# EVIDENCE OF INTRAMOLECULAR ISOMERIZATION IN A FE(II)-BENZOTRIAZOLE COMPLEX

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ABSTRACT - Benzotriazole forms two linkage isomers with the $Fe(CN)_5^{3-}$ ion, displaying reversible spectro-electrochemistry. Relaxation times obtained from cyclic voltammetry support an intramolecular mechanism for the isomerization kinetics.

The study of benzotriazole (Bt) complexes has been stimulated by the remarkable efficiency of the N-heterocyclic ligand as a corrosion inhibitor, particularly for copper and its alloys[1]. In mildly acidic or neutral solution, the molecule has available two nitrogen atoms, N1 and N2, for coordination with transition metal ions. However, up to the present, no case of linkage isomerism in benzotriazole complexes has been published in the literature.

In this work, we report definite spectroscopic and kinetic evidence of the isomerization equilibrium 1, in the pentacyanoferrate(II)-benzotriazole system.

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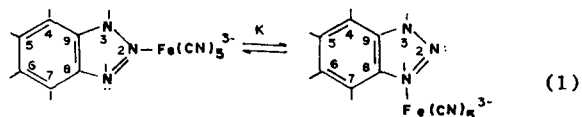
The reaction of benzotriazole with the $Fe(CN)_5H_2O^{3-}$ ion takes place very rapidly in aqueous solution, with a specific rate of 330 $M^{-1}s^{-1}$, obtained from stopped-flow kinetics, at 25 °C, 0.100 M KCl and 10^{-2} M acetate buffer. The substituted product has a characteristic absorption band at 383 nm (ε = 4100 $M^{-1}cm^{-1}$), assigned to a $d_\pi - p_\pi *$ CT transition, in comparison with the literature[2].

In the ^{13}C nmr spectra of D_2O solutions of the benzotriazole complex, nine peaks were observed, in contrast with the three peaks of the free ligand, at 139.96 (C8,9), 126.93 (C5,6) and 115.93 ppm (C4,7). The spectra support the existence of two isomers in solution, since, for symmetry reasons, three peaks were expected for the N2 form, and six for the N1 analog. Accordingly, the peaks at 126.09, 121.47 and 114.15 ppm, were tentatively assigned to the N2-isomer. The corresponding peaks for the N1-isomer were observed at 126.30 (sh, C8), 123.76 (C9), 122.08 (C6), 121.3 (sh, C5), 115.39 (C7) and 113.34 ppm (C4).

Two groups of peaks, of relative intensity 1.3:6.7, were observed at 8.92 and 7.57 ppm, respectively, in the ^1H nmr spectra of the benzotriazole complex. The first one is shifted 0.87 ppm downfield from the free ligand, and was assigned to the proton at C7 in the N1-isomer, based on the magnetic anisotropy of the $Fe(CN)_5^{3-}$ moiety[3]. The other group of peaks is shifted upfield, and was ascribed to the remaining protons in the mixture of isomers.

The benzotriazolepentacyanoferrate(II) complexes can be oxidized reversibly, to a violet-blue product having a ligand-to-metal CT band at 570 nm. Typical spectral changes are shown in the spectro-electrochemical measurements of Fig. 1.
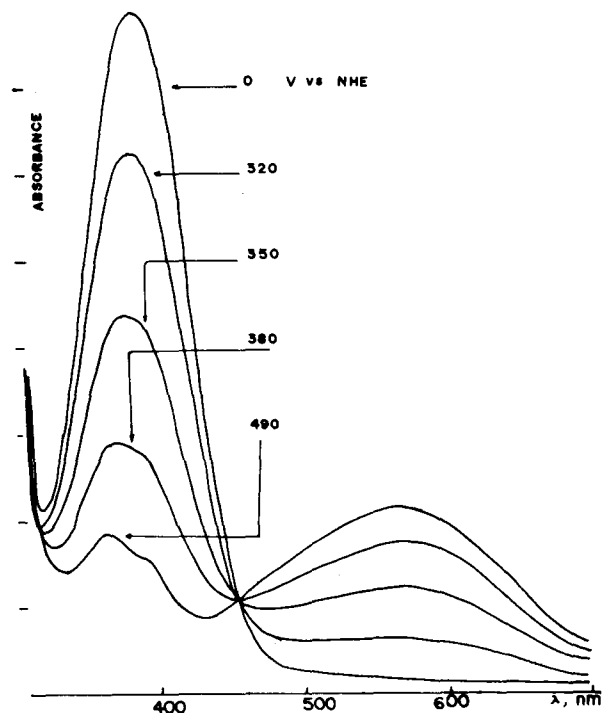

Fig. 1 - Spectro-electrochemical changes of a 1.4×10^{-3} M solution of $Fe(CN)_5Bt^{3-}$, at 25°C 0.50 M KCl, 10^{-2} M acetate buffer, recorded on a Cary 14-PARC 173 potentiostat system.

Cyclic voltammograms of the benzotriazole complexes are shown in Fig. 2. A single wave was observed at low scan rates, e.g. 10 mV.s^{-1}, with $E_{1/2}$ = 0.434 V vs NHE, and D = 4.3 x 10^{-6} cm^2.s^{-1}. The voltammograms can be fitted by eq. 2, using the work functions χ previously described[4], where a = nFv/RT, v = scan rate (V.s^{-1}) and the other terms have the conventional meaning.

$$i = nFAC(\chi Da)^{1/2} \qquad (2)$$

Two peaks of oxidation were detected in the cv at high potential scan rates. Theoretical analysis in terms of eq. 2 provided excellent fittings, indicating that the oxidation process is electrochemically reversible. Based on their relative intensities, the oxidation waves with $E_{1/2}$ = 0.43 and 0.53 V vs NHE were assigned to the N1 and N2 isomers, respectively. The equilibrium constant evaluated from the cv at 200-500 mV.s^{-1}, was 2.40 ± 0.05 at 25°C, in agreement with the nmr results.

The pattern observed at intermediate scan rates, e.g. 50 mV.s^{-1}, is typical of a reversible electrochemical process, preceded by a chemical reaction. The relaxation constants (k_r) evaluated in terms of eq. 3, were 2.14 ± 0.18 s^{-1}, at v = 20-120 mV.s^{-1}.

$$\frac{i_d}{i} = 1.02 + \frac{0.471}{K}(\frac{a}{k_r})^{1/2} \qquad (3)$$

In eq. 3, K is the equilibrium constant of isomerization, and i_d is the diffusion controlled current. By comparison with the limiting substitution rates, k_{-L} = 5.3x10^{-3} s^{-1}, determined in the presence of dimethyl sulfoxide (at 25 °C, 0.100 M KCl), we concluded that the isomerization mechanism is essentially intramolecular.

Considering the cathodic part of the cv, we have observed a linear behavior of the peak currents vs v$^{1/2}$, up to v = 100 mV s^{-1}. Above this scan rate, increasing negative deviations were noted, indicating incomplete relaxation of the oxidized system. At the same time, the cathodic wave, corresponding to the N2 isomer, became more evident in the cv. The relaxation constant evaluated in this case was 0.45 ± 0.08 s^{-1}.

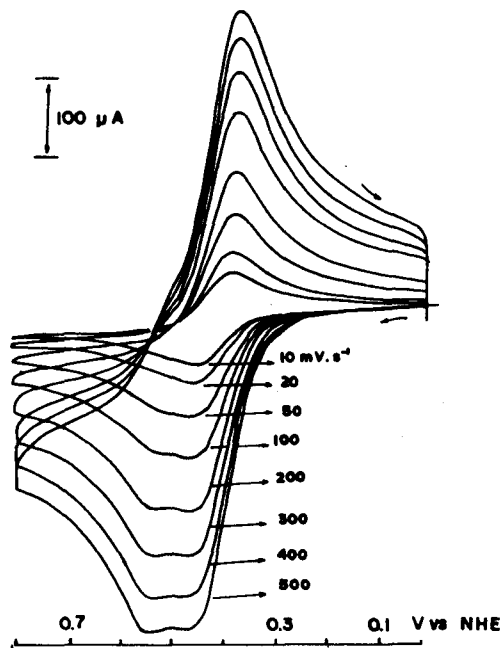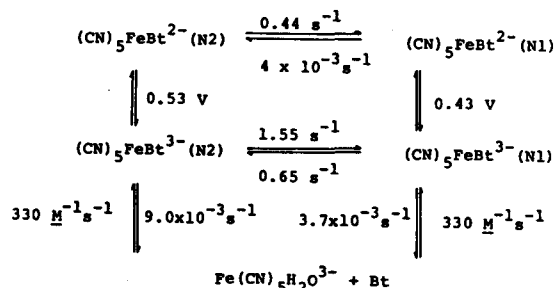Fig. 2 - Cyclic voltammograms of the Fe(CN)$_5$ Benzotriazole complex (2x10^{-3}M, 25 °C, 0.10 M KCl, 10^{-2}M acetate buffer), generated with a PARC 175/175 system.

Based on simple kinetic and thermodynamic calculations, we obtained the following picture for the cyanoiron-Bt system:

This study provided definite evidence of coordination mobility of the benzotriazole ligand. Several other iron and ruthenium benzotriazole complexes are under investigation in this laboratory.

References

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