



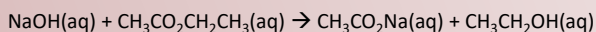
Effect of Carbonate on General Base-Catalyzed Reaction

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Introduction

The general base-catalyzed reaction



is thought to occur by water's attack on ethyl acetate's carbonyl carbon, with hydroxide removing water's proton, and subsequent removal and protonation of the ethoxy group to form ethanol and leave acetate behind. The reaction has been studied in teaching labs and research, and evidently the presence of carbon dioxide wrecks havoc on the kinetic study. The purpose of this investigation was to distinguish between carbon dioxide reacting with NaOH and lowering its concentration, and a specific effect of carbonate in the mechanism.

Terry studied this reaction in the conditions of unequal initial reactant concentrations and arrived at a rate constant of $6.72 \pm 0.02 \text{ M}^{-1}\text{min}^{-1}$ at 25°C . [1]

Approach

Attempts to follow the reaction conductometrically were unsuccessful. We then tried quenching aliquots of reaction solution with HCl and back-titrating with NaOH. This risks acid-catalysis of the reaction. We also tried keeping aliquots cooled on ice until titration. Ultimately we opted for immediate direct titration of the aliquots with HCl.

We titrated to phenolphthalein (PP) endpoint and continued the titration to bromocresol green (BCG) endpoint. A complication in data analysis is that three bases are present—hydroxide, carbonate, and acetate—and only two endpoints were measured.

We finally got around this by performing spikes with sodium carbonate. Titration results could be corrected for the known amount of Na_2CO_3 added, and thus $[\text{OH}^-]$ and $[\text{C}_2\text{H}_3\text{O}_2^-]$ could be calculated at each time from the two endpoints. The fact that at the BCG endpoint, acetate is only 60% protonated was taken into account. (See α_0 Acetic in alpha plot)

Direct titration data were analyzed as follows

$$n_{\text{HCl}}^{\text{PP,corr}} = n_{\text{HCl}}^{\text{PP}} - n_{\text{Na}_2\text{CO}_3}$$

$$n_{\text{HCl}}^{\text{BCG,corr}} = n_{\text{HCl}}^{\text{BCG}} - n_{\text{Na}_2\text{CO}_3}$$

$$n_{\text{OH}^-} = n_{\text{HCl}}^{\text{PP,corr}}$$

$$\alpha_0 n_{\text{C}_2\text{H}_3\text{O}_2^-} = n_{\text{HCl}}^{\text{BCG,corr}}$$

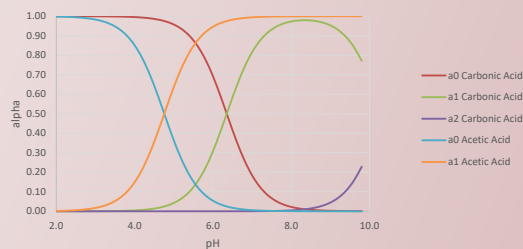
This allowed us to calculate the concentration of OH^- and $\text{C}_2\text{H}_3\text{O}_2^-$ in the 20- mL aliquots of reaction mixture at each time. The integrated rate laws pertaining to $[\text{NaOH}]_0 = [\text{Ethyl Acetate}]_0$ as well as for $[\text{C}_2\text{H}_3\text{O}_2^-]_0 = 0$ are shown below.

In each case the data were fitted to a linear model that forced the regression line through the well-known intercept $1/[\text{OH}^-]_0$. The slope with its 95% confidence limits was obtained. The results are shown graphically below.

The value of k calculated from $[\text{OH}^-]$ data seem to hold together better than those calculated from $[\text{C}_2\text{H}_3\text{O}_2^-]$ data. A smooth curve is drawn as a guide to the eye. [2]

The value of k follows an apparent decreasing trend as $[\text{Na}_2\text{CO}_3]$ increases from zero to ten times the initial concentration of $[\text{OH}^-]$. The like-charged CO_3^{2-} repels hydroxide, lowering its effective concentration near ethyl acetate. The results suggest CO_3^{2-} is less effective than OH^- as a general base catalyst.

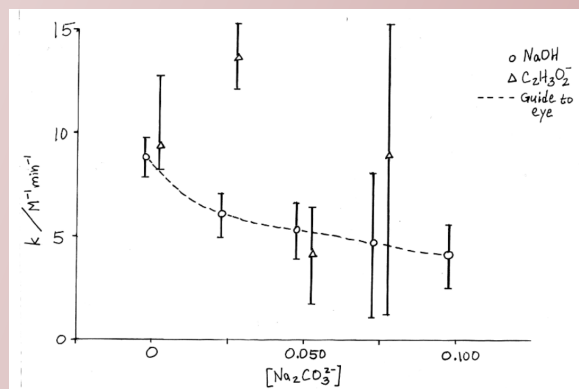
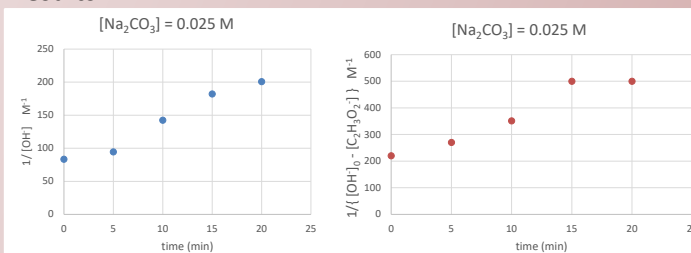
The Equations



$$\frac{1}{[\text{OH}^-]} = \frac{1}{[\text{OH}^-]_0} + kt$$

$$\frac{1}{[\text{OH}^-]_0 - [\text{C}_2\text{H}_3\text{O}_2^-]} = kt$$

Results:



Future Work

- * Design the experiment for tighter 95% confidence limits
- * Optimize the exclusion of CO_2 from reaction mixture by the use of $\text{Ba}(\text{NO}_3)_2$
- * Identify an elegant control reaction that is unaffected by presence of CO_2
- * Add carbonate by bubbling $\text{CO}_2(\text{g})$ for direct lowering of $[\text{OH}^-]$
- * Achieve a titration with 3 endpoints to determine OH^- , CO_3^{2-} and $\text{C}_2\text{H}_3\text{O}_2^-$
- * Develop equations for OH^- , CO_3^{2-} and $\text{C}_2\text{H}_3\text{O}_2^-$ from PP and BCG endpoints
- * Compare the effect of a different dianion salt such as Na_2SO_4

Notes and References

[1] EM Terry Ph.D. Thesis, 1913

[2] Note, the value of k calculated from $[\text{C}_2\text{H}_3\text{O}_2^-]$ (Δ) not shown for $[\text{Na}_2\text{CO}_3] = 0.100 \text{ M}$, as its value and uncertainty exceed the scale of the graph.

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