

Thermodynamics, kinetics and mechanism for Palladium(II) oxalate complex formation

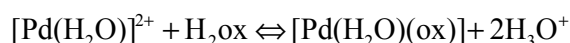
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Spectrophotometric study of complex formation between $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and oxalate ions ($\text{ox}=\text{C}_2\text{O}_4^{2-}$) was performed in aqueous solution under variable temperature and ionic strength. Thermodynamic parameters ($\log_{10} K_{1\text{H}} = 3.38 \pm 0.08$, $\Delta H^0 = -33 \pm 3 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S^0 = -48 \pm 11 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $T = 298.2 \text{ K}$, $I = 1.00 \text{ M HClO}_4$) were determined for following reaction:



Stability constants of complexes $[\text{Pd}(\text{H}_2\text{O})_2(\text{ox})]$ and $[\text{Pd}(\text{ox})_2]^{2-}$ ($\log_{10} K_1^0 = 9.04 \pm 0.06$, $\log_{10} K_2^0 = 13.1 \pm 0.3$) were determined under conditions of zero ionic strength and temperature 298.2 K and calculated using SIT theory from their dependence on ionic strength of the solution. Formation of complex $[\text{Pd}(\text{H}_2\text{O})_2(\text{ox})]$ can be described by two-step reaction mechanism, where the rate-determining step is formation of monodentate complex $[\text{Pd}(\text{H}_2\text{O})_3(\text{ox})]^+$ with H_2ox and Hox^- species. This can be described by parameters of equilibrium reaction ($\log_{10} K_{1\text{H}}' = 1.15$, $\Delta H^0 = -3 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S^0 = -12 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), which are of the same reaction order as thermodynamic data for Pd(II) complexes with other monodentate ligands containing carboxylate group^{1,2}. This reaction step is followed by closing of the chelate ring and thermodynamically stable 1:1 complex is created ($K_{1\text{H},\text{rc}} \approx 2.19$). Chelate effect as a result of increased stability of complex $[\text{Pd}(\text{H}_2\text{O})_2(\text{ox})]$ can be explained by dominance of enthalpic contribution (~ 75 %) over entropic contribution (~ 25 %) which is the opposite behaviour than is usually observed for most of the metal complexes.

REFERENCES

1. Shi T., Elding L. I., Inorg. Chem. 36, 528 (1997)
2. Lubal P., Elding L. I., J. Sol. Chem. 35, 769 (2006).