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Redox Potentials of Cobalt (III/II) Complexes with Sulfonated Heterocyclic Azo Compounds

Akio YUCHI,* Katsuhito MATSUI, Tomosuke ISHIZUKI, and Hiroko WADA
Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466

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Synopsis. Cyclic voltammograms of the cobalt(III) complexes with sulfonated azo compounds indicated one quasi-reversible electrode process at the Pt or Au electrode at −0.3—0 V vs. SCE in aqueous solutions, which was assigned to a metal-centered redox reaction. The formal potentials are linearly correlated with the logarithmic protonation constants of the ligands.

Since the first application of 1-(2-pyridylazo)-2-naphthol (β-PAN) and 4-(2-pyridylazo)resorcinol (PAR) to spectrophotometric determination of cobalt,[1,2] a variety of heterocyclic azo compounds have been synthesized and examined for the improvement.[3]

In early stages, there had been a discrepancy as to the oxidation state of cobalt in the relevant complexes. Various physicochemical studies on the isolated compounds established the $\mathrm{Co^{III}L_2}$-type complexes as the final products in spectrophotometry of cobalt.[4,5] Later, the $\mathrm{Co^{II}L_2}$-type complexes were also identified as a reaction intermediate,[6] and isolated by the reaction of $\mathrm{Co^{III}L_2}$ with hyperoxide in dimethyl sulfoxide.[7] This paper describes the relative stabilities between these cobalt(III) and cobalt(II) complexes as studied by cyclic voltammetry in aqueous solutions, using sulfonated PAN derivatives.[8]

Experimental

β-TAN-7S was newly synthesized by the same procedure as that for β-TAN-6S,[9] and recrystallized from acetic acid solution. Yield 39%. Found: C, 40.3; H, 2.60; N, 10.9%. Calcd for $\mathrm{C_{13}H_8N_3O_4S_2Na{\cdot}2H_2O}$: C, 39.7; H, 3.08; N, 10.7%. All the pyridylazo compounds were prepared as described previously.[10,11]

Each sample solution for cyclic voltammetry was prepared by mixing cobalt(II) salt solution with twice amounts of an azo dye at pH 5. Potassium periodate was added for β-TAN-7S and α-PAN-4S to oxidize any residual Co(II) species. Then, the ionic strength was adjusted at 0.1 mol dm^{-3} with sodium nitrate, since cobalt complexes have relatively low solubilities in potassium nitrate solution.

Cyclic voltammograms were obtained with a Yanaco P-1100 polarographic analyzer using a three-electrode system of a working electrode (the Au electrode for β-TAN-7S and the Pt electrode for the others), a mercury-pool auxiliary electrode, and a saturated calomel electrode (SCE).

Results and Discussion

The protonation constant of β-TAN-7S at phenolic oxygen atom (K_1) was spectrophotometrically determined and given in Table 1, together with those of the other azo compounds. Compared with the parent compounds ($\log K_1 = 8.7$ for β-TAN, 12.2 for β-PAN, and 9.8 for α-PAN), basicity is decreased by the introduction of a sulfo group, except for α-PAN-3S and α-PAN-8S, which have a hydroxy or azo group adjacent to a sulfo group. In general, K_1 value is larger for β- and pyridyl derivatives than α- and thiazolyl derivatives.

The spectral characteristics of the ligands and cobalt(III) complexes are summarized in Table 1. An absorption maximum lies at a longer wavelength for α- and thiazolyl derivatives than for β- and pyridyl derivatives. Although the reactions of cobalt(II) with these reagents consist of two steps and are not simple,[6] kinetics of the formation of cobalt(III) complexes under aerobic conditions were qualitatively studied by monitoring change in absorbance at a wavelength characteristic for the product. The reaction was completed within one min for β-PAN-6S, β-PAN-7S and α-PAN-8S and within several hours for α-PAN-3S, α-PAN-5S, α-PAN-6S, and α-PAN-7S. Cobalt(III) complexes of α-PAN-4S or β-TAN-7S, however, were not quantitatively formed without potassium periodate.

Electrochemical data determined by cyclic voltammetry for cobalt(III/II) complexes are summarized in Table 1. All the complexes showed both cathodic and anodic peaks at −0.3—0 V vs. SCE in aqueous solutions.

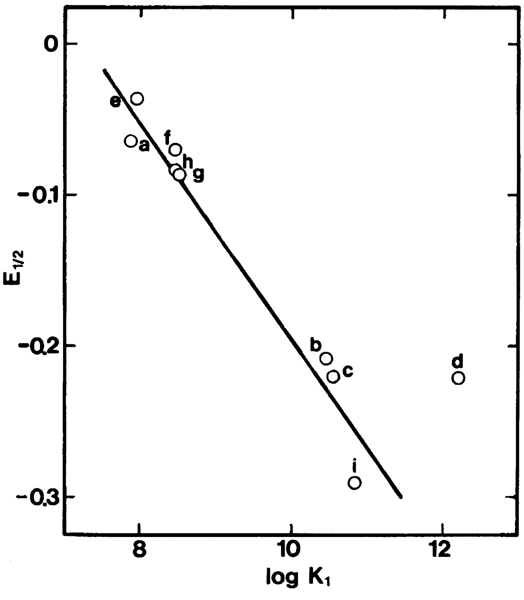
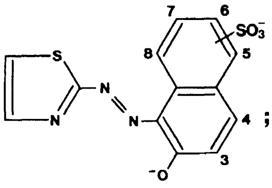


Fig. 1. Plot of $E_{1/2}$ vs. $\log K_1$. Ligand: (a) β-TAN-7S, (b) β-PAN-6S, (c) β-PAN-7S, (d) α-PAN-3S, (e) α-PAN-4S, (f) α-PAN-5S, (g) α-PAN-6S, (h) α-PAN-7S, (i) α-PAN-8S.

Table 1. Protonation Constant, Spectral Characteristics, and Electrochemical Parameters of Cobalt Complexes with Sulfonated Azo Compounds at 25 °C and 0.1 mol dm^{-3} NaNO$_3$

Reagent$^{a)}$	$\log K_1$	HL$^-$		CoL$_2^-$		$E_{1/2}$$^{d)}$	$\Delta E_p$$^{e)}$
		λ_{max}/nm	$\varepsilon$$^{c)}$	λ_{max}/nm	$\varepsilon$$^{c)}$	V	mV
β-TAN-7S	7.85	480	1.6	607	2.3	−0.065	88
β-PAN-6S	10.45$^{b)}$	465	1.8	565	2.3	−0.208	77
β-PAN-7S	10.55$^{b)}$	466	1.9	567	2.2	−0.220	72
α-PAN-3S	12.20$^{b)}$	470	2.4	581	2.4	−0.221	82
α-PAN-4S	7.95$^{b)}$	477	2.2	582	2.8	−0.037	80
α-PAN-5S	8.45$^{b)}$	485	2.0	595	2.6	−0.070	83
α-PAN-6S	8.50$^{b)}$	492	2.0	594	2.6	−0.086	76
α-PAN-7S	8.45$^{b)}$	487	2.0	590	2.6	−0.084	72
α-PAN-8S	10.85$^{b)}$	491	1.9	613	2.4	−0.290	80

a)



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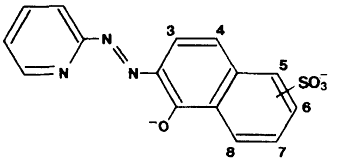

β-TAN-XS

α-PAN-XS

b) Ref. 11. c) ×10^4 mol^{-1} dm^3 cm^{-1}. d) vs. SCE. e) Separation between cathodic and anodic peaks.

The separations of the two peaks were 72—88 mV at a sweep rate of 20 mV s^{-1}, and the peak height ratios (i_{pc}/i_{pa}) were 0.87—1.15 at 25 °C. The formal potentials ($E_{1/2}$), obtained by averaging the peak potentials, were independent of pH in neutral region. All these indicate quasi-reversible one-electron electrode process, which is reasonably assigned to a metal-centered redox reaction.[12)]

Figure 1 shows good correlation between $E_{1/2}$ and $\log K_1$ except for α-PAN-3S, which also exhibited exceptional behavior on the complexation with nickel(II).[11)] The cobalt(III) complexes with the ligands of higher K_1 values are more stabilized against the corresponding cobalt(II) complexes. Since thiazolyl and α-derivatives have lower K_1 values as mentioned above, cobalt(III) complexes are less stabilized than pyridyl and β-derivatives. Actually a series of TAN derivatives yielded stable cobalt(II) complexes without any reducing reagents.[13)] Finally, it is worth while to point out that, within the ligands examined, the cobalt(III) complexes of low $E_{1/2}$ are formed more rapidly, although there is no theoretical necessity.

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8) All the ligands are abbreviated as (α- or β-)-(P or T)AN(-XS), where α- and β- designate 1- and 2-naphthol derivatives, P and T refer to pyridyl and thiazolyl rings, and X in -XS, when present, indicates the position of the sulfo group. Their structural formulas are given in Table 1. These are generally expressed as L, and charges of the ligands and complexes are omitted for clarity.

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