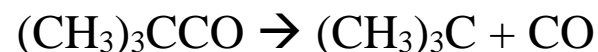


Direct Absolute Measurements of the Rate Constants of Unimolecular Decomposition of Acyl Radicals by Time Resolved Infrared Diode Laser Spectroscopy



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Introduction

Acyl radicals RCO are important intermediates formed after reaction of aldehydes with OH or NO₃ radicals. Like most alkoxy radicals, under atmospheric conditions, they can react via 3 different reaction pathways : unimolecular thermal decomposition, possibly in the fall-off range, isomerization, and reaction with O₂. Since isomerization is negligible for small radicals, the ozone creating potential of acyl radicals is only determined by the ratio between decomposition and reaction with O₂.

Using our newly developed Pulsed Laser Photolysis / Tunable Diode Laser spectrometer (Hanoune et al. 2001), we have measured directly the decomposition rate constant of two acyl radicals (2,2-dimethylpropionyl or pivaloyl (CH₃)₃CCO, and isobutyryl (CH₃)₂CHCO), between 300 and 318 K and between 4.7 and 34 Torr. Reactions were monitored by probing the build-up of CO. It was found to be necessary to work in presence of O₂ to avoid Cl regeneration.

Our data complement the few existing measurements performed at higher pressure. Jagiella et al. (2000) measured the ratio between decomposition and O₂ reaction in a photochemical reaction chamber combined with long-path FTIR analysis between 293 and 317 K at atmospheric pressure. Concurrently, Tomas et al. (2000) measured the same ratio by flash photolysis coupled to UV absorption spectrometry at atmospheric pressure between 323 and 453 K, with a few additional measurements in the fall-off domain (433 K, 40 and 150 Torr).

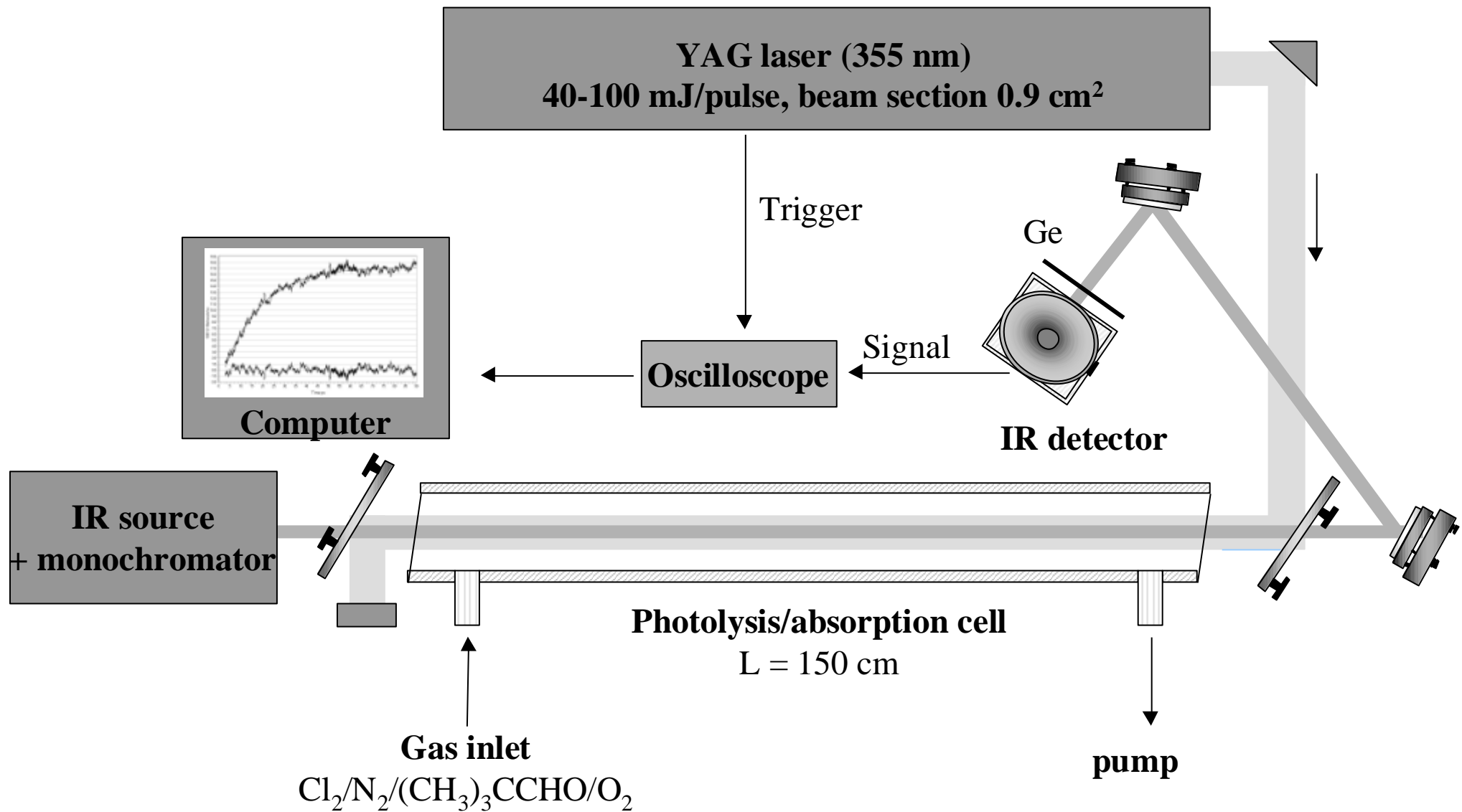
Experimental

The laser photolysis/tunable infrared diode laser system is shown in Fig. 1. The photolysis/absorption cell (stainless steel, i.d. 3.6 cm, length 1.5 m) can be heated up to 500 K. The YAG laser (Quantel 981C) delivers at 355 nm a maximum of 300 mJ per pulse (usually set to about 100 mJ only) into a 0.9 cm diameter beam, at a repetition rate usually set at 1 Hz or slower, to ensure refreshment of the gas mixture between shots.

The strongly astigmatic beam of the infrared diode (Laser Photonics L5736) is refocused (with an almost parallel beam of less than 3 mm diameter) and carefully adjusted to probe only the photolysis zone. Detection is achieved by a photoconductive HgCdTe detector, the signal is amplified by an ac-coupled amplifier, averaged (typically less than 50 times) by a digital oscilloscope (Tektronix TDS 520B), and stored on a computer for further analysis.

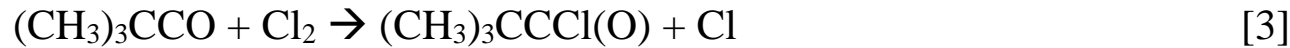
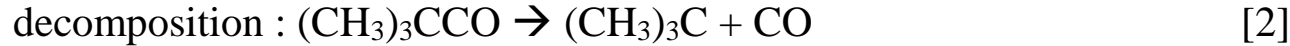
The diode emission frequency was tuned to the R5 or R6 transitions of CO fundamental band, at 2165.601 and 2169.198 cm^{-1} . It was found unnecessary to stabilize the laser frequency during an acquisition sequence (typically 1 mn). Absolute intensity calibration was regularly performed with calibrated diluted CO mixtures.

N_2 buffer gas and O_2 are controlled by mass flow controllers. Carefully degassed pivalaldehyde ($\text{CH}_3)_3\text{CCH}(\text{O})$ is injected into the cell through a needle valve, as well as Cl_2 (5% diluted in He). Their flow rates are determined by measuring the rate of pressure increase in the cell.



Analysis

The following reactions are considered in the analysis :



This system leads to the following mathematical behavior for the CO build-up curve :

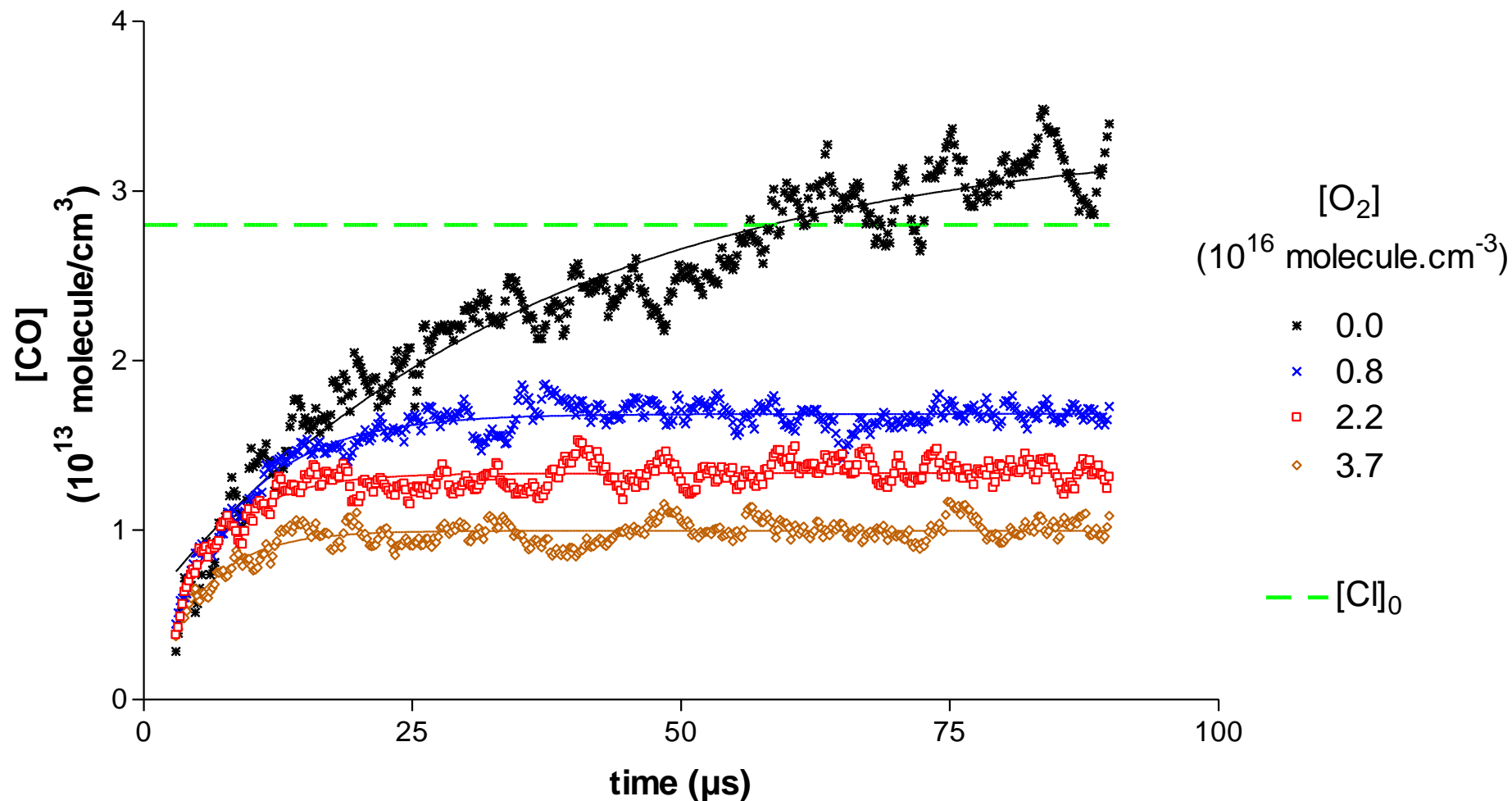
$$[\text{CO}] = [\text{Cl}]_0 \times \frac{k_2}{K^{1st}} \times \left\{ 1 + \frac{K^{1st}}{k_1^{1st} - K^{1st}} \exp(-k_1^{1st} \cdot t) - \frac{k_1^{1st}}{k_1^{1st} - K^{1st}} \exp(-K^{1st} \cdot t) \right\}$$

with $k_1^{1st} = k_1 \cdot [\text{RCHO}]$ and $K^{1st} = k_2 + k_3 \cdot [\text{Cl}_2] + k_4 \cdot [\text{O}_2]$

Taking $k_1 = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Ullerstam et al. 2001), $k_3 = 4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (value for CH_3CO , Tyndall et al. 1999) and $k_4 = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (value for CH_3CO , as in Tomas et al. 2000), and considering our experimental concentrations (see table), it follows that after a few μs , this equation reduces to a simple rising exponential:

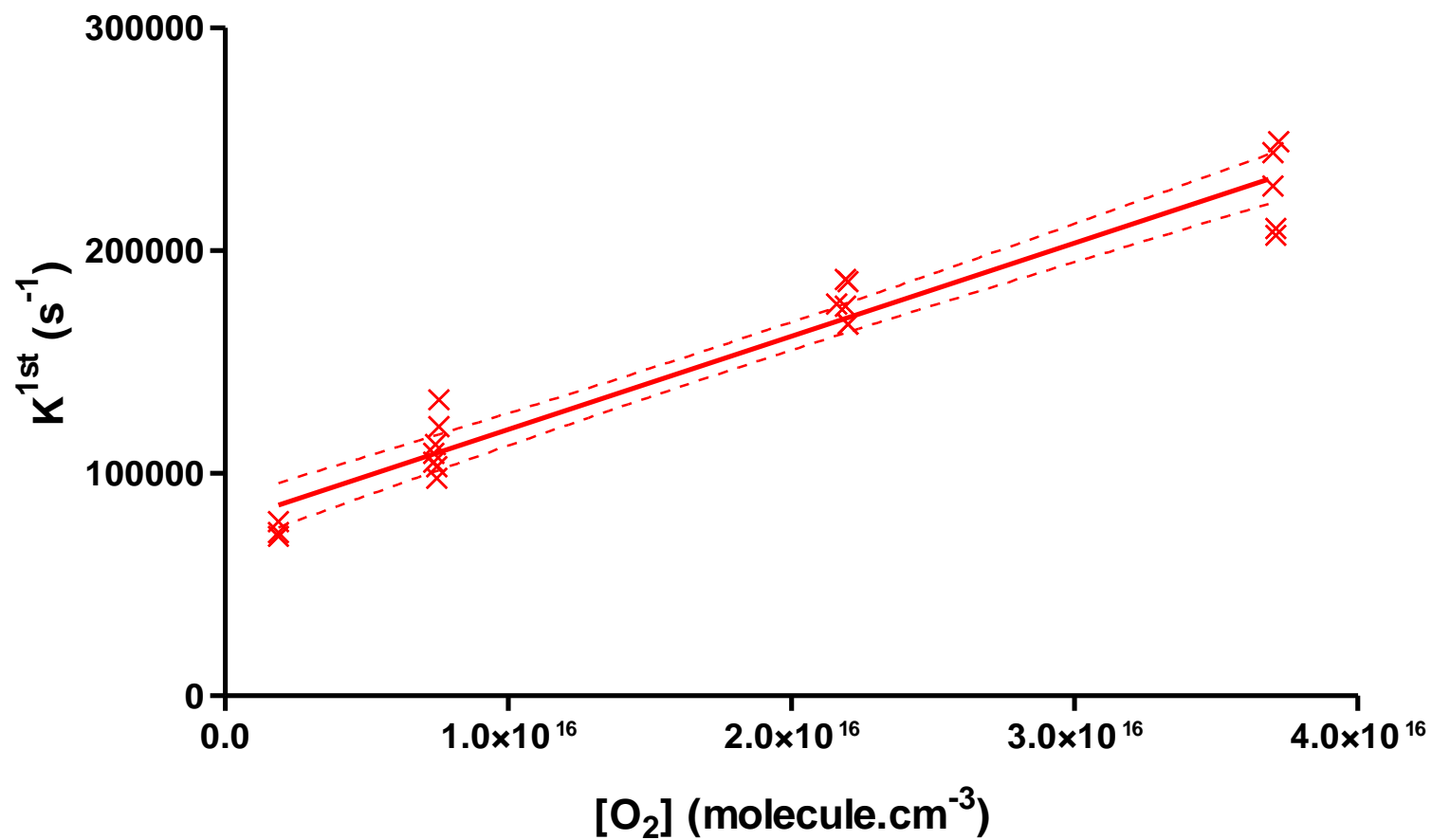
$$[\text{CO}] = [\text{Cl}]_0 \times \frac{k_2}{K^{1st}} \times \left\{ 1 - \frac{k_1^{1st}}{k_1^{1st} - K^{1st}} \exp(-K^{1st} \cdot t) \right\}$$

k_2 and k_4 are derived from a linear regression of the apparent rate constant K^{1st} for different oxygen concentrations, after correction for $k_3 \cdot [\text{Cl}_2]$.



CO build up kinetics versus reaction time .

Experimental conditions : $[(CH_3)_3CCH(O)] = 1.7 \times 10^{16} \text{ molecule.cm}^{-3}$, $[O_2] = 0 - 3.7 \times 10^{16} \text{ molecule.cm}^{-3}$, $[Cl_2] = 3.3 \times 10^{14} \text{ molecule.cm}^{-3}$, temperature 302 K, total pressure 34 Torr, YAG laser fluence 140 mJ/cm^2 . Note the non-exponential behavior in absence of O_2 .



Typical plot of K^{1st} vs. $[O_2]$ in the case of $(CH_3)_3CCO$.

$T = 302 \text{ K}$, $P = 34 \text{ Torr}$

$k_2 = 72500 \pm 5800 \text{ s}^{-1}$

$k_4 = 4.2 \pm 0.3 \times 10^{-12} \text{ cm}^3 \cdot molecule^{-1} \cdot s^{-1}$

(CH₃)₃CCO : Experimental conditions and results

T (K)	P (Torr)	[RCHO] (x 10 ⁺¹⁶)	[O ₂] (x 10 ⁺¹⁶)	[Cl ₂] (x 10 ⁺¹⁴)	[Cl] (x 10 ⁺¹³)	<i>k</i> ₂	<i>k</i> ₄ (x 10 ⁻¹²)
299	4.7	0.5	0 - 2	2.5	1.8	15600 ± 7200	3.9 ± 0.6
301	13.5	1.7	0 - 3	4.3	2.9	41100 ± 8400	5.3 ± 0.4
299	19.7	1.0	0 - 4	6.3	4.6	51200 ± 19800	2.8 ± 0.8
302	34	1.7	0 - 4	2 - 7	1 - 6	72500 ± 5800	4.2 ± 0.3
317	14	1.2	0 - 6	5 - 6	4	90200 ± 17000	3.6 ± 0.5
318	4.6	0.5	0 - 2	2.3	2.3	28500 ± 2800	4.9 ± 0.3

Units : concentrations in molecule.cm⁻³, *k*₂ is expressed in s⁻¹, *k*₄ in molecule⁻¹.cm³.s⁻¹. Uncertainties listed are the 1σ from the linear regressions.

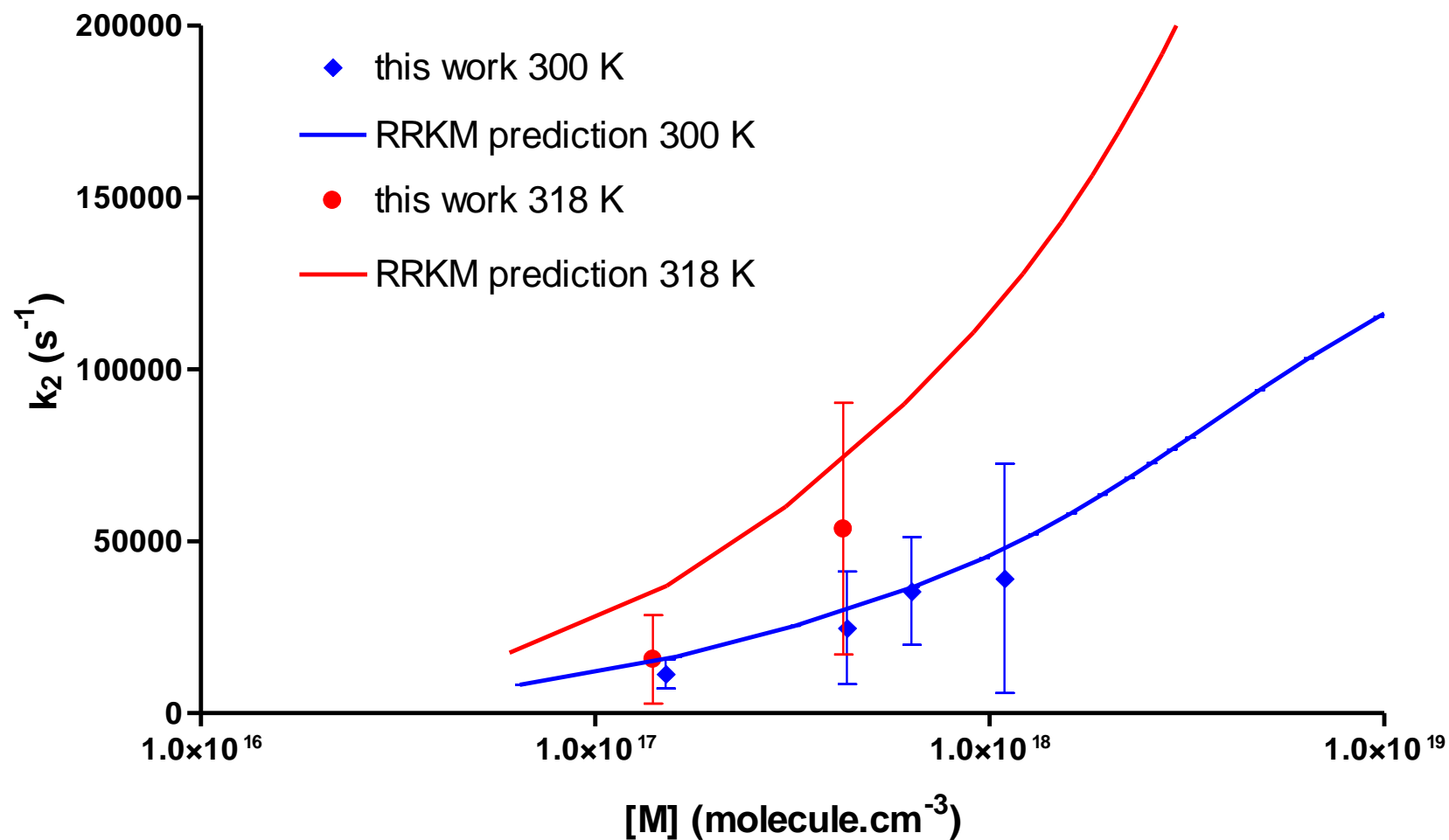
(CH₃)₃CCO reaction with O₂

If we consider that *k*₄ is constant over the pressure range at each temperature, then we derive

$$k_4 = 4.0 \pm 1.0 \text{ molecule}^{-1}.\text{cm}^3.\text{s}^{-1} \text{ at } 300 \text{ K}$$

$$k_4 = 4.2 \pm 1.0 \text{ molecule}^{-1}.\text{cm}^3.\text{s}^{-1} \text{ at } 318 \text{ K}$$

These average values do not change significantly the decomposition rate constant *k*₂.



(CH₃)₃CCO decomposition rate constant.

Experimental results and theoretical fall-off curves (taken from Tomas et al. 2000).
Buffer gas is N₂+O₂.

Conclusion

We report here the first direct determination of the thermal decomposition rate constant of the pivaloyl radical $(\text{CH}_3)_3\text{CCO}$ in the low pressure range (below 34 Torr). Our measurements compare favorably with the extrapolations from RRKM calculations and high pressure determination from Tomas et al. (2001), and will be useful for refining the fall-off curve. We also determined the rate constant of $(\text{CH}_3)_3\text{CCO}$ with O_2 in the same pressure and small temperature range.

We are currently investigating the thermal decomposition of isobutyryl $(\text{CH}_3)_2\text{CHCO}$ as well. In contrast with pivaloyl, no regeneration of Cl atoms in absence of oxygen is noticed, since the CO build up is well-behaved (simple rising exponential). On the contrary, in presence of oxygen, the CO build-up curves are not exponential. In addition, from the absolute level of CO signal, we suspect that another channel of Cl-abstraction is possible, which complicates the analysis :



In this case, we performed the measurements by varying the Cl_2 concentrations. k_2' values determined range at 295 K from 3000 s^{-1} at 14 Torr to 9400 s^{-1} at 151 Torr, and at 322 K from 5200 s^{-1} at 14 Torr to 8500 s^{-1} at 60 Torr, with uncertainties on the determination of about $\pm 2000 \text{ s}^{-1}$. These values agree reasonably well with the fall-off calculations by Tomas et al. (2000), but still need to be confirmed by further experiments at higher temperature and/or pressure.

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