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MÖSSBAUER SPECTROSCOPIC STUDY ON 1′-MONOHALOBIFERROCENES

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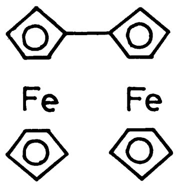
In a series of 1′-monohalobiferrocenes, it has been found that their triiodide salts show a trapped valence state of iron atoms, although the monocations of 1′,1‴-diiodo- and dibromobiferrocene show an averaged valence state in the temperature range from 4.2 K to 298 K.

Mixed valence binuclear ferrocenes have been classified into two categories by the extent of delocalization or the degree of interaction between ferrocene and ferricenium moieties.1,2) One of them is a trapped valence-type compound which has two kinds of the independent valence state of iron atoms corresponding to iron(II) and iron(III). The other is an averaged valence-type compound which has only an equivalent non-integral valence state of iron atoms on the Mössbauer time scale.3) It is known that various monocation salts of biferrocene (1) show the trapped valence-type Mössbauer spectra in the temperature range from 4.2 K to 300 K,4,5) while the triiodide salt of 1′,1‴-diiodobiferrocene (2, X = I) shows the averaged valence-type Mössbauer spectra from 4.2 K to 300 K. In the series of 1′,1‴-dihalobiferrocenes, we have already reported that the triiodide salt of dibromobiferrocene (2, X = Br) also shows the averaged valence state of iron atom in the temperature range between 4.2 K and 298 K, while the Mössbauer spectra for the monocation of dichlorobiferrocene (2, X = Cl) are of the trapped valence-type as in the case of biferrocene.6,7)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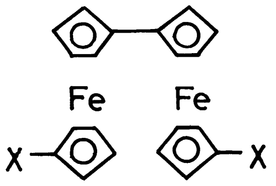
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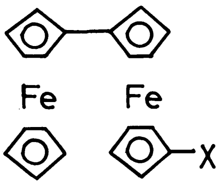
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In the present study, a series of 1′-monohalobiferrocenes (3) was prepared to compare the valence state of iron in the monosubstituted biferrocenes with that in the disubstituted biferrocenes. The effects of the halogen-substitution on the oxidation states of iron were studied by means of Mössbauer spectroscopy and cyclic voltammetry.

1'-Monohalobiferrocenes were prepared by the reaction of 1,1'-dihaloferrocene and 1-haloferrocene with activated copper bronze.[8)] Oxidation of the monohalobiferrocenes was carried out by treating them with iodine equivalent to 3/2 of the corresponding molar amount of monohalobiferrocene in dry benzene. ^{57}Fe-Mössbauer measurements were carried out by using a ^{57}Co(Rh) source moving in a constant acceleration mode. Cyclic voltammograms of the monohalobiferrocenes were obtained using a Hokuto Denki HB-107A function generator and a Hokuto Denki HA-201 potentiostat combined with a standard three-electrode configuration. A working electrode, a platinum button (Beckman) and a Ag/AgCl reference electrode, were connected via a salt-bridge containing $n\text{-}Bu_4NClO_4$ (0.1 mol dm^{-3}) in CH_3CN. The half-wave potentials, given in Table 1, were estimated from the values of peak potentials.

Table 1. CV data of 1'-monohalobiferrocenes and related compounds in CH_3CN

Compound	$E_{1/2}(1)$ / V	$E_{1/2}(2)$ / V	$\Delta E_{1/2}$ / V
Monochlorobiferrocene	0.47	0.82	0.35
Monobromobiferrocene	0.46	0.83	0.37
Monoiodobiferrocene	0.47	0.82	0.35
Dichlorobiferrocene	0.51	0.81	0.30
Dibromobiferrocene	0.51	0.81	0.30
Diiodobiferrocene	0.49	0.80	0.31
Biferrocene	0.36	0.68	0.32

All the monohalobiferrocenes studied here undergo two successive reversible one-electron oxidations to yield the corresponding mono- and dications, respectively. The half-wave potentials are summarized in Table 1 together with those of biferrocene and dihalobiferrocenes. The halogen-substitution of biferrocene results in increases in both of the half-wave potentials, $E_{1/2}(1)$ and $E_{1/2}(2)$. In the series of dihalobiferrocenes, the difference between $E_{1/2}(1)$ and $E_{1/2}(2)$, i.e. $\Delta E_{1/2}$ remains constant at a value of 0.30-0.31 V.

On the other hand, in the series of monohalobiferrocenes, one of the half-wave potentials, $E_{1/2}(1)$, decreases by 0.02-0.05 V compared with that of dihalobiferrocenes. The difference between $E_{1/2}(1)$ and $E_{1/2}(2)$

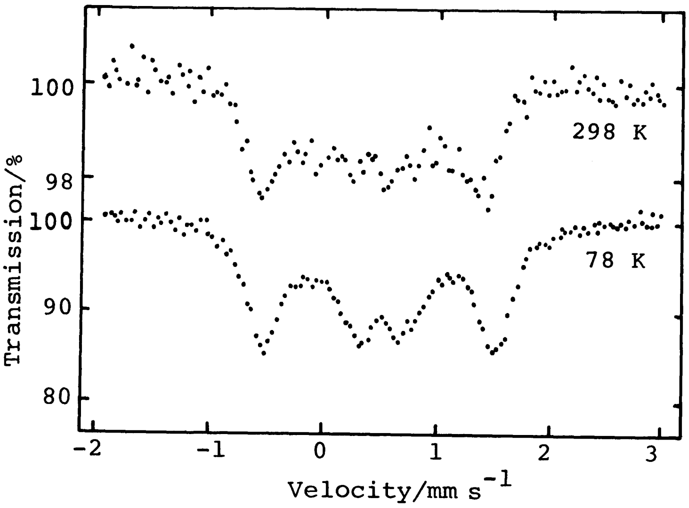

Fig. 1. Mössbauer spectra of 1'-monochlorobiferrocenium$^+I_3^-$.

expands to 0.35-0.37 V, although it was pointed out in our previous report that the value of the half-wave potential can not always be a good criterion for the classification of the type of valence state in a series of mixed valence biferrocene derivatives.[7)]

Mössbauer spectra of monochloro-, monobromo-, and monoiodobiferrocene monocation triiodide salts are shown in Figs. 1, 2, and 3, respectively. The Mössbauer spectra for the triiodide salts of 1′-monohalobiferrocene indicate an essentially trapped valence-type absorption in the temperature range from 78 K to 298 K, as in the case of 1′,1‴-dichlorobiferrocene or biferrocene triiodide salt, although a slight converging between the ferrocene-type and ferricenium-type peak components is found at 298 K.

Since the monocations of 1′,1‴-diiodo- and dibromobiferrocene, as reported previously, have only an equivalent valence state of the iron atoms, it is concluded that the intervalence electron transfer rate between the two iron atoms in these dihalobiferrocene compounds is greater than 10^7 s^{-1}, i.e. the reciprocal of the lifetime of the Mössbauer nuclear excited state. Careful inspection of the Mössbauer spectra for the monobromo derivative indicates that there is a small temperature dependence of the valence state of iron atoms, while there is no change in 1′-monochloro- and iodobiferrocene monocations.

The results that all the 1′-monohalobiferrocene triiodide salts show a trapped valence-type Mössbauer spectra at 78 K

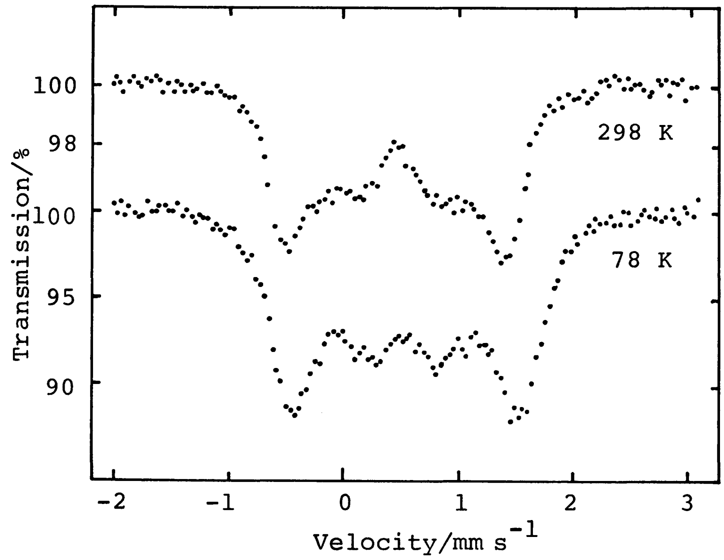

Fig. 2. Mössbauer spectra of 1′-monobromobiferrocenium$^+I_3^-$.

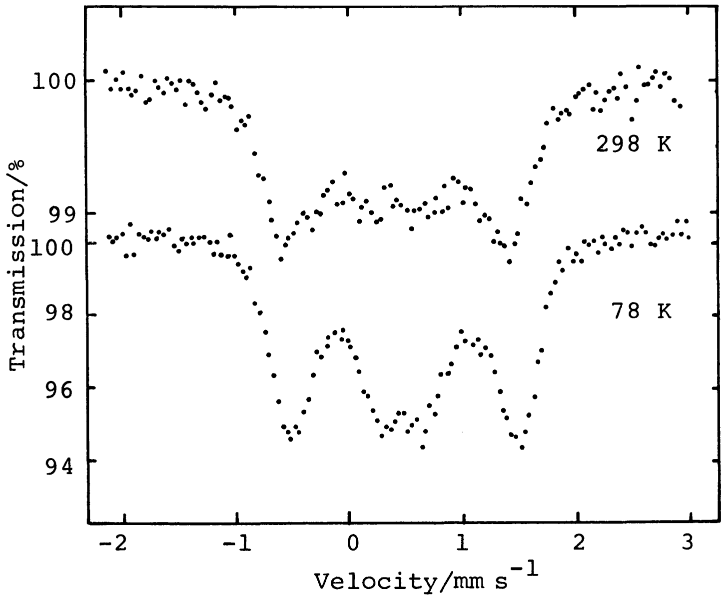

Fig. 3. Mössbauer spectra of 1′-monoiodobiferrocenium$^+I_3^-$.

and 298 K suggest that an asymmetric substitution in 1′ and 1‴ positions of biferrocenium monocation may cause a large difference between the potential minima for the valence (e_{2g}) electrons of iron atoms producing a trapped valence state, and that the difference is a little smaller in the case of 1′-monobromobiferrocenium triiodide showing an appreciable relaxation phenomenon (valence-averaging) between the two iron atoms.[9,10]

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