The Oxidative Decomposition of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$

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$\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ ($\text{X}=\text{Cl}$, Br , and I) was decomposed with molecular oxygen in several solvents. It was found that the iron atom of the complex was oxidized, and oxygen molecule consequently was reduced and activated in every case regardless of the kind of solvents. The process for the coordination of oxygen molecule to the complex, however, depended much on the nature of solvents: in solvents such as alcohols or acetone, the direct substitution of oxygen molecule with the halogen atom of the complex took place, while in solvents such as dimethyl sulfoxide, the complex was decomposed by the solvent to form $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3$, to which oxygen molecule was then coordinated. The resulting activated oxygen oxygenated the allyl ligand or abstracted the hydrogen atom from the substrate.

A great number of reactions of organometallic complexes with molecular oxygen are known^{1)~3)}, and they are classified by Khan and Martell⁴⁾ into two categories: reactions in which molecular oxygen acts as an oxygenating agent, and those in which molecular oxygen serves as only an oxidizing agent to form negatively charged species such as water and hydrogen peroxide. This classification is simply based on products resulted from the reactions, and does not seem adequate in terms of the mechanism of reactions. Almost all of these oxygen reactions include the coordination of oxygen molecule to the complexes with incidental electron transfer from the latter to the former to give negative forms of oxygen molecule such as O_2^- , O_2^{2-} , and so on. Direct charge transfer reactions also occasionally happen to produce such forms of oxygen. The resulting activated oxygen can react with the substrate as an oxygenating or oxidizing agent, depending on the nature of the substrate and the reaction conditions. It is desirable, therefore, to consider the reaction of complexes with oxygen in two ways: coordination and activation of oxygen molecule, and the reaction of the oxygen molecule with a substrate.

The behavior of oxygen molecule in the first coordination step have been reported by many

investigators^{5)~7)}. When the oxygen molecule is stabilized on complexes, they are called as oxygen-carrying complex. When the oxygen is enough activated, on the other hand, it reacts with the substrate (the second step). Oxygenation is known in reactions of PPh_3 ⁸⁾, SO_2 ⁹⁾, NO ¹⁰⁾, CO ¹¹⁾ etc. with molecular oxygen in the presence of metal complexes, and oxidation is observed in enzymatic reactions^{12), 13)} and in autoxidations of organic substrates with metal phthalocyanines¹⁴⁾, poly(phthalocyanines)¹⁵⁾ and porphyrins¹⁶⁾. These two reactions are of interest in simulating the oxidation reaction *in vivo*. It is also important to know the behavior of the activated oxygen in the complicated reactions including both oxygenation and oxidation processes.

The mode of oxidative decomposition of some air-sensitive complexes was found to belong to such a type of reaction. This paper describes the decomposition of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ with molecular oxygen.

Experimental

Materials: $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ ($\text{X}=\text{Cl}$, Br , and I) was prepared by converting $\text{Fe}(\text{CO})_5$ into $\text{Fe}_2(\text{CO})_9$ under radiation of a high voltage mercury lamp, and reacting the resulting complex with an allyl halide^{17), 18)}. This reaction and the subsequent recrystallization from pet=

roleum ether were carried out under pure nitrogen atmosphere. The complexes obtained were identified by IR spectra and elemental analyses.

Solvents used, such as benzene, toluene, acetone, methanol, ethanol, 1-propanol, *t*-butyl alcohol, diethyl ether, tetrahydrofuran, *N,N*-dimethylformamide and dimethyl sulfoxide were purified according to conventional methods.

Procedure: In the decomposition of complexes, the amount of oxygen absorbed was measured using a Toshiba-Beckmann's Dissolved Oxygen Analyzer Model 777. At first, a reaction vessel (25 ml) with a sensor of the oxygen analyzer was filled up with a solvent so that there was no gaseous part in the vessel, and molecular oxygen was bubbled into until the predetermined partial pressure of oxygen was established. After the dissolved oxygen pressure became constant, 0.5~1.0 ml of a solution of the complex prepared under nitrogen, so that the solution contained the calculated concentration of the complex, was charged into the reaction vessel. The rate of absorption of oxygen was determined in the initial period of reaction; in this case, the change of partial pressure of oxygen by the addition of the complex solution was taken into account.

The evolution of carbon monoxide in the interaction of a complex with a solvent was measured using gasmetry. Reaction products were analyzed qualitatively with GLC and GLC-MS methods.

The electrochemical behavior of the complex was measured by cyclic voltammetry using tetraethylammonium perchlorate as a supporting electrolyte on a platinum electrode.

Results and Discussion

Interaction of π -C₃H₅ Fe(CO)₃X with molecular oxygen.

π -C₃H₅ Fe(CO)₃X was gradually decomposed in the presence of molecular oxygen. According to the observation of UV spectra, as oxygen molecule was consumed, the absorption (about 390 nm) of an original complex decreased and a new absorption appeared at about 525 nm indicating the formation of green-colored divalent iron. Consequently, the decomposition of complexes is ascribed to the oxidation of them with molecular oxygen. The interaction of

Fig.-1 Cyclic voltammograms of oxygen and /or π -C₃H₅Fe(CO)₃Br.

complexes with oxygen molecule is explained by cyclic voltammograms. **Figs.-1 (a)** and **1 (b)** show the voltammograms of oxygen molecule and of π -C₃H₅ Fe(CO)₃Br in absence of oxygen, respectively, in which each peak means the following molecular reactions:

$$E_{1/2} = -0.82 \text{ V}$$

$$E_{1/2} = -0.43 \text{ V } (-0.39 \text{ V})^{19)}$$

$$E_{1/2} = -0.72 \text{ V } (-0.72 \text{ V})^{19)}$$

When molecular oxygen was bubbled into the solution of π -allyl Fe(CO)₃Br, the voltammogram **1 (c)** was obtained. **Fig.-1 (c)** illustrates the decrease of height of peaks (1), (2) and (3), and the appearance of new peaks (4) and (5). The peak (4) was not observed at first sweep, but at second sweep. This is attributable to the reduced peak of species formed in the oxidation at (4'), and means following reactions:

The peak (5) is considered to be the reduction peak of the coordinated oxygen molecule to the complex, because it is observed only in the presence of molecular oxygen, and disappears after the purge of molecular oxygen with nitrogen (**Fig.-1 (d)**). The repeated bubbling and purging of oxygen lowered peak height of the complex gradually, but retained the relation as shown in **Figs.-1 (c)** and **1 (d)**. These results confirm the substitution of halogen atom of the complex with oxygen molecule introduced and the reversible coordination of oxygen molecule as follows:

Table-1 Effect of halides of complexes on the rate of oxygen consumption.

X	Rate of oxygen consumed $\times 10^6 \text{ M} \cdot \text{s}^{-1}$
Cl	8.23
Br	3.04
I	2.37

Reaction conditions: [complex], $4 \times 10^{-3} \text{ M}$; $[\text{O}_2]$, 300 mm; solvent, acetone; temperature, 30°C .

Table-2 Effect of solvents on the rate of oxygen consumption.

Solvent	ϵ	Rate $\times 10^6 \text{ M} \cdot \text{s}^{-1}$
Benzene	2.28	0.13
Toluene	2.38	0.16
Acetone	20.8	0.58
Methanol	32.6	1.01
Ethanol	24.3	1.48
Propanol	19.3	2.41
<i>t</i> -Butyl alcohol	12.2	0.25
Diethyl ether	4.22	3.61
Tetrahydrofuran	7.39	54.6
<i>N,N</i> -dimethylformamide	36.7	264
Dimethyl sulfoxide	48.9	910

Reaction conditions: [complex], $8 \times 10^{-3} \text{ M}$; $[\text{O}_2]$, 300 mm; temperature, 30°C .

Table-1 shows the effect of halides of complexes on the rate of consumption of oxygen: the rate being $\text{Cl} \gg \text{Br} > \text{I}$. This order coincides well with those of electronegativity of halogens and of rates of reaction between $\pi\text{-C}_3\text{H}_5 \text{ Fe}(\text{CO})_3\text{X}$ and NO leading to the formation of stable nitrosyl complexes having eighteen electrons:

This may also support the proposal of substitution reaction with oxygen molecule described above.

Solvent effect.

The decomposition of $\pi\text{-C}_3\text{H}_5 \text{ Fe}(\text{CO})_3\text{Br}$ was carried out in various kinds of solvents. **Table-2** shows the rate of oxygen consumption with dielectric constants (ϵ) of solvents, and **Fig.-2** illustrates the rate against $(\epsilon - 1/2\epsilon + 1)$ of solvents. The solvents used seem to be classified into three groups: the first group is

Fig.-2 Correlation of the rate of oxygen consumption with $-1/2\epsilon + 1$ of solvents.

Reaction conditions: same as in **Table-2**.

characterized by hydrophobic nature, such as benzene, toluene and diethyl ether; the second group, hydrophilic solvents such as methanol, ethanol, propanol, *t*-butyl alcohol and acetone; and the third group, for instance, tetrahydrofuran, *N,N*-dimethylformamide and dimethyl sulfoxide. The rate of decomposition of the π -allyl complex, in general, was much greater in third group of solvents than in the second group or first group. In every group, the higher value of $(\epsilon - 1/2\epsilon + 1)$ of solvents, the higher rate of decomposition was observed. This result implies that the loosening of Fe-X bond is preferable to the above-mentioned substitution with oxygen. The extraordinary fast decomposition in a solvent belonging to the third group, however, must be explained by other additional reason.

Fig.-3 shows the evolution of carbon monoxide as measure of the stability of complexes in solvents. The complex was essentially stable in solvents of the first and second groups. But it was instable in solvents of the third group and was decomposed with evolution of carbon monoxide, during of which the color of solution changed from brown to red. The amount of carbon monoxide increased with time to approach a limited value which seemed to be a little over mole per mole of the complex. This is considered to be the same phenomenon as

Fig.-3 Amount of carbon monoxide evolved in the interaction of the complex with solvent.

Reaction condition: $[\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Br}]$, $4 \times 10^{-3}\text{ M}$; temperature, 30°C .

observed in the reaction of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ with dimethyl sulfoxide reported by Nesmeyanov and Kristskaya:²⁰⁾

According to the paper¹⁹⁾, the $(\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3)_2$ shows red color and is in equilibrium with the green-colored $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3$ formed by electrochemical reaction of $\text{Na}(\text{C}_3\text{H}_5\text{Fe}(\text{CO})_2)$ and $\text{Na}(\text{Mn}(\text{CO})_5)$ in the presence of Al_2O_3 :

The fastest rate of decomposition in a solvent of the third group, consequently, can be explained by the fast reaction of oxygen molecule with $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3$ which derived from the $(\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3)_2$ formed by the interaction of the complex with the solvent.

The decomposition products of complexes

Table-3 Main decomposition products of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Br}$ with oxygen.

Solvent	Products
Benzene	Polymer of ligand, Acetone
Acetone* ¹⁾	Polymer of ligand, $\text{C}_6\text{-com=}$ pounds, Benzene, $\text{CH}_3\text{COCH=C}(\text{CH}_3)\text{-CH}_2$
Ethanol	Polymer of ligand, Propylene, $\text{C}_6\text{-compounds}$, Benzene, Acetone, $\text{CH}_3\text{CH}_2\text{OCOOCH}_2\text{CH}_3$
N,N-dimethylformamide	Polymer of ligand, Propylene, $\text{C}_6\text{-compounds}$, Benzene, Acetone

*¹⁾ A little diacetone alcohol (MS: 59, 43, 57) may be produced.

were analyzed only qualitatively, because of the existence of 5 to 10 or more kinds of products which could not be separated. **Table-3** shows some of products which are thought as main products from the peak areas of gas chromatograms. In every solvent, the residue after the complete decomposition contained iron oxides and a polymer unsaturated hydrocarbon consisting of ligand. In addition to this, products based on the allyl ligand such as propylene, $\text{C}_6\text{-com=}$ pounds and benzene were also obtained. The benzene is considered to be formed by the hydrogen abstraction of cyclic dimer of the allyl by the activated oxygen. As oxidation products, on the other hand, acetone, 4-methyl-3-penten-2-one (mass numbers: 98 (P), 83, 58, 55, 43) (the reaction in acetone), and diethyl carbonate (mass number: 118 (P), 103, 87, 73, 49, 45) (the reaction in ethanol) were formed. These products are considered to be derived from the reaction of ligand and/or a solvent with the oxygen species, probably a negatively charged oxygen molecule activated by the coordination. The details of these dehydrogenation and oxygenation reaction will soon be reported by us in this Journal.

Decomposition mechanism.

The kinetical runs of decomposition reaction are shown in **Tables-4** and **5**. The rate of oxygen consumed in acetone, a solvent of the second group is expressed by

$$-d[\text{O}_2]/dt = k[\text{complex}][\text{O}_2]$$

and consistent with the electrochemical results that the coordination of oxygen molecule to the complex was a rate-determining step. On the other hand, in dimethylsulfoxide, the rate

Table-4 Rate of oxygen consumption in acetone solvent.

Complex $\times 10^3\text{ M}$	O_2 mm	$-d(\text{O}_2)/dt \times 10^6 \text{ M}\cdot\text{s}^{-1}$
4.0	300	3.04
6.0	"	4.61
8.0	"	5.83
12.0	"	9.73
8.0	160	2.65
"	350	6.93
"	400	8.12
"	500	10.1

Reaction conditions: solvent, acetone; temperature, 30°C .

Table-5 Rate of oxygen consumed in dimethyl sulfoxide solvent.

Complex $\times 10^3$ M	O ₂ mm	DMSO M	$-d(O_2)/dt$ $\times 10^3$ M $\cdot$ s ⁻¹
4.0	300	2.37	0.76
8.0	"	"	1.57
12.0	"	"	2.15
8.0	160	"	1.51
"	400	"	1.63
"	450	"	1.60
"	300	0.18	0.11
"	"	1.05	0.64
"	"	2.37	1.57
"	"	4.91	3.21
"	"	10.0	6.09
"	"	14.1	9.10

Reaction conditions: solvent, dimethyl sulfoxide diluted with benzene; temperature, 30°C.

was independent on the pressure of oxygen and showed the first order dependency on both the concentration of the complex and of the complex and of the solvent. This is in good agreement with the result

$$-d(O_2)/dt = k'(\text{complex})(\text{solvent})$$

described in the previous section, which showed that the decomposition of complexes by such a solvent occurred before the coordination of oxygen molecule.

The decomposition mechanisms are proposed as follows: in a solvent of first and second groups

and in a solvent of third group

The activation energy of decomposition reaction was about 8 to 12 kcal/mol (**Table-6**). and was comparable to those of oxygenation of complexes^{21), 22)} and the similar oxidative decomposition²³⁾.

Table-6 Activation energies of decomposition of $\pi\text{-C}_3\text{H}_5\text{-Fe}(\text{CO})_3\text{Br}$

Solvent	ΔE , kcal/mol
Benzene	12.2
Acetone	7.55
N,N-dimethylformamide	10.7
Dimethyl sulfoxide + benzene (1 : 4)	9.24

Reaction conditions : [complex], 8×10^{-3} M; [O₂], 300 mm; temperature, 0 to 50°C.

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π -アリル $\text{Fe}(\text{CO})_3\text{X}$ の酸化分解

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π -アリル $\text{Fe}(\text{CO})_3\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) を数種の溶媒中で酸素分解した。錯体の鉄イオンが酸化され、その結果酸素が還元・活性化され、これが溶媒に無関係であることが見いだされた。しかし酸素の錯体への配位過程は溶媒の性質に大きく依存した：アルコールやアセトンのような溶媒中では酸素が錯体のハロゲン原子と直接置換し、一方ジメチルスルホキシドのような溶媒中では錯体が溶媒によって分解されて π -アリル $\text{Fe}(\text{CO})_3$ となり、これに酸素が配位した。得られる活性化酸素はアリル配位子を酸素化し、又は基質から水素原子を引き抜いた。