CHEMISTRY LETTERS, pp. 1207-1212, 1976. Published by the Chemical Society of Japan

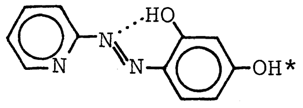
DIVALENT AND TRIVALENT COBALT COMPLEXES OF 4-(2-PYRIDYLAZO)RESORCINOL IN AQUEOUS SOLUTIONS

Katsura MOCHIZUKI, Taira IMAMURA, Tasuku ITO, and Masatoshi FUJIMOTO
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

In the course of the reaction in aqueous solutions between Co^{2+} and 4-(2-pyridylazo)resorcinol (PAR), the formation of an intermediate Co(II)-PAR complex and the subsequent oxidation to the Co(III) complex are observed by a rapid-scan spectroscopic method combined with stopped-flow technique. The ligand substitution reaction of Co(II)-PAR complex with EDTA and that of Co(II)-EDTA complex with PAR are inferred.

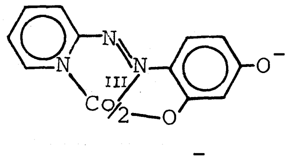
One of the interesting problems on the cobalt complexes of 4-(2-pyridylazo)-resorcinol (PAR) is the oxidation state of cobalt. One of the present authors (M.F.) provided a clear evidence for the presence of Co(III) complexes and the absence of Co(II) complexes in the solution prepared from Co^{2+} and PAR by the measurements of magnetic susceptibility.1) This result has been supported by the studies on the substitution reaction with EDTA2) and also by the proton magnetic resonance studies of the isolated complex.3,4) However, reliable studies on the Co(II)-PAR complex have not been reported so far.

In the present study, we have observed the formation of an intermediate Co(II)-PAR complex during the course of the reaction between Co^{2+} ion and PAR in aqueous systems, using a rapid-scan spectrometer equipped with a stopped-flow cell (A Union Giken rapid-scan spectrophotometer Model RA-1300). PAR was synthesized and purified.4)



LHH*

Figure 1 shows a typical example of the spectral change for the reaction of Co^{2+} and PAR. Each spectrum was rapidly scanned at appropriate time intervals after the solution containing $Co(ClO_4)_2$ in excess was rapidly mixed with a PAR solution by stopped-flow technique at pH 5.46.



$[CoL_2]^-$

Figure 2 shows the change in absorbance with time at 510 nm during the course of the reaction. These two figures clearly indicate that two kinds of relaxation are involved.

At the initial stage, spectrum of the reaction mixture changes rapidly with an isosbestic point at 450 nm. The absorption around 400 nm due to the free ligand PAR decreases with the increase of a new absorption due to the complex around 500 nm. This rapid spectral change ceases in ca. 40-50 ms after mixing. Then a relatively slow spectral change occurs with another isosbestic points at 330 and 435 nm. Final equilibrium attains in ca. 3 min under this condition.5) The final spectrum coincides with the spectrum of $[Co^{III}(PAR)_2]^-$, which is obtained under the same conditions either with an equilibrated solution prepared by mixing Co^{2+} and PAR in the molar ratio of 1 : 2,3) or with an aqueous solution of the isolated complex having the composition of $[Co^{III}L(LH^*)]$;6) Hereafter "PAR" stands for L^{2-}, LH^-, LH^{*-}, and/or LHH* (see the structural formulae).

The final product of the reaction was found to be adsorbed on an anion-exchange resin (QAE-Sephadex A-25), but not on a cation exchanger (SP-Sephadex C-25). The adsorption behaviors on the ion exchangers, together with the spectral evidence, indicate that the final product is an anionic species $[Co^{III}L_2]^-$. This accords also with the results obtained by the solvent extraction study on this system.3,7)

All these results suggest the first spectral change corresponds to the complex formation of Co^{2+} with PAR and the second one involves the oxidation of Co(II)-PAR complex to $[Co^{III}L_2]^-$.

In fact, the rate of the first step was found to be enhanced under the same condition with increase in the initial concentration of Co^{2+} ion (Table 1). The results on the substitution reaction of Co-PAR complexes with EDTA, which will be mentioned later, also provide evidence for the presence of Co(II) state in the initial stage of

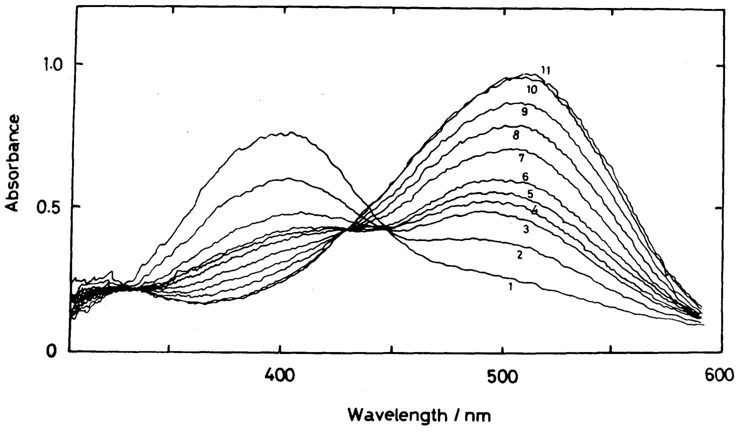


Fig. 1. Change in rapidly-scanned spectrum.

Recorded at (1) 0, (2) 10, (3) 25, (4) 50, (5) 100 ms, (6) 0.5, (7) 5, (8) 20 s, (9) 1, (10) 2, and (11) 3 min after mixing. 7.64×10^{-4} M $Co(ClO_4)_2$ are mixed with 3.31×10^{-5} M PAR at pH = 5.46 (hexamine buffer), ionic strength $\mu = 0.1$ ($NaClO_4$) and 23 °C. Scan rate: 300 nm/5 ms.

the present reaction. Furthermore, the experiments concerning the effect of H_2O_2 on the reaction between Co^{2+} and PAR have revealed that the second relaxation involves the oxidation of Co(II)-PAR complex. When the solution of PAR containing 6% H_2O_2 was mixed with a Co^{2+} solution under the same conditions as in Fig. 1, only the second step was accelerated by several times, leaving the first step essentially unaffected.[8)]

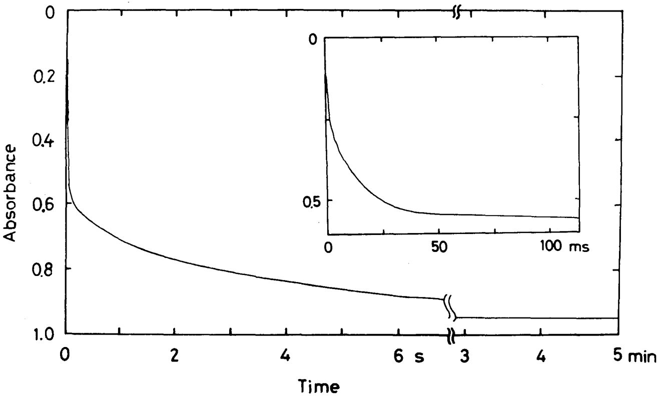


Fig. 2. Stopped-flow signal at 510 nm. The experimental conditions are the same as those for Fig. 1. Inset shows an expanded signal for the initial stage of the reaction.

On the basis of these observations, the following mechanism is proposed for the present reaction. PAR exists in the form of LH^- and LHH* under the given conditions.[9)]

$$LHH^* \xrightleftharpoons{K_{a(LHH^*)}} LH^- + H^+ \qquad (1)$$

$$Co^{2+} + LH^- \rightleftharpoons [Co^{II}L] + H^+ \qquad (2)$$

$$[Co^{II}L] + LH^- \rightleftharpoons [Co^{II}L_2]^{2-} + H^+ \qquad (3)$$

$$[Co^{II}L_2]^{2-} \longrightarrow [Co^{III}L_2]^- + e^- \qquad (4)$$

In view of the inertness of Co(III) complexes against substitution, it seems plausible to conclude that the oxidation of the Co(II) complex occurs after the incorporation of the second PAR molecule.

It has been pointed out that the red color of the Co(III)-PAR complex remains

Table 1. Rate constants for the complex formation of Co(II) and PAR at various concentrations of Co(II).

$[Co(II)]_0$/M	k_{obs}/s^{-1}
3.82×10^{-4}	41.7
7.64×10^{-4}	79.3
1.15×10^{-3}	105.5
1.53×10^{-3}	133.3
1.91×10^{-3}	142.8

$[PAR]_0 = 1.79 \times 10^{-5}$ M, pH = 6.86 ± 0.05, ionic strength $\mu = 0.1$ ($NaClO_4$), and 25 °C. From the rate equation $k_{obs} = k_f[Co(II)]_0 + k_d$, the values of k_f and k_d were estimated to be $k_f \simeq 8.0 \times 10^4\ M^{-1}\ s^{-1}$ and $k_d \simeq 15\ s^{-1}$.

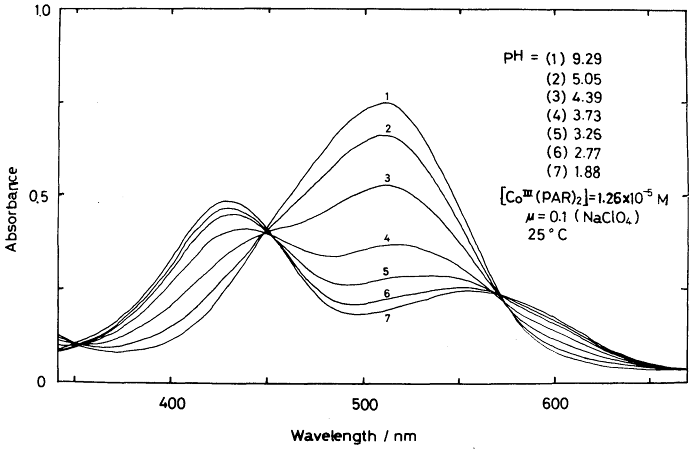


Fig. 3.
Spectra of [Co^{III}(PAR)$_2$] as a function of pH.

unchanged at least for a week, even when the solution is acidified down to pH 1 or lower.$^{10)}$ On the contrary, the spectrum of [Co^{III}(PAR)$_2$] was found to depend on the pH of the solution (Fig. 3). The spectra shown in Fig. 3 are obtained at appropriate pH either with the equilibrated solutions prepared from Co^{2+} and PAR in the molar ratio of 1 : 2 or with aqueous solutions of the isolated [Co^{III}L(LH*)]. Though Nonova and Evtimova have observed the same pH-dependency of the spectrum as in Fig. 3, they ascribed this spectral change to the ligand dissociation and the formation of the Co(II)-PAR complex and determined thereby the stability constant of the Co(II)-PAR complex.$^{11)}$ The spectral change shown in Fig. 3 is evidently caused by protonation-deprotonation of the para-hydroxyl group of the coordinated PAR in the Co(III) complex. The ion-exchange behaviors indicate that the complex ions present at pH 6 or higher are anionic, while those at pH 2 or lower are cationic. Obviously, two protons are dissociated from the two coordinated LH*$^-$, when the pH of the solution is varied from 2 to 6. The Co(III)-PAR complexes are in the form of [CoL$_2$]$^-$ (λ_{max} = 510 nm, ε_{max} = 57000) at pH 6 or higher, and [Co(LH*)$_2$]$^+$ (λ_{max} = 430 nm, ε_{max} = 37500; λ_{max} = 558 nm, ε_{max} = 18300) at pH 2 or lower.

Feature of the spectral change depicted in Fig. 3 suggests the formation of the neutral species [Co^{III}L(LH*)], since two sets of the isosbestic points are observed at 452 and 568, and 448 and 574 nm. However, the values of absorbance at 450 and 571 nm are nearly independent of the pH of the solution as if one set of isosbestic points appears. This can be explained qualitatively by the reasonable assumption that [Co^{III}L(LH*)] shows an average spectrum of [Co^{III}L$_2$]$^-$ and [Co^{III}(LH*)$_2$]$^+$.

Acid dissociation constants for

$$[\mathrm{Co^{III}(LH^*)_2}]^+ \underset{}{\overset{K_{a1}}{\rightleftharpoons}} [\mathrm{Co^{III}L(LH^*)}] + \mathrm{H^+} \qquad (5)$$

and

$$[\mathrm{Co^{III}L(LH^*)}] \underset{}{\overset{K_{a2}}{\rightleftharpoons}} [\mathrm{Co^{III}L_2}]^- + \mathrm{H^+} \qquad (6)$$

were determined from the result shown in Fig. 3. The plots of the absorbance vs. pH at 420, 510, and 600 nm indicated that the values of pK_{a1} and pK_{a2} are not quite different from each other. The average value for pK_{a1} and pK_{a2} was found to be 4.1.$^{12)}$

In order to ascertain if Co(II)-PAR complexes are stable in deoxygenated media, we carried out spectrophotometric measurements using a device connected to vacuum system. In this apparatus, the solutions of Co^{2+} and PAR were separately degassed beforehand by freezing several times. Then the solutions were mixed and introduced to the optical cell in vacuo. However, this approach failed to detect the presence of Co(II)-PAR complex, the resulting spectrum being completely identical with that of $[Co^{III}(PAR)_2]$ species. It can be concluded that $[Co^{II}(PAR)_2]$ complexes are oxidized even by a trace amount of oxygen, provided the dissolved oxygen would play an essential role on the oxidation to Co(III) complex.

It has been reported that the color of the solution prepared by mixing Co^{2+} ions with PAR does not change upon addition of EDTA under the condition generally used in the analytical experiments.[3,13,14] This phenomenon has recently been explained reasonably by the formation of Co(III) complexes in the solutions, since Co(III) complexes are usually inert against substitution.[2] On the other hand, it has been reported also that Co(II)-EDTA does not react with PAR at all.[2] However, we have observed in the present study that EDTA does react with the Co(II)-PAR complex and that Co(II)-EDTA complex does react with PAR, resulting in the formation of $[Co^{III}(PAR)_2]$ complex.

The solution containing Co^{2+} in excess was rapidly mixed with a yellow PAR solution at pH 5 with a microsyringe. The red color of the solution thus formed turned orange upon subsequent rapid addition of EDTA, indicating the liberation of the yellow free ligand PAR. This observation clearly indicates the presence of labile Co(II) state immediately after the rapid mixing of Co^{2+} and PAR. The orange color of the solution thus formed changed again to red upon standing for ca. 24 h. The spectrum of the final solution was identical with that of $[Co^{III}(PAR)_2]$.

When the yellow solution of PAR (5.72×10^{-5} M) is mixed with the almost colorless solution of Co(II)-EDTA (3.06×10^{-5} M) in equal volume at pH 2-8, the color of the solution changes very slowly from yellow to reddish orange. Final equilibrium attains at room temperature in three days or more, depending on the pH of the solution. The resulting spectrum indicates the formation of $[Co^{III}(PAR)_2]$. The reaction was found to be faster as the pH of the solution is lower. This observation can reasonably be explained by the scheme shown below.

$$[Co^{II}EDTA] + 2\,PAR \rightleftharpoons [Co^{II}(PAR)_2] + EDTA \qquad (7)$$

$$[Co^{II}(PAR)_2] \longrightarrow [Co^{III}(PAR)_2] + e^- \qquad (8)$$

Though the stability of the Co(II)-EDTA complex is so high as log K_f = 15.71-16.55,[15] the reaction of this complex with PAR produces irreversibly more stable and inert Co(III)-PAR complex. Therefore, the divalent cobalt is finally eliminated completely from the Co(II)-EDTA system.

REFERENCES AND NOTES

1) T. Iwamoto and M. Fujimoto, Anal. Chim. Acta, 29, 282 (1963).
2) R. Yamashita, T. Yotsuyanagi, and K. Aomura, Bunseki Kagaku, 20, 1282 (1971) and the literatures cited therein.
3) M. Široki, L. Marić, Z. Štefanac, and M. J. Herak, Anal. Chim. Acta, 75, 101 (1975).
4) T. Ito, K. Mochizuki, T. Komazawa, and M. Fujimoto, presented at the 1976 Summer Meeting in Hokkaido of the Chemical Society of Japan and the Japan Society for Analytical Chemistry, Kitami, July, 1976, Abstract p. 12.
5) Similar two-step spectral changes with discrete isosbestic points were also observed for the reaction of Co^{2+} with 1-(2-pyridylazo)-2-naphthol (PAN).
6) The complex $[Co^{III}L(LH^*)]$ was isolated as fine black powders from the solution by mixing stoichiometric amounts of Co^{2+} and PAR and adjusting the pH around 4.
7) T. Yotsuyanagi, K. Goto, and S. Nagayama, Bunseki Kagaku, 18, 184 (1969).
8) The absorpn. spectra of free PAR and $[Co^{III}L_2]^-$ were found to be unchanged around pH 5 at room temp. upon addn. of H_2O_2 (Final concn. of H_2O_2 was 3%). PAR decomposes upon heating up to boiling when the soln. contains H_2O_2. Except for the initial stage the spectral change in the course of this reaction is not similar to that obsd. in the reaction without H_2O_2. The reaction goes to completion ca. 30 min after the initiation, resulting in the colorless soln. This indicates the complete decompn. of the free or the coordinated PAR. It may be due to the side reactions, which involve the complicated redox reactions. However, it can be safely concluded that the rate of the second step is enhanced upon addn. of H_2O_2, since the decompn. proceeds more slowly than the second oxidation step.
9) Acid dissocn. consts. are reported to be $pK_{a(LHH^*)}$ = 5.50 and $pK_{a(LH^-)}$ = 12.31. See, W. J. Geary, G. Nickless, and F. H. Pollard, Anal. Chim. Acta, 39, 71 (1962).
10) S. Funahashi and M. Tanaka, Bull. Chem. Soc. Jpn., 43, 763 (1970).
11) D. Nonova and B. Evtimova, Anal. Chim. Acta, 62, 456 (1972).
12) It is difficult to determine spectrophotometrically the values of pK_{a1} and pK_{a2} separately, because $[Co^{III}L(LH^*)]$ shows approximately an average spectrum of $[Co^{III}(LH^*)_2]^+$ and $[Co^{III}L_2]^-$, i.e., the values of the pK_{a1} and pK_{a2} are not quite different from each other. On standing overnight around pH 4 the solution gave even in 10^{-5} M a reddish orange flocculent precipitate, probably $[CoL(LH^*)]$. Corsini et al. have determined pK_{a1} and pK_{a2} in dioxane-water mixture (50%) by potentiometric titration to be 4.8 and 6.0, respectively. See, A. Corsini, Q. Ferdinando, and H. Freiser, Analyt. Chem., 34, 1090 (1962).
13) Y. Shijo and T. Takeuchi, Bunseki Kagaku, 13, 536 (1964).
14) T. Yotsuyanagi, R. Yamashita, and K. Aomura, Analyt. Chem., 44, 1091 (1972).
15) "Stability Constants of Metal-Ion Complexes," Supplement No. 1, ed. by L. G. Sillén and A. E. Martell, Special Publication No. 25, The Chemical Society, London, 1971, p. 625.

(Received September 20, 1976)