A reinvestigation of the kinetics and the mechanism of the $CH_3C(O)O_2$ + HO_2 reaction using both experimental and theoretical approaches

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Received 3rd January 2005, Accepted 13th March 2006 First published as an Advance Article on the web 28th March 2006 DOI: 10.1039/b518321a

The kinetics and the mechanism of the reaction $CH_3C(O)O_2 + HO_2$ were reinvestigated at room temperature using two complementary approaches: one experimental, using flash photolysis/UV absorption technique and one theoretical, with quantum chemistry calculations performed using the density functional theory (DFT) method with the three-parameter hybrid functional B3LYP associated with the 6-31G(d,p) basis set. According to a recent paper reported by Hasson *et al.*, [J. Phys. Chem., 2004, 108, 5979–5989] this reaction may proceed by three different channels: $CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2$ (1a); $CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3$ (1b); $CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)O + OH + O_2$ (1c). In experiments, $CH_3C(O)O_2$ and HO_2 radicals were generated using Cl-initiated oxidation of acetaldehyde and methanol, respectively, in the presence of oxygen. The addition of amounts of benzene in the system, forming hydroxycyclohexadienyl radicals in the presence of OH, allowed us to answer that channel (1c) is <10%. The rate constant k_1 of reaction (1) has been finally measured at (1.50 \pm 0.08) \times 10⁻¹¹ cm^3 molecule⁻¹ s⁻¹ at 298 K, after having considered the combination of all the possible values for the branching ratios k_{1a}/k_1 , k_{1b}/k_1 , k_{1c}/k_1 and has been compared to previous measurements. The branching ratio k_{1b}/k_1 , determined by measuring ozone *in situ*, was found to be equal to (20 ± 1) %, a value consistent with the previous values reported in the literature. DFT calculations show that channel (1c) is also of minor importance: it was deduced unambiguously that the formation of CH₃C(O)OOH + O₂ (X ${}^{3}\Sigma_{e}$) is the dominant product channel, followed by the second channel (1b) leading to $CH_3C(O)OH$ and singlet O_3 and, much less importantly, channel (1c) which corresponds to OH formation. These conclusions give a reliable explanation of the experimental observations of this work. In conclusion, the present study demonstrates that the $CH_3C(O)O_2 + HO_2$ is still predominantly a radical chain termination reaction in the tropospheric ozone chain formation processes.

1 Introduction

Aldehydes (RCHO) are important trace constituents of the atmosphere. They have both natural and anthropogenic sources, with small primary sources associated with vehicle exhaust and industrial activity and large secondary sources associated with the oxidation of volatile organic compounds.^{2,3} Abstraction of the aldehydic H-atom by OH radicals gives acyl radicals, RC(O), which combine with O_2 to give acylperoxy radicals, RC(O)O2. Acylperoxy radicals play several important roles in atmospheric chemistry. $RC(O)O_2$ radicals react rapidly with NO to give NO₂ which is then photolyzed leading to ozone formation. RC(O)O2 radicals react with NO₂ to form stable peroxyacylnitrates, $RC(O)O_2$. NO₂, which are severe irritant compounds in photochemical smog, and may be efficient reservoirs of NO_x in the troposphere, as they may transport NO_x far from its sources.⁴ In air masses with low $[NO_x]$, acylperoxy radicals undergo reactions with HO_2 and in a lesser extent with other peroxy radicals. Reactions of RC(O)O2 with HO2 radicals are important radical chain termination reactions and are a source of ozone and carboxylic acids in the atmosphere.

Among all aldehydes, acetaldehyde has been one of the most studied as it is present in the atmosphere in large concentrations (from 1.5×10^{10} molecule cm⁻³ in rural areas^{5,6} up to 4×10^{11} molecule cm⁻³ in urban or industrial areas^{7,8}). Several studies on the reactivity of the acetylperoxy radical have been performed for the past years,^{1,9–12} using different techniques, and up to recently, the kinetics and the mechanisms of the CH₃C(O)O₂ reactions were considered as well-established.¹³ In contrast, the kinetics and the mechanism of the reaction of CH₃C(O)O₂ with HO₂ radicals are still a matter of controversy, as the four principal investigations on the rate constant of this reaction or on its different reaction channels all differ on many different points.^{1,9,11,12}

For instance, Hasson *et al.*¹ recently suggested that the mechanism of the reaction of $CH_3C(O)O_2$ with HO_2 radicals proceeds neither *via* the only two channels (1a) and (1b) but *via* the three following channels:

 $CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2$ (1a)

 $CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3$ (1b)

 $CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)O + OH + O_2 \quad (1c)$

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This observation was important as the existence of the third channel (1c), already demonstrated in fluorinated-peroxy radical reactions with HO_2 ,¹⁴ was proposed for the first time for this type of peroxy radicals. According to the authors,¹ this channel, leading to the formation of OH and CH₃C(O)O radicals, may reach up to 40% of reaction (1). This result means that this reaction would not be considered any more as a full radical chain termination reaction in the tropospheric ozone chain formation processes, according to the following reactions:

$$OH + CH_3CHO \rightarrow CH_3C(O) + H_2O$$
 (2)

$$CH_3C(O) + O_2 + M \rightarrow CH_3C(O)O_2 + M$$
(3)

$$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2$$
(4)

$$CH_3C(O)O + M \rightarrow CH_3 + CO_2 + M$$
 (5)

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{6}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$
 (7)

$$NO_2 + h\nu \rightarrow NO + O(^{3}P)$$
 (8)

 $O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$ (9)

$$O_3 + NO \rightarrow O_2 + NO_2 \tag{10}$$

As acetaldehyde is often used as the model for the reactivity of aldehydes in chemical modeling of atmospheric chemistry, it is important to consider if channel (1c) is existing and to confirm or not the branching ratio k_{1c}/k_1 measured by Hasson *et al.*¹

We report here the results of a reinvestigation of the kinetics and the mechanism of the $CH_3C(O)O_2 + HO_2$ reaction, using both experimental and theoretical approaches. Experiments were performed at room temperature and atmospheric pressure, using flash photolysis technique coupled to UV absorption spectrometry. In addition, some new numerical simulations of the older experiments performed by Tomas et al.¹² in our group on the same $CH_3C(O)O_2 + HO_2$ reaction also allow us to investigate the mechanism proposed by Hasson *et al.*¹ and to propose a new value for the rate constant k_1 . In order to detect any presence of OH radicals in our system, formed according to channel (1c), an original method was developed: it consists in adding amounts of benzene in the initial gas mixture. The choice of benzene is fully justified as it does not initially react with chlorine atoms $(k(Cl + C_6H_6) = 1.3 \times$ 10^{-16} cm³ molecule⁻¹ s⁻¹ at 298 k_1^{5} and may form hydroxycyclohexadienyl C₆H₆OH radicals in the presence of OH:

$$C_6H_6 + OH + M \rightarrow C_6H_6OH + M$$
(11)

Hydroxycyclohexadienyl radical formation has been followed at 290 nm, a free UV spectral window where peroxy radicals almost do not absorb.

The quantum chemistry calculations were performed using the density functional theory (DFT) method with the threeparameter hybrid functional $B3LYP^{16}$ associated with the polarized double-zeta 6-31G(d,p) basis set.

2 Experimental section and computational details

The experimental system used is described in detail elsewhere¹⁷ and is dealt with briefly here.

2.1 Flash photolysis experiments

A conventional flash photolysis UV absorption spectrometer was used to monitor peroxy radical absorptions at room temperature and atmospheric pressure. The reaction cell consists of a 70 cm long, 4 cm diameter Pyrex cylinder. A continuous flow of a reactant gas mixture was irradiated periodically by two argon flash lamps. The flash lamp energy is approximately 250 J. The half-life for the light pulse is 5 μ s, although problems with scattered light prevent data collection for approximately 50-100 µs after the flash. The analyzing beam was obtained from a deuterium lamp, passed through the cell, dispersed using a monochromator (2 nm resolution), detected by a photomultiplier, and transferred to a PC for averaging and analysis. About 30-40 absorption time profiles were acquired to reach a satisfactory signal to noise ratio. The total gas flow was adjusted so that the cell was replenished completely between flashes thereby avoiding photolysis of reaction products. Decay traces were simulated by numerical integration of a set of differential equations representative of an appropriate chemical mechanism, selected parameters (rate constant, absorption cross section, and initial radical concentration) were adjusted to give the best nonlinear least squares fit.

Radicals were generated by photolysis of Cl_2 at wavelengths longer than the Pyrex cut-off, using $Cl_2/CH_3CHO/CH_3OH/O_2/N_2$ mixtures:

$$Cl_2 + h\nu (\lambda > 280 \text{ nm}) \rightarrow 2 \text{ Cl}$$
 (12)

$$Cl + CH_3OH \rightarrow HCl + CH_2OH$$
 (13)

 $k_{13} = 5.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}^{18}$

$$Cl + CH_3CHO \rightarrow HCl + CH_3C(O)$$
 (14)

 $k_{14} = 7.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}^{18}$

For acetaldehyde, it has been shown that reaction (14) occurs predominantly (>95%) *via* abstraction of the aldehydic hydrogen.^{19,20}

The concentration of Cl₂ was monitored using its wellknown absorption at 330 nm ($\sigma = 2.55 \times 10^{-19}$ cm² molecule⁻¹).²¹ Liquid reactants, CH₃CHO and CH₃OH, were introduced into the reaction cell using bubblers, by passing a fraction of the diluent flow through the liquid maintained at constant temperature (273 K).

Acetylperoxy and hydroperoxy radicals were formed by adding an excess of oxygen to ensure rapid and stoichiometric conversion of radicals formed by reactions (13) and (14) into peroxy radicals:

$$CH_3C(O) + O_2 + M \rightarrow CH_3C(O)O_2 + M$$
(3)

 $k_3 = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}^{18}$

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O$$
(15)

$$k_{15} = 9.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}^{18}$$

Typical concentration ranges used were: $[Cl_2] = 2-4 \times 10^{16}$ molecules cm⁻³ (Messer, 5% in N₂, purity >99.9%), $[CH_3CHO] = 0.3-0.6 \times 10^{16}$ molecules cm⁻³ (Aldrich, 99.5+%), $[CH_3OH] = 0.2-1.6 \times 10^{16}$ molecules cm⁻³ (Aldrich, 99.8+%), $[O_2] = 2.3 \times 10^{19}$ molecules cm⁻³ (Messer, 99.995%), $[N_2] = 1 \times 10^{18}$ molecules cm⁻³ (Messer, 99.999%).

The total initial concentration of Cl atoms, and therefore of peroxy radicals, was determined by (i) replacing acetaldehyde and methanol under the same experimental conditions by methane, producing CH₃O₂ radicals alone (the UV absorption cross sections of CH₃O₂ being well-known),¹³ (ii) keeping only acetaldehyde (or methanol), producing only CH₃C(O)O₂ (or HO₂) radicals, their cross sections being also well-known.¹³ Under these experimental conditions, initial radical concentrations were varied between 4 and 8×10^{13} molecule cm⁻³. Considering that the rate constant ratio $k_{14}/k_{13} = (1.35 \pm 0.05)$ is well-established,¹⁸ initial concentrations of CH₃C(O)O₂ and HO₂ radicals can be anticipated controlling the concentration of precursors:

$$\frac{[CH_{3}C(O)O_{2}]}{[HO_{2}]} = \frac{k_{14}}{k_{13}} \times \frac{[CH_{3}CHO]}{[CH_{3}OH]}$$
(I)

During experiments, this ratio has been varied from 1.5 to 0.375. Particular attention was given to the amount of acetaldehyde used during experiments, to minimize the potential perturbations due to the equilibrium (16), demonstrated by our group in a previous work:¹²

CH₃CHO + HO₂ + M
$$\Leftrightarrow$$
 CH₃CH(OH)O₂ + M
(16,-16)
 $K_2 = \frac{k_2}{k_{-2}} = 1.9 \times 10^{-27} \exp[+6925/T] \text{ cm}^3 \text{ molecule}^{-1}$

As described above, to accurately know the initial concentrations of CH₃C(O)O₂ and HO₂ radicals, it was first therefore necessary to know with a very good precision the concentration of radical precursors (CH₃CHO and CH₃OH). In this work, it was demonstrated for the lowest concentrations of acetaldehyde, that its gaseous concentration in the reaction cell (controlled by a mass flow controller) was differing by a factor of 1.7 (lower) compared to the expected value calculated from that of the nitrogen flow circulating in the acetaldehyde bubbler, by measuring its UV absorption at 280 nm (σ (CH₃CHO) = 4.6 × 10⁻²⁰ cm² molecule⁻¹).²² This information may be crucial when considering the initial radical concentration ratio in the simulations, and was attributed to the non-linearity of the mass flow controller when using very small flows.

In order to evaluate the proportion of OH radicals formed by channel (1c), some benzene was initially added in the gas mixture. The choice of benzene was justified as it does not initially react with chlorine atoms ($k(\text{Cl} + \text{C}_6\text{H}_6) = 1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K})^{15}$ and may form hydroxycyclohexadienyl C₆H₆OH radicals in the presence of OH:

$$C_6H_6 + OH + M \rightarrow C_6H_6OH + M$$
(11)

The concentration of benzene, introduced into the reaction cell by passing a fraction of the diluent flow through the liquid maintained at constant temperature (285 K), was maintained at 2×10^{18} molecule cm⁻³.

No UV absorbing products were generated when gas mixtures containing all reactants except Cl_2 were irradiated suggesting that the present work is free from complications associated with the formation of absorbing radical species from the photolysis of the aldehydes.

2.2 Computational details

The quantum chemistry calculations were performed using the GAUSSIAN03 computer program package.²³ Full geometry optimization and force field analysis (vibrational wavenumbers) were performed using the density functional theory (DFT) method with the three-parameter hybrid functional B3LYP¹⁶ associated with the polarized double-zeta 6-31G(d,p) basis set. All electronic structure calculations were carried out at the UHF level, with the constraint of destroying the $\alpha - \beta$ and spatial symmetries of the wavefunction in the case of overall closed shell systems separating into radical species. Structures associated with the stationary points of the lowest triplet and singlet (vide infra) potential energy surfaces (PES) were checked to correspond effectively to minima or saddle points through the analysis of the eigenvalues of the Hessian matrix. Minima are characterized by non negative eigenvalues and saddle points by the existence of only one negative eigenvalue. This negative eigenvalue is associated with an imaginary wavenumber in the normal mode analysis. Transition states of reactive processes are dividing surfaces in the phase space corresponding to a minimum of the reactive flux. In the configuration space, the transition states are considered to be located at the saddle point along the reaction paths. Minimum energy paths (MEP) determination is requested to connect the various minima between them through the appropriate saddle point. The choice of the DFT-B3LYP/ 6-31G(d,p) method has been retained since it looks a good compromise between accuracy and computer time. Moreover, this level of theory has proven so far to give reliable transition state energies.²⁴⁻²⁶

3 Results and discussion

In the first part, new numerical simulations of the former experiments performed by Tomas et al.¹² on the CH₃C(O)O₂ + HO₂ reaction, and simulations of the new experiments performed in this work using the same technique, were carried out using the new chemical mechanism (including the third channel (1c)) proposed by Hasson *et al.*,¹ to suggest a new value for the rate constant k_1 . In the second part, as experimental decays could not be well-simulated including channel (1c) in the simulation mechanism, the branching ratio k_{1c}/k_1 was investigated by adding amounts of benzene in the reaction system, to measure the potential formation of hydroxycyclohexadienyl radicals by addition of OH radicals on the benzene ring. In the third part, the branching ratio k_{1b}/k_1 was investigated by measuring the ozone formation and a final value of the rate constant k_1 , accounting for the complete mechanism, was proposed and compared to the previous recommended value.13 Finally, theoretical calculations were performed to give a reliable explanation for the experimental observations of this work.

3.1 Impact of the OH formation channel (1c) on the kinetics of the $CH_3C(O)O_2 + HO_2$ reaction

The necessity of investigating channel (1c) occurred when studying the global kinetics of reaction (1) as, in our system, this third channel leads to the formation of OH radicals which react with methanol and acetaldehyde to produce additional amounts of $CH_3C(O)O_2$ and HO_2 radicals, and leads to the formation of $CH_3C(O)O$ radicals which instantaneously decompose and react with O_2 to form CH_3O_2 radicals:

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2$$
(1a)

$$\rightarrow CH_3C(O)OH + O_3 \tag{1b}$$

$$\rightarrow CH_3C(O)O + OH + O_2$$
(1c)

$$CH_3C(O)O + M \rightarrow CH_3 + CO_2 + M$$
 (5)

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{6}$$

$$OH + CH_3CHO \rightarrow CH_3C(O) + H_2O$$
(2)

$$CH_3C(O) + O_2 + M \rightarrow CH_3C(O)O_2 + M$$
(3)

 $OH + CH_3OH \rightarrow CH_2OH + H_2O$ (17)

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O \tag{15}$$

As all the quoted peroxy radicals absorb in our analysis wavelength window, they may all change the shape of the experimental decays and thus change the extrapolated value of the rate constant k_1 .

First, reaction (1) has been studied simulating experimental traces recorded at 207 and 240 nm (see Fig. 1), with the mechanism presented in Table 1, taking into account the three channels (1a) (1b) and (1c) with the different branching ratios proposed by Hasson *et al.*¹ and using UV absorption cross-sections recommended by Tyndall *et al.*¹³ The rate constant k_1 was measured at 207 nm where both CH₃C(O)O₂ and HO₂ radicals absorb strongly, resulting in a decay well-adapted to the measurement of k_1 . Then, the mechanism was verified at 240 nm, where CH₃O₂ and O₃ absorb strongly. Ten determinations of k_1 were performed, resulting in the following rate constant at room temperature:

$$k_1 = (2.20 \pm 0.07) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Unfortunately, as can be seen in Fig. 1B and 1C, decay traces recorded at 240 nm could not be well-simulated with this new value of the rate constant k_1 , extracted from the simulation of the new mechanism of Hasson *et al.*¹ As a result, to propose a rate constant k_1 allowing the simulation of all experimental curves, and particularly those recorded at both 207 and 240 nm, it was first necessary to evaluate the proportion of OH radicals generated according to channel (1c).

3.2 Determination of the branching ratio k_{1c}/k_1

Channel (1c) was investigated by initially adding benzene in the gas mixture as it may fast form hydroxycyclohexadienyl radicals C_6H_6OH in the presence of OH radicals.

$$C_6H_6 + OH + M \rightarrow C_6H_6OH + M$$
(11)

Decay traces were recorded at 290 nm where C₆H₆OH radicals absorb strongly ($\sigma = 8.91 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$),²⁷ whereas absorbance of all other molecular species and peroxy radicals is weaker. Initial concentrations of both $CH_3C(O)O_2$ and HO_2 radicals were measured at 207, 240 and 290 nm before adding benzene. After adding benzene, the signal recorded at 290 nm is still very weak, as it is corresponding only to the different negative (Cl₂, CH₃CHO) and positive (CH₃C(O)O₂, CH₃O₂ and O₃) contributions to the total absorbance, leading finally to a poor signal-to-noise ratio (Fig. 2). Nevertheless, varying the value of the branching ratio $\gamma_1(OH) = k_{1c}/k_1$ (leading to the formation of OH radicals) from 0 to 0.40, let us demonstrate that 0.10 appears as an upper limit for $\gamma_1(OH)$ at room temperature and that it was impossible to correctly simulate experimental traces using $\gamma_1(OH) = 0.40$ with the mechanism presented Tables 1 and 2 (see Fig. 2).



Fig. 1 Decay traces recorded at 207 nm ([A]: 12.5 ms) and 240 nm ([B]: 12.5 ms and [C]: 500 ms) following the irradiation of Cl₂/ CH₃CHO/CH₃OH/O₂/N₂ gas mixtures at 298 K. Solid lines are results of simulations using the chemical mechanism detailed in Table 1 with γ_1 (OH) = 0.40 at $k_1 = 2.2 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

No.	Reactions	Rate constants ^{<i>a</i>}	Ref.
18	$2CH_3C(O)O_2 \rightarrow 2CH_3C(O)O + O_2$	$k_{18} = 1.4 \times 10^{-11}$	13
5	$CH_3C(O)O + M \rightarrow CH_3 + CO_2 + M$	Fast thermal decomposition	35
6	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	$k_6 = 1.8 \times 10^{-12}$	36
19a	$2CH_3O_2 \rightarrow 2CH_3O + O_2$	$k_{19} = 3.5 \times 10^{-13}$	13
19b	\rightarrow CH ₃ OH + CH ₂ O + O ₂	$k_{19a}/k_{19} = 0.37$	13
20	$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$k_{20} = 1.92 \times 10^{-15}$	36
21	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_{21} = 3 \times 10^{-12}$	18
22a	$CH_{3}C(O)O_{2} + CH_{3}O_{2} \rightarrow CH_{3}C(O)O + CH_{3}O + O_{2}$	$k_{22a}^{22} = 1.25 \times 10^{-11}$	13
22b	\rightarrow CH ₃ C(\tilde{O})OH + CH ₂ O + \tilde{O}_2	$k_{22b}/k_{22} = 0.90$	13
1a	$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2$	$k_{1a} = 1.50 \times 10^{-11}$	This work
1b	\rightarrow CH ₃ C(O)OH + O ₃	$k_{1b}/k_1 = 0.20$	This work
1c	\rightarrow CH ₃ C(O)O + OH + O ₂	$k_{1c}/k_1 < 0.10$	This work
23	$CH_{3}O_{2} + HO_{2} \rightarrow CH_{3}OOH + O_{2}$	$k_{23} = 5.2 \times 10^{-12}$	18
2	$CH_3CHO + OH \rightarrow CH_3CO + H_2O$	$k_2 = 1.49 \times 10^{-11}$	18
17	$CH_3OH + OH \rightarrow CH_2OH + H_2O$	$k_{17} = 9.4 \times 10^{-13}$	18
3	$CH_{3}CO + O_{2} + M \rightarrow CH_{3}C(O)O_{2} + M$	$k_3 = 5 \times 10^{-12}$	18
15	$CH_2OH + O_2 \rightarrow CH_2O + HO_2$	$k_{15} = 9.6 \times 10^{-12}$	18
^a Unity: in	cm^3 molecule ⁻¹ s ⁻¹ .		

Table 1 Mechanism used to simulate the flash photolysis of Cl₂/CH₃CHO/CH₃OH/N₂/O₂ mixtures at 298 K

3.3 Determination of the rate constant k_1 and the branching ratios for the reaction (1)

Considering the upper value of 0.10 for the branching ratio γ_1 (OH), experimental decays recorded at 207 and 240 nm without benzene were reconsidered for simulation. As ex-



Fig. 2 Decay traces recorded at 290 nm, following the irradiation of CH₃CHO/CH₃OH/C₆H₆/Cl₂/O₂/N₂ gas mixtures at 298 K. Solid lines are results of simulations using the chemical mechanism detailed in Tables 1 and 2, varying γ_1 (OH) from 0.40 to 0.

plained before, the rate constant k_1 was measured at 207 nm where both CH₃C(O)O₂ and HO₂ radicals absorb strongly whereas the branching ratio leading to the formation of O₃ $(\beta_1(O_3) = k_{1b}/k_1)$ was measured at 240 nm on a 500 ms time scale. Indeed, O₃ absorbs strongly at this wavelength (see Fig. 3) and at such a time scale, only small amounts of CH₃O₂ radical (generated by the decomposition of the CH₃C(O)O radical arising from the CH₃C(O)O₂ self-reaction, in the presence of oxygen) remain and are easily taken into account using the mechanism presented in Table 1. Ten determinations of k_1 and $\beta_1(O_3)$ were performed, resulting in the following rate constant and branching ratio values at room temperature:

$$k_1 = (1.50 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

 $\beta_1(O_3) = (0.20 \pm 0.01)$

The branching ratio $\gamma_1(OH)$ was finally measured at 240 nm fixing the new values of k_1 and $\beta_1(O_3)$ in the model. Ten determinations of $\gamma_1(OH)$ were performed, resulting in the following value at room temperature:

$$\gamma_1(OH) = (0.05 \pm 0.04)$$

This value of $\gamma_1(OH)$ was validated verifying that both values of the rate constant k_1 and of the branching ratio $\beta_1(O_3)$,

Table 2 Reactions added to the mechanism detailed in Table 1 to simulate experimental decays obtained following the photolysis of the $Cl_2/CH_3CHO/CH_3OH/C_6H_6/N_2/O_2$ mixtures at 298 K

No.	Reactions	Rate constants ^a	Ref.
11	$C_6H_6 + OH + M \rightarrow C_6H_6 - OH + M$	$k_{11} = 1.2 \times 10^{-12}$	37
24	$C_6H_6-OH + O_2 \rightarrow adduct$	$k_{24} = 1.3 \times 10^{-15}$	38
-24	Adduct $\rightarrow C_6H_6-OH + O_2$	$k_{-24}^{-2} = 5 \times 10^3$	38
25	$2C_6H_6-OH \rightarrow \text{products}$	$k_{25} = 2.8 \times 10^{-11}$	27
26	$C_6H_6-OH + OH \rightarrow \text{products}$	$k_{26}^{25} = 1-5 \times 10^{-10}$	27
27	$C_6H_6-OH + HO_2 \rightarrow products$	$k_{27}^{20} = 1 - 10 \times 10^{-11}$	27
28	$C_6H_6-OH + adduct \rightarrow products$	$k_{28}^{27} = 1 - 10 \times 10^{-11}$	27
29	$C_6H_6-OH + CH_3C(O)O_2 \rightarrow \text{products}$	$k_{29}^{20} = 1 - 10 \times 10^{-11}$	39
30	2 adduct \rightarrow products	$k_{30}^{20} = 1-2 \times 10^{-12}$	27
31	Adduct + $HO_2 \rightarrow products$	$k_{31}^{50} = 5-20 \times 10^{-12}$	27
32	$CH_3C(O)O_2 + adduct \rightarrow products$	$k_{32} = 5-20 \times 10^{-12}$	39
33	$CH_3O_2 + adduct \rightarrow products$	$k_{33}^2 = 1 - 2 \times 10^{-12}$	40
^{<i>a</i>} Unity: in cm ³ n	nolecule ⁻¹ s ⁻¹ excepted k_{-24} in s ⁻¹ .		



Fig. 3 Decay traces recorded at 207 nm ([A]: 12.5 ms) and 240 nm ([B]: 12.5 ms and [C]: 500 ms) following the irradiation of Cl₂/ CH₃CHO/CH₃OH/O₂/N₂ gas mixtures at 298 K. Solid lines are results of simulations using the chemical mechanism detailed in Table 1 with γ_1 (OH) = 0.05 and $k_1 = 1.50 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

measured, respectively, at 207 and 240 nm, do not significantly change maintaining the value of $\gamma_1(OH)$ at 0.05. This latter value is in good agreement with the previous evaluation of $\gamma_1(OH)$ carried out with benzene as scavenger of OH radicals, validating the upper limit measured for this branching ratio ($\gamma_1(OH) < 0.10$).

3.4 Accuracy of results

Several factors influence the accuracy of the results obtained in the flash photolysis experiments. The chemistry associated with peroxy radical reactions is very complicated (see Table 1). To quantify the sensitivity of the rate constant k_1 and the branching ratio leading to the formation of ozone of the CH₃C(O)O₂ + HO₂ reaction to the parameters used for analysis, a systematic analysis of the propagation of errors was performed as described previously.¹⁷

The main sources of systematic errors on the rate constant k_1 arise from the absorption cross sections of CH₃C(O)O₂ and HO₂, from the extrapolation of the fit to time zero and from the branching ratio $\gamma_1(OH)$ leading to the formation of OH. Uncertainties associated with $\sigma(CH_3C(O)O_2)$ and $\sigma(HO_2)$ are estimated to be 10% (more variation did not allow to correctly simulate experimental curves), resulting in approximately 13% uncertainty in the value of k_1 . Uncertainties associated with the extrapolation of the fit to time zero is essentially due to the self-reaction rate constant of the CH₃C(O)O₂ radical (fast initial decay). Uncertainties associated with this rate constant are estimated to be 30% resulting in approximately 9% of errors in the value of k_1 . Variations of the branching ratio γ_1 (OH) by a factor of 2 result in a variation of 5% in the value of k_1 . Combining the uncertainties described above, we estimate a global systematic uncertainty of 17% in the value of k_1 .

This analysis was also conducted for the branching ratio $\beta_1(O_3)$ leading to the formation of ozone. Uncertainties associated with $\sigma(CH_3C(O)O_2)$ and $\sigma(HO_2)$ are estimated to be 10%, resulting in approximately 8% of errors in the value of $\beta_1(O_3)$. Variations of 10% in the ozone absorption cross sections $\sigma(O_3)$ result in a variation of 10% in the value of $\beta_1(O_3)$. Variations of the branching ratio $\gamma_1(OH)$ by a factor of 2 result in a variation of 5% in the value of $\beta_1(O_3)$. Combining the uncertainties described above, we estimate a global systematic uncertainty of 14% in the value of $\beta_1(O_3)$.

3.5 Theoretical investigation of the branching ratios of the reaction (1)

The three possible reaction pathways recalled below have been investigated:

$$\begin{array}{l} {\rm CH_3C(O)O_2\,+\,HO_2\,\rightarrow\,CH_3C(O)OOH\,+\,O_2\,(X\ ^3\Sigma_g^-)\ (1a)} \\ {\rm CH_3C(O)O_2\,+\,HO_2\,\rightarrow\,CH_3C(O)OH\,+\,O_3\,(X\ ^1A_1)\ \ (1b)} \\ {\rm CH_3C(O)O_2\,+\,HO_2\,\rightarrow\,CH_3C(O)O\,+\,OH\,(X\ ^2\Pi)} \\ {\rm +\,O_2\,(X\ ^3\Sigma_g^-)\ \ \ (1c)} \end{array}$$

This reaction between the two radicals $CH_3C(O)O_2$ and HO_2 , involves singlet and triplet PES. Spin conservation entails that reaction (1a) evolves on the lowest triplet surface and reactions (1b) and (1c) on the lowest singlet surface. The determination of the different stationary points on those PES coupled to MEP determinations leads to the energy correlation diagram depicted in Fig. 4. The energies displayed in this diagram correspond to relative DFT results with zero point vibrational energies included.

Triplet channel (1a).

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2 (X^3\Sigma_g^-)$$
 (1a)

DFT calculations show that this reaction is highly exothermic $(\Delta H_{\rm rxn}(298 \text{ K}) = -43 \text{ kcal mol}^{-1}, (-49.8 \text{ kcal mol}^{-1} \text{ according}$ to the recommended thermodynamics data²⁸ and the work of Bozelli²⁹ on peracetic acid). The exploration of this pathway shows that the first step is the barrierless formation of a prereactive complex PRCT weakly stabilised with respect to the reactants (-5 kcal mol⁻¹). This PRCT is characterized by a long-range interaction between the hydrogen atom of HO₂ and the terminal oxygen atom of the acetylperoxy group



Fig. 4 Relative energetic diagram of reaction pathways (1a), (1b) and (1c). The energies E(0 K) in kcal mol⁻¹ include zero-point energy corrections.

CH₃C(O)O₂ ($r(H \cdots O_3) = 1.88$ Å) (Fig. 5). This prereactive complex evolves, *via* a very small barrier TS1 (only 0.6 kcal mol⁻¹ above PRCT energy). This path corresponds to the total transfer of the H atom of HO₂ leading to the triplet molecular oxygen O₂ (X ${}^{3}\Sigma_{g}^{-}$) and the peracetic acid molecule CH₃C(O)OOH (Fig. 5).

Singlet channels (1b) and (1c). The exploration of the singlet surface shows, first, the presence of a long distance prereactive complex (PRCS) almost located 7 kcal mol^{-1} below



Fig. 5 Selected geometric structures for the pre-reactive complex PRCT and the transition state TS1.

the reactants. This PRCS is characterized by a rather long range interaction between the H-atom of HO₂ and the carbonyl oxygen of CH₃C(O)O₂ ($r(H \cdots O_1) = 1.89$ Å) (Fig. 6). After passing through a transition state TS2 (4.4 kcal mol⁻¹ below the reactants), the calculations show a minimum corresponding to a cyclic tetroxy adduct "AD" located almost 17 kcal mol⁻¹ below the reactants (the main features of the geometric structure are described in Fig. 6). It can be seen that the H-bonding interaction still exists ($r(H \cdots O_1) = 1.80$ Å in TS2 and 1.78 Å in AD). Moreover, it turns out that the distance O₂···O₃ is now equal to 1.50 Å, which is a rather large value for an O–O distance (usually around 1.40 Å). We expect that this bond is already weakened in this cyclic adduct and will break more easily.

This cyclic adduct AD can evolve into two different ways:

Channel (1b).

$$CH_{3}C(O)O_{2} + HO_{2} \rightarrow AD \rightarrow CH_{3}C(O)OH + O_{3} (X^{1}A_{1})$$
(1b)

The whole exoergicity of reaction (1b) is calculated in this work $\Delta H_{\rm rxn}(0 \text{ K}) = -19.8 \text{ kcal mol}^{-1}$ which corresponds to an enthalpy at 298 K equal to $\Delta H_{\rm rxn}(298 \text{ K}) = -21 \text{ kcal}$ mol⁻¹. Along this reaction path, the transition state TS3 (2 kcal mol⁻¹ above the molecular adduct AD and 14.8 kcal mol⁻¹ below the reactants) involves a concerted H-transfer from HO₂ to the carbonyl O₁ along with an elongation of the $O_2 \cdots O_3$ bond (from 1.50 to 1.92 Å) (Fig. 6) which will eventually break to form the products ozone O₃ and acetic acid CH₃C(O)OH. In this transition state TS3, the C_1-O_1 bond has partly lost its double bond character (1.21 Å in AD \rightarrow 1.26 A in TS3) to the benefit of the C₁-O₂ bond (1.36 A in AD \rightarrow 1.27 Å in TS3). It is clear that we have to deal with a highly feasible concerted process (the energy variation is small) due to the existence of a hydrogen bond which favours the hydrogen transfer from one oxygen atom to another.

Channel (1c).

$$\begin{array}{l} CH_{3}C(O)O_{2} + HO_{2} \rightarrow AD \rightarrow CH_{3}C(O)O \\ + OH \left(X \ ^{2}\Pi\right) + O_{2} \left(X \ ^{3}\Sigma_{g}^{-}\right) \end{array} \tag{1c}$$



Fig. 6 Selected geometric parameters for intermediate structures and transition states along singlet reaction pathways (1b) and (1c).

Contrarily to both previous reactions, this one is almost thermoneutral, $\Delta H_{rxn}(298 \text{ K}) = -2 \text{ kcal mol}^{-1} (-3 \text{ kcal})$ mol⁻¹ using the recommended thermodynamic data).²⁸ In order to explore the path, the bond O₂–O₃ of the cyclic tetroxy adduct AD has been extended step by step, while optimizing all the other geometric variables. The pathway, which does not present any barrier leads to $HO_3 + CH_3C(O)O$ with an energy of 11.5 kcal mol^{-1} above the adduct AD. The existence of HO₃ is still an open question. Several theoretical studies have been performed on this structure.^{30–34} The atmospheric motivation of these studies is the possible sink behaviour of HO₃ with respect to the species OH (² Π) and O₂ (¹ Δ _g).³¹ The most recent calculations lead to a weak stability less than 1 kcal mol⁻¹³⁴ with respect to OH $(^{2}\Pi)$ + O₂ $(^{3}\Sigma_{g})$, a barrier separating HO₃ from OH (² Π) + O₂ (³ Σ_{g}^{-}) being not higher than 4 kcal mol⁻¹.³² From the method (UHF-DFT) we used, we found the energy of HO_3 2.3 kcal mol⁻¹ below the energy of the products OH $(^{2}\Pi) + O_{2}(^{3}\Sigma_{g}^{-})$ and no significant barrier (around 1 kcal mol^{-1} at the very most) between them. This situation is still puzzling. As a matter of fact, HO_3 has one unpaired electron whereas the products OH $(^{2}\Pi) + O_{2}$ $({}^{3}\Sigma_{g}^{-})$ present three unpaired electrons. Since the dissociation of HO₃ involves a change in the electronic configuration when the coordinate O2-OH is elongated, an avoided crossing should exist between two doublet states. Then, it would be reasonable to find a barrier along this dissociation coordinate.

Consequences about the branching ratios

Without doing any precise rate constant calculations, these ab *initio* results permit to predict that reaction $CH_3C(O)O_2$ + HO₂ should evolve mainly according to channels (1a) and (1b). The participation of channel (1c) is highly unlikely. Examination of the energetic positions of the two pre-reactive intermediates gives a slight preference for channel (1a) with respect to channel (1b). As a matter of fact, PRCS is slightly more stable than PRCT by almost 2 kcal mol^{-1} and the exit transition states TS1 and TS2 are located at the same level with respect to the reactants. Then, we can expect that the recrossing flux towards the reactants coming from PRCS is larger than the one coming from PRCT. If, ignoring the spin multiplicity (1 for singlet, 3 for triplet), we attribute a ratio of 25/20 between the rate constants of channel (1a) and channel (1b), respectively, the three branching ratios with respect to the global rate constant of disappearance of reactants are expected to be roughly in that order: for the triplet channel (1a): 75% (spin multiplicity times 25%), for the singlet channel (1b): 20% and for the singlet channel (1c): negligible. Of course, we will check in a future work if our analysis is quantitatively correct.

4 Conclusions

In this study, both experimental and theoretical approaches have been used to verify the possibility of channel (1c) for the reaction of $CH_3C(O)O_2$ with HO₂ radicals, yielding a certain amount of OH radicals, as proposed recently by Hasson et al.¹ The values obtained in this work for the rate constant $k_1 (k_1 =$ $(1.50 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K})$ and for the branching ratio $\beta_1(O_3)$ leading to the formation of ozone $(\beta_1(O_3) = (0.20 \pm 0.01))$ are in excellent agreement with the values previously reported by Tomas *et al.*¹² ($k_1 = (1.42 \pm$ $(0.07) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } \beta_1(O_3) = (0.20 \pm 0.02))$ and those recommended by the review of Tyndall et al.,¹³ as the new value of $\gamma_1(OH)$ determined in this work ($\gamma_1(OH) <$ 0.10) have only a minor effect on the determination of k_1 and $\beta_1(O_3)$. Quantum chemistry calculations confirm the results obtained experimentally. Therefore, it is difficult to explain the difference between our observations and that reported by Hasson et al.1 even if their system only allows the detection and quantification of stable final products and not all the intermediates (CH₃C(O)O₂, HO₂, CH₃O₂ and C₆H₆OH if formed) as detailed in this work. In conclusion, the present study demonstrates that the $CH_3C(O)O_2 + HO_2$ is still predominantly a radical chain termination reaction in the tropospheric ozone chain formation processes.

Acknowledgements

The authors wish to thank R. Lesclaux (University of Bordeaux) for helpful discussions, and the French National Programme for Atmospheric Chemistry for financial support. M.T.R. and J.C.R. wish to thank the IDRIS-CNRS Center (Orsay, France) for computer facilities.

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