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Tropospheric degradation of 2-hydroxy-2-methylpropanal, a photo-oxidation product of 2-methyl-3-buten-2-ol: Kinetic and mechanistic study of its photolysis and its reaction with OH radicals

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Abstract

This article presents the first study of the chemical reactivity of a photo-oxidation product of the 2-methyl-3-buten-2-ol (MBO) in the troposphere, the 2-hydroxy-2-methylpropanal (HMPPr). Experiments were performed under controlled conditions for pressure (atmospheric pressure) and temperature (296 ± 2 K) in the LISA indoor simulation chamber and in the EUPHORE outdoor simulation chamber to understand the transformations of HMPPr in the atmosphere, using FTIR spectrometry. Reaction with OH radicals was studied in the presence and in the absence of NO_x . All the kinetic studies were carried out by relative rate study using isoprene and/or *n*-butylether as the reference compound. The rate constants found for these reactions were $J = (1.01 \pm 0.39) \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{HMPPr}+\text{OH}} = (1.52 \pm 0.36) \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$. For the reaction with OH radicals, an important production of acetone was observed, with a yield of $R_{\text{acetone}} = 1.06 \pm 0.06$. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Biogenic compound; 2-Hydroxy-2-methylpropanal; 2-Methyl-3-buten-2-ol; OH radicals; Photo-oxidation; Troposphere

1. Introduction

Biogenic volatile organic compounds (BVOCs), emitted by natural terrestrial and seascape sources, account for around 90% of the global hydrocarbon emissions into the Earth's atmosphere (Wayne, 2000). The study of Guenther et al. (1995) gave an estimation of $1150 \text{ TgC year}^{-1}$ for the world-wide emission rate of non-methane BVOC. Several

hundred different compounds have been identified, including well-known unsaturated hydrocarbons such as isoprene, and mono- and sesquiterpenes, and some more recently detected non-terpenoid compounds such as 2-methyl-3-buten-2-ol (MBO) (Guenther et al., 1995). Some studies found local high abundance of MBO in the atmosphere. Thus Goldan et al. (1993) measured on the mountain site of Niwot Ridge (in Colorado) day-time MBO concentrations eight times higher than the emission of isoprene. Guenther et al. (2000) in their North America emission inventory took this compound

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into account and recommended a methylbutenol emission of $3.2 \text{ Tg C year}^{-1}$. MBO is probably emitted in large quantities by some specific pine species (Schade et al., 2000; Harley et al., 1998; Goldan et al., 1993) but no data are available about the emissions elsewhere in the world than in North America.

Gas-phase degradations of this reactive molecule contribute to produce photo-oxidants in the atmosphere. Studies about the reactivity of MBO with OH are numerous (Carrasco et al., 2006; Reisen et al., 2003; Spaulding et al., 2002; Alvarado et al., 1999; Fantechi et al., 1998; Ferronato et al., 1998). Alvarado et al., Spaulding et al., and Reisen et al. identified and semi-quantified the compound 2-hydroxy-2-methylpropanal (HMPPr) as a product of this reaction. And Carrasco et al. (2006) indicated a massive production of about 35% of this compound coming from its reaction with OH. The abundant emission of MBO in the troposphere in addition to its important conversion into HMPPr explains the necessity to study the reactivity of this last compound. In particular, the degradation of HMPPr in the troposphere may be an important source of acetone. Acetone is also a major product from $\text{OH} + \text{MBO}$ (Carrasco et al., 2006; Alvarado et al., 1999; Ferronato et al., 1998). It has been shown (Jaeglé et al., 2001; Jacob et al., 2002) that the photolysis of acetone in the upper troposphere is the dominant source of HO_x radicals ($\text{OH} + \text{HO}_2$ radicals) when $[\text{H}_2\text{O}] < 100 \text{ ppmv}$. HMPPr reactivity could also have strong implications in the global troposphere chemistry.

Only one very recent kinetic study (Baker et al., 2004) has been published on the atmospheric degradation of HMPPr in the troposphere. This study deals with the reaction between HMPPr and OH radicals. No product yields have been published yet. In this work, the kinetic studies of HMPPr photolysis and of its reaction with OH were investigated, as well as the mechanism of the reaction between HMPPr and OH radicals. This overview of HMPPr diurnal reactivity will make it possible to quantify the atmospheric implications of this compound in the troposphere.

2. Experimental

2.1. Methods

Experiments were carried out using two different European simulation chambers: an indoor simulation

chamber (LISA, Créteil, France) and an outdoor simulation chamber (EUPHORE, Valencia, Spain). The following experiments were performed: photolysis and OH-without NO_x reactions in EUPHORE, and OH-with NO_x reactions in LISA.

2.2. Smog chambers

The LISA chamber is a 977L cylindrical Pyrex evacuable reactor, equipped with a multiple-reflection optical system coupled to a Bomem DA8-ME FTIR spectrometer (Doussin et al., 1997). Path length in the chamber was adjusted to 156 m. Between each experiment, the simulation chamber was reconditioned by lowering pressure down to 10^{-3} mbar. Then, the chamber was filled with synthetic air (80% N_2 , 20% O_2) at atmospheric pressure and the temperature was kept at $293 \pm 2 \text{ K}$ during all the experiments. The reactor was surrounded by 40 visible lamps (Philips TL03 40W, $\lambda_{\text{max}} = 420 \text{ nm}$).

The EUPHORE outdoor smog chamber is a half-spherical 204 m^3 Teflon bag using natural sunlight radiation (Becker et al., 1996). In order to stabilise the chamber against wind, the pressure in the chamber is slightly higher than the outside pressure (100–200 Pa above). This induces a compound loss through a regulating valve during experiments. To control this dilution, an inert tracer, SF_6 is added.

The natural irradiation allows realistic photolysis experiments. Moreover, natural irradiation includes short-wavelength UV radiations which are able to photolyse H_2O_2 . The photolysis of H_2O_2 produces OH radicals at low NO_x concentrations. Among several other instruments, the reactor is equipped with an FT-IR spectrometer (Nicolet, MAGNA 550) coupled with a long-path absorption system (path length adjusted to 553.5 m), with NO_x and NO_y analysers.

2.3. Chemicals

MBO (Aldrich, purity $> 98\%$), H_2O_2 (Aldrich, 30%), CO, NO and SF_6 (used in EUPHORE only) were used as commercially available without further purification.

In EUPHORE, ozone was produced by a home-made O_3 generator using a silent discharge in pure oxygen, giving a typical production rate of 20 ppb/min in the simulation chamber.

Nitrous acid was synthesised by the slow addition of a diluted NaNO_2 solution into a diluted sulphuric acid solution (Taylor et al., 1980).

2.4. Synthesis of HMPr

In the LISA simulation chamber, the reactant HMPr was introduced directly after its synthesis in liquid phase. For this synthesis, several methods have been tried. The addition of methyl magnesium bromide in a diethylether solution on the 1-1-dimethoxypropanone (Spaulding et al., 2002) led to undesired side products under different acid catalysis and gave at best the dimer of the wanted hydroxaldehyde (identified by GCMS, and FTIR). The finally adopted method was the ozonolysis of MBO in organic solution. A cold (-78°C) and magnetically stirred solution of MBO (10 mL) in dichloromethane (50 mL) was ozonolysed (around 6 h) until a blue colour persisted (Kozmina and Paquette, 1996). The excess ozone was flushed from the solution with a nitrogen flow during 20 min. To reduce the previously formed ozonides into carbonyl compounds, triphenylphosphine (7.5 g in 100 mL of CH_2Cl_2) was carefully added at -78°C . Then the solution was warmed up to room temperature, and was stirred for an additional 48 h (Lorenz and Parks, 1965; Carles and Fliszar, 1969). The solvent was removed under reduced pressure and replaced by diethylether, in which the excess of triphenylphosphine and the triphenylphosphine oxide are not very soluble. Both were eliminated by crystallisation in cold water. The solvent was evaporated under reduced pressure. The remaining liquid phase was analysed by GCMS. Its composition included the methylhydroxypropanal but also formaldehyde and formic acid. A gaseous mixture of the three compounds was directly introduced in the simulation chamber.

In the EUPHORE simulation chamber, HMPr was synthesised in situ by a total MBO ozonolysis in an excess of ozone.

2.5. Chemical analyses

2.5.1. FTIR

Knowing the FTIR spectra of formic acid and formaldehyde and their IR cross-sections (see Table 1), methylhydroxypropanal was calibrated by subtracting the contribution of these two compounds. The error on the calibration of HMPr takes into account the standard deviation of the calibration plot and the error on the calibration of formaldehyde and formic acid. The experiments on HMPr reactivity, performed with this source of HMPr, took into account the well-known chemistry of formaldehyde (Finlayson-Pitts and Pitts, 2000) in the simulation chamber. The FTIR-spectrum of this hard-to-synthesise compound is given in Fig. 1. The spectrum is also compared to the absorption bands identified by Alvarado et al. (1999) in this figure. The two spectra are in good agreement except for a supplementary band at 1050 cm^{-1} in Alvarado et al. (1999) corresponding to another product, and a thin residual band at 1106 cm^{-1} in our spectrum which characterises a remaining trace of formic acid.

Acetone, CO and CO_2 were expected as HMPr oxidation products. Integrated Band Intensities (IBI) of the main infrared absorptions of these compounds are given in Table 1.

2.5.2. Uncertainties

All the linear regressions described in this article (including FTIR calibrations) take into account the uncertainties on both coordinates, x and y , for each measurement. This method avoids systematic bias on the slope of the plot as proved in Brauers and Finlayson-Pitts (1997). For this purpose, a Matlab iterative routine developed by Peltzler (2000) has been directly used. Errors correspond to twice the standard deviations.

In the kinetics studies, where the variable type was $\text{Ln}([\text{Prod}]_0/[\text{Prod}])$, the error for each measurement was first calculated following the procedure

Table 1
IBI of the main IR absorption bands, values are given in log.

Compound	Main absorption band (cm^{-1})	IBI (cm molecule^{-1})	Reference
HMPr	2780–3010	$(1.02 \pm 0.16) \times 10^{-17}$	This work
Acetone	1260–1150	$(1.02 \pm 0.02) \times 10^{-17}$	Picquet-Varrault et al., 2002
Formaldehyde	3000–2630	$(1.33 \pm 0.06) \times 10^{-17}$	Picquet-Varrault et al., 2002
Formic acid	1840–1704	$(5.91 \pm 1.15) \times 10^{-17}$	Barnes and Hjorth, 2004
	1186–1040	$(4.58 \pm 0.92) \times 10^{-17}$	

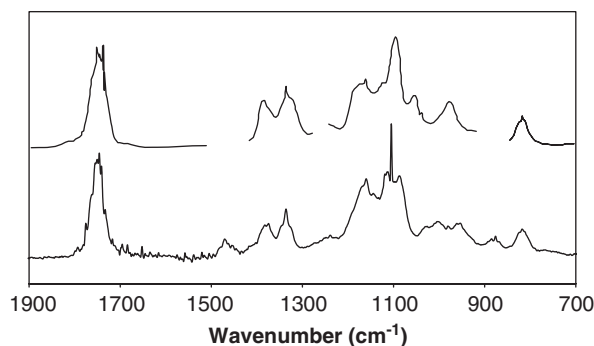


Fig. 1. HMPPr infrared spectra. The upper spectrum was obtained by Alvarado et al. (1999) after subtraction during a MBO + OH reaction. The lower spectrum was obtained in this work after organic synthesis.

described in the first part of Brauers and Finlayson-Pitts (1997).

3. Results and discussion

3.1. Photolysis

The study of HMPPr photolysis was carried out in the EUPHORE chamber (latitude 39°29') on 27/05/03 to expose the compound to natural irradiances. Temperature and pressure were equal to 293 ± 2 K and 1005.3 mbar. The weather conditions were favourable and J_{NO_2} decreased from 9×10^{-3} to $7 \times 10^{-3} \text{ s}^{-1}$ between 13 and 15 h GMT. A total of 0.6 ppm of HMPPr was initially introduced in the chamber. Then 27 ppm of cyclohexane was added to scavenge any OH radicals formed (Grosjean and Grosjean, 1994).

When the reaction began (at 13 h GMT), HMPPr disappeared according to two different processes: the photolysis itself, and a dilution through the Teflon bag, characterised by, respectively, J and τ rate constants. Supposing that J is a constant during the timescale of the experiment (between 13 and 15 h GMT, J_{HCHO} decreases only from 2.6×10^{-5} to $2.3 \times 10^{-5} \text{ s}^{-1}$, for example), the kinetic equation can be integrated as follows:

$$-\frac{d[\text{HMPPr}]}{dt} = (J + \tau)[\text{HMPPr}] \Rightarrow \ln \left[\frac{[\text{HMPPr}]_0}{[\text{HMPPr}]_t} \right] = (J + \tau)(t - t_0).$$

By plotting $\ln([\text{HMPPr}]_0/[\text{HMPPr}]_t)$ vs. time, a straight line is observed with $J + \tau$ as slope. The

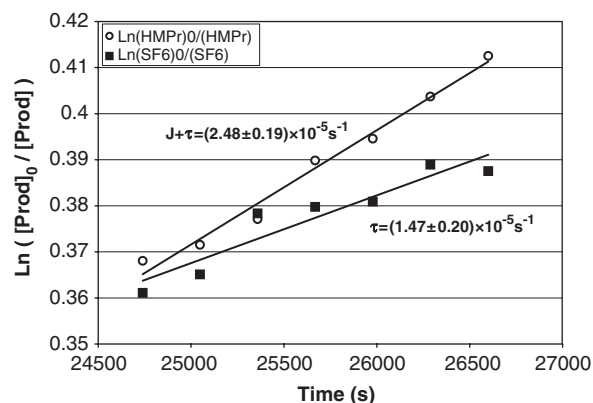


Fig. 2. Natural photolysis of HMPPr in the EUPHORE simulation chamber. White dots represent $\ln(\text{HMPPr})_0/(\text{HMPPr})$ vs. time. Black squares represent $\ln(\text{SF}_6)_0/(\text{SF}_6)$ vs. time. The difference between the two slopes gives the value of J .

dilution tracer, SF_6 , only disappeared by dilution.

$$-\frac{d[\text{SF}_6]}{dt} = \tau[\text{SF}_6] \Rightarrow \ln \left[\frac{[\text{SF}_6]_0}{[\text{SF}_6]_t} \right] = \tau(t - t'_0).$$

In the same way, $\ln([\text{SF}_6]_0/[\text{SF}_6]_t)$ vs. time was plotted to obtain the value of τ . Both plots are given in Fig. 2. Two straight lines are indeed obtained whose slopes give $J + \tau$ and τ , which confirms that the J_{HMPPr} variation has no noticeable effect during the timescale of the experiment: $J + \tau = (2.48 \pm 0.19) \times 10^{-5} \text{ s}^{-1}$ and $\tau = (1.47 \pm 0.20) \times 10^{-5} \text{ s}^{-1}$. The value of J is deduced from these two results: $J = (1.01 \pm 0.39) \times 10^{-5} \text{ s}^{-1}$.

3.2. Reaction with OH radicals

3.2.1. Kinetics

A relative rate experiment was performed in LISA using isoprene as the reference compound and another was carried out in EUPHORE using *n*-butylether as the reference compound. Experimental conditions are reported in Table 2. OH radicals were obtained by photolysing HONO in LISA and H_2O_2 in EUPHORE. Temperature and pressure were adjusted to 293 ± 2 K and to atmospheric pressure.

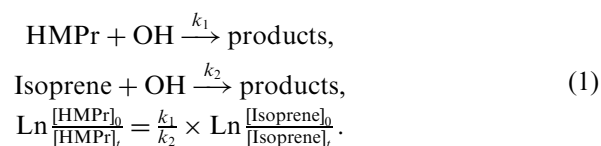
It was checked that both HMPPr and isoprene were stable in the LISA chamber over the timescale of a typical experiment in different conditions: with light, without OH radical sources, and without light, with OH radical sources (less than 3% of HMPPr and isoprene disappeared under these conditions after 30 min in the chamber). In the

Table 2
Conditions of the kinetic and mechanistic HMP_r + OH experiments

Simulation chamber		Initial mixing ratios (ppm _v)	<i>T</i> (K)	P (mbar)
Relative rate experiments	LISA	[HMP _r] ₀ = 0.8 [Isoprene] ₀ = 0.3	295 ± 2	Atmospheric pressure
	EUPHORE	[HMP _r] ₀ = 0.5 [<i>n</i> -But] ₀ = 0.1 UA	293 ± 2	
Mechanistic experiments	LISA	[HMP _r] ₀ = 0.9	298 ± 2	Atmospheric pressure
	Presence of NO _{<i>x</i>}	[HONO] ₀ = 0.8	297 ± 1	
		[HMP _r] ₀ = 0.7		
		[HONO] ₀ = 13.4		
	EUPHORE	[HMP _r] ₀ = 0.5	295 ± 2	
	Absence of NO _{<i>x</i>}	[H ₂ O ₂] ₀ = 2.5	295 ± 2	
		[HMP _r] ₀ = 0.50 [H ₂ O ₂] ₀ = 1.3		

EUPHORE chamber, the dilution also had to be taken into account.

LISA: In the LISA chamber, the only sink for HMP_r and isoprene is their reaction with OH radicals. Indeed, photolysis was tested at 420 nm (wavelength corresponding to the photolysis of HONO) on these VOC and it was checked that they were insensitive to this wavelength:



According to Eq. (1), ratio k_1/k_2 is given by the slope of the plot $\text{Ln}([\text{HMP}_r]_0/[\text{HMP}_r]_t)$ versus $\text{Ln}([\text{Isoprene}]_0/[\text{Isoprene}]_t)$ where $[\text{HMP}_r]_0$ and $[\text{Isoprene}]_0$ are the initial concentrations and $[\text{HMP}_r]_t$ and $[\text{Isoprene}]_t$ are varying concentrations during the reaction (see Fig. 3). Knowing $k_2 = 1.01 \pm 0.10 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997, most recent determination) and the ratio k_1/k_2 , the k_1 value was deduced. Relative error on k_1 was obtained by adding relative errors on k_2 and on ratio k_1/k_2 . The ratio k_1/k_2 was found equal to 0.135 ± 0.014 , giving a rate constant equal to $k_1 = (1.36 \pm 0.42) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

EUPHORE: In the EUPHORE chamber, the reference compound disappears by its reaction with OH radicals and by dilution. The sinks of HMP_r are numerous: the reaction with OH radicals and also the dilution and the photolysis. The last two processes are very likely negligible in comparison to the reaction with OH because of the high concentration of OH radicals in the chamber.

However, we preferred to take into account all the possible decomposition pathways in the linear regression. The weather conditions were sunny and stable (J_{NO_2} decreased from 9.2×10^{-3} to $8.3 \times 10^{-3} \text{ s}^{-1}$ between 13 and 15 h GMT) so that J can be reasonably considered as a constant during the timescale of the experiment:

$$\begin{aligned} -\frac{d[\text{HMP}_r]}{dt} &= (k_1[\text{OH}] + \tau + J)[\text{HMP}_r], \\ -\frac{d[n\text{But}]}{dt} &= (k_3[\text{OH}] + \tau)[n\text{But}], \\ -\frac{d[\text{SF}_6]}{dt} &= \tau[\text{SF}_6]. \end{aligned}$$

The kinetics equation above leads after integration to the following relationship:

$$\begin{aligned} \text{Ln} \frac{[\text{HMP}_r]_0}{[\text{HMP}_r]_t} - (\tau + J) \times t \\ &= \frac{k_1}{k_3} \times \left(\text{Ln} \frac{[n\text{But}]_0}{[n\text{But}]_t} - \tau \times t \right) \\ \Rightarrow \frac{1}{t} \times \text{Ln} \frac{[\text{HMP}_r]_0}{[\text{HMP}_r]_t} &= \frac{k_1}{k_3} \times \frac{1}{t} \\ &\times \text{Ln} \frac{[n\text{But}]_0}{[n\text{But}]_t} + \left(\tau + J - \frac{k_1}{k_3} \times \tau \right). \end{aligned}$$

By plotting $1/t \times \text{Ln}([\text{HMP}_r]_0/[\text{HMP}_r]_t)$ vs. $1/t \times \text{Ln}([n\text{But}]_0/[n\text{But}]_t)$, a straight line is observed with $k_1/k_3 = 0.43 \pm 0.02$ as slope and $\tau + J - k_1/k_3 \tau = (1.2 \pm 0.3) \times 10^{-5} \text{ s}^{-1}$ as initial value (see Fig. 3). Because of the important dispersion, the intercept of the plot cannot be used to determine the value of J . Knowing $k_3 = 3.30 \pm 0.27 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Harry et al. (1999) most recent determination) and the ratio k_1/k_3 , the k_1

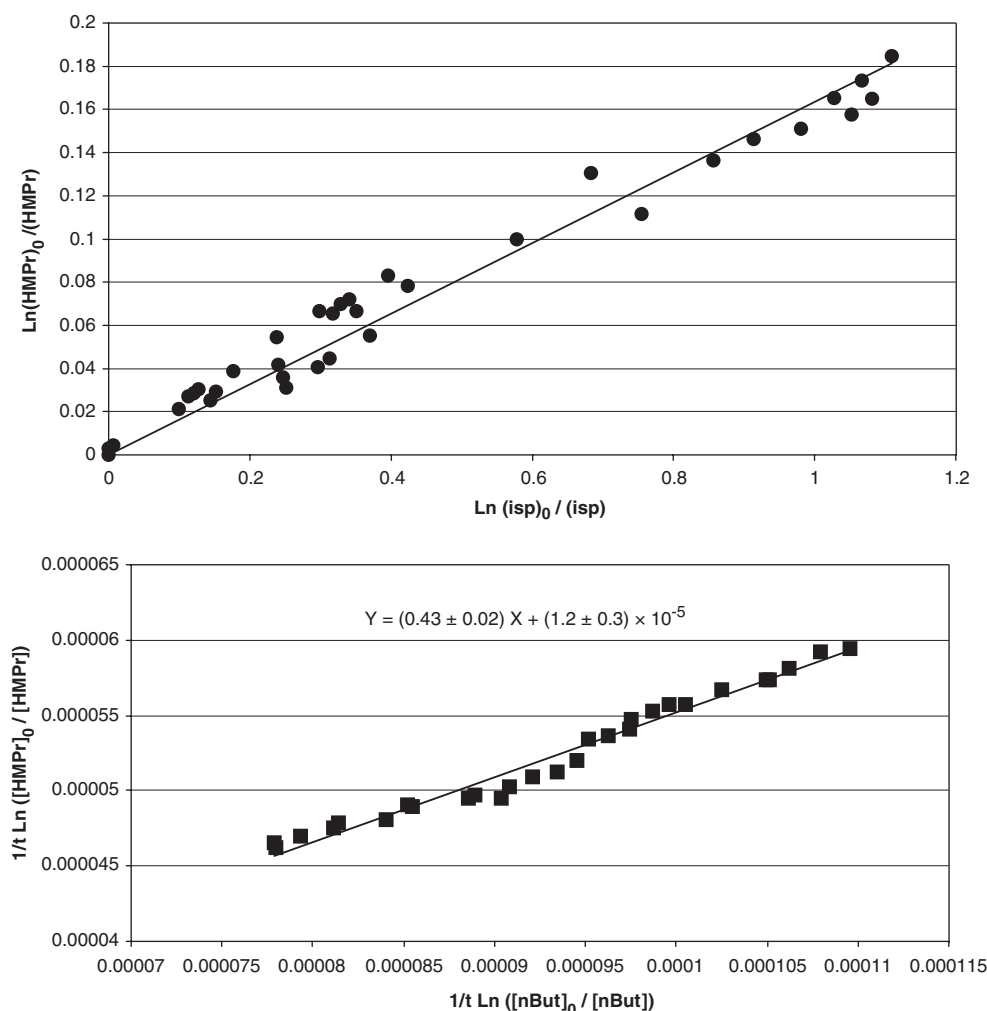


Fig. 3. Reaction of HMPPr with OH radicals. Above: kinetic study by relative rate technique using isoprene as the reference in the LISA chamber. Below: kinetic study by relative rate technique using *n*-butylether as the reference and correcting data by a dilution factor and a photolysis factor in the EUPHORE simulation chamber.

value was deduced. Relative error on k_1 was obtained by adding relative errors on k_3 and on ratio k_1/k_3 . A rate constant equal to $k_1 = (1.42 \pm 0.18) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was found.

Comparison between the two k_1 determinations, made in LISA and in EUPHORE: These two experiments, performed with two different reference compounds and two different sources of OH radicals lead to the respective values $k_1 = (1.36 \pm 0.42) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in LISA and $k_1 = (1.42 \pm 0.18) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in EUPHORE. The average value of these two determinations is $k_1 = (1.41 \pm 0.26) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is in good agreement with the recent publica-

tion of Baker et al. (2004). In Baker et al., HMPPr was generated in situ from the reaction of OH with MBO. Then the rate constant for OH + HMPPr was determined relative to the rate for OH + MBO. A rate constant equal to $k_1 = (1.40 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was found.

3.2.2. Mechanism

Four experiments were performed to study the mechanism of the reaction between HMPPr and OH radicals: two in the LISA chamber and two in the EUPHORE chamber (see more details in Table 2). The only source of NO in the LISA chamber came from the photolysis of HONO. A production of

acetone, CO and CO₂ was observed in each case. The productions of CO and CO₂ were impossible to identify. Indeed, these compounds have also been produced by the degradation of formaldehyde coming from HMP_r synthesis.

In the LISA chamber, formation yields of acetone were determined by calculating the slopes of the curves [Acetone] vs. $-\Delta[\text{HMP}_r]$. In EUPHORE, this method is usually not applicable because mixtures are subject to dilution and to photolysis. However, the previous kinetics study proved that the reaction of HMP_r with OH was much faster than its photolysis or than the dilution process. Furthermore, the rate constant of acetone production by this process is very similar to the rate constant of the reaction HMP_r+OH. Indeed, $k_{\text{OH}+\text{acetone}}$ is equal to $k_{\text{HMP}_r+\text{OH}}$ multiplied by the acetone yield (around 100% as proved hereunder). Thus, it was reasonable to assume that the acetone production by the reaction between HMP_r and OH was predominant. Acetone dilution and its reaction with OH ($k_{\text{acetone}+\text{OH}} = 2.23 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 300 K, DeMore et al., 1997) were also neglected and it was assumed that no other compound present in the gaseous mixture

produced acetone. In this case, formation yields of acetone were determined by calculating the initial slopes of the curves [Acetone] vs. $-\Delta[\text{HMP}_r]$, as in the LISA chamber (see Fig. 4).

All the four experiments show a HMP_r production yield of 100%, with a better precision on the experiments carried out in LISA. Thus, a yield of $R_{\text{acetone}} = 1.10 \pm 0.26$ was found in the absence of NO_x in the EUPHORE chamber and a yield of $R_{\text{acetone}} = 1.06 \pm 0.06$ in the presence of NO_x. A mechanistic scheme of the HMP_r+OH reaction is proposed in Fig. 5. In this scheme acetone can be formed by a direct recombination of the radical (CH₃)₂(OH)C–C°=O or by an intermediate reaction with oxygen. The proportions of the two acetone production pathways were not quantified because CO and CO₂ could not be measured. However, no nitrate formation was noticed in the LISA chamber despite a factor [NO₂]/[NO] favourable to the reaction peroxy radical+NO₂→nitrate (factor around 4 during the experiments). This observation may suggest that the peroxy radical could be far from abundant and as a result, the direct recombination of the radical (CH₃)₂(OH)C–C°=O could be preferred to its reaction with oxygen. Some further experiments are necessary to confirm this hypothesis.

4. Atmospheric implications

The complete diurnal reactivity of HMP_r was presented in this paper. Kinetic studies showed rate constants of $J = (1.01 \pm 0.39) \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{OH}+\text{HMP}_r} = (1.52 \pm 0.36) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for, respectively, photolysis and reaction with OH radicals. Thus, corresponding life times are $\tau_{\text{hv}} = 25 \text{ h}$ and $\tau_{\text{OH}} = 11 \text{ h}$ at OH concentration of $2 \times 10^6 \text{ molecule cm}^{-3}$ (Atkinson and Arey, 2003). This indicates that during daytime HMP_r essentially disappears from the troposphere through its reaction with OH. Moreover, this reaction leads to a complete conversion into acetone. In Carrasco et al. (2006), it was shown that HMP_r and acetone were both produced by complementary pathways by the decomposition of a major biogenic compound, MBO. This implicates that through its additional primary and secondary chemistry, the potentially abundant compound MBO is completely converted into acetone in the troposphere.

In their publication, Jacob et al. (2002) calculated a global source of acetone coming from MBO equal to $1.8 \pm 1.8 \text{ Tg year}^{-1}$, by assuming that the worldwide MBO emissions are equal to the North

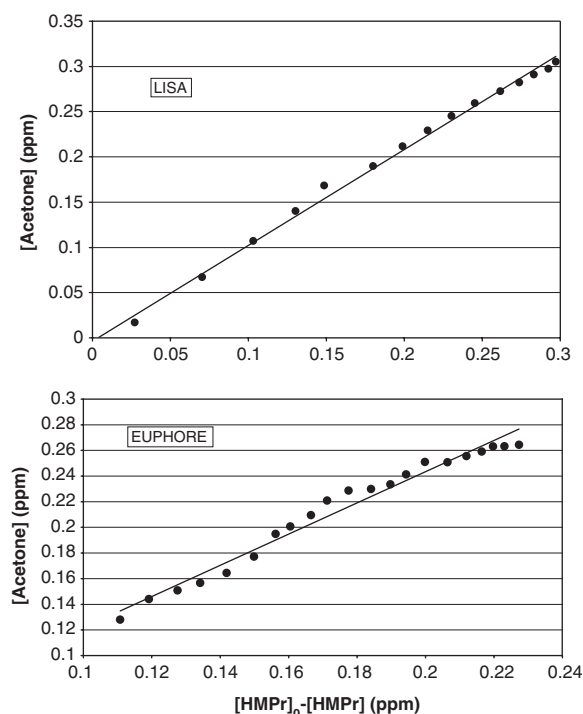


Fig. 4. Production of acetone during a reaction between OH and HMP_r in the LISA and in the EUPHORE simulation chambers.

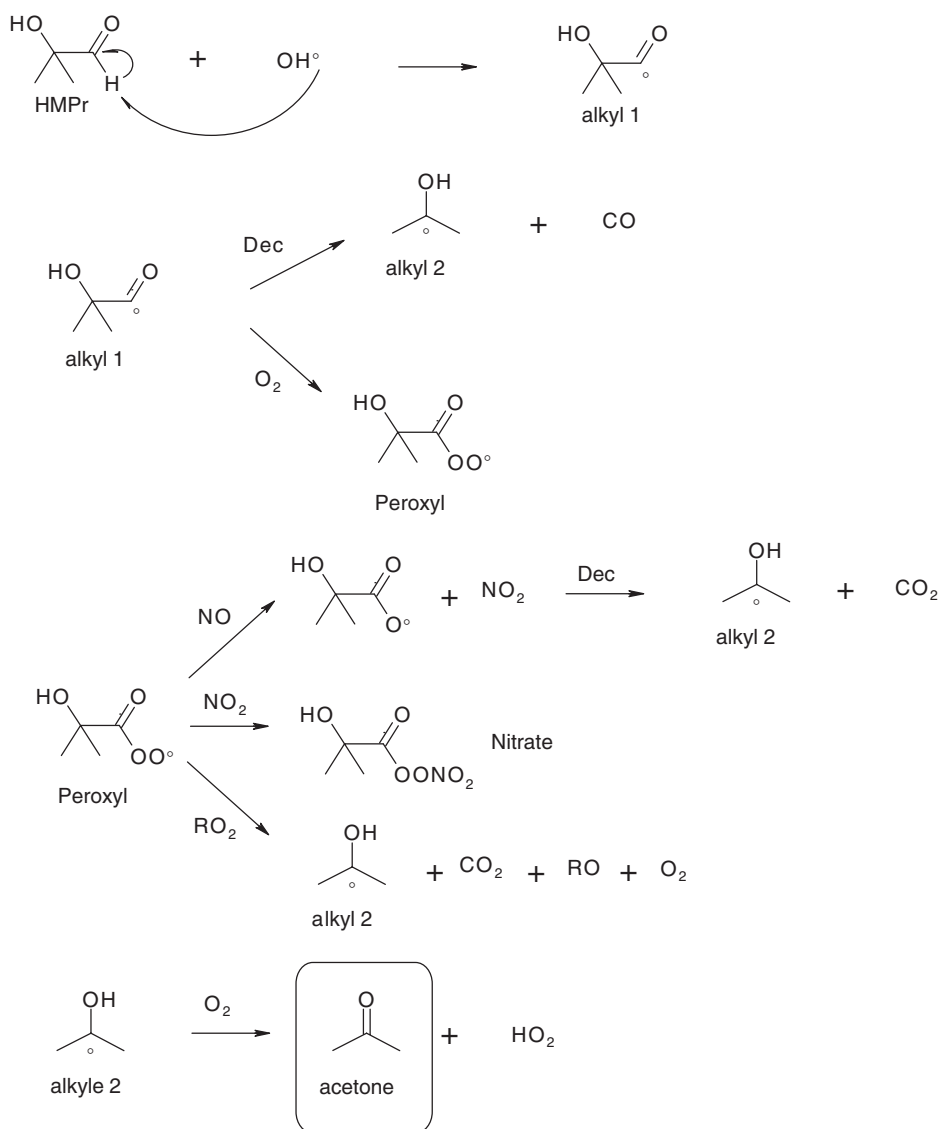


Fig. 5. Mechanism of the reaction between HMPr and OH radicals in the presence of NO_x; $R_{\text{acetone}} = 100\%$ (Dec: decomposition).

American ones and by considering a conversion of 58% from MBO to acetone (Alvarado et al., 1999). Nevertheless, worldwide MBO emissions are probably not restricted to the only North American ones and our work shows that the MBO conversion into acetone is complete when HMPr reactivity is taken into account. We can conclude that the contribution of MBO to the global acetone budget may be more important than calculated by Jacob et al. (2002). To evaluate the extent of this potentially important acetone source, further field experiments are required.

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