

Photocatalysis of ethanol oxidation by tetrachloroferrate(III) supported on Dowex 2-X8

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FeCl₄⁻ heterogenized on a Dowex 2-X8 anion exchange resin catalyzes the photooxidation of ethanol to acetaldehyde under visible and near-UV irradiation (>345 nm). The rate of reaction is proportional to the oxygen partial pressure up to 1 atm. Oxidation is suggested to occur through the formation of 1-hydroxyethylhydroperoxide, initiated by the photodissociation of a chlorine atom. The hydroperoxide re-oxidizes the iron(II) species, both the oxidation and reduction steps producing acetaldehyde. This mechanism is consistent with the increases in yield with ethanol concentration in ethanol–toluene mixtures towards an asymptotic limit. Copyright © 2014 John Wiley & Sons, Ltd.

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Introduction

Among the objectives of green chemistry is that of oxidizing alcohols to aldehydes or ketones using molecular oxygen in place of permanganate and other strong oxidizing agents.^[1] A variety of catalytic systems have been studied for this purpose, using thermal or photochemical reaction conditions.^[2–4] In either case the goals include finding cheap catalysts and using a minimum amount of energy. Additionally, molecular oxygen represents the environmentally and economically preferred oxidizing agent,^[5–7] and several recent studies have probed the potential use of oxygen to selectively form acetaldehyde from ethanol.^[8,9] The use of sunlight for photochemical conversions, though uncommon for preparative chemistry, can be expected to be more common in the future.^[10]

Thermal catalysis of alcohol oxidation has been carried out with a variety of systems, generally involving a transition metal ion and additional components. Thermal catalysis has been shown to be effective for aromatic alcohols such as benzyl alcohol,^[4] but relatively ineffective for aliphatic, especially primary, alcohols.^[4] For example, the oxidation of 1-heptanol was attempted with a catalyst consisting of a mixture of FeCl₃·6H₂O, TEMPO (2,2,6,6-tetramethylpyridine N-oxide) and silica gel. After 24 h at 80 °C under 5 atm of O₂, 11% conversion to the aldehyde was obtained, and no aldehyde at all was formed under air.^[4]

More success in the oxidation of aliphatic alcohols has been achieved with photochemical processes,^[3] however, photooxidation has been carried out overwhelmingly with TiO₂ catalysts, which are essentially nonabsorptive in the visible. Some progress has been made towards potential sunlight-driven catalysis by doping TiO₂ with other elements.^[2] In one study of ethanol photooxidation using vanadium-doped titanium dioxide, it was demonstrated that CH₃CHO was produced in quantities detectable using NMR analysis.^[2]

With the objective of photooxidizing alcohols using a heterogeneous catalyst that absorbs light in the visible part of the spectrum, we investigated FeCl₄⁻ heterogenized on a Dowex 2-X8 anion exchange resin. The lowest lying ligand-to-metal charge transfer (LMCT) band in the FeCl₄⁻ spectrum is centered at approximately 360 nm,^[11,12] with a significant tail into the blue. There has been relatively little use of tetrachloroferrate(III) as a photooxidation

catalyst,^[11] although FeCl₃, the LMCT band for which is approximately 20 nm further into the UV,^[12,13] has been used for this purpose both homogeneously^[4,14–17] and heterogeneously.^[13] Maldotti *et al.* reported the use of heterogenized tetrachloroferrate (III) to photochemically oxidize or chlorinate cycloalkanes stoichiometrically, the outcome depending on experimental conditions,^[18] regenerating FeCl₄⁻ with hypochlorite ion in a separate process. For this study we heterogenized tetrachloroferrate(III) essentially as outlined by Maldotti *et al.*^[18]

An additional objective was to obtain as high a yield of acetaldehyde as possible with a minimum of further oxidation to acetic acid. This goal has remained elusive, despite a variety of recent approaches,^[19–26] including the use of metal nanoparticles,^[20] metal oxide catalysts^[23] and homogeneous hypervalent iodine compounds.^[6]

Experimental

Heterogenized tetrachloroferrate(III), FeCl₄⁻/Dowex, was prepared according to the method of Maldotti *et al.*^[18] by stirring 1.0 g of Dowex 2-X8 resin (Cl⁻ form, BioRad AG-2X8, 16–50 mesh, 3.2 meq. per dry gram) in an acetonitrile solution of anhydrous iron(III) chloride (0.6 g in 50 ml) for 2 h, during which time the solution color virtually disappeared and the resin acquired a dark orange hue. After filtration, the resin was air-dried. This amount of iron chloride was sufficient to saturate the resin, the capacity of which after the addition of FeCl₃ was 2.1 mmol of FeCl₄⁻ per dry gram. For most experiments the resin was ground to a powder.

UV–visible spectra were recorded with a Cary 50 spectrophotometer. GC–MS measurements were carried out with a Shimadzu QP-5000 instrument with an Agilent DB624 column (30 m, 0.32 mm × 1.8 μm cyanopropylphenyl/dimethylpolysiloxane film). The oven start temperature was 40 °C and a 20 °C min⁻¹ linear temperature gradient

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was applied to a final temperature of 260 °C. A 10:1 split ratio was applied to sample injections. Species were identified from their mass spectra and total ion count peak areas were used to determine concentrations.

The products from the photooxidation of ethanol were, as would be expected, acetaldehyde and acetic acid. A substantial fraction of the acetaldehyde was present as the acetal, $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$, and likewise a substantial fraction of the acetic acid was present as ethyl acetate. Total ion count peak areas were determined for standard solutions of acetaldehyde, 1,1-diethoxyethane, ethyl acetate and acetic acid over a range of concentrations, yielding a direct proportionality in each case, with R^2 between 0.983 and 0.998. When analyzing photolysates, care was taken not to exceed the highest concentrations of the standards, diluting when necessary, to avoid potential problems from detector saturation. The acetaldehyde concentration reported in this paper consists of the sum of acetaldehyde and acetal concentrations, and likewise the sum of ethyl acetate and acetic acid concentrations is reported as the acetic acid concentration.

In a typical experiment *ca* 15 mg of powdered $\text{FeCl}_4^-/\text{Dowex}$ catalyst was suspended in 1.00 ml of ethanol or an ethanol-toluene mixture in a fused silica cuvette. The suspension was stirred while it was irradiated with the focused output from a 100 W mercury lamp (Osram HBO 100 W/3) in an Oriol Q Series housing, passed through a 345 nm lowpass filter. In some experiments a 5 ml sample in an Erlenmeyer flask was exposed to direct sunlight. A balloon containing air or oxygen was affixed to the cuvette with a section of a plastic pipette, which made a firm seal in the cuvette opening. A fan was used to maintain the temperature of the cuvette at 22 ± 2 °C.

Results

Irradiation Time

$\text{FeCl}_4^-/\text{Dowex}$ in contact with ethanol catalyzes the photooxidation to acetaldehyde, with some acetic acid. The amount of ethanol oxidized is close to being directly proportional to the irradiation time. Therefore, one irradiation time (60 min) was selected in order to study the dependence of the photooxidation yield on the reaction parameters discussed below.

Dependence on O_2 Partial Pressure

The $\text{FeCl}_4^-/\text{Dowex}$ catalyst prepared as described above is only modestly successful in catalyzing the photooxidation of ethanol in contact with air, but the yield is considerably higher under an atmosphere of O_2 introduced by means of a balloon, as evident from Table 1.

The extent of photooxidation is seen to be approximately proportional to the partial pressure of oxygen in contact with the suspension. It should be noted that the amount of FeCl_4^- employed is 60 μmol , and since the amount of ethanol oxidized is approximately ten times greater (under O_2), the process is certainly catalytic.

Optimum Amount of Catalyst

When using a suspension of a heterogeneous photocatalyst, the dependence of the reaction yield on the amount of catalyst can be quite complex.^[27,28] We find, however, only a slight dependence of the net photooxidation yield under an O_2 atmosphere on the catalyst mass, as is evident from Table 2. Under these conditions,

Table 1. Extent of photooxidation^a

Balloon	EtOH oxidized (μmol)	EtOH oxidized (%)	Aldehyde (%)
Air	105	0.6	80
Oxygen	604	3.5	73

^aA suspension of 30 mg of $\text{FeCl}_4^-/\text{Dowex}$ in 1.0 ml of EtOH under a balloon containing air or oxygen (60 min irradiation with a 100 W mercury lamp, filtered to remove wavelengths below 345 nm).

Table 2. Net yield (acetaldehyde plus acetic acid) from photooxidation^a

Catalyst mass (mg)	EtOH oxidized (μmol)	EtOH oxidized (%)	Aldehyde (%)
7	550	3.2	81
15	600	3.5	73
30	680	4.0	83

^aPhotooxidation of 1.0 ml of ethanol in the presence of powdered $\text{FeCl}_4^-/\text{Dowex}$ catalyst and an oxygen balloon; 60 min irradiation ($\lambda > 345$ nm) by a 100 W mercury lamp.

no trend in the selectivity for acetaldehyde is found, the average being approximately 80%.

In the presence of air, instead of O_2 , the photooxidation yield is much smaller. The dependence of the reaction yield on the catalyst mass goes through a maximum, as is shown in Fig. 1.

The rate of a photoreaction taking place in a suspension of catalyst has a complex relationship with the amount of catalyst in the suspension.^[27,28] The amount of light reflected, the amount of light transmitted and the absorptivity of the catalyst all play a role, and the net result can be either an asymptotic increase in the photoreaction rate with the amount of catalyst or passage through a maximum, after which more of the catalyst actually decreases the photoreaction rate.^[28] This decrease, when it occurs, is due to more light being reflected from the front surface as the amount of catalyst in the suspension is increased.^[28]

The data in Table 1, referring to oxygen-saturated conditions, are inconclusive, since neither a maximum nor an asymptotic approach to a limiting rate can be inferred. The data in Fig. 1, referring to air-saturated conditions, clearly show a maximum photooxidation rate at approximately 15 mg of $\text{FeCl}_4^-/\text{Dowex}$ per milliliter of solution.

Both asymptotic behavior and passage through a maximum can be modeled with the following equation for the fraction of light absorbed by the catalyst, to which the reaction rate is expected to be directly proportional:^[28]

$$f_A = 1 - e^{-\beta m} - \gamma(1 - e^{-\delta m}) \quad (1)$$

Of the three empirical constants in this equation, γ can be no greater than 1, while β and δ must be greater than zero.^[28] The data in Fig. 1 were fitted to this function, with which they appear to be consistent. From Fig. 1, we predict the optimum amount of powdered catalyst to be approximately 15 mg ml^{-1} .

Photooxidation of Ethanol in Toluene

We had some concerns that ethanol would inactivate the catalyst by displacing a coordinated chloride ion. The Cl^- ion would then be retained on the anion exchange resin, sending $\text{FeCl}_3(\text{EtOH})$ into solution. While this does not occur to any observable extent in the

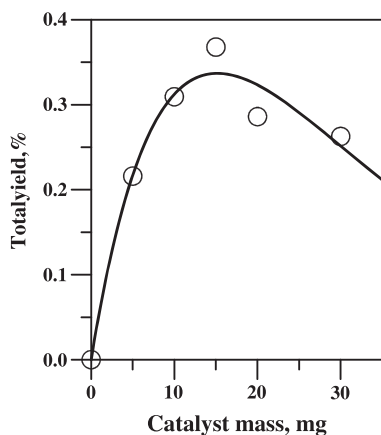


Figure 1. Variation of the extent of photooxidation of ethanol in the presence of air with the mass of $\text{FeCl}_4^-/\text{Dowex}$ suspended (60 min exposure to 100 W Hg lamp, $\lambda > 345$ nm). Solid line represents fit to Eq. (1) in text, with $\beta = 0.069$, $\gamma = 1.00$ and $\delta = 0.064$.

dark, under irradiation, a small amount of the iron complex leaches into the solution. We attempted to reduce the extent of ligand substitution by working with ethanol in a less polar solvent. Since toluene solutions of ethanol have previously been used for the thermal catalysis of alcohol oxidation by iron(III),^[4] we chose this solvent.

The extent of photooxidation varies considerably with the concentration of ethanol in toluene, as can be seen in Fig. 2. The data show a general increase in the extent of photooxidation with the fraction of ethanol, the rate of increase falling at higher ethanol concentrations.

Sunlight Experiments

To establish the feasibility of carrying out the photooxidation of alcohols with sunlight as the only energy source, two 5 ml samples of neat ethanol with $\text{FeCl}_4^-/\text{Dowex}$ in stoppered Pyrex flasks were exposed to unfocused direct sunlight (November) for 3 h. The catalyst was not stirred and the flask contained air rather than oxygen. The results are given in Table 3. The yields should be compared with the first row of Table 1, which refers to the photooxidation of neat ethanol under air. While the rate of oxidation under sunlight is slower, this is to be expected in comparison to irradiation with a similar wavelength range from a focused arc lamp.

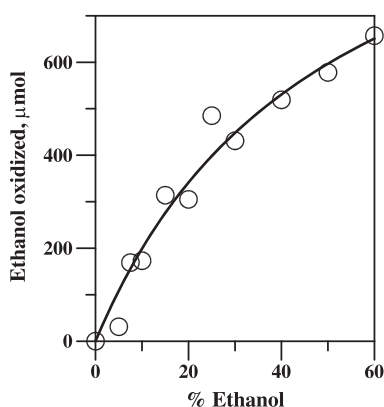


Figure 2. Variation in the extent of photooxidation of ethanol in ethanol-toluene solutions with the fraction of ethanol (60 min irradiation, 100 W Hg lamp, $\lambda > 345$ nm).

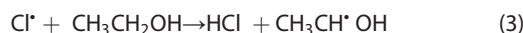
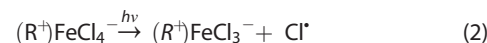
Table 3. Amount of ethanol consumed during 3 h solar irradiation of 5 ml of EtOH (exposed to air) with $\text{FeCl}_4^-/\text{Dowex}$ catalyst

Catalyst mass (mg)	EtOH oxidized (μmol)	EtOH oxidized (%)	Aldehyde (%)
50	76	0.1	75
80	161	0.2	79

Discussion

Mechanistic Considerations

The data are consistent with a photooxidation process involving a hydroperoxide, as has been proposed for the oxidative photodecomposition of dichloromethane catalyzed by FeCl_4^- on Dowex^[11] and the oxidative photodecomposition of chloroform by homogeneous FeCl_4^- .^[12] As was proposed for those systems, the reaction can be expected to be initiated through photodissociation of a chlorine atom following excitation into a LMCT band.^[29] Hydrogen abstraction from the α -carbon of the alcohol and the subsequent reaction of the hydroxyalkyl radical with oxygen yield a peroxy radical (R^+ is used to signify cation resin sites):

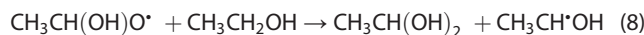
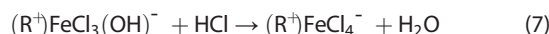
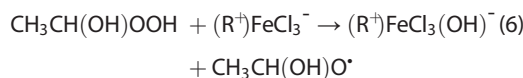


Because the $\text{CH}_3\text{CH}(\text{OH})\text{OO}-\text{H}$ bond energy is 362 kJ mol^{-1} ,^[30] as compared with the $\text{CH}_3\text{CH}_2\text{O}-\text{H}$ bond energy of 397 kJ mol^{-1} ,^[31] the hydroperoxide is not formed through hydrogen abstraction from ethanol, but instead from another 1-hydroxyethylperoxy radical, this self-termination yielding the diradical $\text{CH}_3\text{CH}(\text{O}^{\cdot})\text{OO}^{\cdot}$ as an intermediate step to acetaldehyde and oxygen:^[30,32,33]



The feasibility of the reaction sequence represented by Eqs 3)–(5) can be evaluated to some extent by examining the thermochemistry. The standard enthalpy change for the reaction represented by Eq. (3) is -34 kJ mol^{-1} , given all species in the gas phase, using the value of -56 kJ mol^{-1} calculated for the standard enthalpy of formation of the 1-hydroxyethyl radical.^[31] By use of the ΔH_f° value for the 1-hydroxyethylhydroperoxyl radical of -193 kJ mol^{-1} determined by Denisov and Denisova,^[30] the reaction represented by Eq. (4) is exothermic by 137 kJ mol^{-1} . The disproportionation of Eq. (5) is likewise calculated to be exothermic by 117 kJ mol^{-1} ,^[30] although the initial formation of the diradical by hydrogen abstraction is uphill by 20 kJ mol^{-1} .^[30]

Iron(II) can be readily re-oxidized to iron(III) by hydroperoxides, breaking the weak O–O bond,^[34] which in this system regenerates the FeCl_4^- catalyst and creates another 1-hydroxyethyl chain carrier:



The equilibrium constant for the decomposition of 1,1-dihydroxyethanol, from Eq. (8), to acetaldehyde and water is

Table 4. Comparison data for the catalytic oxidation of alcohols under mild conditions

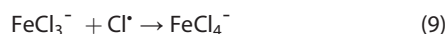
Reference	[3]	[4]	This work
Catalyst	V-doped TiO ₂	FeCl ₃ /TEMPO ^a /silica	FeCl ₄ ⁻ /Dowex 2-X8
Alcohol	Ethanol	1-Heptanol	Ethanol
Concentration	Neat	1 M	1 M
Solvent	—	Toluene	Toluene
Sample volume (ml)	0.002	5	1
Energy source	300 W Xe lamp, 350–450 nm	Heat, 80 °C	100 W Hg lamp, > 345 nm
O ₂ pressure (atm)	12	5	1
Reaction time (h)	1	24	1
Yield (%)	100	11	15

^a2,2,6,6-Tetramethylpyridine N-oxide.

approximately unity.^[35] In ethanol, decomposition of small to medium concentrations of 1,1-dihydroxyethanol to acetaldehyde should therefore be nearly complete. The equilibrium constant for the formation of the acetal, 1,1-diethoxyethane, from acetaldehyde in ethanol has been determined to be 34,^[36] consistent with the large ratio of acetal to acetaldehyde in our photolysates. Neither 1,1-dihydroxyethanol nor the hemiacetal, 1-ethoxyethanol, are detected in any of our samples.

Dependence of Yield on Ethanol Concentration

A simplified picture of the mechanism outlined in Eqs (2)–(8) is obtained by noting that, despite the fact that it is a chain with multiple entries, each molecule of 1-hydroxyethylhydroperoxide formed is responsible for the production of two molecules of acetaldehyde (or its acetal), one produced simultaneously with the hydroperoxide, Eq. (5), and the other during the re-oxidation of Fe²⁺, Eq. (8). At the risk of oversimplification, the steps that regenerate the 1-hydroxyethyl radical, Eqs (5) and (8), may be regarded, once the photostationary state is established, as multiplying the rate of hydroperoxide (and thus acetaldehyde) formation by a factor that is constrained by the rate of self-termination of 1-hydroxyethyl radicals (forming acetaldehyde and ethanol in the process^[37]). The rate is also constrained by the recombination of chlorine atoms with the iron(II) species, i. e. the reverse of Eq. (2):



If the rate of acetaldehyde formation is taken to be a multiple of the rate of hydroperoxide formation, Eq. (3), and the steady-state approximation is applied to Eqs (2), (3) and (9), then the rate of formation of acetaldehyde takes the form

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} = \frac{[\text{EtOH}]}{a[\text{EtOH}] + b} \quad (10)$$

In other words, the rate of acetaldehyde production should be an asymptotic function of the ethanol concentration. This function was fitted to the yield data in Fig. 2, generating an *R*² value of 0.96. Equation (10) assumes that the rate of photodissociation in Eq. (2) is constant and also assumes that the concentration of the iron(II) species, FeCl₃⁻, can be treated as a constant. Note that while the experimental yield increases towards an asymptotic limit with increasing ethanol concentration, as predicted by Eq. (10), dividing Eq. (10) by the ethanol

concentration predicts that the percentage yield should decrease as the ethanol concentration increases, which is again what is observed.

Conclusions

A comparison can be made with other potentially green methods to oxidize alcohols, as is shown in Table 4. Conditions are so dissimilar among the methods compared that it is impossible to establish any of these as superior.

The particular advantages of FeCl₄⁻/Dowex include its simplicity and low cost, the possibility of using sunlight as the sole energy source and the ability to work at room temperature and ordinary pressures. If sunlight is to be employed, the yield can be greatly improved over that of the experiments reported here by focusing the incident solar radiation on the sample volume, by stirring the suspension of catalyst and solution and by using oxygen in place of air. It would, of course, be highly advantageous if photooxidation were to stop at the aldehyde, but this does not happen.

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