# Enthalpy and Activation Energy of the Fructose Mutarotation Determined by Polarimetry

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The optical rotation of solutions containing known initial concentration of β-fructopyranose has been measured as a function of time at various temperatures between 10 and 25°C. Pyranose is transformed, following a first order reaction, into an equilibrium mixture of pyranose and furanose. Since the specific optical rotation of both compounds is known, it is possible to determine rate and equilibrium constants. From these, the enthalpy of the reaction $F_6 \rightarrow F_5$ and the energies of activation of the forward and backward reactions have been calculated: $\Delta H° = 3800$ cal.mole^{-1} and $E_{A+} = 17\ 200$ cal.mole^{-1}, $E_{A-} = 13\ 400$ cal.mole^{-1}. This value of $\Delta H°$ differs significantly from previous calorimetric determinations which gave $\Delta H = 2950$ cal.mole^{-1}.

Mutarotation reactions may be divided into two groups. One consists in a simple α-β conversion, as exemplified by the glucose mutarotation; this type is relatively slow. The other, which is generally faster is a transformation of the ring structure. The transformation of β-fructose from its six-membered pyranose (F_6) modification into the five-membered furanose (F_5) form is an example of the latter. The reaction is not complete but produces an equilibrium mixture according to the scheme

$$F_6 \underset{k_-}{\overset{k_+}{\rightleftarrows}} F_5$$
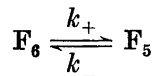
Experiments on fructose mutarotation were described first by Hudson [1] and later by Isbell *et al.*[2] Neither in this nor in later works could the true values of k_+, k_-, or $K = k_+/k_-$ be calculated since only the specific rotation of F_6 was known. F_5 has never been isolated in pure form, but in a kinetic work where F_5 was produced by very fast enzymatic hydrolysis of sucrose, Andersen and Degn [3] were able to deduce its specific rotation. Knowing these values the optical rotation of a mixture of F_6 and F_5 is given by the equation

$$(c_6 + c_5)\, \alpha = c_6 \cdot \alpha_{F6} + c_5 \cdot \alpha_{F5}$$

where the α's are the rotations produced by a column of given length (10 cm) of a solution of unit concentration (100 g/100 ml soln.), the solution being a mixture of F_6 and F_5, or pure F_6 or pure F_5, respectively. The sum of the concentrations c_6 and c_5 is constant and given by the quantity of fructose dissolved in the start of an experiment. Putting

$$C = c_6 + c_5$$

we have the linear relationships

$$c_6 = \frac{\alpha - \alpha_{F5}}{\alpha_{F6} - \alpha_{F5}} \cdot C \text{ and } c_5 = \frac{\alpha - \alpha_{F6}}{\alpha_{F5} - \alpha_{F6}} \cdot C$$

The course of the reaction, as inferred from measurements of α as a function of t, corresponds to the proposed scheme involving two opposed reactions. Indeed, if $\log(\alpha - \alpha_\infty)$ is plotted against t (Fig. 1), a straight line may be drawn through the experimental points, indicating that $\ln(\alpha - \alpha_\infty) = kt + \text{const.}$ or $d(c - c_{eq}) = k(c - c_{eq})dt$. From the slope of the line k may be calculated, where $k = k_+ + k_-$. The final rotation α_∞ yields the equilibrium concentrations c_{5eq} and c_{6eq} from which the equilibrium constant K may be calculated.

If k and K are measured at a series of different temperatures the activation energies E_{A+} of the forward reaction $F_6 \rightarrow F_5$ and E_{A-} of $F_5 \rightarrow F_6$ may be found from plots of $\log k_+$ and $\log k_-$ $vs.$ $1/T$; and the standard enthalpy ΔH° of $F_6 \rightarrow F_5$ from a plot of $\log K$ $vs.$ $1/T$.
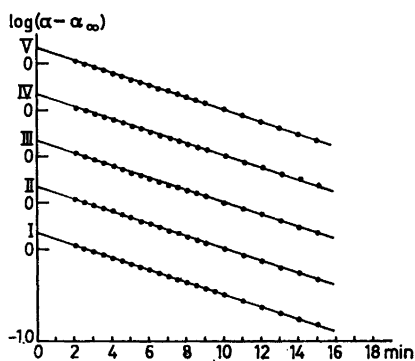

Fig. 1. Plot of $\log(\alpha - \alpha_\infty)$ $vs.$ t for five experiments at 22.5°C. The ordinate has been shifted.
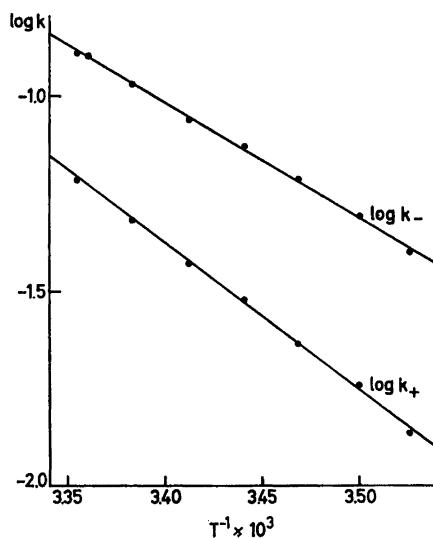
Fig. 2. Plot of $\log k_+$ and $\log k_-$ $vs.$ $1/T$.

EXPERIMENTAL

The measurements were performed with a "Zeiss lichtelektrisches Polarimeter" at 546 mμ. Rotation was measured with a precision of 0.005°. The reaction took place in a 10 cm polarimeter tube, thermostated by circulating water. In every experiment, temperature was measured directly inside the tube. The fluctuations thus found did not exceed 0.02°C.

The reaction mixture was prepared by dissolving β-fructopyranose in acetate buffer at a concentration of 3 g per 100 ml solution at the reaction temperature in every case. The acetate buffer was prepared in a pH-meter adding 0.01 M sodium acetate to 0.01 M acetic acid until a pH of 4.00. This value has been chosen because previous measurements have shown the curve of rate constant vs. pH to pass through a shallow minimum in the range from 3.8 to 4.2.

Experiments at this pH present the double advantage of 1) lowering the reaction rate to a level convenient for precise measurements and 2) minimizing the rate of change of the velocity with pH.

RESULTS

Values from a typical run are shown in Fig. 1 where $\log(\alpha - \alpha_\infty)$ is plotted against t. The fit is seen to be satisfactory. From each curve of this type three figures have been evaluated: k = slope ln 10; $C\alpha$ for $t = 0$ where $c_6 = C$ so that here $\alpha = \alpha_{F6}$; and α for $t \to \infty$ from which c_{eq} and K are obtained. A total

Table 1.

t °C	$C\alpha_{(F6)}$	$C\alpha_\infty$	c_{5eq}/C	$K = \dfrac{c_{5eq}}{c_{6eq}}$	k min^{-1}	k_+ min^{-1}	k_- min^{-1}
25.00	−4.680	−3.155	0.322	0.476	0.189	0.0609	0.128
24.50	−4.679	−3.162	0.321	0.472	0.186	0.0596	0.126
22.50	−4.665	−3.203	0.310	0.449	0.155	0.0480	0.107
20.00	−4.657	−3.251	0.299	0.426	0.124	0.0370	0.0870
17.55	−4.652	−3.300	0.288	0.404	0.104	0.0299	0.0741
15.20	−4.644	−3.355	0.275	0.379	0.0842	0.0231	0.0611
12.60	−4.661	−3.400	0.268	0.366	0.0671	0.0180	0.0491
10.50	−4.657	−3.454	0.256	0.343	0.0534	0.0136	0.0398

number of 39 experiments were made at 8 different temperatures between 10 and 25°C. Average values of $C\alpha_{F6}$, $C\alpha_\infty$, k, c_{5eq}, K, k_+ and k_- are listed in Table 1 for each temperature. The following formulae were used:

$$c_{5eq} = \frac{\alpha_\infty - \alpha_{F6}}{\alpha_{F5} - \alpha_{F6}} \cdot C$$

$$K = \frac{c_{5eq}}{c_{6eq}} = \frac{\alpha_\infty - \alpha_{F6}}{\alpha_{F5} - \alpha_\infty}$$

$$k_+ = kK/(1 + K); \quad k_- = k/(1 + K)$$

The values of α_{F6} are seen to be almost independent of temperature; for α_{F5} the value of 1.7° has been used at all temperatures.[3]
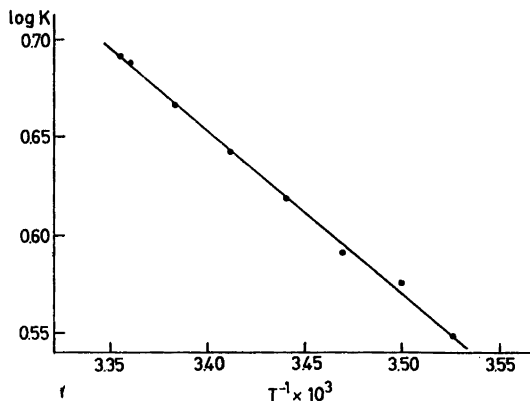
Fig. 3. Plot of log K *vs.* $1/T$.

On Fig. 2 is shown a plot of log k_+ and log k_- *vs.* $1/T$. The activation energies calculated from the slopes are $E_{A+} = 17\ 200$ cal.mole^{-1} and $E_{A-} = 13\ 400$ cal.mole^{-1}, respectively.

The values of log K have been plotted against $1/T$ on Fig. 3. The faint slope of the line yields a standard reaction enthaply $\Delta H° = 3800$ cal.mole^{-1}. This figure must of course equal $E_{A+} - E_{A-}$. It may be compared with the value of 2950 cal mole^{-1} found by direct calorimetric measurement at 25°C.[4] The difference is too large to be explained either by experimental errors or by uncertainty of α_{F5}. It will be realized however, that the calorimetric measurements yield the difference $\Delta H = \overline{H}_{F5} - \overline{H}_{F6}$ at total hexose concentrations ranging from 2 to 5 g/100 ml solution whereas the present measurements permit the calculation of $\Delta H° = \overline{H}_{F5}° - \overline{H}_{F6}°$ in the standard state which is one of infinite dilution. The difference,

$$\Delta H - \Delta H° = \overline{H}_{F5} - \overline{H}_{F5}° - (\overline{H}_{F6} - \overline{H}_{F6}°) = 850 \text{ cal.mole}^{-1}$$

may therefore be interpreted as that of the differential heats of solution of the five- and six-membered forms.

REFERENCES

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