The Electric Properties of Metallocenes and Their Derivatives

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It is well known that electron acceptors, such as tetracyanoethylene, tetracyanoquinodimethane, and *p*-chloranil, form various types of charge transfer complexes with many donor compounds, and that some of these complexes have the properties of semiconductors. Although a great number of ferrocene derivatives have already been synthesized and their chemical properties have been elucidated, only a few reports on the properties of semiconductors in the field of metallocene derivatives have appeared.[1] As has been reported by the present authors,[2] ketazine polymers derived from diacetylferrocene and hydrazine have an interesting property, i. e., their electric resistivities are near to those of organic semiconductors.

Now the present authors wish to report on the electric properties of some metallocenes, polyferrocenyls, and two sorts of charge transfer complexes which consist of one mole of metallocene and two moles of *p*-chloranil.

Samples.—Ferrocene and nickelocene were prepared by the method reported in a previous paper.[3] Terferrocenyl, quater-ferrocenyl and sexiferrocenyl are products of the reaction of ferrocenyllithium and cobaltous chloride reported in previous papers.[4]

The Nickelocene-*p*-chloranil (1 : 2) Charge Transfer Complex.—This complex was prepared by the method reported by Goan and his co-workers.[5] A solution of 2.6 g. of *p*-chloranil in 250 ml. of dry benzene and a solution of 1.0 g. of nickelocene in 10 ml. of dry benzene (2 : 1 in mole ratio) were mixed; the complex immediately precipitated as a crystalline solid. After it had stood for several minutes, it was collected on a filter, washed with benzene, and dried in vacuo at room temperature. Thus 1.7 g. of the complex was obtained (ca. 47% yield) as dark brown glittering fine needles which did not melt at 300°C in air (on Kofler apparatus) nor at 250°C in nitrogen (in a sealed capillary). The ESR observation in acetonitrile gave no signal in the spectrum. (Found: C, 38.72; H, 1.75; Cl, 41.74, 41.69. Calcd. for $(C_{10}H_{10}Ni)(C_6Cl_4O_2)_2$: C, 38.82; H, 1.47; Cl, 41.67%).

The Cobaltocene-*p*-chloranil (1 : 2) Charge Transfer Complex.—According to a method similar to that described above, ca. 1.9 g. of the complex was obtained by mixing a solution containing 2.6 g. of *p*-chloranil in 250 ml. of benzene and a solution of cobaltocene (ca. 1.0 g.) in 50 ml. of benzene under an atmosphere of nitrogen in a dry box. This complex was a brown solid which melted at 150—155°C in nitrogen in a sealed capillary. It decomposed at 125—128°C in air and also after standing for a long period at room temperature. The solution of this complex in acetonitrile gave a sharp ESR signal corresponding to one spin per formula weight, the *g* value being estimated to be 2. (Found: C, 38.64; H, 2.19; Cl, 38.83, 38.78. Calcd. for $(C_{10}H_{10}Co)(C_6Cl_4O_2)_2$: C, 38.81; H, 1.49; Cl, 41.66%).

As is shown in Fig. 1, the infrared spectra of the two complexes show very similar absorption bands, while both are vastly different from that of *p*-chloranil.

Specific Resistivity.—The specific resistivities of the samples were measured in a vacuum with pellets prepared by pressing them at more than 7000 kg./cm^2. For the pellets of the three polyferrocenyls, aluminum foils prepared by vacuum evaporation on thier surfaces were used as electrodes. For the pellets of ferrocene, nickelocene and the two complexes, the electrodes were prepared with an electroconductive paint, "Dotite paint, Type S-1",[6] because of the failure of the application of the aluminum evaporation method. In the latter cases, after the painting of the electrodes on the surfaces of the pellets, they were evacuated under a high vacuum in order to exclude any solvent which might have remained in them.

The relationship between the logarithm of the specific resistivity and the reciprocal of the temperature is shown for three polyferrocenyls in Fig. 2. The specific resistivities at room temperature are listed in Table I. The energy gap, ΔE_g, was determined from the temperature dependence of the resistivity according to the following equation:

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[1] a) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962); b) I. M. Pauskin, L. S. Polak, T. P. Vishnyakova, I. I. Patalakh, F. F. Machus and T. A. Sokolinskaya, *Doklady Akad. Nauk S. S. S. R.*, **149**, 856 (1963); *J. Polymer Sci.*, Part C, No. 4, 1481 (1964).

[2] K. Hata, I. Motoyama and K. Azuma, to be published in this Bulletin; read before the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[3] H. Watanabe, I. Motoyama and and K. Hata, This Bulletin, **38**, 853 (1965).

[4] K. Hata, I. Motoyama and H. Watanabe, ibid., **37**, 1719 (1964); **39**, 790 (1966).

[5] J. C. Goan, E. Berg and H. E. Podall, *J. Org. Chem.*, **29**, 975 (1964).

[6] A product of Fujikura Kasei Co.

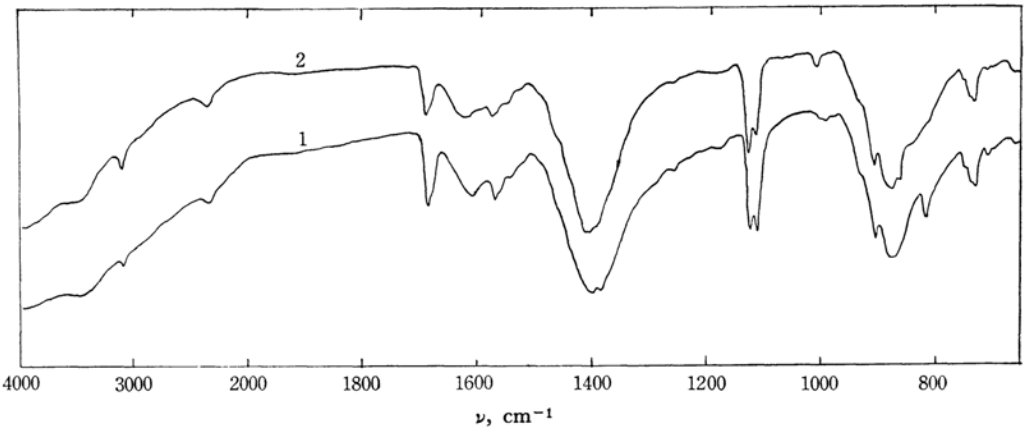

Fig. 1. Infrared spectra of the charge transfer complexes in KBr disk.
1: $(C_{10}H_{10}Ni)(C_6Cl_4O_2)_2$ 2: $(C_{10}H_{10}Co)(C_6Cl_4O_2)_2$

$$\rho = \rho_0 \exp (\Delta E_g/2\boldsymbol{k}T)$$

All of these metallocene derivatives have higher electric conductivities than those of the original metallocenes. The two metallocene-*p*-chloranil complexes have especially high electric conductivities, but they are apt to decompose during the measurements. The electric resistivity shows a minimum at 40—45°C, indicating decomposition at this temperature. Therefore, the energy gaps could not be determined for these substances.

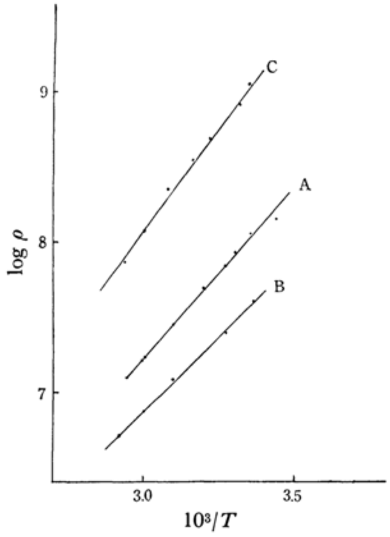

Fig. 2. Temperature dependence of the resistivity.
A: terferrocenyl B: quaterferrocenyl
C: sexiferrocenyl

TABLE I. ELECTRIC PROPERTIES OF THE SAMPLES

Sample	Specific resistivity at room temperature, Ω·cm.	Energy gap ΔE_g, eV.
Ferrocene	10^{12}	—
Nickelocene	10^{11}	—
Terferrocenyl	10^{8}	0.8
Quaterferrocenyl	10^{7}	0.9
Sexiferrocenyl	10^{9}	1.1
Nickelocene-*p*-chloranil complex	10^{5}	—
Cobaltocene-*p*-chloranil complex	10^{6}	—

A solution of the cobaltocene-*p*-chloranil complex in acetonitrile gave a sharp ESR signal, while the nickelocene-*p*-chloranil complex gave no signal. From these facts it may be concluded that the former is present in the form of a charge transfer anion radical, $[C_{10}H_{10}Co^+][C_6Cl_4O_2]_2^{\dot{-}}$, in the solution, and the latter, in the form of a charge transfer anion, $[C_{10}H_{10}Ni^{2+}][C_6Cl_4O_2]_2^{2-}$, as has been pointed out by Goan and his coworkers,[1a,5] and by other investigators.[7] Finally, it can be concluded that these polyferrocenyls and charge transfer complexes have the properties of semiconductors.

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[7] O. W. Webster, W. Mahler and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962); M. Rosenblum, R. W. Rish and C. Bennett, ibid., **86**, 5166 (1964).