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Studies on Ferrocene Derivatives. VII.[1] Solvent Effect on the Oxidation Reaction of *t*-Butylferrocenes

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The oxidation reactivity of *t*-butylferrocenes with air was measured in 1,2-dichloroethane or 1,4-dioxane. Their reactivity in 1,2-dichloroethane was increased with increasing the number of the substituents. It was considered that the oxidation proceeds through air oxidation with catalytic proton. On the other hand, in 1,4-dioxane, the conversion amount to oxidized form of ferrocene or *t*-butylferrocene suddenly incresed in the course of the reaction. In this solvent, the ferrocene nucleus was decomposed to give Fe^{3+} ion. It seems that the substrate was oxidized by Fe^{3+} ion formed.

Ferrocene (Fc) is very stable in air, so that the oxidation from Fe(II) to Fe(III) is difficult. However, in an acidic solution, Fc is readily oxidized to ferrocenium ion[2] with air.

The oxidation reaction of ferrocene derivatives with air (or oxygen gas) in acidic solution has been investigated by several workers.[3,4] The reaction mechanism was considered as follows:[4] ferrocenonium ion[2] is formed by coordination of a proton to iron atom of Fc, and is converted continuously to ferrocenium ion with loss of hydrogen atom by the attack of oxygen (Eq. 1).

$$\mathrm{Fc} \xrightarrow{\mathrm{H^+}} \underset{\text{ferrocenonium ion}}{[\mathrm{Fc\text{-}H}]^+} \xrightarrow{\mathrm{O_2}} \underset{\text{ferrocenium ion}}{\mathrm{Fc}^+} \qquad (1)$$

In our previous paper,[5] the oxidation reaction of (substituted phenyl)ferrocenes was discussed. It was clarified that the reactivity of (substituted phenyl)ferrocenes is influenced by a coordination facility of proton to iron atom. The coordination facility is governed by both the I-effect and the steric effect of the substituent. That is to say, the oxidation reaction proceeds through Eq. 1. In the present work, the oxidation reaction of *t*-butylferrocenes was carried out in the presence of trichloroacetic acid. The reactivity of *t*-butylferrocenes in 1,2-dichloroethane increased with the number of *t*-butyl substituents, and was governed by the coordination facility of proton to iron atom. No steric hindrance by *t*-butyl groups was observed, and the reactivity was controlled by the I-effect of *t*-butyl groups. However, in 1,4-dioxane, the order of the reactivity was different from that in 1,2-dichloroethane. In 1,4-dioxane, the reactivity of ferrocene or *t*-butylferrocene suddenly increased in the course of the reaction. In this paper, we will discuss the mechanism of the oxidation reaction of these ferrocenes in 1,4-dioxane.

Experimental

Preparation of Materials. t-Butylferrocenes were prepared by well known methods[6—9] and the method developed in our laboratory.[10]

$$\mathrm{Fc} \xrightarrow{\mathrm{(CH_3CO)_2O}} \mathrm{Fc\text{-}COCH_3} \xrightarrow{\mathrm{CH_3MgI+I_2}} \mathrm{Fc\text{-}C(CH_3)_3}$$

$$\mathrm{Fc} \xrightarrow{\mathrm{CH_3COCl}} \mathrm{Fc(COCH_3)_2} \xrightarrow{\mathrm{2CH_3MgI+I_2}} \mathrm{Fc[C(CH_3)_3]_2}$$

$$\mathrm{Fc} \xrightarrow{\mathrm{(CH_3)_3CCl}} \mathrm{Fc[C(CH_3)_3]}_n \quad (n=3,4).$$

Table 1. Melting Points of *t*-Butylferrocenes

	Mp/°C [lit]
t-Butyl Fc[a]	—
1,1′-Di-*t*-butyl Fc[a]	28.5—29.0[28][b]
1,1′,3-Tri-*t*-butyl Fc	87.0—89.0[92][b]
1,1′,3,3′-Tetra-*t*-butyl Fc	193.0—194.0[198][b]

a) Ref. 10. b) Ref. 9.

Table 2. ^{1}H NMR Chemical Shifts of *t*-Butylferrocenes[a]

	Chemical shift/ppm[b]									
	H-1	H-2	H-3	H-4	H-5	H-1′	H-2′	H-3′	H-4′	H-5′
t-Butyl Fc[c]	—	4.07	4.01	4.01	4.07	4.14	4.14	4.14	4.14	4.14
1,1′-Di-*t*-butyl Fc[c]	—	4.07	4.01	4.01	4.07	—	4.07	4.01	4.01	4.07
1,1′,3-Tri-*t*-butyl Fc	—	3.86	—	3.94	3.94	—	4.06	4.01	4.01	4.06
1,1′,3,3′-Tetra-*t*-butyl Fc	—	3.85	—	3.92	3.92	—	3.85	—	3.92	3.92

a) Sample concentration is ca. 0.05 mol dm^{-3}. Solv.: $CDCl_3$. Temp.: ambient. b) Downfield positive, TMS internal standard. c) Ref. 10.

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The compounds were identified by melting point and ^{1}H NMR, and the purity was determined by HPLC. The melting point data and ^{1}H NMR chemical shifts are shown in Tables 1 and 2.

Measurements of Oxidation Reactivity. The oxidation reaction and analysis were carried out as described in the previous paper.[5] In the case of the reaction in 1,4-dioxane, HPLC analysis was carried out as follows: after water was added to a sample, unreacted material and internal standard (nitrobenzene) were extracted with 1,2-dichloroethane from a mixture of the reaction solution and water. The extract was analyzed by HPLC as mentioned in the previous paper.[5]

Results and Discussion

Oxidation Reaction in 1,2-Dichloroethane. The conversion of the oxidation of ferrocene and *t*-butylferrocenes in 1,2-dichloroethane is shown in Fig. 1. The order of the reactivity was as follows:

$$\text{Fc} < t\text{-Bu-Fc} < 1,1'\text{-di-}t\text{-Bu-Fc} < 1,1',3\text{-tri-}t\text{-Bu-Fc} < 1,1',3,3'\text{-tetra-}t\text{-Bu-Fc}.$$

The reactivity increased with increase in the number of the substituents. The reason was considered as follows: the electron density of iron atom of ferrocene molecule increases with an increase in the number of the electron-releasing substituents (*t*-butyl groups). It seems that the coordination of catalytic proton to iron atom is accelerated by higher electron density of iron atom. It was considered that the oxidation reaction in this solvent is not controlled by the steric hindrance of *t*-butyl groups and proceeds through Eq. 1.

Oxidation Reaction in 1,4-Dioxane. The conversion of the oxidation of *t*-butylferrocenes in 1,4-dioxane is shown in Fig. 2. The reactivity of ferrocene or *t*-butylferrocene suddenly increased in the course of the reaction. The conversion amount of ferrocene was zero in 1,2-dichloroethane, but the reactivity in 1,4-dioxane was higher. The color of the reaction solution will be noticed. When no remarkable increase of the conversion amount was observed, the solution was green of ferrocenium ion. Whereas, after the conversion amount increased, the solution changed to red-violet. Therefore, it was considered that the sudden increase of the conversion amount did not proceed through Eq. 1, and another mechanism is necessary to explain this reaction.

When sodium hydroxide was added to the red-violet solution, red precipitates were produced. By the addition of potassium thiocyanate (confirmatory reagent for Fe^{3+}) and 1,10-phenanthroline (confirmatory reagent for Fe^{2+}), the solution became orange-red and red, respectively. From these results, both F^{3+} and Fe^{2+} ions must be contained in the red-violet solution after sudden increase of the conversion amounts.[11] On the other hand, in the green solution, where the remarkable increase of the conversion amounts was absent, there were neither Fe^{3+} nor Fe^{2+} ions. Therefore, it seems that the ferrocene nucleus was decom-

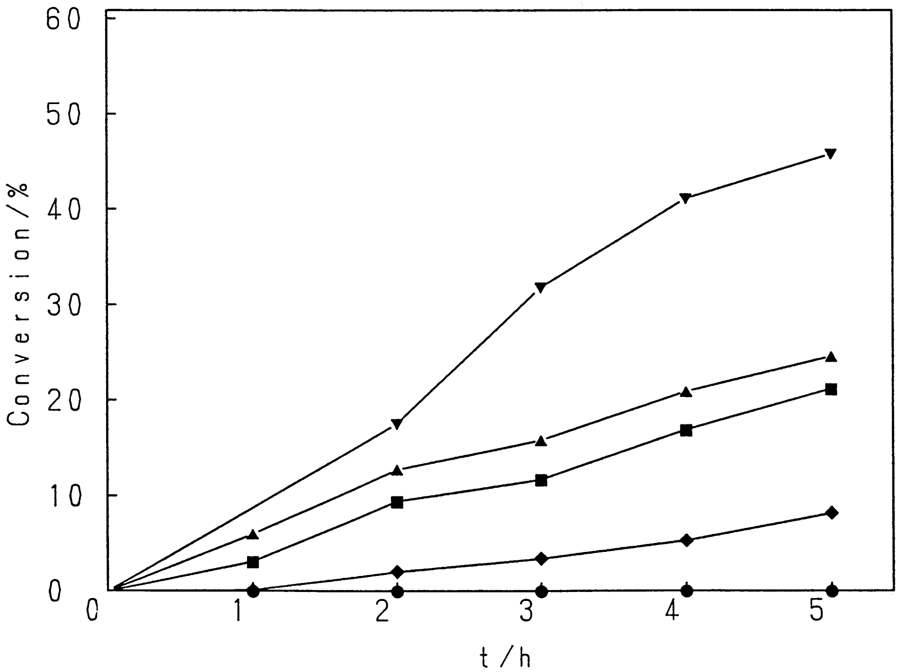

Fig. 1. Conversion of ferrocene and *t*-butylferrocenes in 1,2-dichloroethane. (ferrocenes: trichloroacetic acid=1 : 10, reaction temperature: 40 °C).
●: ferrocene, ◆: *t*-butylferrocene, ■: 1,1′-di-*t*-butylferrocene, ▲: 1,1′,3-tri-*t*-butylferrocene, ▼: 1,1′,3,3′-tetra-*t*-butylferrocene.

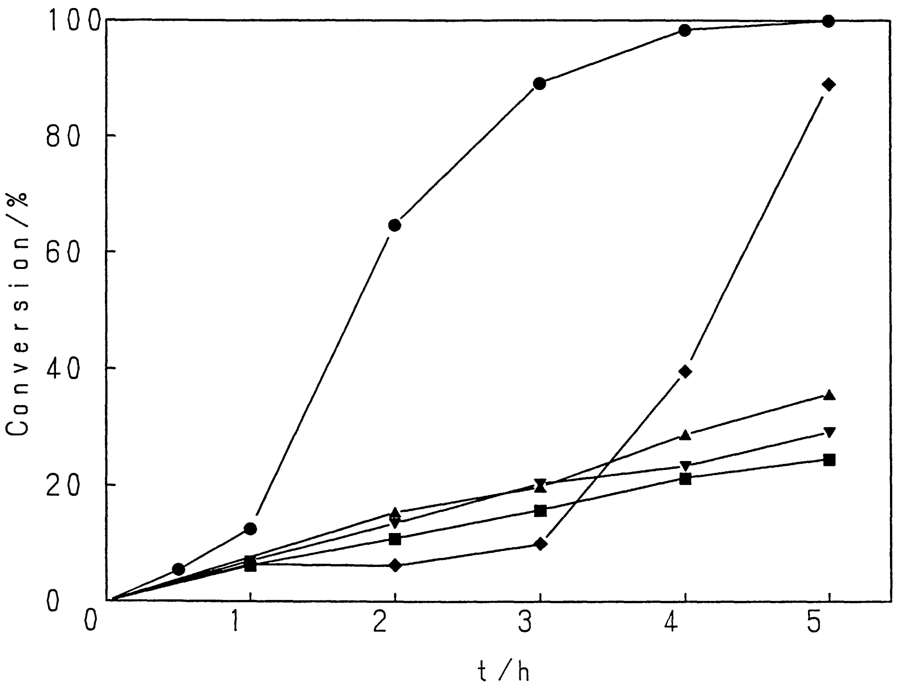

Fig. 2. Conversion of ferrocene and *t*-butylferrocenes in 1,4-dioxane. (ferrocenes: trichloroacetic acid=1 : 10, reaction temperature: 40 °C).
●: ferrocene, ◆: *t*-butylferrocene, ■: 1,1′-di-*t*-butylferrocene, ▲: 1,1′,3-tri-*t*-butylferrocene, ▼: 1,1′,3,3′-tetra-*t*-butylferrocene.

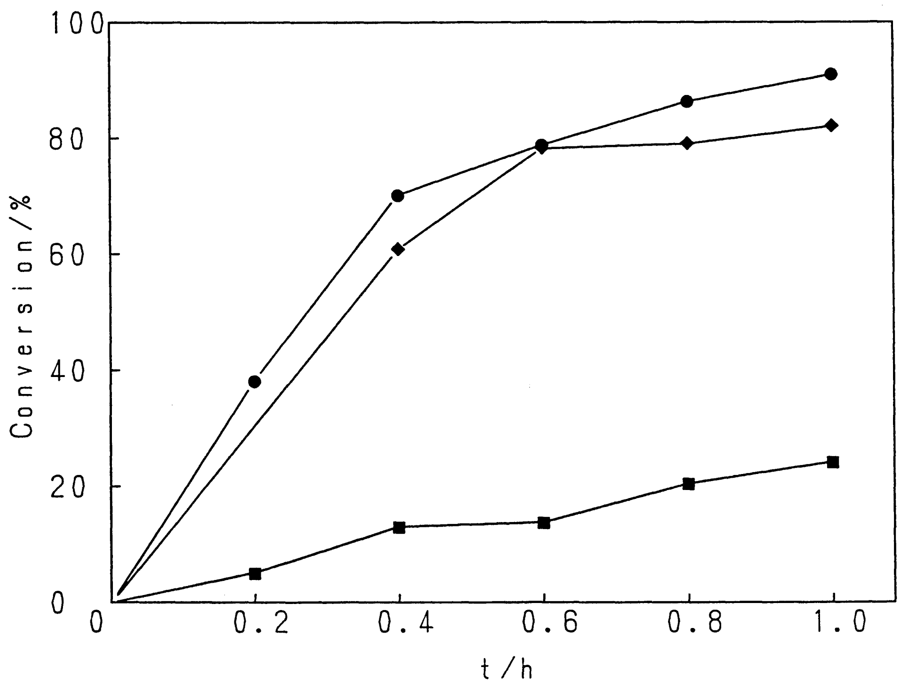

Fig. 3. Conversion of ferrocene in addition of acetic acid or salicylic acid. (ferrocene: trichloroacetic acid=1 : 5, ferrocene: acetic acid=1 : 50, ferrocene: salicylic acid=1 : 1, reaction temperature: 40 °C).
●: trichloroacetic acid, ◆: trichloroacetic acid + acetic acid, ■: trichloroacetic acid + salicylic acid.

posed in the red-violet solution.

The increase of the conversion amounts was not recognized in 1,2-dichloroethane, but it was found in 1,4-dioxane. Another ethereal solvent, dibutyl ether, was used instead of 1,4-dioxane. In a mixed solvent (dibutyl ether: 1,2-dichloroethane=1 : 9 (molar ratio)), which included only 10% ethereal solvent, it seems that the dielectric constant of the solvent is not different from that of pure 1,2-dichloroethane. As shown in Fig. 3, the increase of the conversion amounts was recognized. That is to say, the increase of the conversion amounts is recognized in the presence of ethereal solvents as 1,4-dioxane or dibutyl ether.

Trichloroacetate anion is stable in nonpolar solvent such as 1,2-dichloroethane. However, it was reported that the anion is decomposed to CCl_3^- ion with decarboxylation in aprotic polar solvent such as 1,4-dioxane.[12,13)]

$$CCl_3COO^- \longrightarrow CCl_3^- + CO_2 \tag{2}$$

CCl_3^- ion is carbanion, and is a very strong nucleophilic reagent.[14)] On the other hand, ferrocenium ion is decomposed by the attack of nucleophilic reagent.[15)] Therefore, it seems that CCl_3^- ion is effective species for the decomposition of ferrocenium ion. It was considered that ferrocenium ion was decomposed by CCl_3^- ion.

The oxidation was carried out in methanol. The remarkable increase of the conversion amounts was not recognized as in 1,2-dichloroethane. The reason was considered as follows: CCl_3^- ion was produced even in methanol. However, the ion was converted to chloroform by the attack of methanol proton,[12)] and did not act as nucleophilic reagent for ferrocenium ion. The decomposition process of ferrocenium ion by CCl_3^- ion was supported by this phenomenon observed in methanol.

The decomposition of ferrocene nucleus was confirmed by the following facts. As shown in Fig. 2, the remarkable increase of the conversion amounts was detected only for ferrocene and *t*-butylferrocene. Whereas, for 1,1′-di-, 1,1′,3-tri-, and 1,1′,3,3′-tetra-*t*-butylferrocene, such an increase was not observed. The reason was considered as follows: the Cp(cyclopentadienyl)–Fe bond is relatively strong for di-, tri-, and tetra derivatives and the steric hindrance is increased by *t*-butyl groups. Therefore, the decomposition of ferrocene nucleus of these compounds is difficult, so that the increase of the conversion amount was not remarkable for these three derivatives. The Cp–Fe bond force and the steric hindrance of ferrocene are weakest in all the ferrocenes examined in this study, and the remarkable increase occurred within 1 h from the start of the reaction. Whereas, on *t*-butylferrocene, the increase was observed after 3 h. These phenomena were explained by a similar reason to that mentioned above.

Fe^{3+} ion was formed by the decomposition of ferrocene nucleus. Fe^{3+} ion was a very strong oxidizing reagent for ferrocenes. Ferrocene and *t*-butylferrocenes examined in this study were oxidized perfectly by iron(III) chloride. Hence, when the remarkable increase of the conversion amount was recognized, the oxidation reaction by Fe^{3+} ion seems to proceed as Eq. 3.

$$Fe^{3+} + Fc \longrightarrow Fe^{2+} + Fc^+ \tag{3}$$

Furthermore, in order to block the oxidizing ability of Fe^{3+} ion, the following reaction was carried out: salicylic acid, which forms a complex between Fe^{3+} ion,[16)] was added to the reaction solution together with trichloroacetic acid. No remarkable increase of the conversion amounts was recognized, and the reaction proceeded slowly (Fig. 3). (By the addition of acetic acid possessing no complex-forming ability, the increase of the conversion amounts was not stopped.) The reaction solution was washed with water, and UV spectra of the washings (light violet) showed a sharp absorption at 305.5 nm. The solution of iron(III) chloride and salicylic acid absorbed at the same position. From these results, it seems that Fe^{3+} ion formed by the decomposition of ferrocene nucleus was masked as a complex of salicylic acid in the presence of salicylic acid.

It was considered that the remarkable increase of the conversion amounts for ferrocene or *t*-butylferrocene was caused by the following mechanism: ferrocene nucleus was attacked by CCl_3^- ion formed by the decomposition of trichloroacetate ion in 1,4-dioxane. The nucleus was decomposed to form Fe^{3+} ion. Fe^{3+} ion oxidized ferrocenes, and the increase of the conversion amounts was remarkable. As mentioned above, the reaction solution contains Fe^{2+} and Fe^{3+} ions. It seems that Fe^{3+} ion was reduced to Fe^{2+} through Eq. 3 or by the action of Cp^- ion[15)] formed by the decomposition of ferrocene nucleus.

Conclusion

In 1,4-dioxane, the oxidation of ferrocene or *t*-butylferrocene proceeds as follows:

1. CCl_3^- ion is produced by the decomposition of trichloroacetate ion.
2. The ferrocene nucleus is decomposed by CCl_3^- ion to form Fe^{3+} ion.
3. The substrate is oxidized faster by Fe^{3+} ion than ferrocenonium ion is oxidized by air.

Consequently, in 1,4-dioxane, the conversion amount of ferrocene or *t*-butylferrocene suddenly increases in the course of the reaction.

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