

OXIDATION OF ACETYLFERROCENE AND 1,1'-DIACETYLFERROCENE WITH CERIUM(IV) SULPHATE IN SULPHURIC ACID MEDIUM

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Oxidation of acetylferrocene and 1,1'-diacetylferrocene with cerium(IV) sulphate has been studied in aqueous sulphuric acid solutions having the overall acidity $H_0 = +1$ to -2 . The first step in oxidation of the both ferrocene derivatives consists in a fast one-electron oxidation giving the corresponding unstable ferricenium cations. Their disappearance from the solution is connected with destruction of the sandwich molecule and further redox reactions. Complete destruction of acetylferrocene necessitates two equivalents of the oxidizing agent, the same reaction of 1,1'-diacetylferrocene proceeds by action of three equivalents of the oxidizing agent. On the basis of detailed kinetic measurements mechanism of the oxidation and destruction of the both derivatives has been suggested, and rate constants of decomposition of the sandwich molecules have been determined.

In our previous communication¹ we dealt with oxidative destruction of ferrocene-1,1'-disulphonic acid. To verify validity of conclusions of this study, we have tried now to carry out a similar study of oxidation of acetylferrocene and 1,1'-diacetylferrocene. The both compounds were studied from various points of view, there are also some pieces of information²⁻⁴ about their one-electron oxidation products — acetylated ferricenium compounds. So far, however, it was impossible to explain the excessive consumption of oxidizing agent in oxidations of these derivatives which can amount to even more than eight equivalents per one mol of ferrocene derivative⁵ and, furthermore, some dependences between the oxidation and destruction of the both compounds.

EXPERIMENTAL

Reagents. Acetylferrocene and 1,1'-diacetylferrocene were prepared and purified according to Graham⁶ and Riemschneider and Helm⁷, respectively. Aqueous solutions of sulphuric acid with defined acidity (H_0) were prepared according to Hammett and Deyrup⁸. The other chemicals used were of *p. a.* purity grade.

Chromatography. For chromatographic analyses alumina thin layer (activity II according to Brockmann) was used with benzene-diethyl ether mixture 1 : 1 as eluent.

Analytical determinations. The presence of Fe^{3+} and Fe^{2+} was determined qualitatively by reaction with thiocyanate ion and *o*-phenanthroline, respectively. The iron concentration

was determined chelatometrically or spectrophotometrically in the form of the complex with *o*-phenanthroline.

Apparatus. Photometric and potentiometric measurements were carried out with the apparatus described in our previous communication¹. All the measurements were carried out at 25°C.

RESULTS

Preparation of Solutions for Measurements

Acetylferrocene and 1,1'-diacetylferrocene are little soluble and not very stable in water and aqueous sulphuric acid. Furthermore, the dissolution procedure is rather lengthy. After a number of preliminary experiments the procedure exemplified by the following typical case proved to be the most advantageous: 0.114 g acetylferrocene or 0.087 g 1,1'-diacetylferrocene is dissolved in 25 ml diethyl ether, and 1.0 ml or 1.5 ml samples, respectively, are measured therefrom and introduced in 100 ml vessels. After evaporation of the solvent each vessel contains 0.02 mmol of the respective dry ferrocene derivative. Immediately before measurement the sample is dissolved in 0.5 ml glacial acetic acid and diluted with sulphuric acid of the required concentration. The amount of sulphuric acid is chosen in such a way that sum of the volumes of acetic and sulphuric acids and oxidizing agent solution gives solutions of the required concentration.

Colour Changes in Oxidation of Acetylferrocene and 1,1'-Diacetylferrocene

The acetylferrocene and 1,1'-diacetylferrocene solutions are orange in colour due to absorption in the regions 440 and 456 nm, respectively. Addition of oxidizing agent results in an immediate colour change to blue-green. This colour change is due to the new absorption band typical for all ferricenium compounds (inclusive of the substituted ones) in the region 620 nm. The blue-green colouration disappears after a time, and a yellow to orange colour appears again. This change is due to the presence of the original ferrocene derivatives and their decomposition products and possibly to the presence of excess oxidizing agent. If concentrations of initial solutions of ferrocene derivatives exceed $5 \cdot 10^{-3}$ M, then a precipitate separates during reaction with excess oxidizing agent.

The Reaction Stoichiometry

Overall consumption of oxidizing agent per one mol of acetylferrocene or 1,1'-diacetylferrocene (parameter *n*) depends on the arrangement of experiment and experimental conditions.

When following the time decrease of the oxidizing agent by the method of recording the currentless curves potential-time¹ in the systems containing excess oxidizing agent we found that, within about one hour, 7 mol and 9 mol oxidizing agent are consumed per one mol of acetylferrocene and 1,1'-diacetylferrocene, respectively (Figs 1a,b). After 24 h of reaction the consumption approaches 9 and 10 mol, respectively, of the oxidizing agent. In the both cases the final reaction mixture contains Fe³⁺ ions, their amounts corresponding to total destruction of the sandwich molecules. The oxidation of the formally bivalent iron in the both ferrocene derivatives consumes only one equivalent, the rest being due to very complex subsequent reac-

tions of the oxidizing agent with cyclopentadienyl rings and/or their substituents. From Figs. 1a,b it follows furthermore that the consumption of the first equivalent is very fast, that of the rest being substantially slower. Hence, the first reaction step consists in a rapid one-electron oxidation of the ferrocene derivatives giving the respective acetylated ferricenium cations. This conclusion is also confirmed by direct potentiometric titration of acetylferrocene and 1,1'-diacetylferrocene with cerium(IV) sulphate in the presence of hexachloroplatinate(IV) or reineckate. The titration curves show only one inflection point for $n = 1$, because the formed acetylated ferricenium compounds are insoluble⁴, and, hence, stabilized against further oxidative decomposition by transition to the second phase of the systeme.

Further information about stoichiometry of the reactions is afforded by the results of stepwise photometric titrations of acetylferrocene and 1,1'-diacetylferrocene by integer equivalents of cerium(IV) sulphate (Figs 2a,b). In the both cases addition of the first equivalent of the oxidizing agent causes complete oxidation of the present acetylferrocene (1,1'-diacetylferrocene) to the respective ferricenium cations. These cations are gradually decomposed (extinction decrease of the solution). Addition of the second equivalent of the oxidizing agent after complete disappearance of the ferricenium cations from the solution makes itself felt by repeated formation of the acetylated ferricenium cations in amounts corresponding to one half and two thirds of the original amount in the case of acetylferrocene and 1,1'-diacetylferrocene, respectively, as it follows from comparison of the first two maxima in the Figs 2a and 2b, respectively. It was proved qualitatively by chromatography that in the stepwise process of oxidation and destruction no other ferrocene derivatives are formed

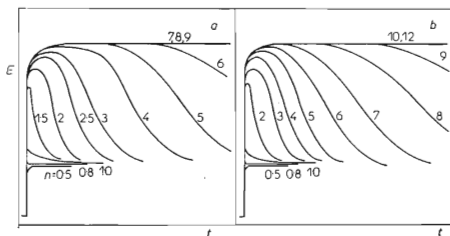


FIG. 1

A Part of the Fan-Shaped Set of Currentless Potential-Time Curves for Various Values of the Parameter n

a) Acetylferrocene ($2 \cdot 10^{-3} \text{ M}$, $H_0 = 0$); b) 1,1'-diacetylferrocene ($2 \cdot 10^{-3} \text{ M}$, $H_0 = -2$).

(e.g. by oxidation of the substituent). From these facts it is obvious that two equivalents of the oxidizing agent are sufficient for complete destruction of acetylferrocene molecule, whereas the minimum amount of the oxidizing agent necessary for complete destruction of 1,1'-diacetylferrocene is 3 equivalents. This conclusion contrasts only apparently with the further course of the curves Fig. 2a,b since starting with the second addition the oxidizing agent is always present in excess and is consumed

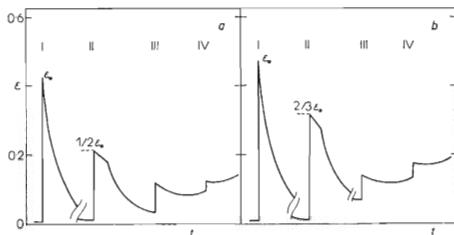


FIG. 2

Gradual Photometric Titrations of Acetylferrocene and 1,1'-Diacetylferrocene with Cerium(IV) Sulphate

a) Acetylferrocene ($2 \cdot 10^{-2} \text{M}$, $H_0 = 0$) b) 1,1'-diacetylferrocene ($2 \cdot 10^{-2} \text{M}$, $H_0 = -2$)
d 2 cm, λ 620 nm.

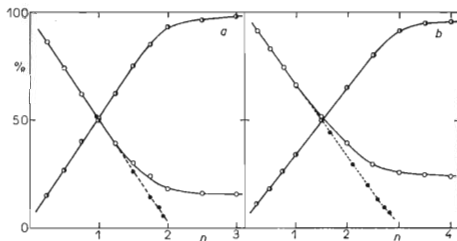


Fig. 3

Dependence of Content of Acetylated Ferrocene Derivatives and Iron Ions on the Parameter n in Solutions after Disappearance of the Acetylated Ferricenium Ions

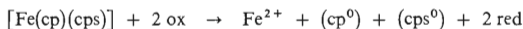
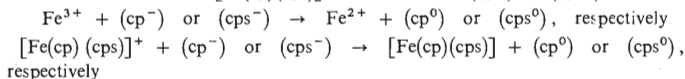
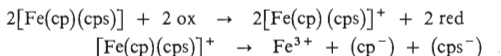
○ a) Acetylferrocene, b) 1,1'-diacetylferrocene, the oxidant was added by integer multiples of n ; ● a) acetylferrocene, b) 1,1'-diacetylferrocene, the oxidant was added in the way that it was never in excess ● content of a) Fe^{2+} , b) Fe^{3+} under the conditions as in (○), acetylferrocene ($2 \cdot 10^{-2} \text{M}$, $H_0 = 0$), 1,1'-diacetylferrocene ($2 \cdot 10^{-2} \text{M}$, $H_0 = -2$).

not only for oxidation of the ferrocene derivatives but also for redox reactions of their decomposition products. If experimental conditions of the stepwise titration are modified in such a way that the oxidizing agent is never present in excess, then it is found that its overall amount corresponds to two equivalents for complete destruction of acetylferrocene, three equivalents being necessary for oxidative destruction of 1,1'-diacetylferrocene (Figs 3a,b).

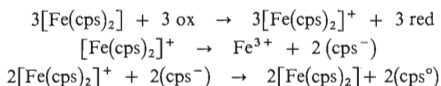
Another important finding concerns the fact that after destruction of acetylferrocene by two equivalents of the oxidizing agent the ions of „free” iron are present in the form of Fe^{2+} , whereas after decomposition of 1,1'-diacetylferrocene by 3 equivalents of the oxidizing agent Fe^{3+} ions are present in the reaction mixture.

On the basis of the above pieces of information the reaction stoichiometry can be described by the following equations:

Reactions of acetylferrocene



Reactions of 1,1'-diacetylferrocene



where cp, cp^- and cp^0 mean the cyclopentadienyl ring, cyclopentadienide ion and its one-electron oxidation product, respectively, and cps, cps^- and cps^0 have the same meaning for the acetylated cyclopentadiene system.

Thus it can be stated that the liberated cyclopentadienyl rings act as reducing agents, as it was the case with ferrocene-1,1'-disulphonic acid, too¹. There is, however, an important difference in that they act as one-electron reducing agents with respect to acetylated ferricenium ions, however, to stronger oxidizing agents (as cerium(IV) ion) they behave as poly-electron reducing agents, the reaction being relatively fast even to higher degrees. In this way it is possible to explain the differences in over-

all consumption of the oxidizing agent used either in stoichiometric amounts or in over-stoichiometric ones.

Kinetics of Decomposition Reactions

Decomposition of the acetylated ferricenium ions was followed spectrophotometrically by their concentration decrease manifested by gradual disappearance of the absorption maximum in the region 620 nm (Figs 4a,b). Linear course of the dependence $\log(\epsilon/\epsilon_0) \sim t$ indicates that the decomposition obeys the 1. order reaction laws. The reaction could be followed without complications up to the values $n \leq 1$ only. At higher values of the parameter n the solutions gradually turn brown due to formation of the abovementioned oxidation products of decomposition products. If deformation of the curves due to these effects is taken into account, then the sets of curves in Figs 4a,b are very similar to the dependences found for oxidation of ferrocene-1,1'-disulphonic acid¹. The dependences for $n \leq 1$ represent parallel straight lines crossing the ordinate axis at distances proportional to n . For $n > 1$ the dependences are composed of two parts. The first one correspond to a slower decomposition of the acetylated ferricenium ions, the second one with the slope identical with that for $n \leq 1$ represents the decomposition connected with reduction of the acetylated ferricenium ions by action of the decomposition products. It can be shown that ratios of slopes of the both parts are 2 : 1 and 3 : 1 for acetylferrocene and 1,1'-diacetylferrocene, respectively, which agrees with the reaction stoichiometry.

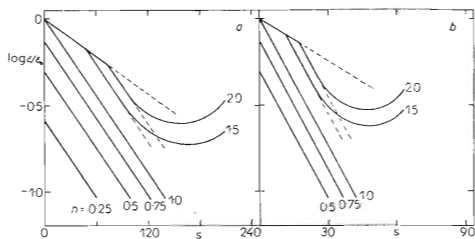


FIG. 4

Time Dependence of Decrease of the Acetylated Ferricenium Ions for Various n Values
 a) Acetylferrocene ($2 \cdot 10^{-2} M$, $H_0 = 0$, $\lambda = 620$ nm; b) 1,1'-diacetylferrocene ($2 \cdot 10^{-2} M$, $H_0 = -2$) $d = 2$. The values at the ordinate axis are quotients of actual extinction and extinction at the time $t = 0$.

The rate constants k (Table I) were calculated from the measured dependences for $n \leq 1$ for the both ferrocene systems and various acidities of the medium. From the Table it can be seen that increasing acidity results in increasing stability of the acetylated ferricenium ions. Increase in acidity by one H_0 unit causes the constant k to decrease roughly to one half. An abrupt decrease of the constants k for the solutions $H_0 = -3$ is due to change in electronic situation in molecules of the both ferrocene derivatives, as the acetyl groups are protonated in these media. Decomposition of acetylferricenium ion is slowed down to such an extent that it is possible to determine the redox potential of the system acetylferrocene/acetylferricenium ion which is equal to +0.48 V under the reaction conditions.

DISCUSSION

In our opinion the oxidative destruction of the sandwich molecules of acetylferrocene and 1,1'-diacetylferrocene has similar course to that of ferrocene-1,1'-disulphonic acid¹. Differences can be seen in the following points: *i*) The cyclopentadienyl rings liberated in the decomposition participate in the reaction as poly-electron reducing agents with respect to cerium(IV) ions, being one-electron reducing agents with respect to the acetylated ferricenium ions. *ii*) Decomposition of acetylferricenium and 1,1'-diacetylferricenium ions produces Fe^{2+} and Fe^{3+} ions, respectively (in the absence of oxidizing agent). This fact is due to the following equilibria being shifted in opposite directions:

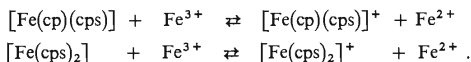


TABLE I

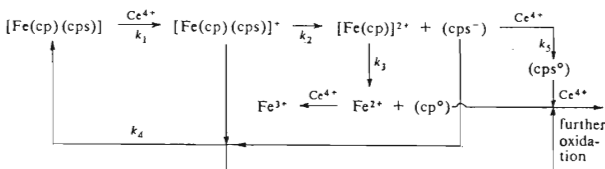
Values of Rate Constants k (s^{-1}) of Decomposition of Acetylferricenium and 1,1'-Diacetylferricenium Ions at Various Values of the Acidity Function H_0 at 25°C

Ion	H_0				
	+1	0	-1	-2	-3
	k, s^{-1}				
Acetylferricenium	$1.3 \cdot 10^{-2}$	$8.5 \cdot 10^{-3}$	$3.9 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$1.0 \cdot 10^{-4}$
1,1'-Diacetylferricenium	—	$2.6 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$	$6.6 \cdot 10^{-2}$	$4.2 \cdot 10^{-3}$

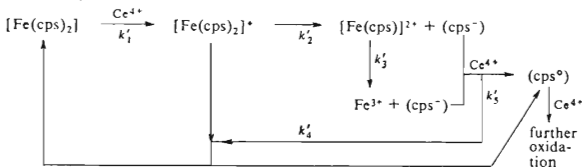
the first one completely to the right whereas the second one to the left. Or in other words – the oxidation ability decreases in the series $[\text{Fe}(\text{cps})_2]^+ > \text{Fe}^{3+} > > [\text{Fe}(\text{cp}) \cdot (\text{cps})]^+$. Of course, the equilibrium is established very quickly, so that it does not affect kinetics of the process.

On the whole, the oxidative decomposition of the both ferrocene derivatives can be described by the following schemes:

Acetylferrocene



1,1'-Diacetylferrocene



From the first scheme it follows that Eq. (1) can be written for decomposition of acetylferrocenium ion (the braces $\{\}$ denote actual concentrations of the species).

$$\begin{aligned}
 -d\{[\text{Fe}(\text{cp})(\text{cps})]^+\}/dt &= k_2\{[\text{Fe}(\text{cp})(\text{cps})]^+\} + \\
 &+ k_4\{[\text{Fe}(\text{cp})(\text{cps})]^+\}\{\text{cps}^-\} - k_1\{[\text{Fe}(\text{cp})(\text{cps})]\}\{\text{Ce}^{4+}\}. \quad (1)
 \end{aligned}$$

In this equation the term containing the rate constant k_1 can be neglected, as it represents a practically immediate one-electron oxidation of acetylferrocene. In the presence of Ce^{4+} ions the term containing the constant k_4 will not make itself felt, too, because the (cps^-) concentration is zero due to rapid reaction with the ions of the oxidizing agent. However, this term is significant for the systems not containing Ce^{4+} ions, i.e. for $n \leq 1$ and for $n > 1$ from the moment when the Ce^{4+} ions are exhausted in the system (the steeper parts of the curves in Fig. 4a). In these cases the (cps^-) ions are consumed by reaction with the yet undecomposed ions acetylferri-

cenium. As they also do not accumulate in the system, the steady state condition (Eq. (3)) can be applied to Eq. (2) expressing their time change according to the above-given scheme, and for $Ce^{4+} = 0$ we obtain Eq. (4).

$$d\{cps^{-}\}/dt = k_2\{[Fe(cp)(cps)]^{+}\} - k_4\{[Fe(cp)(cps)]^{+}\} \{cps^{-}\} - k_5\{cps^{-}\} \{Ce^{4+}\} \quad (2)$$

$$d\{cps^{-}\}/dt = 0 \quad (3)$$

$$k_2\{[Fe(cp)(cps)]^{+}\} = k_4\{[Fe(cp)(cps)]^{+}\} \{cps^{-}\} . \quad (4)$$

Introducing the above-given simplifications into Eq. (1) we obtain the final form:

$$\text{for } \{Ce^{4+}\} \neq 0 \quad -d\{[Fe(cp)(cps)]^{+}\}/dt = k_2\{[Fe(cp)(cps)]^{+}\} \quad (5a)$$

$$\text{for } \{Ce^{4+}\} = 0 \quad -d\{[Fe(cp)(cps)]^{+}\}/dt = 2k_2\{[Fe(cp)(cps)]^{+}\} . \quad (5b)$$

Analogous formal kinetic expressions follow from the second scheme for 1,1'-diacetylferrocene:

$$-d\{[Fe(cps)_2]^{+}\}/dt = k'_2\{[Fe(cps)_2]^{+}\} + k'_4\{[Fe(cps)_2]^{+}\} \{cps^{-}\} - k'_1\{[Fe(cps)_2]^{+}\} \{Ce^{4+}\} \quad (6)$$

and

$$d\{cps^{-}\}/dt = k'_2\{[Fe(cps)_2]^{+}\} + k'_3\{[Fe(cps)]^{2+}\} - k'_4\{[Fe(cps)_2]^{+}\} \{cps^{-}\} - k'_5\{cps^{-}\} \{Ce^{4+}\} . \quad (7)$$

These relations can be simplified in the same way as those for acetylferrocene, *i.e.* with the presumptions:

$$d\{cps^{-}\}/dt = 0 \quad \text{and} \quad k'_3 \gg k'_2$$

to give the following final form:

$$\text{for } \{Ce^{4+}\} \neq 0 \quad -d\{[Fe(cps)_2]^{+}\}/dt = k'_2\{[Fe(cps)_2]^{+}\} \quad (8a)$$

$$\text{for } \{Ce^{4+}\} = 0 \quad -d\{[Fe(cps)_2]^{+}\}/dt = 3k'_2\{[Fe(cps)_2]^{+}\} . \quad (8b)$$

From the given equations it is seen that decomposition of acetylferrocenium ion and 1,1'-diacetylferrocenium ion is two and three times faster, respectively, in the absence

of oxidizing agent than the same reaction in the presence of the oxidant, which agrees very well with experiment. This the constants k_2 and k'_2 are two and three times smaller, respectively, than the values k from Table I.

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