Multiphase Processing of Isoprene Oxidation Products: Kinetic and Product Studies

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Motivation

➢ Isoprene represents a significant fraction of non-methane hydrocarbon in the troposphere. Its emissions have recently been estimated to be in the range of 500 and 750 TgC yr^{-1} (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.
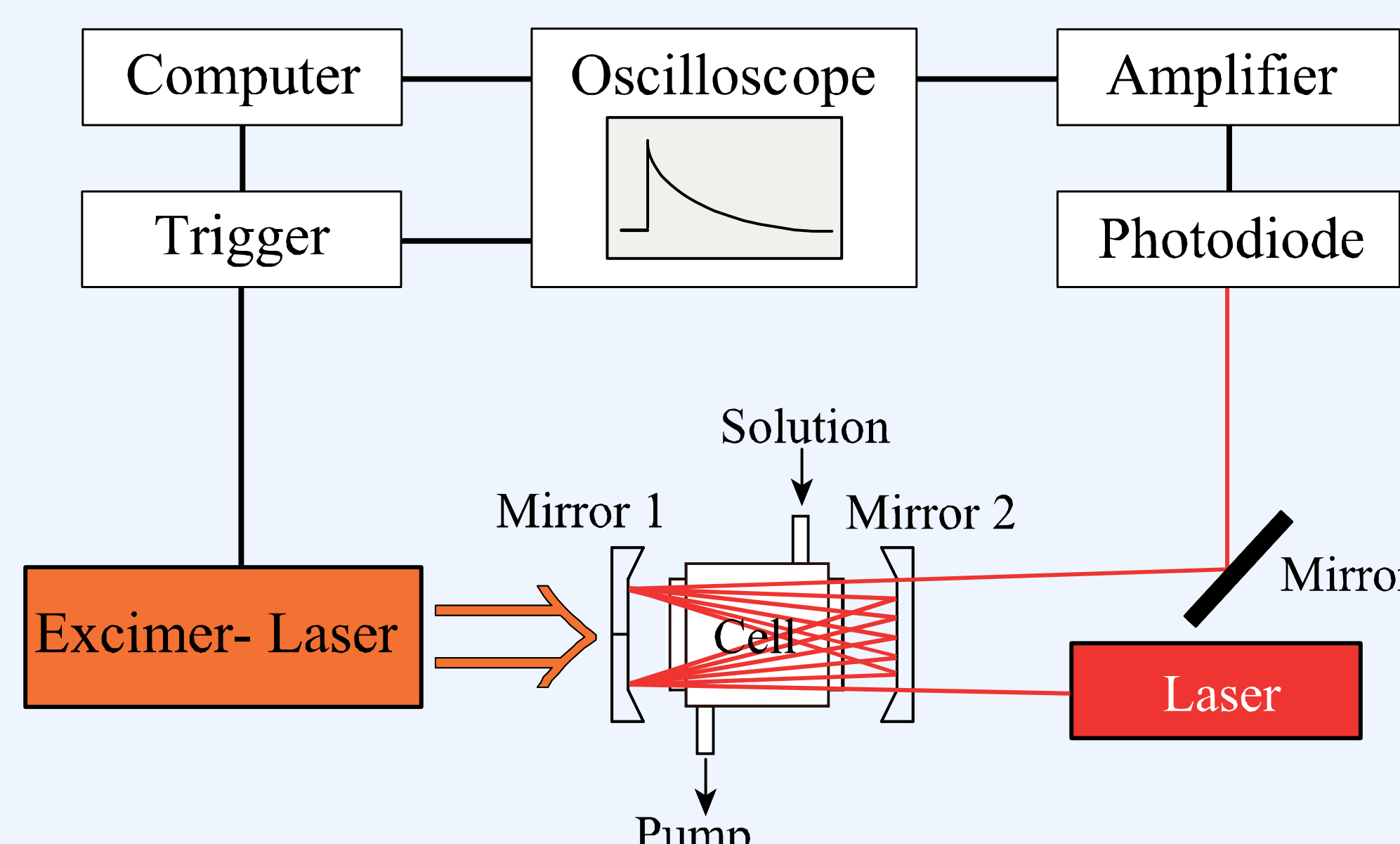
Experimental

Figure 1: Scheme of the laser photolysis setup used for the kinetic and product studies in aqueous solution.
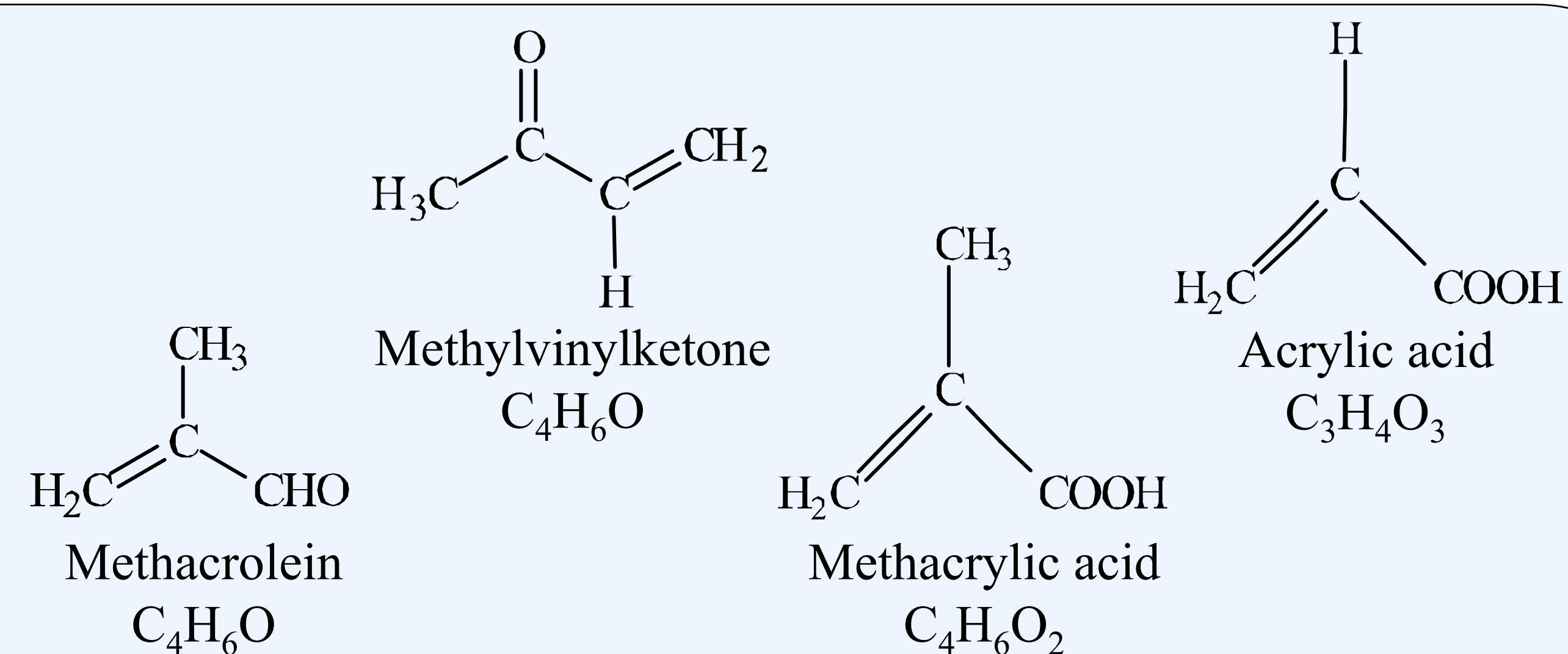
➢ Radicals generated by laser photolysis of precursor compounds such as H_2O_2, $NaNO_3$ and $K_2S_2O_8$ at $\lambda = 248$ nm.

➢ Product studies were done in a quartz cuvette positioned in front of the excimer laser in Figure 1. The following concentrations were used: $[H_2O_2] = 0.02$ mol/L and [methacrolein] = [methyl vinyl ketone] = $1 \cdot 10^{-4}$ 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, NO_3 and SO_4^- in aqueous solution.

	Compound	Aqueous phase					Gas phase	
		k_{2nd} $M^{-1}s^{-1}$	$k_{2nd,Reference}$ $M^{-1}s^{-1}$	Reference	E_A kJ/mol	A $M^{-1}s^{-1}$	k_{2nd} $M^{-1}s^{-1}$	Reference
OH	Methacrolein	$(1.0 \pm 0.1) \cdot 10^{10}$	$(8.0 \pm 0.7) \cdot 10^9$	[1]	10 ± 6	$(6.2 \pm 0.6) \cdot 10^{11}$	$1.9 \cdot 10^{10}$	[4]
	Methyl vinyl ketone	$(7.4 \pm 0.7) \cdot 10^9$	-		8 ± 6	$(2.5 \pm 0.2) \cdot 10^{11}$	$1.9 \cdot 10^{10}$	[4]
	Methacrylic acid	$(1.2 \pm 0.1) \cdot 10^{10}$	-		11 ± 4	$(1.2 \pm 0.1) \cdot 10^{12}$	-	
	Acrylic acid	-	$1.5 \cdot 10^9$	[2]	-	-	-	
NO_3	Methacrolein	$(3.0 \pm 0.6) \cdot 10^7$	-		4 ± 4	$(1.5 \pm 0.1) \cdot 10^8$	$2.7 \cdot 10^6$	[5]
	Methyl vinyl ketone	$(1.9 \pm 0.3) \cdot 10^7$	-		15 ± 2	$(6.9 \pm 0.3) \cdot 10^9$	$3.6 \cdot 10^5$	[5]
	Methacrylic acid	$(7.2 \pm 1.7) \cdot 10^7$	-		-	-	-	
	Acrylic acid	$(2.2 \pm 0.1) \cdot 10^7$	-		28 ± 7	$(1.6 \pm 0.2) \cdot 10^{12}$	-	
SO_4^-	Methacrolein	$(1.7 \pm 0.7) \cdot 10^8$	$(1.2 \pm 0.1) \cdot 10^9$	[1]	-	-	-	
	Methyl vinyl ketone	$(1.0 \pm 0.2) \cdot 10^8$	-		-	-	-	
	Methacrylic acid	-	$1.1 \cdot 10^9$	[3]	-	-	-	
	Acrylic acid	-	-		-	-	-	

[1] Buxton et al., 2000; [2] Buxton et al., 1988; [3] Neta et al., 1988; [4] Atkinson, 1986; [5] Kwok et al., 1996

Methylvinylketone C_4H_6O

Acrylic acid $C_3H_4O_3$

Methacrolein C_4H_6O

Methacrylic acid $C_4H_6O_2$

➢ High reactivity of OH radicals with the unsaturated isoprene oxidation products in aqueous solution. Corresponding NO_3 and SO_4^- 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 ($k_{ozone} \approx 10^4$ $M^{-1}s^{-1}$, 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. NO_3 radical reactions with these two compounds are even slower in the gas phase.

Product studies

➢ The reaction solution (V = 3mL) containing H_2O_2 and the organic reactant were placed in a quartz cuvette in front of the excimer laser ($\lambda = 248$ nm; $E_{laser} = 500$ mJ).

➢ Test experiments in the absence of H_2O_2 and without laser irradiation were performed to see the influence of dark reactions and the photolysis of the organic reactants at $\lambda = 248$ nm.
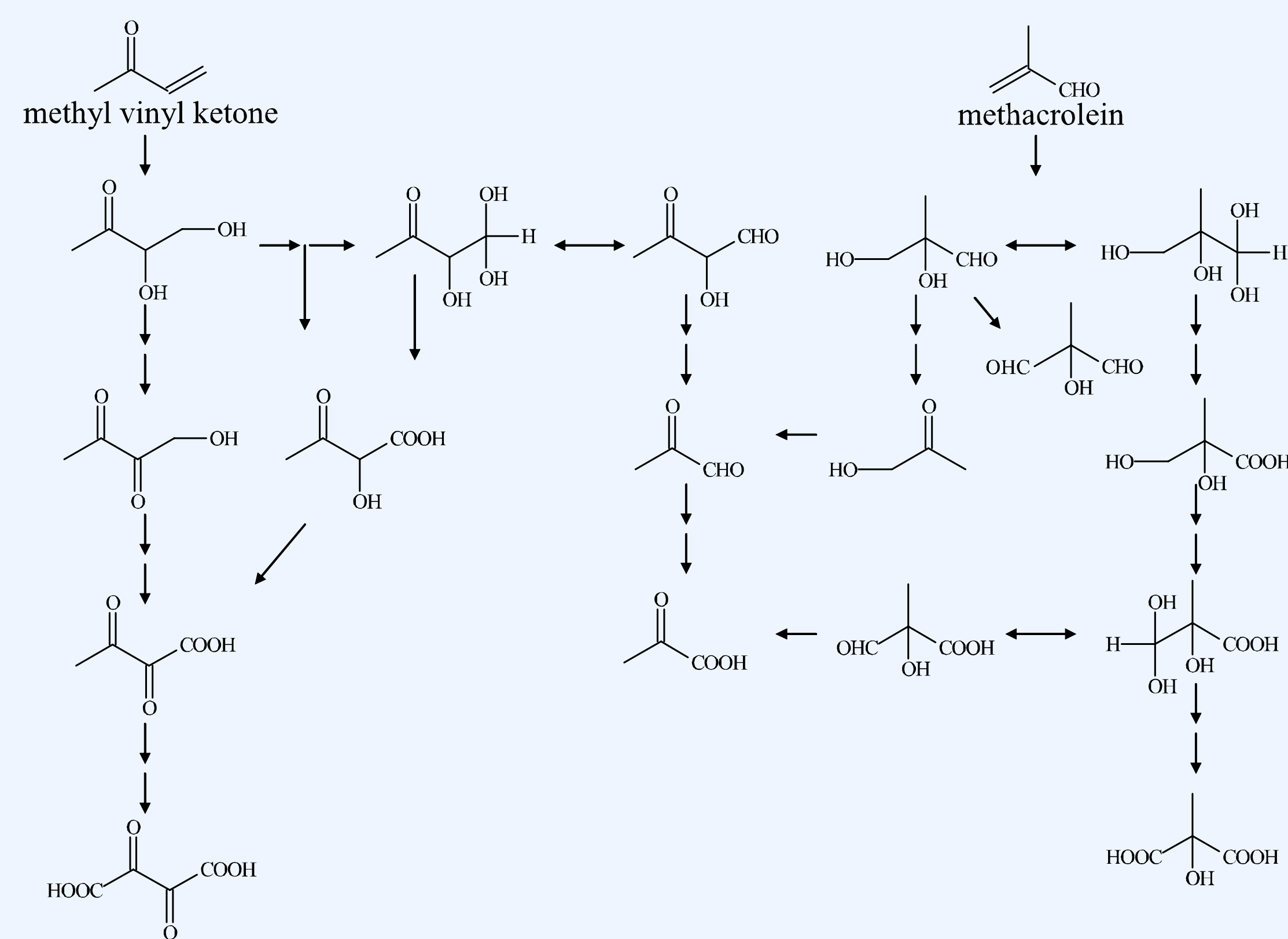

Figure 2: Simplified hypothetical oxidation scheme for methacrolein and methyl vinyl ketone in aqueous solution.
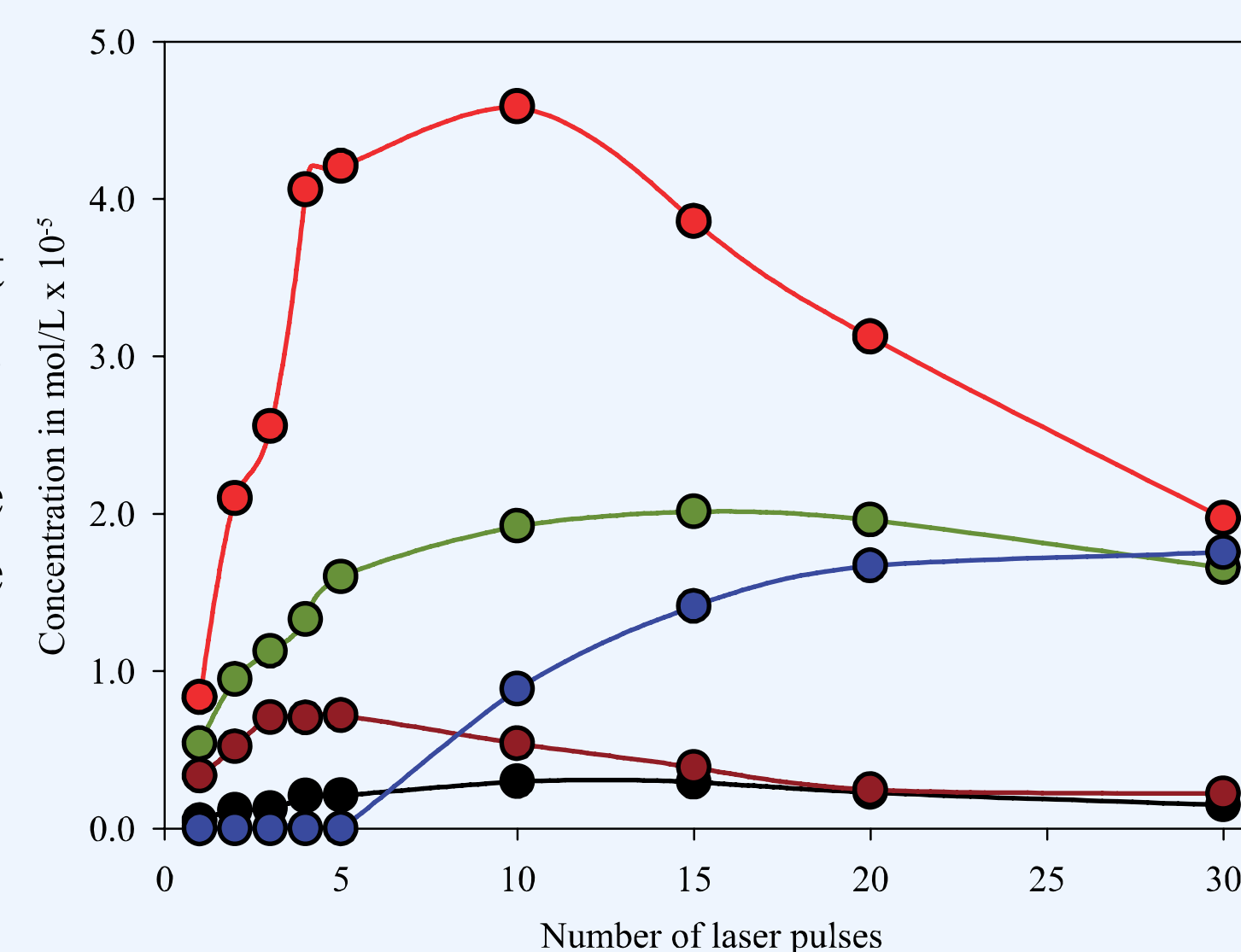

Figure 3 (left): Products formed after the oxidation of methacrolein by OH in aqueous solution: **glyoxal**, **methylglyoxal**, **hydroxyacetone**, **pyruvic acid** and **glycolaldehyde**.
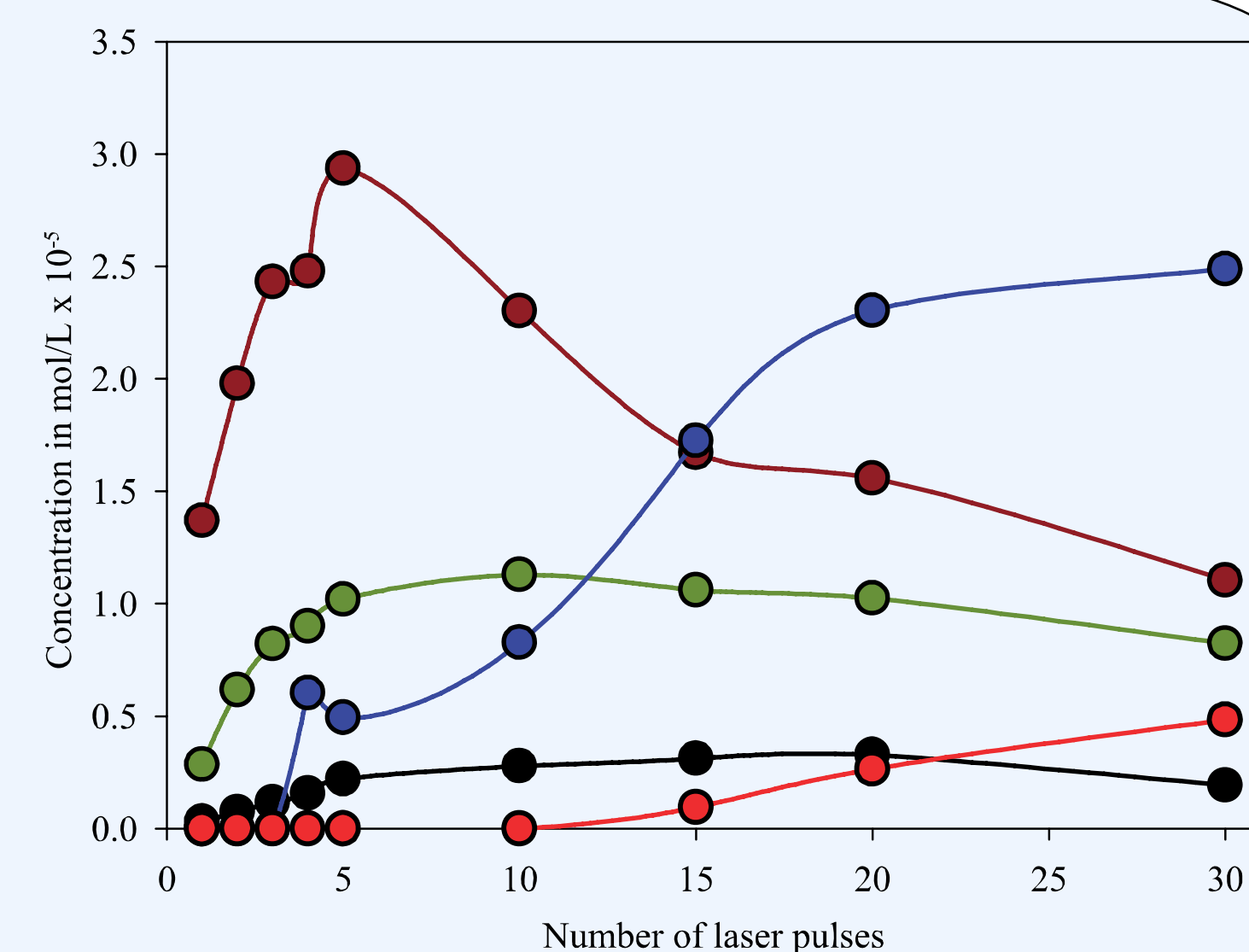
Figure 4 (right): Products formed after the oxidation of methyl vinyl ketone by OH in aqueous solution: **glyoxal**, **methylglyoxal**, **hydroxyacetone**, **pyruvic acid** and **glycolaldehyde**.

➢ Different C3 carbonyl compounds (see Figures 3 and 4) were identified as reaction products. The same compounds were also found in a study from Lui et al., 2009 in aqueous solution.

➢ Furthermore, different functionalized C4 carbonyl compounds (see Figures 5 and 6) were found. Concentrations of these products could not be calculated due to missing standards. These compounds are potential tracer for multiphase oxidation processes of isoprene in the atmosphere.
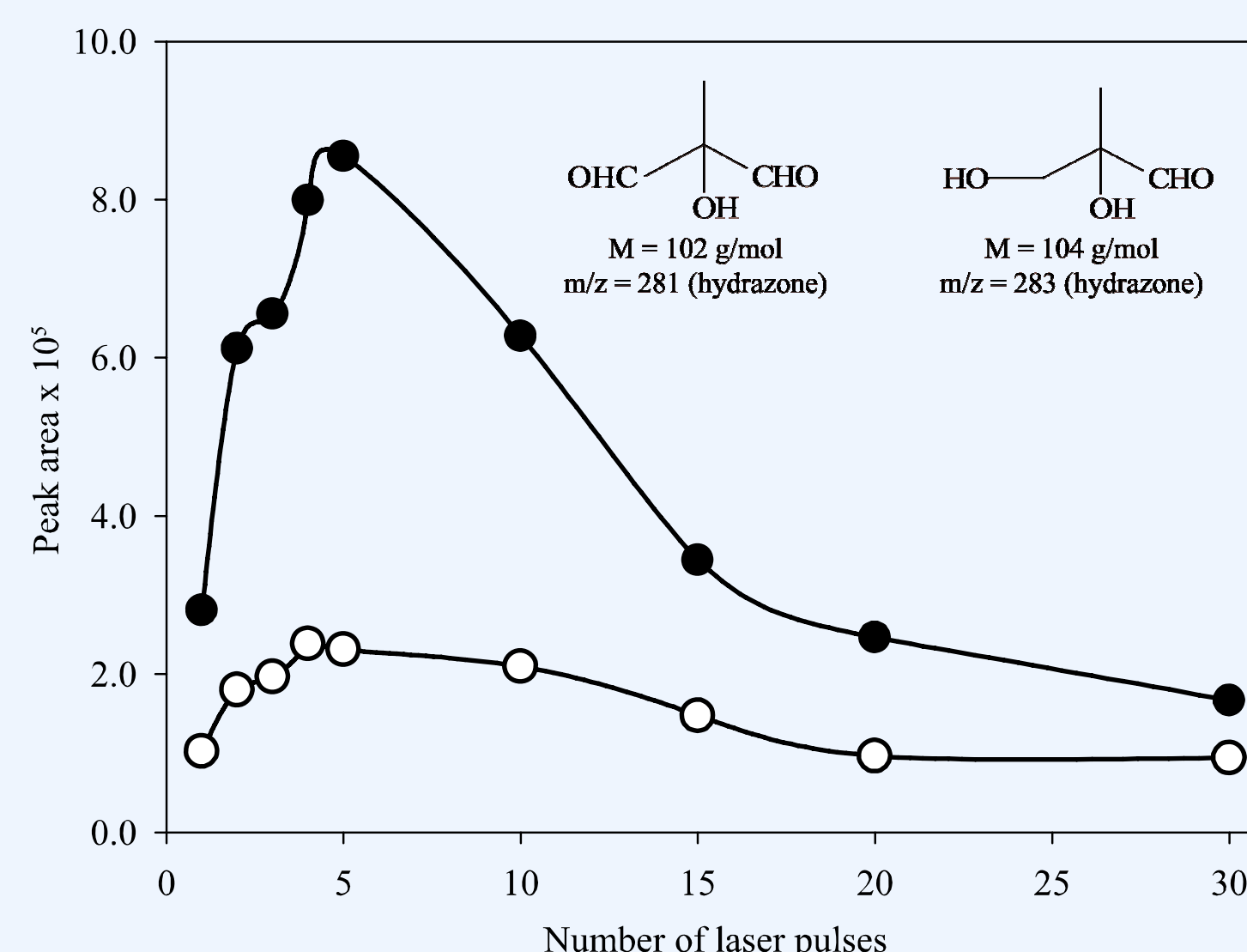

Figure 5 (left): Possible formation of proposed 'early' methacrolein oxidation products with four carbon atoms in Figure 2. m/z = 281 (○) and m/z = 283 (●).
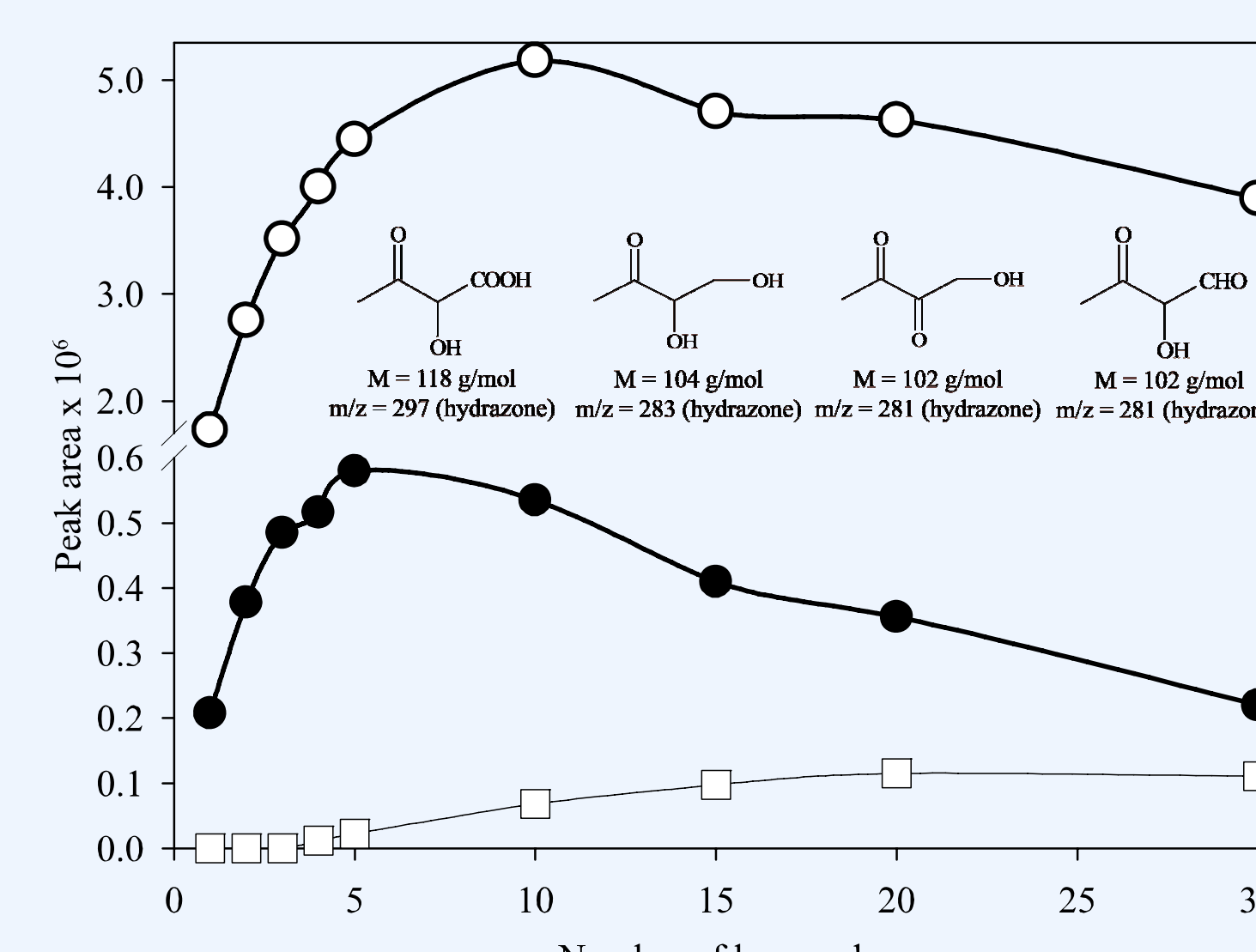
Figure 6 (right): Possible formation of proposed 'early' methyl vinyl ketone oxidation products with four carbon atoms in Figure 2. m/z = 281 (○), m/z = 283 (●) m/z = 297 (□).

Summary and Outlook

➢ Fast oxidation of isoprene degradation products by free radicals in aqueous solution.

➢ Identification of short chain mono- and polyfunctional carbonyls and carboxylic acids as oxidation products of methacrolein and methyl vinyl ketone 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.

➢ Results from the kinetic measurements and product studies will be implemented in atmospheric models to investigate the importance of these oxidation pathways for the formation of particle mass constituents such as carboxylic acids.

References

Atkinson, R., *Chem. Rev.* **1986**, 86, 69-201.
Buxton, G. V. et al., *J. Atmos. Chem.* **2000**, 36, 111–134.
Buxton, G. V. et al., *J. Phys. Chem. Ref. Data* **1988**, 17, 513–886.
Guenther, A. et al., *Atmos. Chem. Phys.* **2006**, 6, 3181–3210.
Kroll, J. H. et al., *Environ. Sci. Techn.* **2006**, 40, 1869-1877.
Kwok, E. S. C. et al., Int. J. Chem. Kinet. **1996**, 28, 925-934.
Lui, Y. et al., *Atmos. Chem. Phys.* **2009**, 9, 5093–5105.
Neta, P. et al., *J. Phys. Chem. Ref. Data* **1988**, 17, 1027–1284.
Pedersen, T.; Sehested, K., *Int. J. Chem. Kinet.* **2001**, 33, 182–190.
Surratt, J. D. et al., *Environ. Sci. Techn.* **2007**, 41, 5363– 5367.