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Motivation

- Acetone is an ubiquitous compound in the tropospheric gas phase ($c = 0.2\text{-}3$ ppbv) [1]
- In the upper troposphere it is mainly removed by photolysis whereby HO_x and PAN (Peroxyacetyl-nitrate) can be produced
- Reactions with OH radicals in the aqueous phase can lead to the generation of semi-volatile compounds
- Therefore it serves as precursor for the formation of SOA (secondary organic aerosol)
- Phase transfer processes as well as degradation reactions in the aqueous phase are still not completely understood
- An increased uptake of acetone could in turn influence the HO_x budget of the troposphere
- The results of previous studies [2], [3], [4] and [5] on the decomposition of acetone in the aqueous phase are shown in Figure 1
- By comparing the studies larger differences can be found so that there is a need for further investigations

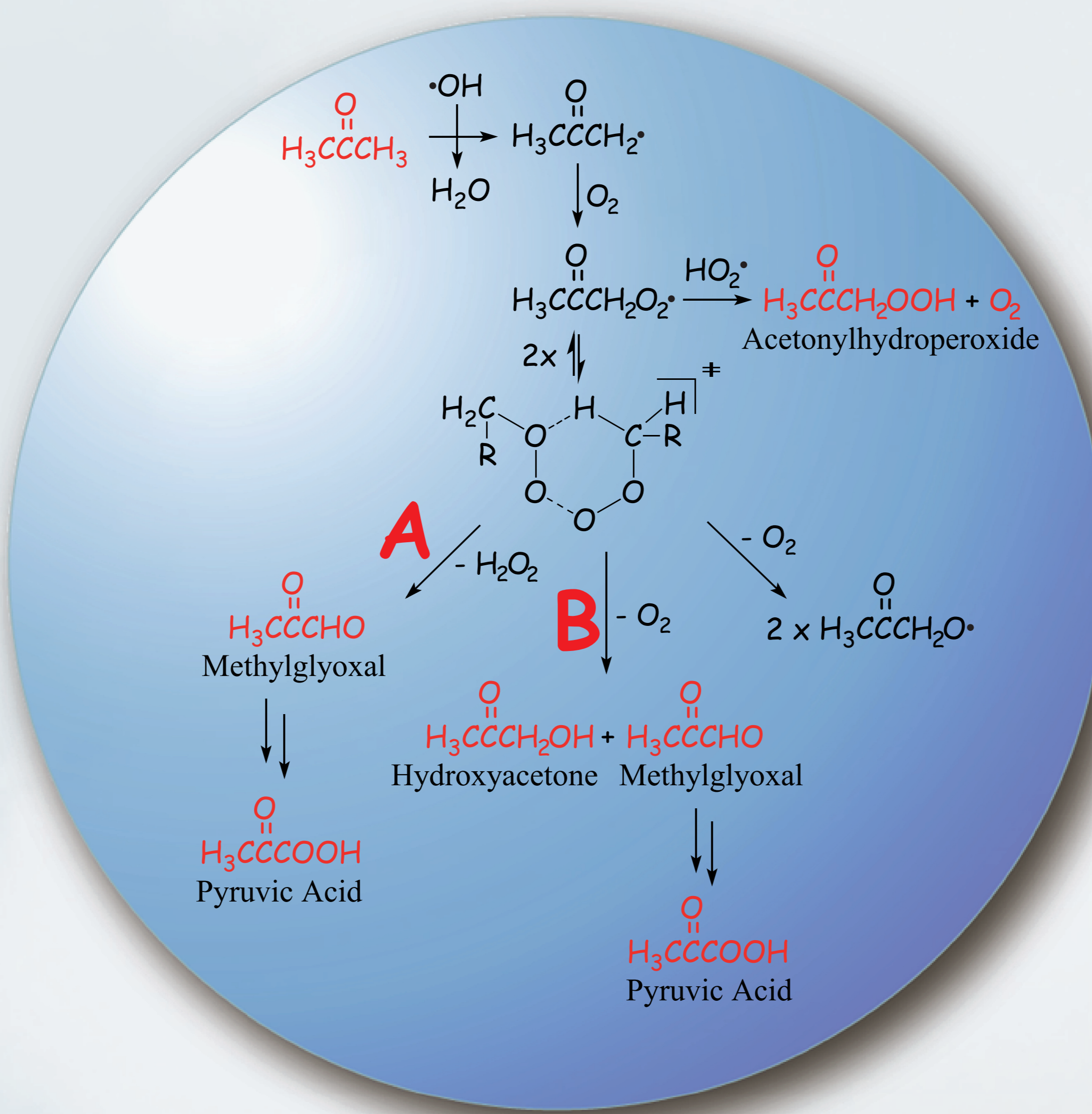


Figure 1: Reaction scheme (based on [2], [3], [4] and [5])

Experimental

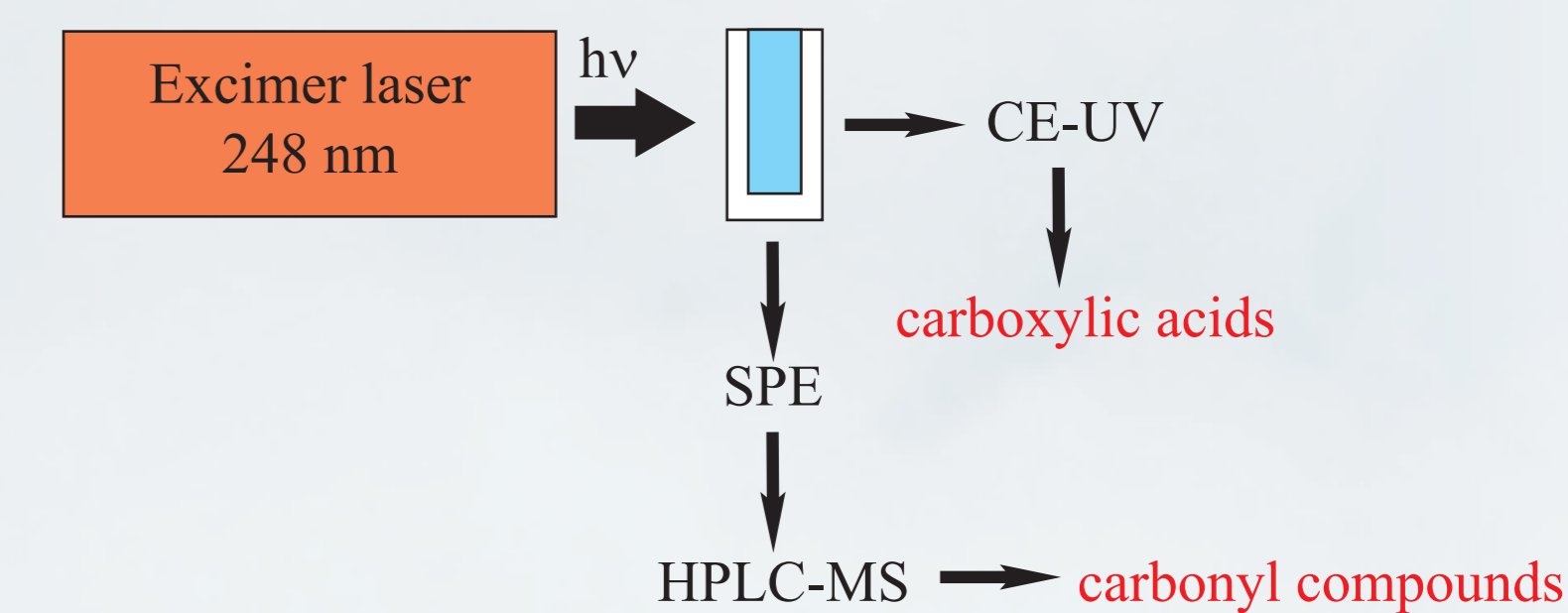


Figure 2: Scheme of the experiments

a) Laser photolysis

- OH radicals were generated by laser photolysis of hydrogen peroxide (1 mM)
- Excimer laser, KrF ($\lambda = 248$ nm)
- The acetone concentration was set to 0.1 mM

b) Analysis of carbonyl compounds

- Derivatization of carbonyl compounds with 2,4-DNPH
- SPE with Oasis HLB cartridge (3cc/60 mg, 30 μm): 2 ml of the sample were added and eluted with 1.25 ml of acetonitrile
- UltiMate 3000 HPLC-MS system, Dionex
- C₁₈-Phenyl column (Phenomenex Gemini 5u, 150 x 2 mm, particle size = 5 μm)
- Eluents: water/acetonitrile, both with 0.2 % acetic acid
- Detection: ESI-MS with Single Quad in negative mode

c) Analysis of carboxylic acids

- CE-UV Spectra Phoresis 1000, Thermo Separation Products with fused silica capillary
- Buffer: aqueous solution of 10 mM p-aminobenzoate, 8 mM diethylenetriamine, 3.5 mM NaOH and 1 % (v/v) methanol [6]
- Voltage: -29.4 kV
- Detection: indirect, $\lambda = 254$ nm

d) Ratio of path A and B

- For comparison with the other studies the ratio between the pathways A and B (Figure 1) were calculated
- Therefore the increase of the concentration of methylglyoxal and hydroxyacetone at 1-5 laser pulses was used
- The result of this work, shown in Table 2, is consistent with that of Stefan and Bolton [4]
- The favoured way of decomposition of the tetroxide is the formation of methylglyoxal and hydroxyacetone

Table 2: Ratio of the reactions A and B

Reference	A in %	B in %
[2]	69	31
[4]	29	71
[5]	64	36
this work	37	63

Results

a) Optimization of initial concentrations

- The concentration of OH radicals formed due to photolysis was calculated for different initial concentrations of hydrogen peroxide
- The following equation was used

$$[\text{OH}] = \frac{E_{\text{laser}} \lambda_{\text{laser}} \phi}{hcV N_A} \left(1 - 10^{-(k_{\text{H}_2\text{O}_2} c_{\text{H}_2\text{O}_2} + k_{\text{acetone}} c_{\text{acetone}}) d} \right)$$

- The fraction of OH radicals reacting with acetone was simulated with GePaSi (Table 1)

- For the simulation the following kinetic model was used:

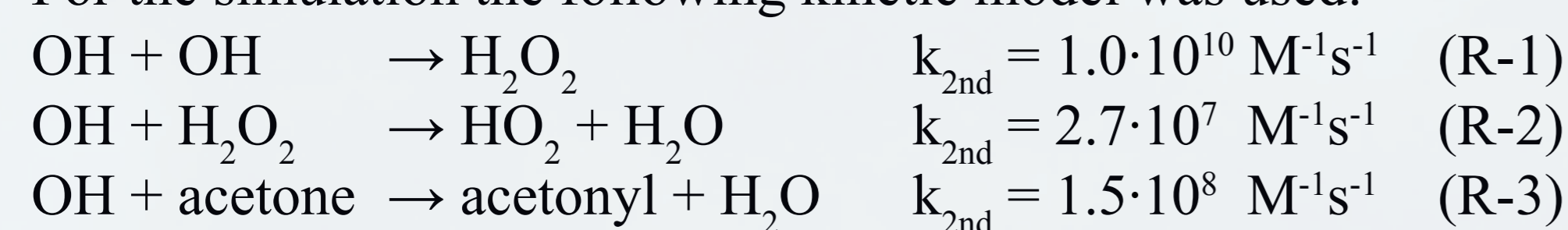


Table 1: Initial concentration of hydrogen peroxide and the formed OH radicals, as well as the fraction of the three possible reactions

$[\text{H}_2\text{O}_2]_0$ in M	$[\text{OH}]$ in M	(R-1) in %	(R-2) in %	(R-3) in %
$1 \cdot 10^{-2}$	$8.3 \cdot 10^{-5}$	50	47	3
$1 \cdot 10^{-3}$	$7.5 \cdot 10^{-6}$	41	38	21
$1 \cdot 10^{-4}$	$5.2 \cdot 10^{-7}$	12	13	75

- The ratio of the concentrations of hydrogen peroxide to acetone has to be decreased to increase the fraction of OH radicals reacting with acetone
- The initial concentration of hydrogen peroxide was set to 1 mM to obtain a detectable conversion of acetone

b) Results of the photolysis experiments

- The concentration of acetone and the forming oxidation products was measured dependent on the number of laser pulses
- The decomposition of acetone was not detectable until 20 laser pulses
- Detected products were: methylglyoxal and hydroxyacetone as primary products; pyruvic acid and acetic acid as second generation products; formic acid, glycolic acid and oxalic acid are late products

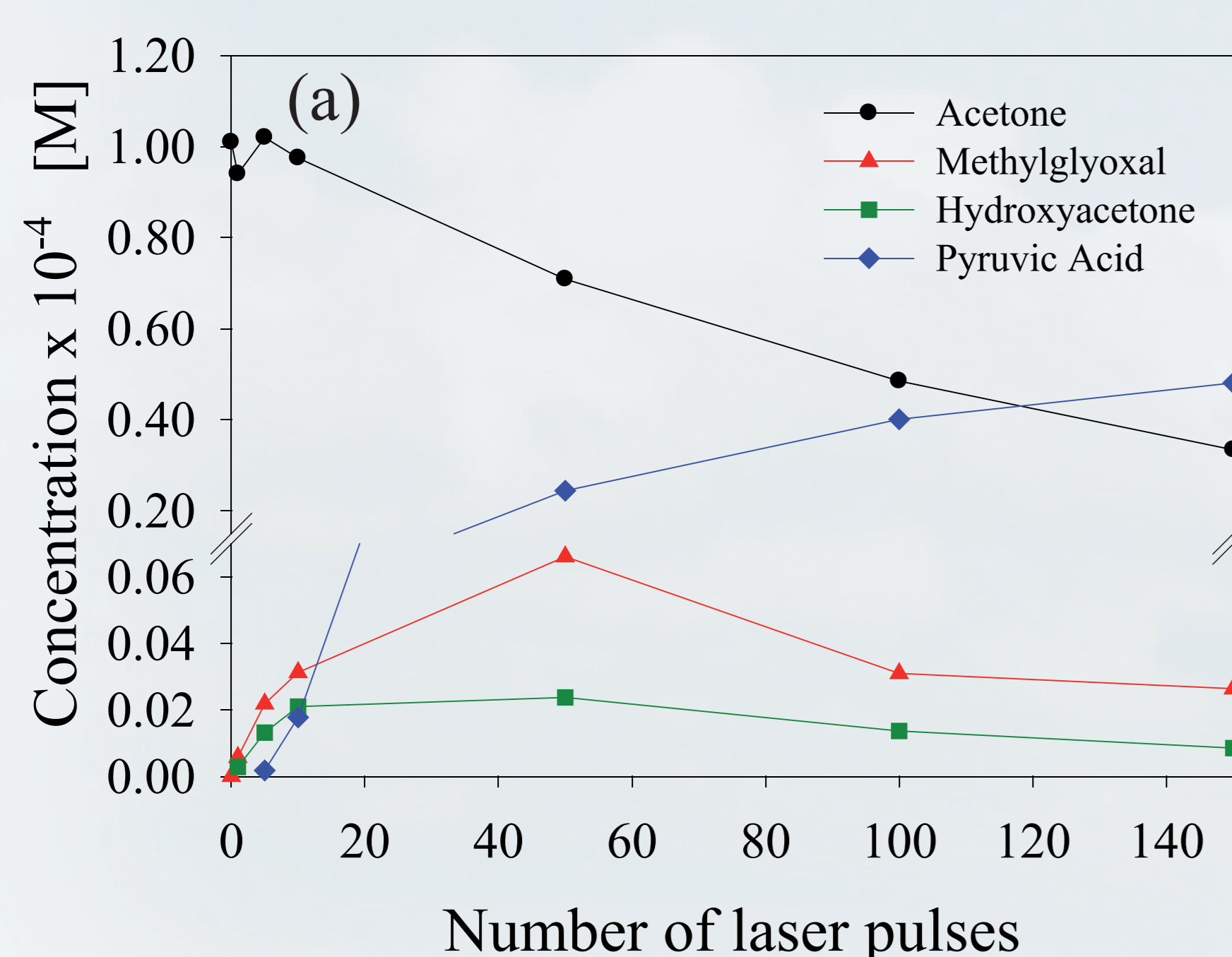


Figure 3: Concentration distribution of acetone and the oxidation products dependent on the number of laser pulses: (a) measured as derivatives with 2,4-DNPH with HPLC-MS and (b) carboxylic acids measured with CE-UV

c) Reaction scheme

- The formation of the products can be explained with mechanisms of Schuchmann and von Sonntag [7]
- Main mechanisms are the bimolecular decomposition of a tetroxide formed of two peroxy radicals (Figure 1) and the elimination of HO_2

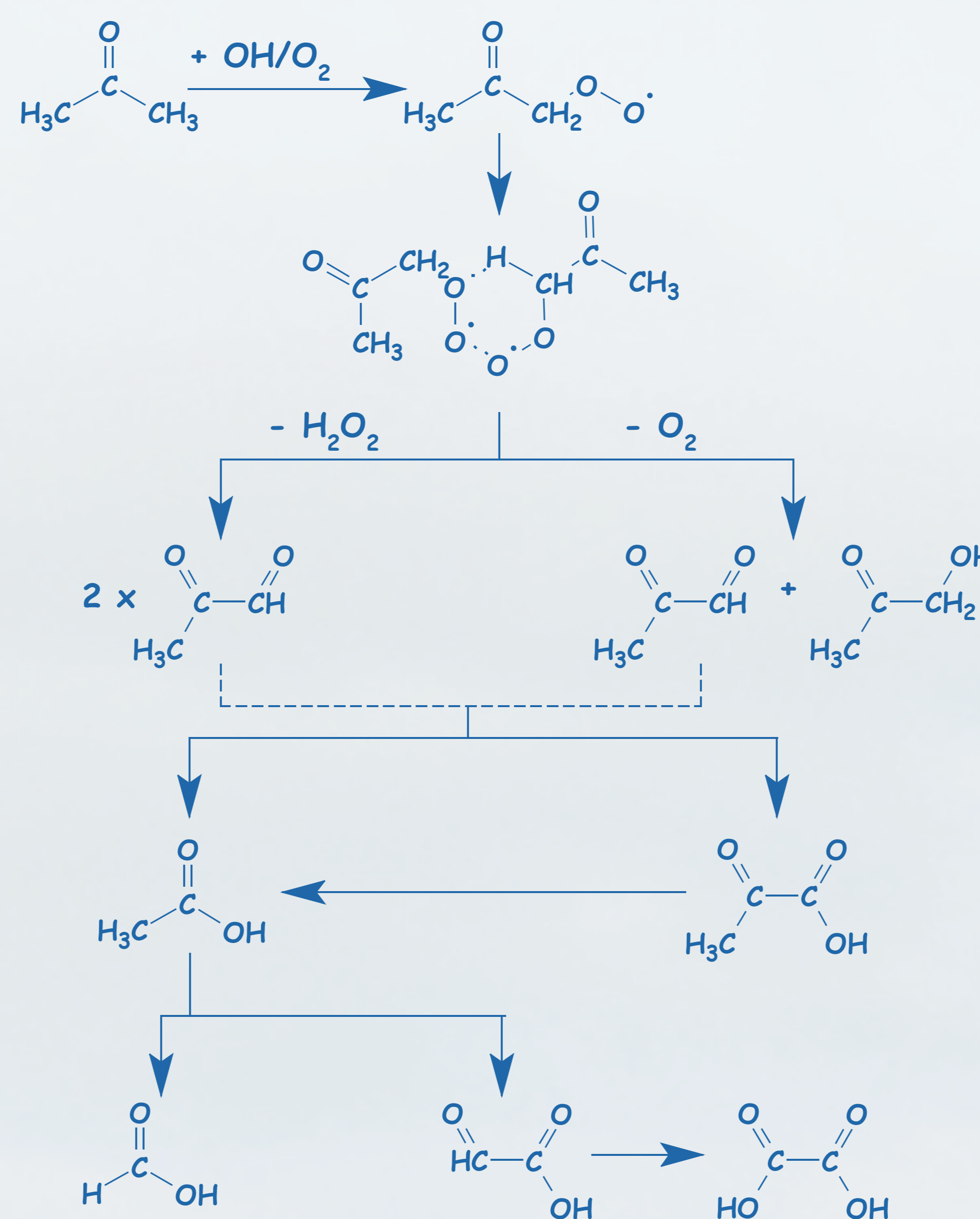
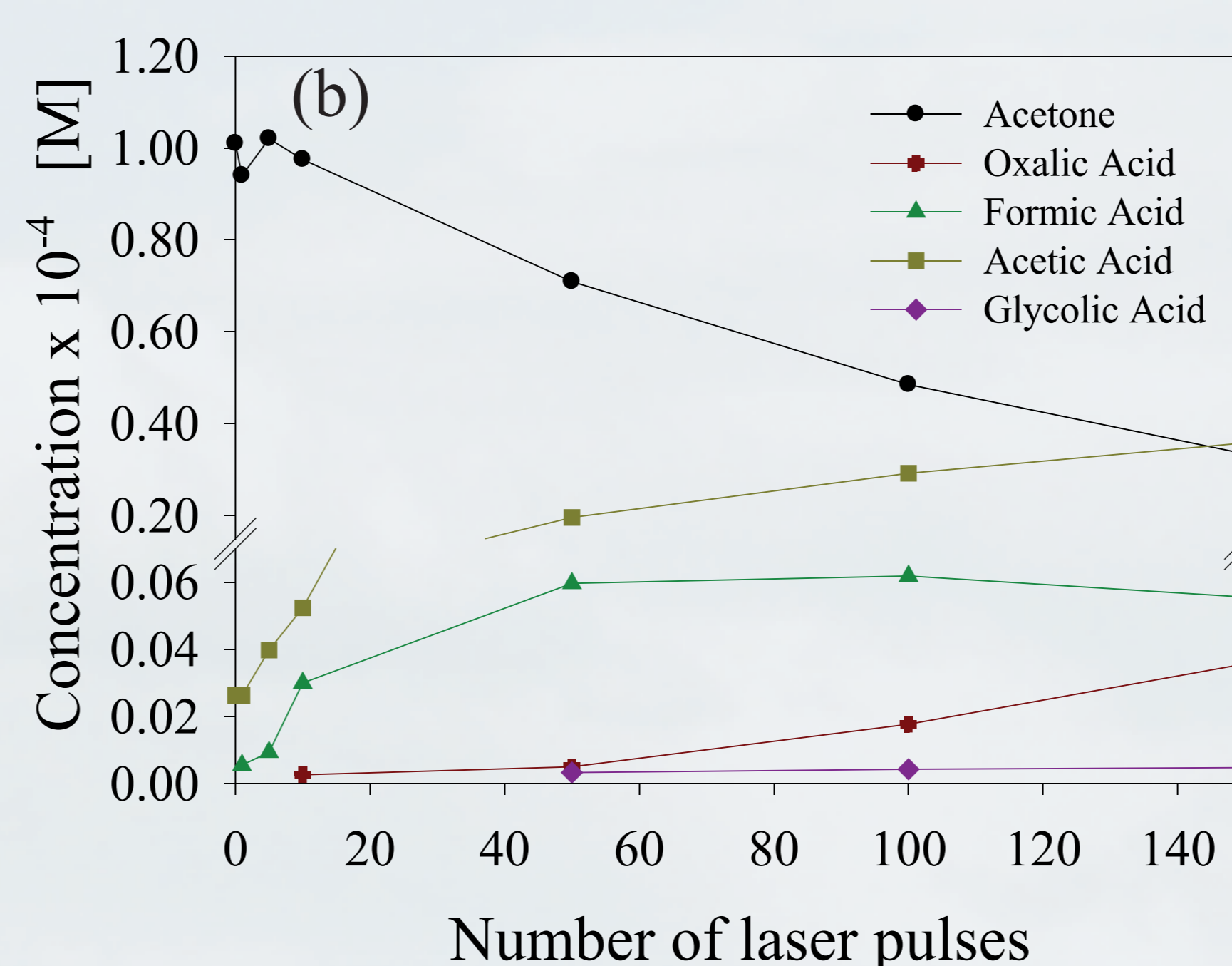


Figure 4: Developed reaction scheme on the basis of the measurements and reaction mechanisms of Schuchmann and von Sonntag [7]



Summary and Outlook

- The OH radical initiated degradation of acetone in aqueous phase was measured
- The amount of OH radicals reacting with acetone is dependent on the ratio of the initial concentrations of hydrogen peroxide to acetone
- A reaction scheme was developed from the distribution of the concentrations of acetone and the oxidation products
- The results of this work together with reaction kinetics (e.g. recombination of peroxy radicals) can be implemented in atmospheric models

References

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