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Electron spin resonance spectra of ferricenium salts

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Fritz, Keller and Schwarzhans[1] have shown that because of too short a spin-lattice relaxation time the ESR spectrum of $FeCp_2^+$ cannot be observed at 77 K. Substitution, however, increases the spin-lattice relaxation time, and ESR spectra of several substituted ferricenium cations can be found at 77 K[2,3,4].

Recently, Horsfield and Wassermann[5] claimed that an ESR signal of ferricenium trichloroacetate can be observed at 77 K if the salt is prepared in a special way. We have repeated the preparation of ferricenium trichloroacetate according to the method of Aly *et al.*[6,7], and found the same ESR spectra for this compound ($g_{\parallel} = 3.10 \pm 0.05$ and $g_{\perp} = 1.90 \pm 0.05$) at 77 K as did Horsfield and Wassermann[5]. But on cooling the samples to 20 K, we also found a much stronger spectrum superposed on the former and identical with the g-values found by Prins *et al.*[2,3,4] for the $FeCp_2^+$ cation. After prolonged storage of the ferricenium trichloroacetate we found that the ESR signals at 77 K had vanished, but the strong spectrum at 20 K had remained the same.

Our results clearly demonstrate that the ESR signal with $g_{\parallel} = 3.1$ and $g_{\perp} = 1.9$ is much weaker than the signals detected at 20 K, and prove that the former signal must be attributed to an impurity and the latter to the $FeCp_2^+$ cation. A comparison with g-values of substituted ferricenium cations indicates that the impurity may be a disubstituted ferricenium cation. Its g-values are close to those of the 1,1′-diacetylferricenium cation[8], $g_{\parallel} = 3.4$ and $g_{\perp} = 1.8$, and suggest that the impurity may well be the 1,1′-ditrichloroacetylferricenium cation.

In addition, we would like to comment on the unusual proton acid radical anion which is supposed to be present in the ferricenium salts of Aly *et al.*[6,7]. These authors described the synthesis of ferricenium salts by oxidation of ferrocene in the presence of proton acids, and stated that during the oxidation an electron was transferred from ferrocene to an antibonding orbital of the anion. Although in this way the formation of a paramagnetic radical anion might be expected, the authors detected an ESR signal (g-value of the trichloroacetic acid adduct 2.016 ± 0.015) only in a few cases. ESR studies of carboxylic acid radical anions in the solid state, however, have shown[9] that these radical anions are unstable above 140 K. The formation of carboxylic acid radical anions at room temperature is therefore highly unlikely.

In our opinion it is much more probable that the oxidation of ferrocene takes place with oxygen:

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O$$

(E_0 = 1.23 V, whereas the oxidation potential of ferrocene is 0.59 V), and that the counterion of the $FeCp_2^+$ cation is the trichloroacetate anion. Besides, the g-values of 2.016 of the ESR signal detected by Aly *et al.* is different from those of other carboxylic acid radical anions (g = 2.0029 ± 0.0003)[9] and is in fact equal to that of $FeCl_4^-$ (g = 2.015 ± 0.005), which may have been formed by a decomposition reaction of the ferricenium cation.

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