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Rate of Electron Exchange between Cuprous and Cupric Ions in Concentrated HCl by Electron Spin Resonance[*1]

R. Allan STEWART[*2] and L. W. REEVES

Department of Chemistry, University of British Columbia, Vancouver, British Columbia

and Shizuo FUJIWARA

Department of Chemistry, The University of Tokyo, Hongo, Tokyo

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Contrary to previous reports, the linewidth of the electron spin resonance spectrum of cupric ion as measured in gauss between points of maximum slope is a sensitive function of ionic strength, chloride ion concentration and cuprous ion concentration. Assuming that electron spin relaxation rates do not change greatly on the addition of cuprous ion, it is possible to derive an electron exchange rate for the reaction:

$$\mathrm{Cu^{+} + Cu^{2+} \longleftrightarrow Cu^{2+} + Cu^{+}}$$

of $k=1.53\times 10^{9}$ l/mol/sec. This value is in good agreement with a previous determination of the same rate constant by McConnell and Weaver using the ^{63}Cu nuclear magnetic resonance (0.5×10^{8}). The results for the linewidth changes can be rationalized in all cases by assuming that bridge chloride ions between two cupric ions or one cupric and one cuprous ion change drastically in concentration as such factors as ionic strength or chloride ion concentration changes. The g value of the electron (free) decreases as chloride ion is added, indicating delocalization of the unpaired electron onto chloride ligands.

While nuclear magnetic resonance (NMR) studies of chemical exchange are widespread, little attention has been paid to the study of electron exchange processes by electron spin resonance (ESR). A recent authoritative review of the subject of exchange studies by magnetic resonance lists only 8 studies1) carried out by ESR. These 8 investigations are comprised solely of investigations of electron transfer between radical ions and parent molecule. The ESR spectra of these species are composed of many hyperfine transitions, but some attempt has been made to compute lineshapes at various exchange rates, and to compare them with experimental curves.2) Part of the reason for the absence of more activity in this field is the shortage of suitable systems and the complexity of the ones avaiable. A system which has been studied by an NMR method3) is the cuprous-cupric electron exchange in aqueous solutions of the chloride. Although this system is complicated, it has the attraction that a single broad ESR line is observed, and the exchange process can be clearly demonstrated to dominate changes in linewidth. The study of linewidths of $\mathrm{Cu^{2+}}$ ions in aqueous solutions has already been investigated to some extent.4)

Solutions of cupric chloride do not obey Beer's law5,6) due to the formation of chloride complexes.

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[*2] Research carried out while a Research Fellow of the Ministry of Education of Japan at the Department of Chemistry, Faculty of Science, University of Tokyo (1964—66).

1) "Advances in Magnetic Resonance," ed. by J. S. Waugh, Vol. 1 (1965), p. 33.

2) J. E. Harriman and A. M. Maki, *J. Chem. Phys.*, **39**, 778 (1963).

3) H. M. McConnell and H. E. Weaver, *ibid.*, **25**, 307 (1956).

4) S. Fujiwara and H. Hayashi, *ibid.*, **43**, 23 (1965).

5) W. V. Bhagwat, *J. Indian Chem. Soc.*, **17**, 52 (1940).

6) T. Moeller, *J. Phys. Chem.*, **48**, 111 (1944).

McConnell and Davidson,7) by optical methods, established the presence of chlorine bridged complexes containing more than one copper ion, *e. g.*, $Cu_2Cl_5^-$, in aqueous solution. The bridge chloride ion promotes electron exchange between the two copper ions, giving rise to an intense coloration. It is probable that these bridge chloride ions are also responsible, in view of the anomalous spectral coloration, for the electron exchange process $Cu^+ \leftrightarrow Cu^{2+}$ in solutions of mixed oxidation states.

The present study is an attempt to compare directly the same exchange rate obtained by both NMR and ESR methods, and to study related processes which influence the ESR linewidth.

Experimental

Solutions were prepared by standard volumetric methods. The exclusion of air from sample tubes prevented the oxidation of cuprous ion to cupric ion. Samples were measured immediately after preparation of the solutions, but in any case, remained stable in closed tubes for periods in excess of one month. The solubility of $CuCl_2$ decreases in solutions of high HCl concentration, so that measurements were limited to more dilute regions. The cuprous ion is more stable in highly acid solutions. The ESR linewidth varies from 50 to 400 gauss as cupric and chloride ion concentrations are changed. This is in contradiction to a statement of Kozyrev,8) and the published results of Al'tschuler and Kozyrev,9) who observed no change from the value of 140 gauss. A JES-118 ESR spectrometer operating in the X-band at room temperature, manufactured by the Japan Electron Optics Company, was used for measurement, and DPPH was the external reference material.

Results and Discussion

It has been pointed out1,2) that the electron exchange problem in magnetic resonance can be considered as a simple modulation of the electron Larmor frequency by the various nuclear spin states responsible for hyperfine interaction. In this sense, the analogy with the influence of chemical exchange on nuclear magnetic resonance in the interruption of scalar coupling to other nuclei is almost complete. The problem of the natural relaxation processes in electron spin resonance is a complicated one, but it is sufficient that it be considered as a separate relaxation rate process, which is additive to any electron site exchange. This latter effect can be attacked by the time tested methods of chemical kinetics. Precautions must be taken that other relaxation mechanisms do not change greatly over the range of concentrations investigated.

In the present case, the single broad ESR line observed in solution has been interpreted as originating from incomplete averaging of the hyperfine coupling to ^{63}Cu and ^{65}Cu nuclei by relaxation mechanisms which have been previously discussed.4,10) The gyromagnetic ratios of the two copper isotopes are almost the same, and the spin quantum numbers are identical.

At constant $CuCl_2$ concentration in concentrated HCl, the ESR linewidth (maximum slope to maximum slope in gauss) was measured for a series of solutions of increasing CuCl concentrations. The results are plotted in Fig. 1 for a great excess of chloride ion (concentrated HCl). The concentration of cupric chloride was maintained at 1 molar. There was a sharp and linear decrease in linewidth of 55 gauss/mol/*l*, indicating that an exchange process, first order in Cu^+ ion is taking place, which results in exchange narrowing. An electron exchange rate can be obtained1) by converting to appropriate frequency units. A value for the electron exchange rate constant $k = 1.53 \times 10^8$ *l*/mol/sec was obtained for the process

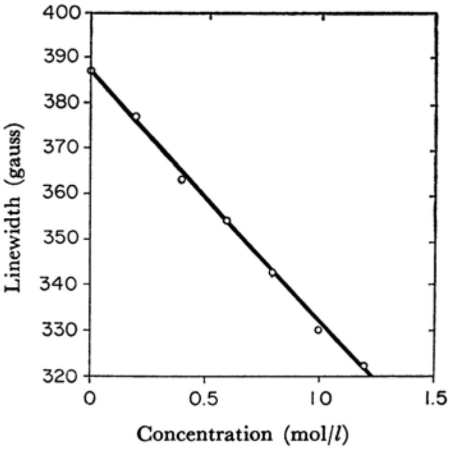

Fig. 1. Linewidth of 1 molar $CuCl_2$ in excess HCl as a function of added CuCl.

$$Cu^{2+} + Cu^+ \underset{k}{\longleftrightarrow} Cu^+ + Cu^{2+}. \qquad (1)$$

This ESR value is quite close to the value $k = 0.5 \times 10^8$ *l*/mol/sec obtained from ^{63}Cu NMR studies by McConnell and Weaver.3) The linewidth of the cupric ion resonance is very sensitive to chloride ion concentration in excess of 5 molar, and independent of concentration below this. The results of this study are plotted graphically in Fig. 2 for 1 molar cupric ion (chloride ion added by way of HCl). The pH was found to have little effect on the width or *g* value of the resonance line. The large increase in linewidth in Fig. 2 of the cupric ion resonance is interpreted as being due to

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7) H. M. McConnell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3168 (1950).

8) B. Kozyrev, *Discussions Faraday Soc.*, No. **19**, 137 (1955).

9) S. Al'tschuler and B. Kozyrev, "Electron Paramagnetic Resonance," Academic Press, London (1964).

10) D. Kivelson, *J. Chem. Phys.*, **33**, 1094 (1960).

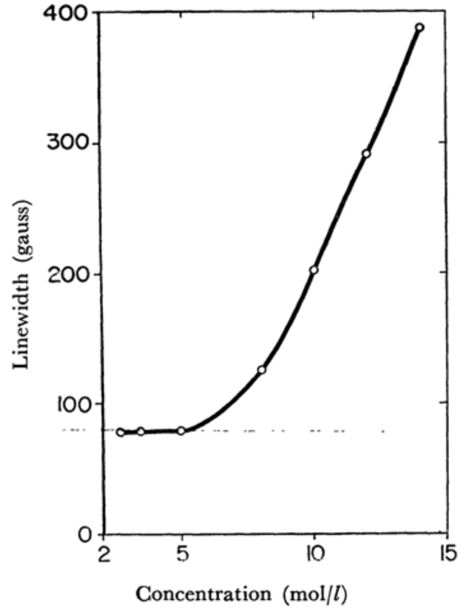

Fig. 2. Linewidth of 1 molar $CuCl_2$ *versus* Cl^- ion (HCl) concentration.

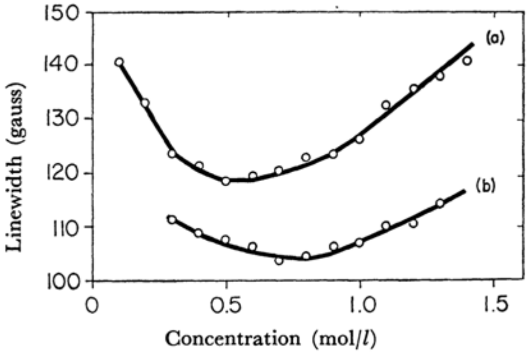

Fig. 3. Curve (a). Linewidth of Cu^{2+} ion resonance *versus* $CuCl_2$ concentration.
Curve (b). Curve (a) with 1 molar CuCl added.

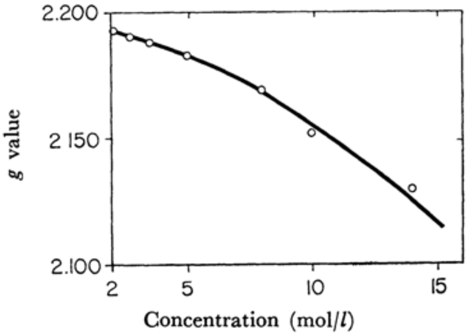

Fig. 4. *g* Value of Cu^{2+} ion resonance *versus* Cl^- ion (HCl) concentration.

a change in the average species present in solution as Cl^- ion is added.⁷⁾ As copper ion becomes more highly complexed by Cl^- ion, the symmetry of the complexes present in solution changes, resulting in a change in the basic ESR relaxation mechanism for copper ion, that of spin-orbit coupling.

In excess HCl, the linewidth of the cupric ion resonance as a function of cupric ion concentration is plotted in Fig. 3, curve (a). The excess chloride was limited to approximately 10 molar by solubility considerations for cupric ion in more concentrated solutions. The linewidth passes through a minimum at approximately 0.55 molar cupric ion. These results are understandable in terms of the two electron exchange mechanism

$$Cu^{2+} + Cu^{2+} \longleftrightarrow Cu^{2+} + Cu^{2+} \qquad (2)$$

if the maximum concentration of bridge chloride ions occurs near that of the minimum linewidth. The rate of electron exchange represented by Eq. (2) is most rapid at this point. Simultaneous electron exchange occurs between two cupric ions, thereby affecting the linewidth of the electron resonance. The rate of this exchange is expected to be slower than that for the process represented by Eq. (1), where only one electron changes site. It is also interesting to note that in Fig. 3, curve (b), where 1 molar cuprous chloride is added to the solutions of curve (a), that the linewidths are always considerably reduced (by 15 to 25 gauss), and the minimum linewidth is displaced by 0.2 mol/*l* to higher cupric ion concentrations. This displacement is thought due to the effect of ionic strength. The ionic strength was kept constant in various copper solutions previously investigated⁴⁾ through the addition of zinc nitrate (chosen because of its similar ionic properties to copper). The linewidth was found to behave in a similar but more simple fashion with change in other linewidth-influencing factors (such as cupric and chloride ion concentrations) at constant ionic strength.

The *g* value measurements for the cupric ion as a function of concentration are also of some interest. These are plotted as a function of chloride ion (HCl) concentration for a 1 molar cupric ion concentration in Fig. 4. There is a large monotonic decrease in the *g* value of the unpaired electron as the chloride ion concentration increases. This is illustration of the increasing coordination of cupric ion by chloride ion, and the delocalization of electron spin density onto the ligand chloride ions. Stability constants of the various cupric and cuprous chloride complexes are very imperfectly known,¹¹⁾ but the stable complex in very concentrated chloride solutions is known⁵,⁶⁾ to be $CuCl_4{}^{2-}$. The hydrated cupric ion has a much more localized unpaired electron spin and the *g* value is higher.

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11) "Stability Constants," The Chemical Society, London, Special Publication No. 17, ed. by L. G. Sillén.