

viously synthesized by methods which have been described elsewhere.⁴

TABLE I
DISTILLATION ANALYSIS OF A MIXTURE OF
POLYOXYETHYLENE GLYCOLS

Type of glycol	Taken, g.	Found, %	Actual, %	n_D^{20} pure glycol
Ethylene	6.16	29.5	29.5	1.4324
Dioxyethylene	None	0	Absent	1.4477
Trioxyethylene	4.34	20.8	20.8	1.4568
Tetraoxyethylene	6.00	28.8	29.9	1.4604
Pentaoxyethylene	None	0	Absent	1.4629
Hexaoxyethylene	4.35	20.85	19.9	1.4647

TABLE II
DETAILS OF THE ANALYSIS^a

Fraction	Found, g.	n_D^{20}	Distn. temp., °C.	Glycol
1	5.87	1.4324-1.4325	46-48	Ethylene
2	0.21	1.3425-1.4332	48-49	
3	.34	1.4330-1.4564	97-98	
4	3.91	1.4564-1.4568	99-104	Trioxoethylene
5	0.46	1.4568-1.4599	106-108	
6	5.43	1.4599-1.4605	125-144	Tetraoxyethylene
7	0.37	1.4605-1.4622	147-165	
8	.25	1.4622-1.4642	162	
9	3.52	1.4642-1.4646	163-167	Hexaoxyethylene
10	0.50	Residue	

^a Total weight, 20.85 g.; pressure, 0.001-0.002 mm.

The distillations were carried out in small flasks equipped with a form of Widmer column,⁵ *i. e.*, a vacuum-jacketed vertical tube with circular indentations (one ring for every 7 mm. length) of outside diameter 1 cm. The inside diameter of the outside tube was about 14 mm. A very slow rate of distillation was used, but otherwise only the ordinary precautions for fractionating under reduced pressure were applied.

(4) Perry and Hibbert, *Can. J. Research*, **14B**, 77 (1936).

(5) Widmer, *Helv. Chim. Acta*, **7**, 59 (1924).

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The Mutarotation of *d*-Glucose in Absolute Methanol

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Numerous investigators have studied the mutarotation of *d*-glucose in an effort to determine the number as well as the amount of isomers present in a solution of *d*-glucose. Some^{1,2,3} draw conclusions from their work that more than two forms

(1) Riiber and Minsas, *Ber.*, **59**, 2266 (1926).

(2) Worley and Andrews, *J. Phys. Chem.*, **31**, 742, 882, 1880 (1927); **32**, 307 (1928).

(3) Hendrick and Steinbach, *ibid.*, **42**, 335 (1938).

of glucose are present in solution. If the mutarotation of glucose involves only two isomers, the observed reaction rate should be that for two opposing reactions and the kinetic data should fit a first-order equation. The presence of a third form in concentrations comparable to the other two forms would cause the reaction to deviate considerably from the first order. For aqueous solutions the mutarotation of *d*-glucose appears to follow a first-order reaction exactly as observed by many investigators.^{4,5,6}

Since methanol acts less readily than water as a catalyzer for the reaction, it is logical to assume that the mutarotation in this solvent would be much slower than in water. If this is the case and the same mechanism is operative in methanol as in water, any divergence from a first-order process would be more easily observed. Worley and Andrews² claimed that one run in methanol with α -*d*-glucose showed a lag for over an hour at 25°. However, no data were given to support this claim. Aside from their work, little has been reported on methanol solutions and, since previous investigations are not too consistent, it was decided to study the mutarotation of *d*-glucose in absolute methanol at 25, 35 and 45°.

Discussion of Results

Anhydrous α - and β -*d*-glucose were obtained through the courtesy of the Corn Products Refining Co. of Argo, Ill. The alpha sugar was further purified by the method of Hudson and Yanovsky⁷ while the beta sugar was treated by the method of Hudson and Dale.⁵ The physical constants of the purified sugars agreed with accepted literature values. The absolute methanol was a synthetic product further dried with metallic sodium and fractionally distilled. The concentration of the solutions ranged from 0.6 to 1.3 g. of sugar per 100 ml. of solution. The course of the mutarotation was followed polarimetrically in jacketed tubes using a sodium arc as a source of illumination.

The velocity constants ($k_1 + k_2$) for the reaction were calculated from Hudson's⁸ equation which is based on the assumption that there is a simple equilibrium between the alpha and beta isomers of *d*-glucose. Of the numerous runs made,

(4) Isbell and Pigman, *J. Research Natl. Bur. Standards*, **18**, 141 (1937).

(5) Hudson and Dale, *THIS JOURNAL*, **39**, 320 (1917).

(6) Nelson and Beagle, *ibid.*, **41**, 559 (1919).

(7) Hudson and Yanovsky, *ibid.*, **39**, 1015 (1917).

(8) Hudson, *ibid.*, **26**, 1065 (1904).

the average values obtained for both alpha and beta glucose are given as follows, expressed in common logarithms with the time expressed in minutes:

Temp. °C.	25	35	45
$(k_1 + k_2) \times 10^4$	1.8 ± 0.4	3.4 ± 0.3	9.0 ± 0.5

Worley and Andrews² noted a divergence from a first-order reaction for about twenty minutes for both alpha- and beta-*d*-glucose in water at 0°. Since the velocity of mutarotation in absolute methanol is 0.00018 at 25° compared to 0.00073 for water at 0°, the divergence should extend over a period of about one hundred and fifty minutes. During the present investigation, in no case was a lag noticed during the first two hours of mutarotation of the alpha sugar in absolute methanol and no acceleration during a like period in the case of the beta sugar.

Though the velocity constants ($k_1 + k_2$) are the lowest and most consistent so far reported in the literature, they are not constant enough to calculate an exact value for the energy of activation for the mutarotation of *d*-glucose in methanol. However, using the average values for ($k_1 + k_2$) at 25, 35 and 45°, a mean value of 15,000 cal./mole is obtained from the Arrhenius equation. If the lowest values obtained at 25° (0.00014) and 45° (0.00085) are used, an activation energy of 17,000 cal./mole is obtained. This value agrees with that obtained for the mutarotation in water solution⁹ and appears to justify the assumption that the mechanism of mutarotation is the same in methanol as in water.

The initial rotations for both alpha- and beta-*d*-glucose were obtained graphically by extrapolating the first-order equation to zero time. The initial specific rotation of alpha-*d*-glucose in absolute methanol was found to be $[\alpha]_D +115.5 \pm 0.5^\circ$, compared to $+111.0^\circ$ for the same sugar in water solution. The corresponding value for the beta-*d*-glucose was $[\alpha]_D +17.0 \pm 0.5^\circ$, compared to $+19.5^\circ$ for a water solution. These values were the same for all three temperatures investigated within experimental error.

The specific rotation for the equilibrium mixture of alpha- and beta-*d*-glucose was found to be $[\alpha]_D +66.5 \pm 0.3^\circ$ in absolute methanol compared to $+52.6^\circ$ in water. If it is assumed that only two forms of sugar are present, the equilibrium mixture of *d*-glucose in methanol contains 50.1%

(9) G. F. and M. C. Smith, *J. Chem. Soc.*, 1413 (1937).

of the alpha form and 49.9% of the beta form. In water solution the equilibrium mixture contains 36.4% alpha and 63.6% beta-*d*-glucose. These results are in qualitative agreement with other workers^{2,7} who found that the percentage of alpha-*d*-glucose in the equilibrium mixture was increased in absolute methanol. However, Worley and Andrews² report 44.3% alpha- and 55.7% beta-*d*-glucose in the equilibrium mixture. To check the composition of the equilibrium mixture, samples were made up from the pure alpha and beta sugars in proportions reported by Worley and Andrews and also in the proportions found in this investigation. The sample with the composition reported here gave the equilibrium rotation immediately and showed no change of rotatory power on standing. The sample with the composition reported by Worley and Andrews gave an initial reading of $+58.4^\circ$ and on standing slowly changed, giving a final equilibrium rotation of $+66.3^\circ$.

The results of this study do not exclude the possibility of forms other than the alpha- and beta-*d*-glucose being present in solution. However, if there are other forms present, their concentration must be too small to be detected by this method. A recent communication by Cantor and Peniston¹⁰ indicates that the amount of the aldehyde isomer in an aqueous solution of *d*-glucose is considerably less than 0.3%.

(10) Cantor and Peniston, *THIS JOURNAL*, **62**, 2113 (1940).

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The Mutarotation of alpha-*d*-Glucose in Ethanol-Water Mixtures at 25°¹

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The mutarotation of alpha-*d*-glucose in water solutions has been investigated many times under various conditions, but the studies of this phenomenon in non-aqueous solutions are not so numerous. Recent work in this Laboratory² using pure methanol as a solvent confirmed the previously observed fact that physical quantities associated with this phenomenon are markedly different in various solvents. Since marked changes were noticed in absolute methanol, it was decided to investigate the mutarotation in ethanol. Due to the slight solubility of alpha-*d*-glucose in

(1) Presented before the Division of Physical and Inorganic Chemistry at the Cincinnati meeting, April, 1940.

(2) Rowley and Bailey, *THIS JOURNAL*, **62**, 2562 (1940).