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Photochemical and spectroscopic studies of complexes of iron(III) with citric acid and other carboxylic acids ☆

Harmon B. Abrahamson *, Ahmad B. Rezvani [1], J. George Brushmiller

Department of Chemistry, University of North Dakota, Grand Forks, ND 58202-9024, USA

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Abstract

The quantum yields for the photoreduction of iron(III) carboxylate complexes vary with the nature of the carboxylate ligand and solution pH. With [carboxylate] = 0.05 M, [Fe(III)] = 0.30 mM and pH = 2.9, the quantum yields are in the order oxalate (0.32) > tartrate > malate > citrate > isocitrate > succinate > formate (0.12). Fe(III) acetate shows no photoactivity. The photoreduction of Fe(III) to Fe(II) is accompanied by the oxidative decarboxylation of the carboxylate ligand, and can even be observed in the solid state. The efficiency of the photoreduction reaction in solution depends on two factors: the pH and the initial ligand-to-metal ratio. For a lower ligand:Fe(III) ratio (=5; [carboxylate] = 0.0015 M, [Fe(III)] = 0.30 mM) the order from highest to lowest is oxalate > tartrate > citrate > malate > isocitrate when the pH of the reaction media is 2.7. Increasing the pH to 4.0 leads to 50% increases in the quantum yields for all listed carboxylates except oxalate, which decreases by 50%. More detailed studies of pH and ligand/iron ratio were done using citric and isocitric acids. The pH dependence is interpreted in terms of a photoactive Fe(III) citrate dimer formed above pH 2 and a photo-inactive monomer present between pH values of 0.5 and 3.0. Magnetic susceptibility data collected as a function of solution pH show that the paramagnetism of the iron carboxylate solutions decreases with increasing pH, presumably because of increased Fe–Fe coupling. The organic intermediate in the photochemical decomposition of Fe(III) citrate can be monitored by HPLC and is shown to be acetone dicarboxylic acid (ADA). The ultimate decarboxylation product of Fe(III) citrate is acetone.

Keywords: Photochemistry; Spectroscopy; Iron complexes; Carboxylic acid complexes

1. Introduction

Iron is of great importance in biological systems [1]. It participates in a wide variety of atom, molecule and electron-transport reactions [2], usually in oxidation states II and III. This is in spite of the strong tendency of aqueous solutions of Fe(III) to hydrolyze and precipitate insoluble ferric hydroxides at biological pH values [3]. In both animals [4] and plants [5], polycarboxylic acids serve important roles in combating this tendency, and are active in iron solubilization, transport and utilization.

In particular, citric acid, $C(OH)(COOH)(CH_2COOH)_2$, is an α-hydroxy tricarboxylic acid that functions as an Fe(III) transport agent in biological systems [6]. This organic acid is capable both of lowering iron levels through chelation or increasing its availability through redox reactions. In animals (including humans), citric acid helps increase the bioavailability of iron in a diet [4]. Citrate is also an important intermediate [7] in carbohydrate metabolism, along with isocitrate.

In plants, the interaction of carboxylic acids and iron is strongly affected by light. Iron chlorosis symptoms develop in the leaves of many plants that are grown in the presence of low iron levels or are kept away from UV and blue light [8]. Citric acid appears to counteract these problems by carrying iron from the roots to the plant tops, where the Fe(III) citrate complex is efficiently photoreduced, releasing the iron in the leaves [5]. UV and blue light are most effective in promoting the reduction of Fe(III).

Many studies have been conducted on the influence of light on plant growth and development, and the photochemical reduction of Fe(III) in the presence of carboxylic acids. The photoreaction involves reduction of Fe(III) to Fe(II) and concomitant oxidation of the

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* Corresponding author.

[1] Present address: Department of Chemistry, Tarbiat Modarress University, Tehran 14488, Iran.

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carboxylic acid, often accompanied by evolution of carbon dioxide. α-Hydroxy carboxylic acids, such as citric acid, are particularly susceptible to these oxidative decarboxylation reactions [9].

$$[Fe^{III}(RCH(OH)COO^-)]^{2+} \longrightarrow Fe^{2+} + RCHO + CO_2 \quad (1)$$

The additional energy required to drive this endothermic process can conveniently be supplied by near-UV or blue light.

The ability of citric acid and other organic acids to promote photoreduction of Fe(III) to Fe(II) has been known for over a century ([8] and refs. therein). While the ultimate products, and in some cases, the organic intermediates, were identified early on, only 'recently' before the summary of Balzani and Carassiti in 1970 [10] was the nature of the photoactive species given any real attention. At that time, apart from work on oxalates [11,12] which are used as standard photochemical reactions (actinometers), the only systematic investigation had been done on Fe(III) formate [13]. Since then, reports from a USDA group at Beltsville [9] and a Russian group [14] have appeared.

These more recent studies, as well as the earlier work, have ignored the question of the true nature of the absorbing species in solution even though some observed pH effects [14]. Other work has shown that though the stoichiometry of Fe(III) citrate is 1:1 in aqueous solution, the dominant species changes from a mononuclear complex to a dimer as the pH is raised [15]. The existence of a dimer in solutions of higher ionic strength in the pH range 2–4 has been confirmed by more recent work [16].

The genesis of the current project was in erratic values of the rates of thermal electron-transfer reactions measured in iron carboxylate compounds. When it was recognized that the erratic results were dependent on lighting, the photochemical reactions became the primary focus. In the present study, quantitative photochemistry is carried out to measure the relative photoactivity of the Fe(III) carboxylate complexes, especially with regard to changes in pH (and speciation). Magnetic measurements, electronic and IR spectra of the organic acid complexes of Fe(III) are used to investigate the chemistry and some of the factors influencing the photoreduction of the iron. HPLC is used to follow the decomposition of the Fe(III) citrate by detection of the organic product. We first present our results on a variety of carboxylates, and then report on more detailed studies of the Fe(III) citrate system. Finally, we reinterpret previous results in the light of these considerations.

2. Results

2.1. Photochemical reactions in aqueous solution

The overall reaction (Eq. (1)) requires a 2:1 Fe:acid stoichiometry, and can be written in balanced form

$$2Fe^{3+} + (RCH(OH)COO^-) \longrightarrow 2Fe^{2+} + H^+ + RCHO + CO_2 \quad (2)$$

since the iron reduction is a one-electron process, while the organic acid is oxidized in a two-electron fashion. Since it is difficult to isolate the iron carboxylate complexes as solid salts of definite stoichiometry and degree of hydration, solution photochemistry is performed using a mixture of a stock solution of Fe(III) sulfate in 0.1 M H_2SO_4 and a solution of the desired carboxylic acid in which the pH has been adjusted to the desired level by the addition of NaOH or H_2SO_4. The ratio of carboxylate to iron ranges from a minimum of 5:1 to a maximum of 167:1.

The easiest way to follow the progress of the reactions is to monitor the formation of Fe(II), which is easily done using 1,10-phenanthroline (phen) to form the $Fe(phen)_3^{2+}$ complex. The characteristic visible absorption of this latter complex with a maximum at 510 nm forms the basis for the quantitative determination of Fe(II) in solution [17]. The phenanthroline can be added before or after irradiation, but careful exclusion of atmospheric dioxygen is recommended in either case to prevent reoxidation of the Fe(II). All quantitative measurements of irradiation efficiency reported below use post-irradiation addition of phenanthroline [12]. The oxidized organic products of the reaction can be monitored as well, and HPLC serves best for their quantitative determination (see below).

A number of variables influences the quantum yields measured, the most important ones being the nature of the carboxylate ligand, the Fe/carboxylate ratio, and the pH of the solution. The pH dependence was probed qualitatively for most carboxylates. No significant photoreduction of any Fe(III) carboxylate complex to Fe(II) occurred at pH values below 1.5 for solutions with $[Fe(III)] = 3.0 \times 10^{-4}$ M and using a four- to eight-fold excess of 1,10-phenanthroline. Higher values of pH gave more efficient photochemistry in most cases (see Table 1). A more detailed investigation of the effects of pH and carboxylate concentration was done using citrate and isocitrate (see below).

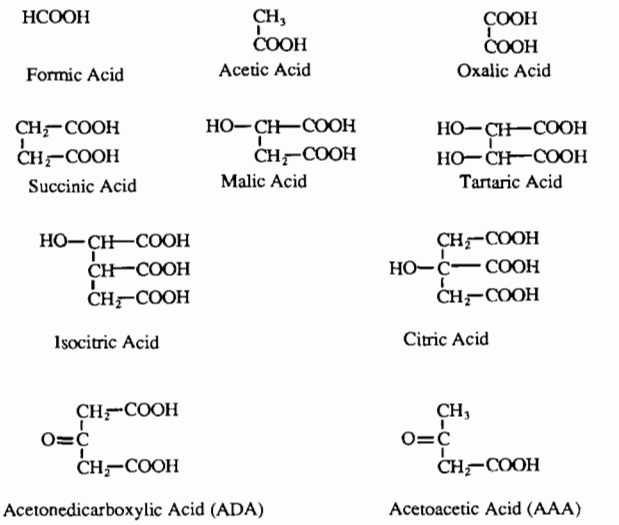
2.2. Ligand dependence

Photolysis of Fe(III) with a number of different carboxylic acids in aqueous solution was performed. The quantum yields for reduction of Fe(III) to Fe(II) in the presence of a large excess of carboxylate (li-

Table 1
Quantum yields for the photoreduction of Fe(III) by various carboxylic acids

Carboxylic acid (CA)	Φ with CA/Fe = 5[a,b]		Φ with CA/Fe = 167[b,c]
	pH = 2.7	pH = 4.0	pH = 2.9
Oxalic acid	0.65	0.30	0.32
L(+)-Tartaric acid	0.40	0.58	
DL-Tartaric acid	0.35	0.50	0.29
meso-Tartaric acid	0.31	0.37	
Citric acid	0.28	0.45	0.17
DL-Isocitric acid	0.14	0.37	
L(−)-Malic acid	0.21	0.29	
D(+)-Malic acid	0.20	0.28	
DL-Malic acid	0.20	0.29	0.26
Succinic acid			0.13
Formic acid			0.12[d]
Acetic acid			nil[e]

[a][Fe(III)] = 3.0×10^{-4} M, [carboxylic acid] = 0.0015 M, I_0 = 7.66×10^{-9} einstein/s.
[b]Φ denotes iron(II) appearance quantum yield (±15%); [*o*-phenanthroline] = 2.0×10^{-3} M.
[c][Fe(III)] = 3.0×10^{-4} M, [carboxylic acid] = 0.050 M, I_0 = 1.38×10^{-8} einstein/s.
[d]pH = 2.5.
[e]No photoreduction observed in the pH range 1.5–11.



Scheme 1. Structural formulas of representative carboxylic acids.

gand:Fe = 167) are given in Table 1 (right column). Under these conditions, oxalate > tartrate > malate > citrate > succinate > formate ≫ acetate. (See Scheme 1 for structures of the acids from which the ligands are derived.) The quantum yields for Fe(III) reduction with smaller excesses of each carboxylate (ligand:Fe = 5) are given in Table 1 at two different values of pH. At pH 2.7, the quantum yield for Fe(III) reduction with different carboxylate ligands decreases in the order: oxalate > tartrate > citrate > isocitrate > malate. The quantum yields were determined only for the conversion of the initial 20% of the total Fe(III) present; this was achieved within 1 to 3 min of irradiation time. At pH 4.0, all of these quantum yields increase by about 50%, except that for oxalate, which decreases by 50%. Some other important trends are apparent. The photoreduction is sensitive to the location of OH in the α-hydroxy tricarboxylic acid (citrate versus isocitrate). The quantum yields also differ for different diastereomers of the same acid (tartrate), although mirror-image optical isomers have identical activities (malate), as might be expected.

2.3. Photochemical reactions in the solid state

In order to verify that decarboxylation takes place, and to try to identify changes in structure upon photolysis, some of the Fe(III) carboxylates were subjected to photochemistry in the solid phase. Unfortunately, we were unable to synthesize pure crystalline solids of the Fe(III) carboxylates. Consequently, we performed this aspect of the study on precipitated solids subjected to vacuum freeze-drying, a technique used previously for isolating solids in polymeric iron carboxylate systems [18].

A solid sample of Fe(III) citrate prepared in this way from a pH 3.8 solution is photoactive. Upon 366 nm irradiation: (a) the 3450 cm^{-1} band (O–H stretch) decreases; (b) a new band at 2343 cm^{-1} (m, sp) appears, characteristic of CO_2(g) trapped in the solid; (c) the asymmetric carboxylate band (1635 cm^{-1}) is shifted to a lower frequency (1600 cm^{-1}), while a shoulder, consistent with a ketonic product (1710 cm^{-1}), appears; (d) the symmetric carboxylate band (1380 cm^{-1}) is broadened and shifted to a higher frequency (1400 cm^{-1}); (e) the 690 cm^{-1} band assigned to asymmetric stretch of the Fe–O–Fe unit [19] disappears.

Data for the IR spectral changes observed in the C–O stretching region when other iron carboxylate complexes are irradiated in KBr pellets are shown in Table 2. Note that in all of the cases where Fe(III) is photoreduced to Fe(II) in solution, i.e. citrate, isocitrate, malate and tartrate,, the $\Delta\nu$(asym − sym) decreases upon irradiation ($\delta\Delta\nu$ is negative). However, in those cases where the iron is already reduced {Fe(II) citrate} or the ligand cannot be oxidized {Fe(III) ADA}, no change in $\Delta\nu$(asym − sym) is seen.

2.4. Photochemical reactions of aqueous iron(III) citrate and isocitrate

No photoreduction of Fe(III) citrate occurs below pH 1.5 for a solution with an initial concentration of 0.05 M citric acid and 3.0×10^{-4} M Fe(III) (citrate/Fe = 167, see Fig. 1). At pH 2.9, rapid photoreduction of Fe(III) to Fe(II) is observed, but the quantum yield decreases at higher pH values. However, photoreduction was significant at pH values as high as 5.0 when

Table 2
Carboxyl stretching frequencies of organic acid complexes of iron

Compound[a]	Unirradiated			Irradiated[c]			$\delta\Delta\nu$[d]
	ν(asym)	ν(sym)	$\Delta\nu$[b]	ν(asym)	ν(sym)	$\Delta\nu$[b]	
Iron(III) citrate	1640	1380	260	1600	1400	200	−60
Iron(III) isocitrate	1625	1400	225	1600	1400	200	−25
Iron(III) malate	1640	1380	260	1600	1390	210	−50
Iron(III) tartrate	1640	1370	270	1620	1380	240	−30
Iron(II) citrate	1575	1425	150	1575	1425	150	0
Iron(III) ADA[e]	1580	1425	155	1580	1425	155	0

[a]The compound was prepared in solid form by vacuum-freeze-drying an aqueous solution. A KBr pellet of the compound was made for the solid IR spectra.
[b]ν(asym) − ν(sym).
[c]Iron(III) carboxylate was irradiated in the KBr pellet for 90 min.
[d]$\delta\Delta\nu$ is $\Delta\nu$(irradiated) − $\Delta\nu$(unirradiated).
[e]ADA is acetone dicarboxylic acid.

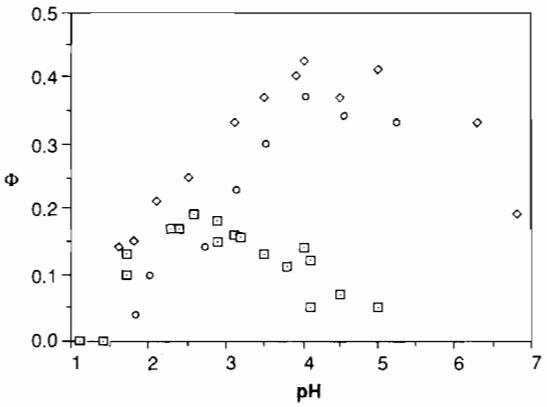


Fig. 1. Comparison of the quantum yields for photoreduction of Fe(III) to Fe(II) as a function of pH in the presence of citric and DL-isocitric acids. Initial concentration of the Fe(III) = 3.0×10^{-4} M, citric acid = 1.5×10^{-3} (◇) or 0.05 (⊡) M, isocitric acid = 1.5×10^{-3} M (○).

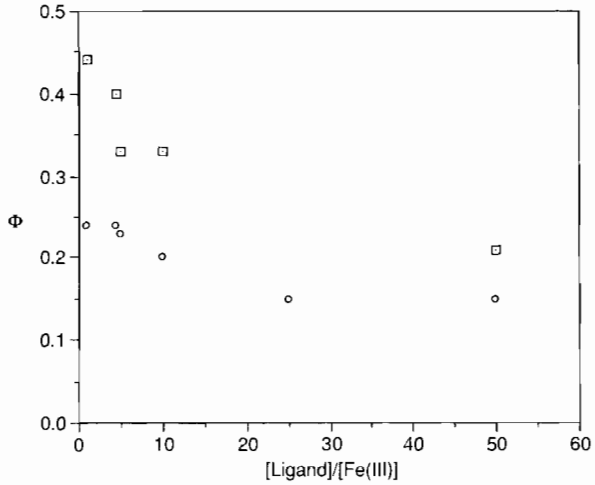


Fig. 2. Quantum yields for photoreduction of Fe(III) to Fe(II) in the presence of citric acid (⊡) or isocitric acid (○) for different concentrations of the acids. Initial reagent concentrations: Fe(III) = 3.0×10^{-4} M and pH = 3.1.

citrate/Fe = 5 for solutions with [citrate] = 0.0015 M (see Fig. 1).

Patterns for response to pH (Fig. 1) and ligand concentration (Fig. 2) are qualitatively the same for citrate and isocitrate. However, the quantum yields in the presence of citric acid are always larger than those in the presence of DL-isocitric acid under the same reaction conditions.

2.5. Photochemical reactions of Fe(III) citrate in a non-aqueous solvent

Acetonitrile was chosen as the non-aqueous solvent because although it is highly polar, it lacks oxygen as a coordinating site. No photoactivity of iron citrate ([citrate] = 0.12 M, [Fe(III)] = 0.025) is observed in completely water-free acetonitrile. However, after a few drops of water are added to an acetonitrile solution containing Fe(III) citrate, photoreduction of Fe(III) can be induced by UV irradiation. Addition of 1,10-phenanthroline also confirmed the formation of Fe(II) in these latter solutions by the formation of the $Fe(phen)_3^{2+}$ complex.

2.6. Magnetic susceptibility of Fe(III) complexes

Magnetic susceptibility of some of the iron carboxylate complexes was determined in solution using the NMR method introduced by Evans [20] and elaborated by others [21,22]. Solutions were prepared in D_2O with a carboxylate/Fe ratio of 8:1. Results of these determinations are given in Table 3. Most of the data are for the citrate complex under a range of pH values; data for acetate and tartrate complexes as well as for the simple mononuclear complex $Fe(CN)_6^{3-}$ are also included. Note that the number of unpaired electrons inferred in the carboxylate complexes is less than the

Table 3
Magnetic data for some complexes of iron[a]

Substance	pH	[Fe] (M)	$\Delta\delta$ (ppm)	μ_{eff}, μ_B (per Fe)	u.p.e.[b] (per Fe)
$K_3Fe(CN)_6$	3.2	0.0610	0.164	1.6	0.92
FeCit[b]	0.8	0.0122	0.280	5.1	4.2
FeCit[b]	0.8	0.0122	0.241	4.7	3.8
FeCit[b]	0.7	0.0122	0.245	4.7	3.8
$Fe_2(Cit)_2$[c]	2.8	0.0122	0.197	4.2	3.4
$Fe_2(Cit)_2$[c]	2.8	0.0122	0.194	4.2	3.3
FeCit and Fe_2Cit_2[c]	2.2	0.0366	0.529	4.0	3.1
$Fe_3(Tar)_3$[c]	4.6	0.0122	0.150	3.7	2.8
FeOAc[c]	2.0	0.0122	0.232	4.6	3.7
$Fe_3O(OAc)_6$[c]	4.5	0.0122	0.076	2.6	1.8
FeCit[d]	1.1	0.0097	0.165	4.3	3.5
FeCit[d]	2.0	0.0097	0.152	4.2	3.3
FeCit[d]	2.8	0.0097	0.134	3.9	3.0
FeCit[d]	4.2	0.0097	0.126	3.8	2.9
FeCit[d]	5.2	0.0097	0.109	3.5	2.7

[a]Determined in D_2O solution by the method of Evans [20], using 2% tert-butanol as a reference substance.
[b]Number of unpaired electrons implied by assuming that the magnetic moment is spin-only.
[c]Solutions contained 0.10 M carboxylate. Speciation indicated is the most likely for the given pH; see Section 3.
[d]These solutions came from the same stock solution, with [citrate] = 0.080 M; pH was adjusted by sequential addition of base.

Table 4
HPLC retention times for ADA, AAA and acetone in different solvent systems[a]

Solvent	pH[b]	Retention time (min)		
		ADA	AAA	acetone
15% Methanol/water	2.0	4.0	5.0	6.0
15% Methanol/water	3.4	3.5	4.5	6.0
Water	2.0	7.5	9.0	18
Water	3.4	4.5	5.0	18

[a]ADA is acetone dicarboxylic acid, AAA is acetoacetic acid. See Section 4 for details of system used.
[b]Adjusted using sulfuric acid.

five expected for high-spin iron, and decreases with increasing pH.

2.7. Determination of organic products

Reversed-phase HPLC (C-18 silica gel column) can be used to detect the organic reaction intermediate(s) of the photochemical decomposition of Fe(III) citrate complexes. The two-electron oxidative decarboxylation of citric acid is known to produce acetone dicarboxylic acid (ADA) [9,23]. The chromatogram (mobile phase: water/H_2SO_4, pH 2) of a solution of Fe(III) citrate (pH = 3.1, citrate:Fe = 5:1, [Fe] = 3×10^{-4} M) has a peak with a retention time of 10 min. Irradiation of the Fe(III) citrate solution results in appearance of a new peak with a retention time characteristic of authentic ADA, 7.5 min. The intensity of this peak is directly proportional to the irradiation time. The concentration of ADA produced was determined through a standard addition method. The concentration of the iron(II) produced was determined spectrophotometrically using *o*-phenanthroline as outlined above. Moderate irradiation (50% conversion) produced ADA and Fe(II) in the expected 1:1 stoichiometry. Longer irradiation times or higher citric acid concentrations gave a higher ratio of ADA to Fe(II). Subsequent non-oxidative decarboxylation steps produce acetoacetic acid (AAA) and ultimately acetone [24], which are seen at longer retention times (Table 4). With the aqueous pH 2 mobile phase, the acetone peak was strongly retained and broadened, making quantitation difficult. In experiments using a different mobile phase optimized for acetone determination (15% methanol/water), acetone production was 60–70% of that expected. The noise level in the acetone determinations was higher, since it has a 30-fold lower absorptivity at 254 nm than ADA.

3. Discussion

3.1. Ligand dependence

For normal aliphatic carboxylate ligands, the presence of hydroxyl group(s) on a polycarboxylic acid gives an easier oxidation route, because the OH group can be transformed into an aldehyde or ketone through a two-electron oxidation (see Eq. (2)). Thus, the quantum yield for the photoreduction of Fe(III) complexed by α-hydroxy carboxylic acids is higher than with the structurally analogous non-hydroxylated carboxylic acids. For example, the Fe(III) complex of malic acid is more photoactive than that of succinic acid (see Table 1). The non-hydroxylated carboxylic acids must participate in one-electron radical chemistry upon oxidation, and the C–C bonds in these compounds are harder to oxidize. Note that Fe(III) acetate shows no appreciable photochemistry under any conditions. This is likely due to the unfavorable energetics of producing a methyl radical in a one-electron oxidative decarboxylation. Other structural features that can accommodate a one-electron reduction give more efficient photochemistry. This means that ligands like oxalate can give relatively higher quantum yields, even from mononuclear complexes, because of the ease of formation of one-electron oxidation products [25,26] from the ligands. The difference between oxalate and the other carboxylates studied here is also apparent in the different response to pH changes (see below).

Table 1 also shows the Fe(II) appearance quantum yields in the presence of different structural and optical isomers of certain carboxylic acids. For example, the

quantum yield in the presence of *meso*-tartaric acid is lower than the other optical isomers (L and DL) of tartaric acid. Similarly, isocitrate gives less efficient photochemistry than its more symmetrical isomer citrate. These differences likely arise from a less favorable conformation for decarboxylation in the dimeric complex which appears to be necessary for photodecarboxylation to take place (see below). As might be expected, there is no significant difference between pure enantiomers or racemic mixtures (see tartaric and malic acids).

The presence of a large excess of carboxylic acid has an adverse impact on the photoefficiency (compare the left and right columns of Table 1). This may indicate an increased competition of excess carboxylate for the second electron instead of our proposed intradimer pathway (see Section 3.6).

Previous work is generally consistent with that reported here. Bennet et al. [9] studied the relative rates of photoreduction of Fe(III) to Fe(II) in solutions containing the organic acids believed to be the major plant acids. They report relative rates for Fe(III) photoreduction by the acids in the order: tartaric > oxalic > citric > malic > aconitic > fumaric > succinic > $FeCl_3$ (control). These data were collected at pH = 4 and used broad-band UV irradiation. Our ordering at pH 4 differs only in the inversion of the order for citric and oxalic acids, which can be ascribed to the sensitivity of Fe(III) oxalate quantum yields to irradiation wavelength [25], which appears not to be the case for citrate. (Faust and Zepp [25] found a quantum yield of 0.28 for Fe(III) citrate at pH 4 with 436 nm irradiation.)

More recently a Russian group [14] has also probed this photochemistry, but with monochromatic irradiation, and found the order of the acids oxalic > glyoxalic > tartronic > tartaric > malic > glycolic > citric with 365 nm photolysis at an unspecified pH. Here the anomaly is the low value reported for citrate (0.052) [14], which is difficult to explain without more experimental details. Note, however, the extreme dependence of quantum yields on pH in the citrate case (see below).

3.2. pH and speciation dependence

The most obvious consequence of pH changes in metal carboxylate complexes is a change in speciation. There was early disagreement on the existence of polynuclear forms of citrate and tartrate complexes of Fe(III). Timberlake determined the equilibrium constants in the Fe(III) tartrate [27] and malate and citrate [15] systems. These measurements indicated that though the iron:carboxylate ratio is 1:1 in acidic aqueous solution, the mononuclear complex gives way to a dimer as the pH is raised. The existence of dimer in Fe(III) citrate solutions of higher ionic strength in the pH range 2–4 has been confirmed [16], although a more complex model [28] uses four mononuclear Fe(III) citrate complexes of varying composition to fit data in the pH range 1–3. Other work on homo- and heterovalent iron(II, III) citrates and tartrates confirms dinuclear formulas for the systems over the pH range 1–6 [29–31].

Most of the discussions of dimer composition focus on species of the sort $[Fe_2(H_{-1}Cit)_2]^{2-}$, where H_3Cit is citric acid; i.e. two additional hydrogen ions have been lost above the six that would dissociate from the acid groups on the two citrate ligands. Some authors view these H^+ ions as coming from the citrate hydroxyl groups, but attempts to build models of dimers where all three acid groups *and* the hydroxyl group are coordinated to an iron atom fail [32], using either CPK models or a computer modeling program like Chem3D [33]. Given the propensity for coordinated water molecules to hydrolyze and form hydroxy or oxo bridges [19], more reasonable formulas for the dimer would be $[Fe_2(\mu\text{-O})(Cit)_2]^{2-}$ or $[Fe_2(\mu\text{-OH})_2(Cit)_2]^{2-}$.

It can be seen in Table 1 that for oxalate, an increase in pH leads to a decrease in quantum yield, while the other polycarboxylates show an increase instead. A detailed study of the pH dependence in citrate and isocitrate (see Fig. 1) shows a maximum quantum yield at pH 4 in both cases with low ligand:Fe ratios (=5). Higher ligand:Fe ratios (=167) shift the maximum to lower pH (~2.7). Other workers [14] have also seen a pH dependence in photolysis efficiency, with succinic, tartaric and pyruvic acids displaying a maximum near pH 3.

The quantum yield data demonstrate the existence of a photoreducible complex for Fe(III) citrate and Fe(III) isocitrate in the pH range 1.5–5, with a maximum near pH 3 or 4. This would make sense if it is the dimeric complex ion which is the photochemically reducible species. Speciation calculations [34] based on Timberlake's stability constants [15] show the dimer reaches a maximum about pH 3 for the concentrations of iron and citrate used in this study. No significant photoreduction occurs at pH values below 1.5 where the neutral mononuclear complex FeCit predominates.

The hydrolysis of Fe(III) at pH values greater than 2.9 cannot completely be ruled out; this could account for the lower quantum yield with increasing pH. (Note that Timberlake did not do equilibrium constant determinations in the region above pH 3.1 because of the slow rate of attainment of equilibrium [15].) Alternatively, this decrease could be due to the formation of trimers or higher nuclearity clusters if these higher clusters were less photoactive. This latter explanation seems most likely on two counts. First, μ-oxo trimers analogous to the basic acetate trimer form from Fe(III) reacted with fully deprotonated dicarboxylic acids [18]. Second, singly reduced $Fe(III)_2Fe(II)$ trimers are very stable [35] and have extensive mixed valence delocal-

ization [36] that could serve to reduce subsequent reactivity (see mechanism).

3.3. Photochemical reactions in the solid state and in a non-aqueous solvent

It is noteworthy that decarboxylation can be induced by photolysis even when the iron carboxylate is in the solid state. The appearance of bands due to free carbon dioxide and others due to structural changes in the metal complex are diagnostic of the same changes that occur in aqueous solution.

Acetonitrile was chosen as the non-aqueous solvent because although it is highly polar, it lacks oxygen as a coordinating site. No photoactivity was observed in completely water-free acetonitrile. These findings indicate that water must be present for photoreduction to occur and likely plays a critical role in the redox reaction. The lack of photoactivity in dry acetonitrile could be due to lack of formation of a μ-oxo dinuclear complex of Fe(III), see above.

3.4. Magnetic behavior of Fe(III) carboxylates

The reduction in magnetic moment of Fe(III) citrate with increasing pH suggests the formation of species exhibiting magnetic coupling. Since the formation of an Fe–O–Fc unit in aqueous solution (pH > 1) is almost impossible to avoid [19], the reduction in paramagnetism of the Fe(III) carboxylate solutions with increasing pH (regardless of how the pH is varied), is expected even in the presence of the carboxylate ligand. However, the magnetic data suggest that with increasing pH, solutions containing Fe(III) carboxylate complexes form dimeric or polynuclear complexes containing two or more Fe(III) ions bridged by an oxygen or hydroxide groups. These polynuclear complexes would exhibit antiferromagnetic behavior due to super exchange coupling of the Fe(III) ions in the complexes. This type of exchange is believed to occur via overlap of the metal d orbitals with the bridging oxygen orbitals in either π super-exchange (antiparallel or parallel) or σ super-exchange (antiparallel) pathways [37]. Similar reductions of expected paramagnetism are seen in the tartrate and acetate data in accord with magnetic moments measured by other techniques ($\mu = 4.30\ \mu_B$ for $Fe_2(tartrate)_2^{2-}$ [38] and $\mu = 3.2\ \mu_B$ for $[Fe_3O(acetate)_6]^+$ [18]). In any event, the chemical shifts are reproducible, and the data suggest that a slow hydrolysis reaction of the Fe(III) citrate is not taking place.

3.5. Organic products

The only surprise in the study of the organic products of the Fe(III) citrate photochemistry was the unexpected stability of the intermediate products ADA and AAA in the photochemistry medium. A more detailed study of the iron chemistry of these two intermediates will be reported separately [24].

3.6. Mechanistic questions

The simple mechanism put forward early on [10] for hydroxy acid complexes involves electron transfer in an excited (mononuclear) complex (Eq. (3)), followed by further oxidation of the organic radical thus formed by additional unexcited Fe(III) (Eq. (4)).

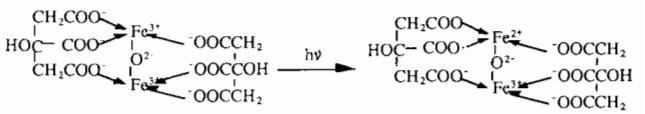
$$[Fe^{3+}(RCHOHCOO^-)]^{2+} \xrightarrow{h\nu} Fe^{2+} + RCHOHCOO^{\cdot} \quad (3)$$

$$RCHOHCOO^{\cdot} + [Fe^{3+}(RCHOHCOO^-)]^{2+} \longrightarrow Fe^{2+} + RCHO + CO_2 + RCHOHCOO^- + H^+ \quad (4)$$

Note that the mechanism is supported by kinetic and stoichiometric data, as well as the fact that the Fe(III) citrate system can photochemically induce the polymerization of vinyl monomers [39,40]. Duka et al. interpret their results [14] in terms of a mononuclear complex with radical formation, in a fashion similar to that proposed by Balzani and Carassiti in their generic mechanism.

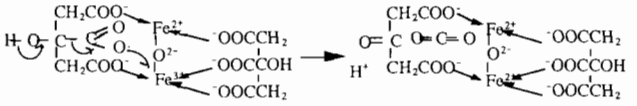
These mechanisms are based on similar work in oxalate systems which continues to the present [25,26,41]. While the inclusion of a free carboxylate radical is a virtual necessity in mechanisms of Fe(III) oxalate systems where mononuclear complexes are the sole light absorbers [42], we feel that the pH and speciation dependence illustrated in the Fe(III) hydroxypolycarboxylates justifies a different approach in those cases.

The simplest mechanism consistent with our data involves initial excitation in a ligand-to-metal charge transfer (LMCT) transition, forming a radical anion carboxylate ligand and Fe(II). At very low pH, this transition reverses, probably by non-radiative decay in the chelated mononuclear complex, and no net photochemistry is observed. At moderate pH, the initial light absorption is by the dinuclear species, and the carboxylate radical anion is formed in the immediate presence of another Fe(III) ion (the other half of the dimer) (Eq. (5)).



(5)

This would allow very rapid completion of the ligand oxidation in a thermal step (Eq. (6)) and the two



(6)

Fe(II) ions produced would be released from the carboxylate coordination, owing to the lower affinity of Fe(II) for oxygen coordinating sites [15]. (The structure of the dimer used in Eqs. (5) and (6) is one that at least appears feasible using computer modelling [32,33].) The acetonedicarboxylic acid thus formed undergoes two subsequent non-oxidative decarboxylations to form the ultimate organic product acetone. The definitive proof of this mechanism awaits a flash-photolysis investigation.

4. Experimental

4.1. Materials

Chemicals were obtained commercially from the following suppliers: acetone dicarboxylic acid, Aldrich; ferric sulfate, Eastman Kodak; ferrous sulfate, Fisher Scientific; *o*-phenanthroline, G.F. Smith; citric acid, formic acid and oxalic acid, J.T. Baker; isocitric acid, malic acids, succinic acid, tartaric acids, acetoacetic acid and lithium salt, Sigma.

Acetonitrile (Fisher, 0.03% water) was purified by stirring it for a few hours over 5 Å molecular sieves, followed by stirring over calcium hydride (1 g/250 ml) until the evolution of H_2 gas was almost diminished, leaving only minute traces of water [43]. The dried acetonitrile was stored under prepurified nitrogen gas. It was then fractionally distilled five times over fresh calcium hydride (0.5 g); 250 ml of acetonitrile yielded 70 ml of completely dry acetonitrile.

4.1.1. Purification of ADA

The acetone dicarboxylic acid obtained commercially was impure, having a melting point of 114–118 °C (Lit.: 138 °C (dec.) [44]) and NMR and IR spectra quite different from those in the literature [45,46]. It contained traces of a water-insoluble material and had a cream color. The commercial acid (20 g) was washed with two 50 ml portions of anhydrous ether which removed most of the color. The washed acid was only partially soluble in 250 ml of boiling anhydrous reagent-grade ethyl acetate (11 g of insoluble material were filtered out). Filtration of the hot mixture (60–70 °C) with suction gave a clear liquor having a faint yellow color; cooling of this liquor resulted in crystallization of a fine white product. To improve recovery, the ethyl acetate liquor was cooled in a dry ice-acetone bath. The recrystallized product was vacuum freeze-dried, yielding about 5 g of the product, with a melting point of 129–130 °C (dec.); Lit. 138 °C [44]. This material was used for almost all the study. ADA was also prepared from sulfuric acid and citric acid by following a published procedure [44]. This gave material of lower purity (m.p. 118 °C after 2× recrystallization) than that obtainable from recrystallization of the commercial material.

4.2. Instrumentation

Solution absorbances were measured using either a Beckman DU 2400 (for 510 nm readings) or a Shimadzu UV–Vis 260. The cell holder was thermostatted using either tap water or a B. Braun Frigomix 1496 circulating bath at 25 °C. The ^1H NMR and ^{13}C NMR spectra were measured using a Varian VXR-300 spectrometer. IR spectra were obtained using a BioRad FTS-40 FT-IR spectrophotometer. The pH of the solutions was measured using an Orion model 399A pH meter equipped with an Orion combination pH electrode.

4.3. Procedures

4.3.1. Spectrophotometric determination of iron(II)

Using *o*-phenanthroline as a chromogen [17], Beer's law was obeyed at 510 nm for iron(II) concentrations up to 1.5×10^{-4} M, but not above this value. The amount of tris(*o*-phenanthroline)iron(II) formed from the reaction between iron(II) and *o*-phenanthroline depends on the pH of the solution as well. For solutions in which the pH was between 2.0 and 6.7, the 510 nm absorbance readings were within experimental error of the expected value, but were lower than expected for pH values outside of this range. Consequently, trapping of iron(II) by *o*-phenanthroline was done in the presence of sodium acetate/acetic acid buffer (pH 4.75).

4.3.2. Magnetic measurements

The procedures outlined by Evans [20] for the determination of magnetic susceptibility by the NMR method were followed. Sample solutions containing iron(III), carboxylate ligand and t-BuOH were sealed in a melting point capillary tube. This tube was placed inside a 5 mm NMR tube containing only the carboxylate and t-BuOH at various pH values which served as the reference.

4.3.3. Photochemistry in solution

Samples were irradiated using a Hanovia 450 W medium-pressure mercury arc lamp. The lamp was placed in a cylindrical jacket of borosilicate glass which was cooled with running water. A Corning combination filter was used to isolate 366 nm light. A cell holder was fixed 2.5 cm away from the light source. The light

intensity of the source was calibrated after every 50 h of use with ferrioxalate actinometry [11,12,47,48].

The following procedures were carried out in total darkness or in a room illuminated by a red light. Solutions containing various concentrations of iron(III) and/or iron(II) with a carboxylate ligand were deoxygenated using an argon purge. After the empty sample cell was purged with argon gas, a 3000 μl volume of deoxygenated iron(III) carboxylate solution was pipetted into the sample cell under a flow of argon gas and the cell was capped. After the absorbance at 366 nm was measured, the cell was placed into the cell holder of the photochemical apparatus for an irradiation at 366 nm. The irradiation time was recorded to the second. The cell containing the irradiated solution was inverted several times. Into the cell was then pipetted a 300 μl volume of the *o*-phenanthroline stock solution under an argon flow. The absorbance at 510 nm was recorded to determine the amount of Fe(II) produced. The sample cell was emptied, rinsed several times with distilled water, and dried with argon flow. Steps above were repeated using different irradiation times. The 510 nm absorbance for an unirradiated control solution was also measured at the end of the experiment to account for any thermal reaction. Quantum yields were corrected for incomplete absorption of the irradiated solution.

4.3.4. Photochemistry in solids

Almost all the iron(III) carboxylate compounds used in this study were insoluble in commonly used IR solvents. Hence the IR spectra used in this study were measured in the solid state, prepared by mixing the sample with potassium bromide (~1:50 wt./wt.). The sample mixture was pressed into a pellet in a conventional barrel, and the spectra were measured directly from the barrel. The pellets were irradiated with the same source used in the solution studies (above).

4.3.5. HPLC experiments

A Waters LC system with differential UV detection (254 nm) was employed. An Alltech Econosphere C18 5U reversed-phase silica gel column (4.6×250 mm) was used with a mobile phase flow rate of 1.0 ml/min. Water adjusted to pH 2 by sulfuric acid was used as a solvent for studies of ADA.

A calibration curve for ADA was made using authentic ADA at known concentrations covering the range expected from the photodecomposition of Fe(III) citrate (<0.0015 M). A solution of Fe(III) citrate (pH=3.1, citrate:Fe=5:1, [Fe]=3×10^{-4} M) was irradiated for a period of time. Then, half of the irradiated solution was used to measure the concentration of the ADA intermediate, and the other half was used to measure the concentration of Fe(II) produced from photodecomposition of Fe(III) citrate (see above).

Experiments to follow the production of acetone, the ultimate decarboxylation product, used the same system with a mobile phase of 15% methanol/water (vol./vol.). Retention times are reduced by a factor of 2–3 in this solvent.

4.4. Preparation of complexes

All of the following complexes were prepared in the dark.

4.4.1. Iron(III) acetate

Iron(III) acetate was prepared by using a modification of the method of Dziobkowski et al. [18]. Sodium acetate dihydrate (5.9 g, 0.05 mol) was suspended in 25 ml of water. The solution was cooled to 8 °C and iron(III) sulfate tetrahydrate (5.9 g, 0.0125 mol) was slowly added with stirring (pH=3.7). A gentle stream of air was used to evaporate the solvent, leaving read–brown solids. The solids were collected, washed with two 5 ml portions of cold water and vacuum freeze-dried. The yield was 2.8 g. The formula for the iron(III) acetate was proposed by the original authors [18] as $[Fe_3(\mu_3\text{-}O)(CH_3CO_2)_6(H_2O)_3]ClO_4\cdot 2H_2O$.

4.4.2. Iron(III) acetonedicarboxylate

The preparation was carried out at a low temperature (8 °C) to avoid decomposition of ADA. ADA (1.46 g) was suspended in 20 ml of water. $NaHCO_3$ was added to raise the pH to 3.8. To this solution, 2.36 g of iron(III) sulfate was added. Additional $NaHCO_3$ was added to maintain the pH at 3.8. Ethanol (200 ml) was then added to the cold aqueous solution to form a precipitate. The resulting precipitate was filtered off, washed with ethanol and vacuum freeze dried.

4.4.3. Iron(III) citrate

Iron(III) citrate was prepared by suspending citric acid monohydrate (10.5 g, 0.05 mol) in 90 ml of water. To this solution 30% sodium hydroxide (5 ml) was added slowly to raise the pH to 3.0. An equimolar amount of iron(III) sulfate tetrahydrate (11.8 g, 0.025 mol) was slowly added to the sodium citrate solution with vigorous stirring, resulting in a pale green (λ_{max}=642 nm, pH 2.6) solution. To a 20 ml portion of this solution, enough H_2SO_4 or $NaHCO_3$ was added to adjust the pH to values between 1 and 7.5. The color of iron(III) citrate at pH 1.2 was yellow, while above pH 2 the color was green. Ethanol, 95% (100 ml), was added to the reaction mixture to form a gel. The resulting suspension was allowed to stand a few hours at 4 °C, forming more gel. The gel was washed with two 10 ml portions of 0.01 M H_2SO_4, and dissolved in 10 ml of cold water and vacuum freeze-dried, yielding about 2 g of the solid product.

4.4.4. Iron(II) citrate

The salt was prepared as reported in the literature [49]. The iron(II) concentration was confirmed spectrophotometrically using *o*-phenanthroline.

4.4.5. Iron(III) isocitrate

Iron(III) isocitrate was prepared by suspending DL-isocitric acid, trisodium salt (1.29 g, 0.005 mol) in 9 ml of water. To this solution an equimolar amount of iron(III) sulfate tetrahydrate (1.18 g, 0.0025 mol) was added, resulting in a pale yellow solution. $NaHCO_3$ was added to adjust the pH to 3.8. The resulting suspension was stirred and allowed to equilibrate for about 2 h. Ethanol, 95% (100 ml), was added to the reaction mixture to form a gel. The resulting gel was allowed to stand a few hours at 4 °C, and then it was washed with two 10 ml portions of water. The precipitate was suspended in 10 ml of the cold water and vacuum freeze-dried, yielding about 1 g of the solid product.

4.4.6. Iron(III) malate

Iron(III) malate was prepared by suspending L-malic acid (6.7 g, 0.05 mol) in 90 ml of water. To this solution 30% sodium hydroxide (5 ml) was slowly added to raise the pH to 3.0. Iron(III) sulfate tetrahydrate (11.8 g, 0.025 mol) was slowly added to the sodium malate solution with vigorous stirring, resulting in a pale yellow, pH 2.6 solution. To a 20 ml portion of this solution, enough $NaHCO_3$ was added to adjust the pH to 3.8. The resulting suspension was stirred and allowed to equilibrate for about 2 h. Ethanol, 95% (100 ml), was added to the reaction mixture to form a gel. The resulting gel was allowed to stand a few hours at 4 °C, and then it was washed with two 10 ml portions of distilled water. The precipitate was suspended in 10 ml of the cold water and vacuum freeze-dried.

4.4.7. Iron(III) tartrate

Iron(III) tartrate was prepared by suspending L-tartaric acid (7.5 g, 0.05 mol) in 90 ml of water. To this solution 30% sodium hydroxide (5 ml) was slowly added to raise the pH to 3.0. Iron(III) sulfate tetrahydrate (11.8 g, 0.025 mol) was slowly added to the sodium tartrate solution with vigorous stirring, resulting a pale yellow (pH 2.6) solution. To a 20 ml portion of this solution, enough $NaHCO_3$ was added to adjust the pH to 3.8. The resulting suspension was stirred and allowed to equilibrate for about 2 h. Ethanol, 95% (100 ml), was added to the reaction mixture to form a gel. The resulting gel was allowed to stand a few hours at 4 °C. The reaction mixture formed more gel, which was washed with two 10 ml portions of millipore water. The gel was suspended in 10 ml of cold water and vacuum freeze-dried.

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