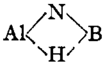
TABLE IV

VAPOR TENSIONS OF LIQUID $[(CH_3)_2N]_3B$

Temp., °C.	21.5	30.1	35.0	39.6	42.9	49.5	58.0
$p_{mm.}$ (obsd.)	3.44	5.82	8.05	10.35	12.44	17.85	27.33
$p_{mm.}$ (calcd.)	3.44	5.93	7.95	10.36	12.46	17.77	27.31
Temp., °C.	58.25	66.3	70.25	77.85	85.3	99.5	
$p_{mm.}$ (obsd.)	27.86	40.51	48.48	67.78	91.85	158.7	
$p_{mm.}$ (calcd.)	27.71	40.65	48.65	67.76	92.11	158.6	

Tris-dimethylamino-borine and Diborane.—Like $[(CH_3)_2N]_2BH$, the compound $[(CH_3)_2N]_3B$ reacted in a stage-wise manner with diborane, quantitatively yielding $(CH_3)_2NB_2H_5$ and $(CH_3)_2NBH_2$. The start of the reaction required a higher temperature—presumably on account of the higher melting point of $[(CH_3)_2N]_3B$—hence it was even less feasible to recognize distinct intermediate compounds. For example, a 67.4-mg. sample (calcd. as 10.56 cc. standard gas) absorbed no more than 17.4 cc. of diborane during 10 minutes at 0–20°, yielding 8.3 cc. of $(CH_3)_2NB_2H_5$ and the previously observed difficultly volatile liquids and solids. These residues were heated with diborane at 85–95°, bringing the total $(CH_3)_2NB_2H_5$ to 30.4 cc. The total absorbed diborane was 25.7 cc., and the yield of $(CH_3)_2NBH_2$ was 1.2 cc. (monomer gas at S.C.); hence the recovery of $(CH_3)_2N$ groups was 99.7%; of B and H atoms, 100.1%. This quantitative realization of the equations $2[(CH_3)_2N]_3B + 5B_2H_6 \rightarrow 6(CH_3)_2NB_2H_5$ and $[(CH_3)_2N]_3B + B_2H_6 \rightarrow 3(CH_3)_2NBH_2$ is clear evidence of the purity of the sample of tris-dimethylamino-borine.

V. The Existence of Aluminum Aminoborohydrides

The recognition of BHB bridge-bonding in the aminodiboranes[2] and the recent evidence for the AlHB bridging in aluminum borohydride[9,10] led to the question whether such a bond system as  also might be stable. In the first experiment on this subject, one gas-volume of $(CH_3)_2NB_2H_5$ and two gas-volumes of aluminum borohydride were heated together for 45 minutes at 100°, yielding a scarcely volatile oily liquid and 0.15 gas volume of diborane. The displacement of the latter suggested that a more direct approach would employ $(CH_3)_2NBH_2$ instead of $(CH_3)_2NB_2H_5$; hence in another experiment 42.5 cc. of $(CH_3)_2NBH_2$ (monomer gas at S.C.) and 45.3 cc. of $Al(BH_4)_3$ were heated 45 minutes at 92°, to give 1.4 cc. of diborane, a trace of highly reactive solid, the oily liquid again, and a mixture which was resolved into 15.5 cc. of $(CH_3)_2NB_2H_5$ and 28.6 cc. of $Al(BH_4)_3$, the latter being isolated in the form of a complex with methyl ether. The reaction balance thus indicated that 1.1 BH_4 groups, per mole of aluminum borohydride, were replaced by $(CH_3)_2NBH_3$ groups, and that the product contained a half-mole proportion of complex-bonded $(CH_3)_2NBH_2$. Attempts to isolate the main product led to a fraction (43% of the Al) in which hydrolytic analysis showed the atomic H:Al ratio to be 10.9 and the N:Al ratio 2.18. This result would suggest mainly $[(CH_3)_2NBH_3]_2AlBH_4$, with a little additional $(CH_3)_2NBH_2$. Larger samples of the oily product were obtained by a process in which $Al(BH_4)_3$ vapor streamed across a sample of $(CH_3)_2NBH_2$ in a U tube, and passed through a Pyrex tube at 120°. Again, however, it was not feasible to isolate single pure components.

The oily liquid products proved to be spontaneously inflammable in air and violently reactive with water. They can be distilled at a practical rate *in vacuo* at 50–60°, without decomposition. With diborane at 90–100°, they react extensively to form $(CH_3)_2NB_2H_5$ and aluminum borohydride—essentially reversing the preparation. They dissolve, apparently without reaction, in dry benzene, carbon tetrachloride or diethyl ether. They react with trimethylamine, but the question whether an amine complex on Al is formed, or a BH_3 group delivered to form $(CH_3)_3NBH_3$, or both effects in succession, has not been fully investigated.

Acknowledgment.—The generous support of this work by the Office of Naval Research is gratefully acknowledged.

LOS ANGELES 7, CALIF. RECEIVED AUGUST 7, 1950

---

(9) Price, Longuet-Higgins, Rice and Young, *J. Chem. Phys.*, **17**, 217 (1949).

(10) Bauer, THIS JOURNAL, **72**, 622 (1950).

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Cuprammonium-glycoside Complexes. VI. The D-Mannosan Complex[2]

BY RICHARD E. REEVES

Complex formation between cuprammonium and D-mannosan produces a visible color change and increased absorption of light in the near ultraviolet, a shift in optical rotation, and a decrease in the conductance of a dilute cuprammonium solution. Measurements at equilibrium conditions by four techniques indicate a single stoichiometric reaction involving one mole of D-mannosan and one mole of cuprammonium. The reaction constant for formation of the cuprammomium-D-mannosan complex is approximately 2.5×10^3 at 25° with the cuprammonium employed in the present work.

The exact nature of cuprammonium-glycol complexes has remained uncertain despite their practical importance in systems involving cuprammonium solutions of cellulose. As an approach to this problem the complex formed by cuprammonium and a glycol grouping in D-mannosan<1,5>β<1,6> was selected for further study because mannosan was the most active complex-forming substance encountered in a survey of several score of sugar derivatives.

Since cuprammonium-glycol complexes are stable only under very restricted conditions, it is ordinarily difficult to differentiate the properties of the complex from those of free cuprammonium and uncombined glycol. In the present studies, taking advantage of the great affinity of D-mannosan for cuprammonium, reaction was driven essentially to completion by employing excesses of glycol.[3] By this means the properties of the cuprammonium-mannosan complex were determined and distinguished from the properties of uncombined cuprammonium and mannosan.

Reaction between glycols and cuprammonium proceeds to equilibrium very rapidly. No data on the kinetics of the reaction have been obtained for equilibrium has been reached even when measurements were made within a minute from the time of mixing the components. The amount of complex at equilibrium is dependent, first, upon the

---

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) The data and calculations of reaction constants for this manuscript are contained in four tables available from the American Documentation Institute, 1719 N St., N. W., Washington 6, D. C., by requesting serial number 3000.

(3) The glycol grouping involved in reaction with cuprammonium is the pair of hydroxyl groups on carbon atoms 2 and 3 in the D-mannosan.

nature of the glycol; and then upon concentration of the reactants according to the laws governing mass action.

Discussion of Experimental Results

Studies based on light absorption in the red and ultraviolet, on optical rotation and on conductivity, are all indicative of a simple reaction between D-mannosan and cuprammonium, and this reaction may be expressed as a simple bimolecular association of the form

$$\text{mannosan} + \text{cupra} \rightleftharpoons [\text{mannosan·cupra}] \quad (1)$$[4]

Spectrophotometric Absorption Studies.—Figure 1 illustrates the spectrophotometric absorption in the region from 320 to 800 mμ for cuprammonium and cuprammonium containing an excess of D-mannosan. The curves show marked divergence in the near ultraviolet and in the red. In the ultraviolet the complex absorbs more strongly than free cuprammonium. The reverse is true in the red end of the spectrum: free cuprammonium absorbs more strongly than the complex.

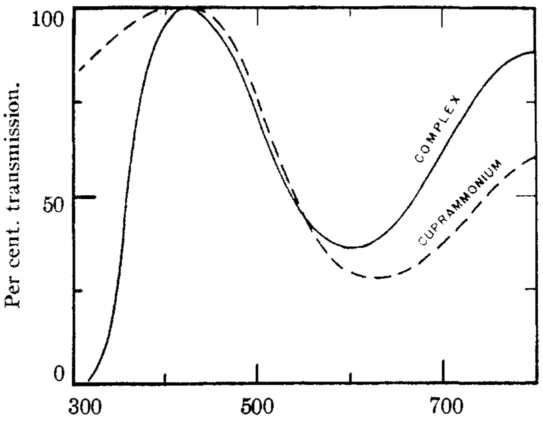


Fig. 1.—The optical transmission of cuprammonium and cuprammonium-mannosan complex in the region 320 to 800 mμ.

Optical density measurements were made at 650 mμ on cuprammonium and on various concentrations of mannosan in cuprammonium. A 0.10-molar solution of mannosan in cuprammonium was employed as standard since in this solution all of the cuprammonium is combined with mannosan. (The solution is 0.010 molar in complex.) Complex concentrations between zero and 0.01 molar were calculated as proportional to the observed optical densities. By this method the average value for the reaction constant was found to be 2.6×10^3.

Optical density measurements were made at 350 mμ with cuprammonium as standard on various concentrations of D-mannosan in cuprammonium. Since the highest concentration of mannosan employed was only 0.016 molar, it could not be presumed in this instance that complex-formation had proceeded to completion. For this most concentrated solution the concentration of complex was calculated to be 0.00942 molar by carrying over a reaction constant of 2.5×10^3 from the preceding experiments. Complex concentrations in the intermediate solutions were calculated in proportion to their optical densities. The average reaction constant obtained by this method was 2.7×10^3.

Optical Rotation Studies.—Mannosan concentrations between 0.003 to 0.10 molar were investigated. In the most concentrated solution the reaction had gone to completion and this solution was hence 0.01 molar with respect to complex and 0.09 molar with respect to D-mannosan. Since the specific rotation of D-mannosan in 3 N ammonia (containing 1% ethanol) was known to be −244°, the specific rotation of the complex (−1090°[5] based on mannosan) was calculated. From these values the concentrations of complex were calculated for each lower concentration of mannosan in cuprammonium. The value found for the reaction constant by this method was 2.2×10^3.

Conductivity Studies.—Specific conductances were measured for solutions of D-mannosan 0.0046 to 0.072 molar, in cuprammonium. In the more concentrated solutions the reaction was driven to a limiting value of 1.46×10^{-3} corresponding to complete reaction. A reaction constant of 2.5×10^3 was carried over from the optical rotation and density results to calculate the concentration of complex in the most dilute solution. The compositions of the intermediate solutions were calculated directly in proportion to their conductivities, conductance being an arithmetically additive function of the concentrations of free cuprammonium and cuprammonium–glycol complex. The value found for the reaction constant by this method was 2.6×10^3.

Conclusions

Although the accuracy of the experimental

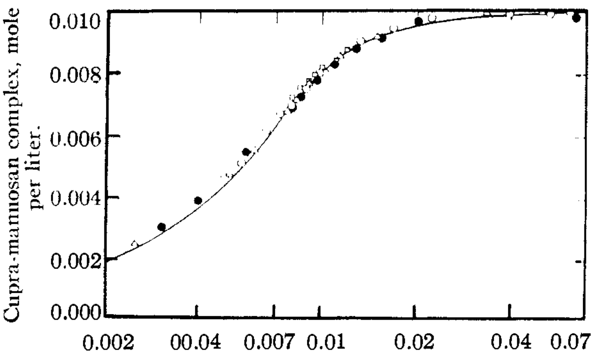


Fig. 2.—The amounts of the cuprammonium-mannosan complex as measured by four different techniques. The curve represents calculated amounts of complex for a bimolecular reaction, $k = 2.5 \times 10^3$: ●, optical rotation; ○, conductivity; △, absorption at 650 mμ; □, absorption at 350 mμ.

---

[4] Since ammonia and water are present in the system in great excess, reaction (1) does not exclude the possible separation of ammonia and/or water during complex formation.

[5] A value of −1115° was obtained previously for mannosan in a different cuprammonium solvent, Reeves, THIS JOURNAL, **71**, 2116 (1949).

observations limits the calculation of reliable reaction constants to mannosan concentrations between 0.008 and 0.016 molar, there is excellent agreement over the entire investigated range between the observed concentrations of complex and those calculated for a bimolecular reaction having an equilibrium constant of 2.5×10^3. The quality of this agreement is illustrated by Fig. 2.

By four independent techniques the reaction between cuprammonium and a glycol grouping in D-mannosan is shown to be a bimolecular association. This is considerably simpler than mechanisms which have been advanced to explain the reaction between cuprammonium and cellulose.[6,7] In fact, the present results appear to warrant a reinvestigation of the latter reaction by a variety of techniques in order to discover whether several types of stoichiometric reactions actually occur when cellulose and cuprammonium combine.

Experimental Methods

The cuprammonium employed in this work has been designated as cupra A in a preceding communication.[8] It is a standard dilute cuprammonium solution containing 0.01 mole of copper, 3 moles of ammonia and 10 ml. of ethanol per liter.

Conductivity measurements were made at 25 ± 0.2° with a commercial 1000-cycle bridge using a dip-type cell. The cell constant, determined against 0.1 *M* potassium chloride, was found to be 0.116.

Optical rotations were measured at 25 ± 2° in a Gaertner polarimeter employing 2-dm. tubes. The mercury blue line (436 mμ) was isolated by means of Corning filters 511 and 038.

Absorption measurements at 650 mμ were made in a Coleman model 11 spectrophotometer. The absorption curves from 320 to 800 mμ and the optical density measurements at 350 mμ were made with the Beckman spectrophotometer. All observations were made at room temperature, which was 25 ± 2°.

Acknowledgment.—Some of the absorption measurements were made by Miss Dorothy C. Heinzelman of the Analytical and Physical Division.

[6] Emil Heuser, "The Chemistry of Cellulose," John Wiley and Sons Inc., New York, N. Y., 1944.

[7] Kurt Hess, "Die Chemie der Zellulose und ihrer Begleiter," Leipzig, 1928.

[8] Reeves and Jung, THIS JOURNAL, **71**, 209 (1949).

NEW ORLEANS, LOUISIANA RECEIVED JULY 5, 1950

[CONTRIBUTION FROM THE EXPERIMENTAL BIOLOGY AND MEDICINE INSTITUTE OF THE NATIONAL INSTITUTES OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

New Tribenzoyl-D-ribopyranosyl Halides and Their Reactions with Methanol

BY ROBERT K. NESS,[1] HEWITT G. FLETCHER, JR., AND C. S. HUDSON

Tribenzoyl-α-D-ribopyranosyl bromide, tribenzoyl-α-D-ribopyranosyl chloride and tribenzoyl-β-D-ribopyranosyl chloride have been obtained in crystalline form. Evidence supporting the assignments of structure and configuration to these three halides, as well as to the previously known tribenzoyl-β-D-ribopyranosyl bromide has been adduced through a study of the behavior of these substances with methanol, both in the presence and in the absence of an acid acceptor. The preparation of crystalline 2,3,4-tribenzoyl-D-ribose is described. Tribenzoyl-β-D-ribopyranosyl bromide is shown to give β-D-ribopyranose tetrabenzoate in 92% yield when reacting with silver benzoate.

In earlier publications[2,3] crystalline tribenzoyl-β-D-ribopyranosyl bromide (II) was described and shown to react with methanol in the absence of a catalyst to give methyl β-D-ribopyranoside tribenzoate (V) in high yield; subsequent researches[4] have shown a variety of benzoylated glycopyranosyl halides to react similarly with methanol. A recent reinvestigation of this general reaction in the D-ribose series has led to the discovery of a second tribenzoyl-D-ribopyranosyl bromide as well as two isomeric tribenzoyl-D-ribopyranosyl chlorides. The present paper will describe the preparation and some of the properties of these new halides.

When β-D-ribopyranose tetrabenzoate[2] is treated with a solution of hydrogen bromide in glacial acetic acid there is obtained in high yield, 71 to 85%, of the previously described[2] tribenzoyl-β-D-ribopyranosyl bromide as well-shaped prismatic crystals. At the same time there is formed in relatively meager quantity (5% yield) a second compound crystallizing in long needles; elementary analysis shows this substance to be an isomer of the major product of the reaction. With anhydrous methanol in the absence of a catalyst this minor product gave methyl β-D-ribopyranoside tribenzoate and thus possesses a pyranose ring like its previously known isomer. The physical constants of this new halide, listed in Table I, are seen to differ markedly from those of its isomer; in contrast to the strongly levorotatory nature of the bromide first prepared, the new substance is dextrorotatory. It seems highly probable, therefore, that the two substances represent an anomeric pair, the levorotatory bromide being a β-D-halide as previously assumed[2] and the new bromide representing tribenzoyl-α-D-

TABLE I

BENZOYLATED D-RIBOPYRANOSYL HALIDES

	M.p., °C.	$[\alpha]^{20}_D$ (abs. $CHCl_3$)	$[M]^{20}_D$
Tribenzoyl-α-D-ribopyranosyl bromide (IV)	164–166	+ 78°	+ 41,000
Tribenzoyl-β-D-ribopyranosyl bromide (II)	152–154	−202°	−106,000
Tribenzoyl-α-D-ribopyranosyl chloride (III)	203–204	+ 60°	+ 28,900
Tribenzoyl-β-D-ribopyranosyl chloride (I)	162–163	−147°	− 70,700

---

[1] Senior Research Fellow, National Institutes of Health, 1948–1950.

[2] R. Jeanloz, H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **70**, 4052 (1948).

[3] R. Jeanloz, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **70**, 4055 (1948).

[4] (a) R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **72**, 2200 (1950); (b) H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **72**, 4173 (1950); (c) R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **73**, 296 (1951).