Academician A. N. NESMEYANOV, Corresponding Member of the USSR Academy of Sciences D. N. KURSANOV,

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Abstract

Full Text

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M. N. NEFEDOVA, V. N. SETKINA, E. G. PEREVALOVA

REPLACEMENT BY A PROTON OF A HALOGEN IN HALOGENOFERRROCENES

In studying the isotope exchange of hydrogen in acidic media, we discovered an unexpected reaction of iodoferrocene with acid. It turned out that, when solutions of iodoferrocene in organic solvents (benzene, methylene chloride) are treated with deuteriotrifluoroacetic acid (95 at.% deuterium), rapid formation of the ferricinium cation and of a complex compound of iodoferrocene with iodine is observed. After reduction with sodium sulfite, the ferricinium cation gives ferrocene containing 9.5 at.% deuterium, which corresponds exactly to replacement of an iodine atom by deuterium. In this case, the deuterium content does not increase with increasing duration of the reaction.

It is evident that, in the interaction of iodoferrocene with deuteriotrifluoroacetic acid, deuterium enters the ferrocene nucleus not as a result of isotope exchange of hydrogen, but as a result of replacement of an iodine atom by deuterium. At the same time ferrocene is oxidized to the ferricinium cation, which, as established earlier ([1]), does not enter into the reaction of isotope exchange of hydrogen with acid. If these processes (cleavage of iodine and oxidation of ferrocene) did not overlap in time, the ferrocene formed would enter into subsequent exchange with the acid, which proceeds at a high rate under the conditions described, and the resulting deuterium content would exceed that calculated for monodeuteroferrocene. Significantly, the iodoferricinium cation was not detected.

The other reaction product—a crystalline molecular complex of iodoferrocene with iodine—upon treatment with sodium thiosulfate forms iodoferrocene containing no deuterium. Similar complex compounds are formed when iodoferrocene is treated with free iodine ([2]).

On the basis of these facts we propose the following mechanism for the reaction described. Since it is known that in acidic media the iron atom in ferrocene is protonated ([3]), it is natural to suppose that the first stage of this reaction is attack of the iron atom by a deuteron. Subsequently the reaction represented by scheme (A) develops,

$$\text{(A)}\qquad C_5H_5FeC_5H_4J + D^+ \rightarrow C_5H_5FeC_5H_4J \cdots D^+ \rightarrow \left[\begin{matrix} C_5H_5FeC_5H_4 \\ \cdots \text{with J and D} \end{matrix}\right]^+ \rightarrow C_5H_5Fe^{\oplus}C_5H_4D + J^{\bullet}$$

$$2\mathrm{J}^{\bullet} \rightarrow \mathrm{J}_2;$$

$$\mathrm{C_5H_5FeC_5H_4J} + n\mathrm{J}_2 \rightarrow \mathrm{C_5H_5FeC_5H_4J} \cdot n\mathrm{J}_2.$$

In the transition state (I), iodine, possessing some negative charge, $-\delta$, approaches the deuteron and exchange of halogen for deuterium takes place. This reaction apparently proceeds by the type of ricochet substitution, similar to the ricochet cyanation reaction of ferricinium salts described earlier by us (^{4}–^{6}). But, in contrast to the reaction described, cyanation begins with attack by the anion CN^- on the iron atom of the ferricinium cation,

having a positive charge (scheme B),

(B) $\mathrm{Fe}^{+} + \mathrm{CN}^{-} \rightarrow \mathrm{Fe} \ldots \mathrm{CN} \rightarrow \left[\text{ ferrocene complex with H and CN }\right] \rightarrow \mathrm{Fc{-}CN} + \mathrm{H}\cdot$

It should be noted that the reaction we have discovered is similar to the reaction of reduction of substituted iodobenzenes by hydroiodic acid. Chogvill and Ridd (8) found that such reduction is an electrophilic substitution of iodine by the proton of the acid with elimination of the iodine cation, i.e., “protodeiodination,” the reverse of the iodination reaction. However, for bromo- and chlorobenzenes analogous reactions are unknown.

In the case of bromo- and chloroferrocenes, replacement of halide by deuterium is also observed, but to a much lesser extent than for iodoferrocene. In the interaction of haloferrocenes with acid, besides replacement of halide by a proton, reactions of isotopic hydrogen exchange and oxidation to the haloferrocenium cation may also occur (oxidation in a nitrogen atmosphere cannot be completely excluded). In the case of iodoferrocene the rate of protodehalogenation so greatly exceeds the rate of the competing reactions that this type of interaction becomes practically the only one. For bromo- and chloroferrocenes, isotope exchange of hydrogen is dominant. The bromo- or chloroferrocene recovered from the reaction amounts to 80–90% of the starting material, and its deuterium content is close to that calculated for isotopic equilibrium. Replacement of halide by a proton in bromo- and chloroferrocenes becomes noticeable only at a higher acid concentration and a longer reaction time than for iodoferrocene. But under these conditions oxidation to the haloferrocenium cation plays no smaller role, and after reduction of the oxidized form a mixture of haloferrocene with ferrocene is isolated.

At concentrations of trifluoroacetic acid in $\mathrm{CH_2Cl_2}$ from 30 to 70 vol.% replacement of halide by a proton plays a noticeable role for bromoferrocene and an entirely insignificant one for chloroferrocene. In the case of dihaloferrocenes, protodehalogenation reactions were not observed. Evidently, electron-acceptor substituents hinder this reaction.

It should be noted that Poson and Morrison (9) observed formation of the ferricenium cation on treating chloroferrocene with $AlCl_3$ in methylene chloride and explained this by the action of traces of $HAlCl_4$.*

Experimental Part

Interaction of iodoferrocene with deuteriotrifluoroacetic acid. To a solution of 0.6 g (0.0019 mole) of iodoferrocene (m.p. 45–46°, from methanol) in 1.5 ml of benzene, in a stream of dry pure nitrogen, was added 1 ml (40 vol.% acid) of deuteriotrifluoroacetic acid (95 atom.% deuterium, b.p. 71–72°), previously saturated with nitrogen. A violet coloration appeared immediately and a black-violet precipitate separated. After 1–2 hours the precipitate was filtered off, and the ferricenium cation was extracted from the filtrate with water. The blue aqueous extract was treated with sodium sulfite until a yellow color appeared and was extracted with ether. After removal of the ether, 0.09 g (0.005 mole) of ferrocene was isolated, m.p. 167–170°; after sublimation, m.p. 170–172°. Its deuterium content was 9.5 atom.% (analysis of the excess density of the combustion water). The precipitate was washed with benzene and purified by sublimation in vacuum.

Found, %: C 20.33, 20.37; H 1.55, 1.57; Fe 9.84, 10.12; I 68.75, 68.49

* Cleavage of chlorine and bromine from the phenyl nucleus was observed under the conditions of the Friedel-Crafts reduction reaction (10) in the preparation of the bis-(arene)chromium cation.

When the precipitate was treated with a saturated aqueous solution of sodium thiosulfate, followed by extraction with ether, iodoferrocene was isolated; after recrystallization from methanol, m.p. 44–45°.

Found, %: I 40.12, 40.23
$C_{10}H_9FeI$. Calculated, %: I 40.69

When chloroform solutions of iodine and iodoferrocene are combined, a dark-violet precipitate forms, which likewise sublimes in vacuo.

Found, %: C 17.28, 17.34; H 1.14, 1.15; Fe 7.68, 7.78

In the case where the reaction of iodoferrocene with trifluoroacetic acid containing 95 at.% deuterium was carried out for 24 hours, the ferrocene isolated after reduction of the aqueous layer contained 9.3 at.% deuterium.

Reaction of bromoferrocene with deuterotrifluoroacetic acid. To 0.2 g (0.0008 mole) of bromoferrocene (m.p. 32–33°) in 1 ml of benzene or CH_2Cl_2, under nitrogen, were added 2.2 ml (67 vol.% acid) of deuterotrifluoroacetic acid (40 at.% deuterium). A blue coloration appeared, but no appreciable precipitate formed. After 24 hours the mixture was treated with water, the aqueous layer was reduced with Na_2SO_3, and extracted with ether. A total of 0.025 g of a mixture of bromoferrocene with ferrocene was isolated. In this mixture, judging from the elemental-analysis data, there was 0.015 g (0.00008 mole, 10%

of the initial bromoferrocene) of ferrocene. From the organic layer, 0.17 g of bromoferrocene was isolated, containing 29.5 at.% deuterium, whereas the value calculated for equilibrium is 32.2 at.% deuterium.

Reaction of chloroferrocene with deuterotrifluoroacetic acid. Completely analogously to the reaction with bromoferrocene, the reaction of 0.2 g of chloroferrocene (m.p. 58–59°, from alcohol) with 1.4 ml (67 vol.% acid) of deuterotrifluoroacetic acid (40 at.% deuterium) in 0.7 ml of benzene or CH_2Cl_2 was carried out. After treatment of the reaction mixture with water, 0.17 g of chloroferrocene was isolated from the organic layer, containing 25.3 at.% deuterium (calculated for equilibrium, 27.2%). On reduction of the aqueous extract with sodium sulfite, 0.015 g of chloroferrocene was obtained, contaminated, according to the elemental-analysis data, with a small amount of ferrocene.

Institute of Organoelement Synthesis
Academy of Sciences of the USSR

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