Supporting Information

TAML/H₂O₂ Oxidative Degradation of Metaldehyde: Pursuing Better Water Treatment for the Most Persistent Pollutants

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Supporting information contains 6 pages, 8 figures and 2 tables.

Table S1. Properties of Metaldehyde.

Distribution / tonnes	$t_{1/2, \mathrm{H_2O}}$	Soil Lifetime	log(K _{OW})	Solubility / mgL ⁻¹	ε ₂₅₄ / M ⁻¹ cm ⁻¹	LD ₅₀ / mgkg ⁻¹
1400 ^a	6150 days ^b	60 days ^c 45 days ^d	$0.12^{1,2}$	200mg/L ^e	21.4 ³	200^{f}

^aUK, tonnes 2008–2012;² ^bHydrolysis half-life resulting from H₂O reaction, compounds having values >14 days have been determined to be potential groundwater contaminants;^{4, 5 c}50–78% oxidized to CO₂ in aerobic soil;^{1 d}To reach 10% mineralization in anaerobic soil;^{1 e}Aq. 20 °C, pH 5, 6.5, 7.2, 9;^{1, 2 f} Oral mouse.⁶

Table S2. Reaction rate comparison with different $[H_2O_2]$.

Cat	pН	[Cat]	$[Met]_0 \times$	$[H_2O_2] \times$	$r \times 10^2$	TON	Met.	CH ₃ COO	t_{∞} /
		$\times 10^7$	$10^4 \mathrm{M}$	$10^{3} / M$	/ min ^{-1b}		Decomp.	H Formed	min.
		Μ					/ %	/ % ^a	
1a	7.0	3.94	3.03	0.31	NA	NA	NA	NA	NA
1a	7.0	3.98	2.95	3.6	5.5	33	4.5	1.6	1000
1a	7.0	3.91	3.00	10.5	13.27	61	8	3.7	1000
1a	7.0	4.00	3.18	5.3	8.36	40	5	1.8	600

^aThe percentage of acetic acid is calculated as a relative percentage compared to starting metaldehyde absolute integral (Ac% = (^{Abs}Int_{1.92})/(^{Abs}Int_{1.34})₀), i.e. if all metaldehyde is converted to acetic acid, the percentage will be 100%; ^bThe rate *r* is calculated from the slope of the line of best fit to the first three measurements of substrate concentration divided by catalyst concentration ($r = d[S]/dt \times 1/[Fe]_0$).



Figure 1S. A: Reduction in the absolute integral of the signal corresponding to the metaldehyde CH₃ groups at 1.34 ppm with time (3% reduction at 760 min). B: Increase in the absolute integral of the signal corresponding to acetic acid CH₃ groups at 1.92 ppm with time (1% production at 760 min as a relative percentage of the initial absolute integral of the metaldehyde CH₃ groups). Symbols distinguish **1a** reaction from controls. Black squares: Metaldehyde; White circles: Metaldehyde and H₂O₂; Black triangles: Metaldehyde, H₂O₂, and **1a**. Conditions: pH 7.5, 0.01 M phosphate buffer in D₂O, [Metaldehyde] = 2.97×10^{-4} M, [H₂O₂] = 5.55×10^{-3} M, [**1a**] = 4.16×10^{-7} M.



Figure 2S. Increase in the absolute integral of the signal corresponding to acetaldehyde CH₃ groups at 2.25 ppm with time (0.6% production at 760 min as a relative percentage of the initial absolute integral of the metaldehyde CH₃ groups). Conditions: pH 7.5, 0.01 M phosphate buffer in D₂O, [Metaldehyde] = 2.97×10^{-4} M, [H₂O₂] = 5.55×10^{-3} M, [**1a**] = 4.16×10^{-7} M.



Figure 3S. Rate *r* dependence on $[H_2O_2]$ in pH 7 0.01 M phosphate buffered D₂O. All conditions are as depicted in Table S3.



Figure 4S. Increase in the absolute integral of the signal corresponding to acetic acid CH₃ groups at 1.92 ppm with time (12% production at 3640 min as a relative percentage of the initial absolute integral of the metaldehyde CH₃ groups). Conditions: pH 7, 0.01 M phosphate buffer in D₂O, [Metaldehyde] = 3.18×10^{-4} M, [H₂O₂] = 5.30×10^{-3} M, [**1a**] = 4.00×10^{-7} M. The vertical lines indicate the addition of an aliquot of **1a** to the reaction mixture every 12 h. The dashed vertical line indicates the addition of both an aliquot of **1a** and an aliquot of H₂O₂ to the reaction mixture at 36 h.



Figure 5S. A: Reduction in the absolute integral of the signal corresponding to the metaldehyde CH_3 groups at 1.34 ppm with time (3.5% reduction at 1480 min). B: Increase in the absolute integral of the signal corresponding to acetic acid CH_3 groups at 1.92 ppm with time (1% production at 1480 min as a relative percentage of the initial absolute integral of the metaldehyde CH_3 groups). Conditions: pH 7, 0.01 M phosphate buffer in D₂O, [Metaldehyde] = 3.45×10^{-4} M, $[H_2O_2] = 5.48 \times 10^{-3}$ M, $[\mathbf{1b}] = 4.33 \times 10^{-7}$ M. An additional aliquot of **1b** was added to the reaction mixture at 12 h.



Figure 6S. Increase in the absolute integral of the signal corresponding to acetic acid CH₃ groups initially at 1.92 ppm (δ changes with time) (4% production at 3650 min as a relative percentage of the initial absolute integral of the metaldehyde CH₃ groups). Conditions: Unbuffered D₂O, [Metaldehyde] = 3.33×10^{-4} M, [H₂O₂] = 5.53×10^{-3} M, [**1a**] = 4.16×10^{-7} M. The vertical lines indicate additions of an aliquot of **1a** every 12 h. The dashed vertical line indicates the addition of one equivalent of H₂O₂ at 36 h after the start of the reaction.



Figure 7S. Downfield shift of the CH₃ peak of acetic acid in the ¹H NMR spectra as the reaction progressed (numbers below peaks show the reaction hours at each measurement). Conditions: Metaldehyde methyl signal used as internal standard. Unbuffered D₂O, [Metaldehyde] = 3.33×10^{-4} M, [H₂O₂] = 5.53×10^{-3} M, [**1a**] = 4.16×10^{-7} M. Every 12 hours an aliquot of **1a** was added. At 36 h an aliquot of H₂O₂ was added.



Figure 8S. ¹H NMR spectra showing the downfield shift of the CH₃ peak of acetic acid upon successive additions of CH₃COOH designed to reproduce the chemical shifts of the spectra in Figure 7S; the experimentally measured pH is shown above the chemical shift axis for each of the seven spectra. Conditions: Unbuffered D₂O, 0.01 M KCl was added to increase ionic strength for pH determination. Trimethylsilyl propanoic acid (TMSP), as the sodium salt was used as an internal standard. DCl was added before the first acetic acid addition to adjust the pH to 7 and convert TMSP to its acid form. To examine if the TMSP signal is also moving with acetic acid additions, chloroform was added as a second internal standard—a slight downfield shift of TMSP was found ($\Delta \delta = 0.0036$ ppm over the range of pH 6.71 to 5.49). For each successive peak, approximately twice the concentration of acetic acid was needed in the model measurement to reproduce the metaldehyde study signals; we attribute this to media differences between the model and degradation study.

References

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