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Catalytic oxidation of cyclohexene by aqueous iron(III)/H₂O₂ in mildly acidic solution: Epoxidation versus allylic oxidation



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ABSTRACT

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Keywords: Fenton Iron(III) Hydrogen peroxide Cyclohexene Epoxidation Allylic oxidation Catalytic oxidation of cyclohexene (organic layer) at 25 °C in a stirred two phase system with fresh $[Fe(OH_2)_6](CIO_4)_3/H_2O_2$ in the pH range 2.0–4.0 (I = 0.1 M, NaCIO_4/HCIO_4) is complete within a 2-minute sampling time before deactivating in contrast to previous reports in the literature. Cyclohexene epoxide is a significant product alongside the more dominant allylic oxidation products; 2-cyclohexen-1-ol and 2-cyclohexen-1-one. Both epoxide and the accompanying allylic products appear over the same time period suggesting that they derive from the same catalytic species. The pH dependence of oxidation product yield (optimizing at \sim pH 3) suggests that the active catalyst derives from reactions involving [Fe(OH₂)₅OH]²⁺ $(PK_a 2.54)$ and is most likely the hydroperoxo ion $[Fe(OH_2)_5OOH]^{2+}$. Yields of cyclohexene epoxide are independent of the presence of dioxygen suggesting that an activated form of H_2O_2 ($[Fe(OH_2)_5OOH]^{2+}$) is responsible. Reduction in the relative yield of the two allylic oxidation products in the absence of dioxygen suggests that they derive from 2-cyclohexen-1-peroxy radicals resulting from iron(II)-promoted Fenton chemistry following homolytic Fe-O or O-O cleavage on $[Fe(OH_2)_5OOH]^{2+}$. A mechanism for the epoxide formation is proposed involving H_3O^+ -assisted heterolytic O–O cleavage on $[Fe(OH_2)_5OOH]^{2+}$ accompanying O atom transfer to the cyclohexene double bond. Accompanying catalysis of H₂O₂ decomposition persists over several hours. For the first time in a Fenton-like system evidence has been obtained for different timescales for the catalysis of oxidation reactions versus catalysis of H₂O₂ decomposition.

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The reactions of hydrogen peroxide with aqueous iron(II) (Fenton's reagent) Eq. (1) and aqueous iron(III) (the Fenton-like reaction) Eq. (2) have been known and studied for many years [1–4].

$$Fe_{aq}^{2+} + H_2O_2 \rightarrow Fe_{aq}^{3+} + HO + OH^-$$

$$\tag{1}$$

$$\operatorname{Fe}_{\operatorname{aq}}^{2+} + \operatorname{H}_2\operatorname{O}_2 \to \operatorname{Fe}_{\operatorname{aq}}^{2+} + \operatorname{H}^+ + \operatorname{HOO} \cdot \tag{2}$$

As an effective source for the non-discriminating hydroxyl radical the Fenton reaction has been much studied and indeed widely employed as a remediation agent for water purification processes, particularly for the oxidative mineralization of various chlorinated aromatic hydrocarbon pollutants [5–14]. However speculation continues as to whether Eq. (1) is truly representative of all the species generated [4,15–19]. Since aqueous iron(III) eventually precipitates from neutral or mildly acidic solution as hydrous oxy-hydroxide species there have been fewer studies on the corresponding Fenton-like reaction in regard to the nature of the species generated and their oxidizing ability in regard to potential environmental applications.

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Most of the studies to date with iron(III) under mildly acidic conditions have focused on its photo [9–10,20] or electrochemical [21] reduction to generate iron(II) for initiating Eq. (1) etc. or its known catalysis of H₂O₂ decomposition [2]. The mechanism of the ferric ion catalyzed H₂O₂ decomposition reaction has been the subject of much debate [22–25] with mono(peroxo)iron(III) and at high [H₂O₂], bis(peroxo) iron(III) complexes, invoked to explain the observed kinetics. Studies by Wynne-Jones et al. [24,25] showed that catalytic decomposition of H₂O₂ optimizes around pH 2.4, decreasing sharply at higher pHs. The rapid formation of yellow–brown colorations upon mixing mildly acidic solutions of aqueous iron(III) and hydrogen peroxide have been well documented and attributed to equilibria (3)–(5)[22–25].

$$\left[Fe(OH_2)_6\right]^{3+} + H_2O_2 \stackrel{K_{HOOH}}{\stackrel{\longleftarrow}{\longleftarrow}} \left[Fe(OH_2)_5(HOOH)\right]^{3+} + H_2O \tag{3}$$

$$\left[Fe(OH_2)_6\right]^{3+} + H_2O_2 \stackrel{K_{OOH}}{=} \left[Fe(OH_2)_5(OOH)\right]^{2+} + H_3O^+$$
(4)

$$\left[Fe(OH_2)_6\right]^{3+} + 2H_2O_2 \stackrel{K_{2HOOH}}{\Longrightarrow} \left[Fe(OH_2)_4(OOH)(HOOH)\right]^{2+} + H_3O^+ + H_2O$$
(5)

Reaction (4) is relevant to the pH range 2–4 with Eq. (3) only relevant below pH 2 and Eq. (5) at high $[H_2O_2]$. Values for K_{OOH} have

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been reported as 3.7×10^{-3} [26] and 2×10^{-3} [23] with values for $K_{HOOH} \sim 3.2 \times 10^{-2} \text{ M}^{-1}$ and for $K_{2HOOH} \sim 6.6 \times 10^{-4} \text{ M}^{-1}$ [23].

In 1999, Pignatello et al. reported the reactions of a photo activated Fenton-like reagent (0.2 mM Fe(III)_{ao}/2.0 mM H₂O₂/I = 0.1 M, NaClO₄/ HClO₄, pH 1–3) with cyclohexane, cyclohexene, 1,1,2-trichloroethane, trichloroethene and tetrachloroethene in a stirred two-phase system at 25 °C [27]. K_{OOH} Eq. (4) was determined spectrophotometrically at 450 nm to be (9.0 \pm 1.5) \times 10^{-3} at pH 2.8 shifting to (1.4 \pm 0.5) \times 10^{-2} at pH 1.45. This latter value is similar to that reported by Lewis et al. [23] for K_{HOOH} and is presumed here to refer to reaction (3). Interestingly the reactions with the chlorinated hydrocarbons; trichloroethene and tetrachloroethene studied at pH 2.8 gave a distribution of carboxylic acid products (particularly high yields of dichloroethanoic acid from trichloroethene) not consistent with solely radical processes initiated by H atom abstraction, e.g. by OH radicals, but rather from the decomposition of an intermediate epoxide [27]. Subsequent investigations with cyclohexene at pH 2.8 led to the detection of significant amounts of epoxide accompanying formation of the expected allylic oxidation products; 2-cyclohexen-1-ol and 2-cyclohexen-1-one [27]. However a surprising observation was the slow appearance of reaction products over several hours. Substitution of water on $[Fe(OH_2)_5OH]^{2+}$, the likely aqua iron(III) species present under the stated conditions [28,29], is fast $(k_{ex}^{298} = 1.4 \times 10^5 \text{ s}^{-1})$ [30] suggesting that assembly of the active catalyst from complexes such as $[Fe(OH_2)_4(HOOH)OH]^{2+}$ Eq. (6) or more likely, given the higher acidity of coordinated H₂O₂[25], its tautomeric form $[Fe(OH_2)_5OOH]^{2+}$ Eq. (7) occurs on the submillisecond timescale.

$$[Fe(OH_2)_5OH]^{2+} + H_2O_2 \rightarrow [Fe(OH_2)_4(HOOH)OH]^{2+} + H_2O$$
(6)

$$H_{2}O_{H_{2}} O_{H_{2}} O_{H_{2}}$$

Furthermore, the formation of epoxide, which is only observed in the presence of iron(III), is not consistent with reactions involving OH radicals e.g. via Eq. (1) and suggests another source for the oxidation. It was speculated [27] that $[Fe(OH_2)_5OOH]^{2+}$ could homolytically cleave at the O-O group to generate the oxo-aquairon(IV) complex; $[Fe(=O)(OH_2)_5]^{2+}$ which actually transfers oxygen to the cyclohexene. However extensive studies by Bakac and co-workers on the chemistry of oxo-aquairon(IV), generated via reaction of ozone with $[Fe(OH_2)_6]^{2+}$, show that it tends to rather promote H atom or hydride abstraction and only transfers oxygen to highly oxophilic substrates such as sulfoxides or phosphines [31,32].

We have re-investigated Pignatello's reaction of aqueous iron(III) (added as a freshly made up acidified solution of $[Fe(OH_2)_6](CIO_4)_3$ adjusted to pH 2-4) and H₂O₂ with neat cyclohexene in a stirred two-phase system [33]. A typical GC trace for the reaction products isolated from the cyclohexene layer at pH 2.7, Fig. 1, confirms the presence of cyclohexene epoxide A ($R_f = 5.78 \text{ min}$) accompanying the formation of 2-cyclohexen-1-ol/cyclohexanol B (not resolved) $(R_{\rm f}=6.23)$ and 2-cyclohexen-1-one C $(R_{\rm f}=6.68).$ The peak at $R_f = 6.91$ is from cyclooctane added as an internal reference. Fig. 2 shows a typical plot (25 °C) at pH 3.0 representing integration of the GC peaks A-C as a function of sampling time after the initial injection of H₂O₂. The product yields were calculated relative to the amount of the internal reference added to each sample. Clearly apparent from Fig. 2 is the rapid formation of products within the first 2-minute sampling time with little or no change thereafter over a 1-hour period. It was initially thought that the loss of activity after the initial 2-minute sampling was due to rapid depletion of H₂O₂ from the reaction solution. However subsequent monitoring of the [H₂O₂] concentration via permanganate titration of aliquots of the aqueous phase in a separate run (shown also in Fig. 2) showed only



Fig. 1. GC trace following sampling of the cyclohexene layer after 2 min at 25 °C. The labeled products are A; cyclohexene epoxide, B; 2-cyclohexen-1-ol/cyclohexanol, C; 2-cyclohexen-1-one. The peak at R_f 6.91 min is from cyclooctane added as reference prior to running the GC. Aqueous layer: $[H_2O_2]_{init} = 10 \text{ mM}$; $[Fe(III)]_{init} = 0.2 \text{ mM}$, pH 2.7.

a slow but steady decrease over the first hour. The addition of further aliquots of stock H_2O_2 solution after 10 and 20-minute reaction, Figure S1, indeed failed to restore the catalytic activity of the solution. However, the addition of aliquots of fresh iron(III) solution did restore some activity over the first 30 min, Figure S2, when amounts of H_2O_2 were still present, Fig. 2. A gradual darkening of the aqueous phase followed by a brown turbidity after 1 h suggested that the loss of catalytic oxygenation activity is due to gradual depletion of soluble mononuclear aqua iron(III) via hydrolytic polymerization to inactive colloidal forms and finally precipitation of insoluble iron(III) oxy-hydroxides [28]. A closer inspection of the H_2O_2 decay profile, Fig. 2, reveals an induction period within the first 2 min correlating with the maximum rate of H_2O_2 activation towards oxygenation. Thereafter, efficient catalysis of H_2O_2 decomposition dominates.

A further insight into the nature of the putative iron(III) oxygenation catalyst came from monitoring the pH dependence of the yields of oxidation products following the initial sampling after 2-minute reaction, Fig. 3. The yields of all products increase sharply in the pH range 2.7-3.2 before decreasing at higher pHs. Interestingly there is a small but noticeable increase in the relative yield of epoxide compared to the allylic oxidation products; the epoxide yield increasing between pH 2.7 and 3.2 to reach ~13% of the total oxidation products seen. Above pH 3.2 the total product yield decreases but the relative yield of epoxide remains steady at ~11%. The speciation profiles of aqua iron(III) at below mM concentrations (data from [29a] shown in Fig. 3 for comparison) indicate a correlation of oxygenation catalytic activity with amounts of the hydroxopentaaqua ion; $[Fe(OH_2)_5OH]^{2+}$ (pK₁₁ = 2.54 at I = 0.1 M, NaClO₄) [29a]. With oxo-aquairon(IV) not proven as an effective epoxidation catalyst [31c], we tentatively propose the following mechanism for alkene epoxidation, Fig. 4. Firstly, an activated complex forms between $[Fe(OH_2)_5OOH]^{2+}$ and cyclohexene which then undergoes intramolecular iron-bound oxygen atom transfer (most electrophilic) to the cyclohexene double bond accompanying (H₃O⁺)assisted O-O heterolysis. Formation of the allylic oxidation products; 2-cyclohexen-1-ol and 2-cyclohexen-1-one will arise via the generally accepted radical autoxidation mechanism (8)



Fig. 2. Time dependence of formation of oxidation products (black symbols) at 25 °C following sampling of the cyclohexene layer respectively at various time intervals [32]: A cyclohexene epoxide; B 2-cyclohexen-1-ol/cyclohexanol; C 2-cyclohexen-1-one. Aqueous layer: $[H_2O_2]_{init} = 10 \text{ mM}$; $[Fe(III)]_{init} = 0.2 \text{ mM}$, pH 3.0. The open circles show the time dependence of the H_2O_2 concentration in the aqueous layer in a separate blank run under the same conditions. Here 5 cm³ aliquots were removed from a 100 cm³ volume of the aqueous layer after the set time interval and quenched by injection into a 25 cm³ solution of 0.1 M HClO₄ for titration with standard permanganate.

involving the trapping of 2-cyclohexene-1 radicals by dioxygen present in the air or from the accompanying H_2O_2 decomposition. Confirmation of this was provided by runs conducted air-free wherein the yields of 2-cyclohexen-1-ol and 2-cyclohexen-1-one are reduced significantly, Table 1, compared to the epoxide; which now assumed >57% of the total products observed at the optimum pH. The flux of 2-cyclohexen-1 radicals most likely derives from iron(II)-promoted Fenton chemistry involving H atom abstraction through OH radicals and/or oxo-aquairon(IV). Both species can be readily generated from $[Fe(OH_2)_5OOH]^{2+}$ either via Fe – O homolysis (e.g. Eq. (9) then Eq. (1)) or O–O homolysis Eq. (10)[34,35]. The most likely pathway is



Fig. 3. pH dependence of the yields of oxidation products at 25 °C following sampling of the cyclohexene organic layer after 2 min: A cyclohexene epoxide; B 2-cyclohexen-1-ol/cyclohexanol; C 2-cyclohexen-1-one. Aqueous layer: $[H_2O_2]_{init} = 10 \text{ mM}$; $[Fe(III)]_{init} = 0.2 \text{ mM}$. The iron(III) speciation data is from ref. 30a (with permission) for I = 0.1 M, NaClO₄, [Fe(III)] = 0.01 mM.

via Eq. (9) given the presence of high spin iron(III) in $[Fe(OH_2)_5OOH]^{2+}$.

$$\operatorname{Fe}(\operatorname{OOH})_{\operatorname{aq}}^{2+} \to \operatorname{Fe}_{\operatorname{aq}}^{2+} + \operatorname{HOO}$$
 (9)

$$\operatorname{Fe}(\operatorname{OOH})_{\operatorname{aq}}^{2+} \to \operatorname{Fe}^{\operatorname{IV}}\operatorname{O}_{\operatorname{aq}}^{2+} + \operatorname{HO}$$
 (10)

The insensitivity of epoxide formation to the presence of molecular oxygen suggests that an activated form of H_2O_2 is responsible for its formation rather than organoperoxy radicals deriving from Eq. (8) which have been reported to generate epoxides from alkenes but in very small yields.

An additional mechanistic possibility is for the H₃O⁺-assisted O-O heterolysis on $[Fe(OH_2)_5OOH]^{2+}$ to take place prior to addition of the 'O' atom across the double bond [36]. Such a reaction would generate a 'perferryl' oxo-aquairon(V) species, [17,22] the oxo group of which would be expected to be very much more electrophilic than oxo-aquairon(IV) or the iron bound peroxooxygen of $[Fe(OH_2)_5OOH]^{2+}$ leading to rapid 'O' addition across the cyclohexene double bond. In polar aprotic solvents in the presence of a number of 2-pyridylmethylamine chelate ligands, evidence has been recently claimed [37] for the formation of short lived highly reactive perferryl oxoiron(V) species, generated via H₂O₂ or peroxycarboxylate oxidation of their iron(II) counterparts. These iron species have been suggested as responsible for the catalysis of alkene epoxidation by H₂O₂ in the presence of ethanoic acid [38] and the insertion of 'O' into unreactive C-H bonds such as in the formation of salicylate from peroxybenzoate [39] or H₂O₂/benzoate [40]. Aqueous iron(V) however has an extremely short lifetime away from strongly alkaline media (lifetime <10 µs below pH 4) [41]. So while we cannot directly rule out an oxo aquairon(V) species as responsible for alkene epoxidation in the present system, its trapping (reduction) by cyclohexene would require an extremely fast and efficient process at the solvent interface capable of competing successfully with its rapid reduction by excess H₂O₂ Eq. (11).

$$Fe^{V}O_{aq}^{3+} + H_{2}O_{2} \rightarrow Fe^{3+}aq + O_{2} + H_{2}O$$
(11)

To date the only example of a stable spectroscopicallycharacterized oxoiron(V) complex is $[Fe(O)(TAML)]^-$ (TAML⁴⁻ = various deprotonated tetraamido macrocycle ligands) reported in



Fig. 4. Mechanism for cyclohexene epoxidation catalyzed by [Fe(OH₂)₅OOH]²⁺.

2007 by Collins et al. [42] and even here it is stable only in polar aprotic solvents at -60 °C.

The rapid appearance of oxidation products observed in this study, including cyclohexene epoxide, before catalyst deactivation contrasts with their reported 'slow' (hours) appearance in the same pH range in the earlier published work [27]. However the rapid processes observed here are entirely consistent with the expected rapid formation and

subsequent reactions of $[Fe(OH_2)_5OOH]^{2+}$ with the cyclohexene organic layer in the stirred two phase system. A slow reaction over several hours is hard to rationalize given the lability of aqueous iron(III) species and known rapidity of reactions (1)-(11)[4] and subsequent aging processes. The rapid stirring of the two phases performed here (rate ~1000 rpm) is in keeping with the experimental conditions previously reported [27] so different rates of mass transfer between the two phases

Table 1

Yields of oxidation products in cyclohexene layer following sampling after 2 min as a function of aqueous phase pH. The values in italics are from runs conducted in the absence of air. [H₂O₂]_{init} = 10 mM; [Fe(III)]_{init} = 0.2 mM.

pН	Moles 2-cyclohexan-1-ol/ cyclohexanol	Moles 2-cyclohexan-2-one	Moles cyclohexene epoxide	Moles total oxidation products	% Epoxide in total products	$\%$ Efficiency total products based on $\rm H_2O_2$	TON total products based on Fe(III)
2.0	1.12×10^{-4}	$1.75 imes 10^{-4}$	1.05×10^{-5}	$2.98 imes 10^{-4}$	3.5	119	60
2.7	3.87×10^{-4}	5.03×10^{-4}	4.66×10^{-5}	9.37×10^{-4}	5.0	375	187
	4.48×10^{-5}	4.71×10^{-5}	3.82×10^{-5}	1.3×10^{-4}	29.3	52	26
3.0	6.91×10^{-4}	1.47×10^{-3}	$1.34 imes 10^{-4}$	2.29×10^{-3}	5.9	916	458
	$4.99 imes 10^{-5}$	$5.04 imes 10^{-5}$	$1.05 imes 10^{-4}$	2.05×10^{-4}	51.2	82	41
3.2	1.39×10^{-3}	1.88×10^{-3}	4.94×10^{-4}	3.76×10^{-3}	13.1	1500	752
	4.67×10^{-5}	5.23×10^{-5}	1.33×10^{-4}	2.33×10^{-4}	57.1	93	47
3.4	9.38×10^{-4}	1.43×10^{-3}	3.45×10^{-4}	2.71×10^{-3}	12.7	584	292
3.6	3.13×10^{-4}	6.25×10^{-4}	1.15×10^{-4}	9.66×10^{-4}	11.9	386	193
4.0	4.27×10^{-5}	8.44×10^{-5}	1.52×10^{-5}	1.42×10^{-4}	10.7	57	28

would seem unlikely as an explanation. Also in the previous work, the photochemical nature of the Fenton-like catalysis was emphasized. Following runs conducted in daylight, in the dark and under mild UV light it appears that the profile of product formation in the present system is not influenced by photo-activation.

For the first time in a Fenton-like system evidence has been obtained for different timescales for the catalysis of oxidation reactions versus catalysis of H_2O_2 decomposition. The active oxidation catalyst is only short lived ($\leq 2 \min$) following the addition of fresh [Fe(OH₂)₆]³⁺ and thereafter quickly deactivates presumed due to depletion of [Fe(OH₂)₅OH]²⁺/[Fe(OH₂)₅OOH]²⁺ from the aqueous phase. The accompanying catalysis of H_2O_2 decomposition however persists over 1–2 h as the iron(III) solution 'ages'. The development of methods for maintaining the flux of mononuclear [Fe(OH₂)₅OOH]²⁺ [Fe(OH₂)₅OOH]²⁺ in solution over longer periods is the subject of ongoing research.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.06.018.

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