Electron Spin Resonance Spectra of Ferricinium

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The e.s.r. spectra of ferricinium salts have been independently investigated by Horsfield and Wassermann and by Prins and his co-workers, but the results do not agree. An attempt is made to explain this.

RESULTS derived from the e.s.r. spectrum of the ferricinium cation are of theoretical interest (see *e.g.*, ref. 1) so it is worth while to attempt to explain the differences between our earlier results [2] and those of Prins and his co-workers.[3,4]

EXPERIMENTAL

The preparation and analysis of ferricinium trichloroacetate, picrate, and iodide have been described.[2,5,6] Solvents were dried and redistilled. The technique of measuring e.s.r. spectra and the apparatus were as before.[2] For temperatures of *ca.* 20 K, 77 K, and higher the Varian Dewar vessel and variable-temperature set up were used. A few tests at 4·2 K were made in the National Physical Laboratory, Teddington, with a previously described [7] apparatus. Optical spectra were measured with a Unicam SP 800 instrument. All solution spectra were taken a few minutes after dissolution. In the case of the frozen solutions, the concentrations relate to *ca.* 20 °C.

Spectroscopic splitting factors, *g*, derived from e.s.r. spectra of ferricinium salts

	Counter ion	Measurements	T/K	$g_{\parallel}$	$g_{\perp}$	Line shape
Ref. 1	Trichloroacetate	Powdered crystals CH_2Cl_2,H_2O (pH 3)	20, 77, 103 77	3·15—3·35	1·82—1·87	Normal
	Picrate	Powdered crystals	77	3·15	1·82	
Ref. 3, 4	I_3^-,BF_4^-	Acetone Dimethylformamide	20	4·35—4·36	1·26—1·30	Abnormal

RESULTS AND DISCUSSION

The line-shape of the signals obtained in the first set of experiments (Table) is in accordance with expectation (*cf.* ref. 8), while the shape of the ' ferricinium spectrum ' given in ref. 4 is highly abnormal. The discrepancy of the ' $g_{\parallel}$ values ' in the first and second lines of the Table

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[1] Y. S. Sohn, D. N. Hendrickson, and M. B. Gray, *J. Amer. Chem. Soc.*, 1970, **92**, 3233.

[2] A. Horsfield and A. Wassermann, *J. Chem. Soc.* (*A*), 1970, 3202.

[3] R. Prins and F. J. Reinders, *J. Amer. Chem. Soc.*, 1969, **91**, 4929.

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[5] M. M. Aly, Ph.D. Thesis, London, 1968.

[6] D. P. Jopling, Ph.D. Thesis, London, 1968.

[7] S. F. S. Reed and D. H. Whiffen, *Mol. Phys.*, 1967, **12**, 159.

[8] F. K. Kneubühl, *J. Chem. Phys.*, 1960, **33**, 1074.

is particularly large and corresponds to differences of *ca.* 500 G.

Pure ferricinium salts are stable in the solid state * if air is excluded. Solutions of ferricinium salts are moderately stable in de-aerated aqueous solution at pH <4 or in de-aerated aprotic solvents, *e.g.*, dichloromethane. Rapid decomposition occurs, on the other hand, at pH >4 (see ref. 6) or in non-aqueous solvents which can act as proton acceptors. That acetone, which is mentioned in ref. 3, is an unsuitable solvent has been suspected before [9] and our experiments confirm this. Dimethylformamide is much worse. This follows from the optical spectra in Figure 1, and similar effects were observed with other ferricinium salts. We conclude that the '$g_{\parallel}$ tensors' in the second line of the Table relate to a decomposition product of the ferricinium cations.

To confirm this we have measured the e.s.r. spectrum of ferricinium picrate without solvent (*cf.* ref. 2) and in frozen solution of acetone and dimethylformamide. The solution spectra in Figure 2 show a low-field signal of apparent g value 4·4, for which there is no counterpart in the spectrum of the powdered crystals. We believe that the relatively strong low-field signal is due to Fe^{3+} ions formed by decomposition of ferricinium (*cf.*, *e.g.*, ref. 10 or the inset of Figure 2) and it is likely that the tail of the Fe^{3+} signal overshadows the low-field ferricinium signals. Alternatively the presence of decomposition products could produce line broadening, so that the signal at *ca.* 2000 G cannot be observed.

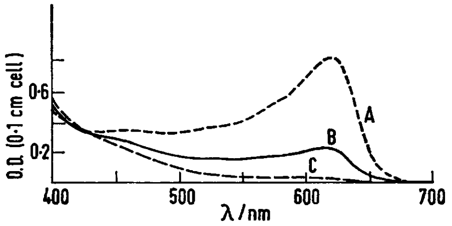

FIGURE 1 Optical spectra of ferricinium trichloroacetate, 0·0173 mol l^{-1} at *ca.* 20 °C. The solvents are: A, water (pH *ca.* 3) and dichloromethane; B, acetone; C, dimethylformamide. The ε values (620 nm) are A, 510 ± 40; B, 154 ± 20; C, <20 l mol^{-1} cm^{-1}

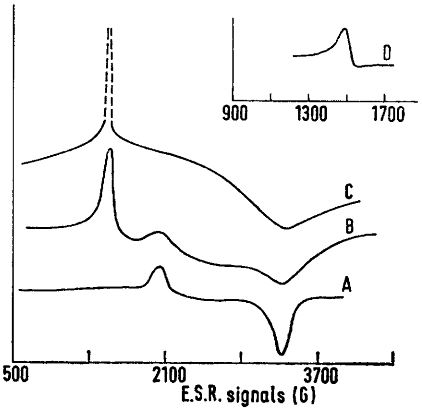

FIGURE 2 E.s.r. spectra of ferricinium picrate at 77 K; A, Powdered crystals, without solvent: $g_{\parallel} = 3{\cdot}15 \pm 0{\cdot}01$; $g_{\perp} = 1{\cdot}82 \pm 0{\cdot}01$; B, solution in acetone, 0·085M: ferricinium signals $g_{\parallel} = 3{\cdot}18 \pm 0{\cdot}03$, $g_{\perp} = 1{\cdot}84 \pm 0{\cdot}02$. Low-field 'decomposition signal': apparent g value, $g = 4{\cdot}41 \pm 0{\cdot}02$; C, solution in dimethylformamide, 0·046M: ferricinium signals: $g_{\parallel}$ not observed; $g_{\perp} = 1{\cdot}92 \pm 0{\cdot}04$. Strong low-field 'decomposition signal': apparent g value $4{\cdot}47 \pm 0{\cdot}02$. (Inset) Aqueous solution of freshly prepared ferric chloride (3×10^{-3}M) in 0·1M-HCl; the apparent g value of the signal is $4{\cdot}27 \pm 0{\cdot}01$

We have also tested ferricinium iodide (see ref. 4): without solvent resolved signals could not be obtained, even at 4·2 K. This must be due to impurities formed during the preparation, which produce line broadening. (Pure ferricinium trichloroacetate crystals give a good spectrum up to 103 K). When ferricinium iodide was tested in acetone or dimethylformamide at *ca.* 20 and 77 K, a similar low-field 'decomposition signal' was observed, as in Figure 2.

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* Ferricinium trichloroacetate crystals (ref. 2) gave a well resolved ferricinium spectrum after 3 years' storage (*ca.* 293 K, in the dark) in an evacuated silica vessel.

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[10] R. Aasa, *J. Chem. Phys.*, 1970, **52**, 3919.