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Kinetic measurements of the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes, ketones and organic acids in aqueous solutions

Correspondence to: H. Herrmann (herrmann@tropos.de)

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Kinetic measurements of the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes, ketones and organic acids in aqueous solutions

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1 *Details on the capillary electrophoresis detection system*

2

3 As described by Scheinhardt et al. (2013), indirect UV detection was used with a
4 measurement wavelength of 260 nm and a reference wavelength of 208 nm. The applied
5 method was an indirect method, because instead of the absorbance of the investigated anions
6 (i.e. small organic mono- and dicarboxylic acids as well as inorganic ions) the absorbance of
7 the electrolyte was recorded. Sulfosalicylic acid was used as electrolyte that absorbs strongly
8 at 208 nm and less at 260 nm. In the presence of an analyte, the absorbance of the electrolyte
9 decreases because the non-absorbing analyte replaces the absorbing electrolyte. This decrease
10 results in a negative peak which can be used to quantify the concentration of the analyte after
11 calibration.

12

1 Table A 1. Pseudo-first order rate constants dependent on the reactant concentration for the
 2 investigated reactions.

Substance	H_2O_2		O_3	
	c / M	k_{1st} / s^{-1}	c / M	k_{1st} / s^{-1}
Glyoxylic acid pH 1	0.50	$(1.95 \pm 0.30) \cdot 10^{-3}$	$1.05 \cdot 10^{-3}$	$(8.53 \pm 0.04) \cdot 10^{-4}$
	0.75	$(3.41 \pm 0.45) \cdot 10^{-3}$	$2.50 \cdot 10^{-3}$	$(8.10 \pm 0.66) \cdot 10^{-4}$
	1.00	$(4.14 \pm 0.39) \cdot 10^{-3}$	$5.00 \cdot 10^{-3}$	$(1.16 \pm 0.06) \cdot 10^{-3}$
	1.25	$(4.92 \pm 0.85) \cdot 10^{-3}$	$7.50 \cdot 10^{-3}$	$(1.54 \pm 0.07) \cdot 10^{-3}$
	1.50	$(6.15 \pm 0.61) \cdot 10^{-3}$	$1.00 \cdot 10^{-3}$	$(2.04 \pm 0.01) \cdot 10^{-3}$
Glyoxylic acid /	---	---	$1.00 \cdot 10^{-3}$	$(1.77 \pm 0.01) \cdot 10^{-3}$
Glyoxylate pH 3	---	---	$2.50 \cdot 10^{-3}$	$(2.20 \pm 0.01) \cdot 10^{-3}$
	---	---	$3.50 \cdot 10^{-3}$	$(2.95 \pm 0.01) \cdot 10^{-3}$
	---	---	$5.00 \cdot 10^{-3}$	$(3.78 \pm 0.01) \cdot 10^{-3}$
	---	---	$7.50 \cdot 10^{-3}$	$(5.09 \pm 0.01) \cdot 10^{-3}$
Glyoxylate pH 7	0.03	$(4.22 \pm 1.07) \cdot 10^{-3}$	$1.00 \cdot 10^{-3}$	$(3.08 \pm 0.02) \cdot 10^{-3}$
	0.05	$(6.59 \pm 1.13) \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	$(5.01 \pm 0.01) \cdot 10^{-3}$
	0.07	$(8.75 \pm 1.59) \cdot 10^{-3}$	$2.50 \cdot 10^{-3}$	$(6.26 \pm 0.02) \cdot 10^{-3}$
	0.10	$(1.15 \pm 0.24) \cdot 10^{-2}$	$3.50 \cdot 10^{-3}$	$(9.80 \pm 0.04) \cdot 10^{-3}$
	0.12	$(1.38 \pm 0.26) \cdot 10^{-2}$	$5.00 \cdot 10^{-3}$	$(1.20 \pm 0.03) \cdot 10^{-2}$
Pyruvic acid pH 1	0.05	$(8.55 \pm 7.33) \cdot 10^{-4}$	$1.00 \cdot 10^{-3}$	$(5.98 \pm 0.02) \cdot 10^{-4}$
	0.10	$(5.01 \pm 4.94) \cdot 10^{-3}$	$5.00 \cdot 10^{-3}$	$(1.17 \pm 0.01) \cdot 10^{-3}$
	0.15	$(8.10 \pm 2.97) \cdot 10^{-3}$	$7.50 \cdot 10^{-3}$	$(1.43 \pm 0.01) \cdot 10^{-3}$
	0.20	$(1.60 \pm 1.01) \cdot 10^{-2}$	$1.00 \cdot 10^{-2}$	$(1.63 \pm 0.01) \cdot 10^{-3}$
	0.25	$(2.41 \pm 1.18) \cdot 10^{-2}$	$1.25 \cdot 10^{-2}$	$(2.16 \pm 0.03) \cdot 10^{-3}$
Pyruvate pH 7	$8.00 \cdot 10^{-3}$	$(1.16 \pm 0.08) \cdot 10^{-2}$	$9.00 \cdot 10^{-4}$	$(2.80 \pm 0.04) \cdot 10^{-3}$
	$1.20 \cdot 10^{-2}$	$(1.31 \pm 0.09) \cdot 10^{-2}$	$2.25 \cdot 10^{-3}$	$(7.62 \pm 0.23) \cdot 10^{-3}$
	$1.60 \cdot 10^{-2}$	$(1.69 \pm 0.13) \cdot 10^{-2}$	$3.50 \cdot 10^{-3}$	$(8.36 \pm 0.99) \cdot 10^{-3}$
	$2.00 \cdot 10^{-2}$	$(2.00 \pm 0.10) \cdot 10^{-2}$	$6.00 \cdot 10^{-3}$	$(1.53 \pm 0.10) \cdot 10^{-2}$
	$2.40 \cdot 10^{-2}$	$(2.32 \pm 0.40) \cdot 10^{-2}$	$7.00 \cdot 10^{-3}$	$(1.62 \pm 0.07) \cdot 10^{-2}$
Glycolic acid pH 1	---	---	$1.00 \cdot 10^{-3}$	$(7.45 \pm 0.10) \cdot 10^{-4}$
	---	---	$5.00 \cdot 10^{-3}$	$(7.86 \pm 0.04) \cdot 10^{-4}$
	---	---	$1.00 \cdot 10^{-2}$	$(1.09 \pm 0.01) \cdot 10^{-3}$
	---	---	$1.75 \cdot 10^{-2}$	$(1.55 \pm 0.01) \cdot 10^{-3}$
	---	---	$2.50 \cdot 10^{-2}$	$(1.69 \pm 0.01) \cdot 10^{-3}$
	---	---	$3.75 \cdot 10^{-2}$	$(2.79 \pm 0.01) \cdot 10^{-3}$

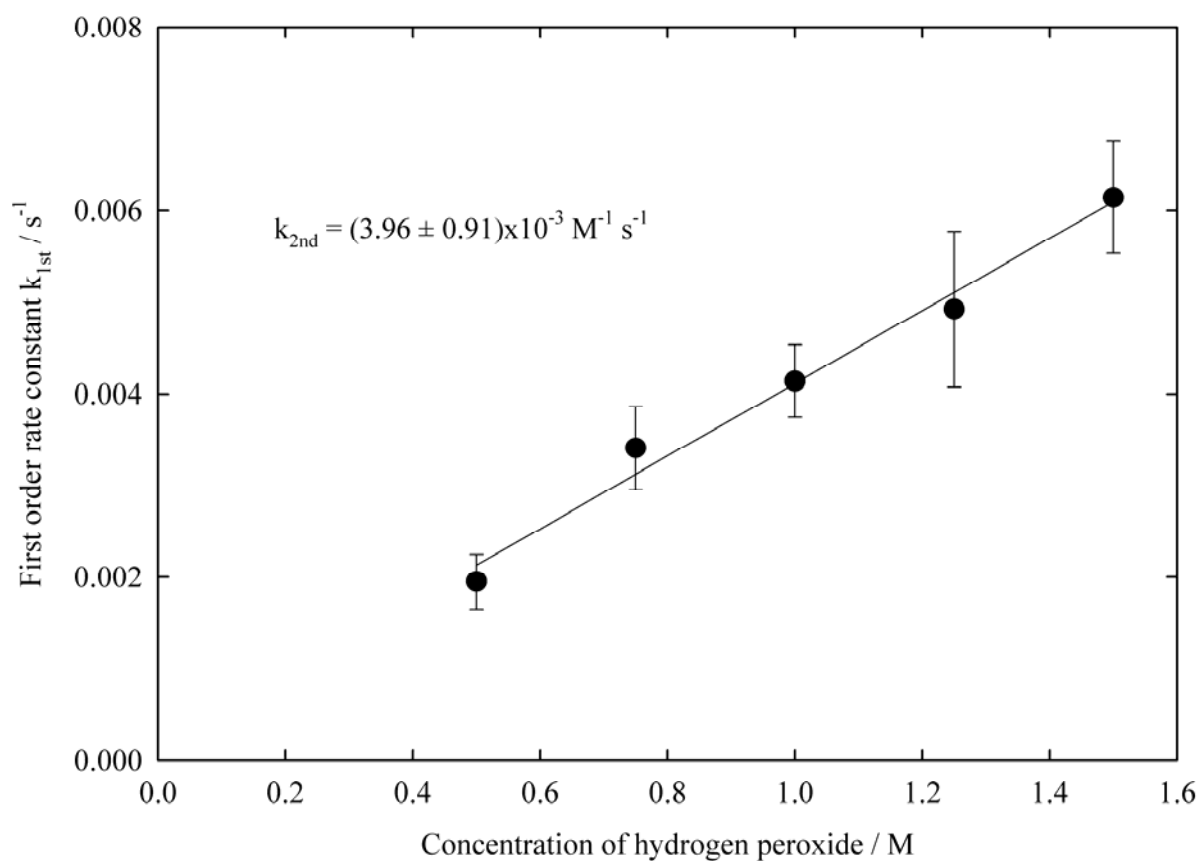
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1 Table A 1 - continued. Pseudo-first order rate constants dependent on the reactant
 2 concentration for the investigated reactions.

Substance	H_2O_2		O_3	
	c / M	k_{1st} / s^{-1}	c / M	k_{1st} / s^{-1}
Glycolate pH 7	---	---	$1.00 \cdot 10^{-3}$	$(1.76 \pm 0.01) \cdot 10^{-3}$
	---	---	$4.00 \cdot 10^{-3}$	$(3.79 \pm 0.04) \cdot 10^{-3}$
	---	---	$7.00 \cdot 10^{-3}$	$(5.65 \pm 0.05) \cdot 10^{-3}$
	---	---	$1.00 \cdot 10^{-2}$	$(8.11 \pm 0.08) \cdot 10^{-3}$
	---	---	$1.50 \cdot 10^{-2}$	$(1.17 \pm 0.01) \cdot 10^{-2}$
Glycolaldehyde	0.02	$(4.88 \pm 0.04) \cdot 10^{-3}$	$1.00 \cdot 10^{-3}$	$(1.03 \pm 0.01) \cdot 10^{-3}$
	0.05	$(4.83 \pm 0.03) \cdot 10^{-3}$	$4.00 \cdot 10^{-3}$	$(2.29 \pm 0.01) \cdot 10^{-3}$
	0.10	$(6.05 \pm 0.05) \cdot 10^{-3}$	$7.00 \cdot 10^{-3}$	$(3.62 \pm 0.01) \cdot 10^{-3}$
	0.15	$(1.01 \pm 0.02) \cdot 10^{-2}$	$1.00 \cdot 10^{-2}$	$(5.14 \pm 0.02) \cdot 10^{-3}$
	0.20	$(1.15 \pm 0.06) \cdot 10^{-2}$	$1.50 \cdot 10^{-2}$	$(8.94 \pm 0.02) \cdot 10^{-3}$
Glyoxal	0.56	$(1.07 \pm 0.01) \cdot 10^{-4}$	$9.00 \cdot 10^{-4}$	$(1.89 \pm 0.01) \cdot 10^{-3}$
	0.84	$(1.58 \pm 0.01) \cdot 10^{-4}$	$1.50 \cdot 10^{-3}$	$(2.14 \pm 0.01) \cdot 10^{-3}$
	1.12	$(1.65 \pm 0.01) \cdot 10^{-4}$	$2.10 \cdot 10^{-3}$	$(2.87 \pm 0.01) \cdot 10^{-3}$
	1.40	$(2.29 \pm 0.01) \cdot 10^{-4}$	$2.40 \cdot 10^{-3}$	$(3.08 \pm 0.01) \cdot 10^{-3}$
	1.68	$(3.06 \pm 0.01) \cdot 10^{-4}$	$2.70 \cdot 10^{-3}$	$(3.25 \pm 0.01) \cdot 10^{-3}$
Methylglyoxal	---	---	$7.05 \cdot 10^{-4}$	$(2.38 \pm 0.02) \cdot 10^{-3}$
	---	---	$9.40 \cdot 10^{-4}$	$(2.76 \pm 0.02) \cdot 10^{-3}$
	---	---	$1.65 \cdot 10^{-3}$	$(4.61 \pm 0.03) \cdot 10^{-3}$
	---	---	$1.18 \cdot 10^{-3}$	$(3.36 \pm 0.02) \cdot 10^{-3}$
	---	---	$2.12 \cdot 10^{-3}$	$(6.45 \pm 0.08) \cdot 10^{-3}$
Methacrolein	1	(0.25 ± 0.02)	$6.00 \cdot 10^{-5}$	1.71 ± 0.09
	1.5	(0.27 ± 0.06)	$7.00 \cdot 10^{-5}$	1.85 ± 0.08
	2	(0.34 ± 0.04)	$8.00 \cdot 10^{-5}$	2.06 ± 0.14
	2.5	(0.36 ± 0.04)	$9.00 \cdot 10^{-5}$	2.36 ± 0.07
	3	(0.38 ± 0.02)	$1.00 \cdot 10^{-4}$	2.58 ± 0.03
Methyl vinyl ketone	---	---	$6.00 \cdot 10^{-5}$	3.78 ± 0.09
	---	---	$7.00 \cdot 10^{-5}$	4.44 ± 0.02
	---	---	$8.00 \cdot 10^{-5}$	5.22 ± 0.04
	---	---	$9.00 \cdot 10^{-5}$	6.05 ± 0.15
	---	---	$1.00 \cdot 10^{-4}$	6.53 ± 0.11

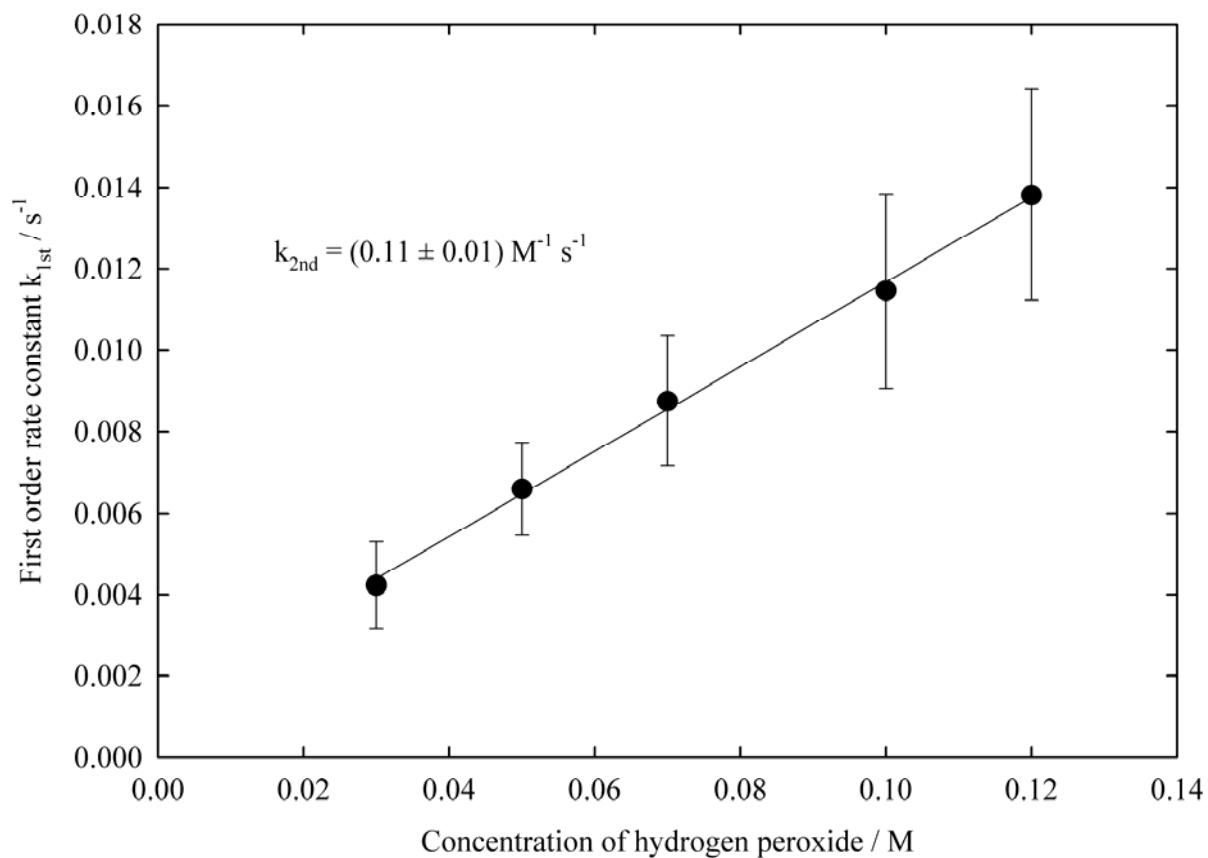
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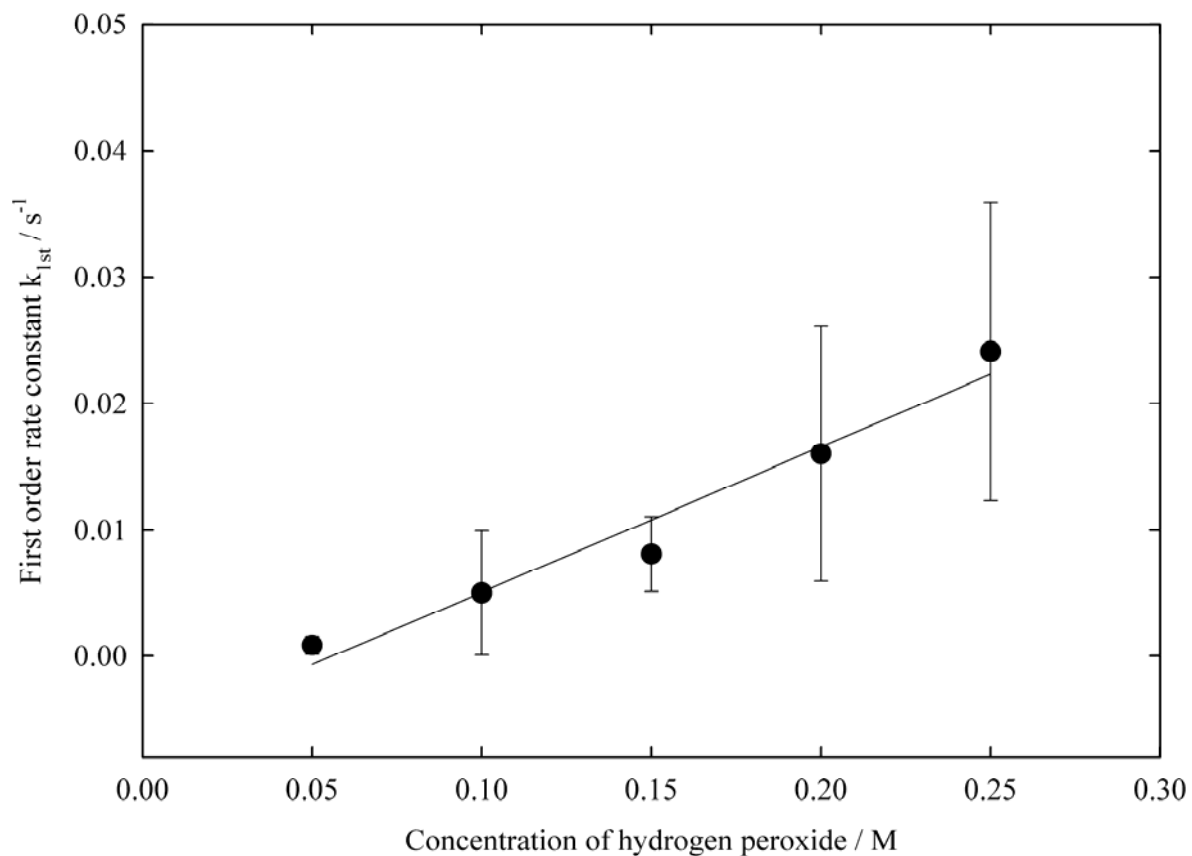


1
2 Figure A 1. First-order rate constants plotted over the concentration for the reaction of
3 glyoxylic acid with H_2O_2 at pH 1. The initial concentration of glyoxylic acid was $2.5 \cdot 10^{-2} M$.
4 The acid was quantified by CE.

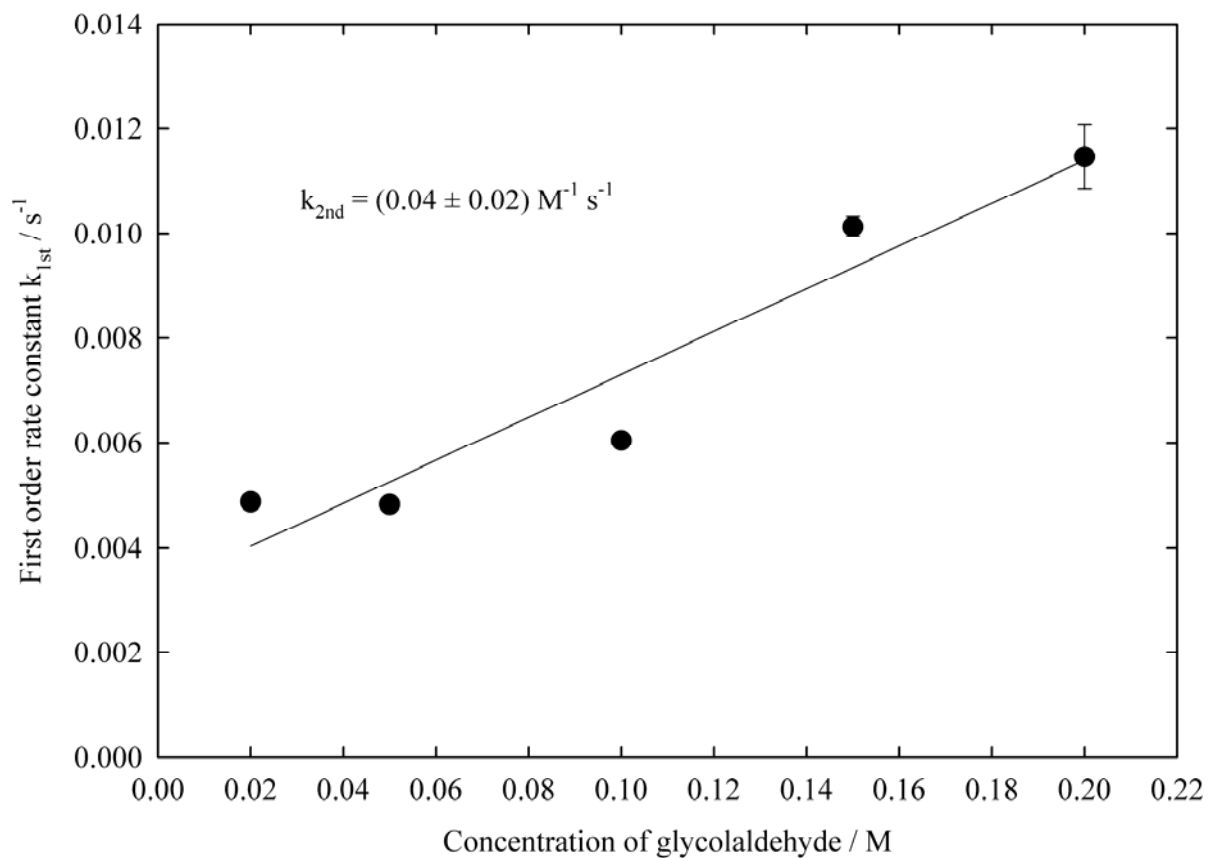
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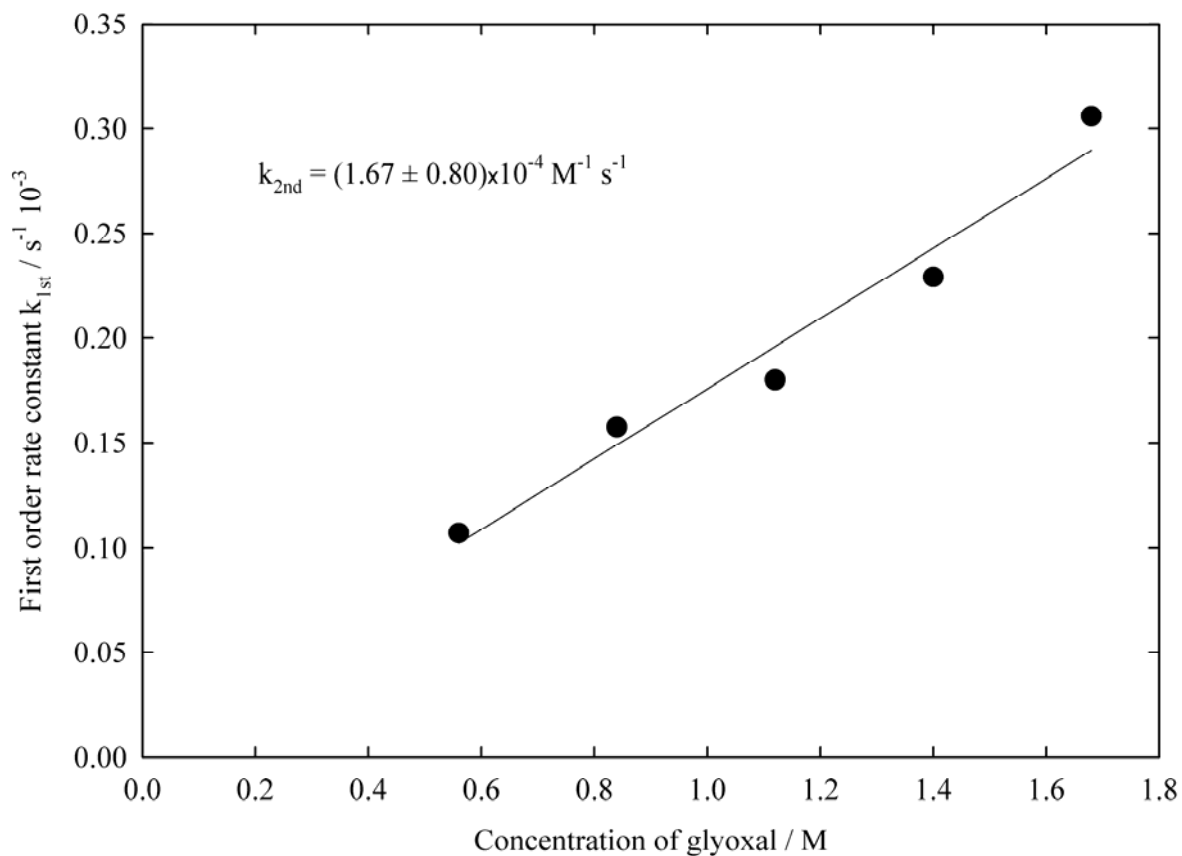
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2 Figure A 2. First-order rate constants plotted over the concentration for the reaction of
3 glyoxylate with H_2O_2 at pH 7. The initial concentration of glyoxylate was $1 \cdot 10^{-3} M$.
4 Glyoxylate was quantified by CE.
5



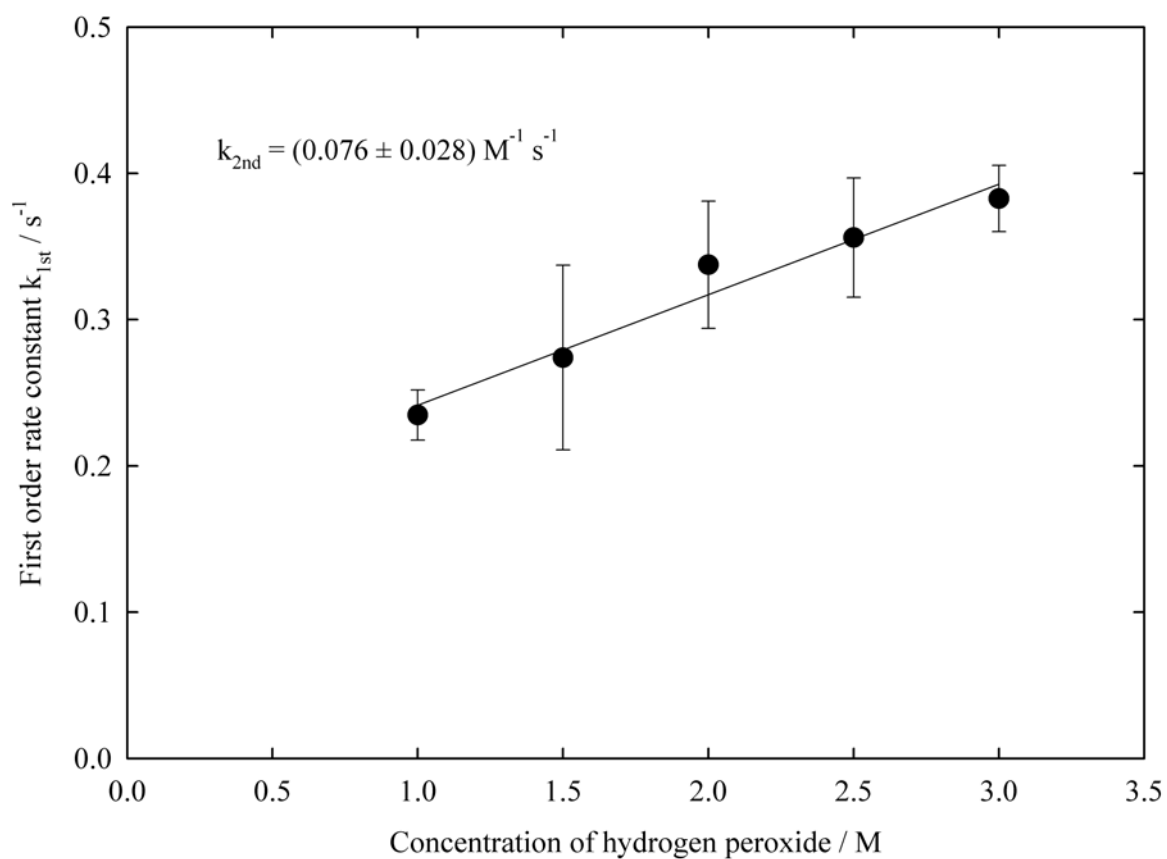
1
2 Figure A 3. First-order rate constants plotted over the concentration for the reaction of
3 pyruvic acid with H_2O_2 at pH 1. The initial concentration of pyruvic acid was $5 \cdot 10^{-3}$ M. The
4 acid was quantified by CE.
5



1
2 Figure A 3. First-order rate constants plotted over the concentration for the reaction of
3 glycolaldehyde with H_2O_2 at pH 5. The initial concentration of hydrogen peroxide was
4 $1 \cdot 10^{-3}$ M. The decay of hydrogen peroxide was monitored at 229 nm.
5

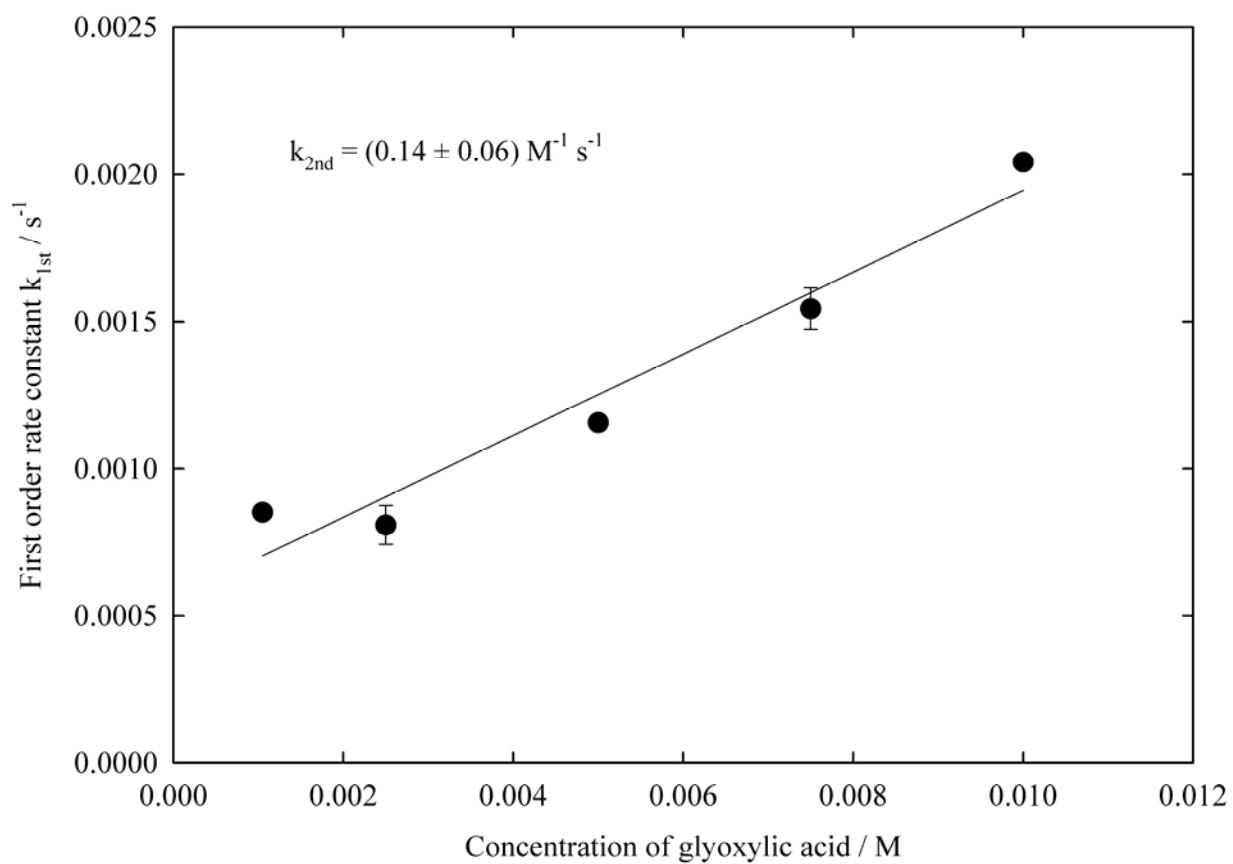


1
2 Figure A 4. First-order rate constants plotted over the concentration for the reaction of glyoxal
3 with H_2O_2 at pH 5. The initial concentration of hydrogen peroxide was $2.8 \cdot 10^{-2}$ M. The decay
4 of hydrogen peroxide was monitored at 233 nm.
5

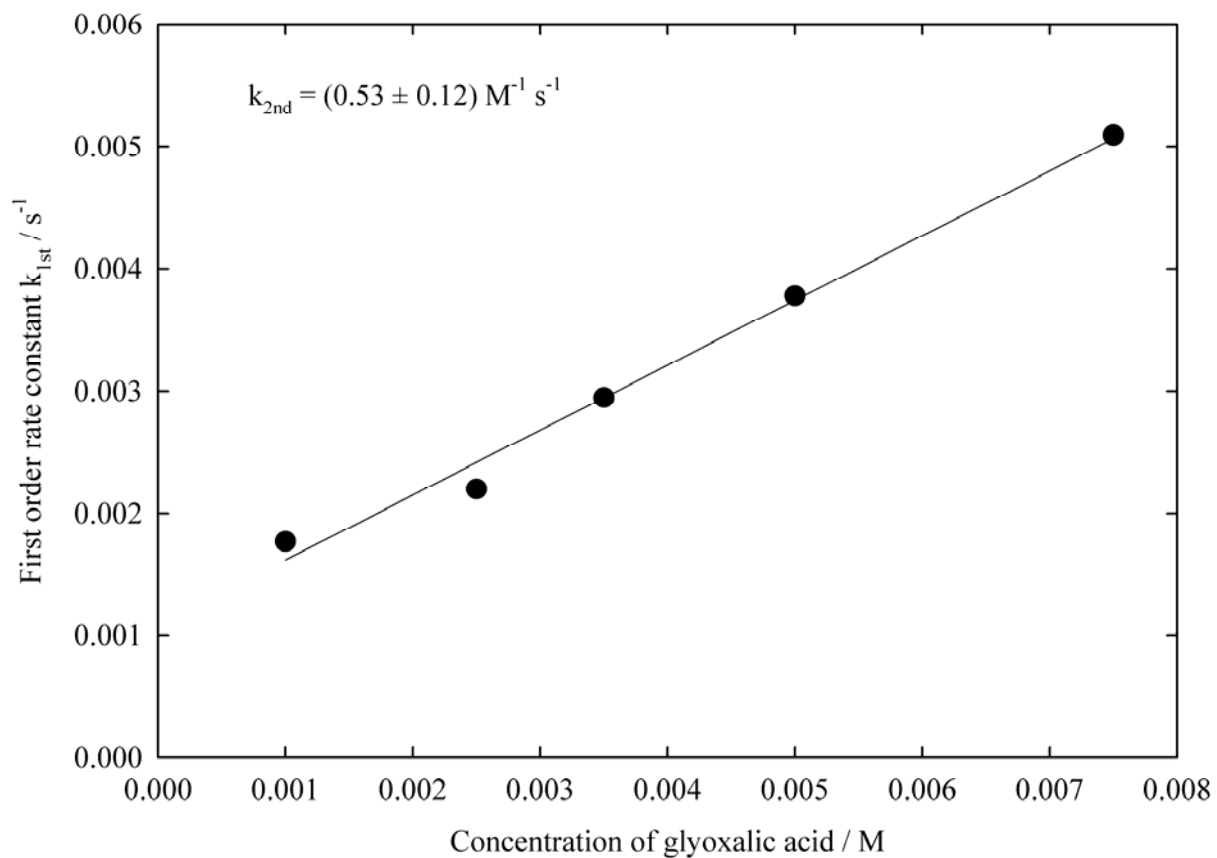


1
2 Figure A 5. First-order rate constants plotted over the concentration for the reaction of
3 methacrolein with H_2O_2 at pH 5. The initial concentration of hydrogen peroxide was
4 $2 \cdot 10^{-2}$ M. The decay of hydrogen peroxide was monitored at 310 nm.

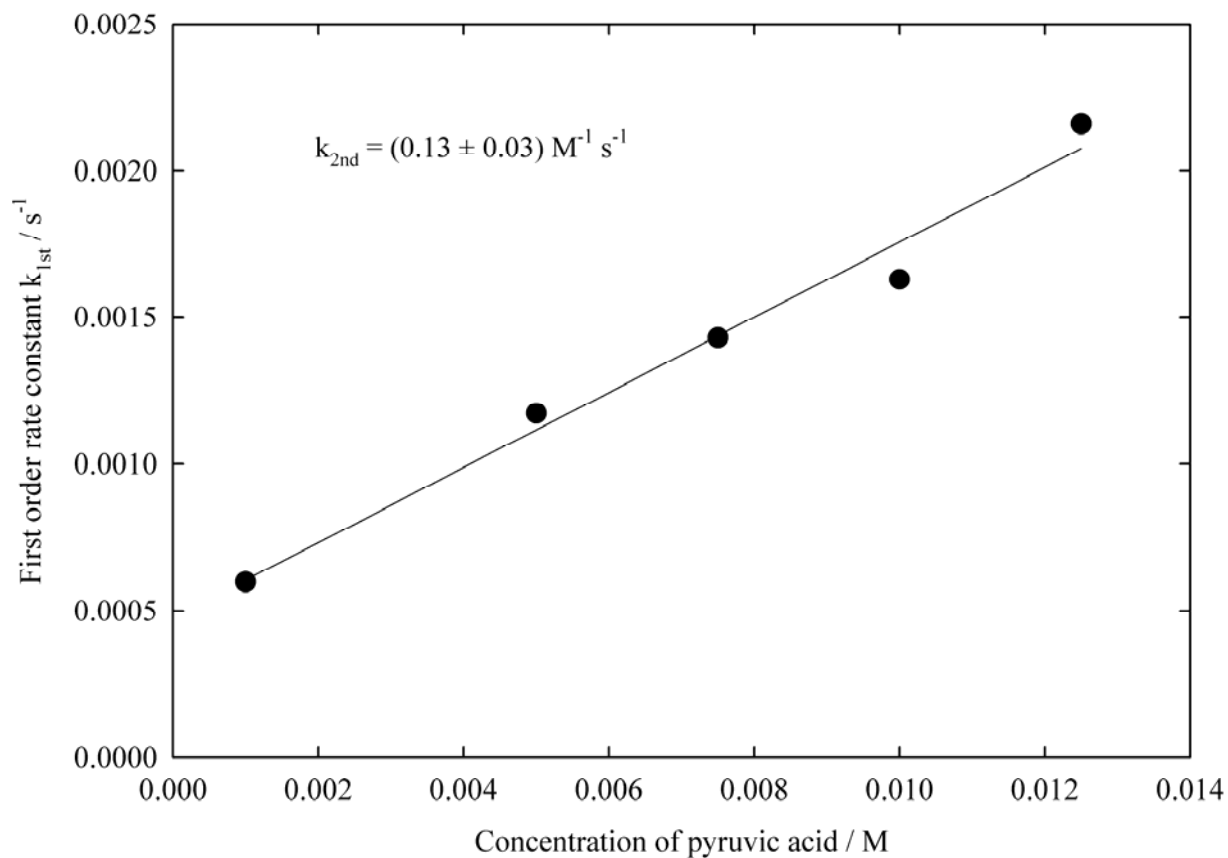
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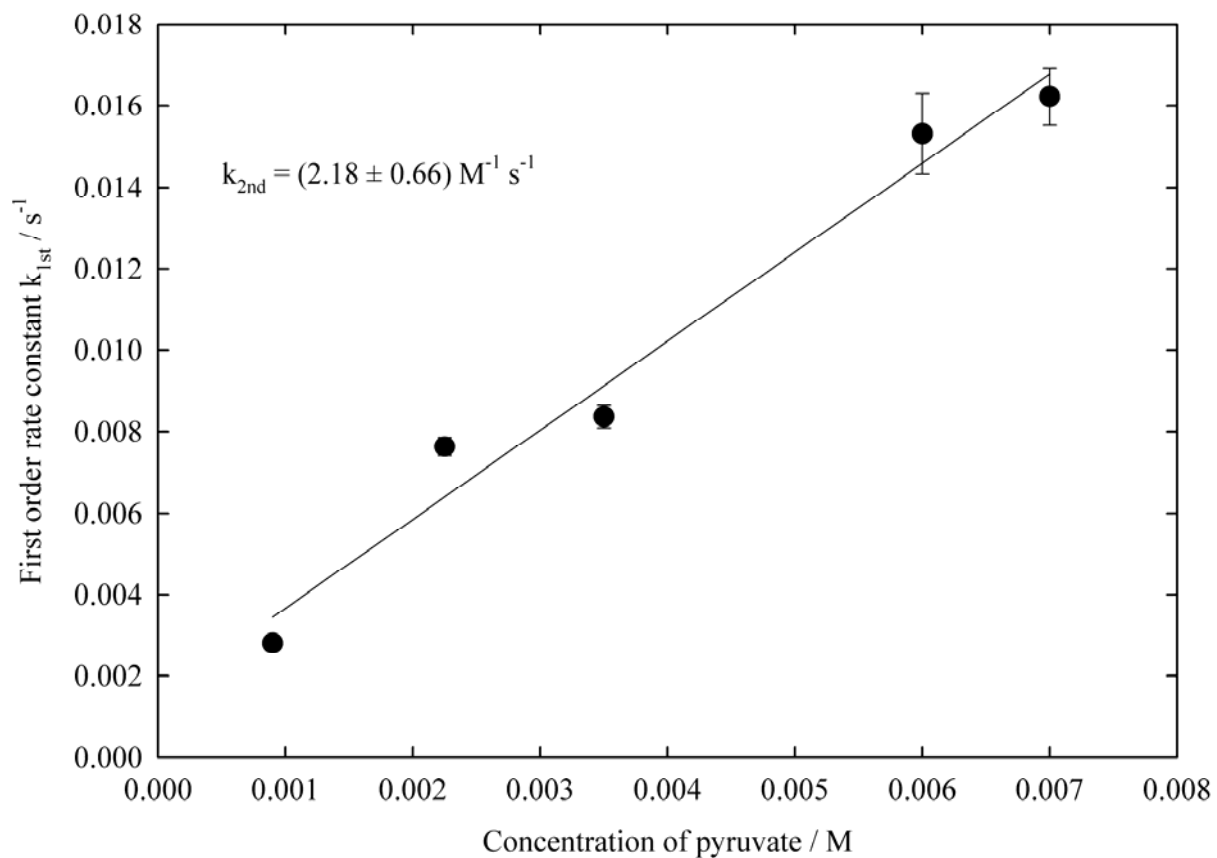
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2 Figure A 6. First-order rate constants plotted over the concentration for the reaction of
3 glyoxylic acid with ozone at pH 1. The initial concentration of ozone was $5 \cdot 10^{-5}$ M.
4



1
2 Figure A 7. First-order rate constants plotted over the concentration for the reaction of
3 glyoxylic acid/glyoxylate with ozone at pH 3. The initial concentration of ozone was
4 $5 \cdot 10^{-5}$ M.
5



1
2 Figure A 8. First-order rate constants plotted over the concentration for the reaction of
3 pyruvic acid with ozone at pH 1. **The initial concentration of ozone was $5 \cdot 10^{-5}$ M.**
4

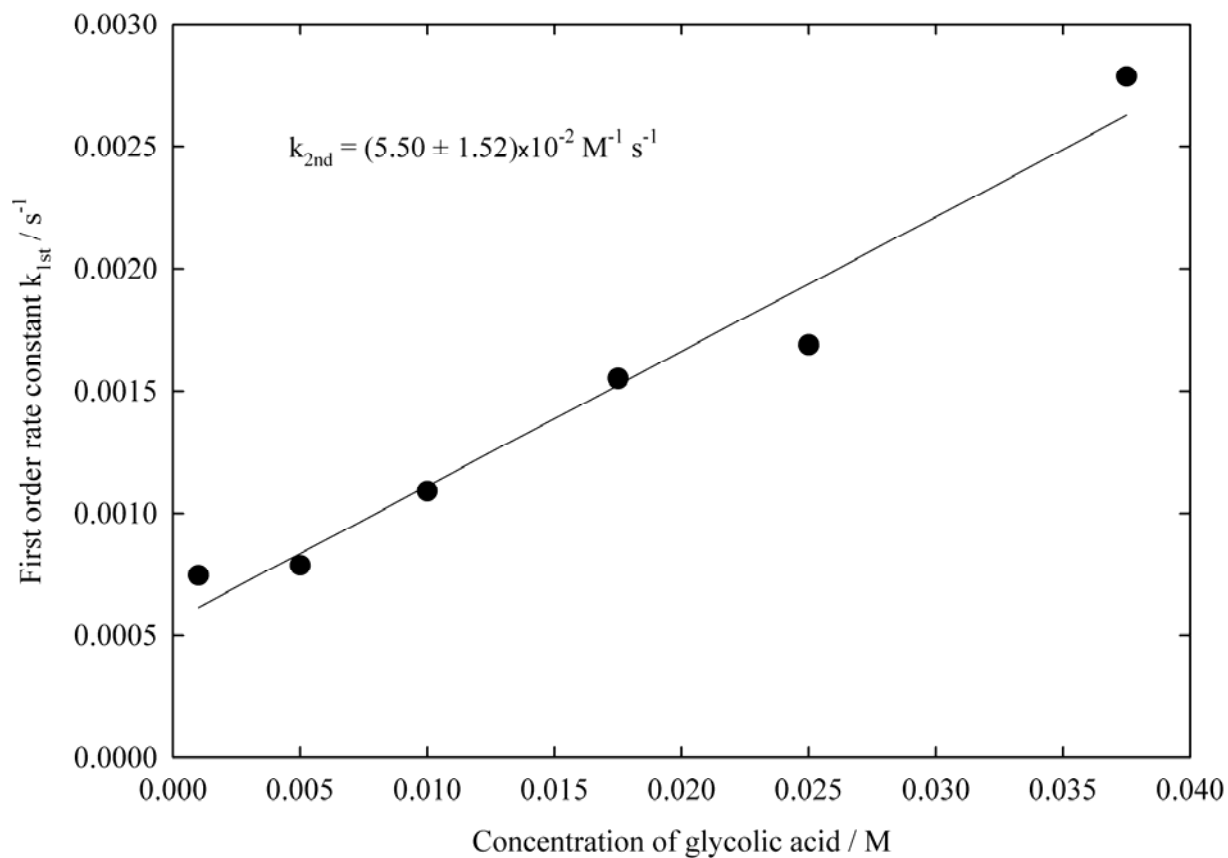


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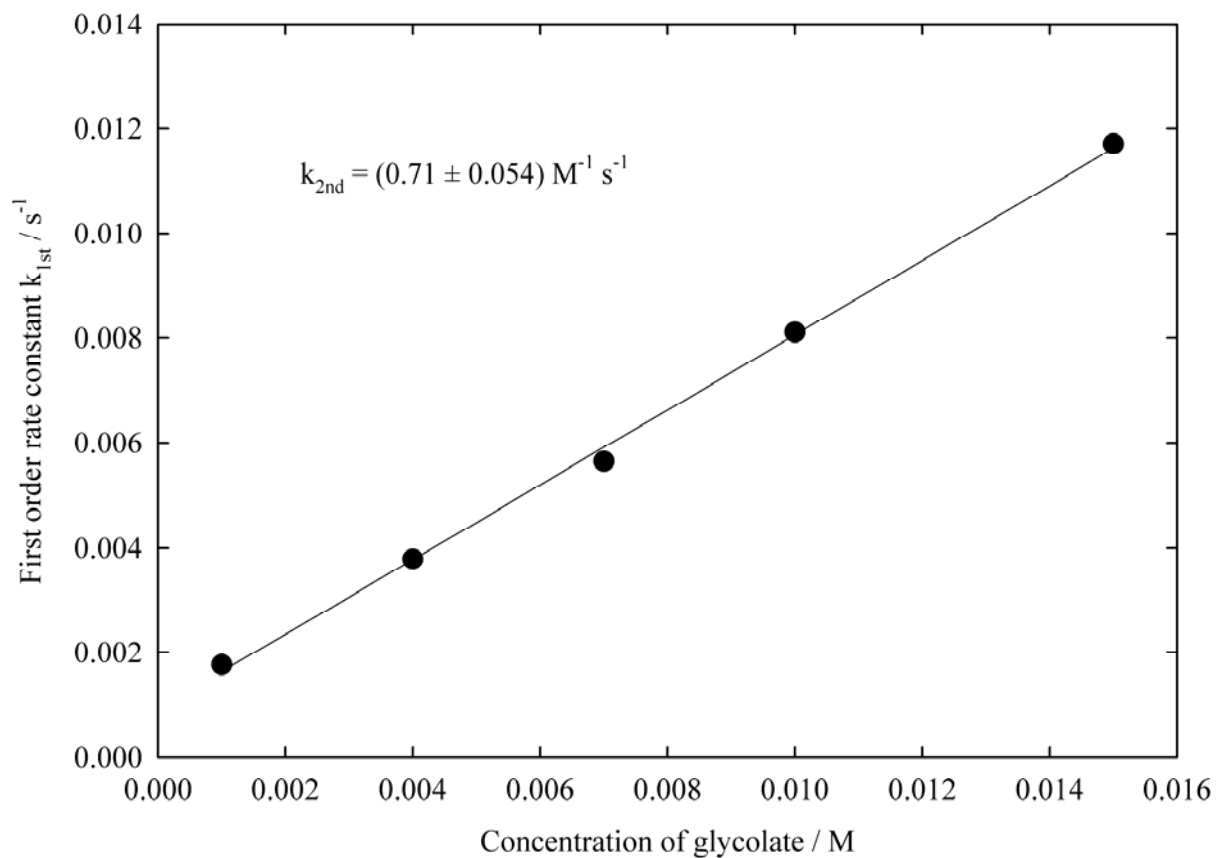
2 Figure A 9. First-order rate constants plotted over the concentration for the reaction of
3 pyruvate with ozone at pH 7. The initial concentration of ozone was $3 \cdot 10^{-5}$ M.

4

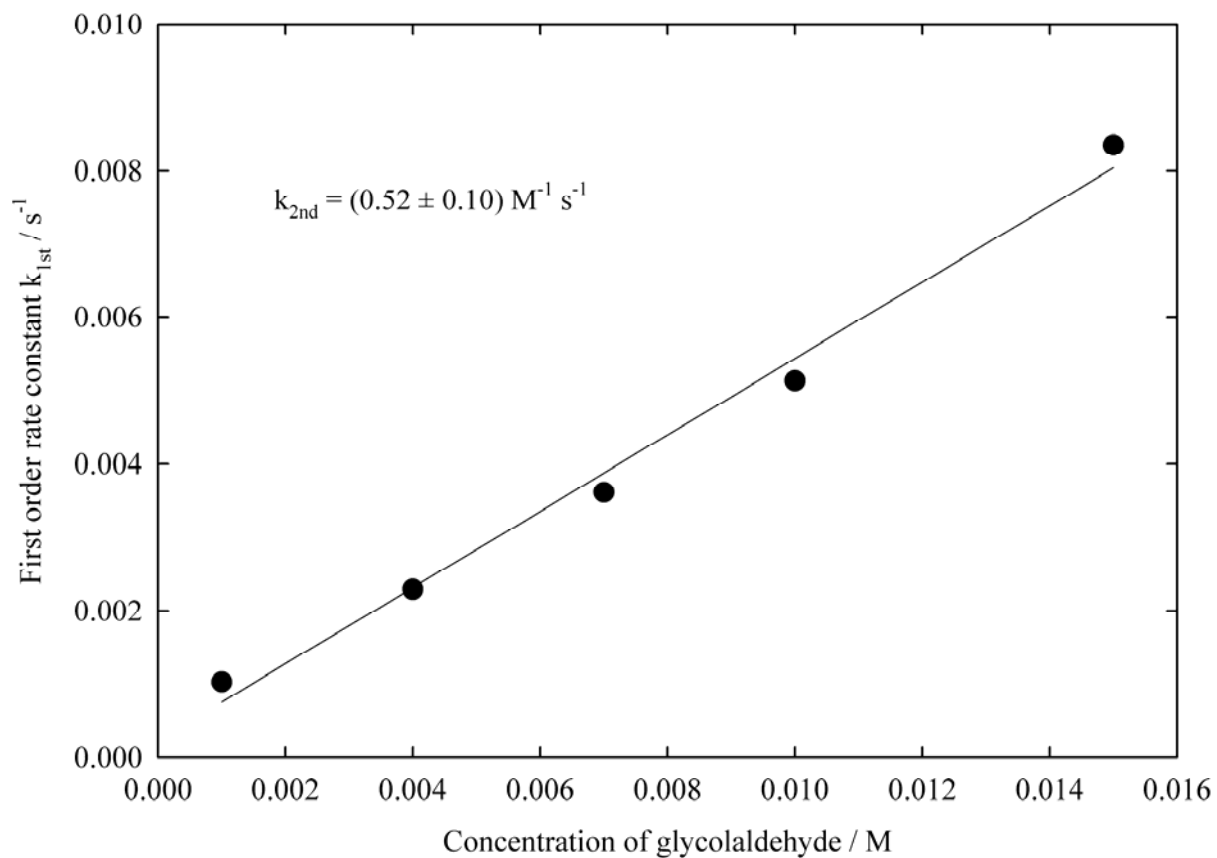
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2 Figure A 10. First-order rate constants plotted over the concentration for the reaction of
3 glycolic acid with ozone at pH 1. **The initial concentration of ozone was $5 \cdot 10^{-5}$ M.**
4

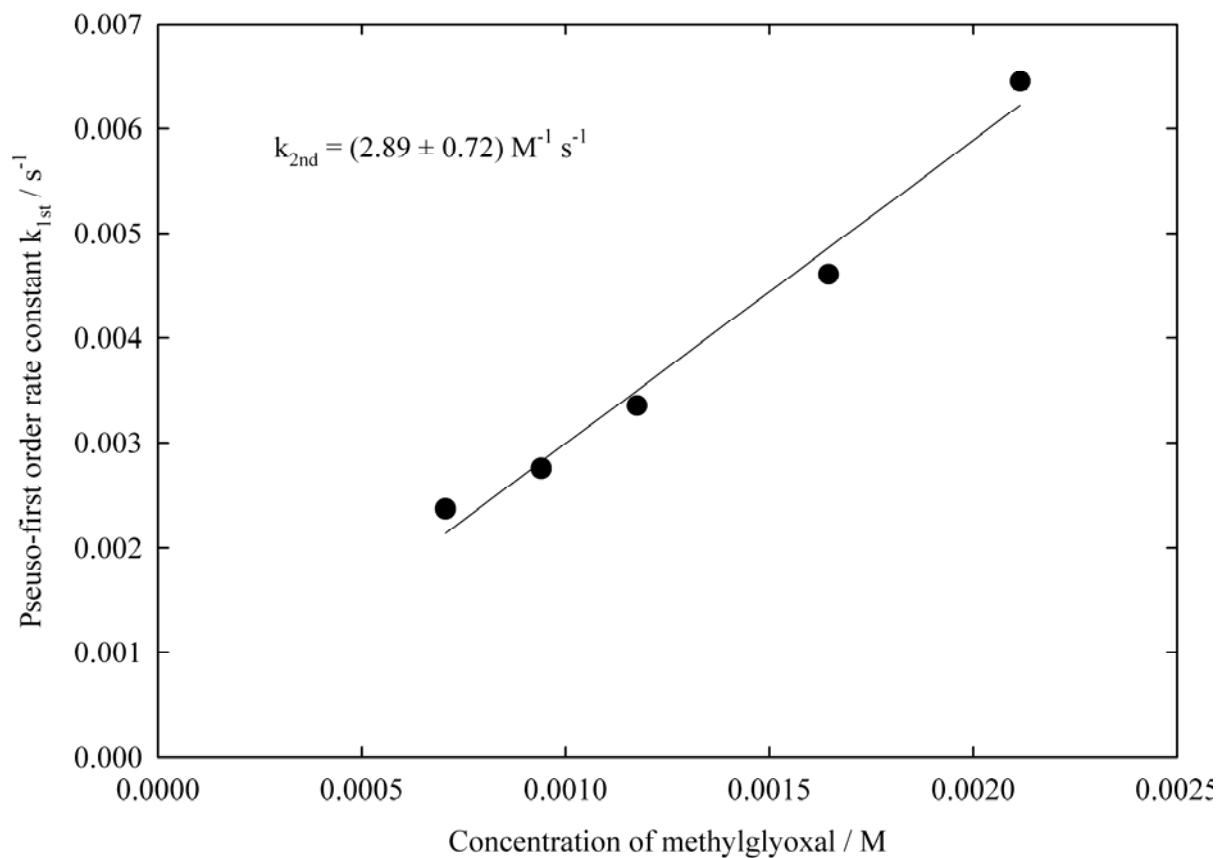


1
2 Figure A 11. First-order rate constants plotted over the concentration for the reaction of
3 glycolate with ozone at pH 7. **The initial concentration of ozone was $5 \cdot 10^{-5}$ M.**
4

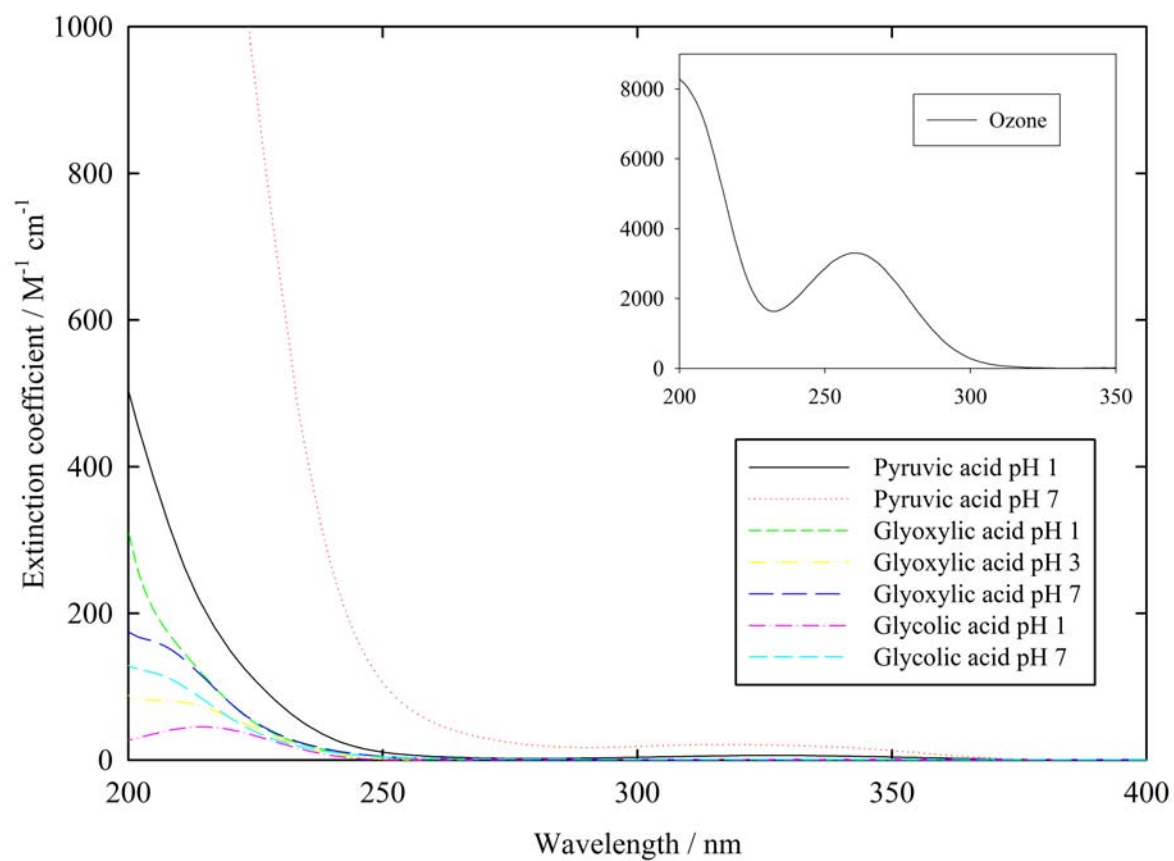


1
2 Figure A 12. First-order rate constants plotted over the concentration for the reaction of
3 glycolaldehyde with **ozone at pH 5**. The initial concentration of ozone was $5 \cdot 10^{-5}$ M.

4
5



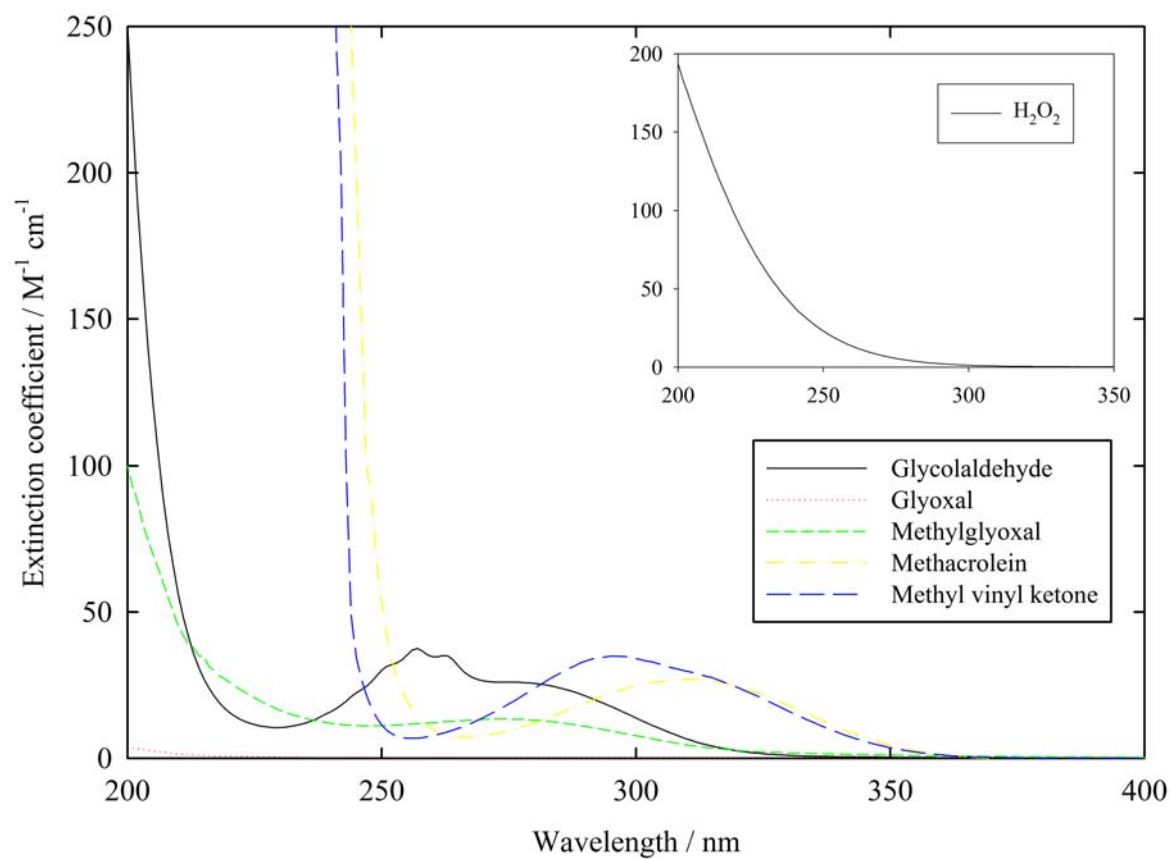
- 1
- 2 Figure A 13. First-order rate constants plotted over the concentration for the reaction of
- 3 methylglyoxal with ozone. The initial concentration of ozone was $3 \cdot 10^{-5} M$.
- 4



1

2 **Figure A 145. UV/Vis-spectra of ozone and the organic acids that were investigated.**

3



1

2 **Figure A 16. UV/Vis-spectra of hydrogen peroxide and the aldehydes and ketone that were**
 3 **investigated.**

4

1 *References*

2 Scheinhardt, S., Müller, K., Spindler, G., and Herrmann, H.: Complexation of trace metals in
3 size-segregated aerosol particles at nine sites in Germany, *Atmospheric Environment*, 74,
4 102-109, 2013.

5