

The AgH⁺ Radical Ion: Electron Spin Resonance Evidence

By R. S. EACHUS and M. C. R. SYMONS*

(Department of Chemistry, The University, Leicester, LE1 7RH)

THE low-temperature irradiation of frozen aqueous acids containing silver (I) salts results in the formation of a new paramagnetic species, which has the properties expected for AgH⁺. The e.s.r. spectrum of this radical was poorly resolved at 77°K, but sharpened markedly on warming.

The (AgH)⁺ radical is thought to be formed either by the direct reduction of silver(I) ions by radiation-produced hydrogen atoms or through tautomeric rearrangement of a complex of the form (AgOSO₃H)²⁻, produced by direct electron trapping.

E.s.r. parameters for the AgH⁺ radical ion and related species

Radical	Nucleus	Hyperfine coupling ^a (in gauss)				<i>g</i> -Tensor ^a				<i>a</i> ² (1s) (H)	<i>a</i> ² (5s) (Ag)	<i>a</i> ² (4 <i>d</i> _{z²}) (Ag)
		<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>A</i> ₁₈₀	<i>g</i> ₁₁	<i>g</i> ₂₂	<i>g</i> ₃₃	<i>g</i> _{av}			
(AgH) ⁺	¹⁰⁹ Ag	-12.8	-11.6	+24.4	+103.6	2.046	2.036	2.002	2.028		0.14	~0.3
	¹ H	-1.3	+0.7	+0.7	+302.3					0.55		
[Ag ⁰ (SO ₄ ²⁻) ₂]	¹⁰⁹ Ag				686				1.9995		0.97	
Ag ⁰ (aq.)	¹⁰⁹ Ag				702				2.000		0.99	
(AgOCH ₃) ⁺	¹⁰⁹ Ag				~120				~2.004		~0.17	

* Derived from the Breit-Rabi relationship⁵

The e.s.r. parameters quoted in the Table for this centre were derived from the spectrum of a frozen solution of Ag₂SO₄ in 7.2M-aqueous H₂SO₄, after irradiation at 77°K, and annealing to 165°K. Our analysis was confirmed with isotopically enriched ¹⁰⁹Ag₂SO₄ in 7.2M-D₂SO₄ in D₂O, and measuring e.s.r. spectra at both X- and S-band frequencies. These results are most readily interpreted if we assume that the anisotropic contribution to the ¹⁰⁹Ag hyperfine coupling arises from direct spin density in the 4*d*_{z²}-orbital. The orbital populations given in the Table were derived on this basis, and the fact that the total spin density is close to unity supports our interpretation. The radical can be formally envisaged as the silver(II) hydride (Ag²⁺-H⁻), where significant mixing of the silver 4*d*_{z²}- and 5s-orbitals reflects the high degree of covalency of this ion, evidenced by the large delocalisation of spin density on to hydrogen. These results are in marked contrast with those for the NaH⁺ centre in barium sulphate, where the unpaired electron is strongly confined to the proton.¹

The e.s.r. spectrum (Figure) of a glassy sample of γ -irradiated 0.1M-Ag₂SO₄ in frozen 7.2M-aqueous H₂SO₄ is characterised by signals from four centres at 77°K. A strong featureless absorption centred close to the free-spin *g*-value, arises from the radiation produced hole-centre in the host matrix.² A broad anisotropic quartet of features spread over approximately 600 gauss and centred at lower field, is associated with the (AgH)⁺ adduct, whilst aquated silver atoms are thought to be responsible for the weaker, poorly resolved doublets at low and high fields.³ [Naturally occurring silver has two isotopes ¹⁰⁹Ag (48.1%) and ¹⁰⁷Ag (51.9%) both of which have nuclear spin *I* = ½, and have nuclear magnetogyric ratios of 1.422 × 10⁻⁴, and 1.237 × 10⁻⁴, respectively.] The remaining detectable paramagnetic species, giving rise to the remarkably narrow-lined doublet of doublets separated by approximately 650 gauss, is thought to be the bis-sulphato-complex [Ag(SO₄)₂]⁴⁻. Each of the hyperfine features from this centre is accompanied by a very weak doublet of satellite lines, separated by approximately

10.6 gauss at low fields and 14.4 gauss at high field, whose intensity with respect to the major feature increases as the microwave power is increased. This is characteristic of

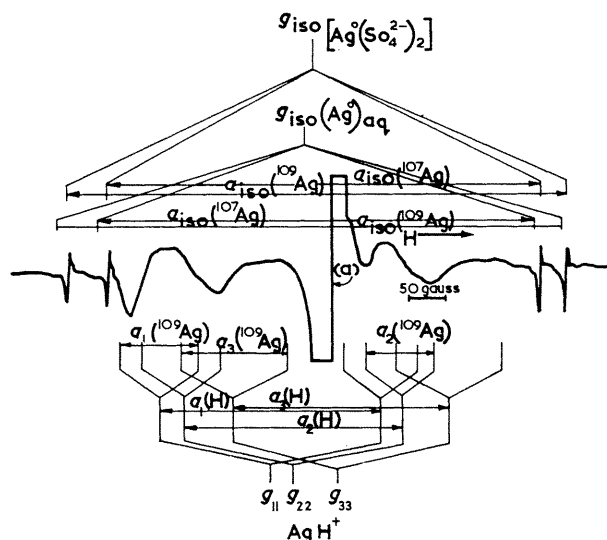


FIGURE. The e.s.r. spectrum of γ -irradiated 0.1 M- Ag_2SO_4 in glassy 7.2 M-aqueous H_2SO_4 measured at 77° K. The feature marked (a) is assigned to the radiation produced hole-centre in the sulphate matrix. For clarity, only e.s.r. features arising from the ^{109}Ag isotope have been indicated for the AgH^+ radical-anion.

features arising from sympathetic neighbouring proton nuclear spin-inversions, generally detected for hydrogen atoms in this matrix.⁴ The concentration of this radical reaches a maximum in the 7.2M-aqueous acid environment, and hyperfine features from this centre were not detectable at acid concentrations lower than 6.5M or greater than 7.9M.

When a frozen solution of silver perchlorate in methanol was exposed to γ -rays, the paramagnetic radiation-damage products stabilised at 77°K were silver atoms, and the CH_2OH and CHO radicals.³ Subsequent annealing of the sample resulted in the formation of the Ag_2^+ ion,³ and a new paramagnetic species characterised by a broad, intense doublet. We have assigned this spectrum to the $(\text{AgOCH}_3)^+$ radical for the following reasons. (i) The silver isotropic hyperfine coupling of approximately 120 gauss is similar to that observed for the AgH^+ radical ion. (ii) No major proton hyperfine couplings were detected; the e.s.r. spectrum of the radical being unaffected, except for a small line-width reduction, when studied in a CD_3OD matrix. (iii) The intensity of hyperfine features from this radical increased with the simultaneous decrease in intensity of features from the CH_2OH centre.

The corresponding species $(\text{AgOCH}_2\text{CH}_3)^+$ is thought to have been formed when a frozen solution of AgClO_4 in ethanol was irradiated at liquid-nitrogen temperature, and subsequently annealed.

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