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FORMATION OF A Mg(II)-O_2^- ADDUCT FROM THE REACTION OF Mg(II) ION WITH SUPEROXIDE ION, O_2^-, IN ACETONITRILE

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Superoxide ion, O_2^-, generated by the electrolytic reduction of molecular oxygen in acetonitrile associates with Mg(II) ion to form the Mg(II)-O_2^- complex. The formation of adduct was verified by ESR spectrometry.

Dioxygen adducts of metal ions are of interest because of their involvement in a variety of biological processes. Recently, by use of superoxide ion, the formation of the dioxygen adducts of some metal complexes such as metalloporphyrins$^{1)}$ was reported. But, it has not hitherto been shown that a dioxygen adduct of magnesium is formed by the reaction either with O_2 or with O_2^- in solutions. In the present study, we have found that O_2^- associates with Mg(II) ion to form the O_2^- adduct in acetonitrile (CH_3CN). In this paper we would like to report these results.

The O_2^- ion was prepared by electrolytic reduction of molecular oxygen in CH_3CN, as described previously.$^{2)}$ Anhydrous $Mg(ClO_4)_2$ was purchased from The G. Federick Smith Co. and used without further purification. ESR spectroscopy was carried out on a JEOL-PE-1X spectrometer (X-band) with 100 kHz field modulation. ESR parameters were obtained by comparison with a Mn^{2+}/MgO marker and DPPH (g=2.0036). The concentration of O_2^- was estimated spectrophotometrically (λ=255 nm, ε=1500 cm^{-1}).$^{2)}$

The electrolytic solutions obtained gave an ESR spectrum at 77 K with g-values ($g_\perp$=2.008, $g_{/\!/}$=2.083)(Fig. 1a), which is typical of O_2^-.$^{2)}$ When 1-10 mM $Mg(ClO_4)_2$ were added to 7.2 mM O_2^- in CH_3CN, the intensity of the spectrum due to O_2^- was decreased and the $g_{/\!/}$ component shifted to a higher field, but any new spectrum could not be observed (Fig. 1b and 1c). The higher field shift of $g_{/\!/}$ component suggests the coordination to metal ions.$^{3,4)}$

When 100 mM $Mg(ClO_4)_2$ was added to 7.2 mM O_2^- in CH_3CN, the ESR spectrum due to O_2^- (indicated by arrows in Fig. 2) further decreased in its intensity and simultaneously a new ESR spectrum appeared as shown in Fig. 2. This new spectrum was not observed in the absence of O_2^- and was thought to be due to the reaction product of O_2^- with Mg(II) ion. Magnesium contains 10% natural aboundance of ^{25}Mg (I=5/2, μ=-0.85470 n.m.) so that, when magnesium interacts with a substance having an odd electron, one strong powder ESR signal near g=2.00 due to ^{24}Mg (spinless nuclei) and a weaker signal with six hyperfine lines due to ^{25}Mg may be detectable. As expected, besides one strong signal at the central position (g=2.003), a signal with six hyperfine splitting was observed upon reaction with O_2^-. The latter signal could be assigned to the perpendicular component ($g_\perp$=2.001, $A_\perp$=87.6G)$^{5,6)}$, but the parallel lines could not be

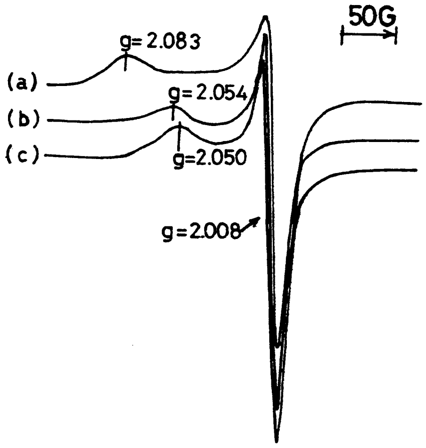

Fig.1. ESR spectra at 77 K of (a) 7.2 mM O_2^- in CH_3CN; (b) 7.2 mM O_2^- plus 1 mM Mg(II); (c) 7.2 mM O_2^- plus 10 mM Mg(II).

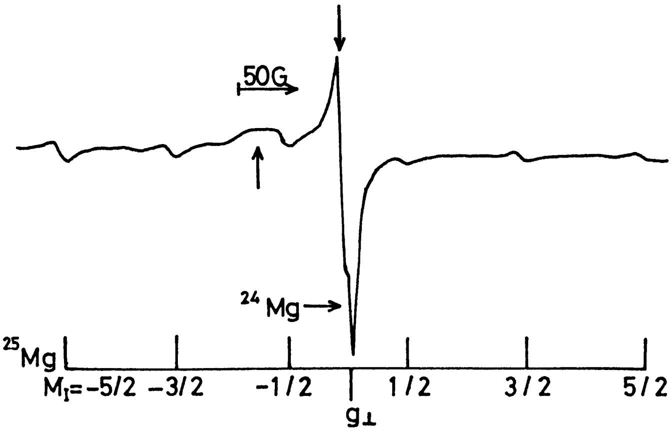

Fig.2. ESR spectrum observed at 77 K after the reaction of 7.2 mM O_2^- with 100 mM Mg(II) in CH_3CN.

observed on account of the weak signal intensity. This new radical species is stable at room temperature for 24 hrs, and its ESR spectrum resembles those of MgH5) and MgOH6) radicals which are trapped in argon or neon matrix at 4 K.

The ESR spectral changes depending on the concentration of Mg(II) ion may be interpreted after the manner of the explanation for the Ba(II)-O_2^- interaction in an aqueous solution.4) That is, at low concentrations of Mg(II) ion (1-10 mM) O_2^- is shown to exist in solution largely as a solvent-shared or a solvent-separated ion pair with the metal. At high concentrations of Mg(II) ion (100 mM) a tightly binding species is mainly present. This radical species might be either the complex, Mg(II)-O_2^- (with or without ClO_4^-), or the complex, Mg(II)-O_2^--Mg(II). The latter species, however, is excluded by the fact of the absence of the spectrum with eleven hyperfine lines.

In conclusion, we presented the first ESR evidence of the formation of the adduct between Mg(II) ion and O_2^- in acetonitrile.

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