

Multiphase Processing of Isoprene Oxidation Products: Kinetic and Product Studies

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Motivation

- Isoprene represents a significant fraction of non-methane hydrocarbons in the troposphere. Its emissions have recently been estimated to be in the range of 500 and 750 Tg yr⁻¹ (440-660 Tg carbon; Guenther et al., 2006).
- Some aspects of SOA formation processes from isoprene and its oxidation products were studied by a number of chamber studies in the past (Kroll et al., 2006, Surratt et al., 2007). However, aqueous phase oxidation processes which may occur after phase transfer of 'early' oxidation product are much less characterized. These processes are a potentially important source for organic particle mass constituents such as mono- and dicarboxylic acids.
- In order to implement the multiphase chemistry in the course of the isoprene degradation in atmospheric models detailed kinetic and product studies were performed. Aqueous phase oxidation processes of isoprene oxidation products such as methacrolein, methacrylic acid, acrylic acid and methyl vinyl ketone by atmospheric radicals were systematically investigated within this work.

Experimental

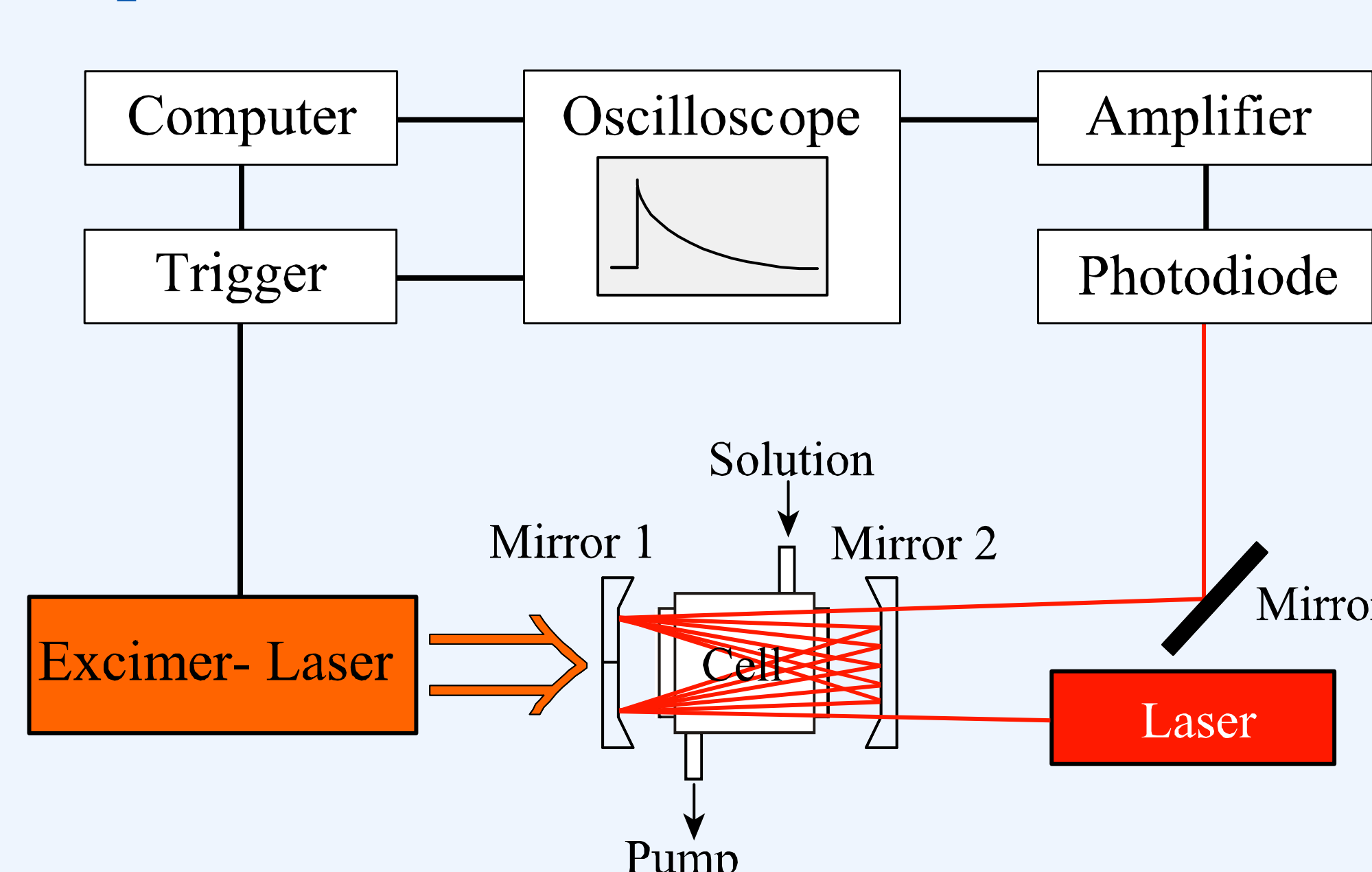


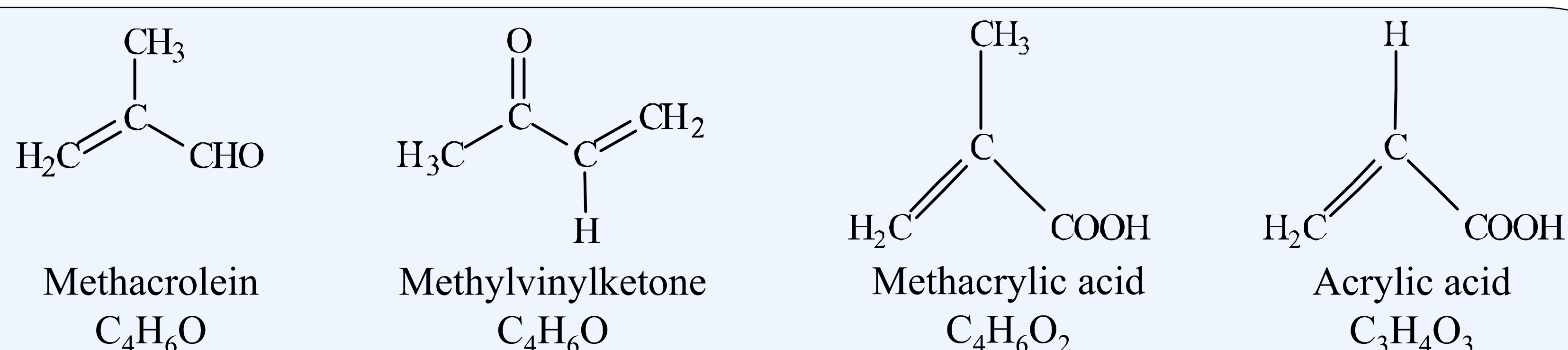
Figure 1: Scheme of the laser photolysis setup used for the kinetic and product studies in aqueous solution.

- Radicals generated by laser photolysis of precursor compounds such as H₂O₂, NaNO₃ and K₂S₂O₈ at λ = 248 nm.
- Product studies were done in a quartz cuvette positioned in front of the excimer laser in Figure 1. The following concentrations were used: [H₂O₂] = 0.02 mol/L and [methacrolein] = 1 · 10⁻⁴ mol/L.
- Product samples were treated as follows:
 - Derivatization with DNPH
 - Solid phase extraction
 - HPLC-MS analysis

Kinetic studies

Table 1: Summary of rate constants (k_{2nd}) and activation parameter for the reactions of methacrolein, methacrylic acid, acrylic acid and methyl vinyl ketone with OH, NO₃ and SO₄⁻ in aqueous solution.

Compound	k _{2nd} M ⁻¹ s ⁻¹	k _{2nd,Reference} M ⁻¹ s ⁻¹	Reference	E _A kJ/mol	A M ⁻¹ s ⁻¹	
OH	methacrolein	(1.0 ± 0.1) · 10 ¹⁰	(8.0 ± 0.7) · 10 ⁹	[1]	10 ± 6	(6.2 ± 0.6) · 10 ¹¹
	methyl vinyl ketone	(7.4 ± 0.7) · 10 ⁹	1.7 · 10 ¹⁰	[2]	8 ± 6	(2.5 ± 0.2) · 10 ¹¹
	methacrylic acid	(1.2 ± 0.1) · 10 ¹⁰	-	-	11 ± 4	(1.2 ± 0.1) · 10 ¹²
	methacrylate	(1.2 ± 0.1) · 10 ¹⁰	5.9 · 10 ⁹	[3]	12 ± 5	(2.1 ± 0.1) · 10 ¹²
	acrylic acid	(5.4 ± 0.8) · 10 ⁹	1.5 · 10 ⁹	[4]	7 ± 1	(1.1 ± 0.01) · 10 ¹¹
	acrylate	(6.5 ± 1.0) · 10 ⁹	-	-	3 ± 1	(2.4 ± 0.06) · 10 ¹⁰
NO ₃	methacrolein	(3.0 ± 0.6) · 10 ⁷	-	-	2 ± 6	(7.2 ± 1.0) · 10 ⁷
	methyl vinyl ketone	(1.9 ± 0.3) · 10 ⁷	-	-	15 ± 2	(6.9 ± 0.3) · 10 ⁹
	methacrylic acid	(7.5 ± 1.3) · 10 ⁷	-	-	-	-
	methacrylate	(2.1 ± 1.2) · 10 ⁸	-	-	-	-
	acrylic acid	(2.2 ± 0.1) · 10 ⁷	-	-	28 ± 7	(1.6 ± 0.2) · 10 ¹²
	acrylate	(8.1 ± 7.8) · 10 ⁷	-	-	-	-
SO ₄ ⁻	methacrolein	(8.0 ± 4.5) · 10 ⁷	(1.2 ± 0.1) · 10 ⁹	[1]	-(2 ± 12)	(2.9 ± 0.9) · 10 ⁷
	methyl vinyl ketone	(1.0 ± 0.2) · 10 ⁸	-	-	4 ± 18	(3.0 ± 1.0) · 10 ⁸
	methacrylic acid	(2.1 ± 0.6) · 10 ⁸	1.1 · 10 ⁹	[5]	11 ± 10	(1.5 ± 0.3) · 10 ¹⁰
	methacrylate	(3.5 ± 1.1) · 10 ⁸	7 · 10 ⁹	[3]	-	-
	acrylic acid	(9.5 ± 1.5) · 10 ⁷	1.1 · 10 ⁹	[3]	2 ± 7	(1.9 ± 0.3) · 10 ⁸
	acrylate	(9.9 ± 1.9) · 10 ⁷	-	-	-	-



- High reactivity of OH radicals with the unsaturated isoprene oxidation products in aqueous solution. Corresponding NO₃ and SO₄⁻ reactions are about two orders of magnitude slower.
- The rate constants of methacrolein and methyl vinyl ketone with ozone in aqueous solution are about five magnitudes lower (k_{ozone} ≈ 10⁴ M⁻¹s⁻¹, Pedersen and Sehested, 2001) compared to the OH radical.
- The reactivity of methacrolein and methyl vinyl ketone with OH in the gas phase is comparable to the aqueous phase. NO₃ radical reactions with these two compounds are even slower in the gas phase.
MACR k_{OH} = 1.9 · 10¹⁰ M⁻¹s⁻¹ (Atkinson, 1986); k_{NO₃} = 2.7 · 10⁶ M⁻¹s⁻¹ (Kwok et al., 1996)
MVK k_{OH} = 1.1 · 10¹⁰ M⁻¹s⁻¹ (Atkinson, 1986); k_{NO₃} = 3.6 · 10⁵ M⁻¹s⁻¹ (Kwok et al., 1996)
- Low activation energies for all investigated reactions, except for NO₃.

[1] Buxton et al., 2000; [2] Gierczak et al., 1997; [3] Maruthamuthu, 1980; [4] Buxton et al., 1988; [5] Neta et al., 1988

Product studies

- The reaction solution (V = 3mL) containing H₂O₂ and methacrolein were placed in a quartz cuvette in front of the excimer laser (λ = 248 nm; E_{laser} = 300mJ; [OH] ≈ 9 · 10⁻⁵ mol/L).

- Test experiments in the absence of H₂O₂ and without laser irradiation were performed to see the influence of dark reactions and the photolysis of methacrolein at λ = 248 nm.

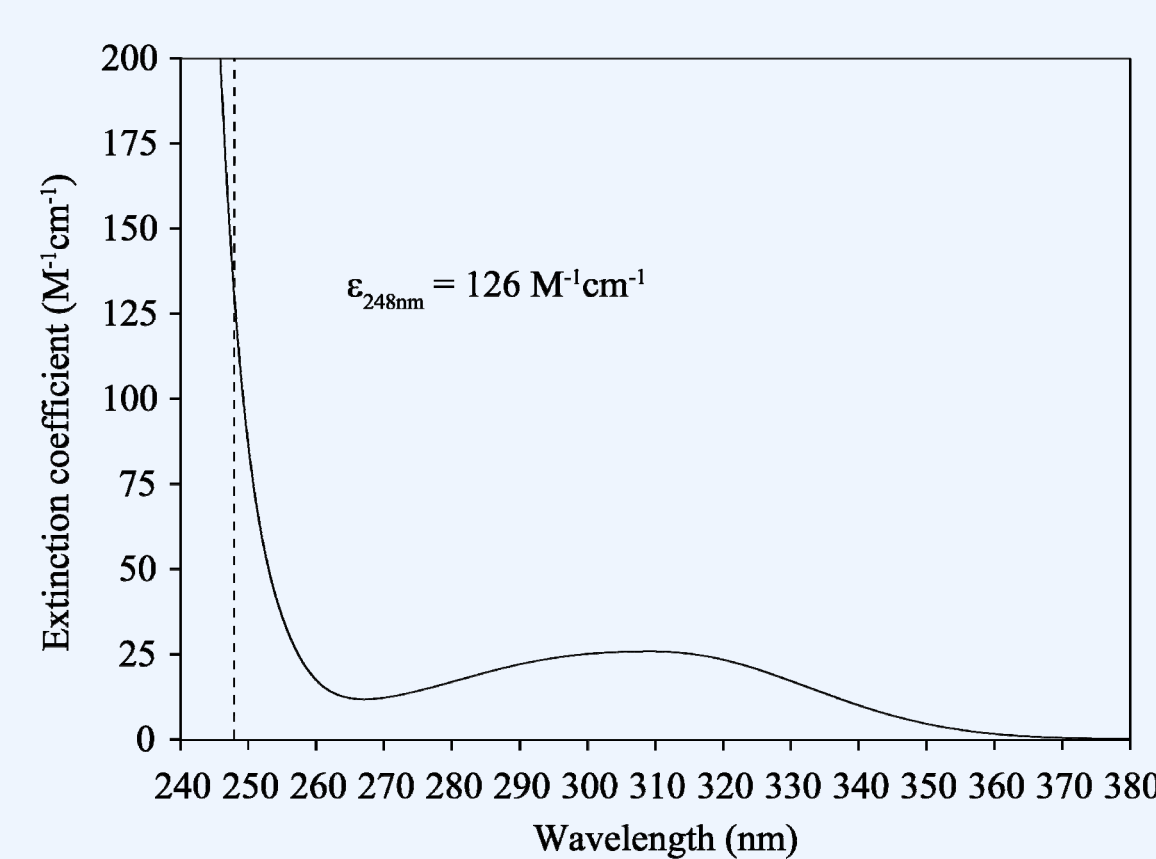


Figure 2: UV-spectra of methacrolein in aqueous solution.

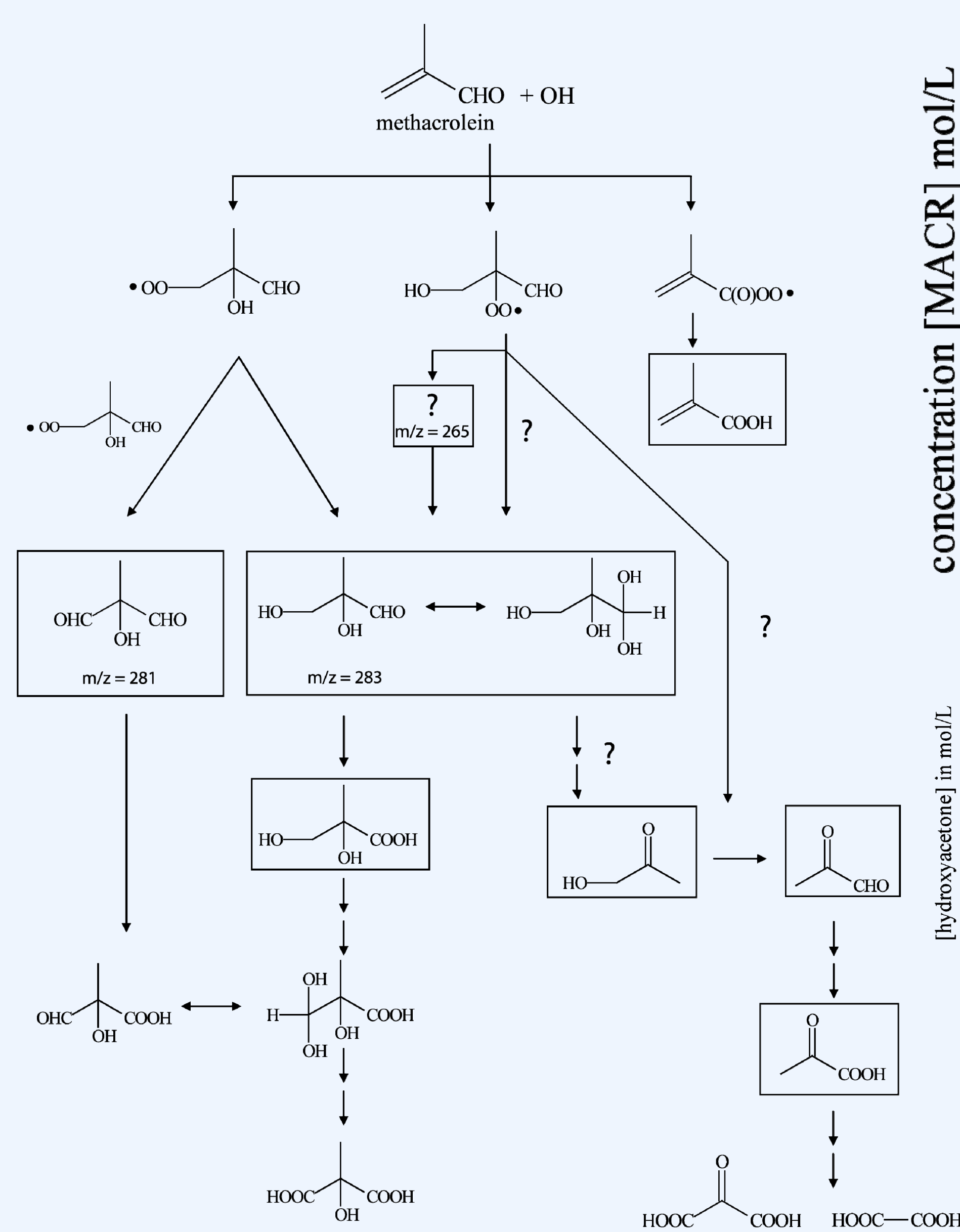
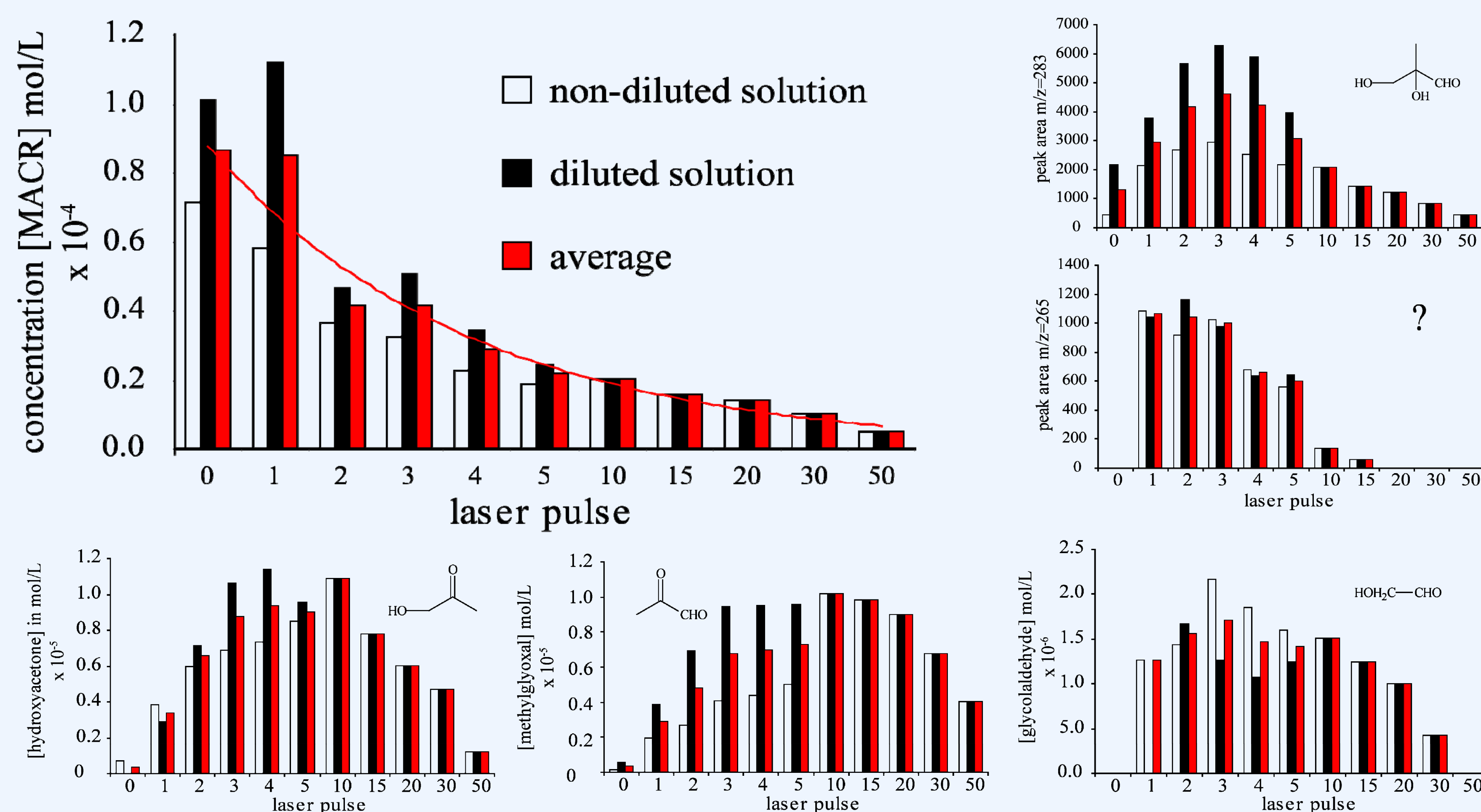


Figure 3: Simplified hypothetical oxidation scheme for methacrolein in aqueous solution based on the experimental results.



- Different carbonyl compounds (see Figures above) have been identified as oxidation products of methacrolein. Similar products were also found in a recent study from Lui et al., 2009.
- Still unclear is the mechanism of the early carbon loss to explain the formation of hydroxyacetone and glycolaldehyde.
- Concentrations of two 'earlier' products could not be quantified due to missing standard compounds. However, these oxidation products are potential tracer compounds for multiphase oxidation processes of isoprene in the atmosphere.

Summary and Outlook

- Fast oxidation of isoprene degradation products by free radicals in aqueous solution.
- Identification of short chain mono- and polyfunctional carbonyls as oxidation products of methacrolein in aqueous solution. Future product studies will be focused on the identification of other polyfunctional products such as alcohols (e.g., tetrols) and dicarboxylic acids. Such products might be also found in field measurements as specific tracer compounds for multiphase chemical processes in the course of the isoprene oxidation. Furthermore, the aqueous phase oxidation scheme of methyl vinyl ketone will be investigated.
- Results from the kinetic measurements and product studies will be implemented in atmospheric models to investigate the importance of these oxidation pathways for the production of organic particle mass.

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