Paramagnetic Ferrocene Acid Adducts. Kinetics of Electron Transfer to Proton Acids

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ON addition of ferrocene to the acids listed in Table 1, adducts A–F are formed; these were purified by recrystallisation or solvent extraction to constant melting points and magnetic susceptibilities. The formulae are based on satisfactory elemental analyses; the formula weights of adducts A and D were confirmed by measuring the unit-cell dimensions of the crystals.* Within the range 200—2000 mμ, the electronic spectra, in water, of the deeply coloured adducts show peaks at 250 mμ ($\log \epsilon = 4{\cdot}07$—$4{\cdot}59$) and 620 m$\mu$ ($\log \epsilon$ 2·44—2·65); adducts D and E show a third peak at 355 mμ, owing to the presence of picric acid. All the adducts are paramagnetic, but electron spin resonance signals could not be observed. Static susceptibilities are field-independent; the magnetic moments, μ_{eff} of the solid adducts at 20° are between 2·57 and 2·89 B.M.; the ratios μ_{eff} (20°)/μ_{eff} (−195°) were between 1·01 and 1·16. The magnetic moments of adduct A in water, nitromethane, and methylene chloride did not increase with increasing dielectric constant of the solvent. In nitromethane solution the magnetic moments of most of the adducts increase with decreasing solute concentration, c; values relating to $c = 10^{-3}$M are in column 6 of Table 1.

Most adducts were prepared with solvents saturated with molecular oxygen, but adduct A was also obtained with degassed solvents; under the experimental conditions the ratio $[O_2]$/[adduct isolated] $< 10^{-3}$. No chloride ions were formed and no reaction occurred on mixing ferrocene with ethyl trichloroacetate.

The results of Zerewitinoff determinations, potentiometric titrations with alkali in water, and conductometric titrations with piperidine in methylene chloride prove the presence of n acid protons (see last column of Table 1). On addition of an excess of dilute alkali to adduct A, alkali trichloroacetate, identified by conversion into *p*-chlorobenzyl thioureatrichloroacetate is formed. The infrared spectra of the adducts are, on the whole, a superposition of the spectra of the components. The spectrum of an adduct prepared from ferrocene and deuterotrichloroacetic acid showed no peaks due to bonds between deuterium and iron or carbon atoms. These experiments prove that there is no proton transfer from the acids to ferrocene.

The molar electrical conductances, Λ, of the adducts in nitromethane are of the order of magnitude to be expected for strong 1 : 1 electrolytes. Dissociation is confirmed by determination of van't Hoff *i*-factors. (Under the same concentration conditions, 10^{-3}—10^{-4} mole/l, the Λ values of the free acids are an order of magnitude smaller). The cation of the electrolytes must be the ferricinium ion, the electronic spectrum of which is known[1] to show the two peaks at 620 and 250 mμ. The magnetic moments indicate that the electron removed from the ferrocene is transferred to the acids. In dilute solution, when the paramagnetic cations and anions are well separated from each other, the magnetic moment should be $\sqrt{2} \times 1{\cdot}73 = 2{\cdot}44$ B.M., if the g-value of cation and anion were close to 2·0. The μ_{eff} values in Table 1 are all larger than 2·44 B.M., which can be accounted for by orbital magnetism of the ferricinium cation. We believe that the electron removed from ferrocene is trapped by acid protons, in the same way as electrons abstracted from alkali-metals in liquid ammonia or amines are trapped by protons of the N–H bonds.[2] These ferrocene acid adducts are regarded as charge transfer salts, $[(C_5\overset{+}{H_5})_2Fe]\ [\overset{-}{(HB)}(HB)_{n-1}]$, where $(HB)_{n-1}$ are formally neutral acid molecules, which may participate in the trapping process. The figures in the last column of Table 1 show that n varies from 1—4. The concentration-dependence of the magnetic moments can be explained by an equilibrium $2e_1 \rightleftharpoons e_2$, where e_1 is the paramagnetic monomeric anion, while e_2 is a spin-paired diamagnetic dimer. The equilibrium seems to be shifted towards the side of e_1 if the concentration is decreased, as with alkali-metal–ammonia solutions.[3]

Chemical evidence for the trapped electrons is

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* These experiments were carried out by Dr. J. H. Milledge.

[1] For references see G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, 1958, **1**, 1.

[2] For references see H. C. R. Symons, *Quart. Rev.*, 1959, **13**, 99.

[3] S. Freed and N. Sugarman, *J. Chem. Phys.*, 1943, **11**, 354.

as follows. In aqueous solution, pH 2—6, metallic silver is formed from silver nitrate, cuprous or ferrous ions from cupric or ferric salts, and iodide from iodine. In these reactions the ferricinium cation does not participate, as shown by the electronic spectra. On addition of picric acid to the aqueous solutions of adduct A, pH $=2{\cdot}5$, the ferrocene–picric acid adducts D and E crystallise out. The latter could also be obtained by direct interaction of ferrocene and picric acid in benzene. It follows, therefore, that an electron trapped by one proton acid can be transferred to a different acid. Another acceptor is the ferricinium cation: if the adducts A–F are dissolved in water at pH > 7 or in methylene chloride containing a strong base, ferrocene is formed. It appears, therefore, that the removal of the proton from HB reverses the original electron transfer.

The kinetics of the reaction between ferrocene and the acids listed in Table 2 were measured by determining the increase of optical density at 620 mμ. The rate is relatively slow and not reproducible if the solvents (second line of Table 2) are degassed or flushed with nitrogen. In the presence of molecular oxygen the rate of adduct formation is reproducible, considerably larger and given by

$$\mathrm{d}x/\mathrm{d}t = kc(a - x)\,(b - x) \qquad .. \qquad (1)$$

where c, $a - x$, and $b - x$ are the concentrations of oxygen, acid, and ferrocene, and k is the rate constant, numerical values of which are in the last line of Table 2. The experiments show that these electron-transfer reactions are catalysed by molecular oxygen,** which is possibly due to the formation of a bridged activated complex. As the ferrocene–acid adducts contain n acid molecules per mole, their formation should occur in n steps. The observed rate is proportional to the first power of the acid concentration and we conclude, therefore, that only one acid molecule participates in the slow stage (2), and that reactions (3), involving the other $n - 1$ acid molecules and "intermediates" $i_1, i_2, \ldots i_{n-1}$ are not rate-determining.

$$\text{ferrocene} + \text{acid} + O_2 \xrightarrow{k} i_1 + O_2 \qquad (2)$$

$$\left.\begin{aligned} i_1 + \text{acid} &\xrightarrow{k_1} i_2 \\ i_{n-1} + \text{acid} &\xrightarrow{k_{n-1}} \text{adduct} \end{aligned}\right\} \qquad .. \qquad (3)$$

The rate of the oxygen-catalysed formation of the ferrocene—trichloroacetic acid adduct in benzene was measured at five temperatures and it was found that the Arrhenius equation with $E = 9{\cdot}5 \pm 0{\cdot}8$ kcal./mole and $A = 10^{4\cdot6 \pm 0\cdot7}$ (l/mole)^2 sec.$^{-1}$ is obeyed.

TABLE 1

Acid	*Solvent*	*Formula, m.p., and ref. designation of adducts*			*μ_{eff} (B.M.) 33·5°, in CH_3NO_2, $c = 10^{-3}$M*	*n*
Cl_3CCO_2H	.. C_6H_6, CCl_4, CH_2Cl_2	$C_{16}H_{13}O_6Cl_9Fe$	126—128°	A	2·98 ± 0·05	3
F_3CCO_2H	.. C_6H_6, none	$C_{16}H_{13}O_6F_9Fe$	Liquid	B	2·91 ± 0·05	3
Cl_2HCCO_2H	.. None	$C_{18}H_{18}O_8Cl_8Fe$	,,	C	2·7 ± 0·1	4
Picric	H_2O	$C_{16}H_{13}O_7N_3Fe$	166—167	D	2·75 ± 0·05	1
	H_2O, C_6H_6	$C_{22}H_{16}O_{14}N_6Fe$	119—120	E	3·1 ± 0·1	2
HBF_4	.. Et_2O	$C_{10}H_{11}BF_4Fe$	228	F	2·90 ± 0·05	1

TABLE 2

Acid	*F_3CCO_2H*	*Cl_3CCO_2H*		*Cl_2HCCO_2H*	*ClH_2CCO_2H**
Solvent	C_6H_6	C_6H_6	CH_2Cl_2†	C_6H_6	C_6H_6
No. of runs ..	5	27‡	13	6	6
k (l^2 mole^{-2} × min.$^{-1}$), 25° ..	0·44 ± 0·10	0·22 ± 0·03	0·86 ± 0·1	0·061 ± 0·012	0·0040 ± 0·0012

* The adduct formed from ferrocene and monochloroacetic acid was not isolated, but characterised in solution by its electronic spectrum, electrical conductance, and paramagnetic susceptibility.

† The dielectric constant of methylene chloride is about four times larger than that of benzene.

‡ One of these runs was performed in the dark and another in intense illumination (λ = 400—600 mμ); there was no detectable photo-effect.

** For other electron transfer processes catalysed by oxygen, see ref. 4.

[4] J. A. N. Scott, B. D. Flockhart and R. C. Pink, *Proc. Chem. Soc.*, 1964, 139; and references there cited to earlier work.

It is of interest to compare the velocity constants, *k*, in the last line of Table 2 with the proton-transfer constants, *K*, of the four acids. Taking the *K*-values given in reference 5, the following linear functional relationships of the Brönsted type is obtained, with $\alpha = -0{\cdot}75 \pm 0{\cdot}1$ and $\beta = 1{\cdot}3 \pm 0{\cdot}1$; $-\log k = \alpha \log K + \beta$. This is compatible with the assumption that in the bridged activated complexes of reaction (2) partial proton-transfer occurs and that this is more easy if the acid is relatively strong. Partially ionic transition states are also in accordance with the fact that the rate of adduct formation increases with increasing dielectric constant of the solvent, as shown by the *k*-values in columns 3 and 4 of Table 2.

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[5] J. Upadhyay, P. Gaston, A. A. Levy, and A. Wassermann, *J. Chem. Soc.*, 1965, 3252.