Thermodynamics of CV + OH --> CVOH

The classic crystal violet kinetic studies by Calvin Richie and coworkers reported kinetic data at 25.0°C for the alkaline bleaching reaction

$$CV^+ + H_2O \rightleftharpoons CVOH + H^+ \qquad K_a = 10^{-9.39}$$

$$H^+ + OH^- \rightleftharpoons H_2O \qquad K'_{w,298} = 10^{13.996}$$

$$CV^+ + OH^- \rightleftharpoons CVOH$$

$$K = K_a * K'_{w,298} = 10^{-9.39} * 10^{13.996} = 10^{4.606} = 4.036 \times 10^4$$

$$\Delta G^o_{298} = -RT \ln K = -6.284\ kcal/mol$$

Ritchie, C. D.; Wright, D. J.; Huang, D. S.; Kamego, A. A., Cation-anion combination reaction. XII. Rates, equilibriums, and activation parameters for reactions of triarylmethyl cations in aqueous solution. J. Am. Chem. Soc. 1975, 97, 1163-1170. 10.1021/ja00838a034

Ritchie, C. D.; Skinner, G. A.; Badding, V. G., Solvent Effects on the Reactions of Stabilized Carbonium Ions with Nucleophiles. J. Am. Chem. Soc. 1967, 89, 2063-2071. 10.1021/ja00985a017

$$CV^+ + OH^- \underset{k_1}{\overset{k_2}{\rightleftharpoons}} CVOH$$

$$K = \frac{k_2}{k_1} = 4.036\times10^4\ M^{-1}$$

$$k_2 = 0.201\ M^{-1}\sec^{-1}\ \text{(Richie 1975)}$$

$$k_1 = \frac{k_2}{K} = \frac{0.201\ M^{-1}\sec^{-1}}{4.036\times10^4\ M^{-1}} = 4.980\times10^{-6}\sec^{-1}$$

$$\Delta G^{\ddagger}_{1,298} = -RT\ln\left(\frac{k_1 h}{k_B T}\right) = -0.5925\frac{kcal}{mol} * \ln\left(\frac{4.980x10^{-6}\sec^{-1} * 6.6261x10^{-34}\,J-\sec}{1.3807x10^{-23}\,J\,K^{-1} * 298.15\,K}\right)$$

$$\Delta G^{\ddagger}_{1,298} = 24.69\ kcal/mol$$

$$\Delta G^{o}_{298} = -6.284\ kcal/mol \qquad \text{(from above)}$$

$$\Delta G^{\ddagger}_{2,298} = 24.69 - 6.284\ kcal/mol = 18.4\ kcal/mol$$