NOTES

The Preparation of 1,5-Dimethylnaphthalene

By Eleanore W. J. Butz

1,5-Dimethylnaphthalene has been prepared by several procedures.[1] A convenient synthesis, by well-known reactions, which can yield only the 1,5-isomer is presented here. No separation of isomeric products is involved at any stage. 5-Methyl-1-tetralone[2] was prepared by the following steps: *o*-bromotoluene → β-*o*-tolylethyl alcohol → β-*o*-tolylethyl bromide → diethyl β-*o*-tolylethylmalonate → β-*o*-tolylethylmalonic acid → γ-*o*-tolylbutyric acid → 5-methyl-1-tetralone.

Reaction of this ketone with methylmagnesium iodide gave a carbinol which was not purified, but was dehydrated directly by heating in a Claisen flask with a crystal of iodine in a slow stream of carbon dioxide at 200° for one hour. The mixture was then distilled at 28 mm. The main product, presumably 3,4-dihydro-1,5-dimethylnaphthalene (b. p. 130–3° at 25 mm.), was accompanied by 10% of 1,5-dimethylnaphthalene (m. p. 76°). Five grams of the liquid distillate was heated with palladium–charcoal at 250° for two hours. Extraction of this mixture with ether yielded 4 g. of 1,5-dimethylnaphthalene (m. p. 76–7°). After recrystallization from ether and methanol, the product was dried at 35° and 80 mm. for one hour; m. p. 80°; picrate, m. p. 137°.

Anal.[3] Calcd. for $C_{12}H_{12}$: C, 92.31; H, 7.69. Found: C, 92.19; H, 7.73.

(1) Vesely and Stursa, *Coll. Czechoslov. Chem. Commun.*, **3**, 430 (1931); Anderson and Short, *J. Chem. Soc.*, 485 (1933); Manske and Ledingham, *Can. J. Research*, **17B**, 14 (1939).

(2) Harvey, Heilbron and Wilkinson, *J. Chem. Soc.*, 423 (1930).

(3) Microanalysis by Arlington Laboratories.

Bureau of Animal Industry
United States Department of Agriculture
Beltsville, Maryland Received July 12, 1940

The Heat of Solution of Gadolinium Sulfate Octahydrate and the Entropy of Gadolinium Ion

By Lowell V. Coulter and Wendell M. Latimer

As an aid to a better understanding of the process of hydration of ions from the thermodynamic viewpoint, additional ionic entropy values for monatomic tripositive ions are of considerable value. As a step in this direction an entropy value for Gd^{+++} has been calculated in the usual manner from entropy, heat of solution and estimated free energy of solution data.

The heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ has been measured by Giauque and Clark[1] and Ahlberg and Clark.[2] On the basis of these measurements Kelley[3] has obtained 155.7 cal./deg. for the entropy which includes the magnetic entropy R ln 8 for each gram ion of Gd^{+++}.

The heat of solution of $Gd_2(SO_4)_3 \cdot 8H_2O$ was measured in a calorimeter already described in This Journal.[4] The sample used in these measurements was prepared from some gadolinium oxalate of about 95% purity which was donated by Dr. Herbert McCoy. The impurity is probably neighboring rare earths which would lead to no appreciable error in the measurements. The oxalate was ignited to the oxide, dissolved in sulfuric acid and recrystallized. After attaining constant water content at room temperature, the hydrated sulfate was, of necessity, powdered to assure a rapid rate of solution. An analysis for volatile constituents of the salt by ignition to the oxide indicated a deficiency of 0.3% as compared with the calculated value. A portion of this may be attributed to the impurities in the sample used. The results of the experiments are tabulated in Table I. The final volume in each case was 1050 cc. As no heat of dilution data are available for this salt, the measured value will be used uncorrected in the following calculations. The error involved from this procedure will be taken into account in the estimated error quoted for the ionic entropy.

Table I

Heat of Solution of $Gd_2(SO_4)_3 \cdot 8H_2O$ at 25°

Sample, wt. g.	Mole	Observed heat absorbed, cal.	Molal heat absorbed, cal.
13.3563	0.01788	−118.66	−6640
13.0707	.01750	−118.56	−6775
			−6710 ± 100

Interpolation of the "I. C. T."[5] values for the solubility of $Gd_2(SO_4)_3 \cdot 8H_2O$ gives 0.041 M for the saturated solution at 25°. Since no activity coefficient data are available for $Gd_2(SO_4)_3$, the activity coefficient was estimated from data for $La_2(SO_4)_3$ and $In_2(SO_4)_3$. For 0.01 M $La_2(SO_4)_3$,

(1) Giauque and Clark, This Journal, **54**, 3135 (1932).

(2) Ahlberg and Clark, *ibid.*, **57**, 437 (1935).

(3) Kelley, "Bureau Mines Bulletin 394."

(4) Pitzer, This Journal, **59**, 2365 (1937).

(5) "International Critical Tables," Vol. IV, p. 227.

Rodebush[6] calculated γ to be 0.15 from freezing point lowering data.[7] An extrapolation with the aid of cryoscopic data obtained by Noyes and Johnston[8] for the same salt resulted in the approximate value 0.05 for γ at saturation at 25°.

In a study of $In_2(SO_4)_3$ solutions Hattox and DeVries[9] determined the activity coefficient of this salt from e. m. f. measurements. By interpolation γ has the value 0.06 for $In_2(SO_4)_3$ at 0.04 M. Taking an average of 0.055 at 0.041 M for γ for $Gd_2(SO_4)_3$ the free energy of solution to form the hypothetical 1 M solution is

$$\begin{aligned}\Delta F &= -RT \ln (\gamma m)^5(2^2 \cdot 3^3) \\ &= -1363.8 \log (0.055 \times 0.041)^5(2^2 \cdot 3^3) \\ &= 15{,}200 \pm 1000 \text{ cal.}\end{aligned}$$

Knowing the heat of solution and an approximate free energy of solution for this salt, the entropy of solution at 25° was calculated to be −73.5 cal./deg. mole. The calculation of the relative partial molal entropy of Gd^{+++}, involving the entropy of $Gd_2(SO_4)_3 \cdot 8H_2O$,[3] the partial molal entropy of $SO_4^{=}$[10] (4.4 cal./deg. mole) and the entropy of water[11] (16.75 cal./deg.) may now be completed as follows

$$\begin{aligned}\bar{S}^\circ_{Gd^{+++}} &= {}^1/_2(\Delta S_{soln.} + S^\circ_{Gd_2(SO_4)_3 \cdot 8H_2O} - 3\bar{S}^\circ_{SO_4^=} - 8S^\circ_{H_2O} \\ &= {}^1/_2(-73.5 + 155.7 - 13.2 - 134.0) = -32.5 \pm \\ &\quad 4 \text{ cal./deg. mole}\end{aligned}$$

The assignment of an entropy value to Gd^{+++} supplements data for two other tripositive ions, Fe^{+++} and Al^{+++}, and now makes possible a comparison of hydration entropies of tripositive ions with mono- and dipositive types. Heretofore, hydration entropies, the calculation of which has already been described,[12] have been found best related to the reciprocal of the ion radius in a linear manner for singly and doubly charged ions.[12,13] If such calculations are made for Gd^{+++}, Fe^{+++} and Al^{+++} a similar relationship exists.

As an empirical rule the entropy of hydration of singly, doubly and triply charged ions may now be approximately represented as follows

$$\Delta S_{hyd.} = -An/r + B_n$$

where A is a constant, common to all ions, having the value 80, n is the number of charges on the ion and B_n has the values 28, 40 and 67 for singly, doubly, and triply charged ions, respectively. What the significance of the above expression may be is not known. However, it does indicate that hydration entropies may be more closely related to the first power of the charge than to the square as previously supposed.[13]

(6) Rodebush, THIS JOURNAL, **48**, 709 (1926).
(7) Hovorka and Rodebush, *ibid.*, **47**, 1614 (1925).
(8) Noyes and Johnston, *ibid.*, **31**, 987 (1909).
(9) Hattox and DeVries, *ibid.*, **58**, 2126 (1936).
(10) Latimer, Pitzer and Smith, *ibid.*, **60**, 1829 (1938).
(11) Giauque and Stout, *ibid.*, **58**, 1144 (1936).
(12) Latimer, Pitzer and Slansky, *J. Chem. Phys.*, **7**, 108 (1939).
(13) Latimer, *Chem. Rev.*, **18**, 349 (1936).

THE CHEMICAL LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
RECEIVED MAY 29, 1940

Bieugenol in a Commercial Geraniol[1]

BY HOWARD A. JONES AND H. L. HALLER

During an examination of commercial geraniol prepared from Java citronella oil for use in Japanese beetle baits, a gelatinous precipitate was formed when a sample of the geraniol was heated. On cooling the geraniol, the product did not redissolve. It was separated by filtration, and the adhering geraniol was removed with alcohol and ether. Chemical examination proved it to be the zinc salt of bieugenol (3,3′-diallyl-5,5′-dimethoxy-6,6′-dihydroxybiphenyl). Eugenol, a known constituent of Java citronella oil, was also shown to be present in the commercial geraniol.

When the geraniol was washed with water, the zinc was removed as a water-soluble salt, but the aqueous solution contained no free or combined phenols. When the water-washed oil was heated, no precipitate was formed. Free bieugenol was isolated from the residue remaining after steam distillation of a sample of the geraniol. Thus it is shown that bieugenol is present as such in the commercial geraniol and that the formation of the insoluble zinc salt is promoted by heat.

The zinc in the geraniol undoubtedly came from the galvanized drums in which geraniol is frequently stored, and the bieugenol probably resulted from the oxidation of eugenol. Commercial geraniol used for Japanese beetle baits contains, in addition to the free eugenol, alcohols, esters, terpenes and sesquiterpenes. Whether or not these compounds or the zinc salt has any role in promoting the formation of bieugenol is not known. Additional information on this point would be of interest as possibly leading to a new method for the preparation of bieugenol as well as other biphenols. Such a study is beyond the scope of our work.

Experimental

Zinc Bieugenol.—A commercial geraniol (1332 g.) was subjected to fractional distillation at a pressure of 2 to 4

(1) Not subject to copyright.

mm. and a temperature in the still of 100 to 150°. The gelatinous precipitate that separated was removed by filtration at an early stage in the distillation. After being washed with ethanol and ether and dried to constant weight in a vacuum desiccator, it weighed 1.17 g., or about 0.09% of the original weight. On ignition the precipitate gave 19.7% ash (calcd. for $C_{20}H_{20}O_4Zn$, 20.8% ZnO). The ash gave qualitative tests for zinc. Another portion of the dried precipitate, after being suspended in water, acidified with dilute sulfuric acid, and extracted with ether, gave after removal of the solvent a white crystalline solid. After several recrystallizations from dilute ethanol it melted at 106°.[2] In ethanol solution the compound gave a deep blue color with ferric chloride. When it was mixed with a sample of pure bieugenol prepared from eugenol by the method of Erdtman,[3] there was no depression of the melting point. On catalytic hydrogenation in ethanol with Adams platinum oxide as catalyst, it was readily reduced with the formation of tetrahydrobieugenol, which after recrystallization from ethanol melted at 151°. Erdtman gives 152° as the melting point of this compound.

Eugenol.—A portion (178 g.) of that fraction of the crude geraniol remaining after three-fourths by volume had been distilled was diluted with ether and extracted with 5% aqueous sodium carbonate and then with 5% aqueous sodium hydroxide. The latter extract was acidified and extracted with ether. The water-washed ether extract was dried over sodium sulfate. After removal of the ether, there remained 4.5 g. of oil having a clove-like odor. It was purified by distillation under reduced pressure. It distilled at 142–142.5° (23.5 mm.). The distillate ($n^{30}D$ 1.5345) gave a deep blue color with ferric chloride. The 3,5-dinitrobenzoate prepared by the method of Phillips and Keenan[4] had a melting point of 130.5°. A mixture with the 3,5-dinitrobenzoate of eugenol gave no depression of the melting point.

The original sample of crude geraniol gave 1.8% total material soluble in 5% sodium hydroxide.

Zinc in Water Washings.—Crude geraniol (445 g.) was diluted with ether and extracted with water. When the water solution had been evaporated practically to dryness, 0.5 g., or about 0.1%, of material was obtained. On ignition an ash was obtained which gave qualitative tests for zinc. A portion of the water-soluble solid was acidified and extracted with ether. The evaporated extract gave no color with ferric chloride.

A portion of the water-insoluble crude geraniol from the water washing gave no precipitate when boiled for about fifteen minutes. A similar portion of the original unwashed crude geraniol gave a voluminous, gelatinous precipitate after boiling for about two minutes.

Bieugenol in Residue from Steam Distillation.—A portion of the crude geraniol (888 g.) was subjected to steam distillation until about 95% by weight had distilled. The residue was extracted with ether, and the ether solution was extracted successively with 5% aqueous solutions of potassium bicarbonate, sodium carbonate and sodium hydroxide. The final extract yielded, after acidification, extraction with ether and removal of the solvent, a product consisting of crystalline material and a brown, viscous oil. The yield was 0.84 g. (about 0.1% of the sample). The mixture was washed with dilute ethanol, and the crystalline residue was recrystallized several times from the same solvent. The product melted at 106° and showed no depression of melting point in admixture with bieugenol prepared by the method of Erdtman.[3]

(2) All melting points are corrected.

(3) Erdtman, *Biochem. Z.*, **258**, 172 (1933).

(4) Phillips and Keenan, THIS JOURNAL, **53**, 1924 (1931).

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C. RECEIVED JULY 8, 1940

Factors Influencing Polysulfone Formation

BY M. S. KHARASCH AND E. STERNFELD

In the course of an investigation involving sulfur dioxide and olefins we were concerned with the possibility of polysulfone formation as an undesirable side reaction. We found that mineral acids, in the presence of a peroxide such as ascaridole, markedly catalyzed this reaction for several olefins which did not readily form polysulfones. Recently, Marvel and Glavis[1] have found peracetic acid a more potent catalyst than acyl peroxides in the formation of polysulfones from vinyl and allyl chlorides. From our experiments, it would seem that a mixture of ascaridole and hydrochloric, hydrobromic, or sulfuric acid is at least as effective as peracetic acid in polysulfone formation from trimethylethylene and allyl or vinyl chlorides.

Allyl bromide does not give a polysulfone under any conditions. What is more remarkable, we found it to be a powerful inhibitor for the formation of polysulfones from other olefins. Thus, allyl chloride mixed with five mole per cent. of allyl bromide does not react to any extent with sulfur dioxide even in presence of ascaridole and mineral acid, whereas without the allyl bromide the yield of allyl chloride polysulfone is practically quantitative. A large excess of ascaridole over the allyl bromide (10 moles to 1) brought about the formation of allyl chloride polysulfone. The yield, however, was poor (less than 20%). Allyl bromide was also a powerful inhibitor for polysulfone formation from cyclohexene and pentene-2 when (following the procedure of Frederick, Cogan and Marvel[2]) aqueous hydrogen peroxide was used as a catalyst. In these cases, the addition of mineral acids overcame this inhibition.

It is difficult to explain the action of allyl bromide as an inhibitor. Attempts to substitute for

(1) Marvel and Glavis, *ibid.*, **60**, 2622 (1938).

(2) Frederick, Cogan and Marvel, *ibid.*, **56**, 1815 (1934).

it other compounds such as nitric oxide, nitromethane, and ethyl or benzyl bromides, which might act as chain breakers, were without avail. On the other hand, cinnamyl bromide was even more effective as an inhibitor than allyl bromide. Two mole per cent. of this compound was sufficient to reduce the yield of allyl chloride polysulfone to less than 3%. The structure $RR_1C{=}CHCH_2Br$ appears to be a prerequisite for this type of inhibitor. This view is substantiated by the facts that hydrogen bromide is not an inhibitor, and that substances such as trichloroethylene and 2,4,4-trimethylpentene-2 do not form polysulfones, yet neither do they inhibit the formation of a polysulfone from allyl chloride.

Experimental Part

Allyl Chloride Polysulfone.—This compound has been described incompletely by Marvel and Glavis.[1] To 10 cc. of liquid sulfur dioxide in a flask or beaker was added 5 g. of allyl chloride, a drop of ascaridole, and a few drops of aqueous or alcoholic hydrogen chloride, hydrogen bromide, or sulfuric acid. The polysulfone began in a few seconds to precipitate as a white viscous mass which hardened in a minute or two. The reaction was complete in less than five minutes. Ether was added; then the mass was broken up, collected on a filter, powdered, washed thoroughly with ether, and dried; yields, 6.5–9 g. (70–100%). The compound has no melting point but decomposes when heated to 210–235°. It is soluble in acetone and chloroform, but insoluble in most other organic solvents.

Anal. Calcd. for $(C_3H_5SO_2Cl)_n$: C, 25.44; H, 3.53; S, 22.78. Found: C, 25.23; H, 3.96; S, 22.82.

Lauroyl, benzoyl, and hydrogen peroxides were ineffective when used in place of ascaridole. Mineral acids could not be replaced in the reaction by acetic or trichloroacetic acid.

Trimethylethylene Polysulfone.—A solution of 7 g. of trimethylethylene, 10 cc. of sulfur dioxide, 0.2 cc. of ascaridole, and 3 g. of hydrogen bromide was allowed to stand in a pressure bottle for twelve hours at room temperature. The bottle was opened, the dark viscous mass dissolved in chloroform, and the polysulfone precipitated with ether. It was dried, powdered, washed thoroughly with ether, and dried again; yield, 6 g. of a dark powder (44%). It melts with decomposition at 125–160°.

Anal. Calcd. for $(C_5H_{10}SO_2)_n$: C, 44.74; H, 7.46; S, 23.89. Found: C, 43.54; H, 7.17; S, 24.36.

A large quantity of halogen acid, 50 mole per cent., was found to be necessary for the formation of trimethylethylene polysulfone. Ascaridole was the only peroxide that brought about the reaction.

Vinyl Chloride Polysulfone.—This compound, described by Marvel and Glavis,[1] was obtained by adding aqueous hydrogen chloride or bromide to a solution of vinyl chloride in sulfur dioxide containing a trace of ascaridole; yield, 50%. The substance decomposes when heated at 245–265°.

Summary

1. The combined effect of acid and peroxides on polysulfone formation of olefins and sulfur dioxide has been studied.

2. It was shown that allyl and cinnamyl bromides do not form polysulfones and act as inhibitors in polysulfone formation from other olefins.

3. Allyl chloride and trimethylethylene polysulfones are described.

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RECEIVED JULY 20, 1940

Condensation of Sulfanilamide with an Enol. N^4-α-Bromotetronyl Sulfanilamide[1]

BY W. D. KUMLER

Sulfanilamide reacts with α-bromotetronic acid when the solid compounds are ground together in a mortar and heated at 110–120°. The original white powder turns red, partially melts and then solidifies. After three crystallizations from 50% acetone–water, a colorless or cream colored compound occurring as fine silky needles was obtained.

Other ways of bringing about the reaction were tried including refluxing the solids while suspended or dissolved in glacial acetic acid, anhydrous dioxane, and toluene. The best results were obtained with toluene. When equal molal quantities of sulfanilamide and α-bromotetronic acid were placed in toluene and refluxed for two hours, a 31% yield of the purified product was obtained.

Sulfanilamide and α-bromotetronic acid might react in several ways. The possibilities are: salt formation, cleavage of hydrogen bromide (the hydrogen coming from either the amino or the amide nitrogen), cleavage of water, the hydrogen again coming from either the amino or amide nitrogen.

The molecular weight of the compound was determined in acetone using a Reiche apparatus. Values of 319, 330 and 329 were obtained which are near the theoretical value of 333 for the molecule formed by splitting out of water. The theoretical molecular weight for the compound formed by splitting out hydrogen bromide is 270 and that for the salt assuming ionization is 176. The compound has a low solubility in water, which would not be the case if it were a simple salt.

(1) Presented before the Division of Medicinal Chemistry at the Cincinnati meeting of the American Chemical Society, April 11, 1940.

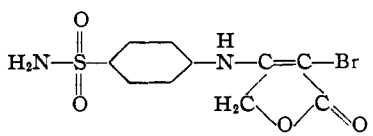
The bromine observed was 24.11 and 23.86, in good agreement with the theoretical value of 24.00 for the compound formed by splitting out water.

The two possibilities are then N^4-α-bromotetronyl sulfanilamide and N^1-α-bromotetronyl sulfanilamide. The N^1-compound would be analogous to a secondary sulfonamide since α-bromotetronic acid is a strong acid pKa 2.23,[2] and such a sulfonamide would be sufficiently acidic to titrate accurately to the phenolphthalein end-point. On the other hand, the N^4-compound would have very weak acidic properties. Our compound has very weak acidic properties and gives a very high equivalent weight at the phenolphthalein end-point.

The N^1-compound would likewise be expected to undergo diazotization at 0°, couple and give a bright color with alkaline α-naphthol, while the N^4-compound would not give a color. Our compound gives no color other than a pale yellow, which was also obtained with a blank. The compound can, however, be hydrolyzed in either 10% hydrochloric acid or 10% sodium hydroxide to give a compound that gives the test for a primary aromatic amine group.

An attempt was made to condense α-bromotetronic acid with a compound in which the amino group in sulfanilamide was blocked, N^4-acetylsulfanilamide. The same conditions were used that gave the best results with sulfanilamide but no evidence of any reaction was obtained and 90% of the N^4-acetylsulfanilamide was recovered unchanged.

The evidence from all sources indicates that the compound is N^4-α-bromotetronyl sulfanilamide.



This compound is of interest because it is a new type of sulfanilamide derivative formed by condensing an enol with sulfanilamide. The compound has a possible tautomeric form but the structure given is the more likely one due to the stability resulting from the resonance forms that are possible with it but not with its tautomer.

Preliminary investigation of the pharmacology of the compound in Dr. Chauncey D. Leake's laboratory in the University of California Medical School indicates that the compound has a very low toxicity. Twelve grams per kilo of body weight were given orally to mice without any fatalities. The compound has a protective action against β-hemolytic streptococcus that is about equal to that of sulfanilamide.

(2) Kumler, THIS JOURNAL, **60**, 859 (1938).

COLLEGE OF PHARMACY
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SAN FRANCISCO, CALIFORNIA RECEIVED JUNE 11, 1940

The Quantitative Analysis of Mixtures of Polyoxyethylene Glycols by Fractional Distillation[1]

BY STANLEY PERRY AND HAROLD HIBBERT

A method for the quantitative separation of the products of hydrolysis of methylated polysaccharides by fractional distillation has been used with some success by Haworth and co-workers[2] in molecular weight determinations by the end-group method. More recently, Hess[3] has modified the method so as to make it even more sensitive for the determination of tetramethyl methyl glucoside. However, the efficacy of a distillation analysis of this type is not very generally recognized, so that it is of some interest that a similar accurate separation has now been found possible with complex mixtures of polyoxyethylene glycols, $HOH_2C(CH_2OCH_2)_nCH_2OH$. Thus, the quantitative separation of these liquid polymers has been obtained by subjecting synthetic mixtures to fractional distillation, the course of the separation being followed in each case by the change in refractive index of the distillate.

The applicability of the process to the separation of unknown mixtures was fully established by collaborative experimentation, the senior author preparing synthetic mixtures which were then separated into their components by the junior author, who was not informed of the number or proportions. Under these conditions, it was not only possible to detect which members were present and which were not, but also to isolate and determine quantitatively the proportion of each with an accuracy of 96 to 99.8%. This is illustrated in the accompanying tables of data.

The mixtures used in these experiments were prepared from carefully purified products pre-

(1) Part LX of the series "Studies on Reactions Relating to Carbohydrates and Polysaccharides."

(2) Haworth and Machemer, *J. Chem. Soc.*, 2270 (1932); Haworth and Percival, *ibid.*, 2277 (1932).

(3) Hess and Neumann, *Ber.*, **70B**, 710 (1937).

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, %	$n^{20}D$ 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.	$n^{20}D$	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	Trioxyethylene
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).

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY
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RECEIVED JUNE 8, 1940

The Mutarotation of *d*-Glucose in Absolute Methanol

BY H. H. ROWLEY AND S. DAVID BAILEY

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 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 Andrews[2] 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 Yanovsky[7] 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's[8] 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,

(1) Riiber and Minsaas, *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).
(4) Isbell and Pigman, *J. Research Natl. Bur. Standards*, **18**, 141 (1937).
(5) Hudson and Dale, THIS JOURNAL, **39**, 320 (1917).
(6) Nelson and Beegle, *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 Andrews[2] 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 solution[9] 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 ± 0.5°, compared to +111.0° for the same sugar in water solution. The corresponding value for the beta-*d*-glucose was $[\alpha]_D$ +17.0 ± 0.5°, compared to +19.5° 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 ± 0.3° in absolute methanol compared to +52.6° 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% 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 Andrews[2] 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° and on standing slowly changed, giving a final equilibrium rotation of +66.3°.

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 Peniston[10] indicates that the amount of the aldehyde isomer in an aqueous solution of *d*-glucose is considerably less than 0.3%.

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

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

DIVISION OF PHYSICAL CHEMISTRY
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RECEIVED APRIL 9, 1940

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

BY H. H. ROWLEY

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 Laboratory[2] 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).

absolute ethanol, it was found necessary to determine these physical properties in mixtures of ethanol–water. Previous work along this line has been reported by Levy,[3] Trey[4] and Hudson and Yanovsky[5] at 20°. The present work was done at 25° and in mixtures ranging up to 93.7% ethanol by weight for values of the velocity constants ($k_1 + k_2$) and up to 98.7% for the equilibrium rotation. By graphical extrapolation it was possible to determine reasonable values for the initial specific rotation, the equilibrium specific rotation and the reaction rate for absolute ethanol.

Discussion of Results

The solutions were made by dissolving a weighed amount of pure anhydrous alpha-*d*-glucose in ethanol–water mixtures of known composition. The mutarotation was followed polarimetrically in jacketed tubes using a sodium arc as a light source. The concentrations ranged from 2.5 g. of sugar/100 ml. of solution for the low alcohol concentrations to 0.6 g. of sugar/100 ml. of solution for the high ethanol concentrations.

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. These values were read directly from large graphs of the original data.

As has been found by many previous workers, the rate of mutarotation of alpha-*d*-glucose follows a first-order reaction which can be expressed by an equation[6] involving the initial rotation, the equilibrium rotation and the rotation at a specific time. The deviation from a first-order reaction found by Worley and Andrews[7] was not found during this investigation. This confirms the findings of Isbell and Pigman[8] and agrees with the results obtained in this Laboratory with absolute methanol solutions.[2]

It is seen from the table that the addition of small amounts of ethanol to water has a much greater effect in reducing the rate of mutarotation than the addition of water to ethanol has in increasing the rate. This is in agreement with the results of Worley and Andrews[7] working with methanol–water mixtures. The extrapolated value for the velocity of mutarotation in absolute ethanol at 25° is less than in methanol (0.00018), as was found qualitatively by Trey.[4]

As the alcohol concentration increases, the value of the equilibrium specific rotation also increases gradually to about 80% ethanol by weight. However, above 80% ethanol the rise becomes much more rapid, giving an extrapolated value of +65.5° for absolute ethanol. Trey[4] reported a specific equilibrium rotation of +62.4° in absolute ethanol. The value reported here is slightly lower than the value of +66.5° obtained in absolute methanol but, allowing for the experimental difficulties, this is not considered significant. Andrews and Worley[7] obtained an almost linear relationship for the change of the specific rotation at equilibrium in methanol–water mixtures. However, their points are scattered and only one value is given for concentrations of methanol above 60% by weight.

The initial specific rotation values were obtained in most cases by extrapolating the first-order equation to zero time. Above ethanol concentrations of 90%, this method could not be used due to experimental difficulties. However, by utilizing the equation for determining the half-life period of a first-order reaction, it is possible to calculate the value of the initial specific rotation in the higher concentrations if the equilibrium rotation is known. As in the case of the equilibrium specific rotation, the specific initial rotation is lowered considerably by the addition of water to ethanol but is raised only slightly by the addition of ethanol to water. The value obtained for absolute ethanol appears to be a trifle higher than the value of +115.5° obtained for absolute methanol.

TABLE I

SUMMARY OF RESULTS

Wt. % C_2H_5OH	Init. rotn. $[\alpha]^{25}D$	Equil. rotn. $[\alpha]^{25}D$	$(k_1 + k_2) \times 10^3$
0	110.5	52.6	10.5
10	110.5	53.1	7.7
20	110.6	53.6	6.3
40	110.8	54.8	4.4
60	111.0	56.3	3.1
80	111.6	58.6	1.7
90	112.6	60.7	0.95
95	114.2	62.6	0.55
100	116.2	65.5	0.10

Attention should be called to the fact that the values given in the "International Critical Tables"[9] for the initial specific rotation and

(3) Levy, *Z. physik. Chem.*, **17**, 317 (1895).

(4) Trey, *ibid.*, **18**, 193 (1895).

(5) Hudson and Yanovsky, THIS JOURNAL, **39**, 1013 (1917).

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

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

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

(9) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. II, 1928, p. 347–348.

equilibrium specific rotation of *d*-glucose in absolute ethanol are in error. The data given in the "Tables" are taken from the work of Hudson and Yanovsky[5] and apply to absolute methanol, not absolute ethanol.

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Note on the Arrangement of Phases in Palladium–Hydrogen

BY D. P. SMITH[1] AND C. S. BARRETT

The existent studies of palladium by methods of X-ray diffraction, now more than a dozen in number,[2] show the system to include two phases, both of face centered cubic type, but of widely differing lattice constants, and having compositions which vary over considerable ranges. Since these investigations have been carried out under conditions not suited to make clear the spatial arrangement of the phases, it seemed desirable to show that, as is to be expected in a diffusion system, the two phases of this typical hydrogen alloy are completely segregated, and that changes in gross composition are accompanied by migration of the phase boundary.

The palladium used was about 99.85% pure and had the form of a ribbon of 5 × 0.05 mm. cross section. This ribbon was suspended vertically in a tube 2 cm. in diameter, consisting of thin celluloid cemented to glass end-pieces, which was borne by an adjustable support provided with a vertical scale. A back reflection camera was employed, with a slit system such that the irradiated area on the specimen extended one millimeter vertically by four millimeters across the strip horizontally. The target was of iron, and the distance between specimen and film was 6 cm. The containing tube was filled to 3.2 cm. above the bottom of the ribbon with 2 *N* sulfuric acid, and during the series of observations the palladium was continuously charged by passing into the immersed portion a current of 5 milliamperes from an adjacent anode of platinum foil. The palladium at the level of the electrolyte had therefore a fixed hydrogen concentration corresponding to a cathodic current density of approximately 0.16 amp./sq. dm.

(1) Associate Professor of Chemistry, Princeton University.

(2) Most recent studies E. A. Owen and J. Idwal Jones, *Proc. Phys. Soc. London*, **49**, 587, 603 (1937); A. Michel, *Bull. assoc. tech. fonderie*, **12**, 302 (1938).

Preliminary exposures, made after some hours of electrolysis, gave the diffraction spectrum of the β phase only, from a region in the palladium one millimeter above the electrolyte level; while at a point several millimeters higher, the spectrum of the α phase was alone observed. It was also found that whereas exposures of three-quarters of an hour were required to yield a visible β phase pattern on an unrotated film, diffraction from the α phase was sufficiently intense to give a clear result in ten minutes. For following the progress of the diffusion, exposures of ten or fifteen minutes were therefore made, and the absence of any pattern was taken as showing the presence of the β phase in the region observed. The results are displayed in Table I, where time is taken from the beginning of measurements, after the full saturation of the metal below the electrolyte, and distance is measured upward from the level of the liquid.

TABLE I

Film	Time, hr.	Distance, mm.	Phase	Rate of boundary migration
12	4.5	4	α	$\lesssim$ 1 mm. in 5 hr.,
13	5.0	1	β	or 0.20 mm./hr.
14	5.7	3	α	
15	22.5	3	β	$\lesssim$ 4 mm. in 23.3 hr.,
16	23.3	5	α	or 0.17 mm./hr.
18	24.3	4	α	
20	46.5	4	β	$\lesssim$ 6 mm. in 47.6 hr.,
21	47.6	6	α	or 0.126 mm./hr.
22	50.7	7	α	

As may be seen from this table, the boundary steadily advanced from the line at which the hydrogen concentration was kept constant, the rate declining from a value exceeding 0.20 mm. per hour to a value less than 0.126.

The method employed could doubtless be made to serve for exact observation of the rate of diffusion, unaffected by factors introduced by the entry and exit of hydrogen at the metal surfaces. Since this, however, would involve a determination of the relation between the cathodic current density and the hydrogen concentration attained in the cathode, and since the diffusion constant obtained would be valid for the metal only in the precise physical condition in which it was examined, we have here contented ourselves with demonstration of the qualitative relationships.

The results show clearly the division of the alloy into two distinct phases, one of which (α) occupies all of the region in which the concentration of hydrogen is below a certain saturation

limit; while the other phase (β) is present alone wherever this limit is exceeded. They also make plain the migration of the phase boundary with continued diffusion. Finally they show that the higher order diffraction lines from the β phase are much less intense than those of the α phase, a fact probably due to the severe cold working which occurs as β is formed from α by a sudden expansion of over 3% (linear) at the advancing phase boundary.

METALS RESEARCH LABORATORY
CARNEGIE INSTITUTE OF TECHNOLOGY
PITTSBURGH, PENNSYLVANIA RECEIVED JUNE 8, 1940

COMMUNICATIONS TO THE EDITOR

STRUCTURE OF CANNABIDIOL. VIII. POSITION OF THE DOUBLE BONDS IN CANNABIDIOL. MARIHUANA ACTIVITY OF TETRAHYDROCANNABINOLS

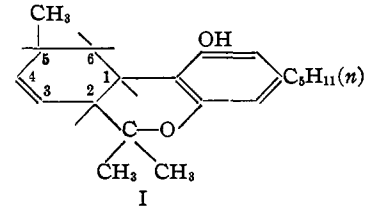
Sir:

Certain mild reagents (previous papers V, VI) convert cannabidiol into a tetrahydrocannabinol $[\alpha]^{32}D$ $-165 \pm 7°$; more vigorous reagents to one with $[\alpha]^{32}D$ $-240 \pm 10°$. It is obvious from the rotations that these forms are not absolutely pure and each is probably contaminated with the other.

The lower-rotating tetrahydrocannabinol can be converted to the higher-rotating by the same reagents and under the same conditions which convert cannabidiol to the higher-rotating form; thus the lower-rotating form is presumably the initial reaction product in the isomerization of cannabidiol and the higher-rotating form a secondary product. Therefore, the lower-rotating form probably has the double bond in the same position as the corresponding double bond in cannabidiol.

Cannabidiol has been shown to have no double bond conjugated to the benzene ring; that its two double bonds are not conjugated to each other is indicated by the very close values of the absorption spectrum of cannabidiol (maximum log ϵ, 3.18), and that of tetrahydrocannabidiol (3.05) and confirmed experimentally by failure of repeated attempts to condense cannabidiol dimethyl ether with maleic anhydride. The double bond in each of the tetrahydrocannabinols has been shown not to be conjugated to the aromatic nucleus by comparison of their physical constants with that of a synthetic tetrahydrocannabinol of unequivocal constitution with the double bond conjugated (see paper VII). Positions 1,2 or 1,6 or 2,3 for the ring double bond in cannabidiol or in the tetrahydrocannabinols are thus excluded.

The migration of the double bond in the tetrahydrocannabinol, if 2,3 or 5,6, should proceed to the most favored position, in conjugation with the benzene ring. As this does not occur, positions 3,4 and 4,5 remain and are considered the most probable. The 3,4 is assigned to the lower-rotating tetrahydrocannabinol (I) and the 4,5 to the higher-rotating (II), for migration from the 3,4 to the 4,5 position (which has the methyl substitution) is more likely than *vice versa*. Through its relationship to the lower-rotating tetrahydrocannabinol, cannabidiol may be postulated as having structure III.



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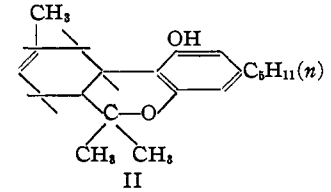

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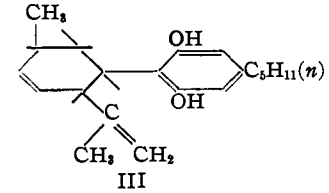

III

The tetrahydrocannabinols have a very potent marihuana activity which is markedly greater