

## **Supporting Information**

### **Atmospheric Chemistry of ketones:**

#### **Reaction of OH radicals with 2-methyl-3-pentanone, 3-methyl-2-pentanone and 4-methyl-2-pentanone**

Yangang Ren<sup>1</sup>, El Mehdi El Baramoussi<sup>2</sup>, Véronique Daële<sup>1</sup>, and

Abdelwahid Mellouki<sup>1,3\*</sup>

#### **Affiliations**

<sup>1</sup> Institut de Combustion, Aérodynamique, Réactivité et Environnement (ICARE), CNRS (UPR 3021), Observatoire des Sciences de l'Univers en région Centre (OSUC), 1C Avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France

<sup>2</sup> Earth Sciences Department, Scientific Institute, Mohammed V- University, Rabat 10106, Morocco

<sup>3</sup> Environment Research Institute, School of Environmental Science and Engineering, Shandong University, Qingdao 266237, China

\*Corresponding author: A. Mellouki (mellouki@cnrs-orleans.fr)

## **1- Techniques**

### **1-1- FTIR and PTR-ToF-MS**

The FTIR is coupled to a White-type multi-path absorption cell system (optical path of 148 m), which was operated in the mid-IR region ( $4000\text{-}650\text{ cm}^{-1}$ ) and the spectra were recorded by co - adding 130 interferograms within 5 min with a  $1\text{ cm}^{-1}$  resolution. Quantitative analysis of infrared spectra was performed by subtraction using reference infrared spectra. PTR-ToF-MS spectra were analyzed by the PTR-ToF Data Analyzer (Müller et al., 2013).

### **1-2- GC-MS**

The STS25 autosampler (PerkinElmer) was also used for VOC sampling with a time period of 1 hour per tube. After collection, compounds in the stainless steel tubes (AirToxics, PerkinElmer) were desorbed using a thermal desorber (TurboMatrix™ 150 ATD) at  $330\text{ }^{\circ}\text{C}$  and transferred under ultra-high purity helium flow into the second stage trap (AirToxics, PerkinElmer), which was cooled at  $-30^{\circ}\text{C}$ , using an inlet split of 30 mL/min. This second trap was heated to  $300\text{ }^{\circ}\text{C}$  to inject the sample in a 60-m PLOT column (Agilent GS-GasPro, diameter 0.320 mm), using an outlet split of 30 mL/min. This process would reduce the background water level and improve the chromatograph peak shape. The temperature of the GC oven was programmed as follows:  $150^{\circ}\text{C}$  held for 10 min, then  $50^{\circ}\text{C min}^{-1}$  to  $300^{\circ}\text{C}$  and held for 20 min. The chromatograms were analyzed using NIST software.

### **1-3- UHPLC-MS**

Carbonyl compounds were also collected with 2,4-dinitro-phenylhydrazine (DNPH)-coated cartridges using a homemade offline auto-sampler. The derivatives created in the DNPH-coated cartridges were extracted using acetonitrile into vial and analyzed by UHPLC/MS with UV detector. The carbonyl compounds were separated with a Shimadzu column Shim-pack XR-ODS III C18 ( $2.2\mu\text{m} \times 50\text{ mm (l)} \times 3\text{ mm (i.d.)}$ ) under  $40^{\circ}\text{C}$  and ionized simultaneously with the help of the DUIS interface (Shimadzu) using two ionization methods: electrospray ionization (ESI), which is suitable for high polarity compounds, and atmospheric pressure chemical ionization (APCI), which is

suitable for low-to-medium polarity compounds. With the UHPLC/MS, the measurements could be performed while switching alternately between positive and negative ionization modes. The mass to charge ( $m/z$ ) was achieved in MS scanning using Quadrupole and qualitative plus quantitative analyzed in LabSolutions software from Shimadzu.

#### 1-4- GC-FID

A gas chromatograph equipped with a DB-1 capillary column and a flame ionization detector (GC-FID, Star 3800 CX, Varian) was used for quantitative analysis of the ketones (2-methyl-3-pentanone, 2M3P, 3-methyl-2-pentanone, 3M2P and 4-methyl-2-pentanone, 4M2P) and references. The column was operated over the temperature range of 403–448 K, and helium was used as carrier gas. Gas samples were automatically collected from the chamber and introduced via a heated sampling loop of 0.25 mL capacity to the gas chromatograph.

## 2. Correction procedure of Products formation

The concentration of each product formed from OH reaction with studied ketones was corrected to account for their losses due to the photolysis and reaction with OH radical and dilution (decay of  $\text{SF}_6$ ).  $[\text{Pro}]_{\text{corr}}$  (in molecule/ $\text{cm}^3$ ) was determined iteratively using the following recursive discrete time equation reported by Galloway et al. (2011):

$$[\text{Pro}]_{i\text{corr}} = [\text{Pro}]_{i-1\text{corr}} + \Delta[\text{Pro}] + [\text{Pro}]_{i-1} \Delta t (k_{\text{OH}+\text{Pro}}[\text{OH}] + k_{\text{loss}} + J_{\text{pro}}) - [\text{ketone}]_{i-1} \Delta t * J_{\text{ketone}} * F$$

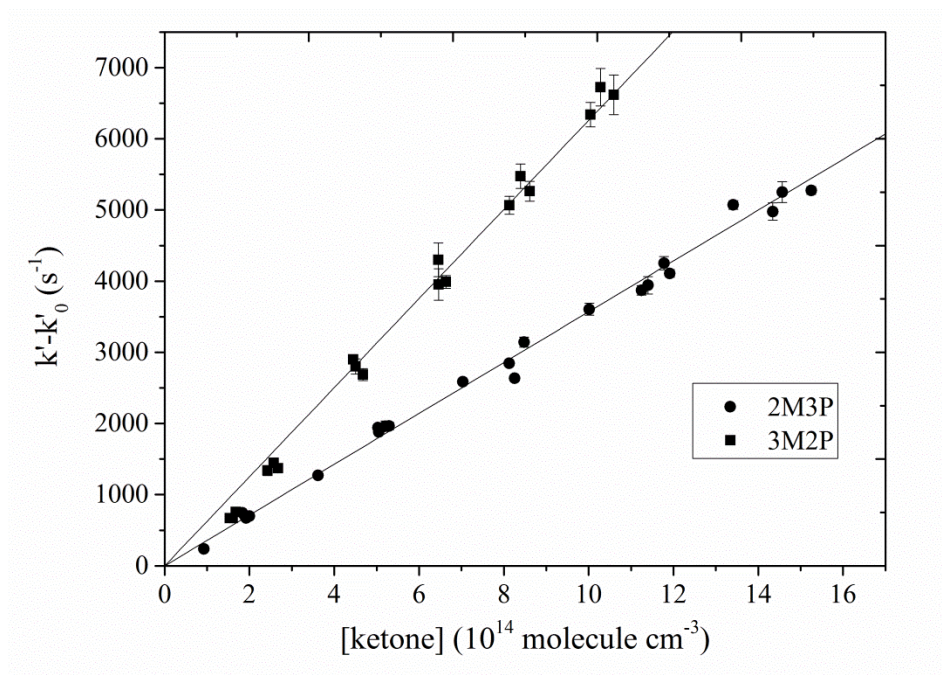
Where  $[\text{Pro}]_{i\text{corr}}$  (in molecule/ $\text{cm}^3$ ) is the corrected concentration of the product at measured time  $i$ ,  $[\text{Pro}]_{i-1}$  and  $[\text{ketone}]_{i-1}$  (in molecule/ $\text{cm}^3$ ) are the measured product and reactant concentration at time  $i-1$ , respectively.  $\Delta t$  (in sec) is the time between measured  $i$  and  $i-1$ ,  $\Delta[\text{Pro}]$  (in molecule/ $\text{cm}^3$ ) is the observed net change in  $[\text{Pro}]$  that occurs over  $\Delta t$ ,  $k_{\text{loss}}$  is the dilution decay rate obtained from  $\text{SF}_6$  (in  $\text{sec}^{-1}$ ),  $J_{\text{pro}}$  and  $J_{\text{ketone}}$  are the photolysis rates of products and reactant upon the light intensity obtained in Table S4, respectively.  $F$  is products formation yield from the photolysis of reactants obtained in Table S4.  $k_{\text{OH}+\text{Pro}}$  is rate constant of the product reaction with OH obtained from

Atkinson et al. (2006);Calvert; et al. (2008) and IUPAC. [OH] is the OH concentration and is estimated from:

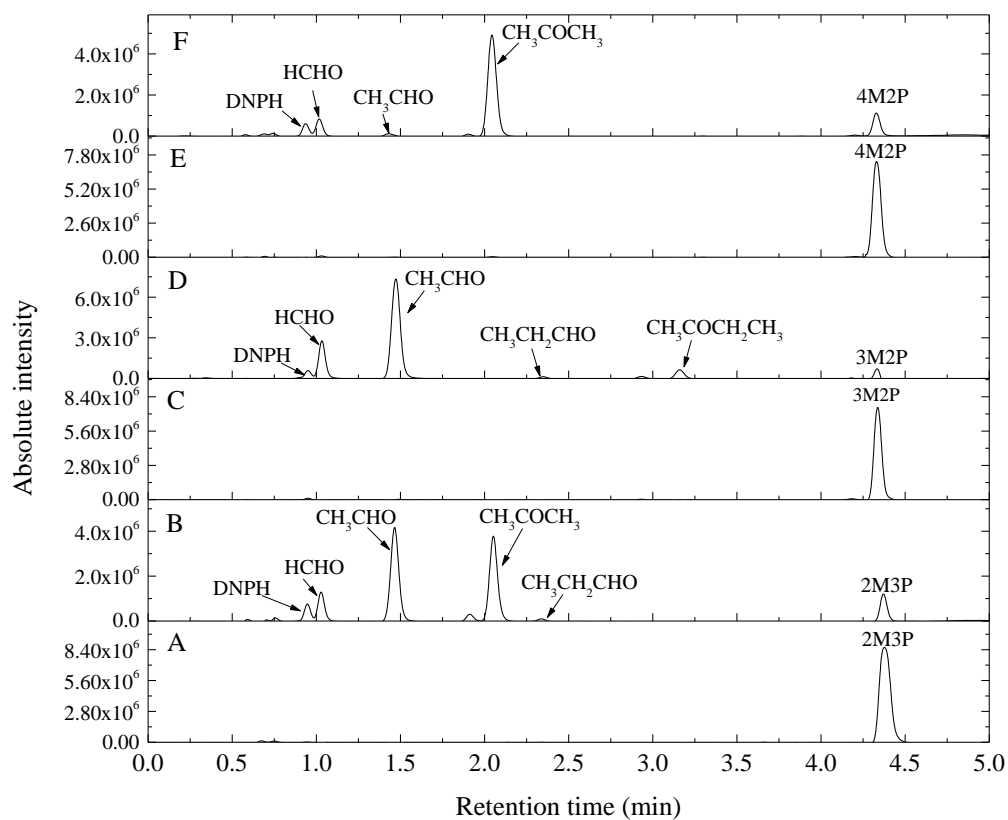
$$[\text{OH}] = - \frac{1}{k_{\text{OH}+\text{ketone}}} \left( \frac{1}{[\text{ketone}]_{i-1}} * \frac{\Delta[\text{ketone}]}{\Delta t} \right)$$

Where  $[\text{ketone}]_{i-1}$  (in molecule/cm<sup>3</sup>) is measured product concentration at time i-1,

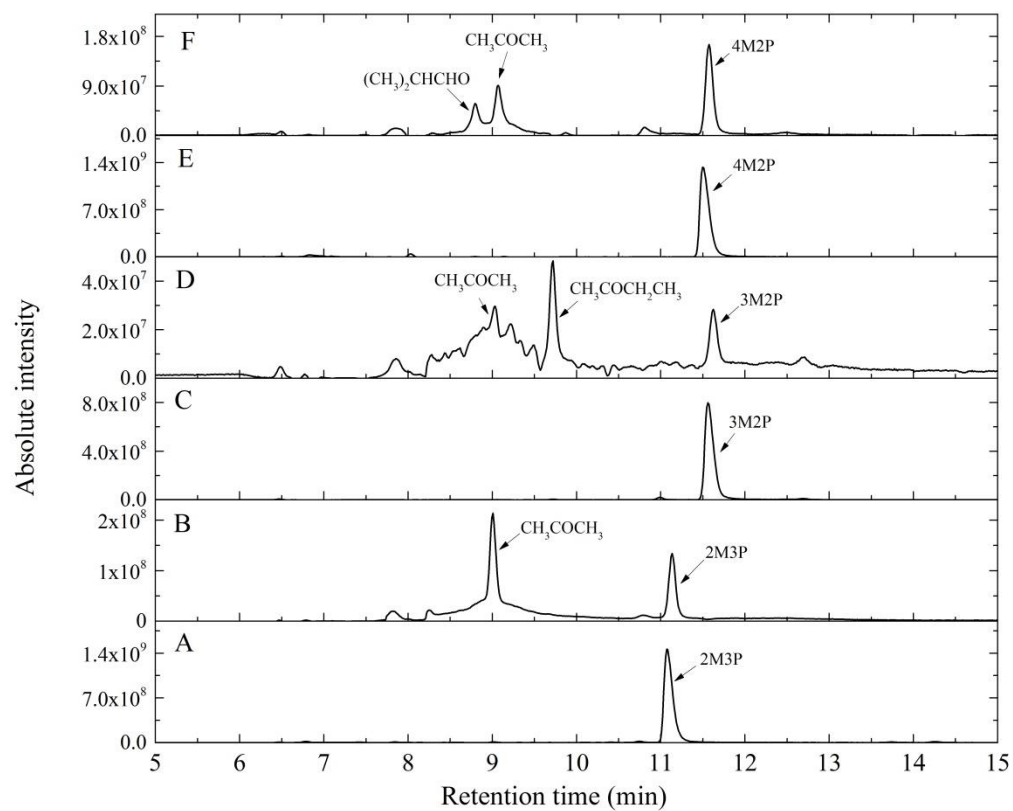
$\frac{\Delta[\text{ketone}]}{\Delta t}$  is the concentration change per time unit.



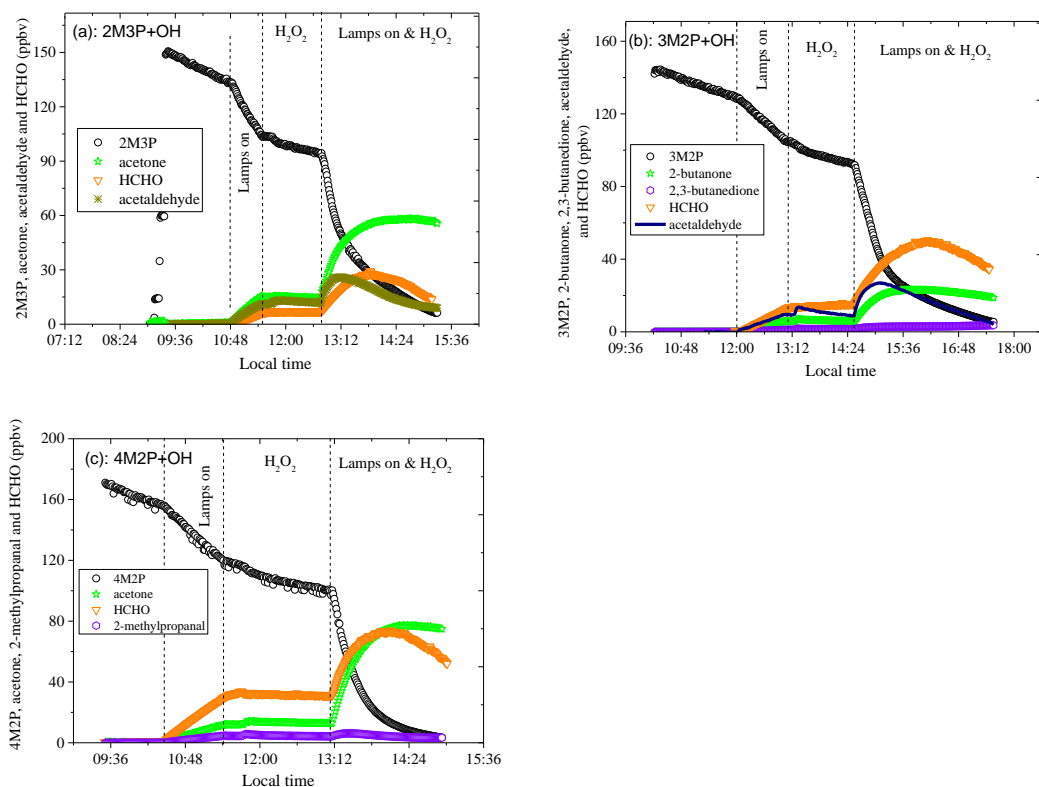
**Figure S1:** Plot of  $(k' - k'_0)$  vs 2M3P and 3M2P concentration at room temperature (296-303 K). The lines represent the linear least-squares fitting. Note:  $k' = k_{\text{ketone}} \times [\text{ketone}] + k'_0$ ,  $k_{\text{ketone}}$  is the rate constant of OH radical reaction with ketones.  $k'_0 = k_{\text{H}_2\text{O}_2} \times [\text{H}_2\text{O}_2] + k_{\text{diff}}$ ,  $k_{\text{H}_2\text{O}_2}$  is the rate constant of OH radical reaction with  $\text{H}_2\text{O}_2$  and  $k_{\text{diff}}$  is the decay rate of OH radical due to the diffusional loss.



**Figure S2:** The chromatogram spectra from UHPLC-MS analysis: (A) before and (B) after 1 hour reaction of 2M3P with OH radical; (C) before and (D) after 1 hour reaction of 3M2P with OH radical; (E) before and (F) after 1 hour reaction of 4M2P with OH radical.



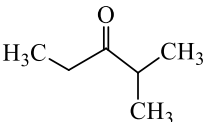
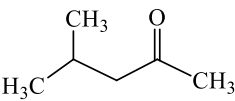
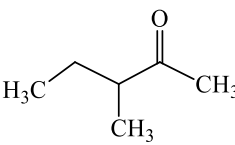
**Figure S3:** The chromatogram spectra from GC-MS analysis: (A) before and (B) after 1 hour reaction of 2M3P with OH radical; (C) before and (D) after 1 hour reaction of 3M2P with OH radical; (E) before and (F) after 1 hour reaction of 4M2P with OH radical.



**Figures S4(a-c):** Time-concentration profiles of reactants (2M3P, 3M2P and 4M2P) and the products formed during the photolysis and OH reaction experiment



**Table S1:** Experimental conditions and rate constants of ketone+OH using RR method.

ketone	Structure	ref.	exp. $T$ (K)	$\frac{k_{ketone\_RR}}{k_{ref}}$ <sup>a</sup>	$k_{ketone\_RR}$ <sup>b</sup> (10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$k_{av}$ <sup>c</sup>
2M3P		propane	1	3.25±0.25	3.39±0.38	3.40±0.45
		cyclohexane	2	3.35±0.24	3.42±0.42	
			3	3.30±0.24		
			4	3.41±0.24		
			1	0.48±0.02		
		2	0.53±0.02	3.40±0.45		
		3	0.48±0.02			
		4	0.53±0.02			
4M2P		propane	1			10.44±0.74
		n-butane	2	9.94±0.44	10.41±0.63	
			3	10.17±0.44		
			4	10.20±0.42		
			1	4.49±0.17		11.99±0.78
		2	4.58±0.12			
		3	4.63±0.12			
		4	4.42±0.10			
		n-hexane	1	2.47±0.06	11.60±0.76	
		2	2.36±0.04			
		3	2.38±0.04			
		4	2.35±0.04			
		cyclohexane	1	1.70±0.04	11.60±0.76	
		2	1.73±0.03			
		3	1.72±0.03			
		4	1.68±0.03			
3M2P		propane	1	5.92±0.75	5.78±0.51	5.90±0.36
		n-butane	2	5.62±0.54	6.05±0.48	
			3	5.52±0.47		
			4	5.42±0.57		
			1	2.75±0.09		
		2	2.62±0.05			
		3	2.68±0.07			
		4	2.50±0.05			
		n-hexane	1	1.19±0.03	5.86±0.54	
		2	1.18±0.02			
		3	1.16±0.02			
		4	1.12±0.02			
		cyclohexane	1	0.88±0.02	5.86±0.54	
		2	0.88±0.01			
		3	0.87±0.01			
		4	0.84±0.01			

<sup>a</sup> The uncertainties for  $k_{\text{ketone\_RR}}/k_{\text{ref}}$  are  $2\sigma$  of least-squares of  $\ln\left(\frac{[\text{ketone}]_0}{[\text{ketone}]_t}\right)$  vs  $\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right)$ .

<sup>b</sup> The uncertainties for  $k_{\text{ketone\_RR}}$  were estimated by combining the uncertainty of  $k_{\text{ketone\_RR}}/k_{\text{ref}}$  with the uncertainty of references

<sup>c</sup> Weighted average  $k_{\text{av}} = (w_1k_1 + w_2k_2 + \dots + w_ik_i) / (w_1 + w_2 + \dots + w_i)$

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 ( $\sigma_{\text{av}}$ ) was given by:  $\sigma_{\text{av}} = (1/\sigma_1 + 1/\sigma_2 + \dots + 1/\sigma_i)^{-0.5}$

**Table S2:** Experimental conditions and the measured rate constants for the reaction of 2M3P+OH with PLP-LIF.

$T$ (K)	$[2M3P]$ ( $10^{14}$ molecule $\text{cm}^{-3}$ )	$k'_0$ ( $\text{s}^{-1}$ ) <sup>b</sup>	$k'$ ( $\text{s}^{-1}$ ) <sup>a</sup>	$k'-k'_0$ ( $\text{s}^{-1}$ )	$k_{2M3P\_LIF} \pm 2\sigma$ ( $10^{-12}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
253	2.3-17.8	111-115	958-6680	845-6567	3.43 $\pm$ 0.05
253	2.4-17.9	115-116	1000-7019	884-6904	3.31 $\pm$ 0.02
253	2.2-16.8	112-143	1021-6989	908-6875	3.46 $\pm$ 0.07
263	2.1-16.1	113-282	940-6382	826-6100	3.30 $\pm$ 0.07
263	2.2-17.0	139-145	987-6180	845-6038	3.35 $\pm$ 0.09
263	2.3-16.9	128	1051-6036	923-5908	3.49 $\pm$ 0.05
273	2.0-15.7	107-113	767-5451	657-5341	3.68 $\pm$ 0.06
273	2.1-16.4	124-126	857-5738	732-5613	3.61 $\pm$ 0.05
296	2.0-15.3	83-135	320-5357	236-5274	3.97 $\pm$ 0.06
297	1.8-14.3	127-142	872-5105	745-4978	4.13 $\pm$ 0.09
297	1.9-14.6	112-113	813-5363	701-5250	3.63 $\pm$ 0.01
303	1.9-13.4	120-122	793-5193	672-5072	3.56 $\pm$ 0.08
325	1.7-13.3	120	784-4349	667-4233	3.26 $\pm$ 0.08
327	0.8-13.4	108-142	218-4613	109-4478	3.41 $\pm$ 0.09
327	1.7-14.3	117	699-4836	582-4719	3.34 $\pm$ 0.02
348	1.6-12.5	111-112	633-3932	522-3820	3.60 $\pm$ 0.06
352	0.9-8.7	107-130	423-3147	297-3026	3.73 $\pm$ 0.07
352	1.7-13.2	110-113	605-4474	493-4363	3.75 $\pm$ 0.09
376	1.1-12.1	124-108	421-4183	305-4067	3.85 $\pm$ 0.14
376	1.5-11.7	122-124	643-3842	520-3701	3.88 $\pm$ 0.10
298					3.57 $\pm$ 0.05
253-376 <sup>c</sup>	$A^c$ ( $10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ): 1.64 $\pm$ 0.09			$E/R^d$ (K): (127.4 $\pm$ 18.6)	

<sup>a</sup>  $k' = k_{\text{ketone}} \times [\text{ketone}] + k'_0$ ;  $k_{\text{ketone}}$  is the rate constant of OH radical reaction with ketones

<sup>b</sup>  $k'_0 = k_{\text{H}_2\text{O}_2} \times [\text{H}_2\text{O}_2] + k_{\text{diff}}$ ;  $k_{\text{H}_2\text{O}_2}$  is the rate constant of OH radical reaction with  $\text{H}_2\text{O}_2$ ;  $k_{\text{diff}}$  is the decay rate of OH radical due to the diffusional loss.

<sup>c</sup> The uncertainties for  $A$  is  $\Delta A = 2A\sigma \ln A$  for the Arrhenius form.;

<sup>d</sup> The uncertainties for  $E/R$  is  $\Delta E/R = 2\sigma E/R$  for the Arrhenius form.

<sup>e</sup> Arrhenius expression using all data from AR and RR methods.

**Table S3:** Experimental conditions and the measured rate constants for the reaction of 3M2P+OH with PLP-LIF.

$T$ (K)	$[3M2P]$ ( $10^{14}$ molecule $\text{cm}^{-3}$ )	$k'_0$ ( $\text{s}^{-1}$ ) <sup>b</sup>	$k'$ ( $\text{s}^{-1}$ ) <sup>a</sup>	$k'-k'_0$ ( $\text{s}^{-1}$ )	$k_{3M2P\_LIF} \pm 2\sigma$ ( $10^{-12}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
263	1.8-11.4	11-359	1711-10419	1600-10061	8.5 $\pm$ 0.5
264	1.8-10.9	138-326	1400-9797	1224-9484	8.5 $\pm$ 0.5
273	1.7-11	131-362	1381-9005	1208-8651	7.9 $\pm$ 0.2
283	1.6-10.3	179-350	807-7616	596-7277	7.1 $\pm$ 0.3
299	1.5-10.1	114-150	818-6484	670-6339	6.2 $\pm$ 0.2
299	1.7-10.6	239-287	949-6895	756-6618	6.1 $\pm$ 0.3
323	1.5-9.3	191-211	737-5366	600-5162	5.4 $\pm$ 0.2
323	1.4-9.1	207-239	890-5218	741-4987	5.4 $\pm$ 0.2
348	1.4-8.8	206-219	717-4700	568-4483	4.8 $\pm$ 0.4
348	1.4-8.7	122-225	714-4613	585-4439	5.0 $\pm$ 0.4
373	1.3-8.3	135-193	646-4001	500-3823	4.6 $\pm$ 0.3
373	1.3-8.1	134-233	619-4095	485-3909	4.7 $\pm$ 0.5
299					6.13 $\pm$ 0.11
263-373 <sup>c</sup>	A <sup>c</sup> ( $10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ): 1.05 $\pm$ 0.14			E/R <sup>d</sup> (K): (537 $\pm$ 41)	

<sup>a</sup>  $k' = k_{\text{ketone}} \times [\text{ketone}] + k'_0$ ;  $k_{\text{ketone}}$  is the rate constant of OH radical reaction with ketones

<sup>b</sup>  $k'_0 = k_{\text{H}_2\text{O}_2} \times [\text{H}_2\text{O}_2] + k_{\text{diff}}$ ;  $k_{\text{H}_2\text{O}_2}$  is the rate constant of OH radical reaction with  $\text{H}_2\text{O}_2$ ;  $k_{\text{diff}}$  is the decay rate of OH radical due to the diffusional loss.

<sup>c</sup> The uncertainties for A is  $\Delta A = 2A\sigma \ln A$  for the Arrhenius form.;

<sup>d</sup> The uncertainties for E/R is  $\Delta E/R = 2\sigma E/R$  for the Arrhenius form.

<sup>e</sup> Arrhenius expression using all data from AR and RR methods.

**Table S4:** The photolysis rate constants of 2M3P, 3M2P, 4M2P, formaldehyde, ethanal, acetone, 2-butanone, 2,3-butanedione and 2-methylpropanal using 14 lamps (254 nm) in the ICARE 7.3 m<sup>3</sup> chamber and the products yields from the photolysis of 2M3P, 3M2P and 4M2P.

VOC	J (10 <sup>-5</sup> s <sup>-1</sup> )	HCHO (%)	Acetone (%)	Ethanal (%)	2B (%)	2,3-BD (%)	2MP (%)
2M3P	8.0±0.2	20.0±0.5	64.6±1.2	50.9±6.7			
3M2P	4.5±0.1	59.8±0.8		62.4±9.8	43.4±0.6	8.2±0.1	
4M2P	5.3±0.1	87.7±2.3	59.2±1.7				115.3±6.0
HCHO	3.9±0.1						
Acetone	6.8±0.2						
Ethanal	6.5±0.3						
2B	10.7±0.2						
2,3-BD	5.2±0.1						
2MP	274.4±1						

The uncertainties are 1σ of the repeat experiments.

2B: 2-butanone, 2,3-BD: 2,3-butanedione, 2MP: 2-methylpropanal

**Table S5:** Reactivity of Alkyl groups R or R' in ketones (RC(O)R') for ketone + OH reaction at 298 K from Le Calvé et al., (1998).

alkyl group R (R')	$10^{12} \times k_{(R)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
CH <sub>3</sub> -	0.1
n-C <sub>2</sub> H <sub>5</sub> -	1
n-C <sub>3</sub> H <sub>7</sub> -	3.9
iso-C <sub>3</sub> H <sub>7</sub> -	2.7
n-C <sub>4</sub> H <sub>9</sub> -	9
sec-C <sub>4</sub> H <sub>9</sub> -	6.3 <sup>a</sup>
iso-C <sub>4</sub> H <sub>9</sub> -	13.7
tert-C <sub>4</sub> H <sub>9</sub> -	1.1
n-C <sub>5</sub> H <sub>11</sub> -	8.8
iso-C <sub>5</sub> H <sub>11</sub> -	10.2

<sup>a</sup> Value recommended from the experimental data of  $k_{3M2P}$  obtained in this work.

**Table S6:** CH<sub>x</sub> (x=1, 2, 3) group rate coefficients  $k_{(\text{CH}_x)}$  for reaction of OH radical with ketones at 298 K from Calvert et al., (2011)(units are  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )

CH <sub>x</sub> group	$\alpha$ - position	$\beta$ -position	$\gamma$ - position	$>\delta$ - position
-CH <sub>3</sub>	0.1	0.37	0.27	0.12
-CH <sub>2</sub> -	0.7	3.5	2.4	1.2
>CH-	2.0	12.7	7.8	2.9

## References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Subcommittee, I.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, *Atmos. Chem. Phys.*, 6, 3625-4055, 10.5194/acp-6-3625-2006, 2006.
- Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and J., W. T.: *The Mechanisms of Atmospheric Oxidation of the Oxygenates*, Oxford University Press, New York, 2011.
- Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S., and Wallington, T. J.: *Mechanisms of Atmospheric Oxidation of the Alkanes*, Oxford University Press, USA, 2008.
- Galloway, M. M., Huisman, A. J., Yee, L. D., Chan, A. W. H., Loza, C. L., Seinfeld, J. H., and Keutsch, F. N.: Yields of oxidized volatile organic compounds during the OH radical initiated oxidation of isoprene, methyl vinyl ketone, and methacrolein under high-NO<sub>x</sub> conditions, *Atmos. Chem. Phys.*, 11, 10779-10790, 10.5194/acp-11-10779-2011, 2011.
- Müller, M., Mikoviny, T., Jud, W., D'Anna, B., and Wisthaler, A.: A new software tool for the analysis of high resolution PTR-TOF mass spectra, *Chemom. Intell. Lab. Syst.*, 127, 158-165, <http://dx.doi.org/10.1016/j.chemolab.2013.06.011>, 2013.