, we present stationary points on the energy hypersurface, four minima and three transition structures, for the title reaction.

$$O_3 + H^\bullet \rightarrow [^\bullet O_3H] \leftrightarrow O_2 + {}^\bullet OH \qquad (1)$$

2 Computational methods

Gaussian-3 (G3) theory is a procedure for calculating total energies of atoms and molecules containing atoms for $Z \leq 18$ (hydrogen to argon) based on ab initio calculations as well as empirically based molecule-independent corrections [16]. G3 theory was assessed on a total of roughly 300 energies from which enthalpies of formation as well as reaction enthalpies, ionization energies, and electron affinities were obtained. Meanwhile, different modifications of G3 theory have been developed, which require less computational time and can be applied to larger systems with more than 150 electrons (20 heavy atoms out of the range between carbon and chlorine) without significant loss of accuracy. The variation, referred to as G3MP2B3, is described in the following [17].

First, the geometries as well as the complete set of vibrational wave numbers are calculated at the B3LYP/6-31G(d) level. The zero-point energies (ZPE) are scaled by 0.96. The B3LYP density functional [18] used for the calculation of the geometries and ZPE is a linear combination of Hartree–Fock exchange, 1988 Becke exchange, and Lee, Yang, Parr correlation functional [19]. Second, a single-point quadratic configuration interaction calculation is performed in the frozen core approximation for the correlation calculation, QCISD(T,FC)/6-31G(d). Third, second-order Mœller-Plesset perturbation theory, MP2(FC), is performed with the basis sets 6-31G(d) and 6-311+G(2df,2p) on Li – Ne, and 6-311+G (3d2f,2p) on Na – Ar, summarized as G3MP2large. Fourth, a spin-orbit (SO) corrections is included for atomic species. Fifth, the higher level correction (HLC) takes into account remaining deficiencies in the energy calculations. The HLC is simply a linear function of the number of valence electrons with α and β spin, $-An_\beta - B(n_\alpha - n_\beta)$, with $n_\alpha \geq n_\beta$. The values of A and B are 10.041 and 4.995 mE_h, respectively, for molecules, and 10.188 and 2.323 mE_h, respectively, for atoms; 1 mE_h = 2.625500 kJ mol^{-1} [17]. In summary, the G3MP2B3 total energy E_0 results to be

$$\begin{aligned} E_0[\text{G3MP2B3}] = {} & E[\text{QCISD(T)/6-31G(d)}] \\ & + E[\text{MP2/G3MP2large}] \\ & - E[\text{MP2/6-31G(d)}] + \Delta E(\text{ZPE}) \\ & + \Delta E(\text{SO}) + \Delta E(\text{HLC}) \end{aligned} \qquad (2)$$

A more accurate but also more expensive method, restricted to small systems, is based on the CCSD(T) electron correlation method (coupled cluster with all single and double substitutions followed by a perturbative estimate of the effect of connected triple excitations) [20]. Different series of calculations are used to achieve complete basis set (CBS) results by means of extrapolation schemes. We follow the strategy of Martin and de Oliveira [21] who abbreviate their CCSD(T)–CBS arrangement of methods by W1. This series of methods is modified for radicals where UCCSD (unrestricted open shell) instead of ROCCSD (restricted open shell) is applied. The protocol for the various steps of W1U is described in the following.

(1) The geometry as well as the complete set of harmonic vibrational wave numbers are calculated at the B3LYP/VTZ level (cc-pVTZ, or VTZ for short, if only first-row atoms are present). The ZPE is scaled for the total energy as well as for thermochemical properties by 0.985. (2) The following single-point calculations are carried out: CCSD(T)/AVDZ, CCSD(T)/AVTZ, and CCSD/AVQZ. (2a) The SCF component of total energy is extrapolated by $A + B/C^l$ from the above SCF components (l = 2, 3, and 4, respectively). (2b) The CCSD valence correlation component is obtained from applying $A + B/l^\beta$ to CCSD/AVTZ and CCSD/AVQZ valence correlation energies (l = 3 and 4, respectively; β = 3.22). (2c) The (T) valence correlation component is obtained from applying $A + B/l^\beta$ to CCSD(T)/AVDZ and CCSD(T)/AVTZ values for the (T) contribution. (3) Core correlation contributions are obtained from CCSD(T)/MTsmall. (4) Scalar relativistic corrections are calculated with the previous step [22]. (5) Spin-orbit coupling effects are considered manually from experimental values [23]. SO splittings (cm^{-1}): O (158.3), OH (139.7); energy corrections (cm^{-1}): O (−79.2), OH (−46.6); 1 kJ mol^{-1} = 83.5935 cm^{-1}. In summary, the W1U total energy E_0 results to be

Table 2 Calculated stationary points, minimum (Min) or transition (TS) structures on the $^{\bullet}O_3H$ energy hypersurface; symmetry, electronic state, equilibrium structural data *r*/Å, *a*/deg.; moments of inertia $I_A, I_B, I_C/10^{-47}$ kg m^2, harmonic vibrational wavenumbers, unscaled, $\tilde{\nu}$/cm^{-1} ; relative electronic energy ΔE/kJ mol^{-1} and enthalpy $\Delta H^{\circ}(T)$/kJ mol^{-1} referenced to O_3 + $H^{\bullet}$. Computational method: CCSD(T)-CBS (W1U) if not stated otherwise.

$O_3 + H^{\bullet}$ Min(**1**) C_{2v} ($^1A_1$)
r(O – O) 1.2562, a(O – O – O) 118.15
$I_A = 7.37968$, $I_B = 61.68924$, $I_C = 69.06892$
$\tilde{\nu}$ 746(a_1), 1193(b_2), 1251(a_1)
G3MP2B3 $\Delta E = 0.0^a$ $\Delta H^{\circ}(0) = 0.0^b$ $\Delta H^{\circ}(298.15) = 0.0^c$
CCSD(T)-CBS $\Delta E = 0.0^d$ $\Delta H^{\circ}(0) = 0.0^e$ $\Delta H^{\circ}(298.15) = 0.0^f$
$^{\bullet}$O1 – O2 – O3 – H-*cis* Min(**2**) C_s ($^2A''$)
r(O1 – O2) 1.2522, r(O2 – O3) 1.5022, r(O3 – H) 0.9737,
a(O1 – O2 – O3) 112.53, a(O2 – O3 – H) 99.44
$I_A = 12.14141$, $I_B = 71.74231$, $I_C = 83.88572$
$\tilde{\nu}$ 244(a″), 470(a′), 727(a′), 1227(a′), 1406(a′), 3680(a′)
G3MP2B3 $\Delta E = -356.7$ $\Delta H^{\circ}(0) = -330.5$ $\Delta H^{\circ}(298.15) = -330.6$
CCSD(T)-CBS $\Delta E = -360.8$ $\Delta H^{\circ}(0) = -333.9$ $\Delta H^{\circ}(298.15) = -338.1$
$^{\bullet}$O1 – O2 – O3 – H TS(**1**) C_1 (^2A)
r(O1 – O2) 1.2440, r(O2 – O3) 1.5373, r(O3 – H) 0.9701,
a(O1 – O2 – O3) 111.74, a(O2 – O3 – H) 99.20, d(O1 – O2 – O3 – H) −87.95
$\tilde{\nu}$ 193**i**, 472, 685, 1236, 1281, 3734
G3MP2B3 $\Delta E = -359.0$ $\Delta H^{\circ}(0) = -335.1$ $\Delta H^{\circ}(298.15) = -336.4$
CCSD(T)-CBS $\Delta E = -358.5$ $\Delta H^{\circ}(0) = -333.7$ $\Delta H^{\circ}(298.15) = -339.1$
$^{\bullet}$O1 – O2 – O3 – H-*trans* Min(**3**) C_s ($^2A''$)
r(O1 – O2) 1.2343, r(O2 – O3) 1.5439, r(O3 – H) 0.9705,
a(O1 – O2 – O3) 110.22, a(O2 – O3 – H) 98.27
$I_A = 11.22038$, $I_B = 75.41439$, $I_C = 86.63477$
$\tilde{\nu}$ 178(a″), 467(a′), 674(a′), 1235(a′), 1377(a′), 3737(a′)
G3MP2B3 $\Delta E = -362.4$ $\Delta H^{\circ}(0) = -336.8$ $\Delta H^{\circ}(298.15) = -336.6$
CCSD(T)-CBS $\Delta E = -361.6$ $\Delta H^{\circ}(0) = -335.2$ $\Delta H^{\circ}(298.15) = -339.1$
$^{\bullet}$O1 – O2 – O3 – H-*cis* TS(**2**) C_s ($^2A''$)
r(O1 – O2) 1.2062, r(O2 – O3) 1.8477, r(O3 – H) 0.9722,
a(O1 – O2 – O3) 115.17, a(O2 – O3 – H) 95.16
$\tilde{\nu}$ 291**i**(a′), 63(a″), 385(a′), 928(a′), 1528(a′), 3720(a′)
G3MP2B3 $\Delta E = -330.4$ $\Delta H^{\circ}(0) = -311.3$ $\Delta H^{\circ}(298.15) = -310.4$
CCSD(T)-CBS $\Delta E = -329.6$ $\Delta H^{\circ}(0) = -309.4$ $\Delta H^{\circ}(298.15) = -312.8$
$^{\bullet}$O1 – O2 – O3 – H-*trans* TS(**3**) C_s ($^2A''$)
r(O1 – O2) 1.2003, r(O2 – O3) 1.8484, r(O3 – H) 0.9711,
a(O1 – O2 – O3) 111.36, a(O2 – O3 – H) 94.52
$\tilde{\nu}$ 265**i**(a′), 130(a″), 381(a′), 901(a′), 1555(a′), 3736(a′)
G3MP2B3 $\Delta E = -334.6$ $\Delta H^{\circ}(0) = -315.1$ $\Delta H^{\circ}(298.15) = -314.5$
CCSD(T)-CBS $\Delta E = -333.8$ $\Delta H^{\circ}(0) = -313.1$ $\Delta H^{\circ}(298.15) = -316.8$
$O_2 + ^{\bullet}OH$ Min(**4**) $D_{\infty h}$ ($^3\sum_g^-$), $C_{\infty v}$ ($^2\Pi$)
r(O – O) 1.2058, r(O–H) 0.9746
$\tilde{\nu}$ 1629(σ_g), 3698(σ)
G3MP2B3 $\Delta E = -349.0$ $\Delta H^{\circ}(0) = -337.1$ $\Delta H^{\circ}(298.15) = -332.1$
CCSD(T)-CBS $\Delta E = -347.2$ $\Delta H^{\circ}(0) = -334.6$ $\Delta H^{\circ}(298.15) = -333.7$

[a] $E = -225.707756$
[b] $H^{\circ}(0) = -225.700667$
[c] $H^{\circ}(298.15) = -225.695985$
[d] $E = -226.064290$
[e] $H^{\circ}(0) = -226.057133$
[f] $H^{\circ}(298.15) = -226.050863$, in units of E_H; 1 E_H = 2625.50 kJ mol^{-1}

$$\begin{aligned} &E_0[\text{CCSD(T)-CBS(W1U)}] \\ &= E[\text{SCF-CBS}] + \Delta E_{\text{val.-correl.}}[\text{CCSD-CBS}] \\ &\quad + \Delta E_{\text{val.-correl.}}[\text{CCSD(T)-CBS}] \\ &\quad + \Delta E_{\text{core-correl}}[\text{CCSD(T)/MTsmall}] \\ &\quad + \Delta E_{\text{relativ.}}[\text{CCSD(T)/MTsmall}] \\ &\quad + \Delta E(\text{ZPE}) + \Delta E_{\text{exp.}}[\text{SO}] \end{aligned} \tag{3}$$

All calculations have been performed using the GAUSSIAN03 computer program [24].

The above-mentioned B3LYP/cc-pVTZ (for W1U) calculations for the energy minimum structures and vibrational wave numbers are the basis for the thermochemical corrections to the electronic total energy E_0. These corrections were calculated at specified states T, p by using standard rigid-rotor harmonic oscillator (RRHO) partition function expressions. In addition to complete sets of structural parameters and vibrational wave numbers $\tilde{\nu}$, principal moments of inertia I_A, I_B, and I_C, heat capacities $C_p^{\circ}(T)$, entropies $S^{\circ}(T)$, and thermal energy contents $H^{\circ}(T) - H^{\circ}(0)$ are available. An an-

Table 3 B3LYP/cc-pVTZ calculated equilibrium structures, r/Å ($^\bullet$ O1–O2–O3–H), and harmonic and anharmonic vibrational wavenumbers $\tilde{\nu}$/cm^{-1} of the free *trans*-$^\bullet O_3H$ radical and the H-bond complex *trans*-$^\bullet O_3H$–OH_2.

	$^\bullet$OOOH		$^\bullet$OOOH–OH_2		Experiment Ar-Matrix [9]
	Harm.	Anharm.	Harm.	Anharm.	
r(O3–H)	0.9704		0.9838		
r(O2–O3)	1.5438		1.5096		
$\tilde{\nu}$					
a″	176	282	204	179	
a′	467	453	517	504	566
a′	674	652	715	694	
a′	1235	1199	1268	1253	1223
a′	1376	1341	1452	1388	
a′	3738	3548	3482	3325	3361

harmonic treatment of vibrational frequencies was carried out for the *trans*-$^\bullet O_3H$, **3**, radical (Table 3).

Enthalpies of formation $\Delta_f H^o(T)$ deserve a special treatment. To calculate enthalpies of formation, we need a few component data first, both experimental and calculated ones [25]. The experimental atomic enthalpies of formation used are $\Delta_f H^o(0)$ = O(246.81) and H(216.02) kJ mol^{-1} [23,26]. The calculation of $\Delta_f H^o(298.15)$ for a molecule proceeds in two steps (Eqs. 4a and 4b) which are exemplified in the following by the hydroxyl radical.

$$\begin{aligned}\Delta_f H^o(0)(\mathrm{OH,calc.}) = {} & \Delta_f H^o(0)(\mathrm{O(g),exp.}) \\ & + \Delta_f H^o(0)(\mathrm{H(g),exp.}) \\ & - \{H^o(0)(\mathrm{O,calc.}) + H^o(0)(\mathrm{H,calc.}) \\ & - H^o(0)(\mathrm{OH,calc.})\} \qquad (4a)\end{aligned}$$

$$\begin{aligned}& \Delta_f H^o(298.15)(\mathrm{OH,calc.}) \\ & = \Delta_f H^o(0)(\mathrm{OH,calc.}) + \{H^o(298.15) - H^o(0)\}(\mathrm{OH,calc.}) \\ & \quad - \{H^o(298.15) - H^o(0)\}(\mathrm{O(ref),exp.}) \\ & \quad - \{H^o(298.15) - H^o(0)\}(\mathrm{H(ref),exp.}) \qquad (4b)\end{aligned}$$

The first step (Eq. 4a) shifts the calculated enthalpy of atomization of OH (T = 0 K), in parentheses, to the experimental enthalpy of formation of atoms, related to the elements (H_2 for H and O_2 for O). The second step (Eq. 4b) takes the temperature dependence of the enthalpy into account where the temperature effect of atoms is taken from the experiment. It should be emphasized that $\{H^o(298.15) - H^o(0)\}$ of O(ref) is the thermal energy content of the O atom (4.35) in O_2, and $\{H^o(298.15) - H^o(0)\}$ of H(ref) is $\{H^o(298.15) - H^o(0)\}$ $(H_2(\mathrm{ref}))/2$ (4.23). With $H^o(0)$ = 1318.37 (H,calc.), 196891.66 (O,calc.), 198639.02 (OH,calc.), and $H^o(298.15)$=198630.35 (OH, calc.) kJ mol $^{-1}$, the interested reader can repeat the calculation of the enthalpy of formation according to Eqs. 4a and 4b. The mean absolute deviations (MAD) between calculated, G3MP2B3 and CCSD(T)-CBS (W1U), and experimental $\Delta_f H^o(298.15)$ values by a set of 32 free radicals are 3.91 kJ mol^{-1} and 2.3 kJ mol^{-1}, respectively [27,28].

The MR–ACPF calculations have been performed according to the algorithm of Gdanitz and Ahlrichs [29], as is implemented in the MOLPRO-2000 [30] suite of programs. Our largest complete-active-space-ansatz for O_3 has been CAS (10,10), distributing ten electrons among ten active orbitals, which comprise 3a$_1$, 3b$_1$, 2b$_2$, and 2a$_2$ orbitals. The corresponding CAS-wavefunction for the X $^1A_1$ ground state consists of 4936 configuration state functions (CSF). The largest CAS-wavefunction in treating the $^\bullet O_3H$ radical has been CAS(13,11), employing seven active orbitals of a′ and four active orbitals of a″ symmetry, which results in 38080 CSFs for the corresponding X $^2A'$ ground state. In order to avoid any bias whatsoever due to configuration selection or wavefunction truncation, the full CAS-wavefunctions have been employed as reference wavefunctions for the subsequent MR-ACPF calculations. This leads to very elaborate CI-expansions amounting to several billion configurations, i.e. 3.79×10^9 configurations for O_3, and due to the C_s symmetry of $^\bullet O_3H$ even 5.45×10^{10} configurations when using the aug-cc-pVQZ basis set. The MR-ACPF energies obtained have eventually been extrapolated using rational function-type approaches proposed by Martin and de Oliveira [21] as described above.

3 Results and discussion

Exploratory optimized scan calculations indicate the early path of the title reaction. The hydrogen atom approaches the ozone molecule on the bisector of the OOO-angle and increases/decreases the ozone states $^1A_1$/$^1B_1$, respectively. Consequently, a state crossing of $^2A_1$ and $^2B_1$ of the reacting system $^\bullet O_3H$ occurs at C_{2v} symmetry. The rhombic structure can undergo a b$_1$ motion (out of planarity) which leads to the avoided crossing region ($^2A'$) on the circle somewhere below the top of the cone in Fig. 1 and further back to planarity to the symmetry reduction $C_{2v} \rightarrow C_s$ to *cis*-$^\bullet O_3H$, **2**, with the state $^2A''$. This conical intersection explains the transition of the reacting system from the state $^2A'$ to $^2A''$.

In the following, the discussion of stationary points in Table 2 is based on the CCSD(T)-CBS (W1U) results.

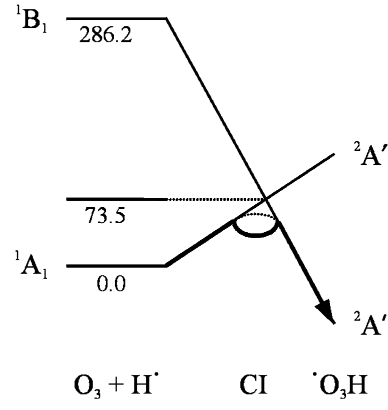


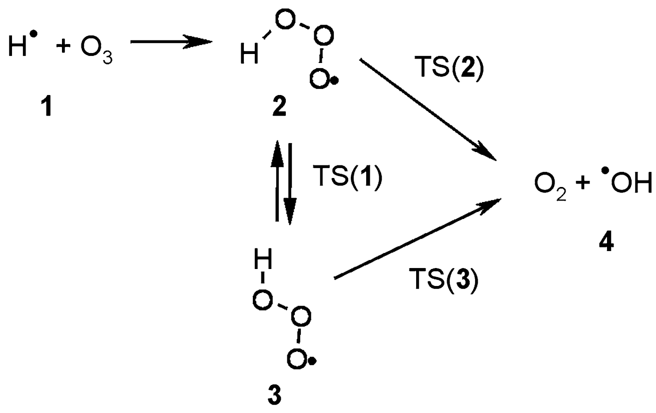
Fig. 1 Qualitative CAS(7,7)/6-31G(d) calculated energy level diagram of the conical intersection (CI) between the ground and first excited singlet states of O_3 in the reaction O_3 + $H^\bullet$ to the $^2A''$ ground state of $^\bullet O_3H$. Energies are given in kJ mol^{-1}

Table 4 Components of atomization enthalpies $H_a^o(0)$/kJ mol^{-1}

	SCF limit	Val. corr. limit	Core corr.[a]	Spin-orbit	Vib. zero-point	$H_a^o(0)$
O_3	−176.5	780.7[b]	0.5	−2.8	−18.8	583.1
$^•O_3H$	258.9	719.1[c]	0.5	−2.8	−45.2	930.5

[a] Including scalar relativ. effects
[b] CBS limit of CAS(10,10)-ACPF (772.6) + CBS limit of CAS extension (8.1)
[c] CBS limit of CAS(13,11)-ACPF (697.6) + CBS limit of CAS extension (21.5)

Formation of **2** from O_3 + $H^•$, **1**, occurs in a strongly exothermic ($\Delta H^o(298.15) = -338.1$ kJ mol^{-1}, Table 2) reaction. *Cis*-$^•O_3H$, **2**, can rearrange via a small barrier (1 kJ mol^{-1}, TS(**1**) in Table 2) to the slightly more stable *trans*-$^•O_3H$, **3**. Both conformers, *cis*-$^•O_3H$ and *trans*-$^•O_3H$, are found to be planar (C_s ($^2A''$)). It is well known that the calculated relative stability as well as the structure (planar or twisted) of $^•O_3H$ strongly depends on the method used [12,14,15]. Path for direct formation of *trans*-$^•O_3H$ from the separated reactants could not be found.



Both conformers of $^•O_3H$ can easily dissociate ($\Delta\Delta H^o(298.15) = 25.3$ and $\Delta\Delta H^o(298.15) = 22.3$ kJ mol^{-1}, for TS(**2**) and TS(**3**), respectively) into the final products O_2 + $^•OH$. Most importantly, the hydrotrioxy radical $^•O_3H$ is found to be stable ($\Delta\Delta H^o(298.15) = -4.4$ and $\Delta\Delta H^o(298.15) = -5.4$ kJ mol^{-1}, for **2** and **3**, respectively) relative to the O_2 + $^•OH$ asymptote as also indicated by the DMBE II potential energy surface [14] where energies rather than enthalpies are used.

The existence of $^•O_3H$ has been proved by Argon matrix infrared studies [9]. This radical appears in the form of hydrogen bond complexes with water as acceptor, $^•OOOH–OH_2$. We calculated at the B3LYP/cc-pVTZ level the harmonic and anharmonic frequencies of the free radical as well as the H-bond complex for comparison. In Table 3, the calculated frequency of the O–H stretching vibration of the radical in the complex is in good agreement with the observed value, 3325 cm^{-1} versus 3361 cm^{-1}, respectively. Observed vibrations typical for $^•OH_3$ are 1223 cm^{-1} and 566 cm^{-1}, calculated at 1253 and 504, and can be assigned to H–O–O and O–O–O bending, respectively.

Table 5 Calculated and experimental enthalpies of formation, $\Delta_f H^o(298.15)$/kJ mol^{-1}, of O_3 ($^1A_1$) and *trans*-$^•O_3H$ ($^2A''$). CAS extrapolations are based on CAS(8,8), CAS(10,10) for O_3, and CAS(9,8), CAS(13,11) for $^•O_3H$

	O_3	$^•O_3H$
G3MP2B3	148.3	31.1 [13]
CCSD(T)-CBS(3-4) W1U	154.0	32.9 [13]
MR-ACPF-CBS(3-4) + CAS extrapolation	154.5	21.2
Experiment	142.7 ± 1.7 [31]	−4.2 ± 21 [7]*

* See note added in proof in the Abstract

Table 6 B3LYP/cc-pVTZ calculated thermodynamic functions for the radicals (a) *cis*-$^•O_3H$ and (b) *trans*-$^•O_3H$ at the RRHO approach. Temperature T/K; heat capacity C_p^o and entropy S^o are given in J mol^{-1} K^{-1}; thermal energy content $H^o(T) - H^o(0)$/kJ mol^{-1}; vibrational wavenumbers $\tilde{\nu}$/cm^{-1} from Table 2 are scaled by 0.985 for the thermodynamic functions

	T	$C_p^o(T)$	$S^o(T)$	$H^o(T) - H^o(0)$
a)	100	37.162	216.756	3.429
	150	41.158	232.563	5.385
	200	44.819	244.902	7.533
	250	48.103	255.249	9.854
	298.15	50.965	263.960	12.237
	300	51.070	264.278	12.332
	350	53.769	272.345	14.952
	400	56.195	279.679	17.698
	500	60.266	292.667	23.524
	600	63.425	303.934	29.713
	800	67.890	322.825	42.864
	1000	70.948	338.306	56.753
	1200	73.220	351.443	71.169
	1500	75.701	368.054	93.515
	2000	78.299	390.208	132.052
	2500	79.806	407.844	171.584
	3000	80.734	422.471	211.710
b)	100	38.878	218.104	3.518
	150	42.526	234.542	5.550
	200	45.970	247.237	7.761
	250	49.099	257.826	10.137
	298.15	51.844	266.705	12.566
	300	51.944	267.023	12.660
	350	54.534	275.219	15.322
	400	56.873	282.650	18.105
	500	60.798	295.771	23.992
	600	63.839	307.127	30.225
	800	68.136	326.109	43.442
	1000	71.082	341.636	57.370
	1200	73.287	354.791	71.807
	1500	75.714	371.409	94.164
	2000	78.283	393.560	132.695
	2500	79.785	411.191	172.214
	3000	80.709	425.818	212.329

The standard enthalpy of formation, $\Delta_f H^o(298.15)$, of the free radical $^{\bullet}OH_3$ was measured to be $-4.2 \pm 21\,kJ\,mol^{-1}$. Numerous computational attempts, where so-called state-of-the-art methods were applied, vary in the range from 17 kJ mol^{-1} to 35 kJ mol^{-1} (Table 1). Most of them are far outside the large experimental interval of uncertainty. Recent successful calculations are no longer single-point jobs but are compound jobs with a manifold of possibilities to adjust the computational results of selected properties to experimental values for a key set of proper systems. For example, G3MP2B3 and CCSD(T)-CBS (W1U) methods have common key sets of radicals with MAD of standard enthalpies of formation as mentioned above. The coupled-cluster-based method yields for O_3 a value of $\Delta_f H^o(298.15) = 154.0\,kJ\,mol^{-1}$, compared with the recently evaluated experimental value of 142.7 [31]. This experimental value can be traced back to 1910 [23,32]. Ozone has a singlet diradical ground state and deserves a special treatment. MR-ACPF-CBS calculations have been performed side by side for both O_3 and $^{\bullet}O_3H$ to eventually consider multiconfiguration effects. Molecular structures and vibrational frequencies are taken from the afore mentioned CCSD(T)-CBS (W1U) calculations as well as core correlation contributions, and SO correction of the oxygen atom is taken from the literature [23]. SCF energies and valence correlation components to the enthalpies of atomization have been extrapolated as mentioned above. In contrast to the coupled-cluster calculations, for MR-ACPF-CBS there is an additional extrapolation, the extension of the reference space (CAS) which yields an increase of the valence correlation energy of $8.1\,kJ\,mol^{-1}$ and $21.5\,kJ\,mol^{-1}$ for O_3 and $^{\bullet}O_3H$, respectively. The analysis of the components of the atomization enthalpies is presented in detail in Table 4. It is interesting to note that for O_3 the SCF enthalpy of atomization yields a negative value of $-176.5\,kJ\,mol^{-1}$ that must be overcome by the valence correlation energy. The importance of multireference ACPF calculations can also be seen in the CI vectors. For O_3 and $^{\bullet}O_3H$ the vectors are 0.866, −0.270 and 10 components between −0.07 and −0.05, and 0.889, −0.178 and 6 components between 0.09 and −0.05, respectively. The final results, the enthalpies of formation $\Delta_f H^o(298.15)$, are summarized in Table 5. The MR-ACPF-CBS calculated enthalpy of formation for *trans*-$^{\bullet}O_3H$ of $21.2\,kJ\,mol^{-1}$ is in the lower range compared with previous calculations presented in Table 1. With this value the dissociation energy $D^o(298.15)$ of the process $^{\bullet}O_3H \rightarrow O_2 + {}^{\bullet}OH$ results to be $16\,kJ\,mol^{-1}$.

Thermodynamic functions, heat capacity $C_p^o(T)$, entropy $S^o(T)$ and thermal energy content $H^o(T) - H^o(0)$ of *cis*-$^{\bullet}O_3H$ and *trans*-$^{\bullet}O_3H$ are presented for the temperature range 100 – 3000 K in Table 6. Together with the corresponding data for the reactants and products in Eq. 1 [23], these values allow third law studies of equilibrium constants.

4 Conclusion

We used three different computational methods, G3MP2B3, CCSD(T)-CBS (W1U), and MR-ACPF-CBS, to calculate the much disputed enthalpy of formation of $^{\bullet}O_3H$; the corresponding values are 31.1, 32.9, and $21.2\,kJ\,mol^{-1}$, respectively. The latter value is close to the upper limit of the confidence interval of the experiment, $-4.2 \pm 21\,kJ\,mol^{-1}$. In view of this situation, further experimental as well as computational studies are recommended (see note added in proof in the Abstract). In addition, the calculation of anharmonic vibrational frequencies for $^{\bullet}O_3H$ yielded good agreement with Ar matrix experiments and facilitates the assignment of individual vibrational modes. This study can be seen as an expanded confirmation and characterization of the free $^{\bullet}O_3H$ radical as a stable intermediate in the title reaction.

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