

Activation of the C–H Bond in Hydrocarbons: the Isolation and Catalytic Activity of a Trinuclear Organoiron Carboxylate Cluster

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Tri-iron cluster compounds of type (1), in the presence of zinc powder, acetic acid, (aqueous) pyridine, and oxygen constitute an efficient and selective system for the oxidation of saturated hydrocarbons.

The majority of model systems developed *in vitro* for the oxidation of hydrocarbons by molecular oxygen feature the use of iron(II) or iron(III) and require the presence of a reducing agent such as ascorbic acid,¹ thiosalicylic acid,² or hydrazo-

benzene,³ generally under well defined conditions of pH. Consideration of the system developed earlier^{4,5} (Fe powder, pyridine–H₂O, acetic acid, H₂S, oxygen) led us to speculate that the iron powder served not only as a reducing agent but

also as the precursor of a cationic iron complex. In like fashion, we envisaged that the organic acid could also function in a dual role, not only as a proton source, but also, in the form of its corresponding carboxylate anion, as a ligand for iron.

Initial support for this hypothesis was obtained by the oxidation of adamantane (1 mmol) with iron(II) sulphate (10 mmol) and zinc powder (10 atom equiv.) in aqueous pyridine (py) (6.6%) containing acetic acid (5 mmol) under an oxygen atmosphere. Adamantanone was isolated from this reaction in the form of its 2,4-dinitrophenylhydrazone derivative (10.5%) and g.l.c. analysis also confirmed the presence of the secondary and tertiary alcohols in 0.9 and 3.8% yield respectively.

In a related experiment we have also shown that iron(II) acetate and iron powder can be used in acetic acid as solvent to effect 27.5% overall oxidation of adamantane. In this latter case, however, the tertiary alcohol comprises a significant part of the reaction mixture (14.1%).

We have also undertaken a detailed study of the original iron powder-acetic acid system.⁴ Further experimentation revealed that hydrogen sulphide, while it undoubtedly functions as an efficient initiator for the reaction, can be omitted merely by raising the temperature to 40 °C. The latter reaction under our standard conditions⁴ gives adamantan-1-ol (4.8%) and a mixture of adamantan-2-ol and adamantanone (11.5%).

Incubation of a mixture of iron powder (10 atom equiv.) and acetic acid (10 mmol) in aqueous pyridine (6.6%) at 30 °C under an argon atmosphere for 20 h followed by filtration to remove unchanged iron (88%) gave a dark brown solution. Addition of adamantane and oxygen gave after 22 h a very small amount of functionalised hydrocarbons (1.45%). In an otherwise identical experiment but with the addition of zinc powder (10 atom equiv.) to the clear filtrate a significant improvement in yield was observed (adamantan-1-ol, 1.25%; adamantan-2-ol and -one, 5.5%). Finally, addition of a second portion of acetic acid (10 mmol equiv.) at the same time as the zinc restored the original activity of the system (adamantan-1-ol, 2%; adamantan-2-ol, 1.5%; and adamantanone, 7.9%). Clearly, the oxidation is catalysed by a soluble complex.

It was possible to isolate, from the reaction of iron powder with acetic acid in aqueous pyridine (py) in air, a beautifully crystalline black complex. Analytical, mass spectral, and titration data served to establish the constitution $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}(\text{OAc})_6(\text{py})_{3.5}$. Such a complex has in fact been described in the literature by ligand exchange with pyridine of the corresponding aquo complex⁶ (1, L = H₂O). The latter, in turn, is readily prepared in 70% yield by reaction of iron(II) chloride with

calcium acetate in aqueous acetic acid.⁷ On the basis of a detailed examination of the magnetic and spectroscopic properties⁸ and the X-ray analysis of an isostructural manganese analogue⁸ the trinuclear iron cluster carboxylate structure (1) is generally formulated.

The isolation of the crystalline cluster immediately provided the opportunity to test the hypothesis that such a species should function as a catalyst. The results of decreasing the cluster concentration, summarised in Table 1, clearly demonstrate, not only that the cluster compound is an efficient catalyst, but also that it is superior to the often employed porphyrin and salen models (see Table 1).

We find that use of diphenyl sulphide as the substrate under standard conditions⁴ leads to a quantitative recovery of starting material, and that diphenyl sulphoxide under these conditions is reduced to an extent of only 5%. It is therefore possible to demonstrate that oxidation of equimolar amounts of cyclohexane and diphenyl sulphide gives cyclohexanol (1.3%), cyclohexanone (7.1%), and unchanged sulphide (92%).

Such a marked proclivity for chemospecific attack on the hydrocarbon in the presence of such 'easily oxidised' substrates is in direct contrast to that expected from the chemistry of a traditional transition metal oxenoid.⁹ The ratio of tertiary H to secondary H substitution in adamantane⁴ is also

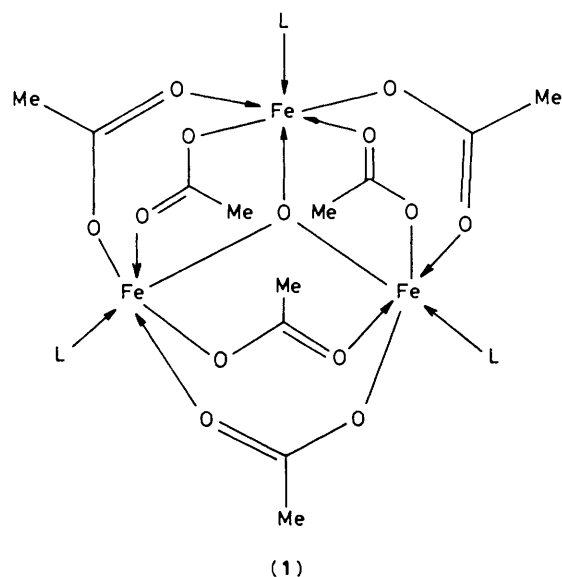


Table 1.^a

Adamantane /mmol	Catalyst/mmol × 10 ⁻³	Conditions	Time/h	Products, adamantane			Total oxidation /% yield	Catalyst turnover no.	
				1-ol	2-ol	2-one			
1.56	(I) L = H ₂ O	120	(A)	23	1.45	2.8	6.75	11	1.4
1.56	(I) L = py	115	(A)	20	1.30	2.5	5.8	9.6	1.3
2.2	(I) L = py	6.2	(A)	20.5	0.7	1.45	5.6	7.8	28
2.2	(I) L = py	2.7	(A)	17	0.5	1.75	5.5	7.75	64
2.2	(I) L = py	0.8	(B)	19	0.7	3.4	5.6	9.7	263
2.2	(I) L = py	0.5	(B)	23	1.6	4.6	7.65	13.8	584
2.2	(I) L = py	0.2	(B)	21	0.7	6.3	4.4	11.4	1232
2.2	(I) L = py	0.1	(B)	23.5	0.8	5.75	3.35	9.9	2087
1.5	Fe(TPP)OAc ^b	7.65	(A)	23	0.4	2.65	3.0	6.05	12
2.2	[Fe(TPP)] ₂ O	72.6	(A)	69	0.6		4.9	5.5	1.7
2.2	Fe(salen) ₂ O ^c	75.5	(A)	68	1.2		1.2	8.6	2.5

^a Experiments were performed under a static oxygen atmosphere at 30–40 °C using either conditions A; zinc (10 atom equiv.), acetic acid (10 mmol) in aqueous pyridine (6.6%) or B; zinc (10 atom equiv.), acetic acid (20 mmol) in pyridine. ^b TPP = Tetraphenylporphyrin. ^c Salen = *N,N'*-ethylenebis(salicylideneaminato).

not in accord with either an oxenoid or a free radical mechanism.⁹

At the present time, we consider that reduction of either the cluster *per se*, or a derived but *non-oxenoid* oxygenated complex therefrom, leads *via* ligand expulsion to a co-ordinatively unsaturated species capable of hydrocarbon functionalisation. Experiments are currently underway to distinguish between these two possibilities.

It is of interest that the same cluster complexes of iron that we find active in a reduced form can also be used for the epoxidation of olefins in a reaction with oxygen *without* reductant.¹⁰

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