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**Atmospheric Chemistry of ketones:**  
**Reaction of OH radicals with 2-methyl-3-pentanone, 3-methyl-2-**  
**pentanone and 4-methyl-2-pentanone**

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## Abstract:

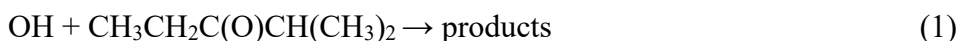
This work reports new kinetic and mechanistic information on the atmospheric chemistry of ketones. Both absolute and relative rate methods were used to determine the rate constants for OH reactions with 2-methyl-3-pentanone (2M3P), 3-methyl-2-pentanone (3M2P) and 4-methyl-2-pentanone (4M2P), three widely used compounds in the industry. This work constitutes the first temperature dependence study of the reactions of OH with 2M3P and 3M2P. The following rate constants values are recommended at 298 K (in  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ):  $k_{\text{OH}+2\text{M3P}} = 3.49 \pm 0.5$ ;  $k_{\text{OH}+3\text{M2P}} = 6.02 \pm 0.14$  and  $k_{\text{OH}+4\text{M2P}} = 11.02 \pm 0.42$ . The following Arrhenius expressions (in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) adequately describe the measured rate constants for OH reactions with 2M3P and 3M2P in the temperature range 263-373 K:  $k_{2\text{M3P}} = (1.93 \pm 0.08) \times 10^{-12} \exp((183.2 \pm 23.9)/T)$  and  $k_{3\text{M2P}} = (1.05 \pm 0.14) \times 10^{-12} \exp((537 \pm 41)/T)$ . Products studies from the reactions of OH with the investigated ketones were conducted in a 7.3 m<sup>3</sup> simulation chamber using PTR-ToF-MS, UHPLC-MS and GC-MS. A series of short chain carbonyl compounds including formaldehyde, acetone, acetaldehyde, 2-butanone and 2-methylpropanal were observed as products. Combining the yields of carbonyls measured with those estimated from the SAR method, we propose various mechanistic degradation schemes of the investigated ketones initiated by reaction with OH radicals.

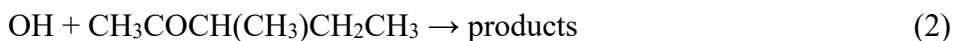
**Keywords:** OH radicals, ketones, kinetics, reaction mechanism

## 1. Introduction

Ketones are widely used in the chemical industry (e.g. as solvents and intermediates); hence, a substantial fraction of these substances can be released into the atmosphere (Calvert et al., 2011; Mellouki et al., 2015). They are also formed in the atmosphere during the oxidation of other hydrocarbons. Significant amounts of ketones are emitted into the atmosphere and thus they are considered as ubiquitous pollutants in the atmosphere where they become available for photochemical transformation (J. B. Burkholder et al., 2015). Their degradation is mainly initiated by their photolysis and reaction with OH radicals. Photolysis is the dominant loss process at high altitudes while the reaction with OH radicals is predominant near the surface. Depending on the chemical structure and their degradation processes, ketones constitute a potential source of free radicals, organic acids, organic nitrates, secondary organic aerosols, and contribute to ozone formation (Mellouki et al., 2015).

Previous kinetic and products studies have mostly focused on the investigation of the reactions of OH with relatively short and straight-chain ketones, e.g. acetone and 2-butanone, 2-pentanone, 3-pentanone, 2-hexanone and 3-hexanone (Calvert et al., 2011). Only a limited number of studies have been performed so far on the OH-initiated oxidation of the long and branched chain ketones e.g. 3-methyl-butanone, 4-methyl-2-pentanone and 5-methyl-2-hexanone (Atkinson and Aschmann, 1995; Atkinson et al., 2000; Cuevas et al., 2004; Le Calvé et al., 1998). In light of the importance of ketones in the atmospheric chemistry, it is of importance to further investigate the degradation processes of ketones having different chemical structures. The present work is dedicated to an experimental investigation of the reactions of OH radicals with three branched ketones: 2-methyl-3-pentanone (2M3P,  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}(\text{CH}_3)_2$ ), 3-methyl-2-pentanone (3M2P,  $\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ ) and 4-methyl-2-pentanone (4M2P,  $\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$ ), which are widely used as solvents or as intermediates in the chemical industry (Williams et al., 2017). We report the rate constant values and the products formed from the reactions of 2M3P, 3M2P, and 4M2P with OH radicals:





This work provides the first determination of the rate constant of OH reaction with 2M3P and the second one for that with 3M2P. In addition, we report the first measurement of the temperature dependence for reaction (1) and (2). The OH-initiated oxidation mechanism of 2M3P and 3M2P have not been investigated earlier, hence, we present in this work the first mechanistic studies of (1) and (2). In addition to the experimental studies, our work aimed at better defining the reactivity and atmospheric fate of the studied ketones toward the OH radicals.

## 2. Experimental and Material

The experiments have been performed using two complementary systems (i) pulsed laser photolysis–laser-induced fluorescence (PLP-LIF) and (ii) two atmospheric simulation chambers (200 L and 7.3 m<sup>3</sup>) at ICARE (CNRS - Orléans, France). The rate constants for the reaction of OH with 2M3P, 3M2P and 4M2P have been measured using both absolute (AR) and relative (RR) rate methods by employing the PLP-LIF and the 200 L simulation chamber. The OH-initiated oxidation mechanisms of the three ketones were investigated in the 7.3 m<sup>3</sup> ICARE simulation chamber.

### 2.1. Relative rate method

All the experiments were performed at ambient temperature ( $T \approx 295 \pm 4$  K) and pressure ( $P \approx 760$  Torr) in the 200 L ICARE chamber, made of FEP Teflon, that has been previously described elsewhere (Bernard, 2009; Bernard et al., 2012; Ren et al., 2018). A GC-FID (supplementary information, SI) was employed here to follow the chemical loss. The reactions rate constants were determined by following the parallel decays of the ketones and reference compounds resulting from the reaction with OH radicals and other additional losses such as photolysis, leaks and sampling:



$k_{1\_RR}$ ,  $k_{2\_RR}$ ,  $k_{3\_RR}$  and  $k_{ref}$  are the rate constants for the reaction of OH with 2M3P, 3M2P, 4M2P and reference compounds, respectively.  $k_{loss}$  is the loss rates of the studied ketones and reference compounds by dilution and on the wall of the chamber.

The typical experimental procedure consisted in:

(1) series of tests prior to the initiation of the reaction: (i) mix in the chamber ketones in air without irradiation for 1 hour to check the possible wall loss; (ii) ketones in air with irradiation (2-4 lamps emitting at 254 nm) for 1 hour to check for their photolysis; (iii) ketones + H<sub>2</sub>O<sub>2</sub> in air without irradiation for 1 hour to verify possible dark reactions. The same tests have been conducted for the reference compounds. These tests showed that there were no significant losses from wall, dark reactions or photolysis of the ketones and reference compounds.

(2) The reactions of OH with the ketones and reference compounds were initiated once OH radicals were generated via photolysis of H<sub>2</sub>O<sub>2</sub> at 254 nm.

Assuming that the ketones and reference compounds are lost only by reaction with OH radicals, it can be shown that:

$$\ln\left(\frac{[ketone]_0}{[ketone]_t}\right) = \frac{k_{ketone\_RR}}{k_{ref}} * \ln\left(\frac{[ref]_0}{[ref]_t}\right) \quad \text{Eq.1}$$

where  $[ketone]_0$ ,  $[ketone]_t$ ,  $[reference]_0$ , and  $[reference]_t$  are the corresponding concentrations of ketone and reference compounds at initial reaction time and t. Hence, plots of  $\ln\left(\frac{[ketone]_0}{[ketone]_t}\right)$  against  $\ln\left(\frac{[ref]_0}{[ref]_t}\right)$  should be straight lines with the slope =  $\frac{k_{ketone\_RR}}{k_{ref}}$  and zero intercept.

## 2.2. Pulsed Laser Photolysis-Laser Induced Fluorescence (PLP-LIF)

The apparatus employed in this work has been described in detail previously in a number of publications from our group (Le Calvé et al., 1998; Mellouki et al., 1995). The decay rate of OH was governed by its reactions with the ketone and H<sub>2</sub>O<sub>2</sub> in addition to its removal from the detection zone by diffusion:



OH  $\rightarrow$  diffusional loss  $k_{\text{diff}}$

$k_{1\_LIF}$ ,  $k_{2\_LIF}$ ,  $k_{3\_LIF}$ ,  $k_{\text{H}_2\text{O}_2}$ , and  $k_{\text{diff}}$  are the OH reactions rate constants with ketones,  $\text{H}_2\text{O}_2$  and the diffusional loss, respectively. All experiments were carried out under pseudo-first-order conditions by maintaining  $[\text{ketone}] \gg [\text{OH}]$ . According to the above reactions sequences, the decay of OH concentration should follow the pseudo-first order rate law:

$$[\text{OH}]_t = [\text{OH}]_0 \exp(-k't) \quad \text{Eq.2}$$

Where  $k'$  is the pseudo-first order rate constant that combines all OH loss processes:

$$k' = k_{\text{ketone\_LIF}} [\text{ketone}] + k_0' \quad \text{where } k_0' = k_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] + k_{\text{diff}} \quad \text{Eq.3}$$

The OH concentration at various reaction times (delay between the photolysis pulses and the probe pulses) were determined by the LIF signal at each decay time. The values of  $k'$  and  $k_0'$  were extracted from the linear least-square analysis of OH LIF signal plotted vs. decay time in the presence and absence of the investigated ketone. The linear least-squares fit of the data  $k' - k_0'$  vs. various ketone concentrations gives the second-order rate constant  $k_{\text{ketone\_LIF}}$ .

The 2M3P and 3M2P were premixed in a 10 L glass light-tight bulb with helium to form (1.0-1.8)% mixtures. The experiments were performed at a total pressure  $P \approx 100$  torr of helium in the temperature range  $T = (253-376)$  K. The ketones concentrations were calculated from their mass flow, pressure and temperature in the reaction cell. Pressure inside the reaction cell was measured with a capacitive manometer connected in the entrance of the cell.

### 2.3. Products studies

The experiments to explore the products formation from the reactions of 2M3P, 4M2P and 3M2P with OH radicals were conducted in the 7.3 m<sup>3</sup> chamber made of Teflon foil and operating at room temperature ( $T = 295$  K) and 760 Torr of purified air (RH <2%). The experimental set-up has been described previously (Ren et al., 2019; Ren et al., 2020).

The analysis of the chemicals (organic reactants and products) was performed with

in-situ Fourier Transform Infrared Spectrometry (Nicolet 5700 Magna spectrometer), online Proton Transfer Reaction - Time of Flight- Mass Spectrometer (PTR-ToF-MS, IONICON 8000), offline analysis by Gas Chromatography-Mass Spectrometry (Perkin Elmer GC-MS Clarus 600 C) and Ultra-High Performance Liquid Chromatograph-Mass Spectrometry (UHPLC-MS, Shimadzu LCMS-2020 Nexera X2). The detailed information of the employed instruments is provided in supplementary information (SI).

## 2.4. Chemicals

H<sub>2</sub>O<sub>2</sub> (50 wt%) solution was obtained from Prolabo and used as received in the chamber experiments while in the PLP-LIF experiments, it was concentrated by bubbling helium through it to reduce the water content for several days prior to use, continually concentrated during the course of the experiments and introduced into the reaction cell by passing a small flow of helium through a glass bubbler containing it. Helium carrier gas (Alphagaz 2, UHP certified >99.9999%) was used without further purification. The used chemicals were high purity commercial samples, 2M3P (≈97%, Aldrich), 4M2P (99.5%, Aldrich), 3M2P (99%, Aldrich), propane (99.95%, Air liquid company), n-butane (99.5%, Air liquid company), hexane (≥97%, Aldrich) and cyclohexane (≥99.9%, Aldrich). All the liquid compounds were further purified by repeating freeze, pump, thaw cycles and fractional distillation before use. GCMS/UHPLC-MS analysis of the used samples did not show any substantial concentrations of reactive impurities.

## 3. Results

### 3.1. Reactions rate constants measurement: RR method

Propane, n-butane, n-hexane and cyclohexane were used as reference compounds. The initial concentrations of the ketones and reference compounds were in the range (2-30) ppm. The reactions rate constants of reference compounds with OH used are:  $k_{\text{propane}}=(1.01\pm 0.15)\times 10^{-12}$  (Atkinson et al., 2006),  $k_{\text{n-butane}}=(2.30\pm 0.35)\times 10^{-12}$  (Atkinson et al., 2006),  $k_{\text{n-hexane}} = (5.07\pm 1.00)\times 10^{-12}$  (Atkinson, 2003) and  $k_{\text{cyclohexane}}=(6.84\pm 1.36)\times 10^{-12}$  (Atkinson, 2003), unit in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at T = 292±2 K.

**Figure 1(a-c)** shows the decay losses of the ketones vs. those of the reference



compounds ( $\ln(\frac{[ketone]_0}{[ketone]_t})$  against  $\ln(\frac{[ref]_0}{[ref]_t})$ ). The linear regression takes into account errors in  $\ln(\frac{[ketone]_0}{[ketone]_t})$  and  $\ln(\frac{[ref]_0}{[ref]_t})$  values. This calculation was carried out based on the program developed by Brauers and Finlayson-Pitts (1997), leading to straight line slope  $\frac{k_{ketone\_RR}}{k_{ref}}$ . The relative rate ratios,  $\frac{k_{ketone\_RR}}{k_{ref}}$ , obtained for the studied ketones are shown in **Table S1** as well as the rate constants values,  $k_{ketone\_RR}$ . The reported uncertainty for each  $k_{ketone\_RR}$  is a combination, in propagation of uncertainty

$$\frac{k_{ketone\_RR}}{k_{ref}} k_{ref} \sqrt{\left[\frac{\sigma_{k_{ref}}}{k_{ref}}\right]^2 + \left[\frac{\sigma_{k_{ketone\_RR}}}{\frac{k_{ketone\_RR}}{k_{ref}}}\right]^2} \quad (\text{Ren et al., 2020}), \text{ of the error in } \frac{k_{ketone\_RR}}{k_{ref}} \text{ and the}$$

error of  $k_{ref}$ . The recommended rate constant values as  $k_{av}$  in **Table S1** are derived from the weighted average of  $k_{ketone\_RR}$  relative to the different references:

$$k_{average} = (w_1 k_1 + w_2 k_2 + \dots + w_i k_i) / (w_1 + w_2 + \dots + w_i) \quad \text{Eq.4}$$

where  $w_i = 1/\sigma_i$ ,  $\sigma_i$  is the error, and  $k_i$  is the rate coefficient obtained with each individual reference.

The error ( $\sigma_{av}$ ) was given by:

$$\sigma_{av} = (1/\sigma_1 + 1/\sigma_2 + \dots + 1/\sigma_i)^{-0.5} \quad \text{Eq.5}$$

### 3.2. Reactions rate constants measurements: AR Method

The possible contribution of secondary OH reaction with the radicals produced in ketone+OH to the measured rate constants were made negligible by using high [ketone]/[OH] ratios, typically in the range (100-10000), and low [OH] initial concentrations. **Figure S1** shows the plot of  $k' - k_0'$  vs. [2M3P] and [3M2] obtained at room temperature and from which  $k_{1\_LIF}$  and  $k_{2\_LIF}$  were derived. The quoted errors for  $k_{1\_LIF}$  and  $k_{2\_LIF}$  include the statistical errors ( $2\sigma$  from the linear least-square analysis) and estimated systematic error (5% due to the uncertainties in the measured concentration).

**Table S2** and **Table S3** summarize the experimental conditions and the pseudo-first order rate constants over the temperature range 253-376 K for 2M3P+OH and 3M2P+OH, respectively. The plots are presented in **Figure 2**. Combining the results obtained from both AR and RR methods, we derived the following Arrhenius

expression in the temperature range  $T = 253\text{-}376$  K:

$$k_1 = (2.33 \pm 0.06) \times 10^{-12} \exp((127.4 \pm 18.6)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (1.05 \pm 0.14) \times 10^{-12} \exp((537 \pm 41)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

### 3.3. Products formation from the ketones + OH radicals

A series of experiments were conducted to investigate the OH-initiated degradation mechanisms of 2M3P, 3M2P and 4M2P in the presence of NO using the photolysis of H<sub>2</sub>O<sub>2</sub> at 254 nm as OH source. The experiments were carried out in the 7.3 m<sup>3</sup> ICARE chamber along with the following analytical techniques: FTIR, PTR-ToF-MS, HCHO monitor, UHPLC-MS and GC-MS. **Table 1** summarizes the experimental conditions and the results obtained. The initial concentrations of the ketones were in the range 90 - 1100 ppb. The typical experimental procedure consisted in monitoring the ketones concentrations, for  $\approx 1$  hour: (i) without irradiation in order to check their possible wall loss; (ii) with irradiation on (254 nm) to check possible photolysis decomposition; (iii) in the presence of H<sub>2</sub>O<sub>2</sub> and NO without irradiation to verify possible dark reactions; (iv) then the photolysis of the later gas mixture initiates the reaction of ketones with OH radicals. No significant wall loss or dark reactions have been observed for the studied ketones. However, the photolysis of 2M3P, 3M2P and 4M2P showed a decrease of these compounds and formation of a series of products. The photolysis rate constants  $J$  and the products formed are shown in **Table S4**. These data were used to correct the 2M3P, 3M2P and 4M2P consumption and products formation from the reaction of OH radicals.

#### 3.3.1. 2M3P+OH

PTR-ToF-MS showed the formation of acetone (CH<sub>3</sub>C(O)CH<sub>3</sub>) and acetaldehyde (CH<sub>3</sub>CHO) at  $m/z$  59.049 (CH<sub>3</sub>C(O)CH<sub>3</sub>H<sup>+</sup>) and 45.034 (CH<sub>3</sub>CHOH<sup>+</sup>), respectively. The formation of formaldehyde (HCHO) was confirmed by the specific and sensitive monitor (Aerolaser 4021). UHPLC-MS analysis indicated the formation of acetone, acetaldehyde, formaldehyde and propanal (CH<sub>3</sub>CH<sub>2</sub>CHO) (**Figure S2**). The formation

of acetone was also confirmed by GC-MS (**Figure S3**). The products formation from the photolysis of 2M3P (**Table S4**) and their losses due to the photolysis (**Table S4**) and reaction with OH radicals (Atkinson et al., 2006; Calvert; et al., 2008) and dilution (decay of SF<sub>6</sub>) were taken into account to derive the formation yields of acetone, acetaldehyde and formaldehyde from 2M3P+OH reaction using the equation reported by Ren et al. (2018) (see details in SI). The amounts of product formed versus the consumption of 2M3P by PTR-ToF-MS, plotted in **Figure 3a**, enabled to calculate the formation yields using the least-squares analyses. The obtained data are summarized in **Table 1**. (e.g. formaldehyde 34.0±6.0%, acetone 79.8±3.0%, and acetaldehyde 104.3±10%).

### 3.3.2. 3M2P+OH

GC-MS showed the formation of acetone and 2-butanone as reaction products (**Figure S3**). 2-Butanone, formaldehyde, acetaldehyde and propanal were detected by UHPLC-MS (**Figure S2**). Formaldehyde was quantified by the Aerolaser A4021 monitor, 2-butanone, 2,3-butanedione and acetaldehyde were quantified using PTR-ToF-MS. The corrected amounts (from the contributions of photolysis and reaction with OH) of the formed products versus the consumption of 3M2P are plotted in **Figure 3b**. The least-squares analyses lead to the formation yields given in **Table 1** (e.g. HCHO 35.4±1.1%, 2-butanone 39.8±1.9%, 2,3-butanedione 2.5±1.8%, and acetaldehyde 109.2±6.1%).

### 3.3.3. 4M2P+OH

Acetone and 2-methylpropanal were detected as products using GC-MS (**Figure S3**). The presence of acetone, formaldehyde and acetaldehyde were confirmed by UHPLC-MS (**Figure S2**). Formaldehyde was quantified by the Aerolaser 4021 monitor, acetone, 2-methylpropanal and acetaldehyde were quantified using PTR-ToF-MS. The amounts of formed products versus the consumption of the 4M2P are plotted in **Figure 3c**. The least-squares analyses lead to the formation yields given in **Table 1** (e.g. HCHO 51.9±3.5%, acetone 87.4±2.2%, and 2-methylpropanal 10.7±4.8%).

## 4. Discussion

#### 4.1. Comparison with literature data

The rate constant values for the reactions of the studied ketones (2M3P, 4M2P and 3M2P) with OH obtained in the present work are compared with the literature data for  $k_2$  and  $k_3$  in **Table 2**. We report here the first determination for  $k_1$ . It has to be noted that the reaction of 4M2P with OH has been already investigated in a previous study from our laboratory using PLP-LIF technique (Le Calvé et al., 1998). **Table 2** shows a good agreement between the values of  $k_1$ ,  $k_2$  and  $k_3$  obtained using both absolute and relative methods. Furthermore, the value of  $k_2$  from this work is in good agreement with the only existing previous relative measurement (Tuazon et al., 2003). There are several studies on  $k_3$  (Atkinson et al., 1982; Cox et al., 1980; Le Calvé et al., 1998; O'Rji and Stone, 1992; Winer et al., 1976). The reported  $k_3$  values from different groups are in fair agreement, except that from Winer et al. (1976) which is lower than the others. Calvert et al. (2011) recommended the Arrhenius expression  $k=8.0\times 10^{-13}\times\exp(828/T)$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and a rate constant of  $k = 12.8\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298K (uncertainty was estimated to be  $\pm 15\%$ ).

#### 4.2. Structure-reactivity Relationships: OH + ketones

The obtained rate constants of the studied reactions at 298 K can be also compared with the calculated ones using three structure-reactivity relationship (SAR) methods:

(1) Using the Kwok and Atkinson proposed SAR in which calculation of H-atom abstraction is based on the estimation of  $-\text{CH}<$ ,  $-\text{CH}_2-$  and  $-\text{CH}_3$  group rate constants. Assuming these groups rate constants depend only on the identity of substituents attached to these groups:

$$k_{(\text{CH}_3-\text{X})}=k_{\text{prim}}F(\text{X}), k_{(\text{X}-\text{CH}_2-\text{Y})}=k_{\text{sec}}F(\text{X})F(\text{Y}), k_{(\text{X}-\text{CH}(\text{Y})(\text{Z}))}=k_{\text{tert}}F(\text{X})F(\text{Y})F(\text{Z}).$$

At 298 K, the following parameters were used to calculate  $k_1$ ,  $k_2$  and  $k_3$ :  $k_{\text{prim}}=0.136$ ,  $k_{\text{sec}}=0.934$ ,  $k_{\text{tert}}=1.94$  (units in  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).  $F_{(-\text{CH}_3)} = 1$ ,  $F_{(-\text{CH}_2-)} = F_{(-\text{CH}<)} = F_{(>\text{C}<)} = 1.23$ ,  $F_{(>\text{CO})} = 0.75$ ,  $F_{(-\text{CH}_2\text{C}(\text{O})\text{R})}=3.9$  (Kwok and Atkinson, 1995). As shown in **Table 2**, the calculated rate constant values are:  $k_{2\text{M3P}}= 3.02\times 10^{-12}$ ,  $k_{3\text{M2P}}=3.38\times 10^{-12}$  and  $k_{4\text{M2P}}=8.86\times 10^{-12}$  (units in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). The agreement between the calculated  $k_{2\text{M3P}}$  and  $k_{4\text{M2P}}$  and the experimental ones is fairly good but a disagreement is observed between the calculated and the measured  $k_{4\text{M2P}}$ . Both the calculated and

experimental values indicate that  $k_{4M2P} > k_{3M2P} > k_{2M3P}$ . This is line with the fact that  $k(-CH<) > k(-CH_2) > k(-CH_3)$  in the  $\beta$  position relative to C=O group.

(2) Additivity method in which the rate constants for OH reaction with ketones  $RC(O)R'$  can be calculated by assuming that the reactivity of the R and R' (alkyl groups) on either side of the C=O are independent and additive:  $k_{RC(O)R'} = k_{(R)} + k_{(R')}$  (Wallington and Kurylo, 1987). Using the rate constants values for various groups,  $k_{(R)}$ , calculated previously from our group (Le Calvé et al., 1998) as shown in **Table S5**:  $k_{(n-C_2H_5)}=1.0$ ,  $k_{(iso-C_3H_7)}=2.7$ ,  $k_{(n-CH_3)}=0.1$  and  $k_{(iso-C_4H_9)}=13.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , we obtain  $k_{2M3P} = 3.7 \times 10^{-12}$  and  $k_{4M2P} = 13.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. As shown in **Table 2**, the calculated and the measured rate constant values  $k_{2M3P}$  and  $k_{4M2P}$  are in excellent agreement. Our measured  $k_{3M2P}$  has been used to derive the rate constant for sec-C<sub>4</sub>H<sub>9</sub> group not available so far:  $k_{(sec-C_4H_9)}=6.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K, (see **Table S5**).

(3)  $k_{(CH_x)}$  additivity method in which the rate constants for the reaction of OH with studied ketones can be calculated using  $k_{(CH_x)}$  ( $x = 1, 2, 3$ ) depending on their relative position to C=O group, e.g.  $k_{2M3P} = k_{\beta(-CH_3)} + k_{\alpha(-CH_2-)} + k_{\alpha(-CH-)} + k_{\beta(-CH_3)} \times 2$ . Using the recommended values of  $k_{(CH_x)}$  from Calvert et al., (2011) for reaction of OH with ketones (see **Table S6**), we derived  $k_1$ ,  $k_2$  and  $k_3$  to be 3.8, 6.2 and  $14.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. These calculated values are in excellent agreement with the experimental ones (**Table 2**).

### 4.3. Temperature dependence of the ketone + OH reaction

This work reports the first temperature dependence measurements for  $k_1$  and  $k_2$ . The temperature dependence of  $k_3$  has been reported previously by our group using the PLP-LIF technique (Le Calvé et al., 1998). The temperature dependences of  $k_2$  and  $k_3$  are significantly negative compared to that of  $k_1$  which is near zero (**Figure 2**). A near zero temperature dependence was observed and reported earlier for other reactions of OH with ketones. Le Calvé et al. (1998) found the temperature dependences for the reactions of OH with 2-butanone and 3-methyl-2-butanone to be near zero, which was explained by the fact that they only contain the deactivated -CH< or -CH<sub>2</sub>- groups in the  $\alpha$  position relative to C=O group and without the CH<sub>x</sub> ( $x=1,2$ ) groups in the  $\beta$

position relative to C=O. This is the same for 2M3P which does not contain CH<sub>x</sub> (x=1,2) in the β position of C=O group. A near zero temperature dependence is reported  $k_1$  in this work which is in line with the observation of Le Calvé et al. (1998). On the other hand, the pronounced negative temperature dependences of  $k_2$  and  $k_3$  are consistent with what was reported earlier for other ketones containing –CH< or –CH<sub>2</sub>- groups at the β, σ or γ position relative to the C=O group which are not deactivated.

#### 4.4. Reaction mechanisms of the OH + 2M3P, 3M2P and 4M2P

The concentration-reaction time profiles of 2M3P, 3M2P, 4M2P and their OH-initiated oxidation products are shown in **Figure S4(a-c)**. The experimental conditions and the results obtained are summarized in **Table 1**. The literature experimental evidence suggests that at T = 298K the ketones react with OH radicals in a similar way as alkanes via H-atom abstraction from different CH<sub>x</sub>- groups (-CH<sub>3</sub>, -CH<sub>2</sub>- and >CH-) resulting in the formation of alkyl radicals (Calvert et al., 2011). Alkyl radicals (R·) will be very quickly converted to alkoxy peroxy radicals (RO<sub>2</sub>) following the reaction with O<sub>2</sub>:



In the presence of NO, RO<sub>2</sub> could react with NO to form organic nitrate but may mainly lead to alkoxy radicals (RO):

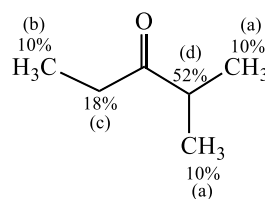


In absence of NO, the RO<sub>2</sub> self-reactions may dominate through reactions (6) and (7):

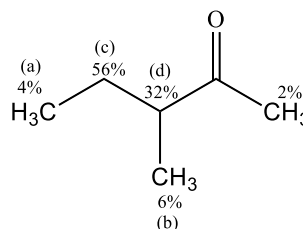


RO· radicals have various reaction channels, they further react with O<sub>2</sub>, decompose and/or isomerizes via a 6-membered transition state complex. These processes depend on the nature and the structure of RO· radicals (Orlando and Tyndall, 2012). Combining the sites attacks estimations derived from the SAR (Kwok and Atkinson, 1995) and the observed reactions products and their yields, we propose the possible reaction mechanisms for the investigated reactions displayed in **Figures 4-6**. The SAR method enables the estimation of the branching ratios of the H-atoms abstraction from the

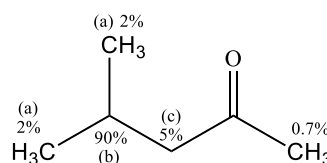
various  $-\text{CH}_3$ ,  $-\text{CH}_2-$  and  $>\text{CH}-$  groups:



$-\text{OH} + \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}(\text{CH}_3)_2$ :



$-\text{OH} + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3$ :



$-\text{OH} + (\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{O})\text{CH}_3$ :

#### 4.4.1. 2M3P+OH reaction mechanism

As shown in **Table 1**, acetaldehyde and acetone were found to be the main products from the reaction of OH radicals with 2M3P, with yields of  $104.3 \pm 10\%$  and  $79.8 \pm 3.0\%$ , respectively. These yields are in excellent agreement with to the ones derived from the SAR estimation of 102% ( $20\% \times 2 + 10\% + 52\%$ ) and 80% ( $10\% + 18\% + 52\%$ ). The formation yield of HCHO was determined to be  $34.0 \pm 6.0\%$ . Hence the carbon content of the formed products occupies  $80.4 \pm 0.7\%$  of the carbon content of the consumed 2M3P. We were not able to detect 2-methyl-pentanedione using the available analytical techniques which led us to conclude that if formed there is a possibility that it could be minor and/or bellow the detection limits of the techniques used.

#### 4.4.2. 3M2P+OH reaction mechanism

As shown in **Table 1**, acetaldehyde and 2-butanone were found to be the main products from the reaction of OH radicals with 3M2P with formation yields of  $109.2 \pm 6.1\%$  and  $39.8 \pm 1.9\%$ , respectively. The reaction occurs mainly through H-atom abstraction from  $-\text{CH}_2-$  and  $>\text{CH}-$  groups (**Figure 5(a-d)**). 2,3-Butanedione was found to be a minor product with a yield of  $2.5 \pm 1.8\%$ , it was mainly formed after H-atom

abstraction from  $-\text{CH}_2-$  group. Propanal was also observed as a minor product using UHPLC-MS at  $m/z=237$  and it is expected to be produced following the H-atom abstraction from  $-\text{CH}_3$  group. By taking into account the experimental yields of formaldehyde, 2-butanone, 2,3-butanedione and acetaldehyde, the total carbon balance is estimated to be  $70.5\pm 1.7\%$ .

#### 4.4.3. 4M2P + OH reaction mechanism

As shown in **Table 1**, acetone, 2-methylpropanal and formaldehyde were found to be the main products from the reaction of OH radical with 4M2P, determined as  $87.4\pm 2.2\%$ ,  $10.7\pm 4.8\%$  and  $51.9\pm 3.5\%$ , respectively. The formation yield of acetone,  $87.4\pm 2.2\%$ , is in reasonable agreement with the yields reported earlier by different groups. Indeed, yields of 68%, 90% and  $78\pm 6\%$  have been reported by Cox et al. (1980), Cox et al. (1981) and Atkinson et al., (1995). In addition, Atkinson et al., (1995) reported the formation of 2-methylpropanal with a yield of  $7.1\pm 1.1\%$ , which is in accordance with the present work. The possible reaction schemes for the four initially formed alkoxy radicals formed after H-atom abstraction from  $-\text{CH}_3$ ,  $-\text{CH}_2-$  and  $>\text{CH}-$  groups at different positions, are shown in **Figure 6(a-c)** as described by Atkinson and Aschmann (1995). The observed products yields indicate that acetone and 2-methylpropanal must arise almost totally following H-abstraction from  $>\text{CH}-$  and  $-\text{CH}_2-$  groups, respectively, as displayed in **Figure 6(a-c)**. Furthermore, the detected acetaldehyde using UHPLC-MS mainly formed from H-abstraction from  $-\text{CH}_3$ . By taking account of the experimental formation yields of formaldehyde, acetone and 2-methylpropanal, the total carbon balance is estimated to be  $59.5\pm 3.1\%$ .

## 5. Atmospheric implications and Conclusion

This work provides new kinetic and mechanistic information on the atmospheric chemistry of ketones, which are essentials for improving atmospheric chemical models. Indeed, both absolute (AR) and relative (RR) rate methods have been used to determine the rate constants of OH reaction with 2-methyl-3-pentanone (2M3P), 3-methyl-2-pentanone (3M2P) and 4-methyl-2-pentanone (4M2P). This work constitutes the first temperature dependence study of the reactions of OH with 2M3P and 3M2P. Taking the



average of the results obtained by both methods, the following rate constants values are recommended at 298 K (in  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>):  $k_{\text{OH}+2\text{M3P}} = 3.49 \pm 0.5$ ;  $k_{\text{OH}+3\text{M2P}} = 6.02 \pm 0.14$  and  $k_{\text{OH}+4\text{M2P}} = 11.02 \pm 0.42$ . We have compared the experimental data obtained in this work with those estimated using three estimation methods. A fair agreement was observed between different set of values. The use of our data enables to derive a new R group rate constant for sec-C<sub>4</sub>H<sub>9</sub> to be used in the group additivity relationships for OH+ketones:  $k(\text{sec-C}_4\text{H}_9) = 6.3 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The reaction of OH with ketones proceeds through initial H-atom abstraction from CH<sub>3</sub>-, -CH<sub>2</sub>- and/or >CH- groups depending on their position relative to the carbonyl group (>C=O) and the ketone chemical structure. Combining the information we obtained during the mechanistic studies on the reactions products and their measured yields along with the site attacks estimation from the SAR method, we have been able to propose various mechanistic degradation schemes of the investigation ketones initiated by reaction with OH radicals. The main reaction products and their formation yields observed experimentally are:

OH + 2M3P: formaldehyde (34.0±6.0%) + acetone (79.8±3.0%) + acetaldehyde (104.3±10%)

OH + 3M2P: formaldehyde (35.4±1.1%) + 2-butanone (39.8±1.9%) + 2,3-butanedione (2.5±1.8%) + acetaldehyde (109.2±6.1%)

OH + 4M2P: formaldehyde (51.9±3.5%) + acetone (87.4±2.2%) + 2-methylpropanal (10.7±4.8%)

This does not exclude the formation of other products that we could not detect with our experimental techniques.

Reactions of hydroxyl radicals with the ketones studied in this work appear to be relatively facile, and hence reaction with OH radicals is expected to be a major atmospheric sink for these species. However, photolysis could also contribute significantly to the atmospheric fate of these ketones during the daytime at high altitude, similarly to other ketones. Reactions with NO<sub>3</sub> radicals and O<sub>3</sub> are unlikely to be significant in comparison. The atmospheric lifetime of a compound with respect to OH radicals is a function of the rate constant and the OH concentration in the troposphere

(lifetime  $\tau = 1/k_{\text{OH}} \times [\text{OH}]$ ). Assuming a tropospheric concentration of  $2 \times 10^6$  molecule  $\text{cm}^{-3}$  for OH radicals in moderately polluted atmospheres (Prinn et al., 1995) the calculated lifetimes of the investigated ketones are 41, 24 and 13 hours for 2M3P, 3M2P and 4M2P, respectively. As a consequence of these short calculated lifetimes, the products of the OH-initiated oxidation of these species will be important in local ozone formation and also possibly in the formation of long-lived nitrogen containing compounds.

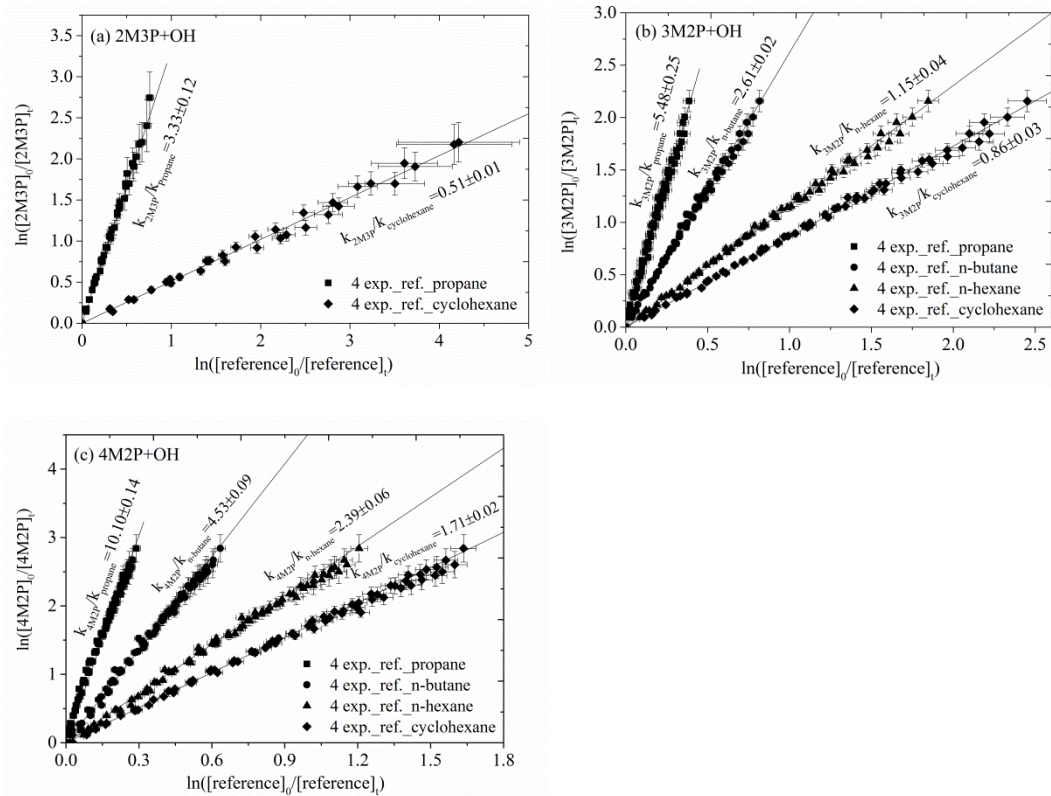
### **Acknowledgements:**

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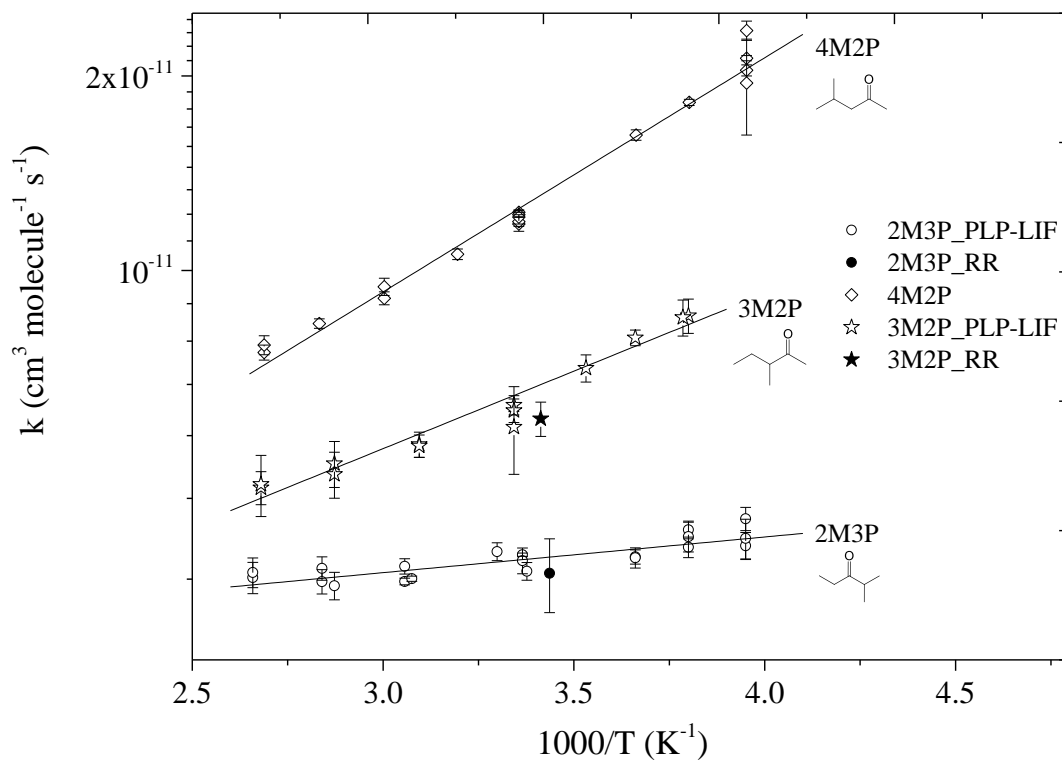
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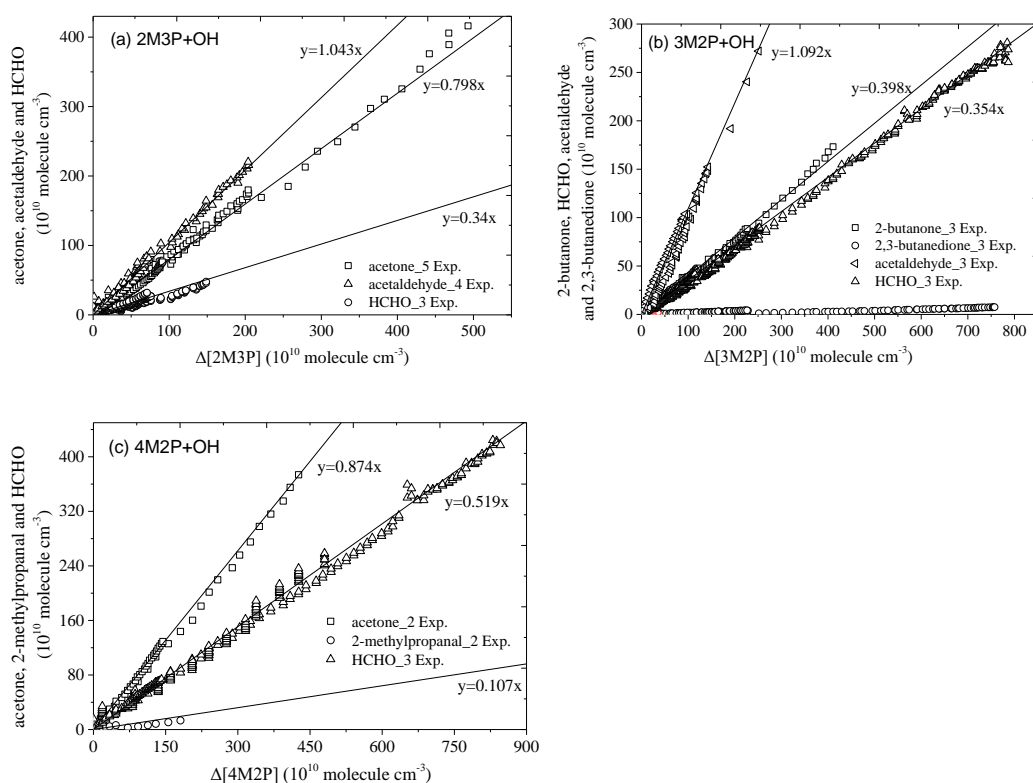
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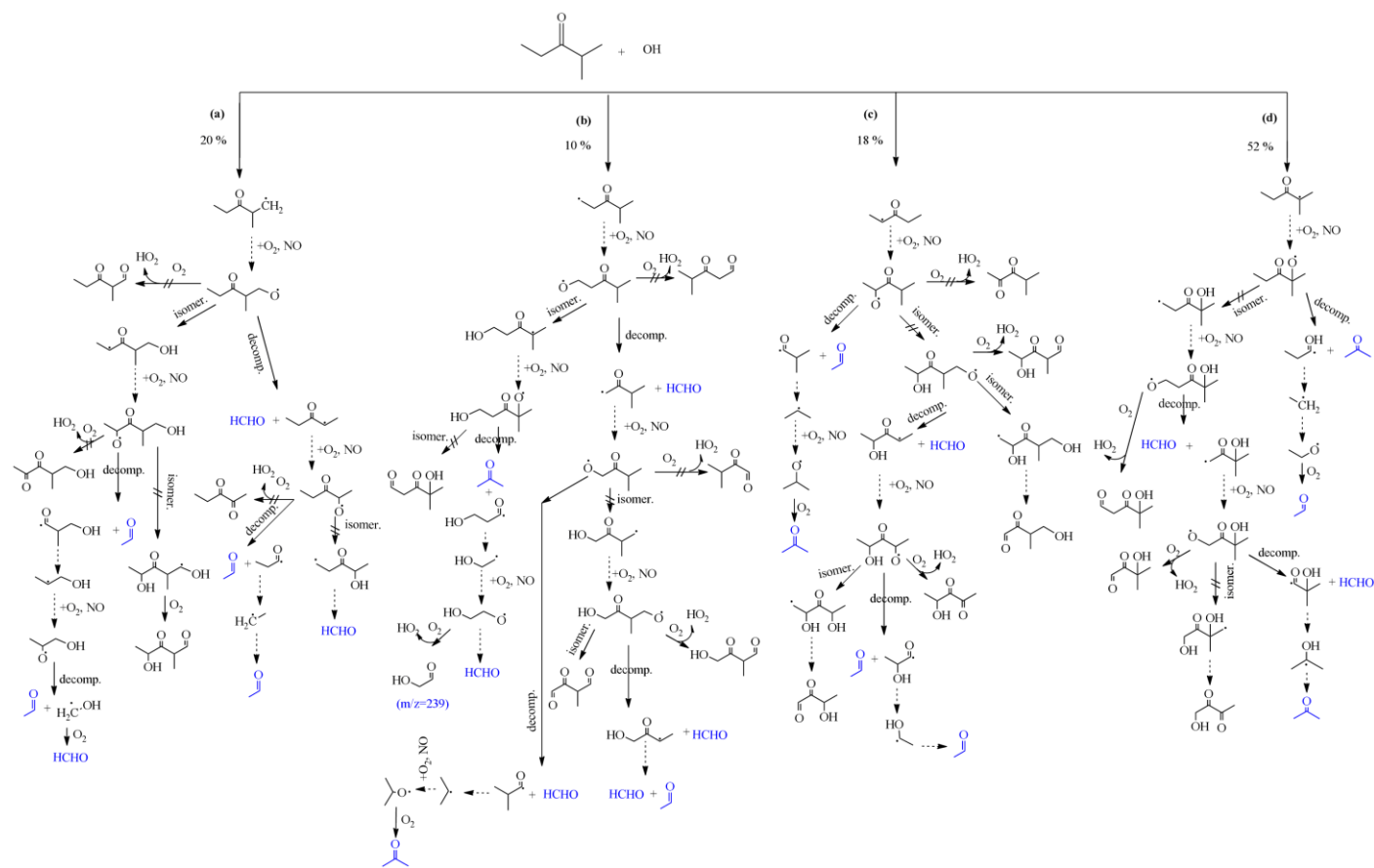
**Figure 1(a-c):** Plots of relative kinetic data from the reaction of 2M3P (a), 3M2P (b) and 4M2P (c) with OH radicals using propane, n-butane, n-hexane and cyclohexane as reference compounds. 4 exp.= 4 runs. ref.= reference



**Figure 2:** Plots of  $k_{2M3P}$  and  $k_{3M2P}$  vs  $1000/T$ . The solid lines represent the Arrhenius parameter least-squares fits to the individual data points at different temperatures. The uncertainty of each point is  $2\sigma$ . The temperature dependence data for reaction of OH radicals with 4M2P are from Le Calvé et al. (1998).

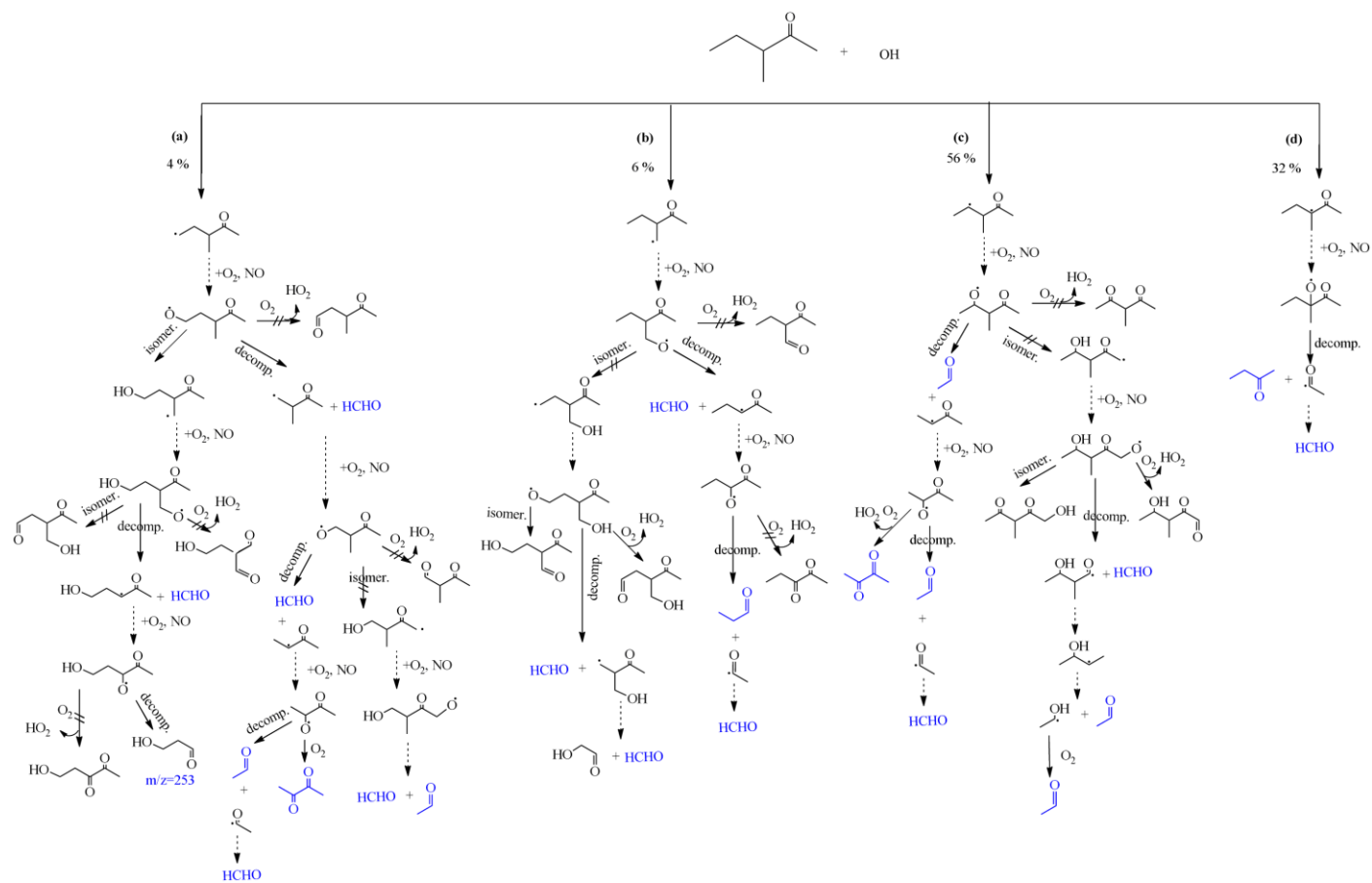


**Figure 3(a-c):** Plots of the amounts of formed products vs the consumed 2M3P (a) and 3M2P (b) and 4M2P (c), respectively. The concentration of products are corrected by their formation from the photolysis (254 nm) of 2M3P, 3M2P, 4M2P and their consumption by reacting with the OH radical, photolyzing (254 nm irradiation), diluting (decay rate of  $\text{SF}_6$ ). The acetone, acetaldehyde, 2-butanone, 2,3-butanedione, 2-methylpropanal were monitored by PTR-ToF-MS and HCHO was followed by the Aerolaser 4021 monitor. Exp. = experiment

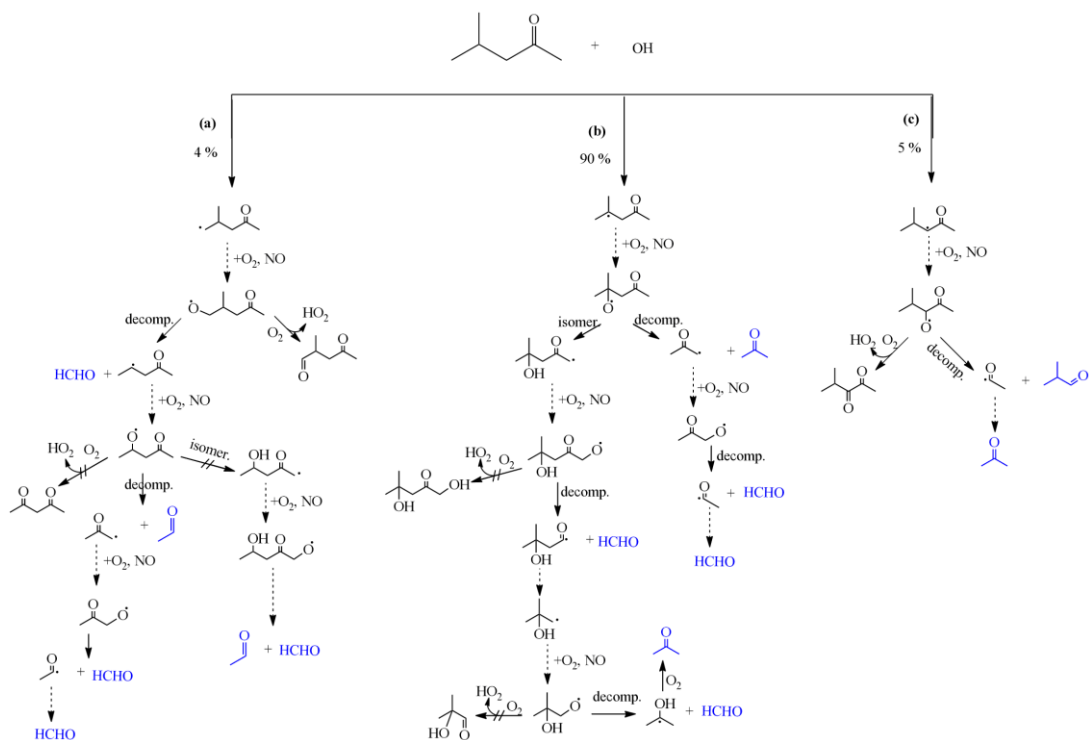


**Figure 4(a-d):** Reaction of OH radicals with 2M3P: proposed mechanism leading to the formation of observed reaction products. Compounds in blue represent products observed experimentally. The expected relative importance of the possible RO·-reaction pathways are indicated by the arrows:  $\rightarrow > \Rightarrow$ ; the intermediary of RO·/ RO<sub>2</sub>· are indicated by  $\dashrightarrow$ .





**Figure 5(a-d):** Reaction of OH radicals with 3M2P: proposed mechanism leading to the formation of observed reaction products. Compounds in blue represent products observed experimentally. The expected relative importance of the possible RO reaction pathways are indicated by the arrows:  $\rightarrow > \Rightarrow \dashrightarrow$ ; the intermediary of RO $\cdot$ /RO<sub>2</sub> are indicated by  $\cdots\rightarrow$ .



1  
 2 **Figure 6(a-c):** Reaction of OH radicals with 4M2P: proposed mechanism leading to  
 3 the formation of observed reaction products. Compounds in blue represent products  
 4 observed experimentally. The expected relative importance of the possible  
 5 RO· reaction pathways are indicated by the arrows:  $\rightarrow > \rightarrow$ ; The intermediary reaction  
 6 of RO·/ RO<sub>2</sub>· is indicated by  $\dashrightarrow$ .  
 7

8 **Table 1:** Experimental conditions and products formation for the reaction of 2M3P,  
 9 3M2P and 4M2P with OH radical at T = 296±2 K and atmospheric pressure.

Exp.	[ketone] <sub>0</sub> (ppb)	Formaldehyde (%) <sup>c</sup>	Acetone (%) <sup>c</sup>	2-butanone (%) <sup>c</sup>	2,3-BD <sup>a</sup> , 2MP <sup>b</sup> (%) <sup>c</sup>	Acetaldehyde (%) <sup>c</sup>
2M3P	1	1094	d	83.1±1.2		d
	2	514	28.1±0.1	81.9±0.6		101.7±5.7
	3	161	33.3±0.1	75.9±0.9		105.3±1.4
	4	206	d	80.5±0.1		107.4±3.8
	5	93	40.6±0.5	77.7±1.0		102.9±7.2
	<b>Average</b>		<b>34.0±6.0</b>	<b>79.8±3.0</b>		<b>104.3±10</b>
Carbon balance <sup>e</sup> (%)				80.4±0.7		
3M2P	1	523	34.5±0.1	40.9±0.4	1.2±0.1 <sup>a</sup>	104.4±1.6
	2	389	35.2±1.1	39.3±1.8	1.8±0.5 <sup>a</sup>	115.7±2.1
	3	92	36.6±1.2	39.1±0.6	4.5±0.7 <sup>a</sup>	107.4±5.5
	<b>Average</b>		<b>35.4±1.1</b>	<b>39.8±1.9</b>	<b>2.5±1.8<sup>a</sup></b>	<b>109.2±6.1</b>
Carbon balance <sup>e</sup> (%)				70.5±1.7		
4M2P	1	580	52.6±0.2	87.3±1.8	7.3±0.2 <sup>b</sup>	
	2	630	51.9±0.3	d	d	
	3	100	51.3±3.5	87.5±1.3	14.1±0.4 <sup>b</sup>	
	<b>Average</b>		<b>51.9±3.5</b>	<b>87.4±2.2</b>	<b>10.7±4.8<sup>b</sup></b>	
Carbon balance <sup>e</sup> (%)				59.5±3.1		

10 <sup>a</sup> 2,3-BD= 2,3-butanedione;

11 <sup>b</sup> 2MP= 2-methylpropanal;

12 <sup>c</sup> Indicated errors are 2σ standard deviations combined with estimated overall  
 13 uncertainties of instruments and statistic errors.

14 <sup>d</sup> The instrument did not function during this period

15 <sup>e</sup> Carbon balance = (yield<sub>1</sub>×number of carbon<sub>1</sub>/100+ yield<sub>2</sub>×number of carbon<sub>2</sub>/100  
 16 + ...)/6×100%.

17

18

19 **Table 2:** Summary of the rate constants for the reaction of OH radicals with the studied  
 20 ketones obtained in this work and in previous studies.

ketone	$k_{SAR}$	k	T (K)	Technique	Reference
2M3P	3.0 <sup>a</sup>	3.40±0.45	291±1	RR (GC-FID)	This work
	3.7 <sup>b</sup>	3.57±0.05	297±1	PLP-LIF	This work
	3.8 <sup>c</sup>				
3M2P	3.4 <sup>a</sup>	6.2±0.3	298	RR (GC-FID)	Tuazon et al., 2003
	6.2 <sup>c</sup>	5.90±0.36	293±1	RR (GC-FID)	This work
		6.13±0.11	299±1	PLP-LIF	This work
4M2P	8.9 <sup>a</sup>	9±3	305±2	RR (GC-FID)	Winer et al., 1976
	13.8 <sup>b</sup>	12.0±0.3	296	RR (GC-FID)	Cox et al., 1980
	14.0 <sup>c</sup>	14.5±0.7	299±2	RR (GC-FID)	Atkinson et al., 1982
		14.0±0.07	297±2	RR (GC-FID)	O'rji and Stone 1992
		12.1±0.5	298	PLP-LIF	Le Calvé et al., 1998
		11.02±0.42	293±1	RR (GC-FID)	This work

21 Unit of  $k_{SAR}$  and k is  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

22 <sup>a</sup> Values calculated using SAR is based on the estimation of  $-\text{CH}_3$ ,  $-\text{CH}_2-$  and  $-\text{CH}$   
 23 group rate constant ( $k_{(\text{CH}_x)}$ ) and which depend only on the identity of substituents  
 24 attached to these groups.

25 <sup>b</sup> Values calculated using SAR is based on the reactivity of R and R' group on either  
 26 side of C=O group for OH reaction with ketones as  $k_{\text{RC(O)R}'} = k_{(\text{R})} + k_{(\text{R}' )}$

27 <sup>c</sup> Values calculated using SAR is based on the rate constants for each  $\text{CH}_x$  ( $x=1, 2, 3$ )  
 28 group of ketones depend on their position relative to C=O.

29 e.g.  $k_1 = k_{\beta(-\text{CH}_3)} + k_{\alpha(-\text{CH}_2-)} + k_{\alpha(-\text{CH}-)} + k_{\beta(-\text{CH}_3)} \times 2$ .

30 PLP-LIF = Pulsed Laser Photolysis-Laser Induced Fluorescence; RR (GC-FID) =  
 31 Relative Rate method (Gas Chromatography-Flame Ionization Detection).

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