

837. *Unstable Intermediates. Part XXIII.*¹ *Solvated Electrons: Stabilisation in Aqueous Alkali-metal Hydroxide Glasses.*

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Aqueous alkali-metal hydroxide glasses after exposure to γ -radiation at 77°K are characterised by an intense absorption band at about 17,000 cm.⁻¹ which is lost on exposure to visible light. Comparison of the electron resonance spectra before and after bleaching suggests that the blue species is paramagnetic, having a symmetrical absorption band of width about 14 gauss and a g -factor of 2.000. The nature of this species is discussed and it is postulated that the entity is an electron trapped at a hydroxide vacancy. The effect of added halide ion on the electron resonance spectra has been examined. A second species, having $g_{\parallel} = 2.002$ and $g_{\perp} = 2.07$ is discussed in terms of an O⁻ radical strongly perturbed by the medium.

THE electron resonance absorption of dilute solutions of metals in ammonia consists of a single, narrow line with a width between points of maximum slope of about 0.02 gauss, and a g -factor of 2.0012, and thus provides disappointingly little information about the structure of the paramagnetic species. Rigid metal solutions^{2a} yield an electron resonance signal assigned to colloidal metal formed during freezing. Addition of sodium iodide to the solutions before freezing was originally thought to trap the solution species,^{2b} but recent work³ suggests that only colloidal metal is detected. In the absence of colloidal metal, blue glasses⁴ have no observable resonance at 77°K. Electrons in solids occupying sites of known structure, similar to those postulated for metal solutions, have been sought in order to learn more about the nature of the solvation shell.

Linschitz, Berry, and Schweitzer⁵ observed a well-resolved optical absorption at 16,500 cm.⁻¹ from a rigid solution of lithium metal in a mixture of triethylamine, methylamine, diethyl ether, and isopentane at 77°K, which they assigned to solvated electrons. This conclusion is open to question,⁶ and the source of the absorption remains obscure.

In recent work⁷⁻¹⁰ on the high energy X- and γ -ray irradiation of aqueous alkali-metal hydroxide glasses at 77°K a species has been detected which has an absorption maximum at about 17,000 cm.⁻¹, is readily bleached by visible light, and appears to be paramagnetic with a characteristic electron resonance spectrum. The species has been variously described as a stabilised free electron,⁷ a free electron in an expanded orbital of solvated metal cations,⁸ an aquated electron,⁹ and an electron trapped in an anion vacancy.¹⁰ Evidence suggesting that the solvated electron might be expected to absorb in this region is provided by the transient species obtained by pulsing electrons into water at room temperature,¹¹ which absorbs at 16,600 cm.⁻¹.

Marx, Leach, and Horani¹² irradiated water vapour with electrons and detected an electron resonance absorption, associated with a blue colour, in the condensate at 77°K. The electron resonance absorption and the blue colour were lost on warming to 150°K. It was postulated that just before vitrification an electron attached to a single water molecule

¹ Part XXII, preceding Paper.

² (a) Levy, *Phys. Rev.*, 1956, **102**, 31; (b) Clark, Horsfield, and Symons, *J.*, 1959, 2478.

³ Catterall and Symons, *J. Chem. Phys.*, 1963, **38**, 272.

⁴ Catterall and Symons, unpublished results.

⁵ Linschitz, Berry, and Schweitzer, *J. Amer. Chem. Soc.*, 1954, **76**, 5833.

⁶ Symons, *Quart. Rev.*, 1959, **13**, 99.

⁷ Schulte-Frohlinde and Eiben, *Z. Naturforsch.*, 1962, **17a**, 445; "Sixth International Symposium on Free Radicals," University of Cambridge, July 1963.

⁸ Jortner and Sharf, *J. Chem. Phys.*, 1962, **37**, 2506.

⁹ Ershov, Pikaev, Glazunov, and Spitsyn, *Doklady. Akad. Nauk S.S.S.R.*, 1963, **149**, 363.

¹⁰ Blandamer, Shields, and Symons, *Nature*, 1963, **199**, 902.

¹¹ Boag and Hart, *J. Amer. Chem. Soc.*, 1962, **84**, 4090; *Nature*, 1963, **197**, 45; Keene, *ibid.*, 1963, **197**, 47.

¹² Marx, Leach, and Horani, "Sixth International Symposium on Free Radicals," University of Cambridge, July 1963.

polarises the surrounding water molecules, and becomes solvated and delocalised over many polar molecules.

EXPERIMENTAL AND RESULTS

Materials.—Solutions were prepared from AnalaR reagents and water of ion-exchange purity. Heavy water was 99.88% by weight deuterium oxide.

Measurements.—Electron resonance spectra were measured at 9.4 kMc/s, using apparatus described elsewhere.¹³ Optical spectra were measured at 77°K with a Unicam S.P. 700 spectrophotometer having cell compartments insulated in the manner prescribed by Rosengren, *et al.*¹⁴

Irradiation.—Samples were irradiated in a 1900c ⁶⁰Co γ -source at a dose rate of 0.326 Mrad. per hour.

Preparation of Samples.—Samples were prepared for optical measurements by glassifying the hydroxide solutions in quartz optical cells of path length 1 mm. Glassification occurred very rapidly on immersion of the cell in liquid nitrogen. After γ -radiolysis at 77°K the cell was transferred to the cell compartment under liquid nitrogen.

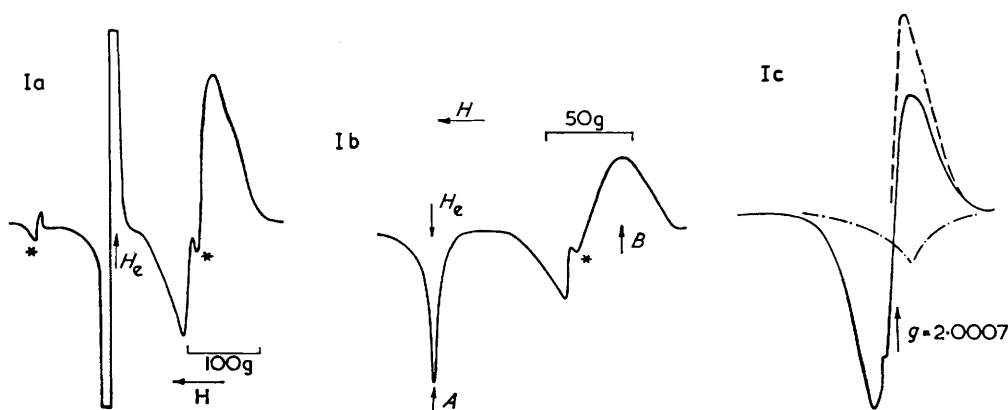


FIG. 1. Electron resonance spectra of γ -irradiated sodium hydroxide glasses at 77°K. (a) 10m-NaOD in D₂O. (b) 10m-NaOD in D₂O after exposure to visible light. (c) The difference spectrum in the free spin region attributed to the solvated electron. H_e; the field corresponding to a *g*-factor 2.0023. * Weak lines from trapped deuterium atoms.

To avoid the strong electron resonance absorption from γ -irradiated Pyrex, glass pellets of the hydroxide solutions were prepared by freezing small droplets of the solution in liquid nitrogen. After irradiation the pellets were collected in Pyrex tubes under liquid nitrogen. All samples were bleached by light from a tungsten filament lamp.

Spectrophotometric Results.—Solutions of sodium, potassium, and rubidium hydroxides in water and deuterium oxide, glassified and irradiated at 77°K, absorbed light throughout the visible region with a maximum at about 17,000 cm.⁻¹ (Table). Bleaching with visible light resulted in loss of the 17,000 cm.⁻¹ absorption and production of a new, broad, absorption edge, strong in the near infrared and red parts of the spectrum, and tailing into the visible. When bleached glass pellets were warmed, just before softening the original blue colour was regenerated, and could be retained by re-cooling to 77°K. The maximum absorption had then returned to 17,000 cm.⁻¹.

Electron Resonance Results.—The γ -damaged hydroxide glasses had complex electron resonance spectra (Fig. 1a), but on bleaching a single symmetrical feature was lost (Fig. 1b). This is tentatively assigned to the blue species although this identification is not compelling. Details of the electron resonance spectra of the blue species and of the bleached residue, which

¹³ Brivati, Keen, and Symons, *J.*, 1962, 237.

¹⁴ Rosengren, Sunner, and Timm, *Acta Chem. Scand.*, 1962, **16**, 467.

we call the "electron deficit centre," are collected in the Table. The effect of added iodide ion on the electron resonance absorption of the blue species is shown in Fig. 2.

Sodium hydroxide chips, γ -irradiated under identical conditions, had a very weak electron resonance absorption and blue colour.

The width of the electron-deficit centre absorption is largely due to g -factor variation, but there is an additional broadening due to hyperfine interaction with surrounding protons. An

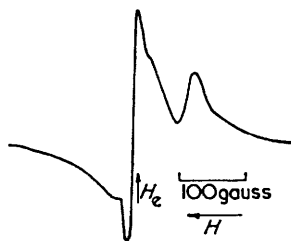


FIG. 2. Electron resonance spectrum of γ -irradiated potassium hydroxide (10m) in water saturated with potassium iodide and glassified at 77°K.

arbitrary measure of the narrowing on substituting deuterium oxide for water in the glasses is given by the width at half height of the perpendicular component of the spectrum. For 10m sodium hydroxide in water and deuterium oxide glasses this width is 37 and 26 gauss, respectively.

Electron resonance data for the two species observed in γ -irradiated alkali hydroxide glasses.

System	ν_{\max} (cm. ⁻¹)	Solvated electron		Electron-deficit centre	
		g -Factor (± 0.0005)	ΔH_{ms} ^a (± 1.0 g.)	g^b (± 0.001)	g^b (± 0.002)
5m-KOH in H ₂ O		2.0000	11	2.002	2.068
10m-KOH in H ₂ O	17,200	2.0005	12	2.002	2.070
20m-KOH in H ₂ O	17,100	1.9997	12	2.002	2.070
5m-NaOH in H ₂ O	17,000	2.0002	16	2.002	2.070
10m-NaOH in H ₂ O	17,000	2.0006	15	2.002	2.070
20m-NaOH in H ₂ O	16,800	1.9995	19	2.002	2.070
10m-NaOH in D ₂ O	17,200	2.0007	7	2.002	2.070
10m-NaOH in H ₂ O-D ₂ O (1 : 1 by volume)		2.0009	12	2.002	2.070
Saturated LiOH in H ₂ O ...		1.9993	15	2.002	2.063
10m-RbOH in H ₂ O	17,300	1.998 (± 0.001)	21 (± 5)	2.002	2.070
2.5m-KI in 10m-KOH in H ₂ O		1.9993	60	2.002	2.070

^a ΔH_{ms} is the width between points of maximum slope of the absorption. ^b Estimated at points A and B as in Fig. 1b.

DISCUSSION

Nature of the Blue Species.—By analogy with F centres in alkali halide crystals, we suggest that the species responsible for the band at 17,000 cm.⁻¹ is an electron trapped at an anion vacancy. The suggested centre differs from the F centre in that the walls of the cavity comprise oriented water molecules rather than cations. It should be stressed that in the glasses under consideration, there are only enough water molecules to solvate the cations and anions provided that they are effectively shared.

In favour of this concept are the following: (a) The g -factors assigned to the trapped electron are almost independent of the nature of the cation, in marked contrast to F centres, and are close to the value found for electrons solvated in liquid ammonia. (b) The line widths (ΔH_{MS}) of the electron resonance spectra are only slightly dependent upon the cations, again in marked contrast to F centres. Thus on going from sodium hydroxide to potassium hydroxide the width changes from 15 to 12 gauss for 10m solutions in water. For the F centre in sodium chloride and potassium chloride the widths are 65 and 23 gauss, respectively. (c) In contrast, the width is reduced by a factor of nearly three on changing

from water to deuterium oxide. (d) The broad absorption band at $17,000\text{ cm}^{-1}$ appears to be independent of the cation, again in contrast to *F* centre bands which are strongly dependent on the lattice parameter. This suggests that the effective lattice parameter is a constant in these systems.

These results demonstrate that the electron is rather strongly insulated from the cations. If the analogy with metal-ammonia solutions is correct, we infer that the broadening due to interaction with protons is dipolar in nature, since the contact interaction for fluid solutions is small.¹⁵

The results summarised above do not appear to support the model favoured by Jortner and Sharf,⁸ and, in particular, it is noteworthy that there is no detectable hyperfine structure, which might have been expected had the electron been trapped at a specific metal ion. Thus, if the model suggested by Jortner and Sharf⁸ were correct, the spin density at the sodium nucleus would have to be less than 0.6%, or the electron would need to be moving rapidly between a variety of cations.

Another alternative is that the blue species is colloidal metal. The most telling experimental evidence against this is that the centre is readily bleached.

Effect of Bleaching.—The fact that, after bleaching, the band at $17,000\text{ cm}^{-1}$ and its associated electron resonance spectrum reappear after controlled warming of the rigid solid, suggests that the new trap occupied on bleaching is very shallow, and that this new species is easily reconverted thermally into the original centre. Perhaps the simplest interpretation of these results is that the photo-excited electron can escape from the original cavity and become trapped at another, which already contains an electron. The resulting species is then analogous to the *F'* centre in alkali halide crystals, and to the e_2 species which has been postulated for metal-ammonia solutions.⁶ *F'* centres are characterised by a broad absorption band on the low energy side of the *F* band in alkali halide crystals, and, by analogy, the comparable centre in the present systems might be expected to have a broad absorption in the near infrared. In fact, a rising absorption in this region has been detected for the bleached glasses, but no clear maximum was found.

Implications of the Model.—Structural implications are discussed in the following Paper.¹⁶ The major significance of our results is that they provide independent evidence in favour of the "solvated electron" model for electrons in polar media, especially water, and furthermore, they suggest that the electron is quite strongly localised. This link arises not only from a comparison of optical spectra with that for electrons in water,¹¹ but also from a comparison of spin-resonance spectra with that of electrons "trapped" in ice.¹²

The problem of trapping electrons in molecular solids has been discussed in terms of the thesis that electrons are unlikely to be trapped even in highly polar rigid solvents, unless preformed cavities are present.¹⁷ The fact that the species under discussion are not formed in irradiated ice may be taken as support for this postulate. The situation, however, is not so clear when rigid alcohols are considered. The nature of the violet species produced in various rigid alcohols by exposure to high-energy radiation¹⁸ or by exposure of solutions containing hydrogen peroxide to ultraviolet light¹⁹ has been extensively discussed.¹⁷⁻²¹ Recent pulse radiolysis studies²² of ethanol and methanol have been interpreted in terms of solvated electrons which give rise to spectra having maxima in the $15,000\text{ cm}^{-1}$ region, and Schulte-Frohlinde and Eiben⁷ have shown that irradiated solid solutions of sodium alkoxides in the corresponding alcohols have

¹⁵ Hughes, *J. Chem. Phys.*, 1963, **38**, 202.

¹⁶ Blandamer, Catterall, Shields, and Symons, Part XXIV, following Paper.

¹⁷ Symons, *J.*, 1963, 1189.

¹⁸ Anderson, Alger, and Webb, *J. Chem. Phys.*, 1959, **30**, 695.

¹⁹ Symons and Townsend, *J. Chem. Phys.*, 1956, **25**, 1299.

²⁰ Symons and Townsend, *J.*, 1959, 263.

²¹ Symons, "Peroxide Reaction Mechanisms," Interscience Publishers, New York, 1962, p. 137.

²² Tauf, Sauer, and Dorfman, *Discuss. Faraday Soc.*, 1963, **36**, 206.

absorption bands in the $17,000\text{ cm}^{-1}$ region. These bands are sufficiently close to those detected in solid alcohols to make clear-cut differentiation difficult.

Interaction with Iodide Ions.—In view of the very large broadening and shift of the spin resonance absorption of metal-ammonia solutions in the presence of iodide ions, it was of interest to see to what extent added iodide might influence the electrons in hydroxide glasses. The results, typified in Fig. 2, show that there are two bleachable paramagnetic resonance bands, one comparable with that for the undoped material and the other having $\Delta H_{\text{MS}} = 60$ gauss and a g -factor smaller than that of the normal line.

The concentration of iodide in these glasses was such that, for a statistical distribution, a large majority of hydroxide ions had either one or no nearest-neighbour iodide ions. We therefore attribute the broad line to electrons in hydroxide ion vacancies having one near-neighbour iodide ion. The broadening and shift are quite comparable to those found for metal-ammonia solutions containing alkali-metal iodides, and presumably arise for the same reasons.¹

Nature of the Electron-deficit Centre.—The simplest interpretation of the residual electron resonance absorption after bleaching is that it is due to the radical ion O^- having effective axial symmetry. Thus the results are independent of the metal hydroxide used, and the parallel and perpendicular components of the spectrum are greatly narrowed by replacing water with deuterium oxide, although no specific feature is altered, in contrast with the radicals trapped in irradiated ice.²³ Thus the species would appear to be associated with many protons rather than specifically with a few.

Interpretation of the g -Tensor assigned to O^- .—If the species concerned is O^- , then orbital motion must be effectively quenched, and the crystal field must have axial symmetry to account for the g -tensor. Qualitatively, the parameters can be accommodated by postulating a splitting of the $2p$ level such that p_z lies well above p_x and p_y . If this splitting is sufficiently large, g_x should be approximately 2.0023 and $g_x = g_y \gg 2.0023$. Since the g -tensor is not a function of the cations it seems likely that this asymmetric field is a property of the surrounding water molecules. If, as seems probable, the O^- radical is formed from a solvated hydroxide ion, and remains in the original solvent cavity, the required interaction might simply reflect an asymmetric solvation of the parent hydroxide ion in which interaction with water molecules along the O-H direction is markedly less than that along other directions. Alternatively, the required axial symmetry, and form of the electron resonance absorption, could arise if there is weak but specific interaction with the oxygen atom of one water molecule. A molecular-orbital description of the resulting unit would require that the unpaired electron be in a σ^* orbital, but still largely associated with the parent O^- radical. The unit bears some resemblance to the $(\text{Hal}_2)^-$ ions formed in alkali halide crystals, and the form of the g -tensor is indeed qualitatively the same as that found for those species.

Mechanism of Formation.—For glasses containing a high concentration of water there are extra features in the electron resonance spectrum, which have been assigned⁷ to hydroxyl radicals, because of the similarity between this part of the electron resonance spectrum and that found for irradiated ice. Under these conditions we have also detected relatively low concentrations of hydrogen and deuterium atoms (see Fig. 1). These were also detected by Ershov and his co-workers,⁹ and it is possible that the trapping sites in these instances are also anion vacancies, as found for example in calcium fluoride crystals.²⁴ It is noteworthy that these features are not found when the water concentration is such that only solvating water molecules are present in the glasses.

It seems probable that hydroxyl ions are the source of O^- radicals, since they are formed by high-energy ultraviolet light, which will be entirely absorbed by the hydroxide ions. The most economic mode of formation of the postulated radicals would be as follows:

²³ Siegel, Baum, Skolnik, and Fluornoy, *J. Chem. Phys.*, 1960, **32**, 1249.

²⁴ Hall and Schumaker, *Phys. Rev.*, 1962, **127**, 1892.

[1964]

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(a) loss of an electron to the bulk crystal leaving a hydroxyl radical: (b) transfer of a proton from this hydroxide radical to a neighbouring hydroxide ion, leaving solvated O^- ; (c) trapping of the electron at the site vacated by the second hydroxide ion, the water molecule becoming part of the solvent shell.

In our hands photolysis with unfiltered ultraviolet light of glasses containing alkali metal phenoxide in low concentration gave electron resonance spectra characteristic of O^- radicals, a new broad feature almost certainly due to phenoxy-radicals, but no optical or electron resonance absorption attributable to solvated electrons. However, on controlled warming after irradiation, a blue colour developed. No decomposition was detected when filters were used to remove the high-energy component (187 $m\mu$) of the ultraviolet light.

These results, which contrast with those reported earlier,⁸ can be readily understood in terms of the present postulates if the rate of generation of electrons from phenoxide ions is greater than the rate of generation of anion vacancies by the high-energy ultraviolet light. Under these conditions all available traps would be filled completely, and one would expect to find only paired electrons trapped at anion vacancies.

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