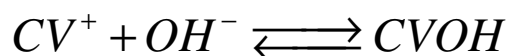


## Thermodynamics of $CV + OH \rightarrow CVOH$

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



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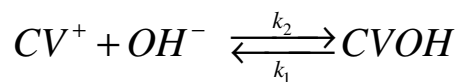


$$K = K_a * K'_{w,298} = 10^{-9.39} * 10^{13.996} = 10^{4.606} = 4.036 \times 10^4$$

$$\Delta G_{298}^o = -RT \ln K = -6.284 \text{ kcal/mol}$$

Ritchie, C. D.; Wright, D. J.; Huang, D. S.; Kamego, A. A., Cation-anion combination reaction. XII. Rates, equilibria, 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



$$K = \frac{k_2}{k_1} = 4.036 \times 10^4 \text{ M}^{-1}$$

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

$$k_1 = \frac{k_2}{K} = \frac{0.201 \text{ M}^{-1} \text{ sec}^{-1}}{4.036 \times 10^4 \text{ M}^{-1}} = 4.980 \times 10^{-6} \text{ sec}^{-1}$$

$$\Delta G_{1,298}^\ddagger = -RT \ln \left( \frac{k_1 h}{k_B T} \right) = -0.5925 \frac{\text{kcal}}{\text{mol}} * \ln \left( \frac{4.980 \times 10^{-6} \text{ sec}^{-1} * 6.6261 \times 10^{-34} \text{ J} \cdot \text{sec}}{1.3807 \times 10^{-23} \text{ J K}^{-1} * 298.15 \text{ K}} \right)$$

$$\Delta G_{1,298}^\ddagger = 24.69 \text{ kcal/mol}$$

$$\Delta G_{298}^o = -6.284 \text{ kcal/mol} \quad (\text{from above})$$

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