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Preliminary communication

Substituent effects in the ESR spectra of ferricenium cations

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In the last few years several studies on the effect of substituents on the electron density in the cyclopentadienyl rings and iron atom of ferrocene have been described[1-3]. Recently it has been demonstrated that electron spin resonance spectra of ferricenium can be measured at low temperatures[4]. Molecular parameters derived from ESR spectra can be of great help in an analysis of electronic effects, and we therefore decided to study the effects of substituents on the ESR spectrum of the ferricenium cation.

The cations of the ferrocene derivatives were prepared by oxidation with iodine or, whenever the oxidation potential of the derivative was too high for iodine, with sulphuric acid. As carbonium ions were formed in sulphuric acid[5], the ferricenium cations of the α-hydroxyalkyl-substituted compounds could be prepared only with iodine. Most compounds were commercially available, a few were prepared according to methods given in the literature[1,6]. The results of our ESR measurements on solid solutions at 20 K are shown in Table 1. Figure 1 indicates how the line positions and line widths were determined.

From the observed g values the orbital reduction factor k and the factor x can be evaluated[4], $x = \zeta/\delta$ in which ζ is the one-electron spin-orbit coupling parameter and δ

TABLE I

g VALUES AND MOLECULAR PARAMETERS FOR SUBSTITUTED FERRICENIUM CATIONS

Substituent	$g_{\parallel}$	$g_{\perp}$	$\Delta H_{\parallel}$, G	$\Delta H_{\perp}$, G	k	x
H [a]	4.35	1.26	140	2500	0.76	1.23
CH_3 [b]	4.17	1.47	160	1500	0.80	0.92
CH_2OH [b]	4.20	1.49	180	1500	0.82	0.90
CH_3CHOH [b]	4.13	1.51	220	1500	0.81	0.87
CH_3OCH_2 [b]	4.13	1.55	200	1500	0.84	0.82
$(CH_3)_2NCH_2$ [a]	4.11	1.55	230	1400	0.83	0.82
1-CH_2-CH_2-CH_2-1′ [b,c]	3.80	1.64	130	400	0.79	0.70
1,1′-$(CH_3)_2$ [b]	3.83	1.67	160	460	0.83	0.66
1,1′-$(C_4H_9)_2$ [b]	3.88	1.68	230	600	0.86	0.65
CH_3CO [a]	3.62	1.76	130	220	0.85	0.54
CHO [a]	3.63	1.77	180	300	0.88	0.53
diindenyliron [a]	2.65	1.99	75	24	(0.80)	0.21

[a] In H_2SO_4. [b] In acetone, counterion I_3^-. [c] 1,1′-trimethyleneferrocene.

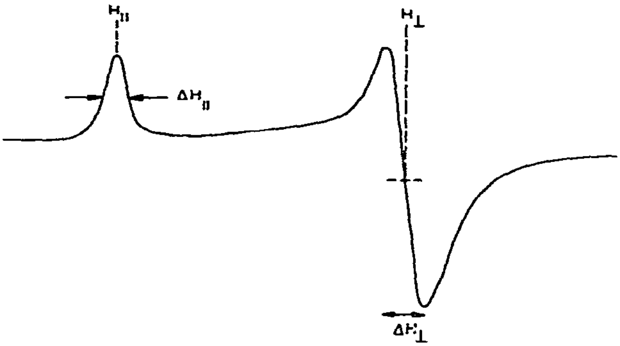

Fig.1. Line positions and line widths in the solid-solution ESR spectra.

measures the strength of the distortion from axial symmetry. Considering the uncertainties of the measurements, the k values of the compounds listed in Table 1 do not vary much. The x values, however, show a considerable spread and this demonstrates that the main effect of a substituent is perturbation of the axial symmetry of the ferricenium cation. This is in accordance with conclusions drawn from Mössbauer[3] and oxidation-potential[1,2] measurements. Substitution in the σ skeleton has only an indirect effect on the π orbitals and will therefore not greatly influence the strength of the interaction between the iron $3d_2$ and e_{2g} ligand π orbitals. The ESR spectra show that all compounds studied can, in a first-order approximation, be treated as axially symmetric compounds. The distortion of the symmetry by the substituents is only weak, which is reflected in the fact that $\delta = \zeta/x$ is one or two orders of magnitude smaller than Δ, where Δ is the axial ligand-field splitting between the e_{1g^*} and e_{2g} orbitals[4].

In addition to the compounds listed in Table 1 we have examined several others, especially those expected to have high δ and low x values. With 1,1′-diacetylferrocene in H_2SO_4 we did not detect any ESR signal. When 1,1′-dicarboxylferrocene was brought into H_2SO_4, gas evolution occurred and an ESR spectrum was recorded with $g_{\parallel} = 3.58$ and $g_{\perp} = 1.76$. This suggests that CO_2 had been formed and that the ESR spectrum belongs to the cation of mono-substituted carboxylferrocene (*cf.* Table 1). When monoacetylferrocene and 1,1′-diacetylferrocene were oxidized in acetone with oxidants such as $(NH_4)_2Ce(NO_3)_6$, $AgClO_4$ and KIO_3 (with a few drops of H_2SO_4 added), ESR spectra were observed with g values and line widths very much the same as those of the α-substituted monoalkylferricenium and 1,1′-dialkylferricenium cations. Thus, acetylferrocene gave a spectrum with $g_{\parallel} = 4.12$ and $g_{\perp} = 1.54$ and 1,1′-diacetylferrocene one with $g_{\parallel} = 3.90$ and $g_{\perp} = 1.65$. We do not know yet what happens in these systems, but it is possible that the acetyl groups are converted into hydroxyl groups.

An additional remark should be made for the diindenyliron cation. Since the $g_{\perp}$ value for this cation is so close to the free-spin value, there is no point in evaluating x from $g_{\perp}$ and then using this x value to evaluate k from $g_{\parallel}$, as was done for the other cations[4]. Therefore we assumed $k = 0.80$ and from $g_{\parallel} = 2.65$ we found $x = 0.21$. With these x and k values $g_{\perp}$ was calculated to be equal to 1.96. Since only first-order contributions to $g_{\perp}$ were taken into account, we think that the difference between this value and the experimental one is within reasonable limits.

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