REACTION OF FERRICINIUM FLUOROBORATE
WITH AMMONIUM THIOCYANATE AND OF FERROCENE
WITH DITHIOCYANOGEN

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Earlier we described the direct cyanidation of ferricinium salts with potassium cyanide or hydrocyanic acid [1-3]. In the present work we have studied the reaction of ferricinium salts with certain derivatives of thiocyanogen, which is the nearest analog of cyanogen.

Ferricinium fluoroborate reacts with ammonium thiocyanate in aqueous solution with partial disruption of the ferrocene nucleus to form the sparingly soluble ferricinium ferrithiocyanate, \((C_{10}H_{10}Fe)_{3}[Fe(SCN)_{6}]\), the structure of which we determined by gamma-resonance spectroscopy [4]. During the reaction a small amount of ferrocene is formed:

\[
(C_{10}H_{10}Fe)BF_{6} + NH_{4}SCN \rightarrow (C_{10}H_{10}Fe)_{3}[Fe(SCN)_{6}] + C_{10}H_{10}Fe
\]

Ferricinium ferrithiocyanate is also formed when ferrocene reacts with dithiocyanogen in chloroform and methylene dichloride:

\[
C_{10}H_{10}Fe(\text{SCN})_{2}(C_{10}H_{10}Fe)_{3}[Fe(SCN)_{6}]
\]

When thiocyanic acid reacts with ferricinium ferrichloride under conditions in which hydrocyanic acid reacts with it to form a nitrile, products from substitution of the hydrogen atoms in the ferrocene nucleus are not formed. After reduction ferrocene is obtained from the reaction mixture in a yield of about 80%. Thus the behavior of the thiocyanate anion in the reaction with the ferricinium compound and of dithiocyanogen in the reaction with ferrocene is similar to the behavior of halogens and their anions [5] and differs widely from the behavior of the cyanide ion and dicyanogen in analogous reactions.

The reactions of ferrocene with halogens and pseudohalogens and of ferricinium salts with the respective anions probably occur through the formation of the intermediate product \(C_{10}H_{10}Fe\sim X\) [6], which then undergoes different transformations depending on the nature of X:

\[
C_{10}H_{10}Fe^{+} \xrightarrow{X^-} C_{10}H_{10}Fe + X
\]

\[
C_{10}H_{10}FeX \xrightarrow{X^-} C_{10}H_{10}Fe + X
\]

\[
C_{10}H_{10}FeCl \xrightarrow{CN^-} C_{10}H_{10}FeCN
\]

The directions of the processes which occur within the \([C_{10}H_{10}Fe\sim X]^{-}\) complex may be compared with the standard oxidation-reduction potentials for the systems: \(C_{10}H_{10}Fe\sim C_{10}H_{10}Fe^{+} + e^-\) and \(X^+ + 2e^- = 2X^-\). The oxidizing capacity of the halogens and the pseudohalogen decreases in the order \(Cl > Br > SCN > I > CN\);

*The specimens used for comparison were tetramethylammonium ferrithiocyanate and ferrothiocyanate, \([N(CH_{3})_{4}]_{3}[Fe(SCN)_{6}]\) and \([N(CH_{3})_{4}]_{4}[Fe(SCN)_{6}]\), the preparation of which is described in the experimental section of the paper.
ferricinium falls between I and CN. In accordance with the $E_0$ values chlorine, bromine, dithiocyanogen, and iodine oxidize ferrocene to the ferricinium cation, while the degree of disruption of the ferrocene system increases with the oxidizing capacity of the agent; dicyanogen does not oxidize ferrocene. The reaction of Cl, Br, and SCN anions with ferricinium salts proceeds with the splitting off of cyclopentadienyl ligands and the formation of complex anions containing iron $\text{[FeHal}_4\text{]}^-$ and $\text{[Fe(SCN)}_6\text{]}^{-3}$ which remove the unreacted ferricinium from the reaction sphere as sparingly soluble salts. The formation of ferrocene evidently occurs as a result of reduction of ferricinium by cyclopentadienyl anions formed by a reaction involving exchange of ligands [9]. With $X = \text{CN}$, because of the lower $E_0$ value for the system $(\text{CN})_2 + 2\text{e}^- \rightarrow 2\text{CN}^-$ compared with the ferrocene $\rightarrow$ ferrocinium system, it becomes possible for an oxidation-reduction process between the $(\text{CN})$ ligand and the adduct (ferrocinium cation) to occur inside the coordination sphere, with subsequent migration of the CN-group to a five-membered ring of the ferrocene.

EXPERIMENTAL

Reaction of Ferricinium Fluoroborate with Ammonium Thiocyanate. When solutions containing 2.73 g of ferricinium fluoroborate [3] in 20 ml water and 25 g ammonium thiocyanate in 50 ml water were mixed a reddish-brown precipitate was formed. It was filtered off, washed with water, dried, and washed free from ferrocene with ether. The yield of ferricinium ferrithiocyanate was 1.6 g (50% calculated on the amount of ferricinium fluoroborate taken). After recrystallization from nitromethane with ether the salt was obtained in the form of a dark green crystalline powder. Found %: C 44.36; H 3.02; N 9.13; S 20.09; Fe 22.54. $\text{C}_{36}\text{H}_{30}\text{N}_{6}\text{S}_{6}\text{Fe}_4$. Calculated %: C 44.90; H 3.14; N 8.73; S 20.03; Fe 23.19.

From the aqueous mother liquor, after reduction with sodium thiosulfate and subsequent extraction with ether, 0.65 g ferrocene was obtained (24% theoretical).

Action of Dithiocyanogen on Ferrocene. A solution of dithiocyanogen in chloroform (obtained from 32 g lead thiocyanate and 5 ml bromine) was gradually added to a solution of 20 g ferrocene in chloroform. The precipitate was filtered off, washed with chloroform, and dried. The yield of ferricinium ferrithiocyanate was 2.4 g (8%). The salt was purified by reprecipitation with benzene from a solution in nitromethane. Found %: C 44.46, 44.57; H 3.06, 3.11; N 8.60, 8.81; S 19.86, 19.86; Fe 23.22, 23.14.

From the mother liquor, after distilling off the solvent, 18.7 g unreacted ferrocene was isolated (90% of the initial amount). Ferricinium ferrithiocyanate was also obtained in the reaction with methylene dichloride. Found %: C 44.24; H 3.03; N 9.22; S 19.91; Fe 23.46.

Tetramethylammonium Ferrithiocyanate $[\text{N(CH}_3\text{)}_4]\text{[Fe(SCN)}_4\text{]}$. This was obtained by mixing aqueous solutions of potassium ferrithiocyanate [10] and tetramethylammonium bromide and recrystallizing from absolute alcohol. The substance is green in the crystalline state, but its solutions in water and alcohol are red. Found %: C 34.86, 34.34; H 5.77, 5.94; Fe 9.37. $\text{C}_{18}\text{H}_{36}\text{N}_{6}\text{S}_{6}\text{Fe}$. Calculated %: C 34.51; H 5.79; Fe 8.92.

Tetramethylammonium Ferrothiocyanate $[\text{N(CH}_3\text{)}_4]\text{[Fe(SCN)}_3\text{]}$. This was obtained by evaporating an aqueous solution containing potassium ferrothiocyanate [11] and tetramethylammonium bromide under vacuum. The light-pink crystals were washed with a small amount of water and alcohol and dried. Tetramethylammonium ferrothiocyanate is readily soluble in water and alcohol; it oxidizes in air, and all the operations were therefore performed under nitrogen. Found %: C 37.48, 37.70; H 7.16, 7.00; N 19.63, 19.34; Fe 7.82, 7.35. $\text{C}_{22}\text{H}_{48}\text{N}_{6}\text{S}_{6}\text{Fe}$. Calculated %: C 37.72; H 6.91; N 20.00; Fe 7.97.

CONCLUSIONS

1. Ferricinium fluoroborate reacts with ammonium thiocyanate to form ferricinium ferrithiocyanate, which is also obtained by the action of dithiocyanogen on ferrocene.

2. Only the cyanide anion reacts with the ferricinium cation, replacing a hydrogen atom by the CN-group on the rebound; the thiocyanate and halide ions break the ferrocene nucleus.

LITERATURE CITED

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*The $E_0$ values in the same order, are respectively 1.359, 1.087, 0.77, 0.62, and 0.18 V [7]. $E_0$ for the ferrocene $\rightarrow$ ferrocinium system is 0.56 V [8].