The characteristics of the half-wave potential have been discussed, and an equation was derived relating the half-wave potentials to the ordinary standard potentials of the metals. The difference between the polarographic half-wave potential of a simple metal ion and the ordinary standard potential of the metal was shown to be a function of three distinct factors: (1) the affinity of the metal for mercury; (2) the solubility of the metal in mercury; and (3) the kinetics of the diffusion processes in the solution and in the mercury drops.

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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

Mutarotation of Tetramethyl-α-d-glucopyranose and Tetramethyl-α-d-mannopyranose

BY B. CLIFFORD HENDRICKS AND ROBERT E. RUNDLE

In a previous paper,[1] a study of the complexity of the mutarotation of *d*-galactopyranose was reported. In this communication a study of the analogous glucose and mannose sugars is presented.

The mutarotation of tetramethyl-α-*d*-glucopyranose has been investigated by Purdie and Irvine,[2] Lowry and co-workers[3-5] and Böeseken and Couvert[6] in water and other solvents. These workers, however, gave direct attention to the reaction order of the sugars' mutarotations at only one temperature. The mutarotation of tetramethyl-α-*d*-mannopyranose has been previously reported,[7] though only incidentally.

A systematic study of the unmethylated α-*d*-glucose[8] does not support the reported[9] complex mutarotation of α-*d*-glucose. The authors proposed to learn whether methylation and mutarotation at or near 0° would give evidence of mutarotation complexity.

Since there is a paucity of data upon tetramethylmannose they prepared and followed the mutarotation of tetramethyl-α-*d*-mannopyranose also.

The two sugars were prepared as indicated in a previous paper.[10] The properties of the tetramethyl-α-*d*-glucopyranose used were: initial rotations, $[\alpha]^0D$ +104.0; $[\alpha]^{25}D$ +104.0; equilibrium rotations: $[\alpha]^0D$ +80.4; $[\alpha]^{25}D$ + 84.8 and m. p. 92.5–93.5°. The constants for the tetramethyl-α-*d*-mannopyranose used were m. p. 49–50°; initial rotations: $[\alpha]^0D$ +11.5; $[\alpha]^{25}D$ +6.3; equilibrium rotations: $[\alpha]^0D$ +2.5 and $[\alpha]^{25}D$ −0.2.

(1) Hendricks and Rundle, THIS JOURNAL, **60**, 3007 (1938).
(2) Purdie and Irvine, *J. Chem. Soc.*, **85**, 1070 (1904).
(3) Lowry and Richards, *ibid.*, **127**, 138 (1925).
(4) Jones and Lowry, *ibid.*, 720 (1926).
(5) Richards, Faulkner and Lowry, *ibid.*, 1733 (1927).
(6) Böeseken and Couvert, *Rec. trav. chim.*, **40**, 354 (1921).
(7) Drew, Goodyear and Haworth, *J. Chem. Soc.*, 1237 (1927).
(8) Isbell and Pigman, *Bur. Standards J. Research*, **18**, 141 (1937).
(9) Worley and Andrews, *J. Phys. Chem.*, **32**, 307 (1928).
(10) Hendricks and Rundle, THIS JOURNAL, **60**, 2563 (1938).

TABLE I

MUTAROTATION OF TETRAMETHYL-α-*d*-GLUCOPYRANOSE AT 25°

2.4298 g. of sugar in 25 ml. of water

Time Min.	Time Sec.	Rotation obsd.	$(k_1 + k_2) \times 10^3$ calcd.
7	15	19.60	
9	0	19.49	
11	15	19.32	9.00
13	50	19.15	8.57
20	30	18.71	8.84
25	0	18.46	8.75
34	50	17.98	8.70
49	0	17.42	8.75
62	25	17.02	8.78
88	15	16.50	8.81
104	0	16.25	9.17
125	0	16.07	9.20
	∞	15.75	
			Av. 8.86 ± 0.34

TABLE II

MUTAROTATION OF TETRAMETHYL-α-*d*-GLUCOPYRANOSE AT 1.0°

2.819 g. of sugar in 25 ml. of water

Time Min.	Time Sec.	Rotation obsd.	$(k_1 + k_2) \times 10^3$ calcd.
9	15	25.32	
10	45	25.30	
18	10	25.24	0.754
25	30	25.18	.644
32	30	25.12	.786
40	50	25.03	.864
58	20	24.90	.829
81	45	24.82	.670
166	30	24.26	.709
255	0	23.78	.707
293	0	23.62	.693
424	0	23.14	.661
575	0	22.64	.660
646	0	22.46	.651
748	0	22.18	.662
	∞	20.68	
			Av. 0.715 ± 0.149

TABLE III

MUTAROTATION OF TETRAMETHYL-α-d-MANNOPYRANOSE AT 25°

1.3911 g. sugar in 25 ml. of water

Time Min.	Sec.	Rotation obsd.	$(k_1 + k_2) \times 10^3$ calcd.
10	15	0.75	
11	15	.70	
12	25	.69	
14	00	.66	15.8
15	30	.63	18.6
20	00	.59	15.1
29	00	.48	18.1
36	50	.43	17.4
45	15	.38	18.3
51	20	.37	16.7
80	00	.30	
	∞	−.28	
			Av. 17.1 ± 2.0

TABLE IV

MUTAROTATION OF TETRAMETHYL-α-d-MANNOPYRANOSE AT 0.0°

0.807 g. of sugar in 20 ml. of water

Time Min.	Sec.	Rotation obsd.	$(k_1 + k_2) \times 10^3$
10	30	0.48	
12	10	.42	
13	30	.41	
65	0	.35	1.39
91	30	.34	1.08
131	0	.30	1.15
263	0	.20	1.14
585	0	.07	1.19
	∞	.02	
			Av. 1.19 ± 0.20

The experimental method followed and technique used were as described in a communication[1] previously cited. In this paper, as there stated, the rotation velocity constant, $k_1 + k_2$, is considered an index of the character of the mutarotation.

Results listed in Tables I, II, III and IV are representative of the results of the numerous experiments made.

The "thermal mutarotation" of tetramethyl-α-d-glucopyranose, using the procedure described previously,[1] was followed over a period of fifteen hours after a temperature change of from 25 to 0°. The calculations from the data for twenty-two observations gave a velocity constant, $(k_1 + k_2) \times 10^3$, of 0.640 ± 0.135. The deviations were random in their distribution with no more indication of trends than that shown in Table II. However, due to smaller changes in specific rotation during mutarotation, the experimental error is larger for methylated sugars. This is especially true for observations for the "thermal mutarotation" of the tetramethylglucose.

Discussion of Results

For purposes of ready comparison the constants of the three methylated sugars are tabulated with their unmethylated analogs in Table V. The data for the latter sugars are taken from the publication of Isbell and Pigman.[8] Those for the methylated galactose are from the paper previously listed.[1]

The mutarotation velocity constants for the methylated glucose show but slightly more variability than do those for the unmethylated sugar, probably due to experimental error. That agreement and the small variation of the velocity of mutarotation constants for the "thermal mutarotation" experiment give no support to the suggested[9] second order type of mutarotation for α-d-glucopyranose. Likewise the mutarotation of tetramethyl-α-d-mannopyranose is as truly of the first order as that of α-d-mannopyranose itself. It should be noted that there is as good an agreement between the heats of activation for the methylated sugars, 16,970 ± 260, as with those of the non-methylated sugars, 17,000 ± 300. These deviations are of about the same order as that introduced by the experimental error.

TABLE V

Sugar	$(k_1 + k_2) \times 10^3$	$(k' + k_2) \times 10^3$	Heat of activation, Q[b]
α-d-Glucopyranose	0.74 ± 0.05 at 0.2°	6.32 ± 0.14 at 20°	17,200
Tetramethyl-α-d-glucopyranose	.72 ± .15 at 1.0°	8.86 ± .34 at 25°	16,963
α-d-Galactopyranose[a]	.93 ± .02 at 0.0°	8.03 ± .04 at 20°	17,100
Tetramethyl-α-d-galactopyranose	.91 ± .06 at .0°	12.1 ± 1.7 at 25°	16,720
α-d-Mannopyranose	2.16 ± .15 at .1°	17.3 ± 0.2 at 20°	16,700
Tetramethyl-α-d-mannopyranose	1.19 ± .20 at .0°	17.1 ± 2.0 at 25°	17,230

[a] The constants for galactose are given only for the second slower phase of its complex mutarotation.

[b] $2.0326 \log \frac{(k_1 + k_2)}{(k_1' + k_2')} = \frac{Q}{1.9864}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Summary

The mutarotations of the tetramethylpyranose forms of both α-d-glucose and α-d-mannose have been investigated at the temperatures 0.0 and 25°.

Neither sugar shows a mutarotation of other

than the first order within the precision limits of the experimental technique used.

The heats of activation of these methylated sugars show a marked agreement with the heats of activation of analogous non-methylated sugars.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF CALIFORNIA]

Sulfophenylarsonic Acids and Certain of their Derivatives. II. *p*-Sulfonamidophenylarsonic Acid

BY J. F. ONETO AND E. L. WAY

In this paper, which is a continuation of our studies of sulfophenylarsonic acids and their derivatives, a number of compounds have been described, two of which (*p*-sulfonamidophenylarsonic acid and *p*-sulfonamidophenylarsine oxide) should be of pharmacological interest.

The preparation of *p*-sulfonamidophenylarsonic acid was effected by application of the Bart reaction to sulfanilamide.

p-Sulfonamidophenylarsine oxide was prepared by two methods: (A) hydrolysis of *p*-sulfonamidophenyldibromoarsine with ammonium hydroxide; (B) interaction between *p*-chlorosulfonylphenyldichloroarsine and ammonium hydroxide. The oxide was converted to *p*-sulfonamidophenylarsonic acid by oxidation with hydrogen peroxide in alkaline solution.

p-Chlorosulfonylphenylarsonic acid, obtained by partial hydrolysis of *p*-chlorosulfonylphenyltetrachloroarsine, reacts with aniline to form *p*-sulfonanilidophenylarsonic acid. This reaction is now being studied in the preparation of substituted anilide and amide derivatives of *p*-sulfophenylarsonic acid.

Experimental Part

***p*-Sulfonamidophenylarsonic Acid.**—This acid was prepared by application of the Bart reaction to sulfanilamide (*p*-aminobenzenesulfonamide). It crystallizes from water in colorless, glistening needles, yield 25%. The acid is somewhat soluble in alcohol and in acetic acid; insoluble in acetone.

Anal. Calcd. for $C_6H_8O_5NAsS$: As, 26.66. Found: As, 26.51.

When heated for two hours under reduced pressure at 185–190°, the acid loses one molecule of water to form the anhydride.

Anal. Calcd. for $C_6H_6O_4NAsS$: As, 28.47. Found: As, 28.36.

The crystalline silver salt of *p*-sulfonamidophenylarsonic acid was obtained when 0.7 g. of the acid dissolved in 10 cc. of boiling water was treated with an excess of 0.25 *N* silver nitrate solution; yield 0.7 g.

Anal. Calcd. for $C_6H_7O_5NAsSAg$: As, 19.31; Ag, 27.81. Found: As, 19.39; Ag, 27.50.

In a second procedure the acid was obtained when 2 g. of *p*-sulfonamidophenylarsine oxide (obtained by treating *p*-chlorosulfonylphenyldichloroarsine with ammonium hydroxide) dissolved in 10 cc. of 10% sodium hydroxide was oxidized with 3 cc. of 30% hydrogen peroxide by heating on the steam-bath for one-half hour. The hot solution was acidified, whereupon the acid crystallized on cooling; yield 0.7 g.

The acid thus obtained was converted to the corresponding dibromoarsine; mixed m. p. 190–191°.

***p*-Sulfonamidophenyldiiodoarsine.**—A hot solution consisting of 1.7 g. of *p*-sulfonamidophenylarsonic acid in 25 cc. of water was treated with 15 cc. of 50% hydriodic acid. The diiodoarsine crystallized on cooling; yield, after recrystallizing from glacial acetic acid, 1.8 g.; m. p. 192–193°.

Anal. Calcd. for $C_6H_6O_2NAsSI_2$: As, 15.45; I, 52.35. Found: As, 15.36; I, 52.70.

***p*-Sulfonamidophenyldibromoarsine.**—A solution prepared from 2 g. of *p*-sulfonamidophenylarsonic acid, 20 cc. of 30% hydrobromic acid and a trace of hydriodic acid was saturated with sulfur dioxide. The resulting crystalline precipitate was recrystallized from glacial acetic acid; yield 2 g.; m. p. 191–192°.

Anal. Calcd. for $C_6H_6O_2NAsSBr_2$: As, 19.16. Found: As, 19.26.

***p*-Sulfonamidophenyldichloroarsine.** (A).—A solution consisting of 2 g. of *p*-sulfonamidophenylarsonic acid, 10 cc. of 37% hydrochloric acid and a trace of hydriodic acid was saturated with sulfur dioxide. The resulting dichloroarsine was recrystallized from glacial acetic acid; yield 1.5 g.; m. p. 176–177°.

Anal. Calcd. for $C_6H_6O_2NAsSCl_2$: As, 24.81. Found: As, 24.85.

(B).—Two grams of *p*-sulfonamidophenylarsonic acid was ground in a mortar with 12 cc. of phosphorus trichloride. After standing for one-half hour, the mixture was treated with ice water and the resulting crude dichloroarsine removed by filtration. The crude dichloroarsine was purified by dissolving in hot 10% hydrochloric acid and precipitating the crystalline substance by the addition of concentrated hydrochloric acid; yield 1.4 g.; mixed m. p. 176–177°.

(C).—One gram of *p*-sulfonamidophenylarsine oxide was dissolved in 10 cc. of hot 10% hydrochloric acid. The crystalline dichloroarsine was precipitated by the