Paramagnetic Ferrocene Acid Adducts*

By

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Ferrocene and proton acids, HB, form deeply coloured paramagnetic adducts. If the acid is HBF_4, $HClO_4$, $HFeCl_4$** or $HGaCl_4$**, the analytical composition of the adducts is compatible with the formula —

$$\{Fe(C_5H_5)_2\} \ldots - \{HB\} \qquad (1)$$

In the case of picric acid, or strong carboxylic acids, e.g., trichloro or trifluoroacetic acid, more than one acid molecule[1] combines with the iron complex. Most of the adducts are well crystallised solids, which can be prepared in a yield of over 90% of the theory and which can be purified to constant melting point[1], analytical composition[1], electronic spectrum[1] and magnetic susceptibility[1]. These species reduce benzoquinone to hydroquinone, bicarbonate to formic acid and nitrous oxide to nitrogen; other reductions have been mentioned before[1].

Conductometric measurement showed that the adducts are strong binary electrolytes, and it follows, therefore, that the adduct formation is accompanied by charge transfer. To obtain information about the nature of the ions, aqueous solutions of the adducts were treated with the potassium salt of a polystyrene sulphonic acid cation exchange resin. The potassium ions were replaced by the iron complex, and the solution was found to be free of iron. If the resin, with the iron complex, was suspended

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* This article is dedicated with many good wishes to Professor *F. Wessely* on the occasion of his 70th birthday.

** The preparation and properties of these acids will be described in a paper together with Dr. *R. J. Clark*.

[1] *M. Aly, R. Bramley, J. Upadhyay, A. Wassermann,* and *P. R. Woolliams*, Chem. Comm., September 1965.

in an aqueous solution of potassium chloride, the iron complex dissolved and an equivalent amount of potassium ions was absorbed. On treatment of an aqueous solution of the ferrocene acid adducts with a polystyrene ammonium salt anion exchange resin in the chloride form, all the iron complex remained in solution, while the anion of the adduct was adsorbed, with simultaneous release of an equivalent amount of chloride. These experiments prove that the iron complex of these adducts is a cation, and that neither the whole, nor a part of it, is an electroneutral or anionic species.

The ferrocene acid adducts, or their cations, prepared with the help of ion exchange resins, can be quantitatively converted into ferrocene by reaction with hydroxyl ions or nitrogen bases. The electronic spectrum of the cations of the adducts is identical with that of the ferricinium cation

$$\left\{\mathrm{Fe}(\overset{+}{\mathrm{C}}_5\mathrm{H}_5)_2\right\} \tag{2}$$

prepared by a one step anodic oxidation of ferrocene[2] and by other conventional oxidation reactions[3]. We believe, therefore, that the cation of the ferrocene acid adducts is species (2). Confirmatory evidence comes from the following considerations: The most probable mechanism which could operate in the conversion of ferrocene into a cation not identical with (2), is a proton transfer from the acid. This reaction would produce C—H or Fe—H bonds, or C—D or Fe—D bonds, if deuterated acids are used. The infrared spectra of these ferrocene acid adducts, including the spectrum of an adduct containing a deuterated acid, do not indicate that these bonds are formed.

If the electron removed from the ferrocene to produce the cation (2), together with an acid proton, were "lost", then ferrocene acid adducts would be conventional ferricinium salts

$$\left\{\mathrm{Fe}(\overset{+}{\mathrm{C}}_5\mathrm{H}_5)_2\right\} \overset{-}{B} \tag{3}$$

where $\overset{-}{B}$ is a diamagnetic anion*, unless such paramagnetic acids as $\mathrm{HFeCl_4}$ were used. This supposition is difficult to reconcile with the fact that adduct formation is not accompanied by evolution of hydrogen; nor is it compatible with other observations relating to the stoicheiometry of these reactions[1] and with kinetic evidence[1]. It is ruled out by the observed magnetic moments[1], which indicate two independent magnetic

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* Such ferricinium salts, e.g., the picrate and the iodide, have been described (see e.g., Ref. 3 and 4). The status of other "ferricinium salts" mentioned in the literature has to be re-assessed in view of our observations. This will be fully discussed elsewhere.

[2] *J. A. Page* und *G. Wilkinson,* J. Amer. Chem. Soc. **74,** 6149 (1952).

[3] *G. Wilkinson, M. Rosenblum, M. C. Whiting,* and *R. B. Woodward,* J. Amer. Chem. Soc. **74,** 2125 (1952).

spins (except in the adduct with $HFeCl_4$*) and by the E.S.R. spectra, which confirm the conclusion to be derived from the magnetic moments, that the paramagnetic cation (g values** at — 180° about 1 and 4) is neutralised by a paramagnetic anion (g value of trichloroacetic acid adduct in dichloromethane 2.016 ± 0.015). The latter signal did not occur with ferricinium salts of type (3). These observations are not in favour of the assumption that the anions of the ferrocene acid adducts are hydrogen atoms, trapped by acid anions. We believe that the anions

$$\bar{\mathrm{H}}\mathrm{B} \tag{4}$$

are proton acids with an electron, accommodated in an antibonding molecular orbital[7].

The hyperfine structure of the E.S.R. spectra could not be resolved and, therefore, the location of the electron in the radical anion (4) is unknown. It should be possible to obtain some insight into the nature of the anion (4) from its electronic spectrum, but measurements with solutions containing the deeply coloured cation (2) did not reveal extra peaks. Unsuccessful attempts were made to replace the cation (2) by a less coloured or colourless ion. These included experiments with cation exchange resins in the potassium or tetramethylammonium form, which adsorb the ferricinium cation, with release of potassium or tetramethylammonium ions. In this metathesis, one could have expected that the potassium or tetramethylammonium salt of anion (4) is formed, but it appears that the odd electron migrates into the resin.

The paramagnetic ferrocene acid adducts are fairly stable in absence of molecular oxygen. In aqueous solution, the rate of decomposition increases with increasing pH. The surprising stability at pH = 2 indicates that the expected reaction $H^+ + \bar{H}B \rightarrow H_2 + \dot{B}$ or $H + HB$ is overshadowed by the substitution $H^+ + \bar{B}H \rightarrow \bar{H}B + H^+$. That the H atom of the radical (4) can be replaced without disturbing the odd electron is shown by the results of tritium-hydrogen exchange experiments, some of which were carried out under conditions excluding the replacement of hydrogens in the cation (2) and with acids, the anions of which were free of hydrogen.

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* The magnetic moment of this adduct is 6.60 ± 0.03 B. M. in nitromethane (33.5°). This result will be discussed elsewhere.

** Prior to this work, attempts to detect the E.S.R. spectrum of species (2) have been unsuccessful (see e.g., Ref. 5 and 6): the reasons for this will be discussed in another paper where details of the results of our experiments will be given.

[4] *V. Engelmann*, Z. Naturforsch. **8 B**, 775 (1954); *I. Pavlik, J. Machacek, B. Stibr* und *O. Soehnel*, Sbornik Vedecych Praci **1964** (11), 37.

[5] *A. M. Maki* und *T. E. Berry*, J. Amer. Chem. Soc. **87**, 4437 (1965).

[6] *R. M. Golding* und *L. E. Orgel*, J. chem. Soc. **1962**, 363.

The actually observed tritium-hydrogen exchange is an additional argument against the supposition that these ferrocene acid adducts are ferricinium salts of type (3).

If our interpretation of these experiments is correct, one would expect that other electron donors, besides ferrocene, should also produce fairly stable radical anions of type (4). Flash photolysis[8] has revealed that proton acids (e.g., formic acid) can act as electron traps, and the existence of an intermediate $\overset{-}{\mathrm{H}}\mathrm{F}$ in the reaction between hydrogen atoms and fluoride ions has been made probable[9]. The life time of such species is many orders of magnitude smaller than that of the paramagnetic ferrocene acid adducts. Kinetic evidence[1] has shown that these adducts are formed in the presence of a suitable catalyst, and that this catalysed electron transfer is characterised by a relatively high energy and low entropy of activation. We believe, therefore, that the synthesis of stable complexes containing anions (4) neutralised by cations different from (2), depends on the detection of the right kinetic, rather than thermodynamic, reaction conditions.

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[7] *C. K. Ingold,* James Flack Norris Award Address, Atlantic City, September 1965.

[8] *J. K. Thomas, S. Gordon* und *E. J. Hart,* J. Physic. Chem. **68**, 1524 (1964); *J. K. Thomas,* Radiation Res. Suppl. **4**, 87 (1964); *J. M. Baxendale,* ibid. p. 114.

[9] *M. Anbar* und *P. Neta,* Trans. Farad. Soc. **63**, 141 (1967).