Radical Anions Formed by Reaction of Cobaltocene with Protic Acids

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Summary Addition of protic acids to cobaltocene in benzene produces two types of cobalticinium salts with either colourless diamagnetic or coloured paramagnetic anions; the latter were characterised by their magnetic, spectral, and chemical properties and are considered to contain anions formed by donation of an electron from cobaltocene to an undissociated molecule of acid.

REACTION of cobaltocene with a several-fold excess of pure trichloroacetic acid in dry de-aerated benzene at 20° for 48 h gave a product from which two salts (I) and (II), m.p.s 126—128°, could be separated by recrystallisation from benzene or dichloromethane. These were formed (> 95% yield) in the proportions 7 : 3 or 1 : 9 when cobaltocene that had been prepared according to two different procedures,[1,2] and thrice sublimed was respectively used. Reaction at −80° over a period of 14 days led essentially to only (II) in about 12% yield.

(I) was stable, as are most conventional cobaltocinium salts;[3] whereas (II) was unstable and decomposed after a few days at room temperature in the solid state. It also decomposed rapidly in solution in tetrahydrofuran although it could be stored in benzene for some days.

Evidence for the radical nature of the anion of (II) was the effective magnetic moment of $1{\cdot}80 \mp 0{\cdot}1$ B.M. that is indicative of a species with one unpaired spin. This moment was deduced from field-independent susceptibilities measured in the solid state and in benzene by the Gouy or n.m.r. methods. Compound (II) also showed a weak, but reproducible, e.s.r. signal with g between 2·001 and 2·004 according to whether the measurements (77 K—293 K) were made with powders, with glasses, or with solutions of benzene, nitromethane or dichloromethane. ΔH_{pp} was between 8 and 50 G and there was no hyperfine splitting. On addition of water to a solution of (II) in benzene containing 0·3M trichloroacetic acid, the e.s.r. signals disappeared and (I) was produced quantitatively together with an equivalent of hydrogen. No magnetic moment or e.s.r. signals could be detected for (I).

(I) had absorption bands in the u.v. characteristic of a conventional cobalticinium salt;[4] λ_{max} (C_6H_6) 275, 400 nm with no absorption above 450 nm; whereas (II) in solution in dichloromethane, nitromethane, or benzene was green with, in addition to the lower wavelength peaks of (I), a peak, λ_{max} (benzene) 665 nm (ϵ *ca.* 60 to 80), attributable to a radical anion. (I) showed no reducing properties, whereas (II) reduced iron(III) chloride to the iron(II) ion (10% conversion, aqueous C_6H_6 system, 0 °C); sodium bicarbonate to formic acid and acetaldehyde (2% conversion, aqueous C_6H_6 system, 0 °C); and benzoquinone to hydroquinone (up to 40% conversion, C_6H_6, 0—20 °C). The low yields in aqueous media are probably due to preferential reaction with protons to give hydrogen. These results indicate that (I) and (II) contain conventional anions and radical anions respectively, and suggest that (II) is analogous to the stable ferricinium acidides† that have

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† This name was suggested to the authors by Professor Sir Christopher Ingold.

been isolated:[5–8] by analogy with the latter, and consistently with elemental analyses, we propose the formulae $(C_5H_5)_2Co^+B^-(BH)_2$ and $(C_5H_5)_2Co^+(BH^-)(BH)_2$ for (I) and (II) ($B = Cl_3C{\cdot}CO_2$).

Cobalticinium salts, which also contain radical anions, were obtained from reaction of cobaltocene with trifluoro-, dichloro-, and mono-chloro-acetic acids, picric acid, and diphenylphosphoric acid. These showed similar properties to (II) and their formation was accompanied by diamagnetic salts similar to (I).

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