Determination of the Equilibrium Constant for Keto–Enol Tautomerism of Ethyl Acetoacetate

Salvador J. Ruggiero and Victor Martinez Luaces

Catedra de Fisicoquimica, Facultad de Quimica, Gral. Flores 2124, Montevideo, Uruguay

Experiments designed to illustrate the determination of equilibrium constants of chemical reactions are a very important part of undergraduate courses.

An experimental procedure for determination of the equilibrium constant for the keto-enol tautomerism of ethyl acetoacetate was presented by Ward¹. An easy and inexpensive method to study this reaction is titrating the enol species as a bromoketoester. This useful method is called Kurt Meyer's titration².

Ward's procedure requires standard sodium thiosulfate aqueous solution, whose concentration must be exactly known. This is a serious disadvantage. Though the procedure is valuable, considerable difficulty is experienced, particularly by beginners, in preparing standard solutions and carrying out the titration. Additionally, this standard solution decomposes rapidly with changes in its concentration³. In Ward's procedure one also needs to determine the exact concentration of ethyl acetoacetate solution in methanol.

The analytical method presented here is based on Ward's procedure with several modifications⁴ to correct the disadvantages noted above. The following modifications are note-worthy:

- 1. Three different concentrations, approximately 0.50, 0.25, and 0.10 M, of the ester in methanol are used.
- 2. Temperature is kept at 25.0 °C (at higher temperatures, the dilatation effect and loss of mass due to evaporation must be considered).

This new procedure is carried out in two steps as described below.

Determination of Enol Content

Samples of 10.00 mL of thermostated 0.50 M solution were transferred to a 250-mL Erlenmeyer flask. Then 4 mL of 0.1 M solution of bromine in methanol was added with shaking followed immediately (1 min or less) by the addition of 0.5 mL of β -naphthol solution (10% in methanol). After that, 2 mL of KI 1 M aqueous solution was added while stirring. The samples were allowed to stand for 30 min in darkness and then titrated with 0.05 M thiosulfate solution (without starch indicator), prepared by exact dilution from a 0.5 M one, to a colorless endpoint if the β -naphthol used is pure or to a brownish tinge if it is slightly oxidized.

The same procedure is followed with the other solutions. The amounts of reagents used for the 0.25 M solution are 25.00 mL of ethyl acetoacetate methanolic solution, 5 mL of bromine solution, 0.5 mL of β -naphthol solution, and 2 mL of KI solution. For the 0.10 M solution we have 25.00 mL of ethyl acetoacetate solution, 2.5 mL of bromine solution, 0.5 mL of β -naphthol solution. In both cases, titration was performed as noted before for the 0.50 M solution.

Determination of Ester Concentration

One hundred milliliters of bromine solution were added to samples of 5.00 mL of the ester. The mixture was allowed to stand until reaction was completed (approximately 24 h).

Afterwards, 14.5 mL of β -naphthol and 10 mL of KI were added in that order. After 15 min with occasional stirring, it was titrated with 0.50 M thiosulfate solution (without starch indicator).

Using this technique it is not necessary to know the exact concentration of ethyl acetoacetate. However, it is convenient to know it approximately in order to estimate the concentration of thiosulfate solution necessary to obtain an adequate volume of titration.

Calculations and Results

If in the enol procedure V is the volume of titration, V_s is the volume of the sample, and M is the molarity of the thiosulfate solution used, and if in the ester procedure V' is the volume of titration, V'_s is the volume of the sample, and M' is the molarity of the thiosulfate solution used, and taking into account that M'/M = 10, then one has

$$K_{\rm eq} = \frac{1}{10 \frac{V' V_{\rm s}}{V V_{\rm s}'} - 1} \tag{1}$$

The upper limit to the error in K_{eq} is given by

$$\Delta K_{\rm eq} = K_{\rm eq}^2 \frac{10V'V_s}{VV'_s} \left[\frac{\Delta V}{V} + \frac{\Delta V_s}{V_s} + \frac{\Delta V'}{V'} + \frac{\Delta V'_s}{V'_s} + \frac{\Delta M}{M} + \frac{\Delta M'}{M'} \right]$$
(2)

where ΔX is the error in X.

From eq 1 it is observed that this procedure does not require the knowledge of the concentration of either the thiosulfate or the ester in order to evaluate K_{eq} . From eq 2 we observe that the accuracy of the method may be changed by modifying the corresponding samples V'_{s} , V_{s} or the thiosulfate solution concentration.

The table shows some typical data for the equilibrium constant. The results are similar to Ward's¹ and Meyer's² data.

The changes recommended make this method more practicable, and manipulations become easier. The use of the present method is therefore preferable to others mentioned in the literature and can be extended to any similar equilibrium process of keto-enol tautomerism.

We acknowledge Oscar N. Ventura for useful discussions concerning this work.

Typical Data for the Keto-Enol Equilibrium Constant Determination at 25 °C

Original conc. ester (molarity)	V _{ester} (mL) V _s	V _{sample} (mL) V _s	V′ _{S2O3²⁻ (0.5 M) (mL) V′}	V _{S2O3²⁻ (0.50 M) (mL) V}	Equilibrium constant
0.5017	5.00	10.00	10.00	12.90	0.0689 ± 0.0006
0.2509	10.00	25.00	10.00	15.70	0.0670 ± 0.0005
0.1003	25.00	25.00	10.00	6.22	0.0664 ± 0.0007

¹ Ward, C. H. J. Chem. Educ. 1962, 39, 95–96.

² Meyer, K. H.; Kappelmeier, P. Ann. 1911, 380, 212-218.

³ Kolthoff, I. M.; Sandell, E. B. *Textbook of Quantitative Inorganic Chemistry*; Macmillan: New York, 1952; pp 592–594.

⁴ Catedra de Fisicoquimica. *Practicas de Termodinamica*; Universidad de la Republica: Montevideo, Uruguay, 1982; pp 119–123.