



Kinetic and Product studies of OH Reactions with a series of Ketones

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2016.10.12

Content

- Part I. Introduction
- Part II. Kinetic studies
 - Absolute Rate method (AR)
 - Relative Rate method (RR)
 - Comparison
- Part III. Products yields and proposed mechanism
- Part IV. Atmospheric implications and Conclusion

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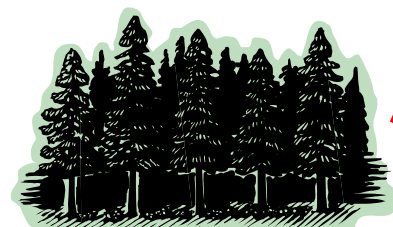
Ketones

Part I

- Emission sources

Ketones are among the most important VOCs in the atmosphere

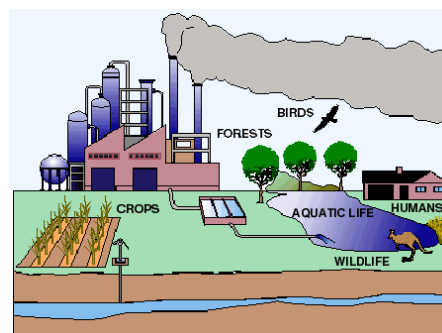
Main fate of ketones is reaction with **OH radical** in the atmosphere



Biogenic

~43 Tg/yr⁻¹

Acetone
2-butanone
4M2P



Anthropogenic

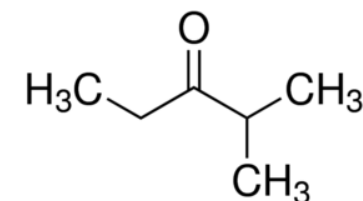
~36 Tg/yr⁻¹

- OH reaction with ketone

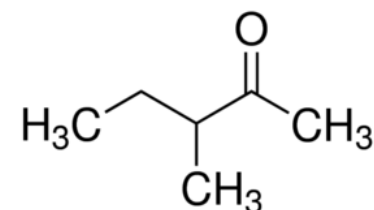
- H-abstraction from -CH_x group
- Structure-Activity Relations (**SARs**) indicate that the reactivity of CH_x group toward OH depends on their relative position to C=O group

(Calvert J.G. et al. 2011, Book)

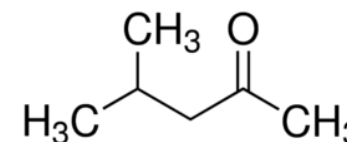
(A. Mellouki et al. Chem. Rev. 2015, 115, 3984–4014)



2-methyl-3-pentanone
(2M3P)



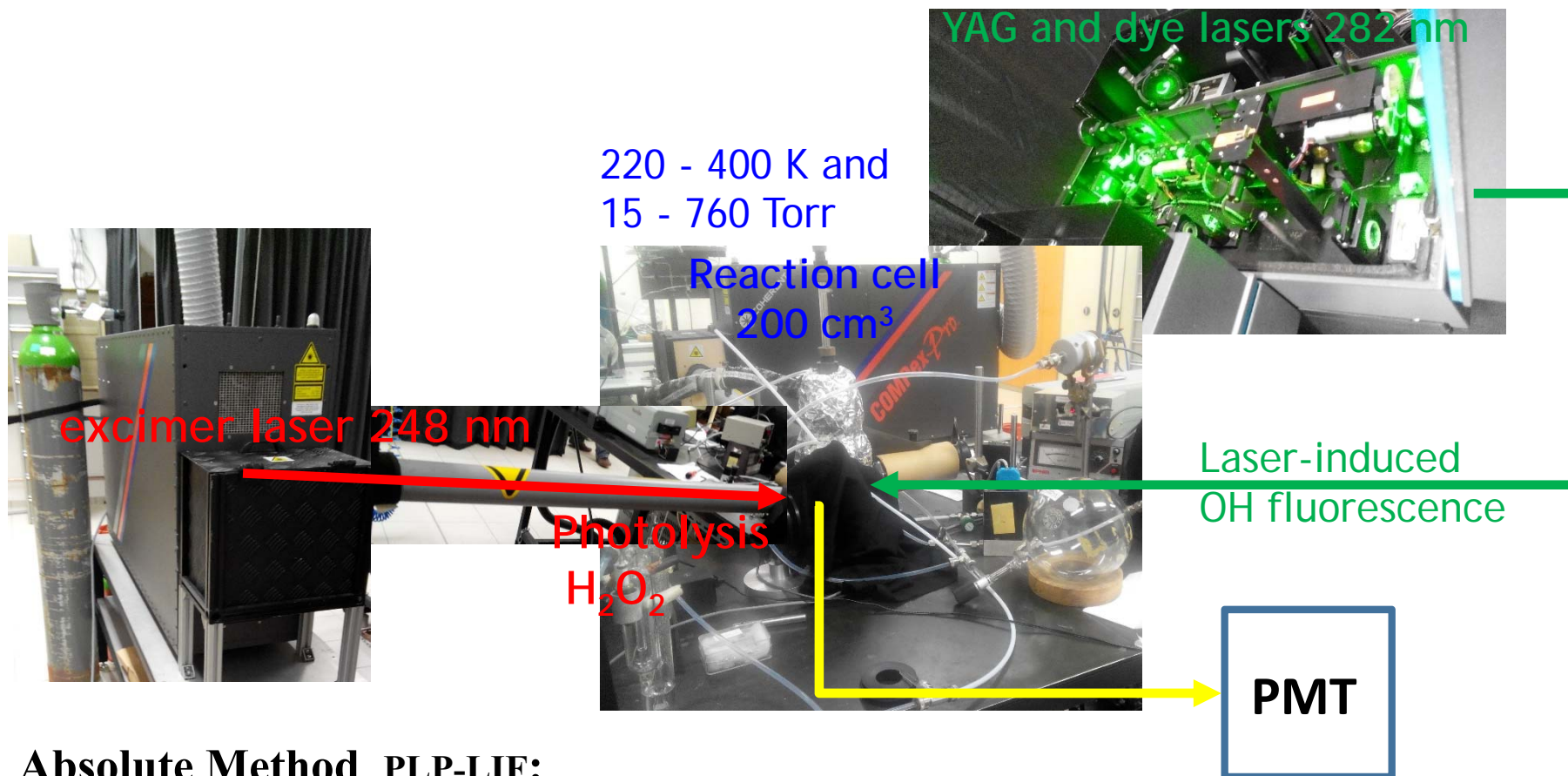
3-methyl-2-pentanone
(3M2P)



4-methyl-2-pentanone
(4M2P)

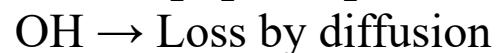
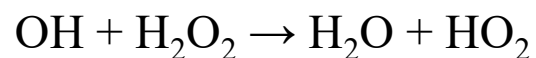
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➤ Absolute Method_PLP-LIF:

The **decay rate of OH** in the reaction cell is monitored:



$$k_{\text{ketone_LIF}}$$

$$k_{\text{H}_2\text{O}_2}$$

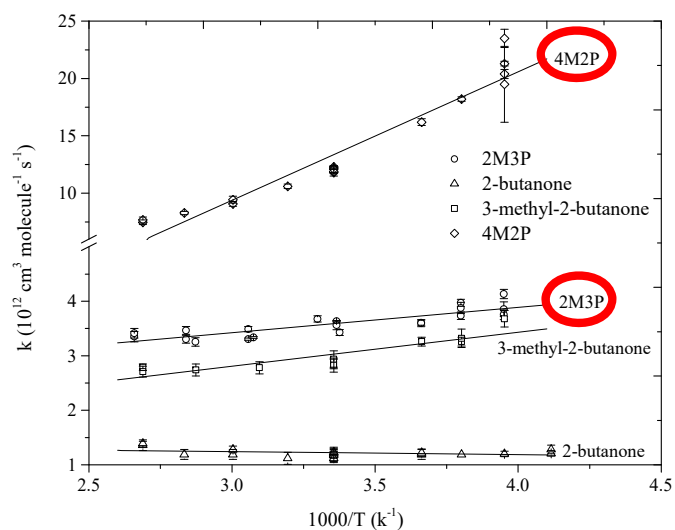
$$k_{\text{diff}}$$

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

$$k' = k_{\text{ketone_LIF}}[\text{ketone}] + k_0'$$

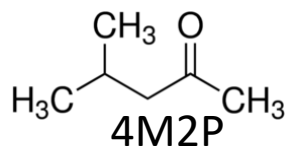
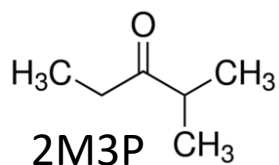
$$k_0' = k_{\text{H}_2\text{O}_2} + k_{\text{diff}}$$

Table 1 Experimental conditions and the measured rate constants for the reaction **2M3P+OH** by absolute method in PLP-LIF.



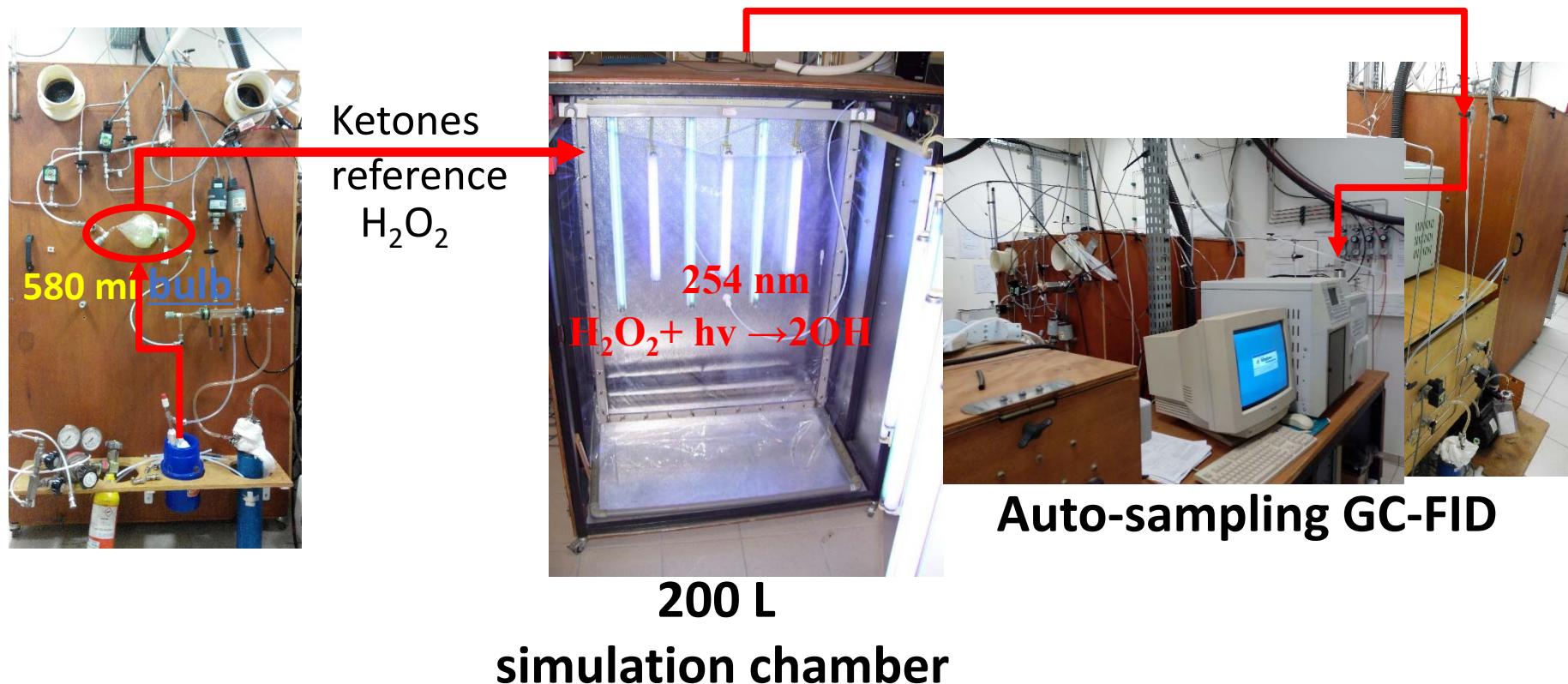
Temperature dependence

- for 2M3P+OH is **near zero**
- for 4M2P+OH is **significantly negative**



T (K)	[2M3P] (10 ¹⁴ molecule cm ⁻³)	k' ₀ (s ⁻¹)	k' (s ⁻¹)	k'-k' ₀ (s ⁻¹)	k _{2M3P-OH} ±2σ (10 ¹² cm ³ molecule ⁻¹ s ⁻¹)
253	2.3-17.8	111-115	958-6680	845-6567	3.43±0.05
253	2.4-17.9	115-116	1000-7019	884-6904	3.31±0.02
253	2.2-16.8	112-1434	1021-6989	908-6875	3.46±0.07
263	2.1-16.1	113-282	940-6382	826-6100	3.30±0.07
263	2.2-17.0	139-145	987-6180	845-6038	3.35±0.09
263	2.3-16.9	128-130	1051-6036	923-5908	3.49±0.05
273	2.0-15.7	107-113	767-5451	657-5341	3.68±0.06
273	2.1-16.4	124-126	857-5738	732-5613	3.61±0.05
296	2.0-15.3	83-135	320-5357	236-5274	3.97±0.06
297	1.8-14.3	127-142	872-5105	745-4978	4.13±0.09
297	1.9-14.6	112-113	813-5363	701-5250	3.63±0.01
303	1.9-13.4	120-122	793-5193	672-5072	3.56±0.08
325	1.7-13.3	120	784-4349	667-4233	3.26±0.08
327	0.8-13.4	108-142	218-4613	109-4478	3.41±0.09
327	1.7-14.3	117	699-4836	582-4719	3.34±0.02
348	1.6-12.5	111-112	633-3932	522-3820	3.60±0.06
352	0.9-8.7	107-130	423-3147	297-3026	3.73±0.07
352	1.7-13.2	110-113	605-4474	493-4363	3.75±0.09
376	1.1-12.1	124-108	421-4183	305-4067	3.85±0.14
376	1.5-11.7	122-124	643-3842	520-3701	3.88±0.10
297					3.54±0.04

C=O deactivates CH_x in α position



➤ Relative Method_200 L chamber:

The decay of ketones and references in the chamber were monitored:

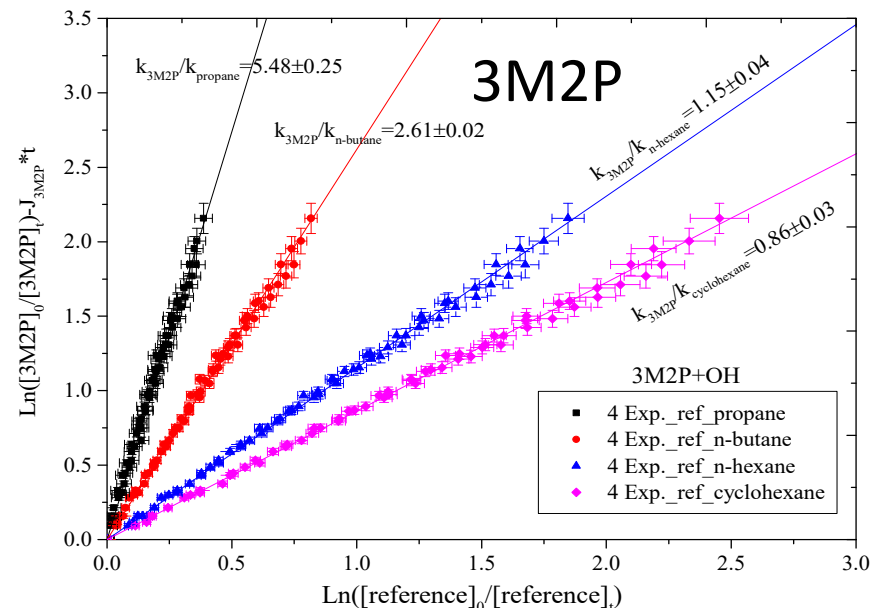
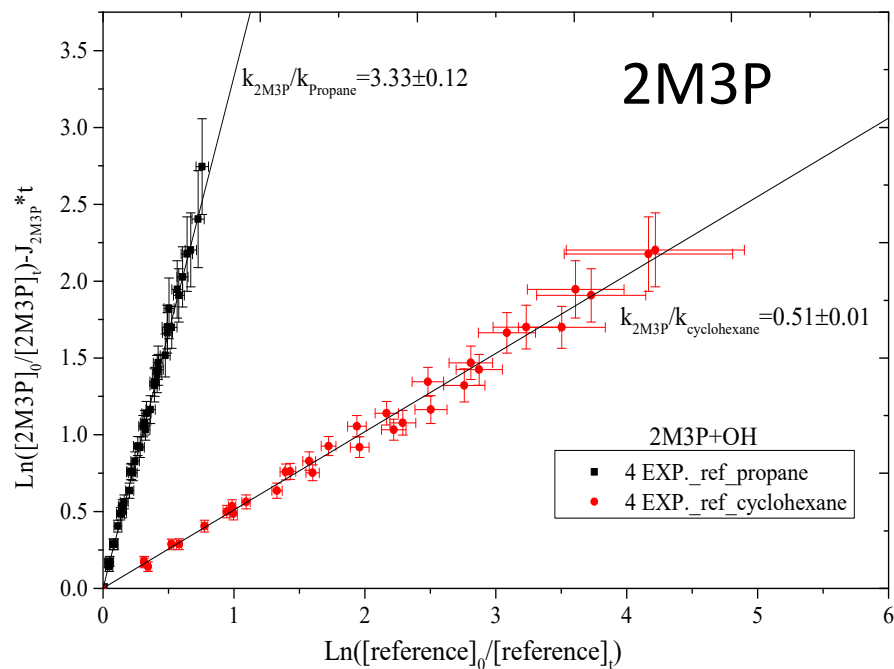


$$k_{\text{ketone_RR}}$$

$$k_{\text{ref}}$$

$$k_{\text{L-ketone}} / k_{\text{L-ref}}$$

- Then: $\ln([\text{ketone}]_0 / [\text{ketone}]_t) - J_{\text{ketone}} * t = k_{\text{ketone_RR}} / k_{\text{ref}} * (\ln([\text{reference}]_0 / [\text{reference}]_t))$



References

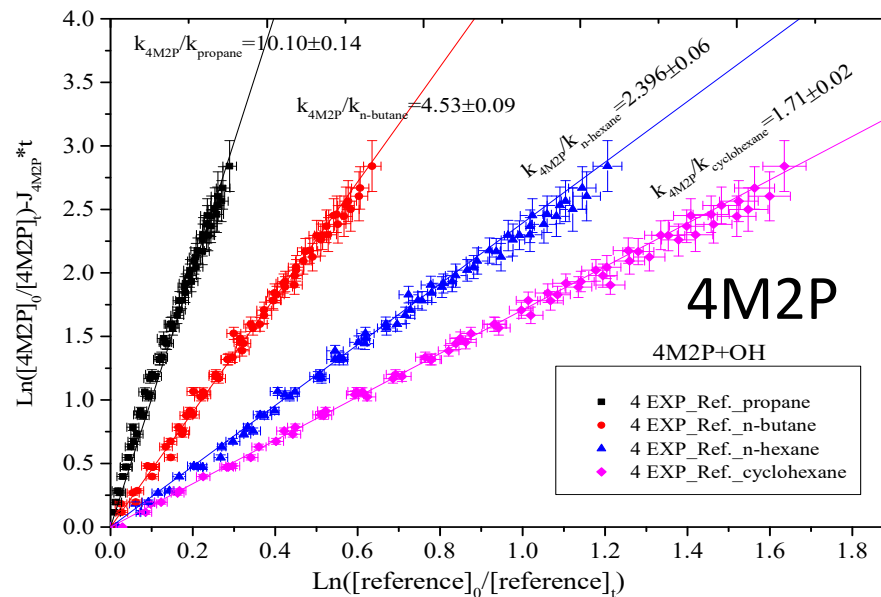
$$k_{(\text{propane}+\text{OH})} = 1.03 \text{ (IUPAC),}$$

$$k_{(\text{n-butane}+\text{OH})} = 2.29 \text{ (IUPAC),}$$

$$k_{(\text{n-hexane}+\text{OH})} = 5.06 \text{ (Atkinson 2003)}$$

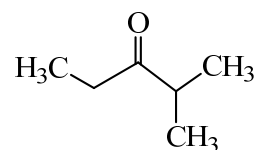
$$k_{(\text{cyclohexane}+\text{OH})} = 6.84 \text{ (Atkinson 2003)}$$

In unit ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

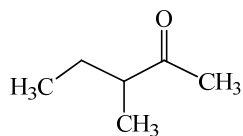
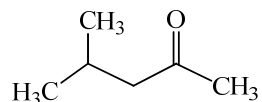


Relative method_200 L chamber

Part II

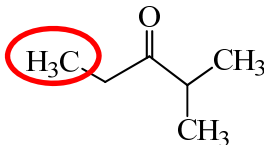
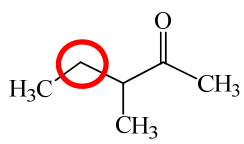
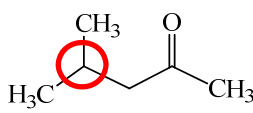


ketone	Ref.	Exp.	T (K)	$k_{\text{ketone_OH_RR}}/k_{\text{ref}}$	$k_{\text{ketone_RR}}$ ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	k_{average}
2M3P	propane	1	291±1	3.25±0.25	3.39±0.38	3.40±0.45
		2		3.35±0.24		
		3		3.30±0.24		
		4		3.41±0.24		
	cyclohexane	1		0.48±0.02		
		2		0.53±0.02		
		3		0.48±0.02		
		4		0.53±0.02		
4M2P	propane	1	293±1		10.44±0.74	11.02±0.42
		2		9.94±0.44		
		3		10.17±0.44		
		4		10.20±0.42		
	n-butane	1		4.49±0.17		
		2		4.58±0.12		
		3		4.63±0.12		
		4		4.42±0.10		
	n-hexane	1		2.47±0.06		
		2		2.36±0.04		
		3		2.38±0.04		
		4		2.35±0.04		
	cyclohexane	1		1.70±0.04		
		2		1.73±0.03		
		3		1.72±0.03		
		4		1.68±0.03		
3M2P	propane	1	293±1	5.92±0.75	5.78±0.51	5.90±0.36
		2		5.62±0.54		
		3		5.52±0.47		
		4		5.42±0.57		
	n-butane	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		
		2		1.18±0.02		
		3		1.16±0.02		
		4		1.12±0.02		
	cyclohexane	1		0.88±0.02		
		2		0.88±0.01		
		3		0.87±0.01		



Comparison

Part II

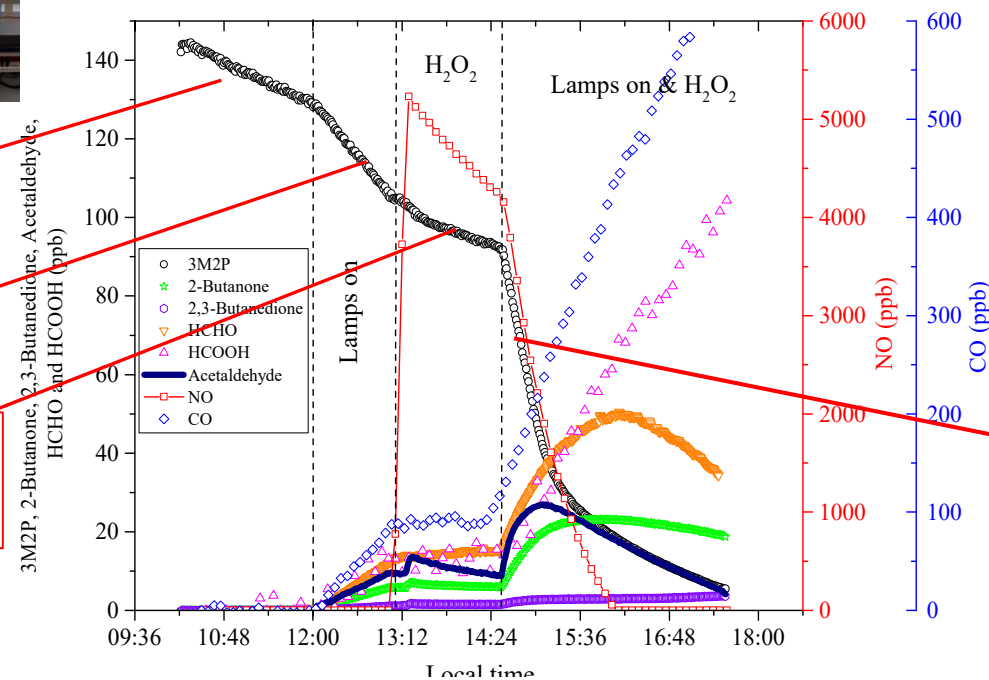
ketone	k (10^{-12} cm ³ molecule ⁻¹ s ⁻¹)	T (K)	Technique	Reference
	3.40 ± 0.45	291±1	RR-GCFID	This work
	3.57 ± 0.05	297±1	PLP-LIF	This work
	6.2 ± 0.3	298	RR-GCFID	Tuazon et al. (2003)
	5.90 ± 0.36	293±1	RR-GCFID	This work
4M2P	9 ± 3	305±2	RR-GCFID	Winer et al. 1976
$k_{2M3P} < k_{3M2P} < k_{4M2P} \rightarrow k(-CH_3) < k(-CH_2) < k(-CH<) \text{ in the } \beta \text{ position of C=O group}$				
	12.0 ± 0.5	290	RR-GCFID	Cox et al. 1980
	14.5 ± 0.7	299±2	RR-GCFID	Atkinson et al. 1982
	14.0 ± 0.07	297±2	RR-GCFID	O'rji and Stone 1992
	12.1 ± 0.5	298	PLP-LIF	Le Calve et al. 1998
	11.02 ± 0.42	293±1	RR-GCFID	This work

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Products experiments

Part III



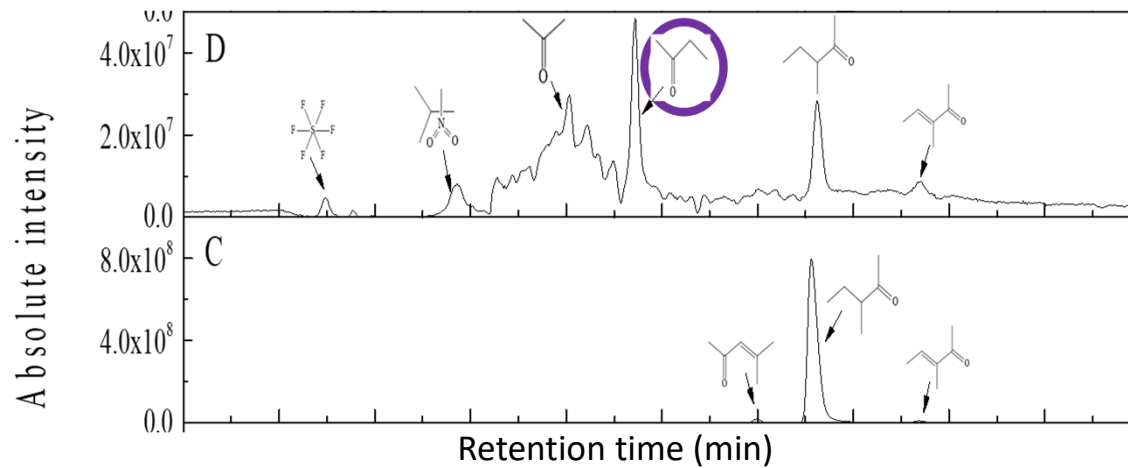
Wall loss

Photolysis of studied ketones

Possible interference of ketones with H₂O₂

Reaction with OH radical in the presence of NO

3M2P+OH_Products

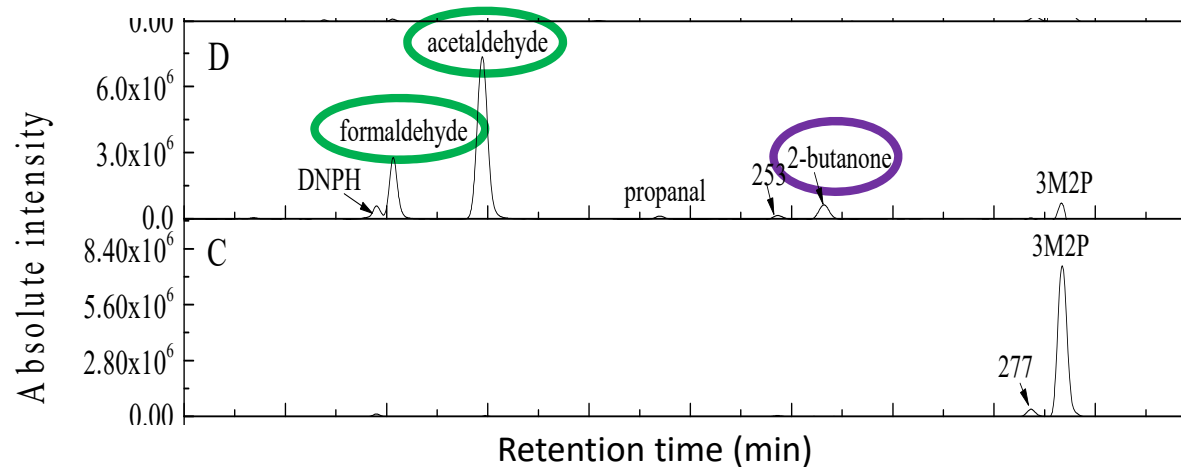


The Chromatogram spectrum from **GC/MS** analysis: (C) before and (D) after 1 hour reaction

CO and HCOOH were also monitored by **FTIR**,

HCHO was monitored by **Aerolaser 4021**

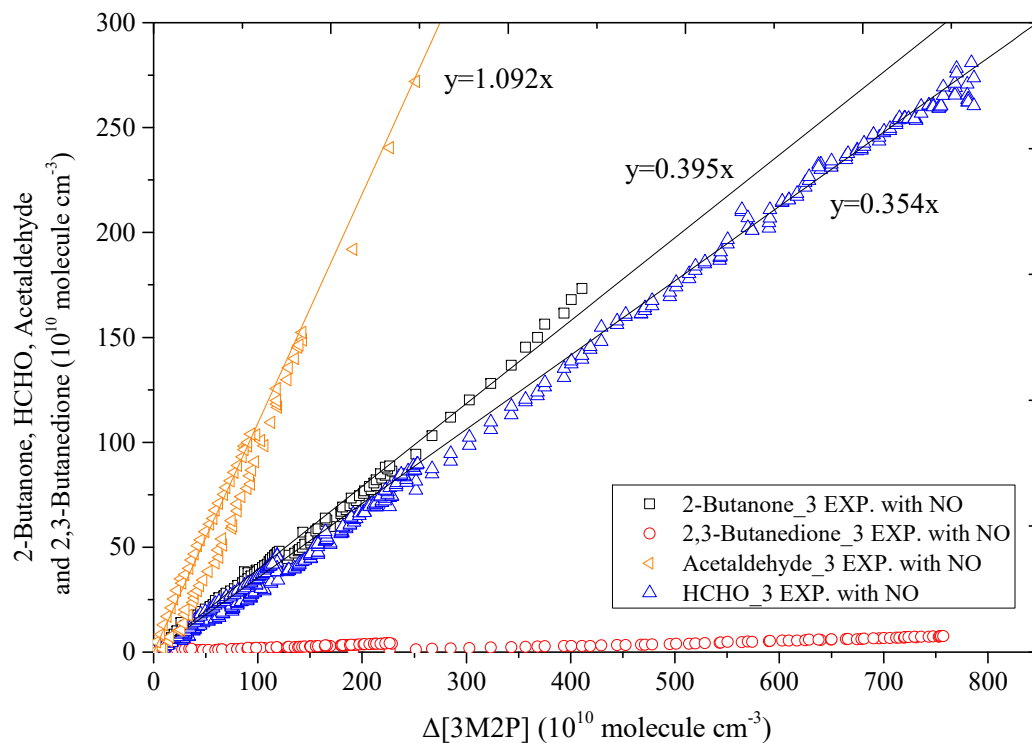
PTR-Tof-MS was used to quantify the concentration



The Chromatogram spectrum from **UHPLC/MS** analysis: (C) before and (D) after 1 hour reaction

3M2P+OH_Products

Part III



Plots of the amounts of **2-butanone, 2,3-butanedione, acetaldehyde and HCHO formed**, corrected for the formation from the photolysis (254 nm) of 3M2P and which were reacted with the OH radical, photolyzed (254 nm) and diluted (decay rate of SF₆), against the consumed 3M2P.

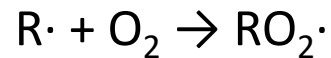
EXP.	[3M2P] (ppb)	[NO] (ppb)	2-Butanone (%)	2,3-Butanedione (%)	Acetaldehyde (%)	HCHO (%)	T (K)
20160317	523	4234	40.9 ± 0.4	1.2 ± 0.1	104.4 ± 1.6	34.5 ± 0.1	296 ± 1
20160322	389	10625	39.3 ± 1.8	1.8 ± 0.5	115.7 ± 2.1	35.2 ± 1.1	295 ± 1
20160412	92	4262	39.1 ± 0.6	4.5 ± 0.7	107.4 ± 5.5	36.6 ± 1.2	298 ± 1
Average			39.8 ± 1.9	2.5 ± 1.8	109.2 ± 6.1	35.4 ± 1.1	
C equilibrium (%)	70.5 ± 1.7						

Proposed mechanism

➤ H-abstraction using SAR calculation:

3M2P+OH: -CH₃ at 5-position 4.3%; -CH₂- at 4-position 56.1%; and >CH- at 3-position 32.1%; -CH₃- at 3-position branch 5.9%; -CH₃ at 1-position 1.6%;

➤ R. radical formed from the H-abstraction

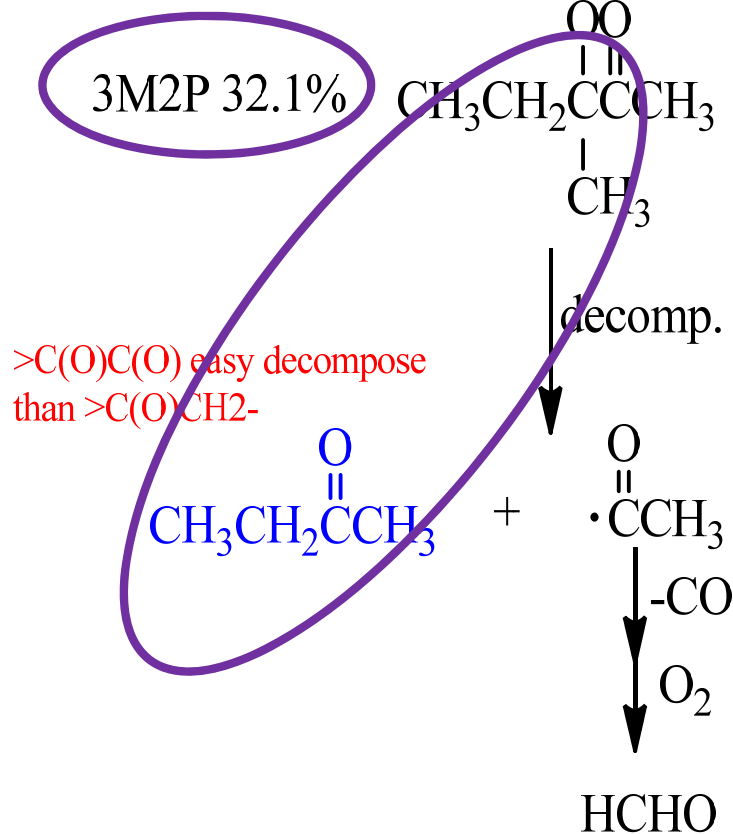


RO radical would mainly proceed: (1) reaction with O₂, (2) decomposition (3) isomerization via a 6-membered transition state.

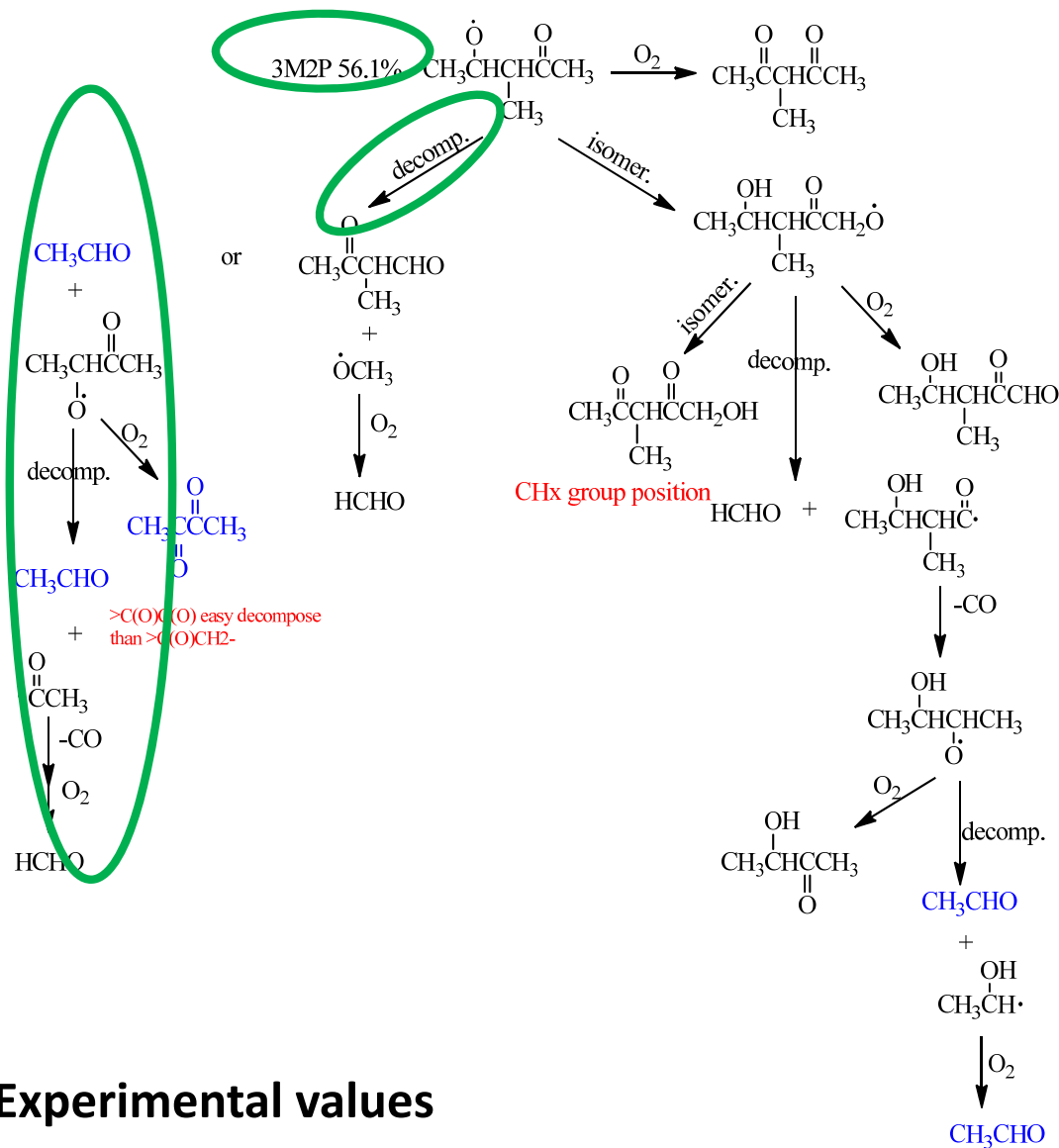
Proposed mechanism

Part III

>CH- at 3-position 32.1%



-CH₂- at 4-position 56.1%



SAR calculation Experimental values

2-butanone:	32.1%	39.8 ± 1.9%
Acetaldehyde:	56.1*2=112.2 %	109.2 ± 6.1%

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➤ Tropospheric lifetimes

- 2M3P: 3.4 days
- 3M2P: 2.0 days
- 4M2P: 1.1 days

(OH concentration of 1×10^6 molecule cm^{-3})

➤ Reactive species from OH reaction with studied ketones

- Formation of HO_2 and RO_2 radical, which in the presence of NO are converted back to OH, resulting in a fast **cycling of radicals** that forms the most important oxidation mechanism in the atmosphere
- The O_3 was expected to be formed from the OH radical initiates reactions with ketones
- A mass of CO is also expected to be produced from the OH reaction with studied ketones.

Conclusion

➤ Confirmed kinetic coefficients: (unit in $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

- 2M3P+OH: $3.40 \pm 0.45/3.57 \pm 0.05$
- 3M2P+OH: 11.02 ± 0.42
- 4M2P+OH: 5.90 ± 0.36

Then indicate that: $k(-\text{CH}_3) < k(-\text{CH}_2) < k(-\text{CH})$ in the β position of C=O group

➤ Products formation yield:

- 2M3P+OH: formaldehyde ($34.0 \pm 6.0\%$), acetone ($34.0 \pm 6.0\%$), acetaldehyde ($104.3 \pm 10\%$)
- 3M2P+OH: formaldehyde ($35.4 \pm 1.1\%$), 2-butanone ($39.8 \pm 1.9\%$), 2,3-butanedione ($2.5 \pm 1.8\%$), acetaldehyde ($109.2 \pm 6.1\%$)
- 4M2P+OH: formaldehyde ($51.9 \pm 3.5\%$), acetone ($87.4 \pm 2.2\%$), 2-methylpropanal ($10.7 \pm 4.8\%$)

➤ Proposed mechanism

- the main pathways for each reaction are proposed

Thanks for your attention!

