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TAML/H$_2$O$_2$ Oxidative Degradation of

Metaldehyde: Pursuing Better Water Treatment for

the Most Persistent Pollutants

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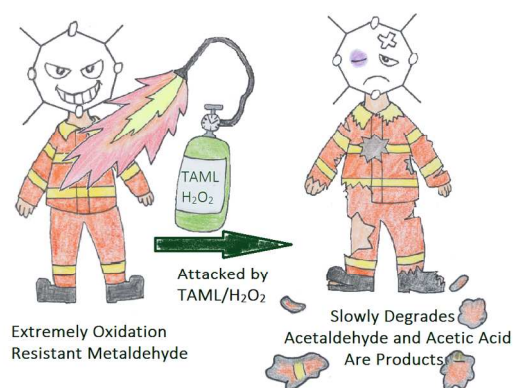
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12   ABSTRACT. The extremely persistent molluscicide, metaldehyde, widely used on farms and

13   gardens, is often detected in drinking water sources of various countries at concentrations of

14   regulatory concern. Metaldehyde contamination restricts treatment options. Conventional

15   technologies for remediating dilute organics in drinking water, activated carbon and ozone, are

16   insufficiently effective against metaldehyde. Some treatment plants have resorted to effective,

17   but more costly UV/H_2O_2. Here we have examined if TAML/H_2O_2 can decompose metaldehyde

18   under laboratory conditions to guide development of a better real world option. TAML/H_2O_2

19   slowly degrades metaldehyde to acetaldehyde and acetic acid. Nuclear magnetic resonance

20   spectroscopy (^{1}H NMR) was used to monitor the degradation—the technique requires a high

21   metaldehyde concentration (60 ppm). Within the pH range of 6.5–9, the reaction rate is greatest

22   at pH 7. Under optimum conditions, one aliquot of TAML **1a** (400 nM) catalyzed 5%

23   degradation over 10 hours with a turnover number of 40. Five sequential TAML aliquots (2 μM

24   overall) effected a 31% removal over 60 hours. TAML/H_2O_2 degraded metaldehyde steadily

25   over many hours, highlighting an important long-service property. The observation of

26   metaldehyde decomposition under mild conditions provides a further indication that TAML

27   catalysis holds promise for advancing water treatment. These results have turned our attention to

28   more aggressive TAML activators in development, which we expect will advance the observed

29   technical performance.

30   Introduction

31   Metaldehyde, the cyclic tetramer of acetaldehyde (Chart 1), is deployed as a molluscicide to

32   control gastropods including slugs and snails. It is one of the most recalcitrant anthropogenic

33   water contaminants with a half-life in water of nearly 17 years.[1] Metaldehyde is toxic and even

34   lethal to humans and other vertebrates at high doses.[2] At low concentrations in water, the broad

35   distribution, moderate water solubility and enduring persistence conspire to make metaldehyde a

36   contaminant of regulatory concern impacting, for example, UK, French and Swedish drinking

37   water sources (Table S1).[3-6] The UK Environment Agency has reported that between 2009 and

38   2011 metaldehyde was found in 81 of 647 reservoirs in England and Wales.[7] In 2009, the UK

39   Drinking Water Inspectorate (DWI) reported that metaldehyde was responsible for one third of

40   the 1103 failures to meet the prescribed concentration or value (PCV) in these two countries.[8]

41

1a   1b   2a
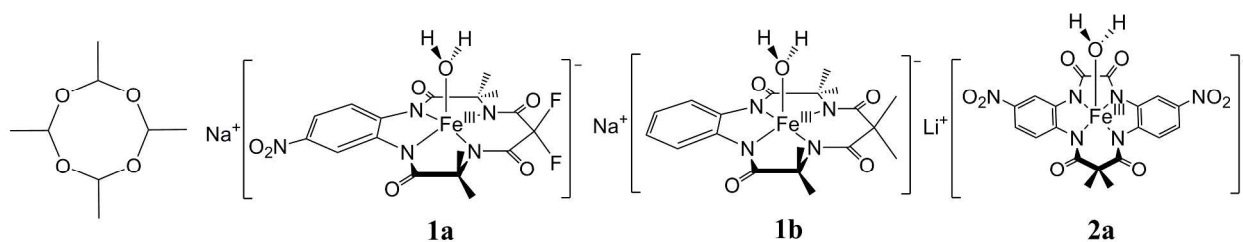
Chart 1. Structure of metaldehyde and the TAML catalysts used in this study. TAML[®] is a
registered trademark covering patented macrocyclic ligand catalysts.[9]

45

46   For most micropollutants, weighing the combined merits of familiarity and technical, cost and

47   environmental performances has led to the conclusion that adsorption on activated carbon (AC),

48   granular (GAC) or powdered (PAC), or oxidative degradation by ozone are the most desirable

49   treatments. Metaldehyde is exceptionally difficult to remove using these technologies. GAC does

50   not reliably achieve the regulatory PCV of 0.1 µg/L if the influent concentration is greater than

51   0.15 µg/L; peak concentrations in the rivers of Yorkshire can reach 0.4-0.6 µg/L.[8, 10-12] Similarly,

52   reaching the PCV with PAC produces substantial AC waste.[13] Ozone by itself is ineffective at

53   meeting the PCV.[8, 14] Thus, a substantial body of research has been dedicated to finding

54 alternative methods. Table 1 lists the performance of selected processes with the relevant

55 operational parameters.

56

57 **Table 1**. Summary of metaldehyde treatment protocols.

E#	Method	$[Met]_0$ / mg L^{-1}	Efficiency[a]	Removal %	pH[b]	Experimental Details
1		0.002–0.02	0.07 $[H_2O_2]$	>95	natural	1500 mJ cm^{-2}, 272 mg L^{-1} H_2O_2[15]
2	UV$_{254}$/H$_2$O$_2$	1	3.50 $[H_2O_2]$	95	natural	600 mJ cm^{-2}, 272 mg L^{-1} H_2O_2[12]
3		1	3.38 $[H_2O_2]$	92	natural	1200 mJ cm^{-2}, 272 mg L^{-1} H_2O_2, 8.7 mgC L^{-1} DOC[12]
4		0.0005–0.003	0.14 $[H_2O_2]$	95	8	Pilot plant, 2600 mJ cm^{-2}, 20.4 mg L^{-1} H_2O_2[16]
5		1	42 $[TiO_2]$	100	natural	600 mJ cm^{-2}, 24 mg L^{-1} TiO_2[12]
6		1	250 $[TiO_2]$	20	natural	1500 mJ cm^{-2}, 0.8 mg L^{-1} TiO_2[12]
7	UV$_{254}$/TiO$_2$	1	2.92 $[TiO_2]$	7	natural	1200 mJ cm^{-2}, 24 mg L^{-1} TiO_2, 8.7 mgC L^{-1} DOC[12]
8		0.01	0.05 $[TiO_2]$	<50	natural	16800 mJ cm^{-2}, 100 mg L^{-1} TiO_2, 3.5 mgC L^{-1} DOC, 120 mg L^{-1} alkalinity[c, 17]
9	O$_3$	0.00005–0.0002	0.002 $[O_3]$	4	NA	Surface water, 4 mg L^{-1} O_3[12]
10	O$_3$/H$_2$O$_2$	0.000.5–0.003	0.14 $[H_2O_2]$ 0.27 $[O_3]$	72	8	Pilot plant, 16–22 mg L^{-1} H_2O_2, 8 mg L^{-1} O_3[16]
11	O$_3$/H$_2$O$_2$ followed by UV$_{254}$	0.0005–0.003	0.17 $[H_2O_2]$ 0.34 $[O_3]$	90	8	Pilot plant, 1200 mJ cm^{-2}, 16–22 mg L^{-1} H_2O_2, 8 mg L^{-1} O_3[16]
12	The Arvia Process	0.011	0.000164 [Nyex]	>99	7	67 g L^{-1} dry Nyex, 4 treatment cycles, converted to CO_2[18]
13	SAFMS[d]	200	190 [SAFMS]	>95	NA	1 g L^{-1} SAFMS, converted to acetaldehyde[19]
14	GAC[d]	64	13 [GAC]	15	6.2	750 mg L^{-1} [11]
15	PAC[d]	62.20	160 [AX-21]	42	7	162 mg L^{-1} AX-21[13]
16		2.475	39 [AX-21]	39	7	24.5 mg L^{-1} AX-21[13]
17	PC[d]	64	76 [PC]	>90	6.2	750 mg L^{-1} PC[11]
18	**1a**/H$_2$O$_2$	58.4	18,000 [TAML] 50 $[H_2O_2]$	31	7	1.004 mg L^{-1} **1a**, 376 mg L^{-1} H_2O_2, converted to 3:1 acetic acid:acetaldehyde[e]

58 [a]We define efficiency in this study as mg$_{Met}$ g$_{material input}^{-1}$ with the identity of the material input
59 considered given in the brackets while noting that O_3, H_2O_2, TiO_2, Nyex, SAFMS, GAC, PAC,
60 PC, and TAML encompass energy inputs not accounted for herein; [b]Natural pH means the pH of

61   the water was not adjusted; [c]Annular photoreactor; [d]Abbreviations: SAFMS: Sulfonic Acid
62   Functionalized Mesoporous Silica, GAC: Granular Activated Carbon, PAC: Powdered Activated
63   Carbon, PC: Tailored Phenolic Carbon; [e]This work.

64

65   UV/H_2O_2 is the most effective metaldehyde AOP treatment and exploits the high reactivity and

66   low selectivity of the hydroxyl radical ($\bullet OH$);[20] > 95% removal can be achieved (Table 1, E1).

67   However, low concentrations of metaldehyde and the presence of NOM (as surrogates, Table1,

68   E2–3) demand increases in expensive UV dosages to reach high removals.[12, 15, 16, 21] UV/TiO_2

69   can completely degrade metaldehyde (Table 1, E5). The approach is very sensitive to dissolved

70   organic carbon (DOC, Table 1, E5 and 7).[12] Other efforts have been made to decrease the energy

71   demands of $\bullet OH$ production. In a pilot trial, O_3/H_2O_2 was found to reduce metaldehyde by 72%

72   (Table 1, E10) with a 33% energy reduction compared to UV/H_2O_2 (Table 1, E4). Ozone/H_2O_2

73   with a follow-up of UV gave an energy optimized reduction of 90% (Table 1, E11).[16]

74   The Arvia process, a continuous adsorption-electrochemical regeneration cycle coupling

75   adsorption to graphite intercalating Nyex™ with electrochemical oxidation, can achieve 99%

76   conversion of metaldehyde (Table 1, E12)—regenerative energy demands are high.[18] In situ acid

77   catalyzed decomposition with sulfonic acid functionalized mesoporous silica (SAFMS) is

78   capable of 95% reduction (Table 1, E13) proceeding via acetaldehyde which is adsorbed by an

79   amine bearing macroporous ion exchange resin.[19] Phenolic resin-derived activated carbons (PC)

80   adsorb metaldehyde (Table 1, E17) better than either GAC (Table 1, E14) or PAC (Table 1,

81   E15);[11] concerns have been raised about leeching of phenolic components into treated water.[18]

82   The challenges of metaldehyde contamination underscore the need for remediation

83   technologies that can deliver better technical, cost, environmental, and health performances.

84   TAML activators (Chart 1) are a family of small-molecule, full functional peroxidase enzyme

85   mimics[22] that catalyze the oxidation of hazardous environmental pollutants including, *inter alia*,

86   polychlorophenols, natural and synthetic estrogens, pesticides, dyes, explosives, and active

87   pharmaceutical ingredients by H_2O_2.[23-33] These catalysts have been investigated for low dose

88   adverse effects using in vitro cellular (10^{-11}–10^{-5} M) and in vivo zebrafish (80 nM–250 μM)

89   development assays—all three catalysts used herein showed no toxicity.[34, 35] We have examined

90   the degradation of metaldehyde (0.3 mM) by H_2O_2 (5–10 mM) catalyzed by **1a, 1b** and **2a** (0.4–

91   2 μM) under ambient conditions by following the rates of metaldehyde consumption, the product

92   production and the efficiencies in catalyst and peroxide. The work proves that TAML/H_2O_2 can

93   slowly degrade metaldehyde in laboratory experiments. We conclude by reflecting on how

94   TAML processes might be advanced to provide a real world solution.

95

96   Experimental

97   *Materials.* All reagents, components of buffer solutions, and solvents were of at least ACS

98   reagent grade and used as received. Metaldehyde (Acros, 99%) was recrystallized in ethanol[36]

99   and stored at 4 ℃. Metaldehyde stock solutions (0.3 mM) were prepared by sonicating

100   appropriate quantities of metaldehyde in buffered D_2O (99.9%, Cambridge Isotope Laboratories,

101   Inc.) at room temperature for 3 h. Phosphate (0.01 M, pH 6.5-7.5) and carbonate (0.01 M, pH

102   9.0) buffers were prepared in D_2O and monitored with an Accumet[TM] AB15 pH meter at room

103   temperature. The stated pH values of these D_2O solutions are uncorrected pH meter readings.

104   TAML[®] activator **2a** was synthesized by published methods.[37] Compounds **1a** and **1b** were

105   obtained from GreenOx Catalysts, Inc. **1b** was purified by column chromatography on C18-silica

106   gel with a water/methanol eluent (95/5, v/v) prior to use. Stock solutions of TAML activators

107   ($2×10^{-4}$ M) were prepared in D_2O (**1a** and **1b**) or H_2O (**2a**), and stored at 4 ℃. Hydrogen

108   peroxide stock solutions were prepared by diluting 30% aqueous H_2O_2 with D_2O. The

109   concentration of H_2O_2 stock solutions were monitored daily by measuring the UV-Vis

110   absorbance at 230 nm ($\varepsilon = 72.4$ $M^{-1}cm^{-1}$).[38]

111   *Instrumental*. UV-Vis measurements were performed on an Agilent 8453 UV-Vis

112   spectrophotometer equipped with an 8-cell transporter and thermostatic temperature controller.

113   Solution temperatures were maintained at 25 ºC in capped quartz cuvettes (1.0 cm). 1D [1]H

114   spectra were recorded at 300 K on a Bruker Avance[TM] III 500 NMR spectrometer operating at

115   500.13 MHz. The water signal was suppressed using the presaturation experiment (zgpr) from

116   the Bruker pulse programs library. Chemical shifts are reported in parts per million relative to

117   TMSP (internal standard for water solutions). Each sample was scanned 128 times over 16.5

118   minutes. The Bruker TopSpin[TM] 3.0 software was used to process the NMR data. Absolute

119   integrals for each proton peak were used for quantification. Each data point with error bars is the

120   average of three measurements. No measurable broadening of signals due to the accumulation of

121   catalyst was observed at the catalyst quantities employed.

122

123   Results and Discussion

124   *The use of NMR spectroscopy as a monitoring tool.* The oxidation of metaldehyde was

125   monitored by ^{1}H NMR. Presaturation[39, 40] was used to suppress water proton signals. Since an

126   internal standard would have been susceptible to TAML/H_2O_2 oxidation, none was added. The

127   quantification of metaldehyde and products was enabled by maintaining consistency of the RF

128   power delivered to the coil in the NMR probe (90º pulse), always tuning/matching the coil before

129   each measurement, using the same number of scans and the same receiver gain. As a result, the

130   intensities of the observed signals are directly proportional to the absolute quantities of the

131   specific protons responsible for each signal.[40, 41]

132   The traditional method of detecting metaldehyde in an aqueous matrix involves solid phase

133   extraction, dissolution in an organic solvent, and quantification by GC-MS.[42, 43] This study

134   employs *in situ* NMR as a monitoring method because it conveys certain advantages over the

135   traditional method, especially because the process is slow, including (1) the reaction can be

136   analyzed without quenching or pre-treatment, (2) extraction of analytes into organic solvents or

137   matrices is not required thereby reducing sources of experimental error, (3) the concentrations of

138   proton-bearing products and substrate can be analyzed at the same time without intensity

139   calibration,[39] (4) small molecules can be detected without derivatization,[44] (5) one sample can be

140   analyzed at multiple time points without destruction, and (6) lower volume reaction mixtures can

141   be analyzed with ease.[45] These characteristics enable the real-time identification and

142   quantification of multiple analytes in a small reaction volume without risk of altering their

143   molecular structures in the analytical procedure. Thus, we show that ^{1}H NMR is a powerful

144   analytical tool for monitoring the degradation of metaldehyde at higher concentrations (~300

145   μM).

146   *General observations.* The oxidation of metaldehyde was monitored by ^{1}H NMR (Figure 1).

147   The identities of the major products, acetic acid and acetaldehyde, were confirmed by spiking

148   with authentic standards. More acetic acid was produced than acetaldehyde. These degradation

149   products possess rat LD_{50} values of 3310 and 661 mg kg^{-1} (oral), respectively, significantly

150   greater than that of metaldehyde (Table S1).[46-49]
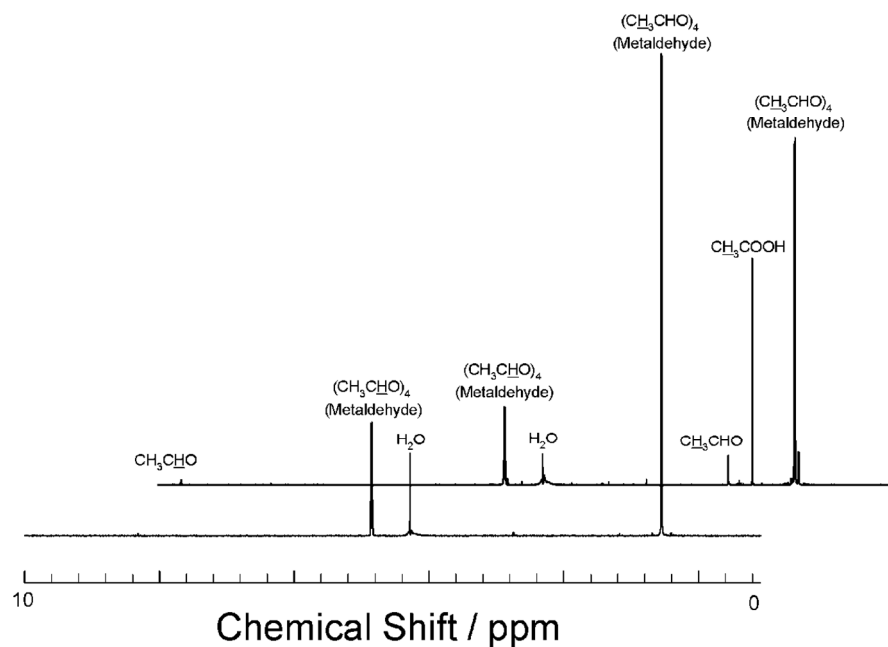
151

152 **Figure 1**. An example of the ^{1}H NMR spectra (in D_2O at pH 7) from which quantitative analyses

153 were derived. Bottom spectrum collected at ca. 20 min, top at 60 h. Conditions: pH 7, 0.01 M

154 phosphate buffer in D_2O, [Metaldehyde] = 3.18×10^{-4} M, [H_2O_2] = 5.30×10^{-3} M (180 ppm =

155 83% of the mineralization requirement), [**1a**] = 4.00×10^{-7} M. An additional aliquot of **1a** (total

156 = 2 μM) was added to the reaction mixture every 12 h and an additional aliquot of H_2O_2 (total =

157 360 ppm) was added at 36 h.

158

159 Reactions were initiated by the addition of one aliquot of H_2O_2 to a solution of a TAML

160 catalyst and metaldehyde in an NMR tube. The samples were stored in dark NMR autosampler

161 holders throughout the measurement periods to minimize metaldehyde degradation by

162 UV/H_2O_2.[12] Little decomposition of metaldehyde was observed in the presence of peroxide alone

163 indicating that the uncatalyzed process does not contribute significantly to the observed

164 degradation (Figures 2A and 1SA). As shown in Figures 2 and 1S, the rate of decomposition of

165 metaldehyde as well as that of the production of acetic acid decreased over the reaction time

166   period of 600 minutes. The production of acetaldehyde follows the same trend as that of acetic

167   acid (Figure 2S).

168   *Comparative performance of three catalysts in pH 7 buffered solutions.* The relative

169   performances of **1b** and **2a** in the degradation of metaldehyde were assessed for comparison with

170   that of **1a** (Table 2). All **1** catalysts share the same basic ligand structure (Chart 1). Catalyst **1a**

171   differs from **1b** by appendage of a nitro group to the aromatic ring and substitution of fluorine

172   atoms for the geminal dimethyl groups of the malonamide residue.[50] These substitutions increase

173   both the rate at which the catalyst is activated by H_2O_2 to form the active catalysts (Ac) and that

174   at which Ac oxidizes a substrate at neutral pH.[50] The overall rate of TAML catalysis is typically

175   a function of one or both of these processes. Addition of electron-withdrawing groups to the

176   macrocycle typically increases the oxidative aggression of the resulting TAML catalyst.

177   Consequently, the rate of metaldehyde oxidation catalyzed by **1a** was expected to be greater than

178   that of **1b** as has been observed for other micropollutants.[29, 32] Indeed **1a** oxidized metaldehyde

179   with a rate, r, of 8.36×10^{-2} min^{-1} where $r = d[S]/dt \times 1/[Fe]_0$, faster than **1b**, $r = 3.40 \times 10^{-2}$ min^{-1}

180   ^{1}. Activator **1a** also did more work than **1b** performing a 5% reduction with a turnover number

181   (TON) of 40 versus a 1.8% reduction with a TON of 14 after 600 minutes. Catalysts **1** and **2a**

182   belong to different generations.[51] In **1**, the amido-*N* nitrogen atoms are attached to six sp^2 and

183   two sp^3 carbon atoms. In **2,** all eight carbons attached to the four amido-*N* nitrogen atoms are sp^2

184   hybridized, thereby significantly reducing the electron donating ability of the macrocycle. The

185   introduction of a nitro group at each aromatic ring further reduces the overall basicity of the

186   macrocycle of **2a** to further augment the reactivity. At neutral pH, **2a** is known to both form Ac

187   from H_2O_2 and oxidize substrates more rapidly than any other TAML catalyst to date.[37]

188   However, **2a** is less effective than either **1a** or **1b** in the degradation of metaldehyde showing a

189   rate of 1.58×10^{-2} min^{-1}, an overall reduction of 1% and a TON of 8 under similar conditions.

190   We attribute this to the shorter lifetime of **2a** versus **1a** or **1b**. Of the three catalysts tested, **1a** is

191   the most effective in the degradation of metaldehyde considering both the amount and the rate of

192   the decomposition.

193

194   **Table 2**. Summary of metaldehyde degradation under different conditions. $[H_2O_2] \approx 5 \times 10^{-3}$ M.

Cat	pH	$[Cat] \times 10^7$ M	$[Met]_0 \times 10^4$ M	$r \times 10^2$ / min^{-1e}	TON	Met. Decomp. / %	CH$_3$COOH Formed / %^{a}	t_∞ / min.
1a	7.0	4.00^b	3.18	8.36	40	5	1.8	600
1b	7.0	4.33^b	3.45	3.40	14	1.8	0.3	600
2a	7.0	3.90^b	3.45	1.58	8	1.0	0.3	750
1a	7.0	4.00^c	3.18	NA	NA	31.0	12	3640
1b	7.0	4.33^d	3.45	NA	NA	3.5	1	1480
1a	NA	4.16^c	3.33	NA	NA	7.0	4	3650
1a	6.5	4.16^b	3.33	5.77	26	3.3	1	770
1a	7.5	4.16^b	2.97	4.19	22	3.1	1	760
1a	9.0	4.16^b	3.42	NA	NA	NA	0.4	770

195   ^{a}The percentage of acetic acid is calculated as a relative percentage compared to starting
196   metaldehyde absolute integral (Ac% = (^{Abs}Int$_{1.92}$)/(^{Abs}Int$_{1.34}$)$_0$)), i.e. if all metaldehyde is converted
197   to acetic acid, the percentage will be 100%; ^{b}An aliquot of catalyst and an aliquot of H$_2$O$_2$ were
198   added to the reaction mixture; ^{c}An aliquot of catalyst was added to the reaction mixture every 12
199   hours, five aliquots of catalyst were added in total and an additional aliquot of H$_2$O$_2$ was added
200   to the reaction mixture at 36 h; ^{d}An additional aliquot of catalyst was added at 12 h; ^{e}The rate r
201   is calculated from the slope of the line of best fit to the first three measurements of substrate
202   concentration divided by catalyst concentration (r = d[S]/dt $\times$ 1/[Fe]$_0$).

203

204   *Effect of pH on the catalyzed oxidation process in buffered solutions*. The trend in the rate of

205   metaldehyde degradation with increasing pH differs substantially from that usually observed for

206   TAML activators functioning in water. Here TAML catalysis follows a two-step stoichiometric

207   mechanism.[26] The resting catalyst (Rc) is activated by H$_2$O$_2$ to form an active catalyst (Ac). Ac

208   then oxidizes a substrate to give a product and regenerate Rc; both the first and second steps are

209   comprised of multiple elementary reactions. The first step, catalyst activation, is typically rate-

210   determining (d[S]/dt ~ k_I[H$_2$O$_2$][Fe]). In this system a linear dependence of the rate (r) of **1a**

211   catalyzed metaldehyde oxidation on [H$_2$O$_2$] (3–10 mM) was observed at pH 7 as would be

212   expected for a system in which catalyst activation is rate determining (Figure 3S, Table S2). The

213   value of the rate constant for TAML catalyst activation, k_I, follows a bell shaped trend with

214   respect to increasing pH.[22, 50] For **1a**, k_I reaches a maximum value around pH 10.5.[50] As a result

215   when catalyst activation is rate determining, the rate of substrate oxidation (d[S]/dt) is expected

216   to increase as the proton concentration decreases if [H$_2$O$_2$] and [Fe] are held constant within the

217   pH range of 6.5-9.[50] At pH 6.5 in D$_2$O, the **1a** catalyzed metaldehyde oxidation r is 5.77 × 10^{-2}

218   min^{-1}, lower than that observed at pH 7 (Table 2). However, the pH 7.5 r is 4.19 × 10^{-2} min^{-1},

219   also less than the pH7 r of 8.36 × 10^{-2} min^{-1} and no oxidation is observed at pH 9. Remarkably,

220   the oxidation of metaldehyde at pH 6.5–7 follows the trend expected for a system in which

221   catalyst activation is the rate-determining step. This seems to be unrealistic given the resilience

222   of metaldehyde. Moreover, the behavior observed within the pH range of 7.5–9 is anomalous.

223   We suspect this behavior has a complex origin which is being further examined. The maximum

224   reaction rate within the pH range of 6.5–9 is achieved at ~ pH 7. A pH range of 7–10.5 is

225   proposed for drinking water in order to achieve water quality objectives and corrosion control.[52]

226

227   *Multiple treatments with* **1**/*H$_2$O$_2$ in pH 7 buffered solutions.* The efficacy of multiple aliquots

228   of **1a** in a solution buffered at pH 7 was determined (Figure 2, Table 2). The reaction was

229   initiated by the addition of one aliquot of H$_2$O$_2$ to a buffered solution of **1a** and metaldehyde. An

230   additional aliquot of the **1a** stock solution was added every 12 h. In total five aliquots of catalyst

231   were added and the reaction was monitored for 60 h. One additional aliquot of H$_2$O$_2$ was added

232   at 36 h. Metaldehyde consumption and acetic acid production ceased prior to each catalyst

233   addition. Both resumed upon each addition of **1a**. We have long interpreted this result as

234   evidence that the catalyst is undergoing inactivation during the slow oxidation process.[53, 54] The

235   net effect of these treatments was a 31% reduction in the concentration of metaldehyde. Upon

236   visual inspection of the data in Fig. 2, it appears that **1a** has a functional lifetime of 500 minutes.

237   Adding successive catalyst aliquots at 500 minutes rather than 720 minutes, would give a total

238   time of 42 hours rather than 60 hours, a 31% reduction of the stated time.

239   More complete metaldehyde degradation could have been achieved through further additions

240   of catalyst. However, we chose to stop at this level of reduction to focus instead on the

241   developments that might remove all of the metaldehyde with one TAML activator aliquot. This

242   work is ongoing; we are optimistic that it will be successful.

243   Kinetic traces of the acetic acid production (Figure 4S) reveal a similar trend to that shown for

244   acetaldehyde in Figure 2B. The acetic acid and acetaldehyde produced accumulate over multiple

245   treatments and reach a final ratio of ca. 3:1, accounting for about half of the decomposed

246   metaldehyde. The performance of **1b** under identical conditions was assessed for comparison.

247   One aliquot of H_2O_2 was added to a buffered solution of **1b** and metaldehyde to initiate the

248   reaction. An additional aliquot of the **1b** stock solution was added at 12 h. In total two aliquots of

249   catalyst were added and the reaction was monitored for 24 h. These treatments effected a 3.5%

250   reduction in the concentration of metaldehyde with a final ratio of acetic acid to acetaldehyde of

251   1.3:1 (Figure 5S); acetic acid is toxicologically preferred over acetaldehyde. For comparison the

252   first two treatments with **1a**/H_2O_2 accomplished a 9% reduction in 24 h. In every way, of these

253   two catalysts, **1a** has superior performance properties.
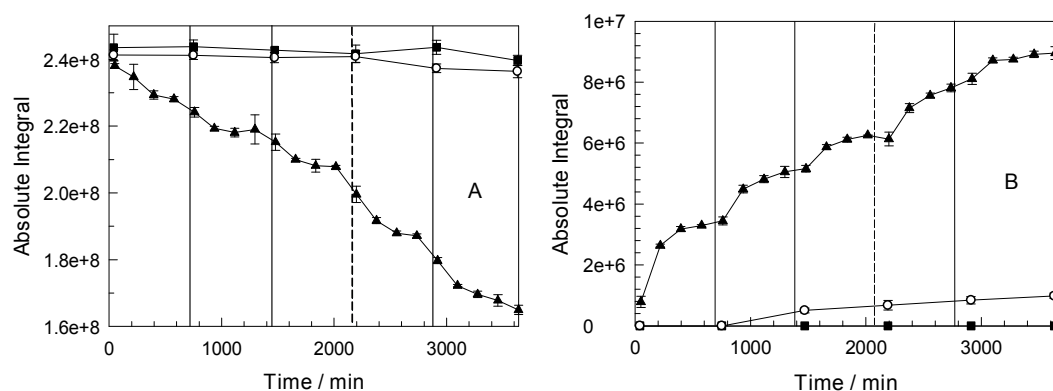
254

255 **Figure 2**. Metaldehyde reduction and acetaldehyde formation in pH 7 buffered D$_2$O. Symbols

256 distinguish **1a** reaction from controls. Black squares: Metaldehyde; White circles: Metaldehyde

257 and H$_2$O$_2$; Black triangles: Metaldehyde, H$_2$O$_2$, and **1a**. A: Reduction in the absolute integral of

258 the signal corresponding to the metaldehyde CH$_3$ groups at 1.34 ppm with time (31% reduction

259 at 3640 min). B: Increase in the absolute integral of the signal corresponding to acetaldehyde

260 CH$_3$ groups at 2.25 ppm with time (3.7% production at 3640 min as a relative percentage of the

261 initial absolute integral of the metaldehyde CH$_3$ groups). Conditions: pH 7, 0.01 M phosphate

262 buffer in D$_2$O, [Metaldehyde] = 3.18 × 10^{-4} M, [H$_2$O$_2$] = 5.30 × 10^{-3} M, [**1a**] = 4.00 × 10^{-7} M.

263 The vertical lines indicate the addition of an aliquot of **1a** every 12 h. The dashed vertical line

264 indicates the addition of both an aliquot of **1a** and an aliquot of H$_2$O$_2$ at 36 h.

265

266 *Treatment with multiple aliquots of **1a**/H$_2$O$_2$ in an unbuffered solution.* The degradation of

267 metaldehyde by multiple aliquots of **1a**/H$_2$O$_2$ in unbuffered D$_2$O was also followed as this

268 approximates the ideal treatment conditions for large-scale water purification (Figure 3A). The

269 reaction was initiated by the addition of one aliquot of H$_2$O$_2$ to an unbuffered solution of **1a** and

270 metaldehyde. An additional aliquot of the **1a** stock solution was added every 12 h. In total five

271 aliquots of catalyst were added and the reaction was monitored for 60 h. One additional aliquot

272   of H_2O_2 was added at 36 hours. These treatments reduced the concentration of metaldehyde by

273   7%. The acetaldehyde produced by each aliquot of **1a** is rapidly consumed by the next aliquot of

274   **1a** (Figure 3B), unlike catalysis in buffered solutions where it accumulates (Figure 2B). The final

275   ratio of acetic acid to acetaldehyde was 6:1, an even more benign product mixture than that

276   produced under buffered conditions. The consumption of acetaldehyde and comparatively acetic

277   acid rich product ratio were interpreted as evidence of increased acetaldehyde oxidation over that

278   which occurs in buffered solutions. Kinetic traces of acetic acid production (Figure 6S) show a

279   trend similar to that observed in the buffered case (Figure 4S). The reduced metaldehyde

280   decomposition is probably due, at least in part, to the lowering of the pH with the progression of

281   the process in the absence of buffer. In a real world system where there would be much less

282   metaldehyde this effect should be minimal. Again, these results indicate the need for a more

283   aggressive, longer-lived TAML activator en route to being able to deal in the real world with this

284   exceptionally persistent contaminant. As the reaction progressed through multiple additions of

285   **1a**, the acetic acid C$\underline{H}_3$ signal drifted downfield (Figure 7S). This is indicative of a decreasing

286   solution pH[45] consistent with the production and equilibrium protonation/deprotonation of acetic

287   acid. The observed downfield shift in this unbuffered study was not observed in the buffered

288   study. Since NMR study volumes (600 μL) were too small for accurate pH measurements, the

289   signal drift was approximately reproduced in a model experiment whereby quantities of acetic

290   acid were sequentially added to D_2O (Figure 8S).

291
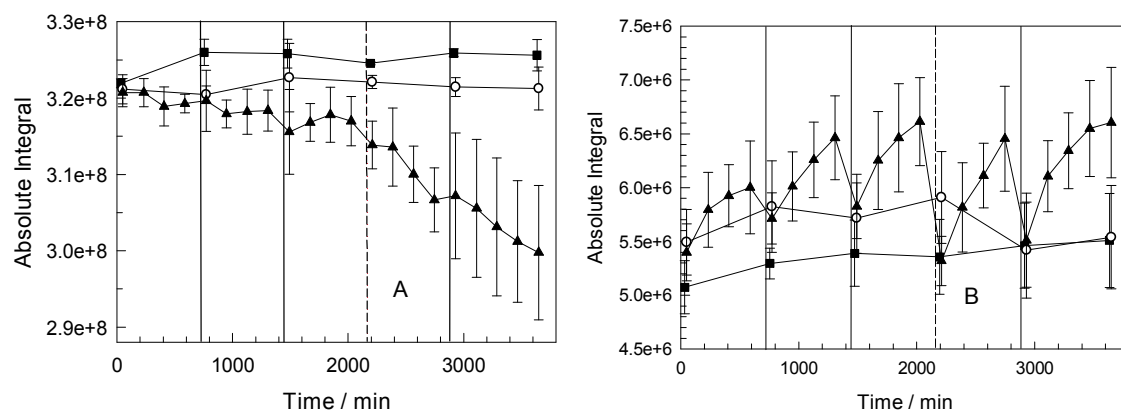
Figure 3. Metaldehyde reduction and acetaldehyde formation in unbuffered D_2O. Symbols

distinguish **1a** reaction from controls. Black squares: Metaldehyde; White circles: Metaldehyde

and H_2O_2; Black triangles: Metaldehyde, H_2O_2, and **1a**. A: Reduction in absolute integral of the

metaldehyde CH_3 groups at 1.34 ppm with time (7% reduction at 3650 min). B: Acetaldehyde

formed according to absolute integral at 2.25 ppm in the ^1H NMR spectra. Conditions: D_2O,

[Metaldehyde] $= 3.33 \times 10^{-4}$ M, [H_2O_2] $= 5.53 \times 10^{-3}$ M, [**1a**] $= 4.16 \times 10^{-7}$ M. The vertical lines

indicate the addition of an aliquot of catalyst to the reaction mixture every 12 h. The dashed

vertical line indicates the addition of both an aliquot of catalyst and an aliquot of H_2O_2 at 36 h.

300

Comparison of TAML/H_2O_2 system with existing metaldehyde degradation processes. We have

long known that TAML/H_2O_2 processes are very efficient in remediating water contaminants.

The data in Table 1 quantify this for metaldehyde. The TAML process displays a peroxide

efficiency of 50 mg_{Met} g_{H2O2}^{-1}, 14 times greater than the 3.50 mg_{Met} g_{H2O2}^{-1} of UV_{254}/H_2O_2 and

350 times greater than the 0.14 mg_{Met} g_{H2O2}^{-1} of O_3/H_2O_2. After the TAML process reported

herein, UV_{254}/TiO_2 is the next most efficient reported catalytic metaldehyde oxidation process.

Metaldehyde is oxidized by **1a**/H_2O_2 with an efficiency of 18,000 mg_{Met} g_{TAML}^{-1}, 72 times

greater than 250 mg_{Met} g_{TiO2}^{-1}, the best reported efficiency of UV_{254}/TiO_2 (noting of course that

309   only the surface of TiO_2 nanoparticles are active). The multiple aliquot process based on

310   **1a**/H_2O_2 shows greater material efficiencies than GAC, PAC, or PC and remediates metaldehyde

311   in situ.

312   While catalyst inactivation complicates comparisons of efficiency between **1a**/H_2O_2, the Arvia

313   process and SAFMS, other qualitative comparisons can be made. Since TAML/H_2O_2 does not

314   rely upon adsorption it is more likely to accommodate a range of substrates of varying structure

315   than is the Arvia process. Since TAML/H_2O_2 is an oxidative process, it is likely to be more

316   general than the acid catalyzed decomposition employed by SAFMS. SAFMS produces

317   acetaldehyde exclusively which is also an ozone disinfection by-product. Acetaldehyde is

318   considered a probable human carcinogen (Group B2)[55, 56] although no international guideline for

319   acetaldehyde in drinking-water has been established. Chlorination of acetaldehyde containing

320   water can result in the formation of chloral hydrate (trichloroacetaldehyde) which may

321   subsequently degrade to chloroform depending on pH, temperature, and maturity of the

322   water.[57] In all cases TAML processes produced more acetic acid than acetaldehyde.

323   Despite the comparative advantages, it is important to note that the metaldehyde degradation

324   rates that we have characterized are slow for this especially persistent pollutant. We evaluate this

325   work at its current state of development as very promising progress, but do not consider the

326   system is ready yet as a real world solution in the particular case of this especially persistent

327   micropollutant. Thus, it is worth asking how much faster a catalyzed process would have to

328   proceed to represent a real-world solution for metaldehyde remediation. A ten-fold increase in

329   the rate would result in the removal of one third of the metaldehyde in ca. 4 hours, all other

330   things being equal. A one-hundred-fold increase in the rate would reduce this time to 24 min; a

331   one-thousand-fold increase to 2.4 min. Is it conceivable that the higher rate increases might be

332 achievable? In seeking shorter reaction times, we are redesigning the catalyst to increase *both* the

333 lifetime and the aggression. The fact that this TAML/ H_2O_2 process is not ready for commercial

334 development for metaldehyde remediation does not have the same meaning for the vast number

335 of micropollutants that are much less oxidatively resistant than metaldehyde. An additional area

336 for study involves the assessment of the interaction of NOM surrogates with TAML/H_2O_2.

337 It is also worth asking about the safety of any TAML process for water treatment. Multiple

338 studies have been published on toxicity endpoints of TAML activators[32, 34, 35] and these studies

339 are ongoing and include mammalian studies. Due to the diverse reactivity of the activated

340 catalyst, catalysis relevant TAML inactivation can only be studied at [TAML] $< 1\times10^{-6}$ M under

341 turnover conditions where the remaining concentration of substrate is greater than zero when all

342 of the catalyst has been inactivated. The final result is a soup of degradation and catalyst

343 inactivation products. The former are present in much larger amounts than the latter making the

344 chemical identification of catalyst derived degradation products complicated. One study showed

345 how a catalyst similar to **1b** was breaking down under oxidative stress.[58] Because of the

346 challenges of chemical characterization, we have chosen to test final process solutions for

347 toxicity.[32] Additional such studies are forthcoming.

348

349 **Supporting Information**. Supporting Information Available. Tables of metaldehyde

350 properties and experimental results with varied conditions (Tables S1 and 2), figures of

351 metaldehyde degradation details (Figures 1-8S). This information is available free of charge via

352 the Internet at http://pubs.acs.org.

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