ACTA CHEMICA SCANDINAVICA 19 (1965) 723–728

Determination of the Enthalpy of the Fructose Mutarotation by Reaction Calorimetry

BJØRN ANDERSEN and F. GRØNLUND

Fysisk-kemisk Institut, Kemisk Laboratorium IV, Københavns Universitet, København, Denmark

The molar enthalpy of formation of beta-fructofuranose from beta-fructopyranose was measured to be 2950 cal. The calorimeter used was of the adiabatic type, in which the temperature of the reaction mixture was sensed by a thermistor and recorded. The sensitivity of about 25 mV/degree C corresponds to roughly 40 cal/mV, and reaction heats of the order of 200 cal were conveniently determined with an overall accuracy of 3 %, using a 5 mV recorder.

Brown and Pickering[1] in 1897 described experiments from which they were able to calculate the enthalpy of the fructose mutarotation. They found 4.64 cal/g giving a molar enthalpy of 835 cal. However, they believed that they were measuring a reaction in which the unstable form of fructose was completely transformed to a stable form. What they actually measured was the transformation of the pyranose ring to an equilibrium mixture of pyranose and furanose. Since we now know that the equilibrium mixture at 25°C contains 31.56 % furanose[2] we can recalculate Brown and Pickering's molar enthalpy to 2645 cal. In the present work, the heat of reaction has been redetermined using more precise equipment, and with a better definition of start and end points of the reaction. Also, the final result gives the molar heat of reaction.

The present paper contains a description of the calorimeter followed by the results of reaction heat determinations.

DESCRIPTION OF THE CALORIMETER

The calorimeter was designed to be of the adiabatic type in which the heat liberated or absorbed by the reaction can be followed by temperature measurements. The container (see Fig. 1) consists of a Dewar vessel evacuated and baked out at 10^{-6} Torr in order to ensure good thermal insulation. Its thermal leak rate was subsequently found to be about 0.3 cal per min and per degree temperature difference, most of which is probably due to conduction through the glass wall. It is closed with a cover turned from plexiglass; and the whole, Dewar and cover, is surrounded by a water mantle through which

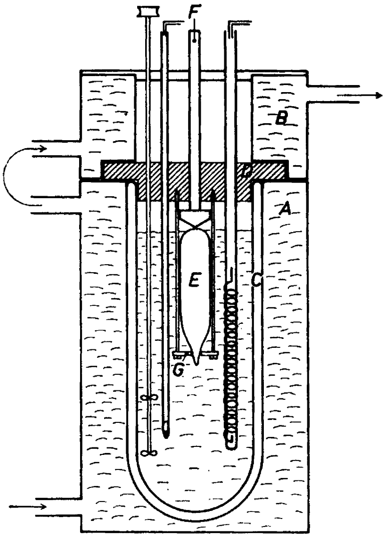

Fig. 1. Cross section of calorimeter. A: water mantle. B: detachable top part of water mantle. C: Dewar. D: perspex cover. E: ampoule. F: impinger. G: cage.

is circulated thermostat water maintained at 25.00°C. In order to minimize heat losses due to evaporation through the cover, the top part of the mantle is covered inside with wet filter paper. Electrical leads and shafts are passed through the thermostated top so that influence of room temperature on the inner compartment is greatly reduced.

A cage made of nickel-plated brass is mounted on the lower side of the plexiglass cover. Inside, a thin-walled glass ampoule containing the fructose may be placed. The reaction is started by crushing the ampoule with a conical impinger driven from above by a plexiglass rod.

Agitation is provided by another plexiglass shaft provided with two propellers. The shaft may be driven at two different speeds, a higher speed for quick dissolution of the contents of the ampoule, and a lower speed used during the reaction in order to minimize the stirring heat. A synchronous motor is used so that the heat evolution due to agitation may be kept constant and be evaluated with sufficient precision.

To calibrate the calorimeter before each experiment, a known amount of electric energy is dissipated in a 54.55 Ω heater. This is made from manganin wire coiled on a glass rod and embedded in araldite. A stabilized voltage of 6.17 V is connected either to a dummy load or to the calorimeter heater. The switch that sends the current either way also operates a digital quartz clock reading $\pm 10^{-4}$ sec. The amount of electric heat delivered may be determined with an accuracy of about 0.2 %.

The temperature sensing element is a 6 kΩ Siemens thermistor type K 17 whose resistance decreases 3.82 % per degree centigrade. Its properties were not found to vary significantly over the period of several months in which the apparatus has been used. A simplified diagram of the circuit is shown in Fig. 2. The bridge is fed from the above mentioned 6.17 V constant voltage supply. The fixed ratio resistors A and B have a very low temperature coefficient (5×10^{-5} deg^{-1}), and the same applies to the 5-decade, 0.1 % resistor X. The error voltage, which is fed into a line recorder with full scale deviation 5 mV, is found to be dependent on the thermistor temperature only, and proportional to this with a satisfactory degree of precision within the temperature range used. The sensitivity is of the order of 25 mV/degree C or about 0.2 degree C for full scale deviation of the recorder. For a typical filling of the calorimeter this corresponds to about 200 cal. The electric effect dissipated in the thermistor is much too feeble to have any significance in the heat balance, but it does necessitate a minimum of agitation to avoid local heating around the measuring point.

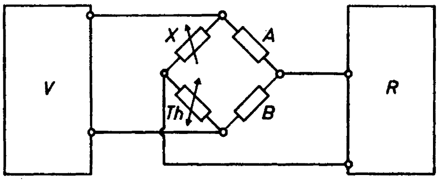

Fig. 2. Schematic diagram of measuring circuit. V constant voltage source (6.17 V). R recorder (5 mV f.s.d.). A and B: ratio resistors, 1000 Ω and 100 Ω, respectively. Th: thermistor, *ca.* 6 kΩ. X: 5-decade resistor 1-100 000 Ω.

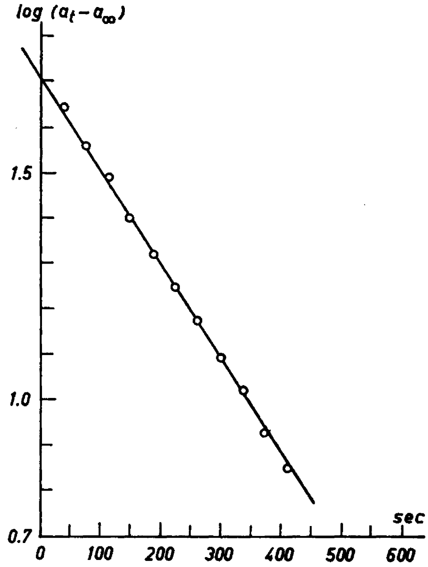

Fig. 3. Plot of log $(a_t - a_\infty)$ *vs.* t where a is the recorder deviation.

EXPERIMENTAL PROCEDURE

600 ml of 0.005 M Na-acetate buffer are transferred into the calorimeter. A glass ampoule is filled with a weighed quantity of β-fructopyranose (10—30 g), sealed, equilibrated in a 25.00°C thermostat for several hours and finally placed inside the cage. The calorimeter is then assembled and left overnight with thermostat water at 25.00°C circulating in order that thermal equilibrium may be established.

Immediately before the experiment, the calorimeter is heated about 0.15 degree per 10 g of fructose by means of the electric heater. This is done in order to compensate the temperature drop produced by the dissolution process, so that during the subsequent mutarotation the inner and outer temperature will be approximately equal. At the same time, the calorimeter constant is determined by recording the temperature. The reaction is started crushing the ampoule, and the time noted on the recorder. During the first 60 sec. vigorous agitation is maintained so that practically all of the fructose is dissolved. After this period agitation is reduced to 55 rpm and the recorder left running for more than one hour. The total fructose concentration is subsequently determined by polarimetric measurement.

The results from a typical run are shown in Fig. 3 where log $(a_\infty - a_t)$ has been plotted against t, a being the recorder deviation as read from the paper. As expected, the points are seen to approach a straight line, the slope of which gives the rate constant, while ΔH of the reaction may be calculated from its intersection with the ordinate axis.

CALCULATION OF THE REACTION HEAT

The overall process in the calorimeter involves two reactions: (a) dissolution of solid fructopyranose (A) into dissolved fructopyranose (B) and (b) mutarotation of part of the latter into fructofuranose (C), so that finally an equilibrium mixture is formed containing the fractions $(1-\xi_e)B + \xi_e C$. In a simplified treatment, (a) could be supposed to take place immediately upon crushing the ampoule so that subsequent temperature changes would be due to (b) exclusively. However, the two reactions overlap somewhat, and we shall try to account for this using an approximate scheme for (a).

The following symbols will be used:

A	solid fructopyranose
B	dissolved "
C	dissolved fructofuranose
k_d	rate constant for dissolution
k_m	$= k_1 + k_{-1}$, overall rate constant for mutarotation
x	concentration of undissolved fructopyranose
y	" " dissolved "
z	" " dissolved equilibrium mixture
c_0	total concentration of fructose, $x + y + z$
ξ_e	fraction of fructofuranose in the equilibrium mixture
V	solution volume
n	$c_0 V$, total amount of fructose in the calorimeter
q_d	molar enthalpy of dissolution of fructopyranose
q_m	" " " formation of fructofuranose from fructopyranose
Q_t	total enthalpy change up to time t

In order to account for the (small) effects of the finite duration of the dissolution, we shall make a rough but seemingly satisfactory assumption for its course. Suppose that the rate of dissolution is proportional to the amount of undissolved fructose A per unit volume. The dissolution will then proceed as a first order reaction with a (high) rate constant k_d:

$$A \xrightarrow{k_d} B$$

The next step might be written

$$B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

but as this leads to rather lengthy expressions for the heat evolved, we shall consider the mutarotation formally as a first order reaction transforming B into an equilibrium mixture $(1 - \xi_e) B + \xi_e C$ with a (relatively small) rate constant $k_m = k_1 + k_{-1}$. The overall reaction scheme may then be written

$$\underset{x(t)}{A} \xrightarrow{k_d} \underset{y(t)}{B} \xrightarrow{k_m} \underbrace{(1 - \xi_e)B + \xi_e C}_{z(t)}$$

The corresponding rate equations are

$$\mathrm{d}x/\mathrm{d}t = -\,k_\mathrm{d}x;\quad \mathrm{d}y/\mathrm{d}t = k_\mathrm{d}x - k_\mathrm{m}y;\quad \mathrm{d}z/\mathrm{d}t = k_\mathrm{m}y$$

and the solutions

$$\begin{aligned} x &= c_0\mathrm{e}^{-k_\mathrm{d}t} \\ y &= c_0\,\frac{k_\mathrm{d}}{k_\mathrm{d}-k_\mathrm{m}}\left(\mathrm{e}^{-k_\mathrm{m}t}-\mathrm{e}^{-k_\mathrm{d}t}\right) \\ z &= c_0\left(1-\frac{k_\mathrm{d}}{k_\mathrm{d}-k_\mathrm{m}}\,\mathrm{e}^{-k_\mathrm{m}t}+\frac{k_\mathrm{m}}{k_\mathrm{d}-k_\mathrm{m}}\,\mathrm{e}^{-k_\mathrm{d}t}\right) \end{aligned}$$

where $c_0 = x + y + z$ is the (constant) amount of A + B + C per unit volume, and $y = z = 0$ for $t = 0$.

In the present type of measurements the kinetics are studied by following not concentrations but heat evolved as a function of time. In fact a direct relation is established between heat evolved and recorder deviation, so that the temperature does not figure explicitly in the final results. It is therefore necessary to calculate the total amount of heat absorbed, Q_t, as a function of time and to compare this with the experimental results.

Q_t arises as a sum of two contributions. $y + z$ moles have dissolved, thereby absorbing $q_\mathrm{d}\ (y + z)$ cal; and z moles of equilibrium mixture C containing $\xi_\mathrm{e}z$ moles of fructofuranose have formed absorbing $q_\mathrm{m}\ \xi_\mathrm{e}z$. Therefore, the heat Q_t absorbed at the time t will be

$$\begin{aligned} Q_t &= V(q_\mathrm{d}\ (y+z) + q_\mathrm{m}\xi_\mathrm{e}\ z) \\ &= c_0V\left\{q_\mathrm{d}+\xi_\mathrm{e}q_\mathrm{m}-\frac{k_\mathrm{d}}{k_\mathrm{d}-k_\mathrm{m}}\,\xi_\mathrm{e}q_\mathrm{m}\mathrm{e}^{-k_\mathrm{m}t}-(q_\mathrm{d}-\frac{k_\mathrm{m}}{k_\mathrm{d}-k_\mathrm{m}}\,\xi_\mathrm{e}q_\mathrm{m})\mathrm{e}^{-k_\mathrm{d}t}\right\} \\ &\simeq n\left\{q_\mathrm{d}+\xi q_\mathrm{m}\left(1-\frac{k_\mathrm{d}}{k_\mathrm{d}-k_\mathrm{m}}\,\mathrm{e}^{-k_\mathrm{m}t}\right)\right\} \text{ for } k_\mathrm{d}t \gg k_\mathrm{m}t \end{aligned}$$

Consequently $Q_\infty = n(q_\mathrm{d} + \xi_\mathrm{e}q_\mathrm{m})$ from which the difference $Q_\infty - Q_t$ is readily formed

$$Q_\infty - Q_t \simeq n\,\frac{k_\mathrm{d}}{k_\mathrm{d}-k_\mathrm{m}}\,\xi_\mathrm{e}q_\mathrm{m}\ \mathrm{e}^{-k_\mathrm{m}t}$$

The approximation becomes increasingly better as time proceeds since $k_\mathrm{d} > k_\mathrm{m}$.

It is seen that a plot of ln $(Q_\infty - Q_t)$ *vs.* t will give a curve approaching a straight line whose slope is k_m, the mutarotation rate constant proper, and intersecting the ordinate axis at $n[k_\mathrm{d}/(k_\mathrm{d} - k_\mathrm{m})]\xi_\mathrm{e}q_\mathrm{m}$. If n, k_d, k_m, and ξ_e (the equilibrium mixture composition) are known, then q_m which is the molar enthalpy of the mutarotation reaction may be determined. The ratio $k_\mathrm{d}/(k_\mathrm{d} - k_\mathrm{m})$ accounts for the finite time of dissolution, assuming the simple kinetics described. With the experimental procedure adopted, it introduces a correction of about 3 %.

It remains to provide a relation between recorder deviation and $Q_\infty - Q_t$. This is established directly by maintaining a known voltage over the heater for a given length of time, and noting the resulting recorder indication.

Table 1.

Experiment No.	Temperature °C	Fructose concentration g/100 ml sol.	Amounts of fructose dissolved, g	ΔH cal/mole
1	25.2	3.62	21.752	3060
2	25.2	3.84	22.813	2890
3	25.1	2.98	18.386	2970
4	25.1	2.76	16.129	2930
5	25.2	3.74	26.467	2820
6	25.4	4.88	32.134	3140
7	25.1	2.28	13.38	2870

The average value is $\Delta H = +2950$ cal/mole with a standard deviation of 110 cal/mole in single measurement, and 40 cal/mole on the average figure.

RESULTS

A series of runs were made in the manner described above, all at a temperature close to 25°C, with fructose concentration varying between 13 and 32 g per 600 ml of buffered solvent. The results are given in Table 1, where the ΔH values give the calculated enthalpy of formation of 1 mole of β-fructofuranose from 1 mole of β-fructopyranose. They are based on the assumption that the equilibrium mixture in the given solvent at 25.00°C contains 31.56 mole % of β-fructofuranose.[2]

Acknowledgement. The authors wish to thank the *Carlsberg Foundation* which donated the recorder employed in this work.

REFERENCES

1. Brown, H. R. and Pickering, S. U. *J. Chem. Soc.* **71** (1897) 756.
2. Andersen, B. and Degn, H. *Acta Chem. Scand.* **16** (1962) 215.

Received December 8, 1964.