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NOTE ON THE THERMAL MUTAROTATION OF *d*-GALACTOSE, *l*-ARABINOSE, AND *d*-TALOSE

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It has been found that on changing the temperature of aqueous solutions of galactose, arabinose, and talose, mutarotations occur which give maximum values similar to the mutarotations of ribose,¹ and β -glucoheptose.² The first stage of these mutarotations, hereafter called thermal mutarotations, is found to be largely due to a change in the concentration of the labile constituents whose presence was discovered by Rüber and Minsaas.³ The later slow change presumably corresponds to a disturbance in the equilibrium of the α - and β -normal isomers such as that previously noted by Hudson.⁴

In order to compare the thermal mutarotations with the ordinary mutarotations new measurements on the above compounds were made at 0 and 20° C. The results obtained with 4-percent aqueous solutions are expressed by the following equations:

α -*d*-Galactose:

$$\begin{aligned} [\alpha]_D^{20} &= 64.9 \times 10^{-0.00803 t} + 5.6 \times 10^{-0.079 t} + 80.2. \\ [\alpha]_D^0 &= 66.3 \times 10^{-0.00093 t} + 2.7 \times 10^{-0.0119 t} + 84.0. \end{aligned}$$

Thermal mutarotation = $0.9 \times 10^{-0.00107 t} - 3.0 \times 10^{-0.0132 t} + 84.0$.
(25.0 \rightarrow 0.3° C).

α -*l*-Arabinose:

$$\begin{aligned} [\alpha]_D^{20} &= 77.3 \times 10^{-0.030 t} + 8.8 \times 10^{-0.138 t} + 104.5. \\ [\alpha]_D^0 &= 78.9 \times 10^{-0.00362 t} + 5.9 \times 10^{-0.0217 t} + 109.2. \end{aligned}$$

Thermal mutarotation = $1.6 \times 10^{-0.00364 t} - 4.9 \times 10^{-0.0271 t} + 109.2$.
(25.2 \rightarrow 0.2° C).

α -*d*-Talose:

$$\begin{aligned} [\alpha]_D^{20} &= 9.3 \times 10^{-0.0263 t} + 37.9 \times 10^{-0.126 t} + 20.8. \\ [\alpha]_D^{10} &= 9.8 \times 10^{-0.00362 t} + 27.5 \times 10^{-0.0255 t} + 25.2. \end{aligned}$$

Thermal mutarotation = $0.15 \times 10^{-0.0036 t} - 5.0 \times 10^{-0.0289 t} + 25.2$.
(25.8 \rightarrow 0.1° C).

¹ Phelps, Isbell, and Pigman, J. Am. Chem. Soc. 56, 747 (1934).

² Isbell, J. Am. Chem. Soc. 56, 2789 (1934).

³ Ber. deut. Chem. Ges. 59, 2266 (1926).

⁴ J. Am. Chem. Soc. 31, 80 (1909).

The thermal mutarotations were obtained by cooling the aqueous solutions rapidly from 25 to 0 ° C, measuring the optical rotations at various times, t , after the temperature change. The ordinary mutarotations of α -*d*-galactose and α -*l*-arabinose are in approximate agreement with those of Lowry and Smith⁵ and Riiber and Sørensen,⁶ while heretofore the mutarotations of α -*d*-talose had not been previously reported in equation form. The exponents representing the velocity constants for the reactions comprising the thermal mutarotations agree approximately with the corresponding constants for the ordinary mutarotations.

Inasmuch as the rapid reactions comprise a large part of the thermal mutarotations, the equilibrium proportions of the labile constituents vary markedly with temperature, indicating that the heat of reaction is considerable. The proportions of the α - and β -modifications change to a lesser degree, and hence the heat of interconversion is smaller.

Assuming that the changes during mutarotation are due to two simultaneous reactions, application of the Arrhenius equation,

$$\ln \frac{k_1}{k_2} = \frac{Q}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

to the exponents representing the rate of change for the rapid reactions at 0 and 20° C gives values for Q corresponding to 15,040, 14,700, and 12,750 calories per mole for α -*d*-galactose, α -*l*-arabinose, and α -*d*-talose; application of the same equation to the slow reactions gives values corresponding to 17,130, 16,800, and 15,820. The mean heat of activation, Q , for the substances corresponding to the rapid change in mutarotation is therefore less than the mean heat of activation for the slow change which comprises the interconversion of the α - and β -normal sugars.

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⁵ J. Phys. Chem. **33**, 9 (1929).

⁶ Kgl. Norske Videnskab. Selskabs, Skrifter, no. 7, 50 (1933).