

added and the mixture agitated with hydrogen chloride gas until it becomes homogeneous. From this solution thorium chloride octahydrate precipitates as pure white crystals, which are filtered off, washed with ether and dried. A sample of the salt when dissolved in water gives a negative thiocyanate test for iron.

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The Action of Monoethanolamine on Ethyl Bromomalonate

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In the course of work being carried out in these Laboratories dealing with the synthesis of diureides, the condensation of monoethanolamine with ethyl bromomalonate was attempted. As ordinarily carried out, we find condensation does not result; rather the bromine atom in the ester is replaced by hydrogen. This reaction is analogous to the action of alkaline reagents and halogen acids on similar compounds containing active halogen atoms.

The ethyl bromomalonate was prepared by the action of bromine on ethyl malonate dissolved in carbon tetrachloride. The product was carefully purified by several distillations through a column under reduced pressure. The fraction boiling at 126–127° under 18 mm. pressure was used.

Forty-six grams of monoethanolamine (0.752 mole) and 90 g. of the ethyl bromomalonate (0.376 mole) were refluxed together for six hours. On cooling, the mixture separated into two layers, the lower one eventually solidifying. The solid material was identified as monoethanolamine hydrobromide. The liquid upper layer was extracted with diethyl ether, thus effecting separation from any excess monoethanolamine, and the ether extract dried over anhydrous magnesium sulfate. The ether was distilled off and the resulting liquid fractionated. A low-boiling fraction, b. p. 58–60° (2 mm.), was shown to be ethyl malonate by its refractive index (n_D^{20} 1.4144) and density (d_4^{20} 1.055). The yield was 11 g. A higher boiling fraction (36 g.), b. p. 92–93° (2 mm.), was identified by its boiling point and density (d_4^{20} 1.426) as unchanged ethyl bromomalonate.

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The Mutarotation of α -D-Glucose in Dioxane-Water Mixtures at 25°

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The mutarotation of α -D-glucose has been an object of study for many years by numerous investigators. Though the majority of the experiments concerned this phenomenon in aqueous solution both with and without catalysts, a few have been studied in mixed aqueous solvents. Worley and Andrews² studied the mutarotation in methanol-water mixtures; Richards, Faulkner and Lowry³ in both methanol-water mixtures and ethanol-water mixtures; Lowry and Faulkner⁴ in pyridine-water mixtures; and more recently Rowley⁵ in ethanol-water mixtures at 25°. The mutarotation of glucose in solution is believed by many to be catalyzed by acids and bases and since water is a complete catalyst, having both acidic and basic properties, the reaction is fairly rapid in pure water. Absolute methanol is amphiprotic and apparently a complete catalyst but much inferior to pure water⁶ as is absolute ethanol.⁵ On the other hand, pyridine is not amphiprotic but is a fairly strong base so mixtures of this solvent and water should be a fair catalyst for the mutarotation.

In continuing the studies of the mutarotation of α -D-glucose in mixed aqueous solvents, it was decided to use an inert organic solvent which probably does not itself catalyze the reaction. Unlike the alcohols, which have been used in previous studies, dioxane has no apparent acid group and its basic properties are probably relatively weak. Thus it might be assumed that its catalytic effect on the mutarotation will be exceedingly small. This appears to be justified by subsequent experimental work. Since α -D-glucose is fairly soluble in mixtures up to ninety weight per cent. of dioxane, the mutarotation of this sugar was studied in dioxane-water mixtures at 25°.

Discussion of Results

The solutions were made by dissolving a weighed amount of pure anhydrous α -D-glucose in dioxane-water mixtures of known composition. The concentration ranged from 4.0 g. of sugar/

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(2) Worley and Andrews, *J. Phys. Chem.*, **31**, 742, 1880 (1927).

(3) Richards, Faulkner and Lowry, *J. Chem. Soc.*, 1733 (1927).

(4) Lowry and Faulkner, *ibid.*, **127**, 2883 (1925).

(5) Rowley, *THIS JOURNAL*, **62**, 2563 (1940).

(6) Rowley and Bailey, *ibid.*, **62**, 2562 (1940).

100 ml. of solution to 0.6 g. of sugar/100 ml. of solution, decreasing as the solubility in the dioxane-water mixtures decreased. In all cases unsaturated solutions were used. The mutarotation was followed polarimetrically in jacketed tubes using a sodium arc as a light source.

Dioxane, of histological grade, was dried by refluxing with sodium and then fractionally distilled in an all glass apparatus. The product boiled at 100.8° and gave a refractive index n_{25}^{25} 1.41836. No special precautions were taken to remove peroxides since freshly distilled samples and those which had been standing for some time gave identical results. Thus the peroxides, which are known to form readily in dioxane, apparently do not influence the mutarotation of glucose.

A summary of the values for the initial specific rotation, the equilibrium specific rotation and the velocity constants ($k_1 + k_2$), expressed in common logarithms with the time expressed in minutes, is given in Table I.

TABLE I

SUMMARY OF RESULTS			
Wt. % dioxane	Init. rotn. [α] ₂₅ ^D	Equil. rotn. [α] ₂₅ ^D	($k_1 + k_2$) × 10 ⁴
0.0	110.5	52.6	105
20.6	111.0	54.2	63.7
40.9	111.1	55.4	36.4
50.8	111.3	56.3	25.9
60.8	111.6	57.1	16.8
70.7		58.0	11.8
80.6	111.7	59.1	7.3
85.4		59.7	5.5
90.3		60.7	3.6
95.3		63.0	1.5
100		(67.0)	(0.5)

The initial specific rotation was obtained by extrapolating to zero time the plot of $\log(\alpha_t - \alpha_\infty)$ against time. With the more dilute dioxane solutions, the extrapolation could be carried out with reasonable precision. However, above concentrations of 50% dioxane, the rate of solution of the glucose is rather slow so the reported extrapolated values are only approximations. A plot of the initial specific rotation against weight per cent. dioxane shows a slight but definite increase as the amount of dioxane increases. Due to experi-

mental difficulties it was impossible to determine whether a sharp rise occurs above 80% dioxane as was found in ethanol-water solutions.⁵

The equilibrium specific rotation increases as the per cent. of dioxane increases as was found in the case of ethanol-water.⁵ The dioxane curve is slightly higher than the ethanol curve and above 80% dioxane the rise becomes more rapid, giving an extrapolated value of about +67° in pure dioxane. Since the solubility of glucose in this solvent is so slight, it is doubtful if this could be checked directly. It is interesting to note that the apparent equilibrium specific rotation value in three pure organic solvents is very close: methanol +66.5°,⁶ ethanol +65.5°,⁵ dioxane +67°.

Since the mutarotation of α -D-glucose is known to be a first order reaction, the velocity constant ($k_1 + k_2$) was calculated from the slope of the straight line obtained when $\log(\alpha_t - \alpha_\infty)$ is plotted against the time. When the velocity constants are plotted against weight per cent. of dioxane, the last four points lie on a straight line allowing extrapolation to the value in the pure solvent.

It is seen from the table that the addition of small amounts of dioxane to water has a much greater effect in reducing the rate of mutarotation than the addition of water to dioxane has in increasing the rate. This is in agreement with the results obtained for methanol-water mixtures² and ethanol-water mixtures.⁵ For mixed aqueous solvents containing less than 30% by weight of methanol, ethanol or dioxane, the rate constant is practically the same for a given concentration of the organic solvent. Above this concentration the catalytic effect of the organic solvent itself is possibly effective for the values for dioxane-water are lower than for either methanol-water or ethanol-water mixtures of equal weight concentration. The extrapolated velocity constant for pure dioxane is less than 0.00005, which is lower than the values found in either pure methanol, 0.00018,⁶ or ethanol, 0.0001.⁵

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