Reactions of Ag^I Ions in Alcohols after Radiolysis at 77 K

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Solutions of silver perchlorate in methanol, ethanol, ethane-1,2-diol, isopropyl alcohol, allyl and propargyl alcohols have been exposed to ⁶⁰Co y-rays at 77 K and the resulting radicals studied using ESR spectroscopy. In addition to CH₂OH solvent radicals, methanolic solutions gave Ag¹¹ centres and a number of discrete Ag^o species. The latter exhibited a range of hyperfine couplings, reflecting various degrees of solvation. Their relative yields were shown to vary according to initial Ag^I concentration and with added sodium perchlorate. After annealing to ca. 120 K, Ag⁰ gave way to the molecular cluster cations Ag_2^+ , Ag_3^{2+} , Ag_4^{3+} and Ag_5^{4+} , previously identified by ESR and optical spectroscopy in a range of systems and shown to be formed by the sequential addition of Ag^I ions. Ag₅⁴⁺ formation was favoured either by high initial Ag^I or high counterion (nitrate or perchlorate) concentration. During the silver aggregation process the solvent radicals (CH_2OH) decayed and the adduct $[Ag.CH_2OH]^+$ was formed $[A_{iso}(Ag) =$ 128 G]. On annealing to the softening point of the matrix these species were lost. No higher-nuclearity molecular centres were detected. However, a weak singlet in the free-spin region grew in. This is tentatively assigned to conduction electron spin resonance (CESR) in pseudo-metallic, Ag_n^0 particles. On further melting the Ag_n^0 signal disappeared and the sample became black, indicating the eventual formation of colloidal silver. Similar reactions were observed in ethanol, ethane-1,2-diol and isopropyl alcohol.

The allyl alcohol system did not give any clearly defined Ag^0 centres, only solvent radicals being observed at 77 K. Two possible silver-solvent adducts were detected after annealing, one with a larger $A_{1so}(Ag)$ value than expected (*ca.* 360 G). Results for propargyl alcohol were similar, except that only one silver-solvent species was formed. Possible structures for these centres are discussed. When both systems were annealed to the matrix softening point, the adduct signals decayed and an isotropic singlet in the free-spin region was revealed. This signal was particularly strong in the propargyl system. The *g* value and linewidth are similar to values recently reported for CESR signals from Ag_n^0 latent-image particles formed in silver halide matrices by photolysis.

The study of silver atoms and silver clusters is of great interest in the fields of surface physics and chemistry, heterogeneous catalysis and the photographic process. These have been prepared in a variety of matrices including inert gases, zeolites, organic and aqueous media.¹ Silver atoms and the paramagnetic molecular cluster cations Ag_2^+ , Ag_3^{2+} , Ag_4^{3+} and Ag_5^{4+} , formed after the radiolysis of aqueous and alcoholic Ag^I solutions at 77 K have been characterised using conjoint ESR and optical techniques.^{2–5} Conduction electron spin resonance (CESR) signals, which have some characteristics in agreement with theoretical electronic models,^{6,7} have been reported for pseudo-metallic silver agglomerates formed in CO₂ and organic matrices at 77 K⁻ using an atomic beam technique^{8,9} and photolytically in silver halide matrices between 90 K and room temperature.¹⁰ Various organo-silver radicals have also been prepared from the reaction

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of silver atoms and ions with a number of saturated and unsaturated organic molecules at cryogenic temperatures. $^{\rm 11-15}$

Here we have used ESR to study solutions of Ag^{I} ions in methanol, ethanol, isopropyl alcohol, ethane-1,2-diol, allyl and propargyl alcohol, exposed to ionizing radiation at 77 K. A more complete picture of the reactions of Ag^{I} ions in these systems has emerged. In some cases, a complete pathway which includes the initial formation of silver atoms and, on subsequent annealing, the formation of molecular silver clusters and pseudometallic silver particles has been established. Several novel silver–solvent radical adducts formed during the course of these annealing studies have also been detected.

Experimental

Salts and solutions were of the highest grade available and were used without further purification. $^{107}AgClO_4$ was prepared by refluxing ^{107}Ag powdered metal (98.2% enrichment, Oak Ridge Laboratories, Tennessee) with perchloric acid (Hopkin and Williams). ^{13}C -enriched methanol was obtained from Amersham International.

Samples were either placed into quartz tubes prior to freezing to 77 K or frozen as small beads by dropping into liquid nitrogen. They were irradiated at 77 K using a Vickrad ⁶⁰Co γ -source with doses of *ca*. 0.8 Mrad. Typical exposures were *ca*. 30 min.

ESR spectra were recorded at *ca*. 77 K using a Varian E109 X-band spectrometer. Samples were annealed above 77 K either using a commercial variable temperature attachment or by decanting liquid nitrogen from the quartz insert Dewar and allowing the sample to warm, with continuous monitoring of the ESR spectrum, before re-cooling to 77 K.

Results and Discussion

It is convenient to consider each type of centre in turn, going from atom-like centres to cationic clusters, to silver aggregates and finally to solvent-radical silver adducts.

Silver-atom Centres

One of the most remarkable results of studies of Ag^0 centres formed by electron capture (1) has been the multiplicity of subtly different centres formed :^{2, 16, 17}

$$Ag_{solv}^{+} + e^{-} \to Ag_{solv}^{0} \to Ag^{0}.$$
 (1)

In our view, these differences reflect the fact that Ag^+ ions are strongly solvated in water and alcohols, and the solvent shell is not initially lost on electron addition. Loss of solvent molecules should occur in stages, giving rise to different centres, some being asymmetric.² Ultimately, the unsolvated atoms are formed. In general, as solvent is shed, the atomic character increases. This was clearly established by measuring the shift in the optical spectra.² However, in some systems, $A_{iso}(^{109}Ag)$ actually decreases on annealing. We have interpreted this in terms of s-p mixing, induced by the asymmetry of the solvates.

In the present work, we have studied the effect of increasing the concentration of $AgClO_4$ in methanol and CD_3OD , and have extended the range of alcohols to include isopropyl alcohol, ethane-1,2-diol and the unsaturated alcohols allyl alcohol and propargyl alcohol.

Methanol

The effect of increasing $[AgClO_4]$ is shown in fig. 1. There is a remarkable difference between dilute and concentrated solutions. For the former, two species dominate. One is the 'unsolvated' atom and the other must be quite strongly solvated. The former has



Fig. 1. First derivative, X-band, ESR spectra for a range of Ag⁰ centres in alcohols formed after the exposure of unenriched AgClO₄ in CD₃OD at various concentrations (*a*)–(*d*) and with added NaClO₄ (*e*) to ⁶⁰Co γ -rays at 77 K. Each centre gives rise to low- and high-field doublets corresponding to the isotopes ¹⁰⁹Ag and ¹⁰⁷Ag, (*I* = 1/2) which have approximately equal natural abundance. For the sake of clarity, only the low-field (-1/2) features are shown.

sharp features, as expected for trapped atoms, but so has the latter, which is most unexpected and contrasts with results for more concentrated solutions. The fact that CD_3OD was used must contribute to the lack of broadening, but the implication must be that only one, highly specific solvate, is present. This is presumably the primary $Ag^+(CD_3OD)_n$ solvate. This means that *n* is a precise number, probably 4, by comparison with other data.^{18, 19}

As $[AgClO_4]$ increases, so ion-ion interaction becomes important, and a range of slightly different solvates are clearly present. Also, features for Ag_2^+ can be detected. At these concentrations reaction (2) becomes important:

$$Ag^{0} + Ag^{+} \rightarrow Ag \cdot Ag^{+}$$
⁽²⁾

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solvent	species	$-A_{iso}(^{109}\text{Ag})/\text{G}^{a, b}$	$-A_{iso}(^{107}\text{Ag})/\text{G}^{a, b}$	$g_{ m iso}$	
MeOD	I	615	533	2.002	
	II	625	541	2.000	
	III	655	568	2.000	
	IV	722	624	2.002	
EtOD	$vii^{c}(\doteq II)$	621	538	1.999	
	$ix^{c}(\neq III)$	661	573	1.999	
PrOH	(≑I)	616	533	1.996	
CH_OHCH_OH		560	485	1.998	
2 2 2	(≑II)	638	553		

Table 1.	ESR	data	for	Ag ⁰	centres	observed	after	the	exposure	of	AgClO ₄	solutions	to	⁶⁰ Co
				-		γ-ray	s at 7'	7 K			-			

^a 1 G = 10⁻⁴ T. ^b Silver has two magnetic isotopes, ¹⁰⁷Ag ($\mu_N = -0.1130$) and ¹⁰⁹Ag ($\mu_N = -0.1299$). They have almost equal abundance. Note that their moments are negative so that the numbers quoted herein are actually -A values. This convention is commonly used to stress the fact that positive spin densities are involved. ^c Nomenclature taken from ref. (2).

The fact that unsolvated atoms are no longer detected suggests that reaction (2) primarily involves attack by unsolvated Ag^{0} rather than by the solvated entities.

Another remarkable fact is that, for dilute solutions, desolvation seems to be 'all or nothing', in that only the two centres are significant. The fact that they coexist even on slight annealing is interpreted in terms of desolvation occurring for the 'hot' Ag⁰ centre before it has time to relax to its equilibrium state. Once this relaxation has occurred, the shedding of solvent molecules requires considerable thermal energy. The changes induced by increasing salt concentration are clearly due to cation-anion interactions, rather than cation-cation interactions, since NaClO₄ had a very similar effect [fig. 1(d)]. Species III is favoured, with properties quite close to gas-phase values, although the lines remain very broad. We assume this is a specific ion pair, which is probably less strongly solvated than the normal cations. Data for these centres are given in table 1.

Isopropyl Alcohol

Only one major Ag^0 centre was obtained for this solvent [see outer features in fig. 5(a) below]. This has parameters close to those for methanol centre II.

Ethane-1,2-diol

Two species with almost equal concentrations were initially detected. One of these has parameters quite close to those for the methanol centre II. The other has a value for $A_{iso}(Ag)$ significantly lower than methanol centre I. No unsolvated atomic centres were obtained.

Allyl and Propargyl Alcohols

It is interesting that neither of these solutions gave significant yields of either Ag^0 centres or cluster centres such as Ag_2^+ or Ag_4^{3+} . This can be understood in terms of reactions (3) and (4), which we have established for the radiolysis of the pure alcohols.

$$CH_2 = CHCH_2OH + e^- \rightarrow CH_2 - CH - CH_2 + OH^-$$
(3)

$$HC \equiv CCH_2OH + e^- \rightarrow HC^- \equiv C - CH_2 + OH^-.$$
(4)

For simple alcohols, ROH, reaction with electrons is slow, and electron trapping (solvation) is favoured. However, for these alcohols, no e_t^- centres were detected, but good yields of the allyl and propargyl radicals, well characterised by their ESR spectra were obtained. Clearly, Ag^+ ions are unable to compete significantly with reactions (3) or (4), so Ag^0 centres are not important.

Silver Cluster Cations

Silver atoms, formed from the cations in a range of solvents, show a remarkable tendency to form cationic clusters:

$$Ag_2^+ + Ag^+ \rightarrow Ag_3^{2+} \tag{5}$$

$$Ag_3^{2+} + Ag^+ \to Ag_4^{3+} \tag{6}$$

[see also reaction (1)]. All the evidence suggests that these are formed in a stepwise manner, the $Ag_4^{3^+}$ cluster being the most stable. Typical spectra are shown in fig. 2 and data are given in table 2. Neutral clusters of up to seven atoms are well established,²⁰⁻²² and are structurally quite well understood. However, it is remarkable that one electron is able, apparently, to hold four cations together, despite the larger charge repulsion. Some degree of solvation must help, but we have never seen any clear explanation for this effect. We have therefore attempted to show that these well defined, stable centres really are $Ag_4^{3^+}$ units and not Ag_4^+ with three bonding electrons. The stoichiometry can be gauged by following the loss of Ag^0 to give Ag_2^+ , and the loss of Ag_2^+ to give Ag_4 species. The results establish that each Ag^0 gives rise to one Ag_4^+ unit. This points strongly to the $Ag_4^{3^+}$ representation.

In another series of experiments, we annealed irradiated samples to give solutions characterised by intense quintets for Ag_4 units and exposed these samples at 77 K to high radiation doses. Marked loss of the quintets was observed, but unfortunately we have not achieved two-electron addition to give the Ag_4^+ species (unless this cluster is not detectable by ESR spectroscopy).

Even more surprising has been the identification of a species thought to be $Ag_5^{4+.5}$ This centre has a far more complex ESR spectrum than those of the other cluster cations [fig. 2(d)]. Computer analysis, after subtraction of features due to Ag_2^+ ions, gave a reasonable fit for three strongly coupled silver nuclei (140 G) and two weakly coupled nuclei (55 G) (table 2). As usual for these cationic clusters, there are significant shifts to low g values, indicating important contributions from p orbitals, although the hyperfine anisotropy is always small.

Although we were able to detect Ag_3^{2+} and Ag_5^{4+} centres under carefully controlled conditions, there is no doubt that the most stable cluster is Ag_4^{3+} , having four equivalent silver nuclei and, probably, a tetrahedral structure. This centre was the final product for all the saturated alcohols. For allyl alcohol and propargyl alcohol, extremely weak features, probably due to various clusters, were observed, but these are not important intermediates. This accords with the absence of Ag^0 centres, which are, presumably, precursors. This means that the species responsible for the intense singlet obtained from the propargyl alcohol system on annealing, which we assign to large silver agglomerates (see below) is not formed from stable cation clusters of the type discussed here.

Silver Agglomerates

When the irradiated solid solutions were annealed close to their softening points, all signals were lost irreversibly, but in some cases single lines close to free-spin were detected. The best example was for the propargyl alcohol system, which is surprising in view of the absence of Ag^0 centres (fig. 3 and table 3). These signals were not obtained



Fig. 2. First-derivative X-band ESR spectra for the silver-cluster cations (a) Ag_2^+ , (b) Ag_3^{2+} , (c) Ag_4^{3+} , (d) Ag_5^{4+} , after the exposure of unenriched $AgClO_4$ (0.05–0.50 mol dm⁻³) in CD₃OD to ⁶⁰Co γ -rays at 77 K and subsequent annealing in the region *ca.* 100–130 K. In (a) and (b), features resulting from the various possible ¹⁰⁹Ag and ¹⁰⁷Ag isotopic combinations can be clearly seen [in (c) and (d) the linewidths were too broad to resolve these]. (Central solvent features are not shown.)

in the absence of silver ions. Also, on annealing to the melting points and re-freezing, the signals were lost, but the samples became black from the formation of colloidal metal particles.

The singlet obtained with the propargyl alcohol system has a width (18 G) and g value (2.0036) similar to CESR signals obtained from silver particles deposited in CO_2 , C_6H_6 and $C_{18}H_{38}$ matrices using an atomic beam technique.^{8,9} We have obtained very similar signals from latent-image silver particles formed during the photolysis of silver halide microcrystals.¹⁰ Data for all these centres are given in table 3.

		$-A(^{109}Ag)/G$					
species	solvent	A_{\perp}	A_{\parallel}	A _{av}	g_{\perp}	g_{\parallel}	$g_{\rm av}$
Ag ₂ ⁺	MeOD EtOD PrOH	307 307 300	312 312 308	310 309 303	1.970 1.977 1.968	1.997 1.999 1.992	1.979 1.984 1.976
Ag_{3}^{2+}	MeOD			195	—		1.975
Ag ₄	EtOD	150	155	150 152	1.951	 1.967	1.962 1.956
Ag_5^{4+a}	MeOD			140(3) 55(2)	1.979	1.946	1.968
	EtOD		—	140(3) 55(2)	1.973	1.943	1.963

Table 2. ESR data for molecular silver clusters observed after the exposure of $AgClO_4$ solutions to ⁶⁰Co γ -rays at 77 K and subsequent annealing

^{*a*} Data derived from a computer simulation.



Fig. 3. First-derivative X-band ESR spectra for pseudo-metallic silver agglomerates formed after the exposure of $AgClO_4$ (0.50 mol dm⁻³) in EtOD and CHCCH₂OH to ⁶⁰Co γ -rays at 77 K and annealing to the matrix softening point.

Table 3. X-Band ESR data for Ag_n^0 centres observed after the exposure of $AgClO_4$ solutions to ⁶⁰Co γ -rays at 77 K and extended annealing (CESR data for Ag_n^0 centres formed in other systems is also given)

matrix	gino	$\Delta H_{\rm nn}/{\rm G}$
 EtOD	2.002	9
CHCCH ₂ OH	2.0036	18 1526
$CO_{2}^{9}, C_{6}H_{6}, C_{18}, H_{38}^{9}$	2.008-2.016	30 12 19 5
AgCl emulsion ¹⁰ AgBr emulsion ¹⁰	2.0042-2.0051 2.0035	12–18.5 19–21

Solvent Radical Adducts

Saturated Alcohols

Some time ago a well defined doublet centre was detected after annealing irradiated solutions of silver salts in methanol.¹¹ This was assigned to Ag^+ —OCH₃ centres. We have also detected centres of this type, but suggest that they are not Ag^+ —OR units but are best interpreted in terms of the structure



(I)

formed by the reaction

$$\mathbf{R}_{2}\mathbf{COH} + \mathbf{Ag}^{+} \to \mathbf{Ag}^{+} \cdot \mathbf{CR}_{2}(\mathbf{OH}).$$
⁽⁷⁾

Some examples are given in fig. 4 and data in table 4. The major reason for this new assignment is that Ag^+ —OMe is better written as Ag^{2+} —OMe⁻. Given that other solvent ligands are also present, such centres should have ESR signals typical of Ag^{II} complexes. Indeed, Ag^{II} centres are often detected as minor products in the systems described herein. Also, RO⁻ radicals, although formed from alcohol molecules on irradiation following electron ejection [reaction (8)]:

$$R_{2}CHOH \rightarrow R_{2}CHOH^{+} \rightarrow R_{2}CHO + (H^{+})$$
(8)

are unstable and convert to R_2 COH radicals very rapidly at 77 K [reaction (9)]:

$$R_2 CHO \rightarrow R_2 COH.$$
 (9)

Since the silver-radical adducts are not formed at 77 K, but only begin to grow in around 130 K, they cannot be formed from RO[•] radicals, nor is there any obvious route starting with Ag^0 centres. However, the adduct doublets grow in as the $R_2\dot{C}OH$ signals are lost, in a 1:1 manner. As shown below, all the ESR evidence supports the $Ag^+ \cdot CR_2(OH)$ formulation, and this structure is used from hereon.

Notable results are: (i) the $Ag^+ \cdot CH_2(OH)$ adducts give no detectable proton coupling, but the lines narrow on going to $Ag^+ \cdot CD_2(OD)$. (ii) A clear doublet splitting appears on each feature for $Ag^+ \cdot {}^{13}CH_2(OH)$. (iii) For $Ag^+ \cdot CH(CH_3)(OH)$ an extra *ca*. 40 G doublet is found, and for $Ag^+ \cdot C(CH_3)_2(OH)$ a 38 G triplet is observed (fig. 5). These splittings must be due to one specific proton in the CH₃ groups. This means that $-CH_3$ rotation is restricted specifically, such that there is good overlap for one C—H bond and



Fig. 4. First-derivative X-band ESR spectra for various silver-solvent adducts formed after the exposure of AgClO₄ (0.05–0.50 mol dm⁻³) in (a) MeOH, (b) EtOH, (c) CH₂OHCH₂OH, (d) CH₂CHCH₂OH, (e) CHCCH₂OH to ⁶⁰Co γ -rays at 77 K and annealing to ca. 120 K (residual solvent features are not shown).

Table 4. ESR	data for	silver-solv	vent	addu	cts obse	erve	d after	the
exposure of	AgClO ₄	solutions	to	⁶⁰ Co	γ-rays	at	77 K	and
subsequent annealing								

			A(¹³		
adduct	$-A(^{109}Ag)/G$	<i>a</i> (¹ H)/G	A_{\parallel}	A_{\perp}	g
Ag ⁺ ·CH _o OH	128		80	30	2.000
Ag ⁺ ·CH(Me)OH	132	40(1H)	_		2.000
Ag ⁺ ·CH(CH ₀ OH)OH	107				2.002
Ag ⁺ · C(Me _s)ÔH	115	38(2H)			2.002
Ag ⁺ ·CH ₃ CHCH ₃	180			—	1.993
Ag ⁺ ·CH _a CCH ^a	90		_		1.994
$Ag \cdot H^{+27}$	104	302	—		—

^a Ref. (24).

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Fig. 5. First-derivative X-band ESR spectra for silver centres formed after the exposure of unenriched $AgClO_4$ (0.05 mol dm⁻³) in (Me₂)CHOH to ⁶⁰Co γ -rays at 77 K. (a) Immediately after irradiation, showing ¹⁰⁹Ag⁰ and ¹⁰⁷Ag⁰ doublets and central (Me₂)COH features, (b) after annealing to ca. 120 K showing features from Ag⁺ · C(Me₂)OH radicals and Ag⁺₂ cluster cations. The (-1) and (+1) features from the latter are clearly resolved into 1:2:1 triplets corresponding to the three possible isotopic combinations (¹⁰⁹Ag⁻¹⁰⁹Ag)⁺, (¹⁰⁹Ag⁻¹⁰⁷Ag)⁺ and (¹⁰⁷Ag⁻¹⁰⁷Ag)⁺. The (-1, -1/2) and (+1, +1/2) features for the Ag⁺ · C(Me)₂OH radicals are concealed under the central features for Ag⁺.

poor overlap for the other two. Such restricted rotation is typical of pyramidal structures.²³ Unfortunately, these structures were lost before any onset of rotation able to make all the methyl protons couple equally. That the $-\dot{C}R_2OH$ unit is pyramidal is expected from the postulated structure, and is required by the small αH coupling, which would have been much larger had the radicals come close to planarity, as they are prior to bonding to Ag⁺.

The centre $Ag^{+}CMe_2(OH)$ is of particular interest in the light of a recent report by Henglein²⁵ that small silver clusters of remarkable stability are formed by radiolysis of solutions of $AgClO_4$ in water and isopropanol solvent. He suggests that reaction (10) occurs, followed by aggregation of silver atoms.

$$Ag^{+} + (CH_{3})_{2}COH \rightarrow Ag^{0} + (CH_{3})_{2}CO + [H^{+}].$$
 (10)

Our results show that this is not a one-step reaction, that the adduct, $Ag'^+CMe_2(OH)$, is relatively stable and shows no unimolecular tendency to give Ag^0 . Probably aggregation occurs *via* reactions between these adducts. Possibly the $(Ag)_n$ species formed in propargyl alcohol is also formed from the silver-radical adducts.

It is interesting to compare these novel σ^1 radicals with those formed from silver atoms and ethenes (11). These have been extensively studied by Kasai and co-workers.^{14, 24} They are clearly symmetrical units with equal bonding to both carbon atoms. The link between the two types of radicals is protonation (12).

$$Ag^{0} + CH_{2} = CH_{2} \xrightarrow{Ag}_{H_{2}C \longrightarrow CH_{2}} (11)$$

$$Ag^{+}(H^{+}) \longrightarrow Ag^{+} - CH_{2}CH_{3}$$

$$H_{2}C - CH_{2}$$
(12)

As yet, such protonation of ethene complexes, or deprotonation of the present σ^1 complexes has not been observed.

Allyl and Propargyl Alcohols

Both form similar doublets, but the splitting has increased to *ca*. 180 G for allyl alcohol and decreased to *ca*. 90 G for propargyl alcohol. If the complexes are σ^1 species comparable with those discussed above, *i.e.* Ag⁺C \leftarrow centres, it is not easy to understand these large differences. For the allyl alcohol doublet, it is possible that there are other features hidden by the central lines. However, these radicals have a larger negative g shift which accords with a larger spin density on silver, so we reject this concept.

The problem is more complex than for the saturated alcohols since two different radicals could be involved. Analysis of the spectra of these two alcohols after irradiation²⁶ shows that for allyl alcohol, CH_2CHCH_2 radicals and $CH_2CHCHOH$ radicals are formed in comparable yields. On annealing, the former radicals are lost as the silver adduct signals grow in, leaving the latter radicals still trapped. Thus, the 180 G centre [centre A, fig. 4(d)] is probably formed from allyl radicals. If these are the units (II)



they could well have a higher spin-density on silver. Alternatively, they may have a cyclic structure such as (III).



However, other results suggest that such radicals might have only small silver hyperfine couplings.²⁶

A second doublet centre was also detected for the propargyl alcohol systems [centre B, fig. 4(d)] with a splitting of *ca*. 360 G, and a large negative g shift. We have no clear assignment for this unusual centre, but stress that these might be the outer features of a multiplet, rather than being a doublet. Possibly some form of silver aggregation is involved.

Only one centre, with A(Ag) = 90 G was seen for the propargyl alcohol solutions. Again, there are two initial solvent radicals, thought to be $H_2CC=CH$ and HC=HCCHOH. The former were lost as the doublet grew in, so the adduct could be (IV). If so, it is difficult to see why, in this case, the silver splitting is reduced.

$$Ag^+ \cdot C \stackrel{H}{\leftarrow} H C \equiv CH$$

(**IV**)

We stress that the σ^1 structure for all these adducts is unusual, although $\sigma_1^2 \sigma_2^1$ (or σ^*) radicals such as Cl_2^{--} are well established. Ag \cdot Ag⁺ was probably the first such radical studied by ESR spectroscopy. The prototype for the present species is Ag \cdot H⁺, formed from hydrogen atoms in sulphuric acid glasses.²⁷ The silver splitting of *ca.* 104 G is clearly comparable with the present centres (except that for allyl alcohol) which accords well with expectation based on orbital energies. The features were narrow and showed a clear anisotropy for the silver splitting (-12.8, -11.6, +24.4 G). This means that there is considerable 5p₂ contribution to the SOMO. The proton coupling of 302 G shows that the spin density on hydrogen is *ca.* 60%. The 5s character is *ca.* 15%, leaving *ca.* 25% 5p-orbital character.

Conclusions

These systems are excellent examples of the power of ionizing radiation coupled with ESR and optical spectroscopy to give detailed information on charge-transfer and radical chemistry. Thus, electron addition to Ag^+ gives Ag^0 centres in a range of solvation states. These give Ag_2^+ and other cluster centres on warming, and very small metallic particles on further annealing. Solvent radicals, formed by radiolysis, attack Ag^+ to give novel silver-alkyl radicals not previously detected. An overall example of this is shown in fig. 5 for $AgClO_4$ in isopropyl alcohol. In fig. 5(*a*) one dominant Ag^0 centre is present together with $(CH_3)_2COH$ radicals, first studied many years $ago.^{28}$ On annealing [fig. 5(*b*)] the Ag^0 centres clearly form Ag_2^+ centres, whilst the Me_2COH radicals form $Ag^+ \cdot CMe_2(OH)$ radicals.

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