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

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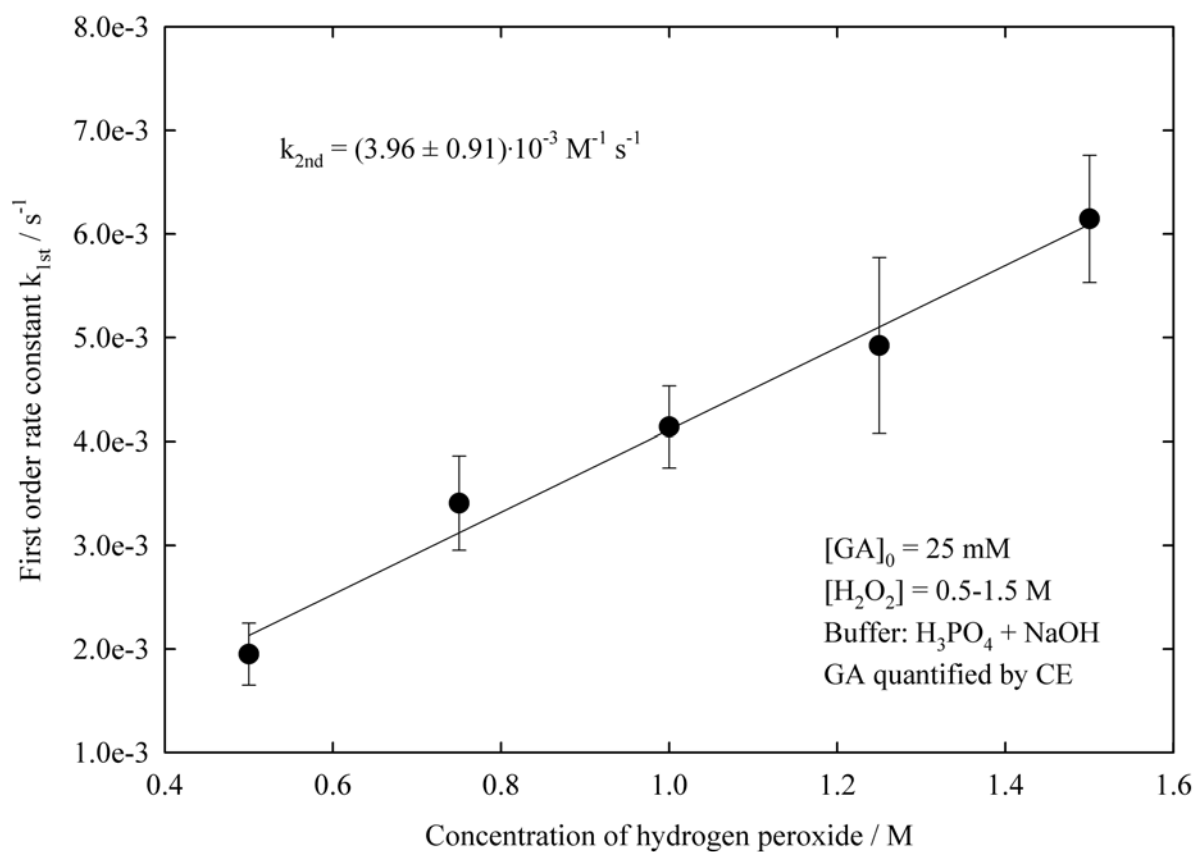
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Electronic supplemental material (ESM)

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

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 / Glyoxylate pH 3	---	---	$1.00 \cdot 10^{-3}$	$(1.77 \pm 0.01) \cdot 10^{-3}$
	---	---	$2.50 \cdot 10^{-3}$	$(2.20 \pm 0.01) \cdot 10^{-3}$
	---	---	$3.50 \cdot 10^{-3}$	$(2.95 \pm 0.01) \cdot 10^{-3}$
	---	---	$5.00 \cdot 10^{-3}$	$(3.78 \pm 0.01) \cdot 10^{-3}$
	---	---	$7.50 \cdot 10^{-3}$	$(5.09 \pm 0.01) \cdot 10^{-3}$
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	---	---	$1.00 \cdot 10^{-3}$	$(7.45 \pm 0.10) \cdot 10^{-4}$
	---	---	$5.00 \cdot 10^{-3}$	$(7.86 \pm 0.04) \cdot 10^{-4}$
	---	---	$1.00 \cdot 10^{-2}$	$(1.09 \pm 0.01) \cdot 10^{-3}$
	---	---	$1.75 \cdot 10^{-2}$	$(1.55 \pm 0.01) \cdot 10^{-3}$
	---	---	$2.50 \cdot 10^{-2}$	$(1.69 \pm 0.01) \cdot 10^{-3}$
	---	---	$3.75 \cdot 10^{-2}$	$(2.79 \pm 0.01) \cdot 10^{-3}$

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

Substance	H$_2$O$_2$		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	---	---	$7.05 \cdot 10^{-4}$	$(2.38 \pm 0.02) \cdot 10^{-3}$
			$9.40 \cdot 10^{-4}$	$(2.76 \pm 0.02) \cdot 10^{-3}$
	---	---	$16.45 \cdot 10^{-3}$	$(4.61 \pm 0.03) \cdot 10^{-3}$
	---	---	$11.75 \cdot 10^{-3}$	$(3.36 \pm 0.02) \cdot 10^{-3}$
	---	---	$21.15 \cdot 10^{-3}$	$(6.45 \pm 0.08) \cdot 10^{-3}$
Methacrolein	1	$(0,25 \pm 0.02)$	$6.00 \cdot 10^{-5}$	1.71 ± 0.09
	1.5	$(0,27 \pm 0.06)$	$7.00 \cdot 10^{-5}$	1.85 ± 0.08
	2	$(0,34 \pm 0.04)$	$8.00 \cdot 10^{-5}$	2.06 ± 0.14
	2.5	$(0,36 \pm 0.04)$	$9.00 \cdot 10^{-5}$	2.36 ± 0.07
	3	$(0,38 \pm 0.02)$	$1.00 \cdot 10^{-4}$	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

$k_{2nd} = (3.96 \pm 0.91) \cdot 10^{-3} \ M^{-1} \ s^{-1}$

$[GA]_0 = 25 \ mM$
$[H_2O_2] = 0.5\text{-}1.5 \ M$
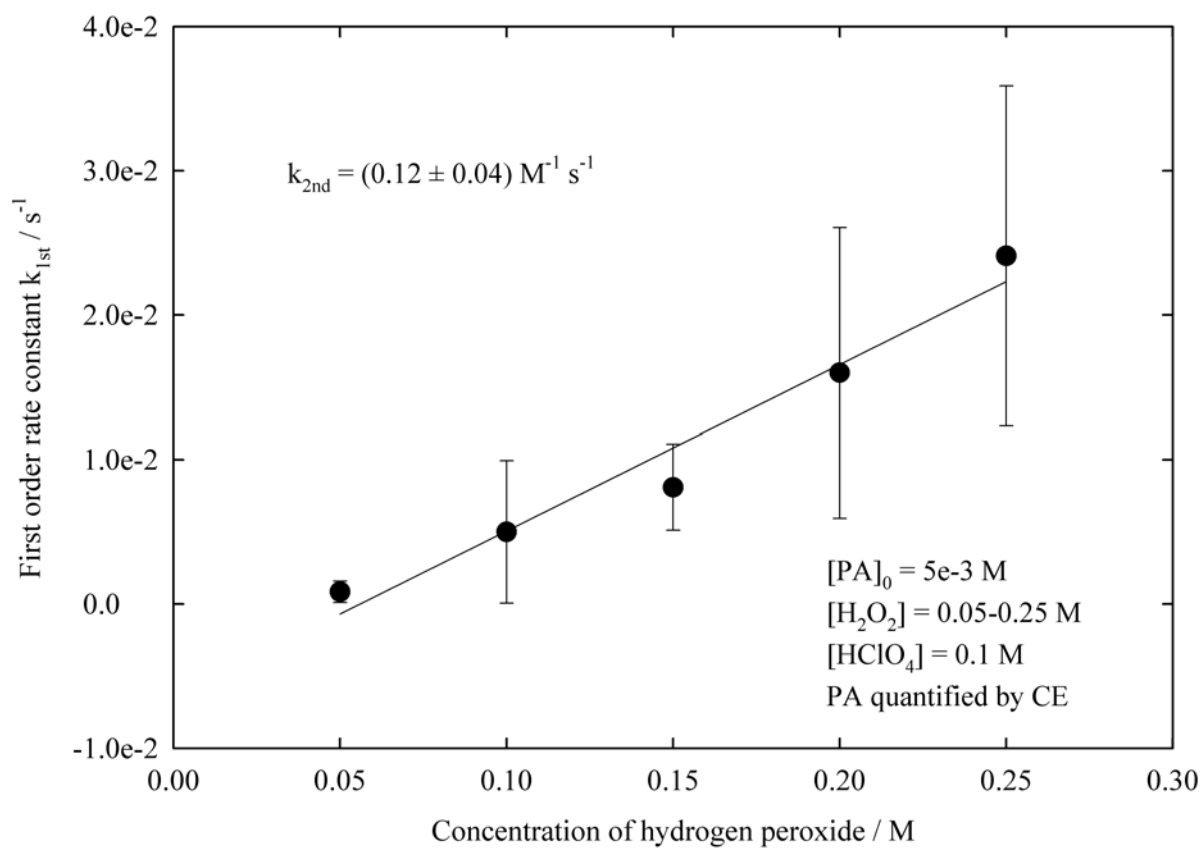Buffer: $H_3PO_4 + NaOH$
GA quantified by CE

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.

4
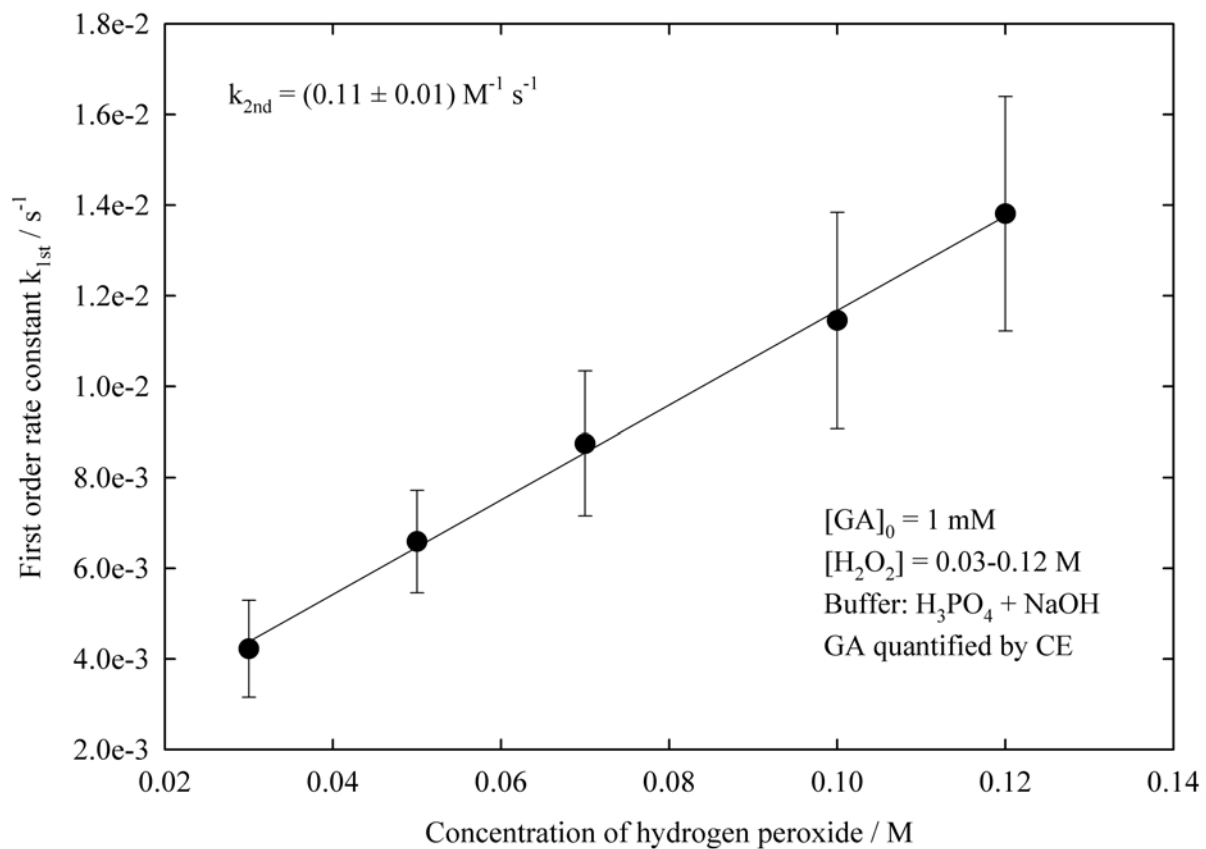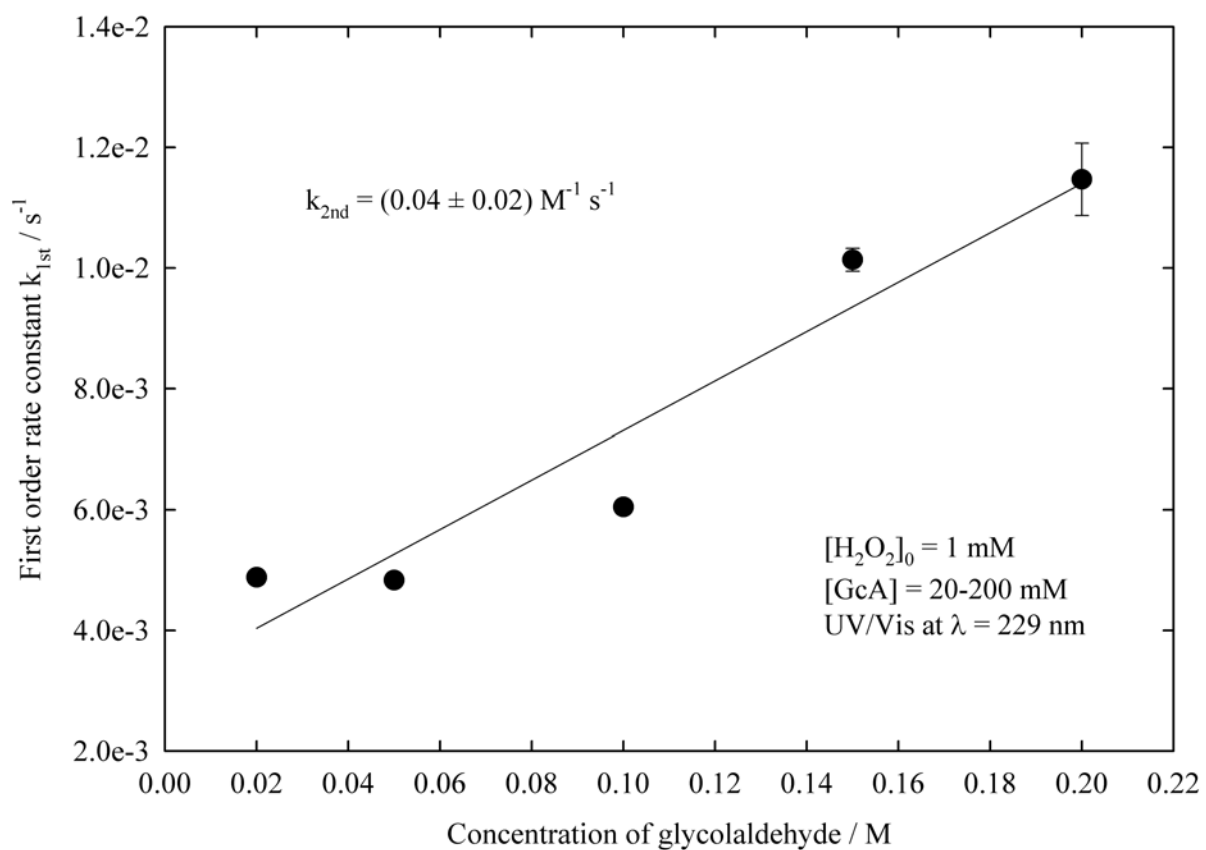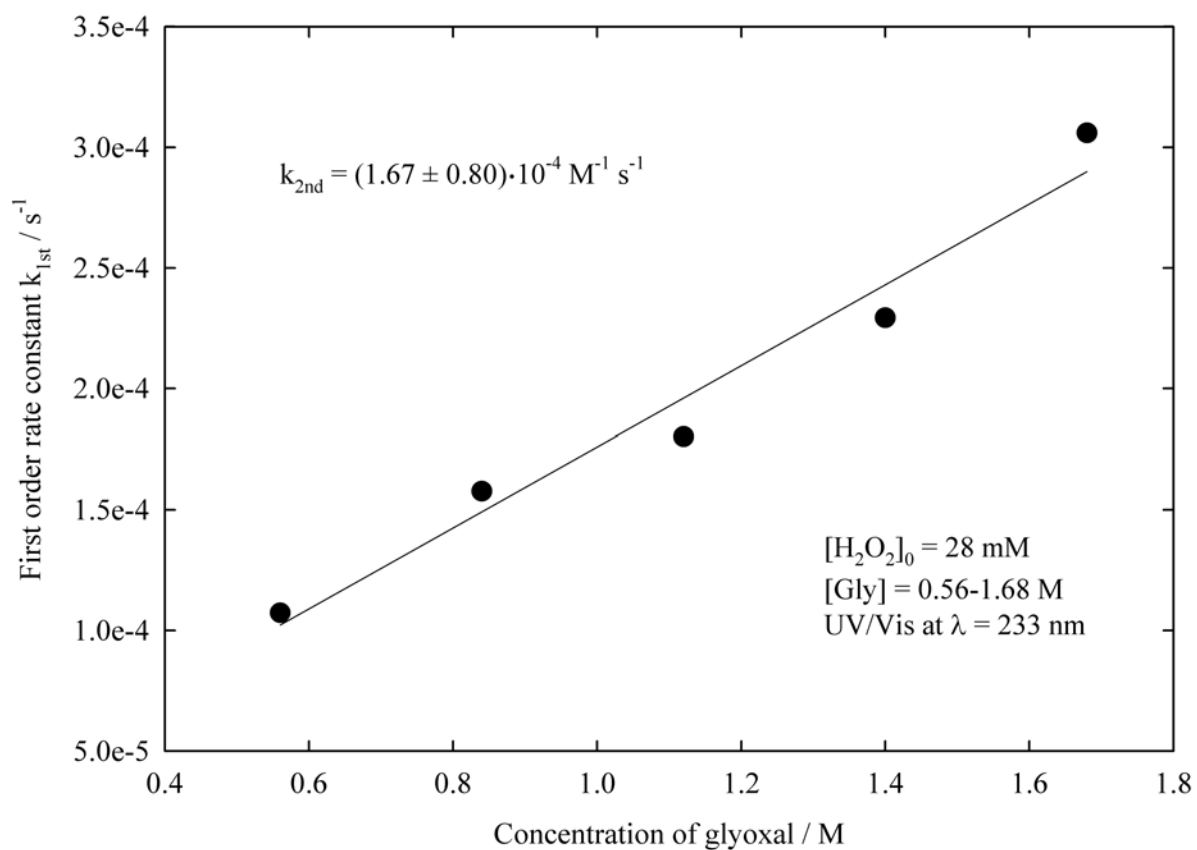
Figure A 2. First-order rate constants plotted over the concentration for the reaction of glyoxylate with H_2O_2 at pH 7.
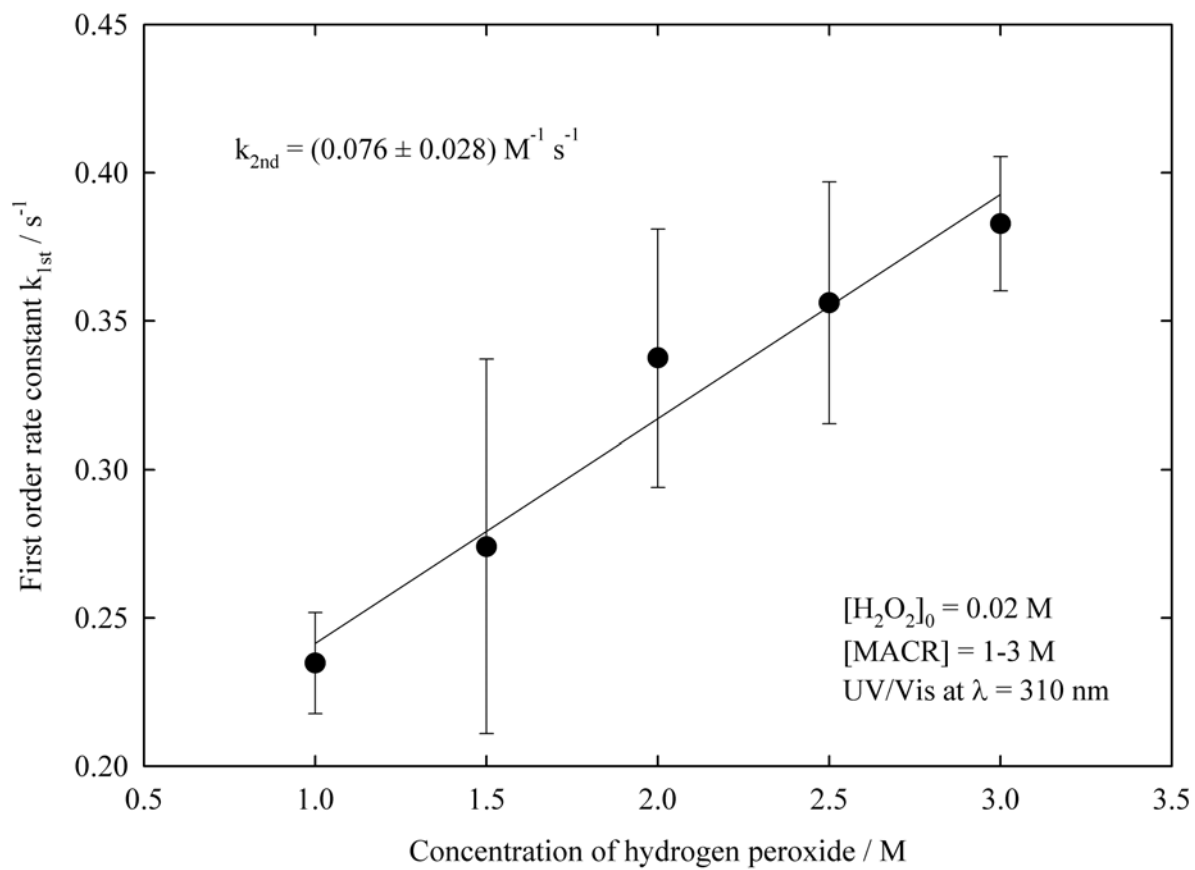
Figure A 3. First-order rate constants plotted over the concentration for the reaction of pyruvic acid with H_2O_2 at pH 1.
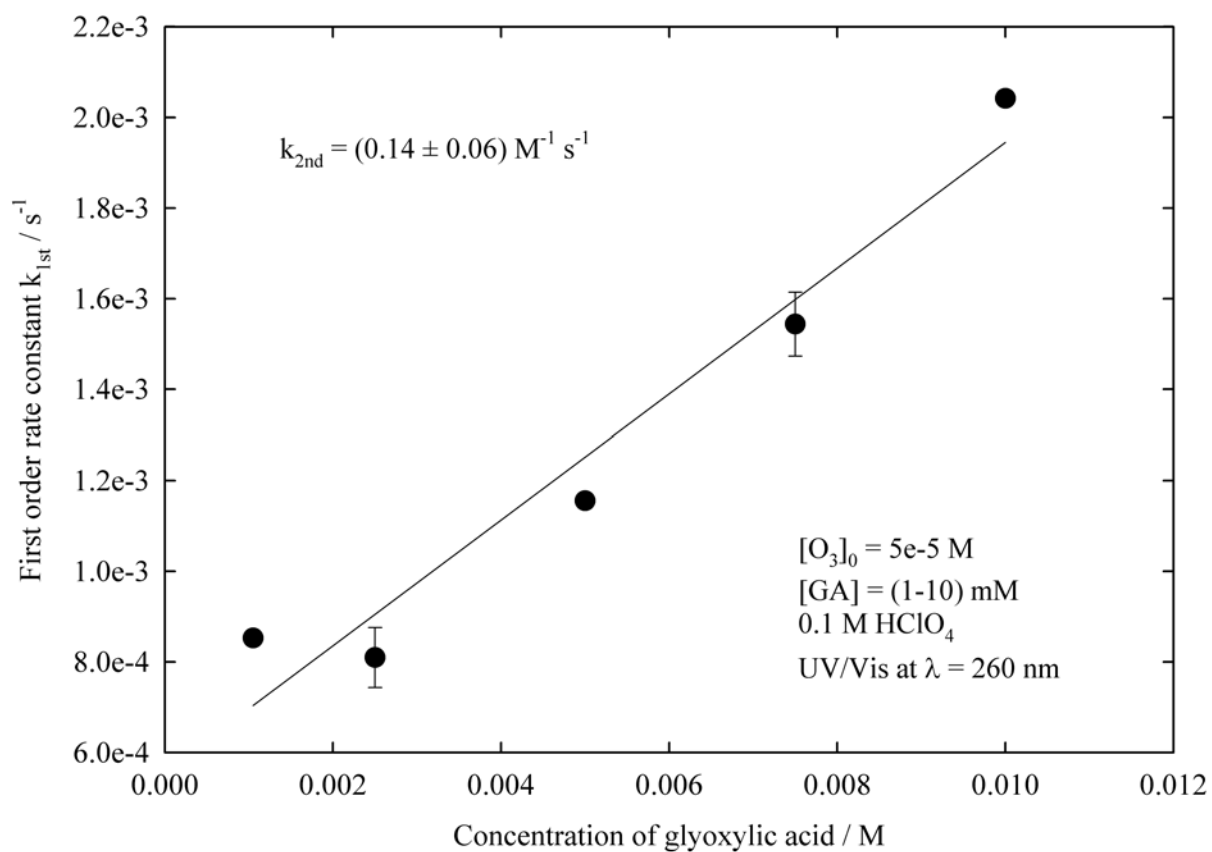
Figure A 4. First-order rate constants plotted over the concentration for the reaction of glycolaldehyde with H_2O_2.

The chart shows a plot with:
- Y-axis: First order rate constant k_{1st} / s^{-1} (ranging from 5.0e-5 to 3.5e-4)
- X-axis: Concentration of glyoxal / M (ranging from 0.4 to 1.8)

$k_{2nd} = (1.67 \pm 0.80) \cdot 10^{-4}$ M^{-1} s^{-1}

$[H_2O_2]_0 = 28$ mM
$[Gly] = 0.56-1.68$ M
UV/Vis at $\lambda = 233$ nm

1

2   Figure A 5. First-order rate constants plotted over the concentration for the reaction of glyoxal

3   with H_2O_2.

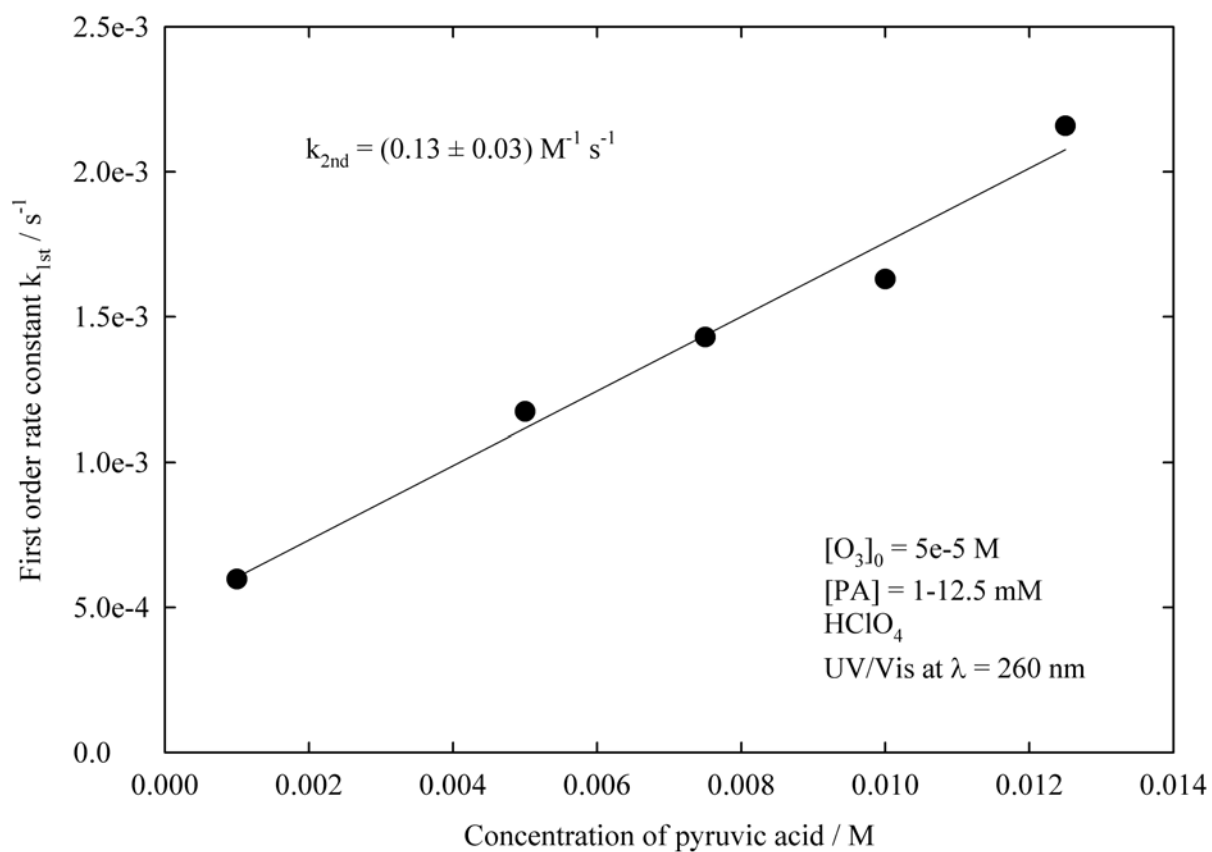$k_{2nd} = (0.076 \pm 0.028)$ M^{-1} s^{-1}

$[H_2O_2]_0 = 0.02$ M
$[MACR] = 1\text{-}3$ M
UV/Vis at $\lambda = 310$ nm

Figure A 6. First-order rate constants plotted over the concentration for the reaction of methacrolein with H_2O_2.

$k_{2nd} = (0.14 \pm 0.06)\ M^{-1}\ s^{-1}$

$[O_3]_0 = 5e\text{-}5\ M$
$[GA] = (1\text{-}10)\ mM$
$0.1\ M\ HClO_4$
UV/Vis at $\lambda = 260\ nm$
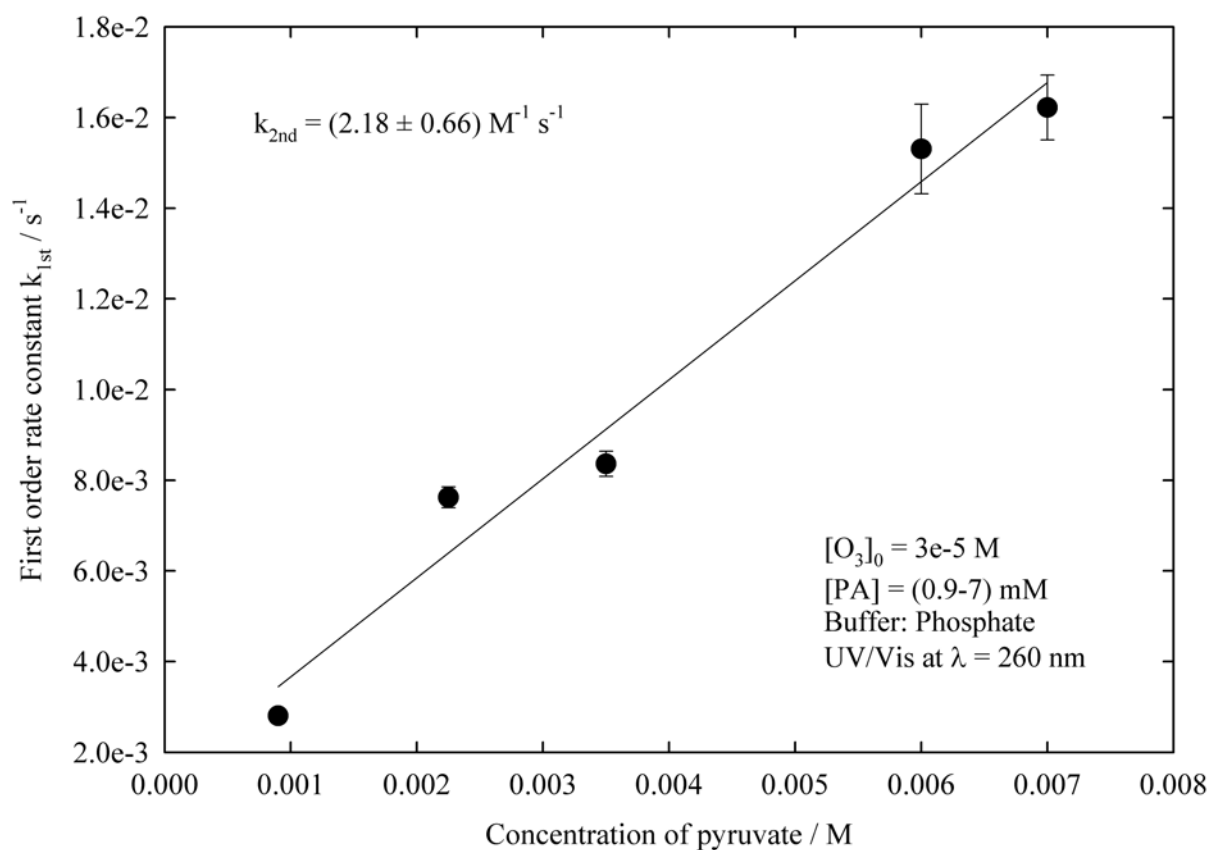
Figure A 7. First-order rate constants plotted over the concentration for the reaction of glyoxylic acid with ozone at pH 1.
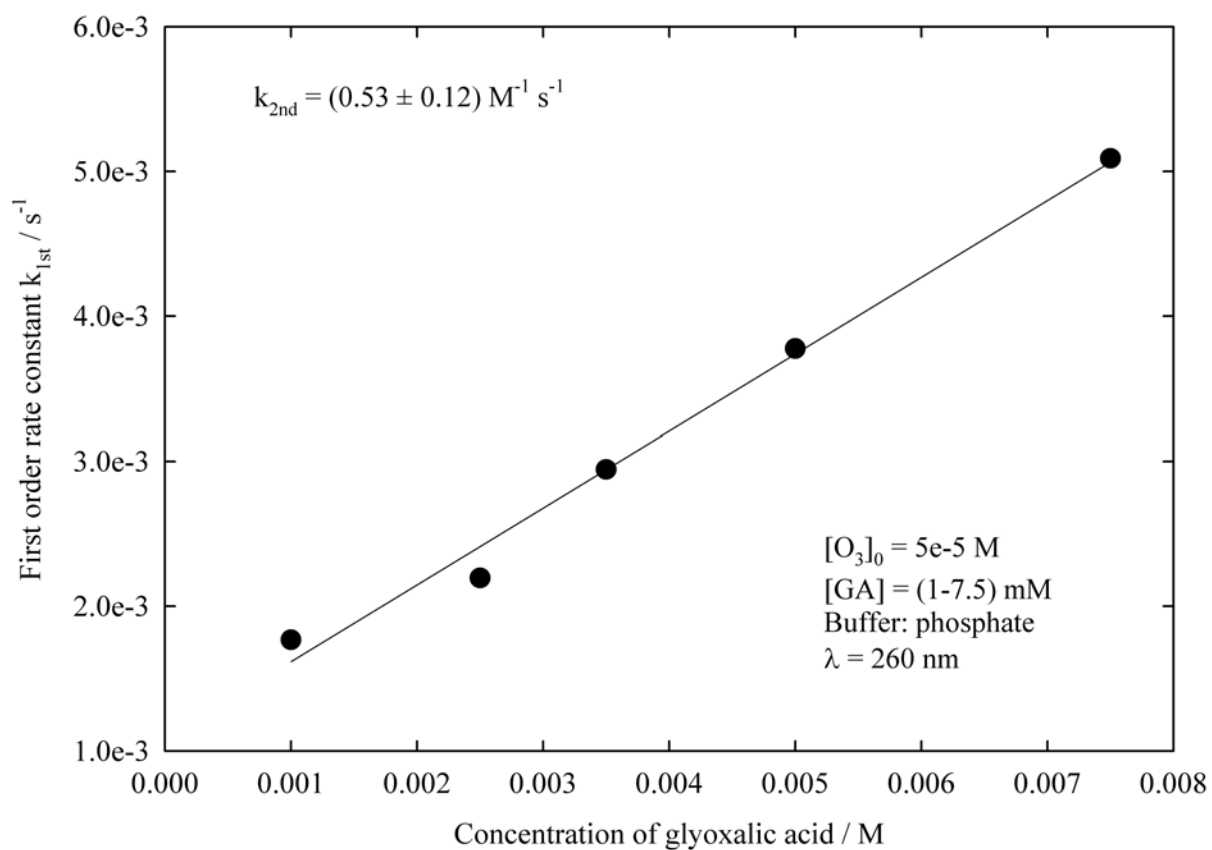
Figure A 8. First-order rate constants plotted over the concentration for the reaction of glyoxylic acid/glyoxylate with ozone at pH 3.
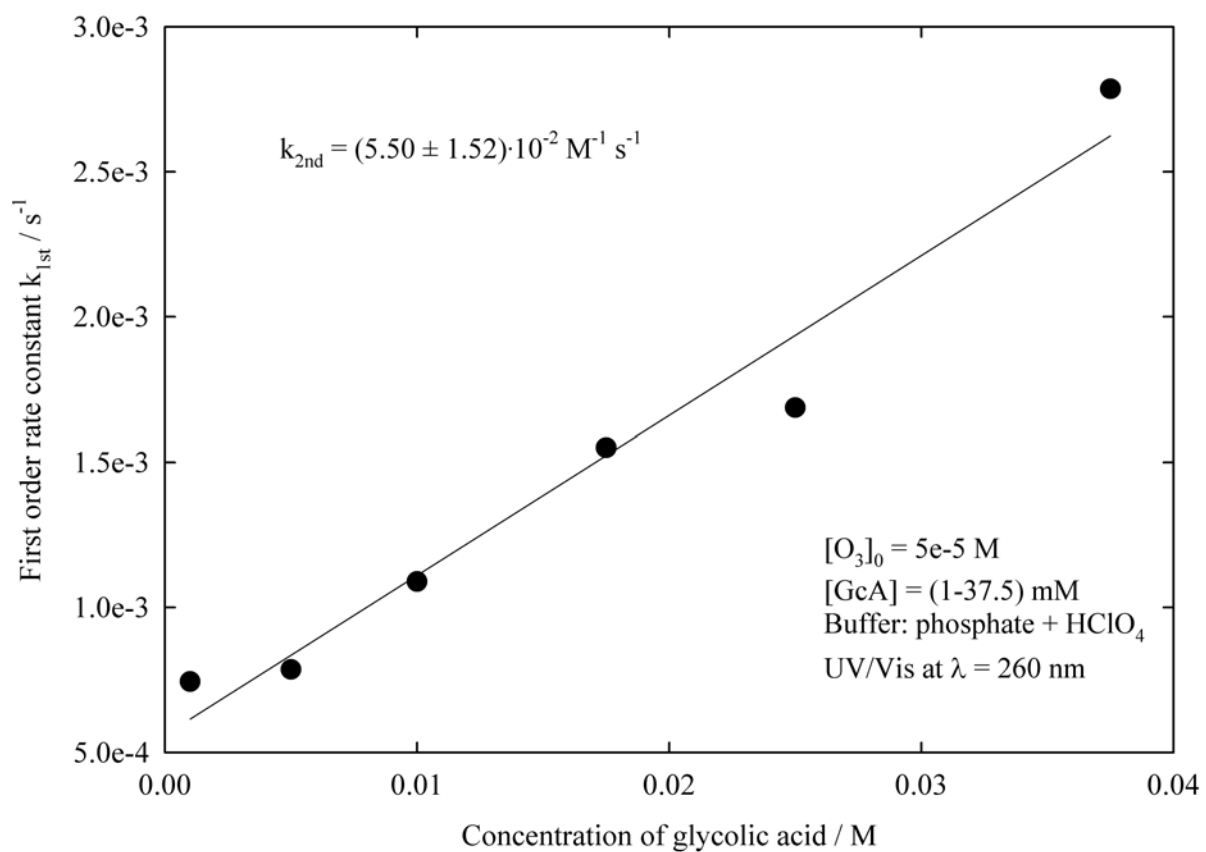
$$k_{2nd} = (0.13 \pm 0.03) \text{ M}^{-1} \text{ s}^{-1}$$

$[O_3]_0 = 5e\text{-}5 \text{ M}$
$[PA] = 1\text{-}12.5 \text{ mM}$
$HClO_4$
UV/Vis at $\lambda = 260$ nm

1

2 Figure A 9. First-order rate constants plotted over the concentration for the reaction of

3 pyruvic acid with ozone at pH 1.

$k_{2nd} = (2.18 \pm 0.66) \ M^{-1} \ s^{-1}$

$[O_3]_0 = 3e-5 \ M$
$[PA] = (0.9-7) \ mM$
Buffer: Phosphate
UV/Vis at $\lambda = 260 \ nm$
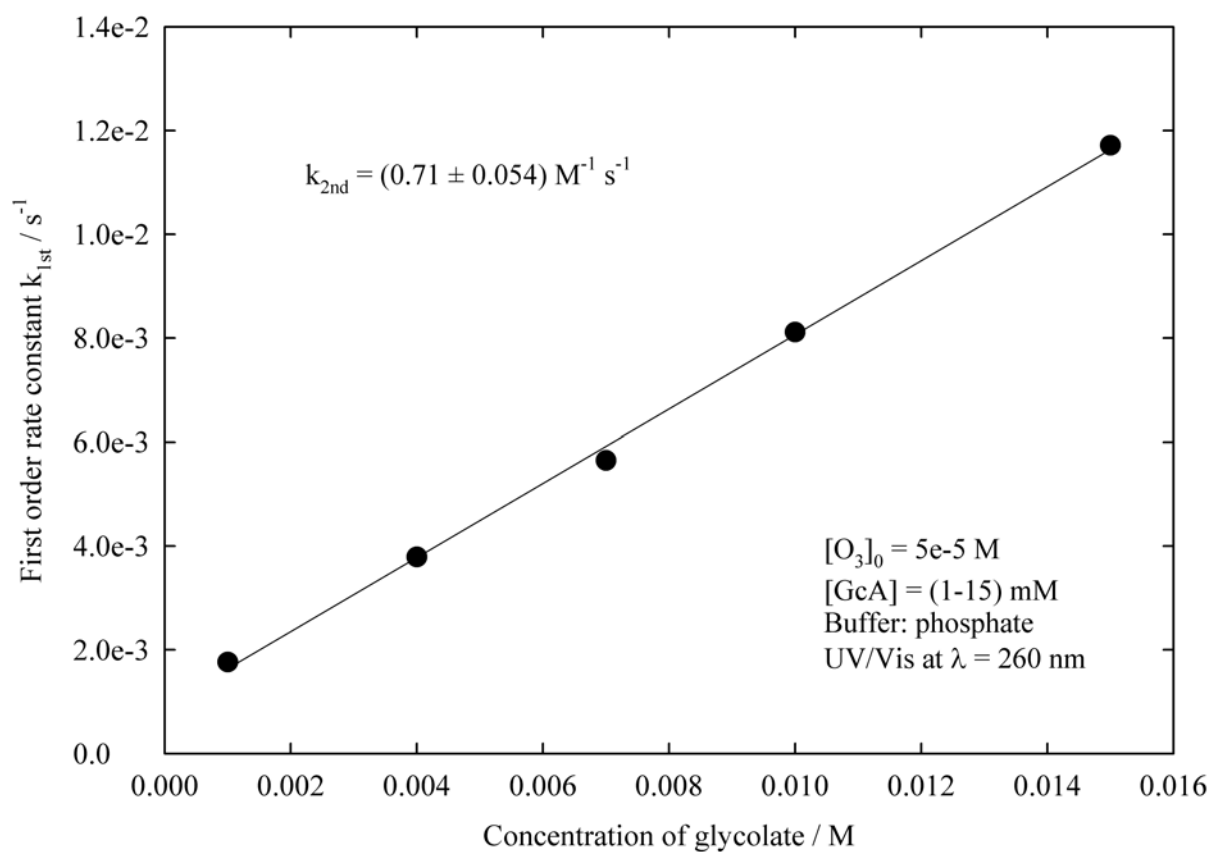
Figure A 10. First-order rate constants plotted over the concentration for the reaction of pyruvate with ozone at pH 7.

Figure A 11. First-order rate constants plotted over the concentration for the reaction of glycolic acid with ozone at pH 1.

The figure contains the following annotations:

$k_{2nd} = (5.50 \pm 1.52) \cdot 10^{-2} \ M^{-1} \ s^{-1}$

$[O_3]_0 = 5e-5 \ M$
$[GcA] = (1-37.5) \ mM$
Buffer: phosphate + $HClO_4$
UV/Vis at $\lambda = 260$ nm

Axis labels: First order rate constant k_{1st} / s^{-1} (y-axis), Concentration of glycolic acid / M (x-axis)

$k_{2nd} = (0.71 \pm 0.054)\ M^{-1}\ s^{-1}$

$[O_3]_0 = 5e\text{-}5\ M$
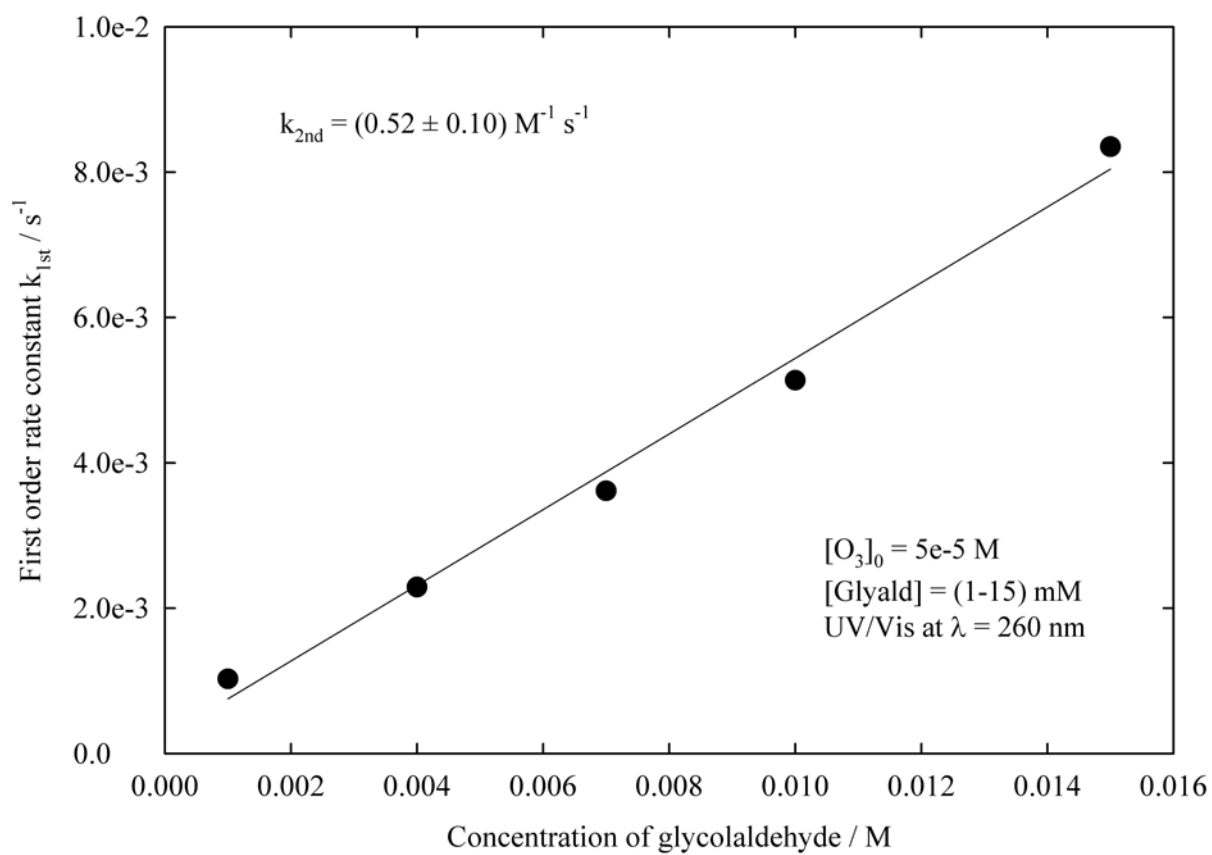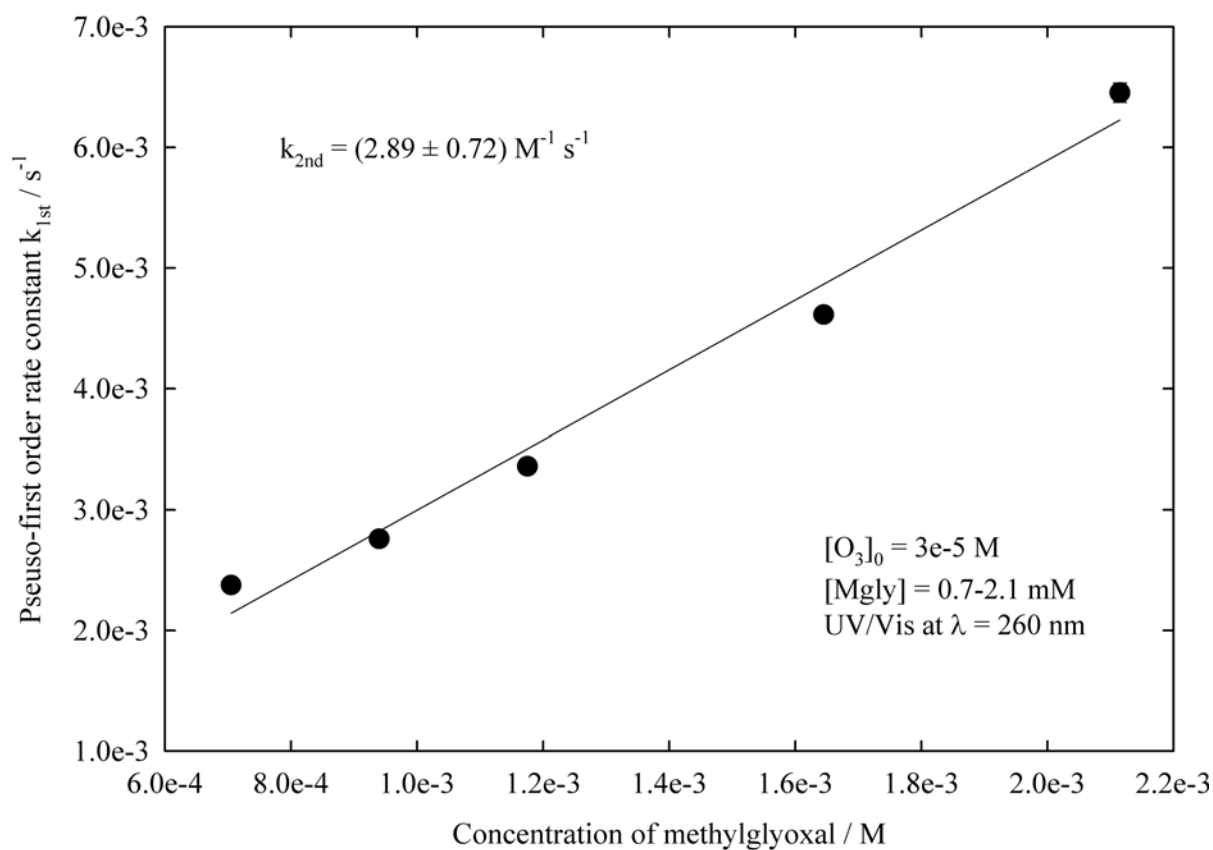$[GcA] = (1\text{-}15)\ mM$
Buffer: phosphate
UV/Vis at $\lambda = 260\ nm$

1

2   Figure A 12. First-order rate constants plotted over the concentration for the reaction of

3   glycolate with ozone at pH 7.

First order rate constant k_{1st} / s^{-1} plotted over the Concentration of glycolaldehyde / M

$k_{2nd} = (0.52 \pm 0.10)$ M^{-1} s^{-1}

$[O_3]_0 = 5e\text{-}5$ M
$[Glyald] = (1\text{-}15)$ mM
UV/Vis at $\lambda = 260$ nm

1

2   Figure A 13. First-order rate constants plotted over the concentration for the reaction of

3   glycolaldeyhde with ozone.

Figure A 14. First-order rate constants plotted over the concentration for the reaction of methylglyoxal with ozone.