

# Cation Interactions of Trapped Electrons in Irradiated Alkaline Ice<sup>1</sup>

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*Line-width studies have been carried out on electron spin resonance spectra of trapped electrons in  $\gamma$ -irradiated alkaline ices of  $H_2O$  and  $D_2O$  as a function of the alkali cation. Contributions to the line width from both alkali cation and proton interactions are demonstrated and analyzed quantitatively. Small anisotropic contributions may also be present. The cation interaction shows that the spin density of the trapped electron is distributed over at least a 3–4- $\text{Å}$ . radius from the trapping center.*

## Introduction

Schulte-Frohlinde and Eiben<sup>2</sup> recently found that the radiolysis of strongly alkaline ices at 77°K. produces trapped electrons and mononegative oxygen ions. These species can be studied by electron spin resonance and appear at different magnetic field intensities,  $g(e^-) = 2.001$  and  $g(O^-) = 2.06$ . These results have been confirmed and extended by other workers.<sup>3–6</sup>

The mechanism by which the mobile electron is stabilized in alkaline ices is of fundamental interest. Jortner and Scharf<sup>7</sup> suggested that the electron was stabilized by an alkali cation–electron interaction by analogy with the mechanism postulated in metal–ammonia solutions. It was pointed out that in metal–ammonia glasses at 20°K. the electron center itself absorbs at 1200  $m\mu$  while the alkali cation–electron center absorbs at 595  $m\mu$ .<sup>8</sup> On the other hand, Schulte-Frohlinde and Eiben<sup>2</sup> emphasized that the shape and peak position of the trapped electron absorption band at 586  $m\mu$  are independent of the nature of the cation in lithium, sodium, potassium, and cesium hydroxide glasses. It has also been argued<sup>4</sup> that an alkali cation–electron interaction should give rise to some discernible hyperfine splitting in the e.s.r. spectrum of the electron center. The absence of such hyperfine splitting has led Blandamer, Shields, and Symons<sup>4</sup> to suggest that the electron is stabilized in an anion vacancy surrounded by water molecules. Differences in the line width of trapped electrons in  $H_2O$  and  $D_2O$  have been observed<sup>3–6</sup> and show that water protons do interact with the trapped electron. In the

present work we have found that line-width contributions from cation interactions are also quite significant. The separate contributions from cation and proton interactions to the trapped electron line width were examined to ascertain what could be learned about the spatial extent of the electron trapping site.

## Experimental

All solutions were made with triply distilled water and reagent grade chemicals.  $D_2O$  was obtained from Matheson and quoted at 99.5 mole %. Sample solutions were deaerated with nitrogen. Frozen samples were prepared in the form of cylinders 3 mm. in diameter as previously described<sup>9</sup> for 2  $M$  solutions, and in spherical form by dropping the solution into liquid nitrogen for 5  $M$  solutions. All frozen samples appeared opaque except for 5  $M$  NaOH solutions which appeared glassy. This difference in phase does not affect the trapped electron spectrum.

Irradiations were performed with  $Co^{60}$   $\gamma$ -rays at a dose rate of 0.11 Mrad/hr. at 77°K. The total dose was 0.16 Mrad.

Electron spin resonance spectra of trapped electrons were obtained with a Varian-4500 spectrometer operating at 9.1 kMc. Irradiated samples were warmed at an approximately linear rate from 77 to 140°K. over a 3-min. period before spectra were recorded. This treatment caused the trapped hydroxyl radicals to decay but left the electron spectrum unchanged. Line widths were measured as the peak-to-peak separation on a first derivative curve of the absorption signal. Care was taken to avoid broadening due to power saturation and excessive modulation.

## Results and Discussion

Measurements of the line widths of trapped electrons in both  $H_2O$  and  $D_2O$  and in the presence of lithium, sodium, and potassium hydroxides have been made and are tabulated in the last column of Table I. The spin and magnetic moments of the pertinent nuclei are listed in Table II. From the data we can clearly see that the line width of the trapped electron is partly dependent on the nature of the cation. Furthermore, the order of increasing line width,  $K^+$ ,  $Na^+$ ,  $Li^+$ , parallels the order of increasing magnetic moment of the cations. The line width is also decreased greatly in  $D_2O$ ; this indicates that the major contribution to the line width arises from proton interactions.

The magnetic moment of the trapped electron in ice will interact with the magnetic moments of the sur-

(9) L. Kevan, P. N. Moorthy, and J. J. Weiss, *J. Am. Chem. Soc.*, **86**, 771 (1964).

(1) Radiolysis of Frozen Solutions. IV.

(2) D. Schulte-Frohlinde and K. Eiben, *Z. Naturforsch.*, **17a**, 445 (1962); *ibid.*, **18a**, 199 (1963). These authors have reversed their original assignment. The high-field line is now identified as the trapped electron.

(3) B. G. Ershov, A. K. Pikaev, P. Ya Glazunov, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **149**, 363 (1963).

(4) M. J. Blandamer, L. Shields, and M. C. R. Symons, *Nature*, **199**, 902 (1963).

(5) T. Henriksen, *Radiation Res.*, **23**, 63 (1964).

(6) P. N. Moorthy and J. J. Weiss, *Phil. Mag.*, **10**, 659 (1964).

(7) J. Jortner and B. Scharf, *J. Chem. Phys.*, **37**, 2506 (1962).

(8) E. Bosch, *Z. Physik*, **137**, 89 (1954).

rounding nuclei. Although no hyperfine structure is observed, this interaction should be the principal broadening mechanism that contributes to the line width of the trapped electron. Such an interaction will pro-

**Table I.** E.s.r. Line Widths of Trapped Electrons in Various Irradiated Alkaline Ices

Salt	Concn., M	Solvent	$\Delta H_{\text{max slope}}$ , gauss
LiOH	2-5	H <sub>2</sub> O	17.5 ± 0.5
NaOH	2-5	H <sub>2</sub> O	15.7
KOH	2-5	H <sub>2</sub> O	14.0
LiOH	2-5	D <sub>2</sub> O	8.5 ± 1.0
NaOH	2-5	D <sub>2</sub> O	7.0 ± 0.5
KOH	2-5	D <sub>2</sub> O	5.0 ± 0.5

duce a Gaussian line shape, and experimentally we find that the line shape of the trapped electron is nearly Gaussian. Broadening due to hyperfine anisotropy is consistent with this line shape and may also make a

**Table II.** Nuclear Spins and Magnetic Moments

Nucleus	Abundance, %	<i>I</i>	$\mu$	$\frac{\mu^2(I+1)}{I} = \alpha$
H <sup>1</sup>	...	1/2	2.793	23.5
D <sup>2</sup>	...	1	0.859	1.47
Li <sup>6</sup>	7.42	1	0.822	
Li <sup>7</sup>	92.58	3/2	3.256	
Li	Natural			16.4
Na <sup>23</sup>	100	3/2	2.218	8.20
K <sup>39</sup>	93.08	3/2	0.391	
K <sup>41</sup>	6.91	3/2	0.215	
K	Natural	3/2	(0.382) <sub>rms</sub>	0.24

small contribution to the line width. Kip, Kittel, Levy, and Portis<sup>10</sup> have previously carried out the theoretical treatment of such a situation in connection with the line widths of F centers in ionic crystals. They find that the line width is given by eq. 1 in which  $\Delta H_{\text{rms}}$

$$(\Delta H_{\text{rms}})^2 = \frac{64\pi^2}{27} \sum \mu_i^2 \frac{I_i + 1}{I_i} |\psi_i|^4 \quad (1)$$

is the root-mean-square line width,  $\mu_i$  is the magnetic moment of nucleus *i*,  $I_i$  is the spin of nucleus *i*, and  $|\psi_i|^2$  is the charge density at the *i*th nucleus.

Since the trapped electron e.s.r. lines are fairly symmetrical, we will assume that not more than 1 gauss of the total line width is attributable to anisotropic interactions and that the remainder of the line width arises from hyperfine interactions with protons (or deuterons) and alkali metal cations. The line width due to hyperfine interactions is given by eq. 1, which may then be used to test the fit of the data with the F-center model.

We assume that the wave function of the trapped electron has the same density at protons in H<sub>2</sub>O as at deuterons in D<sub>2</sub>O. For Gaussian lines the line width at maximum slope is 2.0 times the root-mean-square

line width. Then from the observed line widths in NaOH-H<sub>2</sub>O and NaOH-D<sub>2</sub>O and the ratio of  $\alpha_{\text{D}}/\alpha_{\text{H}} = 1/16$  we have

$$\begin{aligned} 216 &= W_{\text{H}}^2 + W_{\text{Na}}^2 \\ 36 &= W_{\text{H}}^2/16 + W_{\text{Na}}^2 \end{aligned} \quad (2)$$

where  $W_{\text{H}}$  and  $W_{\text{Na}}$  are the respective contributions in gauss to the observed line width at maximum slope from proton interactions and sodium ion interactions.

Values of  $W_{\text{H}}$  may also be calculated from the KOH line widths and from the LiOH line widths. These values agree with those from NaOH within experimental error and give an average value of 13.9 gauss. The agreement found illustrates the applicability of eq. 1. Furthermore, the contributions from the cations are in qualitative agreement with eq. 1 in that they increase in order of their  $\alpha$ -values. The various derived contributions to the line width of trapped electrons in H<sub>2</sub>O are summarized in Table III.

**Table III.** Contributions to the Line Widths of Trapped Electrons in Irradiated Alkaline Ices

System	Contribution, gauss		
	Cation <sup>a</sup>	Proton <sup>a</sup>	Anisotropy
2-5 M KOH in H <sub>2</sub> O	2.4	12.8	~1
2-5 M NaOH in H <sub>2</sub> O	4.9	13.8	~1
2-5 M LiOH in H <sub>2</sub> O	6.5	15.2	~1

<sup>a</sup> Root-mean-square contribution calculated from eq. 1.

Measurements of the *g*-factors of trapped electrons have been reported with a relative error of 0.0001 and show that the *g*-factor varies slightly with the nature of the cation.<sup>6</sup> This is as expected if a significant cation interaction does exist since the *g*-factor shift from the free spin value of 2.0023 depends directly on the spin orbit coupling constant and inversely on the s-p orbital separation of the cations.<sup>11</sup> The order of the slight variations reported is in agreement with such a picture.

The line width of the O<sup>-</sup> species has also been examined. In H<sub>2</sub>O the line width is 40 ± 1.5 gauss and in D<sub>2</sub>O it is 31 ± 1.5 gauss. In both solvents the line width varies slightly in the same order as found for the trapped electron but these variations are within the error quoted. For this very wide line the major contribution to the line width is neither a cation nor a proton interaction; the major contribution is most likely due to a residual orbital moment on the O<sup>-</sup> ion.<sup>3</sup> The change in width in H<sub>2</sub>O and D<sub>2</sub>O implies that there is a 12-gauss contribution to the line width from proton interactions in H<sub>2</sub>O. It is interesting that this is about the same as the contribution from proton interactions that was deduced above for trapped electrons. A cation contribution to the O<sup>-</sup> line width probably exists, but this cannot be clearly ascertained from the data because of the breadth of the line.

The electron is trapped with the same yield in both glassy and polycrystalline ices.<sup>12</sup> The local orienta-

(10) A. F. Kipp, C. Kittel, R. A. Levy, and A. M. Portis, *Phys. Rev.*, **91**, 1066 (1953).

(11) H. Kahn and C. Kittel, *ibid.*, **89**, 315 (1953).

(12) L. Kevan, *J. Phys. Chem.*, **69**, 1081 (1965).

tion of polarized water molecules around the anion is postulated to form an electron trap when the anion is neutralized by proton transfer induced by irradiation.<sup>13</sup> This local orientation is apparently similar in both glassy and polycrystalline phases when formed by rapid freezing, the main difference in these phases being in the long-range order. This is also shown by the fact that the line width is not significantly different in the two phases. The latter observation implies that the charge density of the trapped electron is not extremely delocalized.

However, since a significant cation contribution to the line width is observed, we know that the charge

(13) L. Kevan in "Progress in Chemistry of the Solid State," Vol. 2, H. Reiss, Ed., Pergamon Press, New York, N. Y., 1965, pp. 304-329.

density distribution of the trapped electron cannot be too highly localized. At 2-5 M concentrations the average distance to a cation is about 5-4 Å. By using the theory of Kip, *et al.*,<sup>10</sup> the proton contribution to the line width can be shown to correspond to interaction of the trapped electron with about eight protons.<sup>3,13</sup> Thus the total interaction of the charge density of trapped electrons in alkaline ices encompasses several water molecules and one or more cations. This is consistent with the physical picture of an anion vacancy as the trapping site.

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## Preparation, Reactions, and Structure of Bis(dithio- $\alpha$ -diketone Complexes of Nickel, Palladium, and Platinum<sup>1,2</sup>

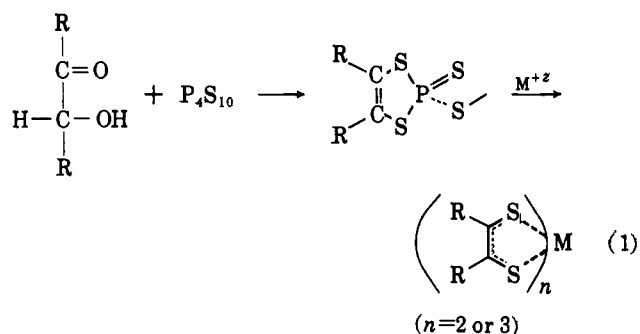
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*Preparation and properties of complexes  $M(RCSCSR)_2$  ( $R = \text{aryl or alkyl}$ ,  $M = \text{Ni, Pd, Pt}$ ) are reported. From theoretical considerations and X-ray and spectroscopic evidence, it is inferred that the compounds are planar bis-chelates of semi- $\alpha$ -dithiodiketones with the metals in the +2 state. Reactions of the complexes with hydrazines, phosphines, alkynes, and olefins are reported. With alkynes, thiophene derivatives are obtained via dithiadienes as intermediates. With a number of diolefins, labile 1:1 adducts are formed, the structure of which is discussed.*

Since their discovery,<sup>3</sup> complexes of the type  $M(RCSCSR)_n$  ( $M = \text{a transition metal}$ ,  $n = 2 \text{ or } 3$ ,  $R = \text{aryl or alkyl}$ ) were available only with difficulties and low yields, *e.g.*, from the reaction of alkynes with certain metal sulfides. A new method of synthesis has now been developed,<sup>4</sup> details of which will be published shortly. It makes these interesting compounds accessible from simple starting materials, according to reaction sequence 1. By this method we have prepared a large number of complexes of this type of most

transition metals. In the present paper some results of our work on complexes of nickel, palladium, and platinum are reported.



*Preparation and Properties.* The bis(dithio- $\alpha$ -diketone complexes of composition  $M(RCSCSR)_2$  with  $R = \text{phenyl, substituted phenyl, or alkyl}$  and  $M = \text{Ni and Pt}$  were prepared according to eq. 1. Bis-(dithiobenzil)palladium was obtained similarly, but the analogous methyl-substituted complex of this metal so far has resisted isolation. All compounds were well crystallized, air stable, and intensely colored solids. The X-ray analysis of bis(dithiobenzil)nickel has now been completed<sup>5</sup> and confirms the initially proposed structure I. The analogous complexes of Pd and Pt are isostructural with the nickel compound, space group  $P2_1/a$ . The methyl-substituted complexes are vacuum sublimable. The dithiobenzil complexes of

(1) Paper VI of the series "Chemistry of the Coordination Compounds"; Paper V: G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 1080 (1964).

(2) Partly abstracted from the Ph.D. Thesis of V. P. M., The University, Munich, Germany, 1964.

(3) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(4) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, U. Müller-Westhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 381 (1964); G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Angew. Chem.*, **76**, 715 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 639 (1964).

(5) M. R. Truter, Leeds, personal communication.