An ESR Study of the Oxidation-Reduction Reaction of Piperidine with a Copper(II) Bis-dithiocabamate Complex

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Copper(II) ion, some copper(II) complexes and some copper proteins are known to undergo oxidation-reduction reactions with various organic compounds.[1] When piperidine is added to a solution of copper(II) bis-*N,N*-dialkyldithiocarbamate complex, the deep greenish-brown color of the complex in the solution disappears gradually. This is thought to bo due to the reduction of copper(II) ion to copper(I) ion in the complex by the strongly basic secondary amine, piperidine. The purpose of this work is to investigate the mechanism of the above oxidation-reduction reaction by detecting the unstable free radicals produced during reaction by an ESR technique. The ESR spectra were measured in solution below −70°C with a Hitachi K-band ESR spectrometer. The sample solution was a mixture of 1 vol of piperidine and 9 vol of 10^{-2}—10^{-3} M toluene solution of copper(II) bis-*N,N*-diethyldithiocarbamate complex. The ESR spectra obtained are shown in Figs. 1 and 2.

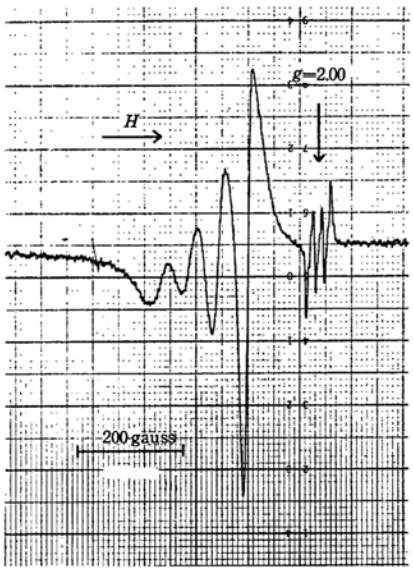

Fig. 1. The ESR spectrum (first derivative, 23808 Mc/s, at about −80°C) of the reaction mixture of piperidine and copper(II) bis-*N,N*-diethyldithiocarbamate in toluene.

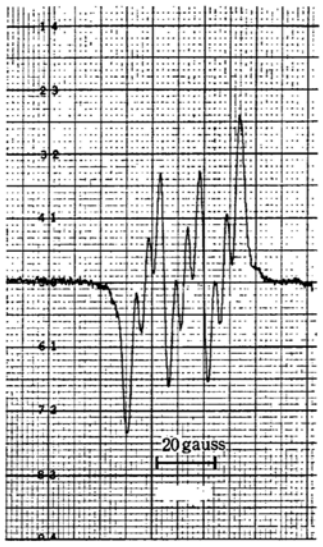

Fig. 2. The enlarged ESR spectrum of the free radical observed in the high field part of the spectrum in Fig. 1.

The ESR spectrum shown in Fig. 2 indicates that the spectrum was due to a free radical, and was composed of two triplets with intensity ratios of 1 : 1 : 1, whose hyperfine splitting constants were 17.6 gauss and 5.4 gauss. It is certain that the nitrogen of piperidine accounts for at least one of the triplets, and, therefore, that the initial step of the oxidation-reduction reaction is an electron transfer from the nitrogen lone pair of piperidine to the copper(II) complex. However, a definite conclusion on the structure of the free radical produced can not be safely drawn at this stage. The problem of investigating the mechanism of this type of oxidation-reduction reaction is very important from the standpoint of organic reactions, coordination chemistry and biochemistry. Interestingly, pyrrolidine and 2-methylpiperidine were also found to undergo a reaction similar to piperidine, but the ESR signals of their free radicals could not be so clearly detected.

Details, together with optical absorption spectral data, will be published elsewhere.

1) E. Frieden, "Horizons in Biochemistry," ed. by M. Kasha and B. Pullman, Academic Press, New York (1962), p. 461; T. E. King, H. S. Mason and M. Morrison (Editors), "Oxidases and Related Redox Systems," John Wiley & Sons, Inc., New York (1965), p. 207.