

Supplementary information

A fast and efficient method for the analysis of α -dicarbonyl compounds in aqueous solutions: development and application

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SI1 Literature review of trapping reagents used for the quantification of α -dicarbonyl compounds in liquid samples.

Trapping reagents	Detection method	Chromatographic method	Matrix type	References
(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA)	MS, ECD, NPD, FPD	GC	Wine, ozonated drinking, surface and waste waters	(Glaze et al., 1989; Yamada and Soniya, 1989; Cancilla and Que Hee, 1992; Cancilla et al., 1992; de Revel and Bertrand, 1993; le Lacheur et al., 1993; Seaman et al., 2006; Serrano et al., 2013; Rodigast et al., 2015)
Dinitrophenylhydrazine (DNPH)	UV, MS	LC	Airborne, fine particulate matter (PM2.5), crude oil - seawater mixture, seawater, surface microlayer, rain fog	(Druzik et al., 1990; Grosjean and Grosjean, 1994; Zhou and Mopper, 1997; Matsumoto et al., 2005; Takeda et al., 2006, 2014; Nakajima et al., 2007; Collett et al., 2008; Wang et al., 2009; Mu et al., 2010; Kampf et al., 2011; Uchiyama et al., 2011; Ervens et al., 2013; Cao and Tarr, 2017; Li et al., 2020)
Phenylenediamine	UV, MS, FID, NPD	GC, LC	Cigarette smoke, oils, beverages, synthetic liquid sample	(Niyati-Shirkhodae and Shibamoto, 1993; Nishiyama et al., 1994; de Revel et al., 2000; Rodrigues et al., 2002; Fujioka and Shibamoto, 2004; Shibamoto, 2006; da Silva Ferreira et al., 2007; Degen et al., 2012; Ramos et al., 2012; Jeong et al., 2017; Kim et al., 2021)
Girard T reagent	UV	LC	Beverages, synthetic aqueous sample	(Mitchel and Birboim, 1977; Wells-Knecht et al., 1995; Lawrence et al., 2017)
Cysteamine	NPD, MS	GC	Food and beverages	(Hayashi and Shibamoto, 1985; Hayashi et al., 1985)
Benzylhydroxylamine (BHA)	MS, FID	GC	Rain, snow, gaseous and particulate	(Matsunaga and Kawamura, 2000; Kawamura et al., 2013)
4-nitro-phenylenediamine	UV	LC	Beer	(Li et al., 2012)
4-methoxy-phenylenediamine	Fluorimetric	LC	Wine, urine	(Maroulis et al., 1985; Ojeda et al., 2014)
Stilbenediamine	UV	LC	Serum	(Khuhawar et al., 2006; Mirza et al., 2007)
4,5-dimethoxy-phenylenediamine	Fluorimetric	LC	Urine, synthetic liquid sample, blood plasma	(Hara et al., 1988; McLellan et al., 1992; Thornalley et al., 1999; Akira et al., 2004; Ogasawara et al., 2016)
1,2-diamino-4,5-methylenedioxybenzene	Fluorimetric	LC	Aqueous synthetic sample, urine, serum	(Hara et al., 1988; Yamaguchi et al., 1989)
2,3-diaminonaphthalene	UV, MS	LC, GC	Drinking and pool water, urine, plasma beverages, cells	(Nagai et al., 2002; Neng et al., 2007; Usui et al., 2007; Chen et al., 2015; Pastor-Belda et al., 2017)
Aminoguanidine	MS	GLC	Synthetic liquid sample, serum	(Hirsch et al., 1995; Glomb and Tschimich, 2001; Araki et al., 2005)
6-hydroxy-2,4,5-Triaminopyrimidine	Fluorimetric	LC	Urine, synthetic liquid sample	(Espinosa-Mansilla et al., 1998; Manini et al., 2006)
3-methyl-2-benzothiazolinone hydrazone	UV	LC	Cloudwater	(Igawa et al., 1989)
Dansylacetamidooxylamine	Fluorimetric	LC	Snow, rain, cloudwater	(Houdier et al., 2011)
BF3/n-butanol	MS, FID	GC	Fine particulate matter (PM2.5), seawater, precipitation	(Kawamura, 1993; Kawamura and Ikushima, 1993; Li and Yu, 2005; Tedetti et al., 2006; Cao et al., 2017; Kalogridis et al., 2018; Liu et al., 2019)
2-thiobarbituric acid	Amperometric	Capillary electrophoresis	Urine, river and pool water	(Zhang et al., 2010)

Table SII. Trapping reagents used for the quantification of α -dicarbonyl compounds in liquid samples. MS: Mass Spectrometry. ECD: Electron Capture Detector. GC: Gas Chromatography. FID: Flame Ionisation Detector. UV: UV absorbance detection. LC: Liquid Chromatography. NPD: Nitrogen-Phosphorus Detector. GLC: Gas-Liquid Chromatography. RT: Room Temperature.

SI2 Chemicals and reagents

Chemicals	Purity	Company
Glyoxal	40 wt. % solution in water	Sigma-Aldrich
Methylglyoxal	40 wt. % solution in water	Sigma
2,3-Butanedione	97%	Aldrich
Phenylglyoxal monohydrate	97%	Aldrich
Glycolic acid	99%	Acros Organics
α -nitrooxyacetone	Laboratory product	Laboratory product
Lactic acid	90% wt. % in water	Fisher Chemical
Mandelic acid	99%	Aldrich
2-Methylactic acid	99%	Aldrich
Valeric acid	99%	Aldrich
Formic acid	99.5%	Optima
Oxalic acid	99%	Aldrich
Glyoxilic acid monohydrate	98%	Acros Organics
Sulfuric acid	95%	Fisher Chemical
Sodium hydroxide	50% wt. % in water	Fisher Chemical
Sodium carbonate	99%	Prolabo
Sodium bicarbonate	99%	Chemlab
Hydrogen peroxide	30% wt. % in water	Acros Organics
Water	18.2 M Ω .cm, TOC < 2 ppb	Laboratory product (Milli-Q water purification system from Millipore)

Table SI2. Chemicals and reagents used during the experiments.

SI3 Synthesis of α -nitrooxyacetone

Non-commercial α -nitrooxyacetone was synthesized according to the method developed by González-Sánchez et al (2021). The synthesis consisted in two nucleophilic substitution steps to produce α -nitrooxyacetone from chloroacetone with iodoacetone as an intermediate product. 1.2 eq-mol of KI was added to a solution of chloroacetone in acetone. The solution was stirred in the dark at room temperature for 20 h. The mixture was filtered and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography (pentane 10:1 ethyl acetate) leading to a deep brown oil. To an acetonitrile solution of iodoacetone, 1.5 eq-mol of AgNO_3 was slowly added under dark conditions at 0 °C and stirred for 20 h at room temperature (still under dark conditions). The precipitate was filtered and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography (pentane 1:1 ethyl acetate) and lead to a yellow oil.

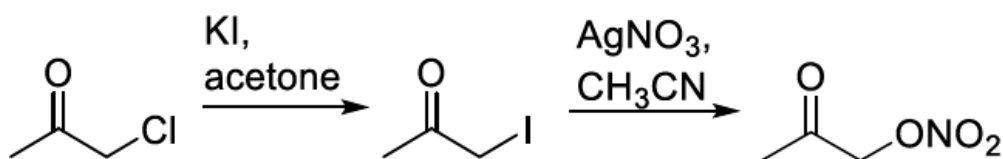


Fig SI3.1: Synthesis of α -nitrooxyacetone.

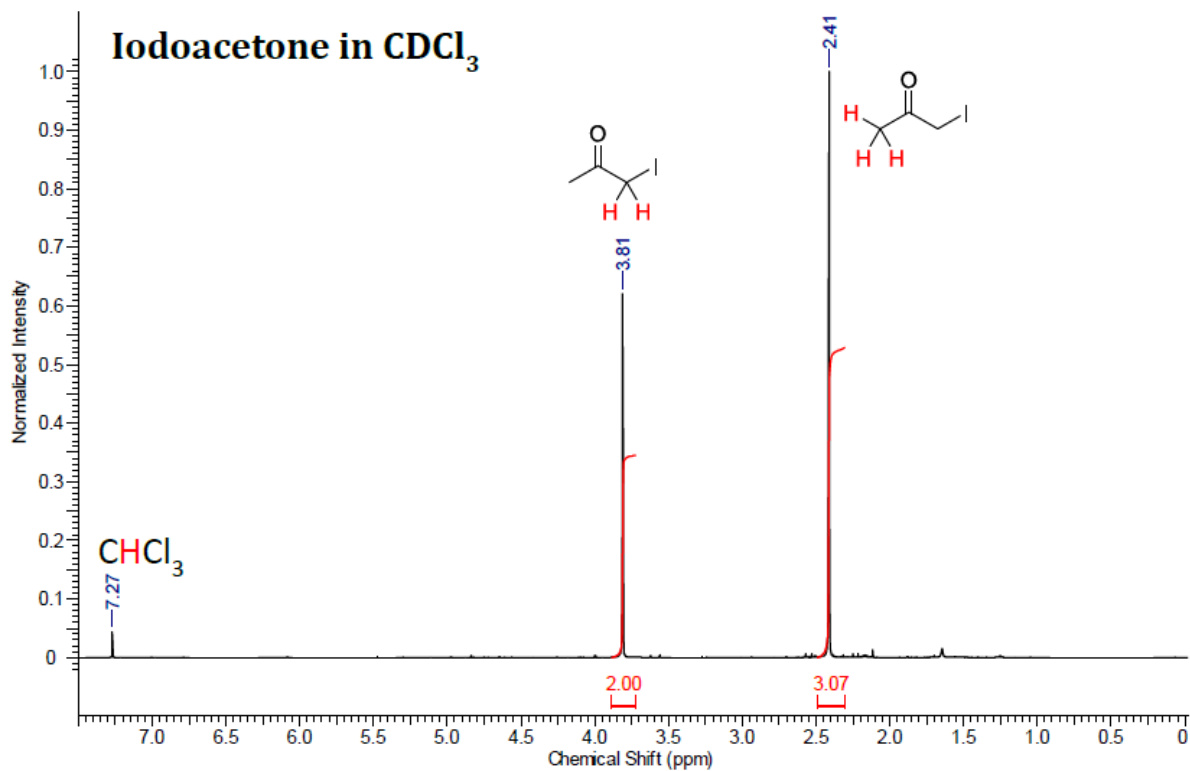


Fig SI3.2: ¹H-NMR spectra of the synthesised iodoacetone in CDCl₃.

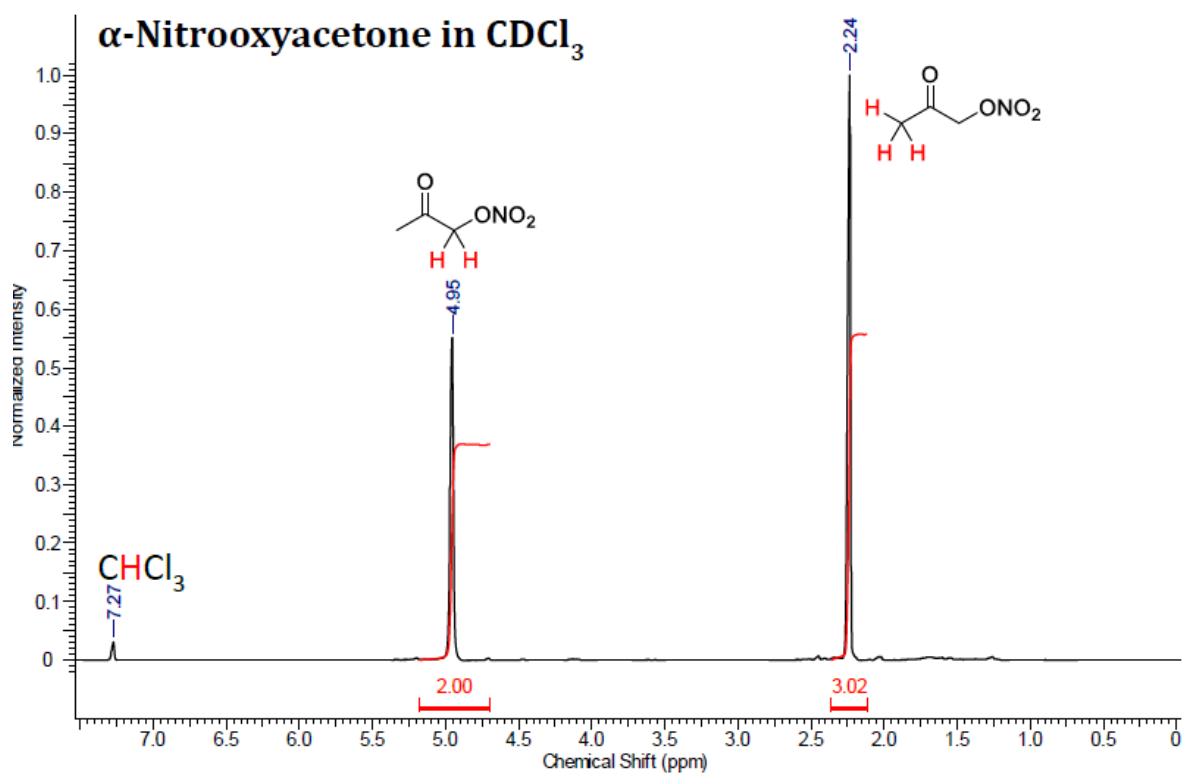


Fig SI3.3: ¹H-NMR spectra of the synthesised α-nitrooxyacetone in CDCl₃.

SI4 Xenon arc lamp irradiance spectrum

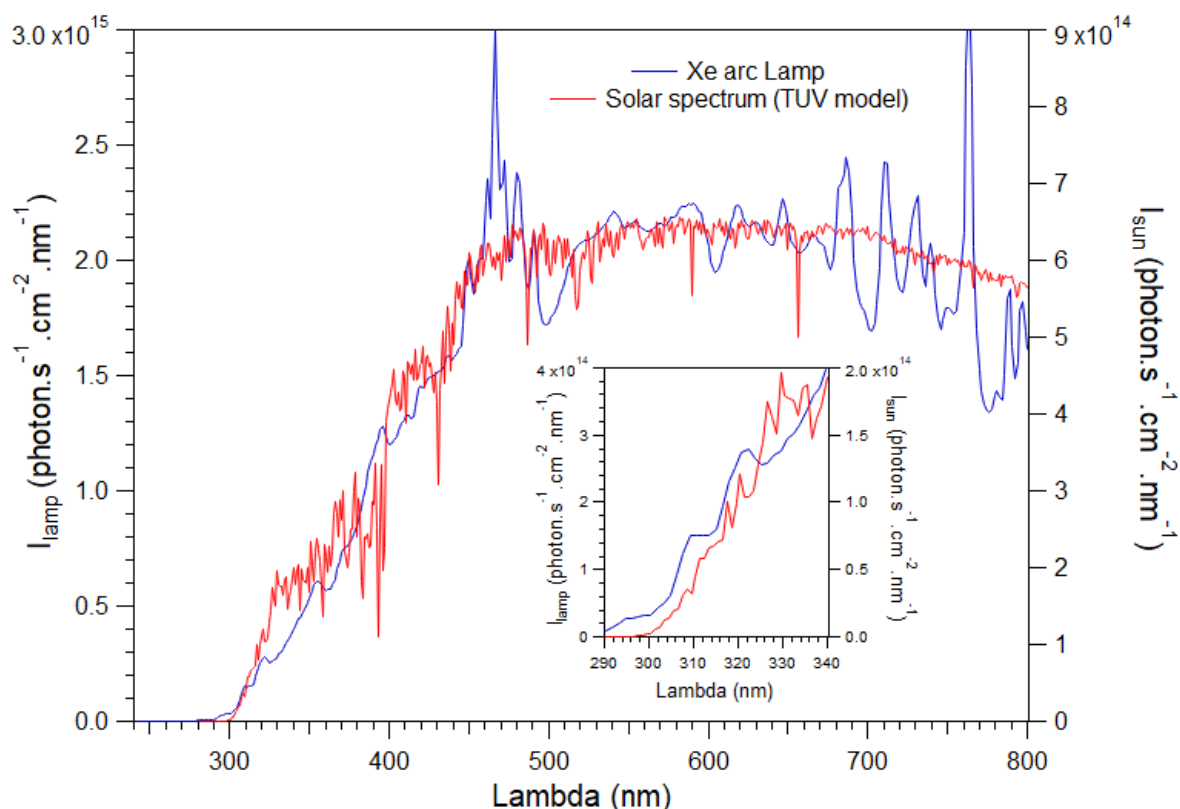


Fig SI4: Irradiation spectra of the Xe 1000 W Arc Lamp equipped with an AM1.5 filter (blue trace, left axis) compared to the solar irradiation spectra (red trace, right axis). Inner graph: zoom in the 290 to 340 nm region.

The actinic flux was taken from the Tropospheric Ultraviolet-Visible (TUV) model at Marseille (43.3 °; 5.4 °; noon; 21/06/2019; ground level). The lamp actinic flux is 3.5 times more intense than the sunlight under these conditions. However, the spectrum was measured at the brightest spot of the lamp, therefore, it does not represent the average intensity received by the photoreactor.

SI5 H₂O₂ analysis

H₂O₂ was monitored by UHPLC-UV analysis (Thermo Scientific Accela 600) at 197 nm in the same way as (Renard et al., 2015). The device was equipped with a Hypersil Gold C18 column (50 x 2.1 mm) with a particle size of 1.9 μm and an injection loop of 5 μL. A binary eluent of H₂O and CH₃CN was used for all analyses at a flow rate of 400 μLmin⁻¹. The elution gradient started from H₂O/CH₃CN 80/20 (v/v) to (70/30) (v/v) in 1 min, held at this proportion for 1 min, and then set back to 80/20 (v/v) within 10 s until the end of the run at 3 min.

SI6 Simulations of the conversion rate constant of α -dicarbonyl compounds to the corresponding α -hydroxy carboxylates under basic conditions

The models developed by Fratzke and Reilly (1986) and by Hine et al. (1971) predict the pseudo first order conversion rate constants k of glyoxal, methylglyoxal and phenylglyoxal as a function of hydroxide concentrations according to equation 1.

$$k = \frac{a_1[\text{OH}^-] + a_2[\text{OH}^-]^2}{1 + a_3[\text{OH}^-]} \quad \text{Equation 1}$$

Where a_1 and a_2 are related to the role of intermediate reactants of the benzilic rearrangement. Using the a_i coefficients provided by the above-mentioned studies, we have plotted pseudo-first-order conversion rate constants of the three α -dicarbonyls as a function of pH (Fig SI6.1). Using pseudo-first-order kinetics, we have also calculated the conversion factors ($C_f = 1 - \exp(-kt)$) versus pH and time for glyoxal at 25°C (Fig SI6.2), methylglyoxal at 25°C (Fig SI6.3) and phenylglyoxal at 35°C (Fig SI6.4). These figures clearly show that under our HPIC_{carbonate} conditions (pH=10.14), none of the dicarbonyls are converted within the analytical time of 10 minutes; whereas under our HPIC_{NaOH} conditions (pH=12.24), only glyoxal is totally converted within the analytical time of 10 minutes, whereas methylglyoxal nor phenylglyoxal are only partly converted.

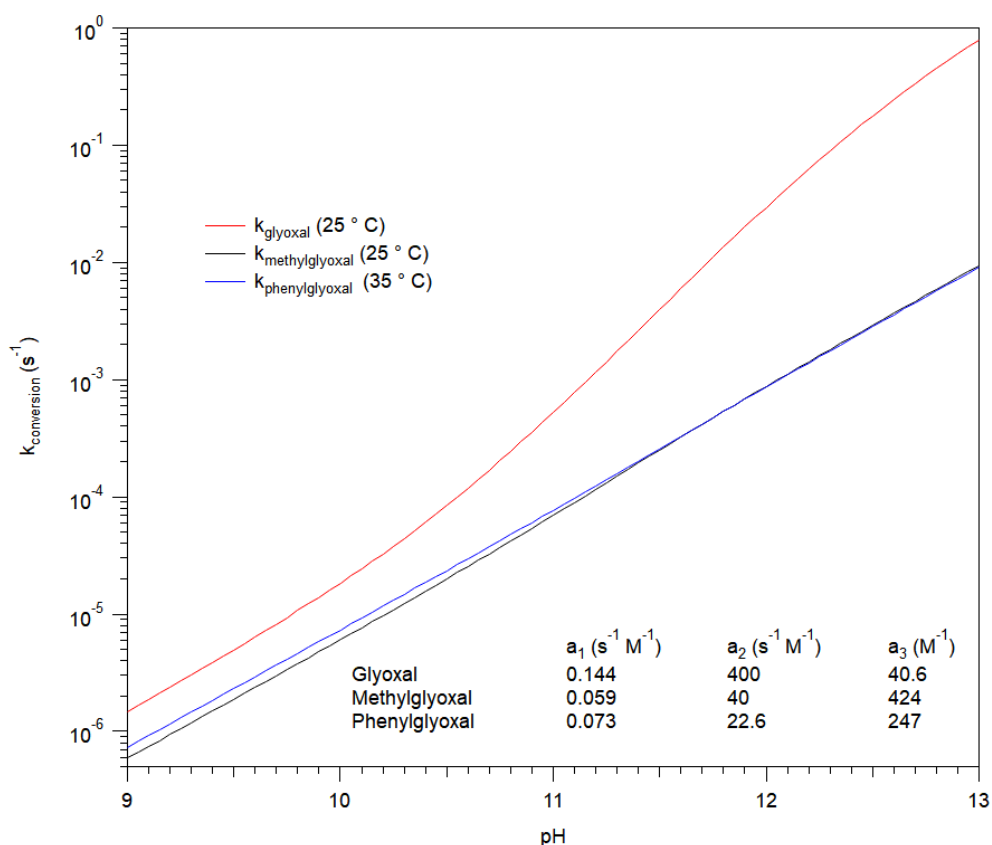


Fig SI6.1 Pseudo first-order conversion rate constant of α -dicarbonyl compounds according to the models proposed by Fratzke and Reilly (1986), Fratzke (1985) and Hine et al. (1971).

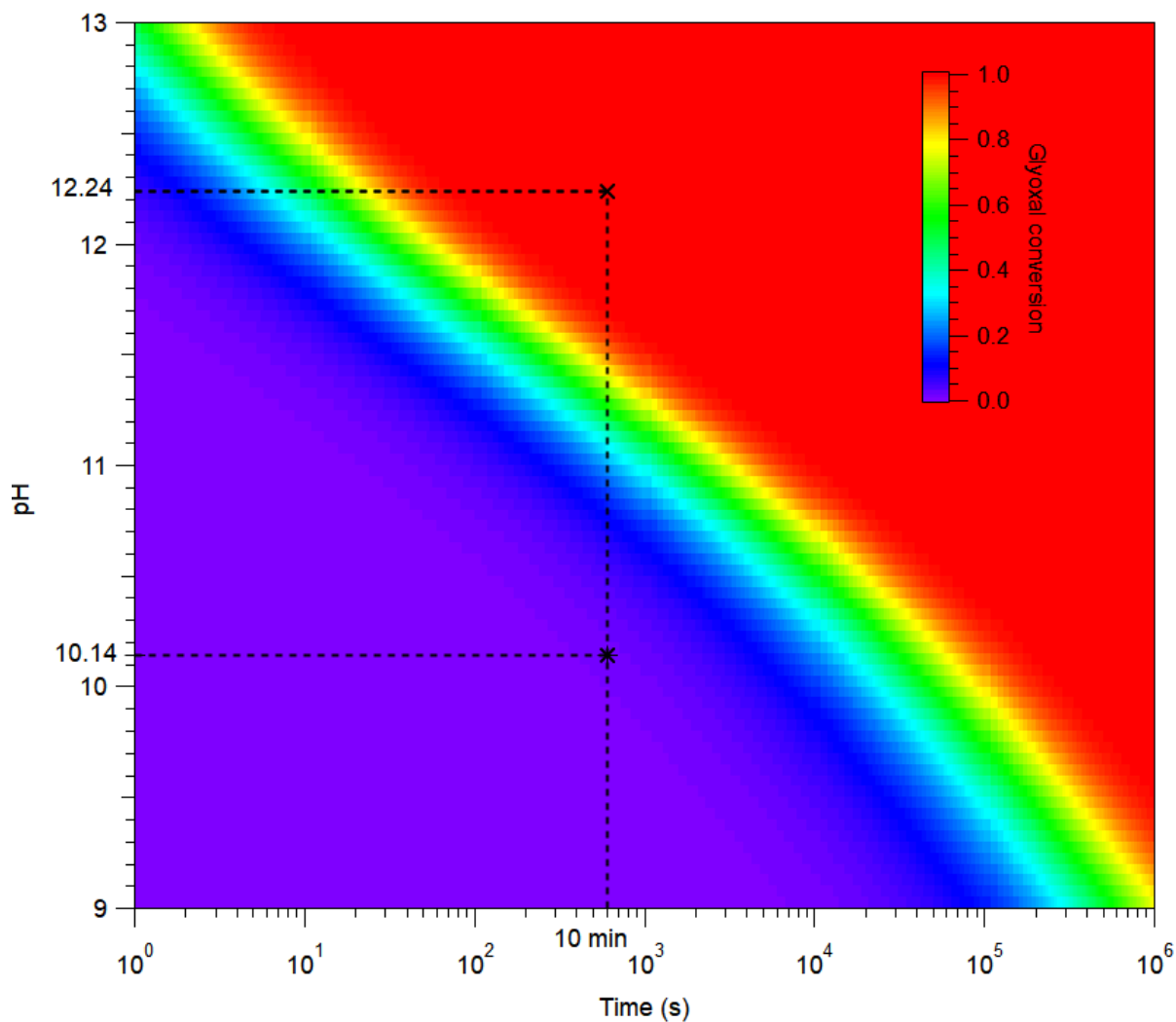


Fig SI6.2: Glyoxal conversion factor as a function of time and pH at 25°C using the model proposed by Fratzke and Reilly (1986). The black crosses show the glyoxal conversion factor under our experimental pH conditions, for an analytical time of 10 min.

Fig SI6.2 shows that at $\text{pH} = 10.14$, the expected glyoxal conversion within 10 min of reaction should be 1.6% and should therefore be negligible in agreement with our $\text{HPIC}_{\text{carbonate}}$ results. However, at $\text{pH} = 12.24$ (and above), the expected glyoxal conversion within 10 min of reaction should be 100% and therefore very significant, in agreement with the work by (Chen et al., 2005) and with our strong signal observed using $\text{HPIC}_{\text{NaOH}}$.

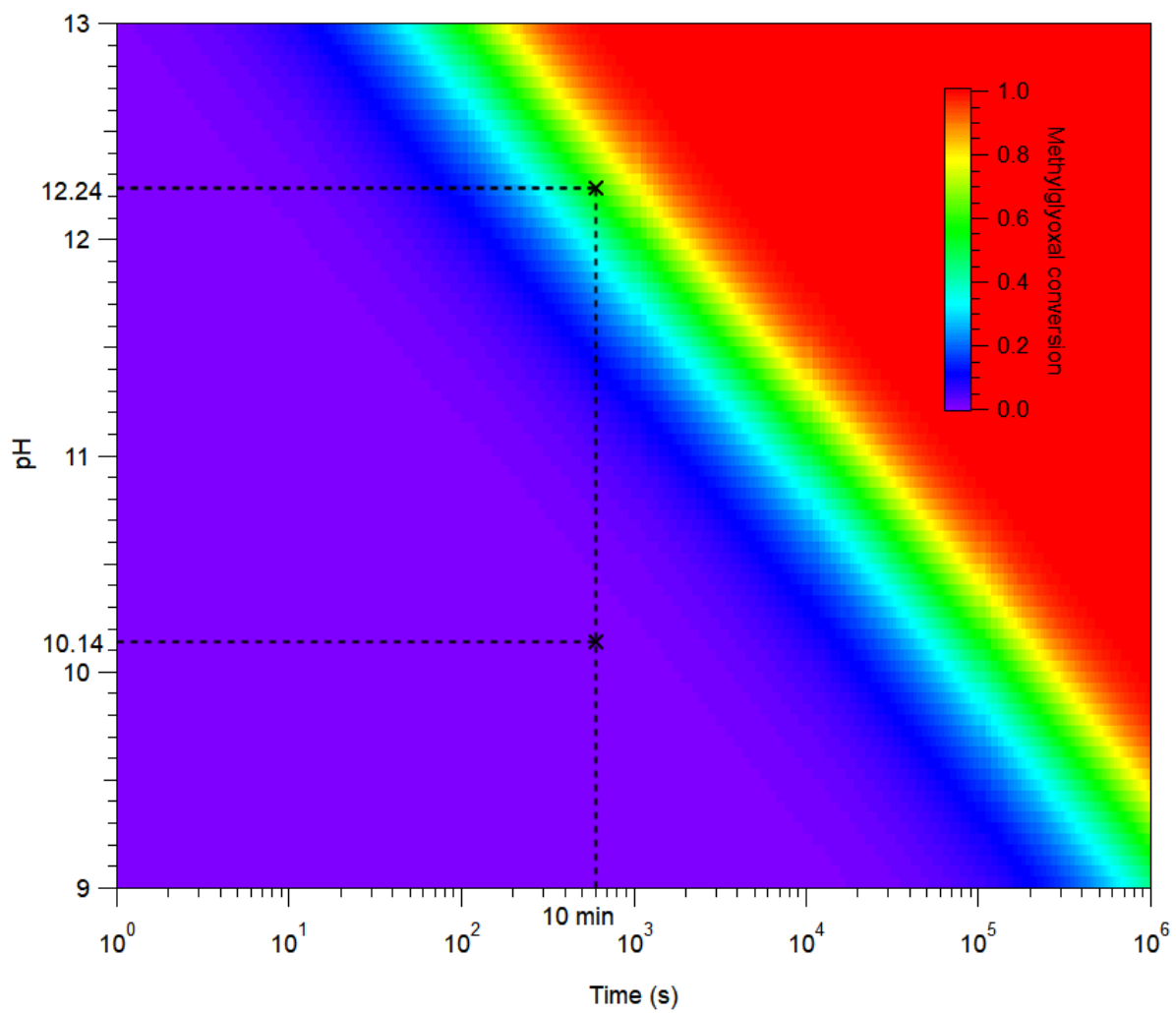


Fig SI6.3: Methylglyoxal conversion factor as a function of time and pH at 25°C using the models proposed by Fratzke and Reilly (1986) and Fratzke (1985). The black crosses represent the methylglyoxal conversion factor under our experimental conditions, for an analytical time of 10 min.

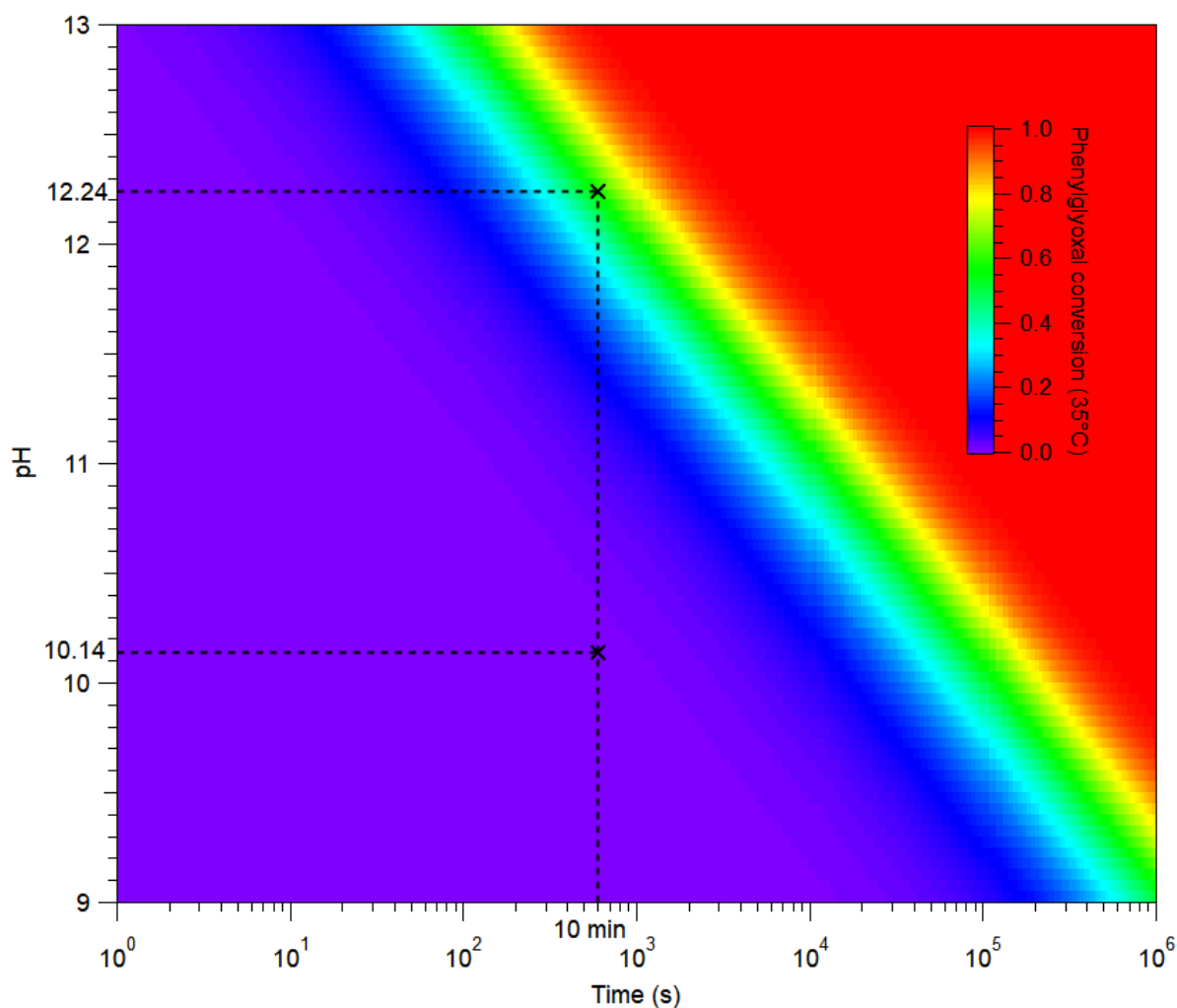


Fig SI6.4: phenylglyoxal conversion factor as a function of time and pH at 35°C, using the models proposed by Fratzke and Reilly (1986) and Hine et al. (1971). The black crosses represent the phenylglyoxal conversion factor under our experimental conditions, for an analytical time of 10 min.

According to the kinetic model predictions of i) Fratzke and Reilly (1986) for methylglyoxal and ii) Hine et al. (1971) for phenylglyoxal, the conversion kinetics of these two compounds are similar. At pH = 10.14, considering an analysis time of 10 minutes the conversion of methylglyoxal and phenylglyoxal should be around 0.6 % and thus negligible, which is consistent with our observations. At pH = 12.24, the expected conversion of methylglyoxal and phenylglyoxal should be around 61% within 10 minutes of reaction, which is also consistent with the lactate and mandelate signals that were detected, respectively.

SI7 Reaction mechanism of diacetyl in alkaline solutions:

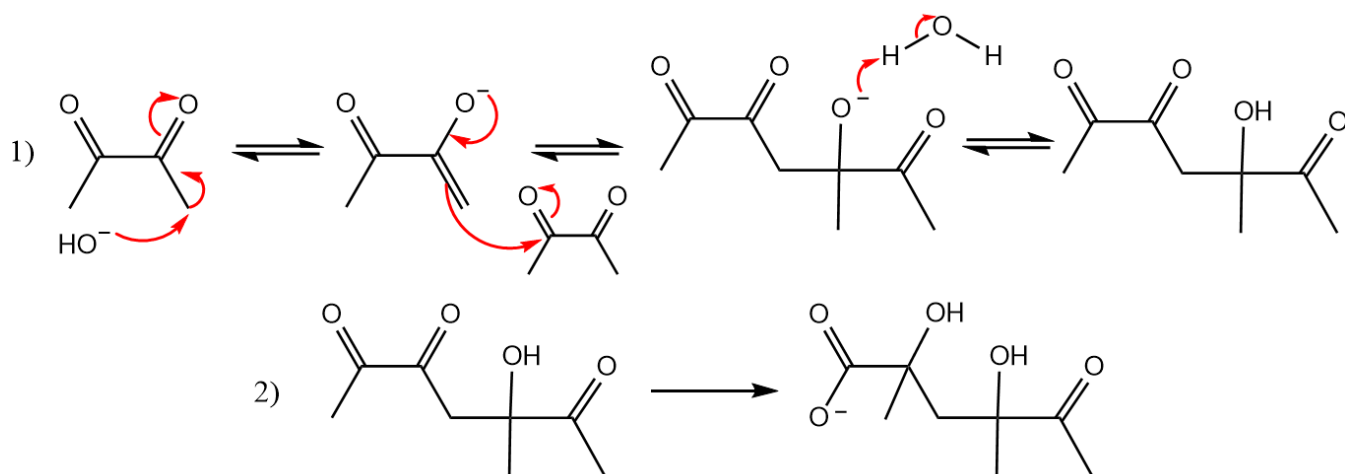


Fig. SI7 – Reaction mechanism of diacetyl in alkaline solutions: 1) base catalysed aldol condensation, 2) benzilic acid rearrangement (Machell, 1960).

SI8 Temperature dependency of the glyoxal conversion rate constant k_{glyoxal} at pH=12.24

Using the model proposed by Fratzke and Reilly (1986) at pH=12.24 for each a_i factor versus T, Figure SI7 shows that the temperature dependency of k_{glyoxal} at pH=12.24 shows an Arrhenius behavior.

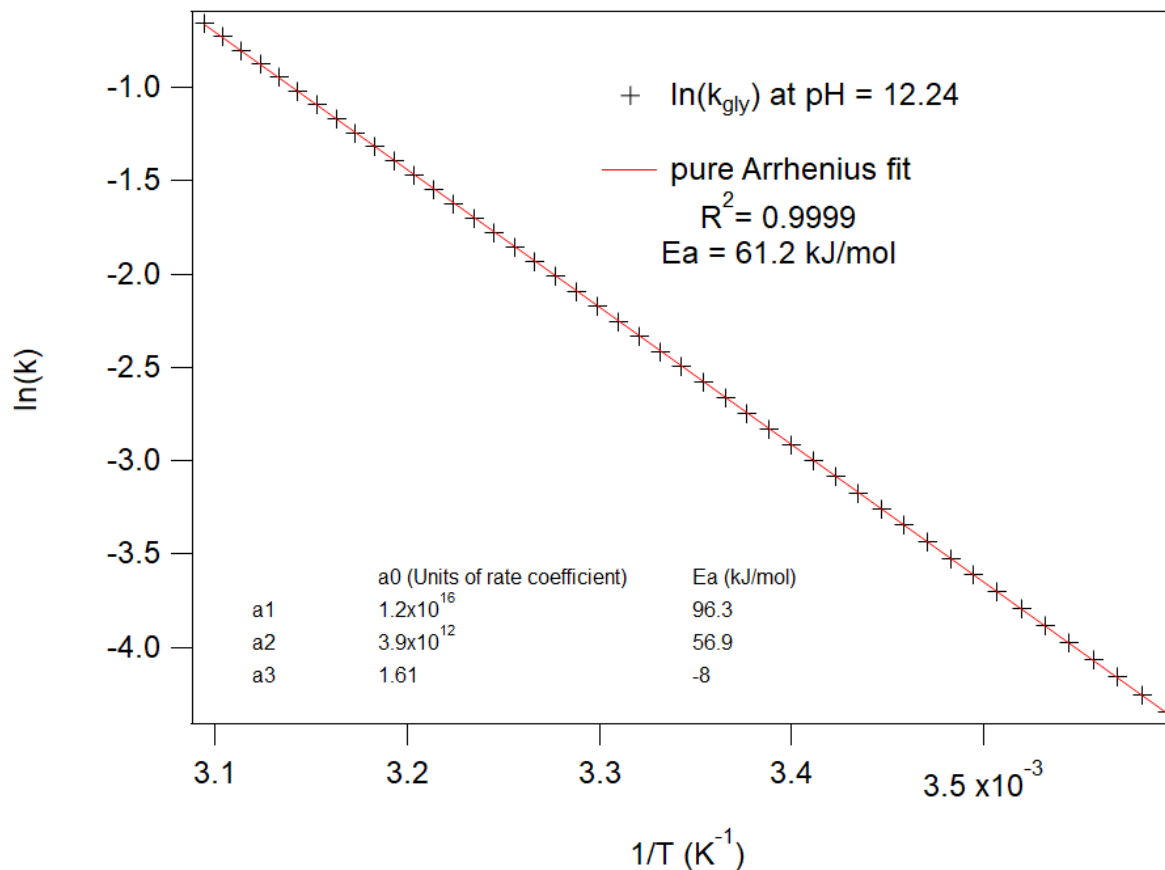


Fig SI8: Arrhenius plot of the conversion kinetics of glyoxal to glycolate at pH = 12.24 from the Fratzke model.

Black crosses represent the logarithm of k_{gly} , the pseudo first order rate constant of glyoxal conversion, at different temperatures using an Arrhenius dependency of each rate coefficient ($a_{1-2-3} = a_0 \exp(-E_a/RT)$), using the values of Fratzke and Reilly (1986). The red line represents a pure Arrhenius dependency of the pseudo first order rate constant of glyoxal conversion ($k = k_0 \exp(-E_a/RT)$).

SI9 Calibration curves of α -dicarbonyl compounds using HPIC_{NaOH} under our optimized conditions

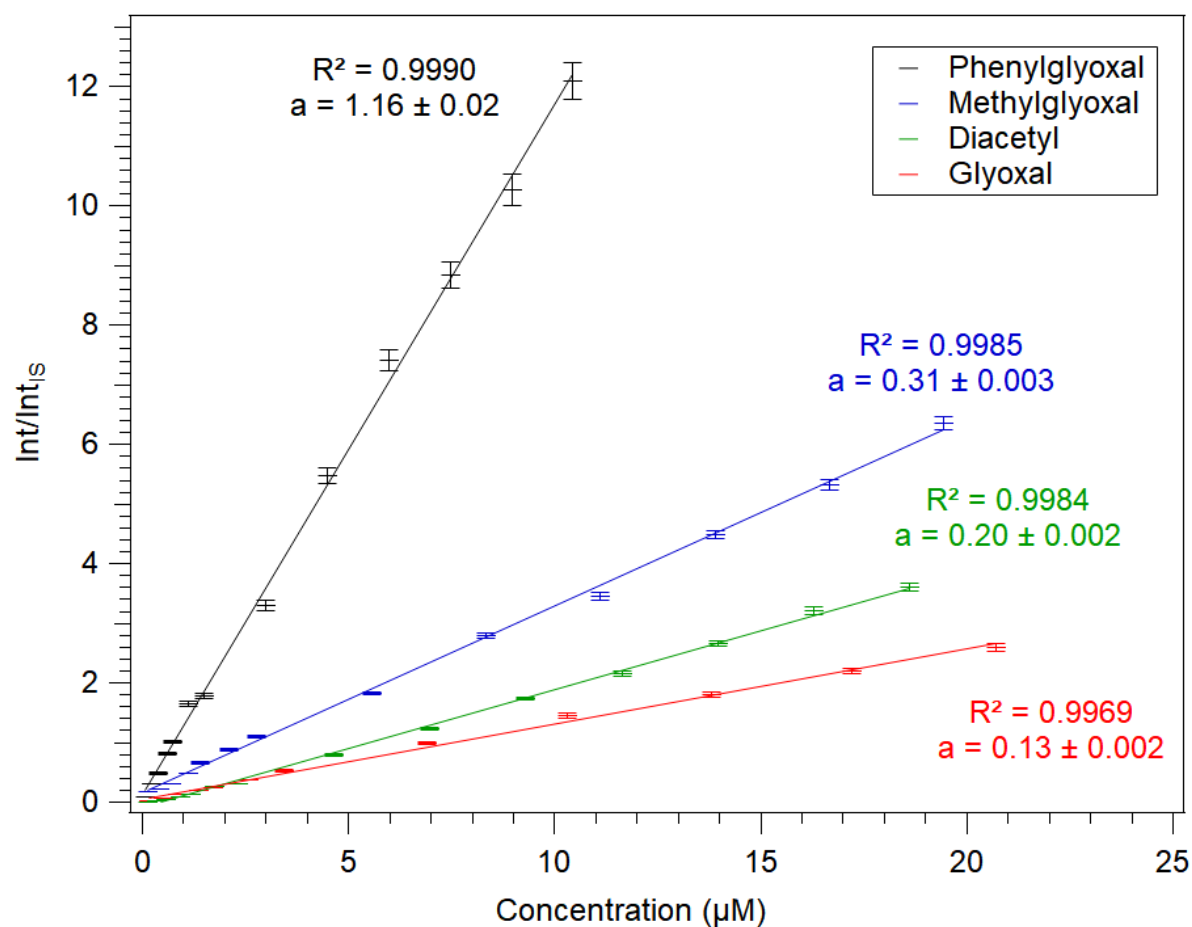
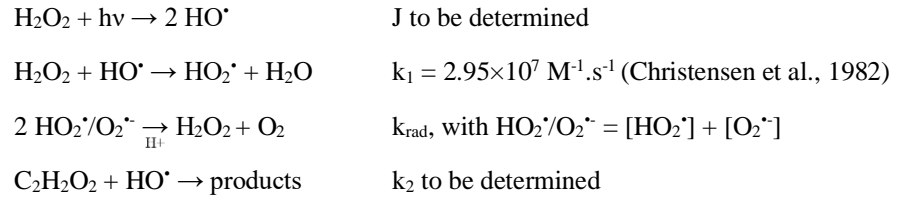


Fig SI9: Calibration curves of the four studied α -dicarbonyls. The chromatographic peak integrated areas (Int) of the measured α -hydroxy carboxylate ions were normalized to those of valerate, the internal standard (Int_s); a is the sensitivity (the regression coefficient of the corresponding linear fit). Error bars represent the standard deviation between triplicates.

SI10 Simulation of the H₂O₂ concentration time profile

The following reactions occur in the batch reactor :



Assuming steady state concentrations for HO[•] and HO₂[•] radicals, one obtains the following equations :

$$[\text{HO}^\bullet] = \frac{2J[\text{H}_2\text{O}_2]}{k_2[\text{Glyoxal}] + k_1[\text{H}_2\text{O}_2]} \quad \text{Eq. S1}$$

$$k_{\text{rad}} \times [\text{HO}_2^\bullet]^2 = \frac{k_1[\text{H}_2\text{O}_2][\text{HO}^\bullet]}{2} \quad \text{Eq. S2}$$

Using Eq. S1 and Eq. S2, one obtains the simulated time profiles of both H₂O₂ and glyoxal:

$$[\text{H}_2\text{O}_2]_{\text{sim}} = [\text{H}_2\text{O}_2]_0 \times \exp\left(-\frac{1}{2}k_1[\text{HO}^\bullet]t - Jt\right) \quad \text{Eq. S3}$$

With [H₂O₂]₀ the initial experimental concentration of H₂O₂.

$$[\text{Glyoxal}]_{\text{sim}} = [\text{Glyoxal}]_0 \times \exp(-k_2[\text{HO}^\bullet]t) \quad \text{Eq. S4}$$

With [Glyoxal]₀ the initial experimental concentration of glyoxal.

Using Eq. S3 and Eq. S4, the simulated time profiles were compared to the experimental data in Fig. 7 for glyoxal and Figure SI9 for H₂O₂.

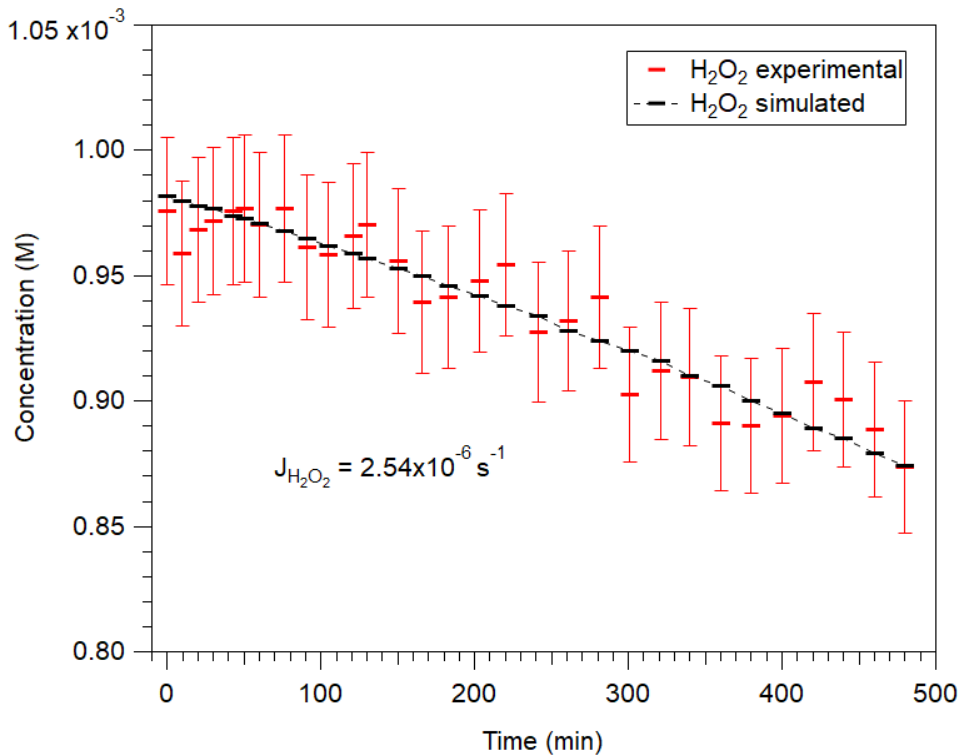


Fig SI10: Experimental and simulated H₂O₂ time profiles during glyoxal aqueous phase photooxidation.

SI11 Correction of the α -dicarbonyl concentrations due to the potential presence of α -hydroxy carboxylate in the sample

The correction was determined for glyoxal. Six samples were prepared, two were composed of 30 μM of glyoxal, 2 were composed of 30 μM of glycolate, and 2 were composed of 15 μM of glyoxal and glycolate. One sample of each pair was converted by addition of a NaOH solution to reach a concentration of 17.5 mM (pH = 12.24). The samples were then analysed using $\text{HPIC}_{\text{carbonate}}$.

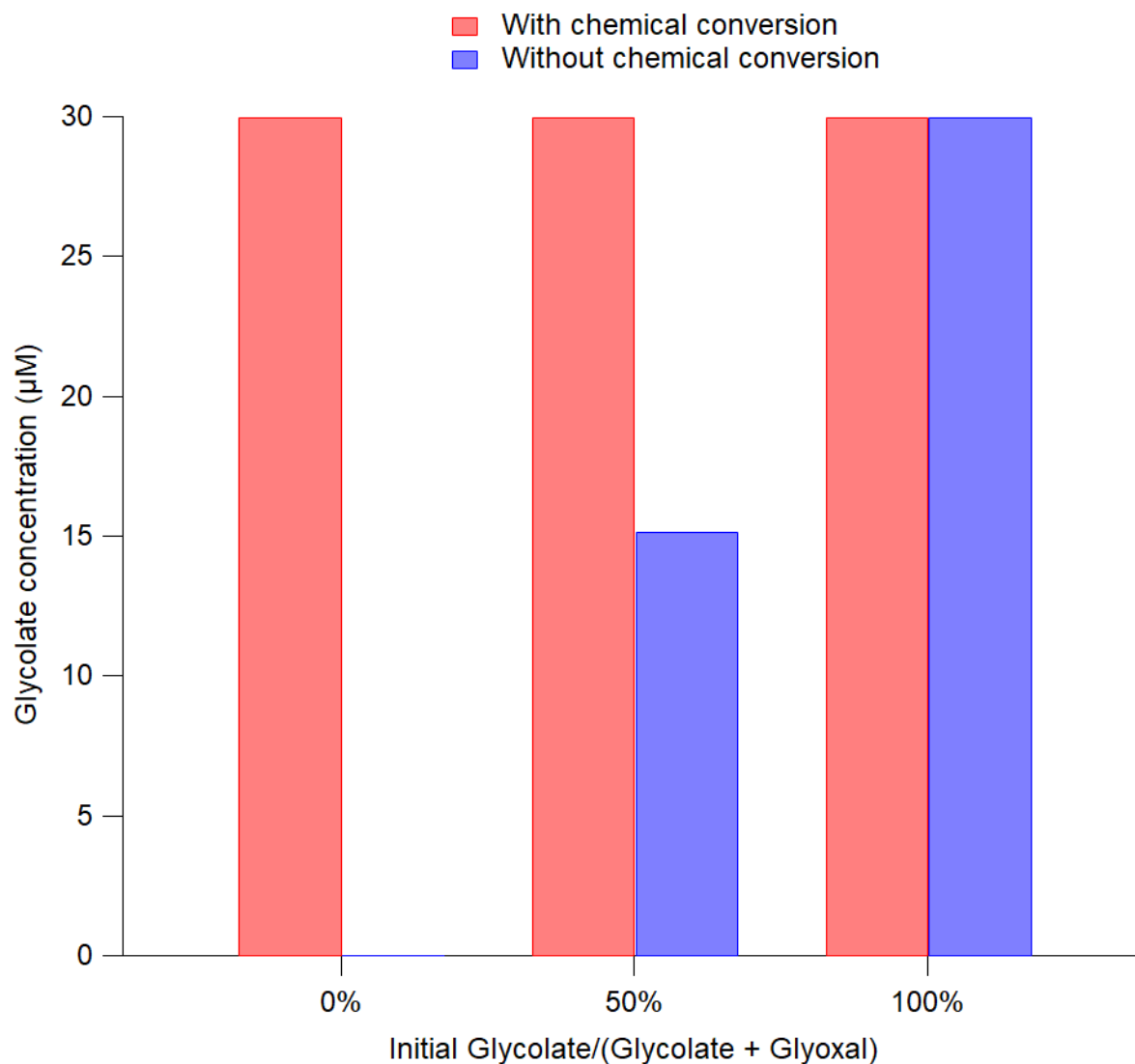


Fig SI11: Glycolate concentrations measured using $\text{HPIC}_{\text{carbonate}}$ of 3 pairs of samples with (red) and without (blue) alkaline conversion prior analysis.

The results show that the converted glyoxal are detected using $\text{HPIC}_{\text{carbonate}}$ at pH = 10.14 illustrating the irreversibility of the reaction when the pH is lowered. The measurement performed with chemical conversion thus represents the sum of converted glyoxal and glycolate initially present. The measurement performed without chemical conversion represents only the glycolate initially present. The real glyoxal concentration is therefore the difference between the two measurements. The same approach can be applied to all α -dicarbonyl compounds.

SI12 Chromatographic conditions for HPLC analysis of α -nitroxyacetone

At a flow rate of 1 mL min⁻¹, the gradient was started at 4 mM NaOH for 10 min, then, it went to 50 mM NaOH in 12 min. It went back to 4 mM NaOH within a minute and finally held at this proportion until the end of the analyses at min 25. The retention times of the compounds were verified with this method using authentic standards. According to Fratzke and Reilly (1986), this method lead to a methylglyoxal conversion of 10%.

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