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**The Role of the Recombination Channel in the Reaction between
the HO and HO₂ Radicals**

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Abstract

The kinetics of the gas phase recombination reaction $\text{HO} + \text{HO}_2 + \text{He} \rightarrow \text{HOOOH} + \text{He}$ has been studied between 200 and 600 K by using the SACM/CT model and the unimolecular rate theory. The molecular properties of HOOOH were derived at the CCSD(T)/aug-cc-pVTZ ab initio level of theory, while relevant potential energy features of the reaction were calculated at the CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ level. The resulting high and low pressure limit rate coefficients are $k_\infty = 3.55 \times 10^{-12} (\text{T}/300)^{0.20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_0 = [\text{He}] 1.55 \times 10^{-31} (\text{T}/300)^{-3.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate coefficients calculated over the $6 \times 10^{-4} - 400$ bar range are smaller at least in a factor of about 60 than the consensus value determined for the main reaction channel $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$, indicating that the recombination pathway is irrelevant.

1. Introduction

The reaction $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ plays a relevant role in atmospheric chemistry. It is a dominant reaction pathway in the removal of the HO and HO₂ radicals, both of which catalytically depletes ozone in the upper atmosphere.¹⁻³ This is also an important process in combustion chemistry. It is a major consumption process of HO₂ in lean combustion and responsible for the depletion of both radicals in burnt gases.^{4,5} In earlier investigations, the recombination reaction via a complex mechanism involving the formation of HOOOH as an intermediate has been proposed.^{1,6,7} In this way, two alternative channels were suggested,^{1,7}





Here, M denotes a third-body bath gas and HOOOH the simplest trioxide species for which the synthesis, structural and spectroscopic characterization, and reactivity have been extensively studied and recently reviewed.⁷⁻¹⁰ Channel (1a) might occur via an energized hydrogen-bonded complex HO–HOO on a triplet potential energy surface, or via the formation of the HOOOH intermediate on a singlet potential energy surface.

Experimental studies of this system suggest pressure dependences between 1 and 1000 Torr, that are not clearly outside the experimental uncertainty, and that only may be explained including reaction (1b) in the overall mechanism. The hydrogen-bonded complex is too weakly bonded to generate any important pressure dependence. Due to the interest in this subject, rate coefficients for the present system have been measured by different techniques.^{1,5,11} A combination of vacuum UV resonance fluorescence and laser-induced fluorescence (LIF) in a discharge-flow apparatus has been employed to determine the reaction temperature dependence.¹ The rate coefficients have been also measured using a discharge flow reactor and detection by laser magnetic resonance and resonance fluorescence in pseudo first order conditions.¹¹ The reverse reaction was studied in shock heated H₂O/O₂/Ar mixtures between 1600 and 2200 K employing laser absorption of HO at 306.7 nm and H₂O at 2.5 μm.⁵ An extensive report of measured rate coefficients for reaction (1) can be found in Refs. 4 and 12.

Theoretical studies of the temperature and pressure dependencies of $k_{1\text{b}}$ are available. Room temperature falloff curves derived from RRKM calculations based on a totally loose transition state (Gorin model)¹³ or using the variational transition state theory with a dipole-dipole potential¹⁴ have been reported. In the last study, it was concluded that the reaction involving HOOOH as an intermediate plays a minor role, except at very high temperatures and/or

pressures. In fact, the calculations predict that above 5000 Torr the recombination reaction (1b) could compete with the dominant reaction channel (1a). However, the long range potential employed in these studies probably overestimates the attractive forces between the HO and HO₂ radicals, thus avoiding the region of the potential energy surface where anisotropic effects associated to the transitional modes are operative. As a consequence, the high pressure region of the falloff curves was overestimated. Hence, considerable controversy of the pressure effects on the rate coefficients of this reaction still remain. However, nowadays it is possible to characterize the potential energy surfaces using accurate ab initio models. Therefore, to establish the importance of reaction $\text{HO} + \text{HO}_2 + \text{He} \rightarrow \text{HOOOH} + \text{He}$ on the global process, a quantum-chemical and kinetic study of this recombination reaction was carried out.

2. Computational details

The high correlated coupled cluster singles and doubles excitations approach, including a perturbational estimate of the triples, CCSD(T), was used to fully optimize the molecular structure of the most stable conformation of HOOOH and derive its harmonic vibrational frequencies.¹⁵ The aug-cc-pVTZ Dunning correlation basis set was selected for these calculations.¹⁶

To employ in the kinetic studies of the $\text{HO} + \text{HO}_2 \rightarrow \text{HOOOH}$ reaction, electronic potential curves along the minimum energy pathways (MEP) were computed with the G3(MP2)B3^{17,18}, G4(MP2)¹⁹ and G4²⁰ ab initio composite models. In the first two models, the B3LYP/6-311++G(3df,3pd) functional was used to obtain molecular structures and harmonic vibrational frequencies, whereas in the G4 model the B3LYP/6-31G(2df,p) level was employed. Transitional frequencies along the reaction coordinate were also calculated with the B2PLYP double-hybrid density functional method²¹ combined with the 6-

311++G(3df,3pd) basis set. In addition, CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ calculations were employed to derive the potential curves. All calculations were performed with the Gaussian 09 package.²²

Well-established kinetic models of the unimolecular reaction rate theory were used for modeling the HO + HO₂ association reaction. The limiting low pressure rate coefficients k_0 were derived using the strong collision low pressure rate coefficients, k_0^{SC} , estimated with a factorized model.^{23,24} The high pressure rate coefficients, k_∞ , were calculated with the statistical adiabatic channel model/classical trajectory (SACM/CT) formulation developed for linear rotor + linear rotor type of reactions.²⁵⁻²⁷ In addition, the simplified SACM version of Refs. 28 and 29 was also employed. For the estimation of the pressure dependence of the rate coefficients in the intermediate falloff range, a recently formulated reduced falloff curves method was used.^{30,31} In all these calculations, theoretical molecular information provided by the quantum-chemical calculations was employed.

3. Results and Discussion

3.1. Molecular structures and harmonic vibrational frequencies

Experimental and theoretical data of the molecular properties of HOOOH have greatly increased in the last years.³²⁻³⁸ In 2002, Engdahl and Nelander reported a matrix isolation study of HOOOH and presented an infrared spectroscopic identification of this trioxide.³² However, the first detection in the gas phase was published in 2005 when Endo and coworkers determined its pure rotational spectra and molecular structure.³³ The geometrical structure of HOOOH has been the subject of different experimental and theoretical studies and now it is well known.³³⁻³⁸ The CCSD(T)/aug-cc-pVTZ equilibrium structure here calculated is shown in Figure 1. This corresponds to the most stable *trans*- isomer of HOOOH with a zigzag skew-chain and the calculated parameters agree very well with those

experimentally determined using Fourier transform microwave (FTMW) spectroscopy and FTMW-millimeter-wave double resonance and triple resonance spectroscopy techniques.³³ In fact, a comparison between calculated and experimental bond lengths and bond angles leads to mean absolute deviations (MAD) of 0.007 Å and 0.3°, respectively. The short O–O bond lengths, 1.435 Å, are similar to those recently predicted for some fluorinated trioxides³⁹ and suggest a relatively large stability. Another important structural characteristic of trioxides is the ROOO dihedral angle. In the case of HOOOH (C_2 symmetry) both dihedral angles are equal to 81.2°. The found values for the O–O bond lengths and dihedral angles have been mainly attributed to dipole and the hyperconjugation effects.^{40,41}

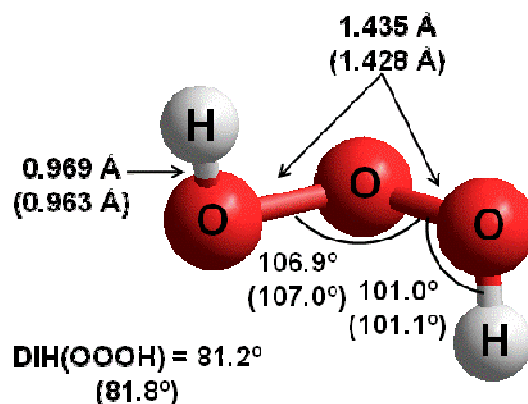


Figure 1. Molecular structure of *trans*-HOOOH derived from CCSD(T)/aug-cc-pVTZ calculations. Experimental values are given in brackets.³³

The HOOOH harmonic vibrational frequencies (unscaled) computed at the CCSD(T)/aug-cc-pVTZ level are listed in Table 1. In addition, approximate mode assignments obtained from the animation of the normal modes are included in this table. The calculated frequencies for HOOOH are in very good agreement with those obtained in an argon matrix.³² In fact, a relatively small MAD value of 69 cm⁻¹ was derived from these data.

Table 1. Harmonic Vibrational Frequencies (in cm^{-1}) and Approximate Assignments of HOOOH Calculated at the CCSD(T)/aug-cc-pVTZ Level.

approximated assignments	experimental	calculated ^a
asymmetric HO stretching	3529.6	3731
symmetric HO stretching	3529.6	3728
HOO bending	1359.1	1391
HOO bending	1347.4	1382
symmetric OO stretching	821.0	896
asymmetric OO stretching	776.3	798
OOO bending	509.1	521
HOO torsion	387.0	417
HOO torsion	346.4	361

^a Reference 32.

3.2. Energetics and potential energy curves for $\text{HO} + \text{HO}_2 \rightarrow \text{HOOOH}$

As above mentioned, several experimental and theoretical studies have dealt with the kinetics of the reaction between HO and HO₂ radicals.^{1,11,13,14,42} The slight pressure dependence observed for this process has been explained via the formation of the HOOOH. However, the transition state leading to the formation of H₂O + ¹O₂ in reaction (1a) is located 44.1 kcal mol⁻¹ above of HOOOH (or 13.6 kcal mol⁻¹ above of the HO + HO₂ radicals) at the CCSD(T)/aug-cc-pVTZ//CCSD/aug-cc-pVDZ level of theory for a singlet potential energy surface. Therefore, except at very high temperatures and in concordance with the investigations of Kaiser and coworkers,^{14,42} the HO and HO₂ radicals recombine forming HOOOH. The above discussion is schematized in Figure 2. It is important to note that the experimental value for the enthalpy of the reaction $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + {}^1\text{O}_2$ is -47.1 kcal mol⁻¹ at 0 K, underestimated at the CCSD(T)/aug-cc-pVTZ//CCSD/aug-cc-pVDZ level, mainly due to

errors in the calculations of the excited species $^1\text{O}_2$. This result is improved to $-42.3 \text{ kcal mol}^{-1}$ at the G4 level. However the analysis of this last reaction is beyond the scope of our work.

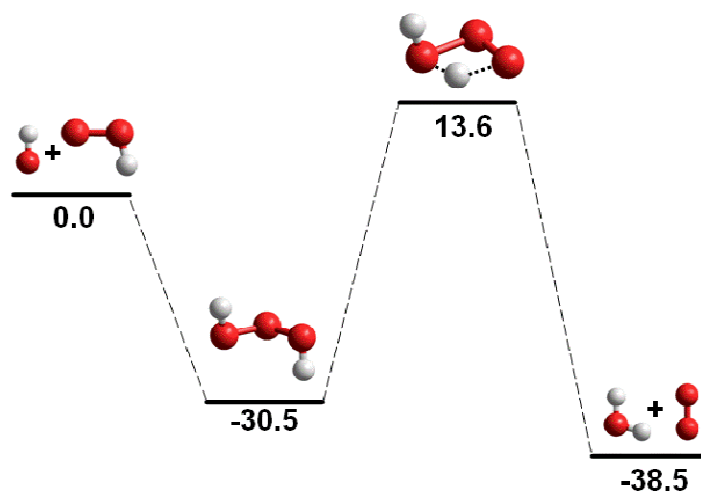


Figure 2. Schematic diagram (in kcal mol^{-1}) for a singlet potential energy surface of the $\text{HO} + \text{HO}_2$ reaction calculated at the $\text{CCSD(T)/aug-cc-pVTZ//CCSD/aug-cc-pVDZ}$ level of theory.

According to $\text{CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ}$ calculations, a bond dissociation energy of $D_e = \Delta_0 H^0 + \Delta E_{\text{ZPE}} = 35.5 \text{ kcal mol}^{-1}$ is predicted for the $\text{HOOOH} \rightarrow \text{HO} + \text{HO}_2$ reaction. The calculated $\Delta_0 H^0$ values of $30.5 \text{ kcal mol}^{-1}$ ($\text{CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ}$) and $30.7 \text{ kcal mol}^{-1}$ ($\text{CCSD(T)/aug-cc-pVTZ}$) agree satisfactorily with the derived from recommended enthalpies of formation at 0 K, $31.89 \text{ kcal mol}^{-1}$,² and with the MP4/6-31G(d,p) value of $29.09 \text{ kcal mol}^{-1}$,¹⁴ but differ significantly from the value of $21.9 \text{ kcal mol}^{-1}$ computed at the CI/ANO level.^{14,43}

Potential energy curves for $\text{HO} + \text{HO}_2 \rightarrow \text{HOOOH}$ along the minimum energy path (MEP) were obtained at different levels of theory. For each O–O bond distance a full optimization of the other HOOOH geometrical parameters was allowed. The resulting normalized curves, V/D_e , at the $\text{G3(MP2)//B3LYP/6-311+G(3df,3pd)}$, $\text{G4(MP2)//B3LYP/6-311+G(3df,3pd)}$, G4 ,

and CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ levels are depicted in Figure 3. The employed D_e values have been derived from the total energies of the HO, HO₂ and HOOOH species. To our knowledge, these are the first potential energy calculations for HOOOH. As can be seen, all selected methods predict long range and smooth potential curves, but not so large as those resulting from dipole-dipole interactions (see below).^{13,14,44} As Table 2 shows, the derived normalized potentials can be well fitted with a Morse function, $V/D_e = [1 - \exp(-\beta(r - r_e))]^2$, with β parameters ranging between 2.75 and 3.05 Å⁻¹.

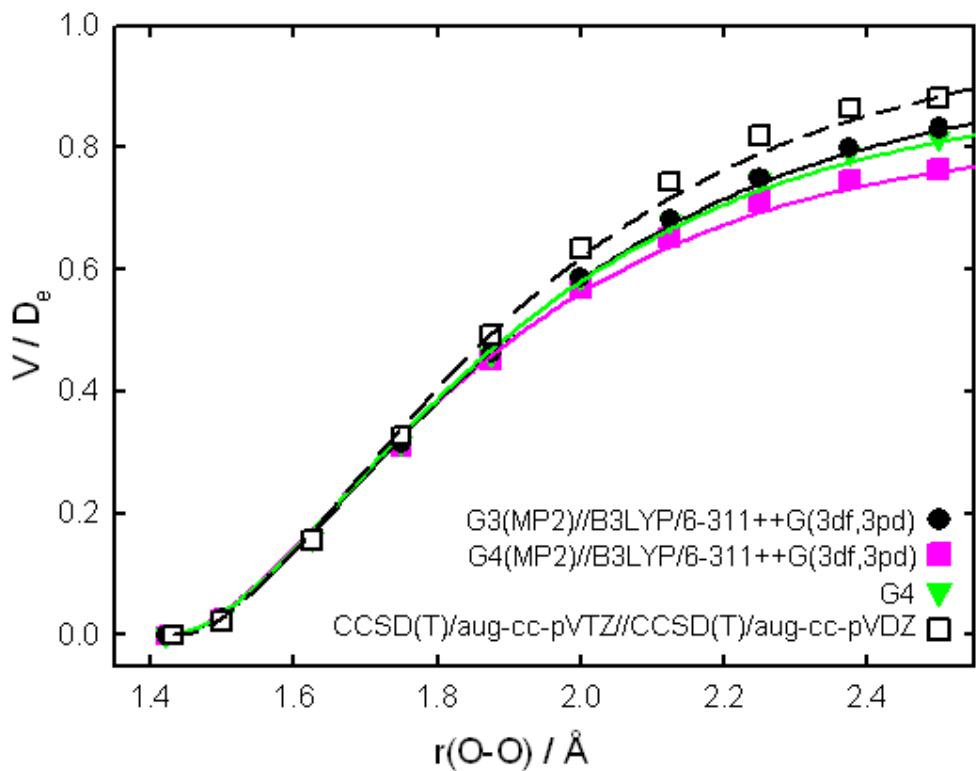


Figure 3. Normalized radial potential curves calculated along the MEP for HO + HO₂ → HOOOH. For the fits see the text.

Table 2. Bond Dissociation Energies (in kcal mol⁻¹) and Morse Parameters β (in Å⁻¹) Derived from the Fits of Figure 3.

level of theory	D_e	β
G3(MP2)//B3LYP/6-311++G(3df,3pd)	35.1	2.75
G4(MP2)//B3LYP/6-311++G(3df,3pd)	35.4	3.05
G4	36.0	2.79
CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ	35.5	2.80

To perform the kinetic study of k_∞ , besides of the above isotropic potential, the anisotropic part of the potential surface arising from the contribution of the degrees of freedom orthogonal to the reaction coordinate must be characterized. These transitional modes change from pure vibrational modes, at the HOOOH equilibrium bond distance, to totally free rotations of the HO and HO₂ radicals at large O–O interfragment distances. Quantum-chemical calculations show that only the four lowest vibrational frequencies exhibit a pronounced decay as the HO–OOH bond distances increase. The values of the transitional frequencies for reaction (1b) along the MEP are listed in Table 3. They can be well described by the expression $\nu_r \approx \nu_e \exp [-\alpha (r - r_e)]$, where α is the so-called anisotropy parameter.⁴⁵ The respective CCSD(T)/aug-CC-pVDZ values are $\alpha_1=1.45$, $\alpha_2=1.24$, $\alpha_3=1.13$, $\alpha_4=0.858 \text{ \AA}^{-1}$. The resulting average value of $1.17 \pm 0.25 \text{ \AA}^{-1}$ is similar to the derived from the analysis of a large number of experimental recombination reactions, $1.09 \pm 0.30 \text{ \AA}^{-1}$,²⁹ with a simplified SACM model.²⁸ For a comparison, similar calculations performed at the B3LYP/6-311++G(3df,3pd) and B2PLYP/6-311++G(3df,3pd) levels (see Table 3) lead to α values of 1.45, 1.16, 0.83, 0.332 \AA^{-1} and 1.56, 1.04, 0.97, 0.451 \AA^{-1} , respectively. The resulting average values of 0.943 \AA^{-1} and 1.01 \AA^{-1} are also reasonable for this type of recombination reactions.

Table 3. Calculated Transitional Frequencies (in cm^{-1}) for Reaction $\text{HO} + \text{HO}_2 \rightarrow \text{HOOOH}$ as a Function of the O–O Bond Length (in \AA).

r(O-O)	v ₁ (torsion)			v ₂ (torsion)			v ₃ (OOO bending)			v ₄ (OOO asymmetric stretching)		
	a	b	c	a	b	c	a	b	c	a	b	c
r _e	364	375	372	423	431	431	507	535	536	734	804	806
1.500	347	340	337	424	446	442	491	512	510	652	674	663
1.625	284	280	272	337	381	347	456	490	478	515	556	548
1.750	-	-	-	256	267	259	412	447	436	526	574	573
1.875	-	-	-	226	226	230	359	400	386	534	588	590
2.000	-	-	-	200	202	210	306	355	338	516	584	582
2.125	-	-	-	182	181	194	257	315	294	479	567	555
2.250	-	-	-	167	160	180	212	279	255	417	541	514
2.375	-	-	-	143	150	163	175	249	221	331	510	462
2.500	-	-	-	106	138	146	170	222	191	216	478	402

a: CCSD(T)/aug-CC-pVDZ (r_e = 1.451 Å). b: B3LYP/6-311++G(3df,3pd) (r_e = 1.422 Å).
c: B2PLYP/6-311++G(3df,3pd) (r_e = 1.423 Å).

3.3. High pressure rate coefficients for HO + HO₂ → HOOOH

The high pressure rate coefficients for the recombination reaction HO + HO₂ → HOOOH were calculated using the SACM/CT approach,²⁵⁻²⁷ employing the potential energy surface properties described in Sections 3.1 and 3.2. The HO₂ radical was treated as a quasi-linear species, forming with the HO a nonlinear adduct with an angle θ between the rotor axis and the molecular axis connecting the center of mass of the fragments.

The procedure to estimate SACM/CT high pressure rate coefficients has been described previously.^{46,47} It has been demonstrated that the high pressure rate coefficients can be factorized as²⁹

$$k_{\infty} = f_{\text{rigid}} k_{\infty}^{\text{PST}} \tag{2}$$

Here k_{∞}^{PST} is the phase space theory rate coefficient which is computed with the isotropic part of the potential, and f_{rigid} is a rigidity factor that accounts for dynamical constraints due to the anisotropy of the electronic potential.

k_{∞}^{PST} can be calculated as

$$k_{\infty}^{\text{PST}} = f_e f_{\text{sym}} (8\pi kT/\mu)^{1/2} (31.153 - 18.158 X + 0.8685 X^2)/\beta^2 \quad (3)$$

where $X = \ln(kT/D_e) - \beta r_{\text{CM}} + 4$.²⁶ For the present reaction, the collisional reduced mass $\mu = 11.22 \text{ g mol}^{-1}$, the electronic degeneracy factor at 298 K $f_e = Q_{\text{elHOOH}}/Q_{\text{elHO}} Q_{\text{elHO2}} = 0.166$ (where a spin-orbit splitting of 139.7 cm^{-1} was considered for OH¹²), the stoichiometric coefficient $f_{\text{sym}} = 1$ and the distance between the centers of mass of the two combining radicals $r_{\text{CM}} = 1.87 \text{ \AA}$ were calculated.

An earlier expression to estimate k_{∞}^{PST} is given by

$$k_{\infty}^{\text{PST}} = f_e (kT/h) (h^2/2\pi\mu kT)^{3/2} Q_{\text{cent}} \quad (4)$$

where Q_{cent} is the centrifugal pseudopartition function.²⁸

On the other hand, f_{rigid} is given by²⁶

$$f_{\text{rigid}} \approx [1 - 2.3 C_{\text{eff}} (\beta r_{\text{CM}})^{1/2} \exp((X - 4)/2.044)] (1 + 0.75 Z + Z^4)^{-1/4} \quad (5)$$

with²⁷

$$Z = (d C_{\text{eff}})^n \quad (6)$$

$$C_{\text{eff}} = \{1 + 0.4[2\alpha/\beta - 1] + [2\alpha/\beta - 1]^2\} \{[2\varepsilon_s^2 \varepsilon_a^2 \varepsilon_t^2 / [B_1 B_2 (B_1 + B_2)]]^{1/3} / 2D_e \{kT/D_e\}^{2\alpha/\beta - 1}\} \quad (7)$$

$$n = 1 - 0.5 \sin^2 \theta + \sin^4 \theta \quad (8)$$

$$\begin{aligned} d = & 1.757 - 1.337 \sin^2 \theta - 0.393/\sin^2 \theta + [(\varepsilon_a/\varepsilon_t)(\varepsilon_s/\varepsilon_t)]^{2/3} (1.444 - 0.509 \sin^2 \theta - 0.07730/\sin^2 \theta) \\ & + (\varepsilon_a/\varepsilon_t)^2 \cos^2 \theta (0.357 - 0.557 \sin^2 \theta + 0.247/\sin^2 \theta) + (\varepsilon_s/\varepsilon_t)^2 \cos^2 \theta (-1.932 + 0.385 \sin^2 \theta + \\ & 1.529/\sin^2 \theta) \end{aligned} \quad (9)$$

In the above equations, $\theta = 87.1^\circ$; $\varepsilon_s = 521$, $\varepsilon_a = 798$ and $\varepsilon_t = 361 \text{ cm}^{-1}$ are the adduct vibrational frequencies for the symmetrical and asymmetrical deformation modes and for the torsional motion, $B_1 = 18.772 \text{ cm}^{-1}$ is the HO rotational constant, and $B_2 = 1.084 \text{ cm}^{-1}$ is the average of the smallest HO₂ rotational constants, all calculated at the CCSD(T)/aug-cc-pVTZ level of theory.

Additionally, using the simplified SACM version of Refs. 28 and 29, f_{rigid} can be calculated by

$$f_{\text{rigid}} = (F_{\text{AM}}/\sigma) \frac{\prod_{m=1}^5 Q_m \prod_{j=1}^4 Q_j}{Q_{\text{rotHO}} Q_{\text{rotHO}_2} Q_{\text{vibHO}} Q_{\text{vibHO}_2}} e^{-\Delta E_{0z}/kT} \approx (F_{\text{AM}}/\sigma) \frac{\prod_{m=1}^5 Q_m}{Q_{\text{rotHO}} Q_{\text{rotHO}_2}} e^{-\Delta E_{0z}/kT} \quad (10)$$

Here, F_{AM} is an angular momentum coupling correction factor, σ is an effective symmetry number, Q_m and Q_j are the pseudopartition functions corresponding to the transitional modes and the conserved oscillators, respectively, Q_{rot} and Q_{vib} are the rotational and vibrational partition functions of HO and HO₂ radicals and, ΔE_{0z} is the adiabatic zero point barrier for the lowest reaction channel. The calculation of the abovementioned factors was performed from the molecular data listed in Tables 1 and 4. The scheme that correlates the highest rotational constant of HOOOH with the lowest rotational constant of HO₂, and the vibrational frequencies corresponding to the transitional modes with the rest of the rotational constants of HO and HO₂ radicals is the following (in cm^{-1}): $1.694 \leftrightarrow 1.055$ ($m=1$), $361 \leftrightarrow 1.112$ ($m=2$), $416 \leftrightarrow 18.773$ ($m=3$), $521 \leftrightarrow 18.773$ ($m=4$), $798 \leftrightarrow 20.505$ ($m=5$). The effective rotational constant was calculated with the expression $B_{\text{eff}}(r) = [B(r) + C(r)]/2 = 0.3299 / [1 + 0.430 (r - r_e) + 0.484 (r - r_e)^2]$, with $r_e = 1.451 \text{ \AA}$, resulting from the CCSD(T)/aug-cc-pVDZ geometries along the MEP.

For both kinetics models, the CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ curve fitted with the parameters $\beta = 2.80 \text{ \AA}^{-1}$ and $D_e = 35.5 \text{ kcal mol}^{-1}$ was employed. The looseness

parameter $\alpha = 1.17 \text{ \AA}^{-1}$ derived at the CCSD(T)/aug-cc-pVDZ level, was used in the f_{rigid} calculations.

Table 4. Calculated Harmonic Vibrational Frequencies and Rotational Constants (both in cm^{-1}) for HOOH, HO and HO₂ at the CCSD(T)/aug-cc-pVTZ Level.

species	frequencies	rotational constants
HOOH	3731, 3728, 1391, 1382, 896, 798, 521, 417, 361	0.313, 0.357, 1.694
HO	3719	18.773
HO ₂	3646, 1428, 1125	1.055, 1.112, 20.505

With the more recent SACM approach given by equations (3) and (5), values of $k_{\infty}^{\text{PST}} = 7.62 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $f_{\text{rigid}} = 0.046$ were obtained at 298 K. As a consequence, according to expression (2), the SACM/CT value of $3.53 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived for k_{∞} . This value becomes about 2.7 times smaller for $\alpha = 0.943 \text{ \AA}^{-1}$ (B3LYP/6-311++G(3df,3pd)), and decreases by about a factor of 2 if $\alpha = 1.01 \text{ \AA}^{-1}$ (B2PLYP/6-311++G(3df,3pd)) is used. On the other hand, from the expressions (4) and (10), $k_{\infty}^{\text{PST}} = 8.68 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $f_{\text{rigid}} = 0.036$ were derived, leading to the SACM value $k_{\infty} = 3.09 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Therefore, the simplified SACM and the SACM/CT results differ by only 12%.

The high pressure rate coefficients calculated between 200 and 600 K using the simplified SACM and the SACM/CT approaches are summarized in Table 5 and can be expressed by

$$k_{\infty} = 3.55 \times 10^{-12} (T/300)^{0.20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{SACM/CT}) \quad (11)$$

$$k_{\infty} = 3.05 \times 10^{-12} (T/300)^{0.18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{Simplified SACM}) \quad (12)$$

Table 5. Calculated High Pressure Rate Coefficients k_{∞}^{PST} and k_{∞} (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and Rigidity Factors for $\text{HO} + \text{HO}_2 \rightarrow \text{HOOOH}$. (T in K).

T	k_{∞}^{PST} [Eq. (3)]	k_{∞}^{PST} [Eq. (4)]	f_{rigid} [Eq. (5)]	f_{rigid} [Eq. (10)]	$k_{\infty}(\text{SACM/CT})$	$k_{\infty}(\text{simplified SACM})$
200	7.40×10^{-11}	8.56×10^{-11}	0.0446	0.0321	3.30×10^{-12}	2.75×10^{-12}
250	7.51×10^{-11}	8.60×10^{-11}	0.0456	0.0343	3.42×10^{-12}	2.95×10^{-12}
298	7.62×10^{-11}	8.67×10^{-11}	0.0463	0.0356	3.53×10^{-12}	3.09×10^{-12}
350	7.75×10^{-11}	8.75×10^{-11}	0.0470	0.0366	3.64×10^{-12}	3.20×10^{-12}
400	7.87×10^{-11}	8.84×10^{-11}	0.0475	0.0371	3.74×10^{-12}	3.28×10^{-12}
450	7.99×10^{-11}	8.94×10^{-11}	0.0480	0.0373	3.84×10^{-12}	3.33×10^{-12}
500	8.11×10^{-11}	9.04×10^{-11}	0.0483	0.0372	3.92×10^{-12}	3.36×10^{-12}
550	8.23×10^{-11}	9.13×10^{-11}	0.0487	0.0369	4.01×10^{-12}	3.37×10^{-12}
600	8.34×10^{-11}	9.23×10^{-11}	0.0489	0.0351	4.08×10^{-12}	3.37×10^{-12}

That is, both SACM theories lead to comparable results. By contrast, the room temperature SACM/CT rate coefficient is 13 - 29 times smaller than theoretical values reported twenty five years ago. In fact, values of $4.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (vibrational/rotational adiabatic capture rate theory),¹⁴ $9.75 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (modified Langevin collision capture model)⁴⁸ and $1.02 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (canonical variational transition state theory, CVTST)¹⁴ have been predicted for k_{∞} . For all these cases the long range of the potential was approached by a dipole-dipole interaction potential,

$$V = -(\mu_1 \mu_2 / r^3) [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2)] \tag{13}$$

Here μ_i are the dipole moments of the reactants (1.67 D for HO ⁴⁹ and 2.09 D for HO_2 ⁵⁰), while θ_i and ϕ_i are the spherical polar angles describing the orientation of r_i with respect to the body-fixed axes, for radical i .¹⁴ Figure 4 shows the high energy region of the Morse potential based on the CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ calculations and the dipole-

dipole potential for angular contribution values of 1.0 and 0.81. The last one has been derived from the present calculations along the MEP.

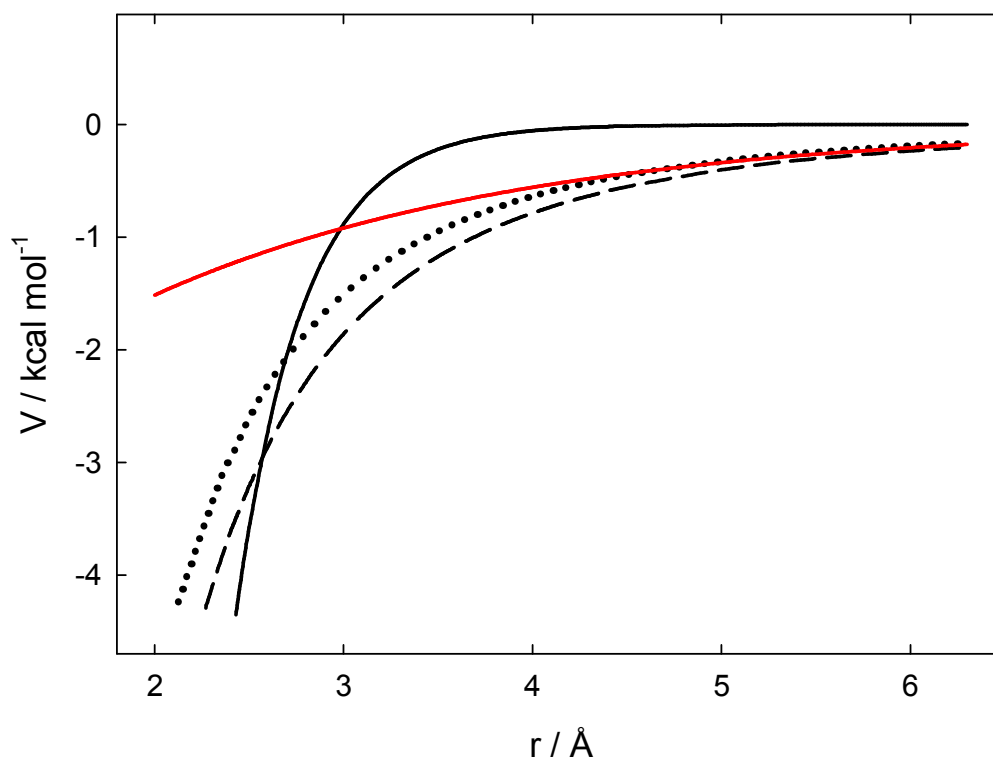


Figure 4. Morse and dipole-dipole potentials for $\text{HO} + \text{HO}_2 \rightarrow \text{HOOOH}$. Black solid line: Calculated with a Morse parameter of $\beta = 2.80 \text{ \AA}^{-1}$. Black dotted line: Calculated with an angular contribution of 1.0 in Equation (13). Black dashed line: Calculated with an angular contribution of 0.81 as obtained from CCSD(T)/aug-cc-pVDZ calculations along the MEP. Red solid line: Fit of the dipole-dipole potential at large elongations with a Morse function with $\beta_{\text{d-d}} = 0.5 \text{ \AA}^{-1}$.

It can be seen that the dipole-dipole potential leads to a pronounced attractive interaction between the reagents. To compare the rate data predicted by both potentials, k_{∞}^{PST} calculations were performed at 298 K. For this, the higher part of the dipole-dipole potential

was fitted with a Morse function using the very low value $\beta_{d-d} = 0.5 \text{ \AA}^{-1}$ (see Figure 4). The simple Equation (3) predicts a value of $7.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ when this parameter is employed. This k_{∞}^{PST} is one order of magnitude larger (see Table 5) than the value derived using the ab initio potential. However, despite the inherent differences between the vibrational/rotational adiabatic capture rate theory and the SACM/CT, similar $f_{\text{rigid}} = k_{\infty}/k_{\infty}^{\text{PST}}$ values of 0.06 and 0.05 were respectively obtained. However, a f_{rigid} nearly a factor of two larger results from modified Langevin collision capture and CVTST calculations.¹⁴ These results indicate that the pronounced rate coefficient discrepancies between earlier and the present calculations are mostly attributed to the unrealistically large dipole-dipole potential employed in Ref. 14.

3.4. Low pressure rate coefficients for $\text{HO} + \text{HO}_2 + \text{He} \rightarrow \text{HOOOH} + \text{He}$

To investigate the pressure dependence of present reaction, the limiting low pressure rate coefficients, k_0 , and the relevant falloff curves are required. k_0 was calculated using Troe's factorized formalism.^{23,24} In this approach, the recombination low pressure rate coefficient is represented by the product $k_0 = \beta_c k_0^{\text{SC}}$, where the collision efficiency β_c depends on intermolecular energy transfer properties and the strong-collision rate coefficient k_0^{SC} is characterized by the equilibrium populations of molecular states. The different terms contributing to k_0^{SC} are explicitly accounted for by²³

$$k_0^{\text{SC}} = (1/K_C) [M] Z_{\text{LJ}} (\rho_{\text{vib,h}}(E_0) k T / Q_{\text{vib}}) \exp(-E_0 / k T) F_{\text{anh}} F_E F_{\text{rot}} F_{\text{rotint}} \quad (14)$$

Here, $K_C = [\text{HO}][\text{HO}_2]/[\text{HOOOH}]$ is the equilibrium constant estimated from the molecular partition functions and the threshold energy $E_0 \approx \Delta_0 H^0 = 30.7 \text{ kcal mol}^{-1}$, Z_{LJ} is the collision frequency between the energized HOOOH adduct and the bath gas $M = \text{He}$, $\rho_{\text{vib,h}}(E_0)$ is the

HOOOH harmonic vibrational density of states at E_0 , Q_{vib} is the HOOOH vibrational partition function, and the F factors are corrections for different effects. F_{anh} takes into consideration the anharmonicity, F_E accounts for the energy dependence of $\rho_{\text{vib,h}}(E_0)$, F_{rot} describes the external rotations contribution, and finally F_{rotint} takes into account the internal rotors behavior. The evaluation of these factors was performed using the molecular data listed in Tables 1 and 4. In particular, the $8.84 \times 10^2 \text{ (kcal mol}^{-1})^{-1}$ and 1.38 values were estimated for $\rho_{\text{vib,h}}(E_0)$ and F_{anh} , respectively. The potential energy curve computed at the CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ level was employed for the F_{rot} calculations (Figure 3). Barrier heights of $4.5 \text{ kcal mol}^{-1}$ and reduced moments of inertia of $0.87 \text{ amu } \text{\AA}^2$ were obtained for the HOO–OH internal rotations from CCSD(T)/aug-cc-pVTZ//CCSD/aug-cc-pVDZ calculations. Lennard-Jones collision parameters for HOOOH of, $\sigma = 3.8 \text{ \AA}$ and $\epsilon/k = 289.3 \text{ K}$, employed in the calculation of Z_{LJ} were derived considering additivity relationships for molar volumes and by molecular resemblance to HOOH,^{12,51} while values of 2.55 \AA and $\epsilon/k = 10 \text{ K}$ were used for He.⁵²

Table 6 summarizes estimated factors in equation (14) and the resulting K_C and k_0 values obtained between 200 and 600 K. The β_c values were derived from the expression $-\langle\Delta E\rangle \approx F_E kT \beta_c / (1 - \beta_c^{1/2})$,²³ assuming that the average energy transferred in up and down HOOOH-He collisions, $-\langle\Delta E\rangle \approx 75 \text{ cm}^{-1}$, does not change between 200 and 600 K.⁵²

Table 6. Contributing Factors to k_0 for Reaction $\text{HO} + \text{HO}_2 + \text{He} \rightarrow \text{HOOOH} + \text{He}$ (Z_{LJ} and k_0 in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, K_C in molecule cm^{-3} , and T in K).

T	Z_{LJ}	F_E	F_{rot}	F_{rotint}	Q_{vib}	β_c	K_C	$k_0/[\text{He}]$
200	3.41×10^{-10}	1.07	20.08	32.81	1.03	0.251	1.23×10^{-8}	5.95×10^{-31}
250	3.63×10^{-10}	1.09	15.74	25.41	1.07	0.213	9.33×10^{-2}	2.75×10^{-31}

298	3.82×10^{-10}	1.11	12.94	20.49	1.13	0.186	2.56×10^3	1.54×10^{-31}
350	4.01×10^{-10}	1.13	10.81	16.70	1.22	0.163	6.46×10^6	9.22×10^{-32}
400	4.17×10^{-10}	1.16	9.28	14.00	1.32	0.145	1.76×10^9	6.07×10^{-32}
450	4.32×10^{-10}	1.18	8.11	11.94	1.45	0.131	1.35×10^{11}	4.25×10^{-32}
500	4.47×10^{-10}	1.20	7.18	10.33	1.61	0.118	4.24×10^{12}	3.06×10^{-32}
550	4.60×10^{-10}	1.23	6.42	9.04	1.79	0.108	6.99×10^{13}	2.30×10^{-32}
600	4.73×10^{-10}	1.25	5.80	8.00	2.00	0.099	7.11×10^{14}	1.76×10^{-32}

The results obtained between 200 and 600 K can be represented by

$$k_0 = [\text{He}] 1.55 \times 10^{-31} (T/300)^{-3.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{15}$$

3.5. Rate coefficients for HO + HO₂ + He → HOOOH + He in the falloff range

The kinetic behavior of the HO + HO₂ + He → HOOOH + He reaction in the intermediate region between the low and the high pressure limits, the falloff range, was theoretically investigated. To this end, we employed the Troe's reduced method,^{30,31} in which the rate coefficients are estimated using the following relationship

$$k \approx k_\infty [x / (1 + x)] F(x) \tag{16},$$

where F(x) are suitable broadening factors and $x = k_0/k_\infty$. These factors account for corrections to the Lindemann-Hinshelwood expression (indicated between brackets in equation (16)) due to the energy and total angular momentum dependencies of the energized adducts and the multistep character of the collisional energy transfer. These broadening factors are given by³¹

$$F(x) = [1 + x] / [1 + x^n]^{1/n} \tag{17}$$

Here $n = [\ln 2 / \ln(2/F_{\text{cent}})] [0.8 + 0.2 x^q]$, $q = (F_{\text{cent}} - 1) / \ln(F_{\text{cent}}/10)$, and the center broadening factor is given by $F_{\text{cent}} = F(x=1)$. For low temperatures applications, a constant value of $F_{\text{cent}} = 0.6$ is usually employed.² However, for a more reliable analysis, F_{cent} can be estimated from the weak, $\log F_{\text{cent}}^{\text{WC}} = 0.14 \log \beta_c$, and strong collision, $F_{\text{cent}}^{\text{SC}}$, contributions: $F_{\text{cent}} = F_{\text{cent}}^{\text{WC}} F_{\text{cent}}^{\text{SC}}$. The strong collision broadening factor is given by $-\log F_{\text{cent}}^{\text{SC}} = (1.06 \log S_T)^{2.2} / (1 + C_1 S_T^{C_2})$, with $C_1 = 0.10 \exp(2.5 B_T^{-1} - 0.22 B_T - 6 \times 10^{-10} B_T^6)$ and $C_2 = 1.9 + 4.6 \times 10^{-5} B_T^{2.8}$.³⁰ The Kassel parameters S_T and B_T were calculated employing the harmonic vibrational frequencies listed in Table 1 and $\Delta_0 H^0 = 30.7 \text{ kcal mol}^{-1}$. To estimate the $F_{\text{cent}}^{\text{WC}}$ factors, β_c values from Table 6 were employed. The F_{cent} values obtained decrease from 0.67 to 0.42 when the temperature increases from 200 to 600 K.

The resulting falloff curves are shown in Figure 5. The two straight lines, drawn for simplicity only for 300 K, allow to visualize the center of the falloff curves, $[\text{He}]_c = k_\infty/k_0[\text{He}]$. It is observed that at room temperature and atmospheric pressure ($\sim 2.5 \times 10^{19} \text{ molecule cm}^{-3}$ or $\sim 1.013 \text{ bar}$) the reaction is close to the high pressure limit. In addition, for a given total pressure, the predicted k decreases as the temperature increases. For comparison, RRKM falloff curves derived by Gonzalez et al. at 300 K are included in Figure 5.¹⁴ As can be seen, these estimations obtained from molecular information provided by MP4/6-31G(d,p) and CI/ANO energetics, give different pressure dependencies. At about one atmosphere of He, the CI/ANO based and our falloff curve are close. Below $\sim 10^{17} \text{ molecule cm}^{-3}$, the present results lie between those obtained in Ref. 14 based on MP4/6-31G(d,p) and CI/ANO quantum-chemical data. Above one atmosphere, the long range dipole-dipole potential employed in the k_∞ estimations of Ref. 14 is the principal reason of the observed differences.

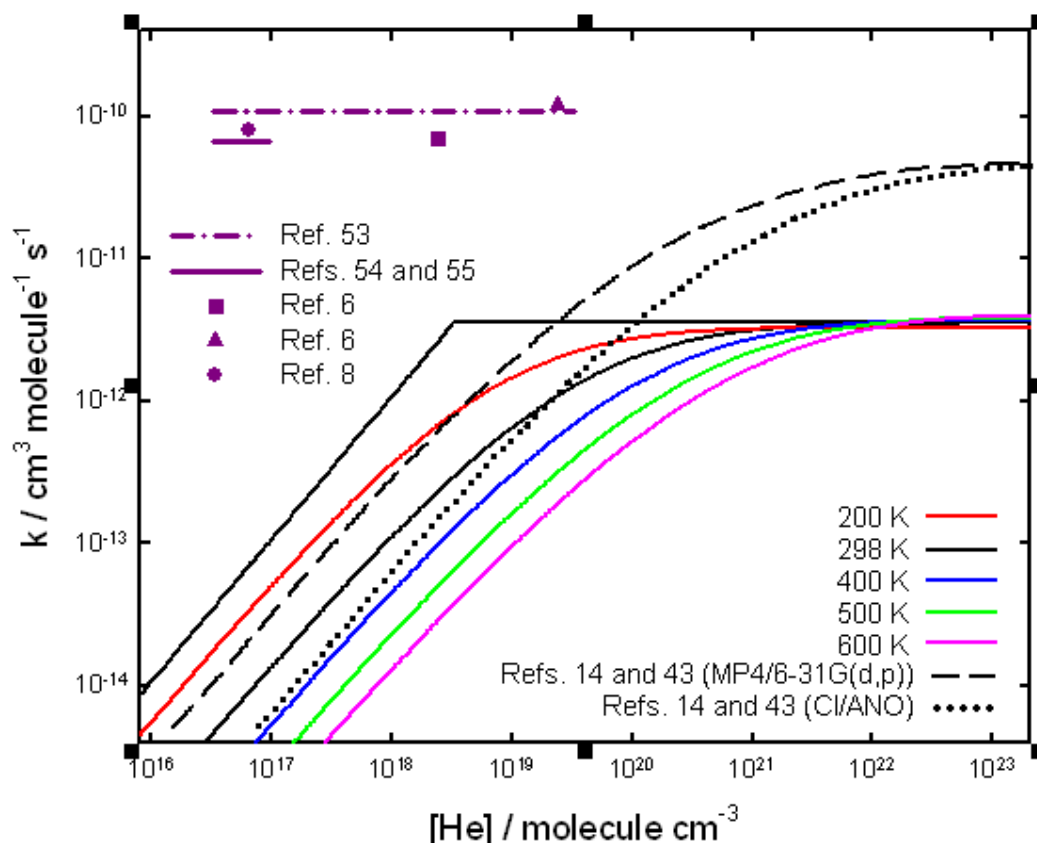


Figure 5. Falloff curves for $\text{HO} + \text{HO}_2 + \text{He} \rightarrow \text{HOOOH} + \text{He}$. Violet: Rate coefficient data for $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ at 298 K.

Finally, representative data for the reaction (1a), $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$, are also shown in Figure 5. These values are quite consistent with the consensus value of $k_{1a} = 4.8 \times 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.²⁻⁴ A comparison of these values with present k_{1b} results clearly indicates that the association process is irrelevant in all experimental conditions. By contrast, it has been suggested that above 5000 Torr ($\sim 1.6 \times 10^{20} \text{ molecule cm}^{-3}$) reaction (1b) could compete with reaction (1a).¹⁴ Therefore, the small pressure dependence observed for the $\text{HO} + \text{HO}_2$ global reaction from $k \sim (5 - 8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (at 1 – 75 Torr of Refs. 6, 11,

54, and 55) to $k \sim (1 - 2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (at about 1 atmosphere^{6,53}), may be probably attributed, as Keyser *et al.* suggested,⁵⁶ to secondary reactions arising from the presence of small concentrations of H and O atoms in the low pressure discharge-flow investigations.

4. Conclusions

The kinetics of the recombination reaction $\text{HO} + \text{HO}_2 + \text{He} \rightarrow \text{HOOOH} + \text{He}$ has been theoretically studied on the singlet potential energy surface. SACM/CT and unimolecular rate theory calculations on CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ electronic potential allow to estimate the rate coefficient over a wide range of pressures and temperatures. The derived high and low pressure rate coefficients between 200 and 600 K are given by $k_\infty = 3.55 \times 10^{-12} (T/300)^{0.20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_0 = [\text{He}] 1.55 \times 10^{-31} (T/300)^{-3.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The present rate coefficients are much smaller than those measured for the $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ reaction, indicating that the association pathway studied here does not play any role in any experimental condition.

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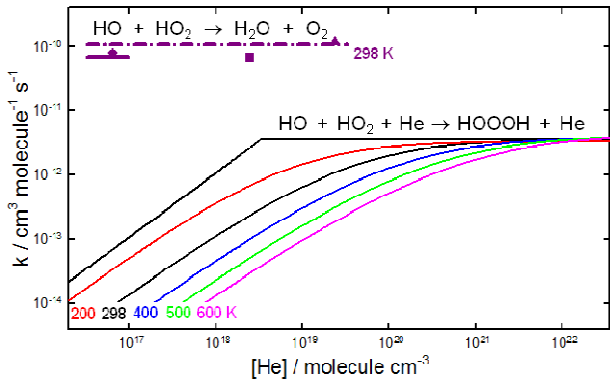
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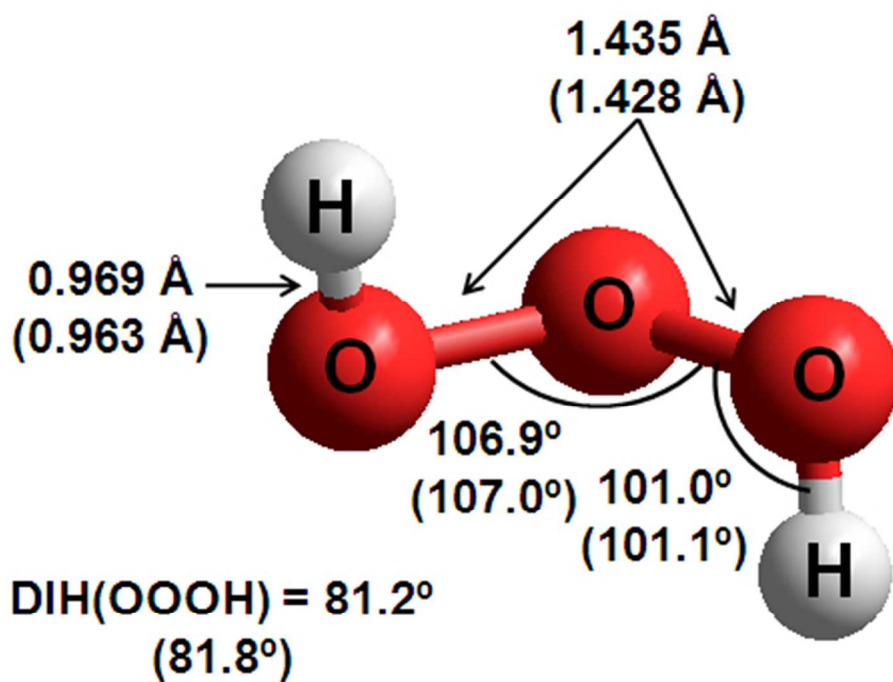
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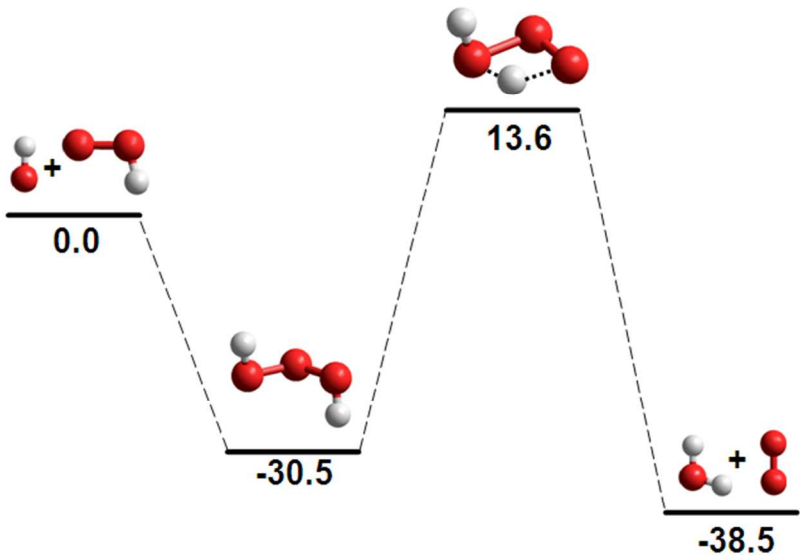
TOC Graphic





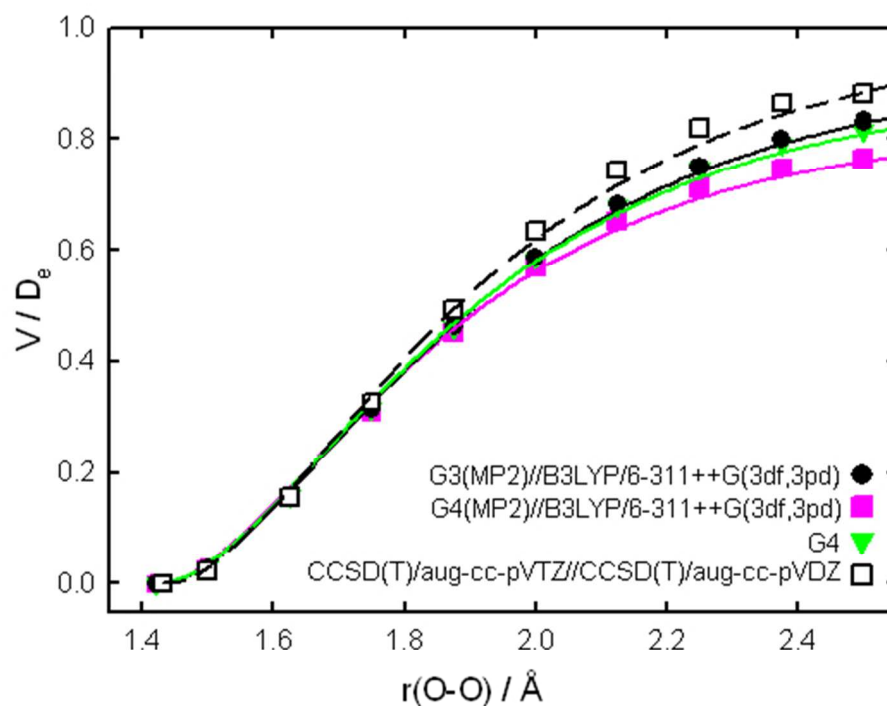
Molecular structure of trans-HOOOH derived from CCSD(T)/aug-cc-pVTZ calculations. Experimental values are given in brackets.³³

Figure 1
129x95mm (96 x 96 DPI)



Schematic diagram (in kcal mol⁻¹) for a singlet potential energy surface of the HO + HO₂ reaction calculated at the CCSD(T)/aug-cc-pVTZ//CCSD/aug-cc-pVDZ level of theory.

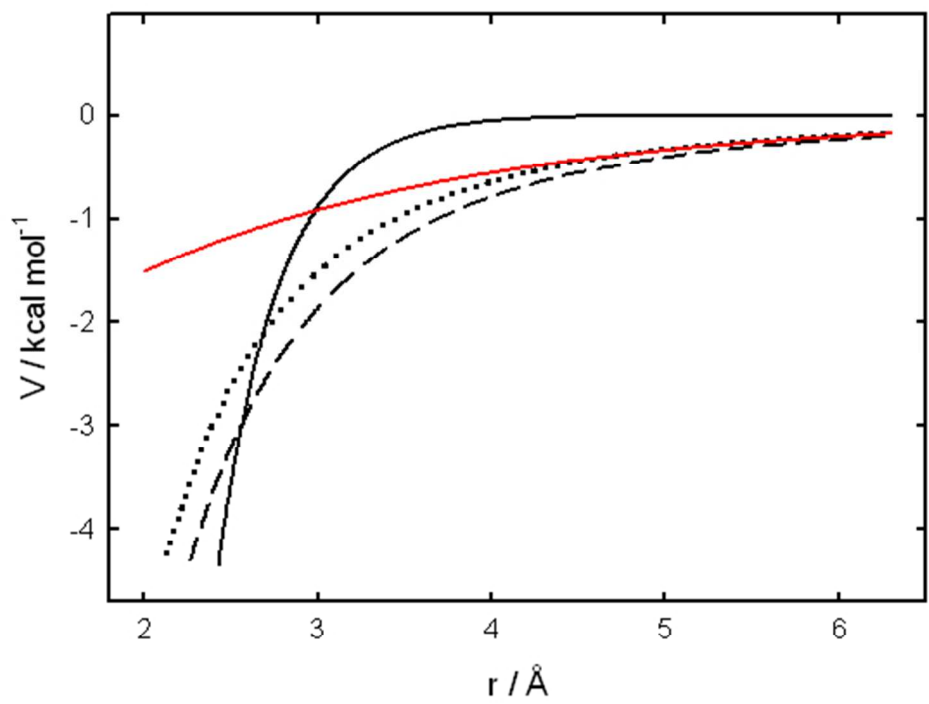
Figure 2
210x129mm (96 x 96 DPI)



Normalized radial potential curves calculated along the MEP for $\text{HO} + \text{HO}_2 \rightarrow \text{HOOOH}$. For the fits see the text.

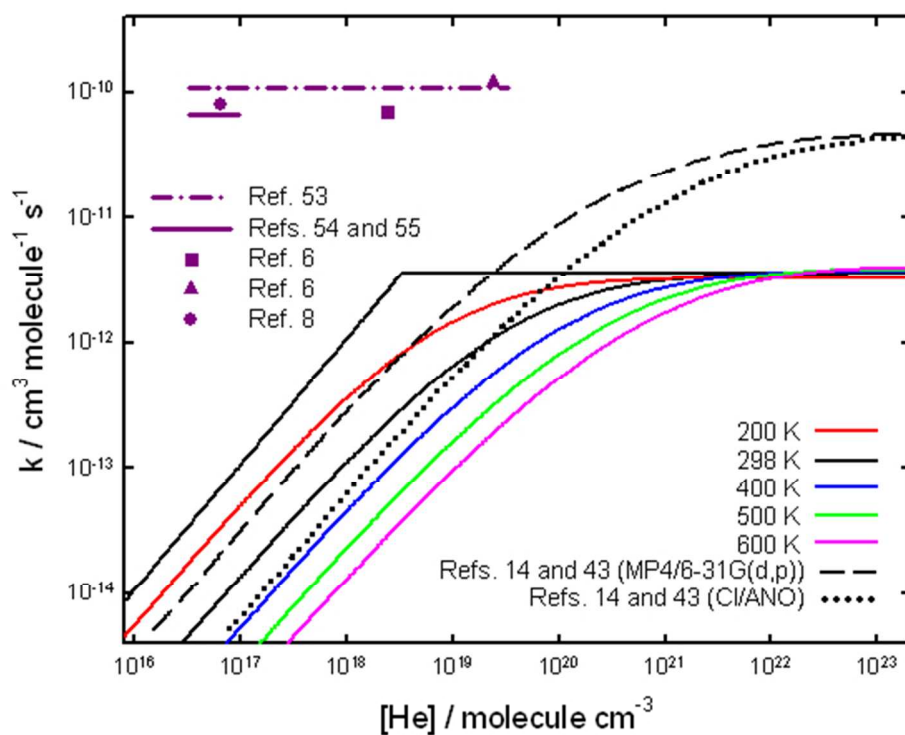
Figure 3

153x118mm (96 x 96 DPI)



Morse and dipole-dipole potentials for $\text{HO} + \text{HO}_2 \rightarrow \text{HOOOH}$. Black solid line: Calculated with a Morse parameter of $\beta = 2.80 \text{ \AA}^{-1}$. Black dotted line: Calculated with an angular contribution of 1.0 in Equation (13). Black dashed line: Calculated with an angular contribution of 0.81 as obtained from CCSD(T)/aug-cc-pVDZ calculations along the MEP. Red solid line: Fit of the dipole-dipole potential at large elongations with a Morse function with $\beta_{\text{d-d}} = 0.5 \text{ \AA}^{-1}$.

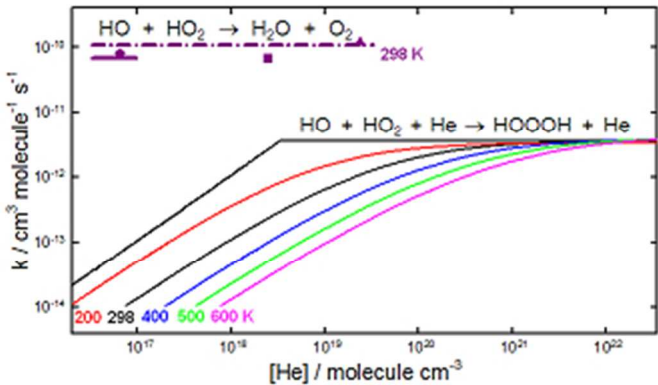
Figure 4
153x115mm (96 x 96 DPI)



Falloff curves for $\text{HO} + \text{HO}_2 + \text{He} \rightarrow \text{HOOH} + \text{He}$. Violet: Rate coefficient data for $\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ at 298 K.

Figure 5

159x130mm (96 x 96 DPI)



TOC Graphic
88x51mm (96 x 96 DPI)