

The aqueous layer coming from the previously described benzene extraction was extracted with three 150-cc. portions of ether and the combined extracts were dried (sodium sulfate). Evaporation of the ether left a residue (0.2 g.) which was very soluble in water. It was crystallized from a mixture of ethyl acetate and petroleum ether (b.p., 60–68°), when it formed white plates melting at 276–280° (dec.). The value for the neutral equivalent indicated that this substance was a dimethyldicarboxyphenol.

*Anal.* Calcd. for  $C_{10}H_{10}O_6$ : neut. equiv. (two), 105. Found: neut. equiv., 107.

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### Esters of Glucose and Lactose

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A number of straight-chain aliphatic acid esters of glucose and lactose were prepared. The crystalline compounds are described below; the others are listed in Table I.

soluble in 95% alcohol, acetone, Skellysolve C, ether, chloroform and benzene; m.p. 77.0–77.4° (cor.),  $[\alpha]^{25}_D + 4.6^\circ$  (*c* 2.5, chloroform),  $-14.2^\circ$  (*c* 2.5, benzene).

*Anal.* Calcd. for  $C_{12}H_{14}O_{11}(CO_2C_3H_7)_3$ : free hydroxyl, none; C, 58.52; H, 7.81. Found: free hydroxyl, none<sup>2a</sup>; free acidity, none<sup>2a</sup>; C, 58.55; H, 8.17.<sup>2b</sup>

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### X-Ray Investigation of *t*-Butyl Chloride and *t*-Butyl Bromide<sup>1</sup>

BY ROBERT S. SCHWARTZ, BENJAMIN POST AND  
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Thermal measurements indicate that both *t*-butyl chloride and *t*-butyl bromide undergo two transitions in the solid state. The sum of the entropies of the transitions is 8.7 e.u./mole for the

TABLE I

PROPERTIES OF POLYSUBSTITUTED GLUCOSE AND LACTOSE ESTERS

Ester	Acyl groups per mol. <sup>a</sup>	Elementary analyses, %				Free acidity, <sup>d</sup> %	$[\alpha]^{25}_D$ ( <i>c</i> 2.5) in $CHCl_3$	M.p., °C. (cor.)	$n^{20}_D$	Physical state and color
		Calcd. <sup>b</sup> C	H	Found <sup>c</sup> C	H					
A. Glucose										
Caprylate	4.7	67.7	10.2	68.2	10.2	1.1	+46.8		1.4587	Light-amber sirup
Caprate	4.8	70.5	10.8	70.9	10.8	1.1	+40.3		1.4612	Light-amber sirup
B. Lactose										
Caproate	7.2	63.2	9.0	63.2	9.0	0.85	+15.3		1.4646	Light-yellow sirup
Caprylate	6.9	66.5	9.9	66.7	10.2	1.5	+14.5		1.4650	Amber sirup
Caprate	7.0	69.3	10.5	69.6	10.7	2.0	+12.6		1.4657	Amber sirup
Laurate	6.5	70.7	10.9	70.2	11.1	Trace	+13.4	110–112		White, waxy solid
Myristate	7.2	73.0	11.4	73.3	11.4	0	+9.4	43.4–46.0		White, waxy solid
Palmitate	7.5	74.5	11.7	74.5	11.7	Trace	+9.0	55.6–58.2		White, waxy solid
Stearate	7.2	75.4	11.9	75.3	12.0	Trace	+7.9	62.5–64.5		White, waxy solid

<sup>a</sup> Calculated from free hydroxyl values obtained by the method of Ogg, Porter and Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945). <sup>b</sup> Based on the number of acyl groups per mol. found. <sup>c</sup> Microanalyses by C. L. Ogg and Mary Jane Welsh.

<sup>d</sup> By Mrs. R. B. Kelly.

All the esters but the lactose butyrate were prepared by slowly adding a chloroform solution of acid chloride (10% excess) to a stirred mixture of the sugar ( $\beta$ -lactose, or anhydrous  $\alpha$ -glucose), pyridine (1.1 moles/mole of acid chloride), and chloroform.<sup>1</sup> After initially cooling with an ice-salt mixture (until one hour after the acid chloride was added) the reaction was carried out six to eight hours at room temperature for the glucose esters and four to thirteen hours at 50–70° for the lactose, depending upon the reaction rate.

**$\alpha$ -D-Glucose Pentamyristate.**—After three recrystallizations from an alcohol-chloroform mixture the ester formed long, fine needles, insoluble in 95% alcohol and acetone, soluble in Skellysolve C and very soluble in ether, chloroform and benzene; m.p. 59.0–59.8° (cor.),  $[\alpha]^{25}_D + 38.3^\circ$  (*c* 2.5, chloroform),  $+33.5^\circ$  (*c* 2.5, benzene).

*Anal.* Calcd. for  $C_6H_7O_6(COC_{13}H_{27})_5$ : free hydroxyl, none; C, 74.09; H, 11.62. Found: free hydroxyl, none<sup>2a</sup>; free acidity, none<sup>2a</sup>; C, 74.19; H, 11.63.<sup>2b</sup>

**Lactose Octabutyrate<sup>3</sup> ( $\beta$ ?)**.— $\beta$ -Lactose was stirred with a mixture of butyric anhydride (70% excess) and pyridine (1.9 moles/mole of butyric anhydride) for eight hours at room temperature, eight hours at 50°, and 23 hours at 90°. After separating the crystals which formed in the sirupy product and recrystallizing four times from a 3:1 alcohol-water mixture, the ester was obtained as fine needles very

chloride, and 7.6 e.u./mole for the bromide. The dielectric constants of the crystalline solids just below the melting point are higher than those of the liquids.<sup>2,3</sup> These data indicate that both crystalline solids are highly disordered above the transition temperatures. The nature of the disorder has been investigated using low temperature single crystal X-ray diffraction techniques.

#### Experimental

Eastman Kodak Co. "white label" *t*-butyl chloride and *t*-butyl bromide were fractionally distilled in a column packed with glass helices. The fraction of *t*-butyl chloride boiling between 50.0–50.5° was used;  $n^{20}_D$  1.3852. The *t*-butyl bromide boiled at 72.7–73.0°;  $n^{20}_D$  1.4278.

Optical observations indicate that both compounds are isotropic at temperatures above transition II and strongly birefringent below this transition. Baker and Smyth,<sup>2</sup> however, have reported that below this transition crystalline *t*-butyl bromide is isotropic.

Samples of the compounds were sealed in thin-walled Pyrex capillary tubes and mounted on the goniometer arcs of a low temperature X-ray camera.<sup>4</sup> Single crystals of the

(1) Cf. G. Zemplén and E. D. Laszlo, *Ber.*, **48**, 915 (1915).

(2) (a) By Mrs. R. B. Kelly. (b) Microanalyses by C. L. Ogg and Mary Jane Welsh.

(3) An apparently unsuccessful preparation was recorded by M. Berthelot, *Ann. chim. phys.* [3] **60**, 98 (1860).

(1) This work supported by the Office of Naval Research.

(2) W. O. Baker and C. P. Smyth, *THIS JOURNAL*, **61**, 2798 (1939).

(3) L. M. Kushner, R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 1091 (1950).

(4) B. Post, R. S. Schwartz and I. Fankuchen, *Rev. Sci. Instr.*, **22**, 218 (1951).

isotropic phase of *t*-butyl chloride and *t*-butyl bromide were grown from the liquids in the capillaries. Oscillation diagrams were obtained at  $-45 \pm 3^\circ$  and  $-35 \pm 3^\circ$ , respectively. The reflections for both crystals could be indexed on the basis of face-centered cubic unit cells with  $a_0 = 8.40 \pm 0.05 \text{ \AA}$ . for the chloride and  $8.78 \pm 0.05 \text{ \AA}$ . for the bromide. Extrapolations from the known densities of the liquids indicate that there are in each case four molecules per unit cell. The computed density of *t*-butyl chloride is 1.04 at  $-45^\circ$  and that of *t*-butyl bromide is 1.34 at  $-35^\circ$ .

### Discussion

A stationary molecule of low symmetry cannot of itself form the pattern unit of a lattice of high symmetry. In such cases some form of disorder, rotational or orientational, must be present. In both *t*-butyl chloride and *t*-butyl bromide there is only one molecule per lattice point. Molecules of both compounds possess axes of threefold symmetry but do not possess the two-fold symmetry axes needed if the molecules are to be stationary in the cubic unit cells found.

Values of  $F_{hkl}$ , based on several postulated types of disorder, were computed for comparison with values of  $F_{\text{observed}}$ . In the case of both compounds, intensities calculated on the basis of molecules rotating freely (or randomly oriented about one mean position)<sup>5</sup> showed variation of calculated  $F$ 's approximately in accord with those observed.

To improve the agreement between  $F_{\text{observed}}$  and  $F_{\text{calculated}}$  calculations were made by assuming rotation or orientational disorder about several positions along the carbon-halogen axis between the central carbon and the center of mass. In the case of the chloride the best fit to the observed data is at a point 0.46  $\text{\AA}$ . from the central carbon. The center of mass is 0.49  $\text{\AA}$ . from the central carbon. The best fit for the bromide was 0.41  $\text{\AA}$ . from the central carbon. The center of mass is 0.87  $\text{\AA}$ . away from the central carbon. Table I shows a comparison of computed and observed data.

TABLE I  
COMPARISON OF CALCULATED AND OBSERVED STRUCTURE FACTORS

<i>hkl</i>	<i>t</i> -Butyl chloride		<i>t</i> -Butyl bromide	
	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$
111	10.0	10.0	10.0	10.0
200	7.3	7.0	7.4	7.5
220	-0.1	..	1.1	1.4
311	0.0	..	-1.0	0.8
222	-0.5	2.9	-1.3	2.8

The distance between the molecular centers is 5.94  $\text{\AA}$ . in the case of the chloride, and 6.20  $\text{\AA}$ . for the bromide. By use of Pauling's value for the van der Waals radius for a methyl group,<sup>6</sup> it is found that the spherical volumes swept out by molecules rotating or randomly oriented about the centers determined above have diameters of 7.5  $\text{\AA}$ . for both cases. It is evident that rotation of the molecules is subject to steric restriction. The available X-ray data indicate that the restriction is not great enough to preclude reasonably good agreement between observed intensities and intensities

(5) W. H. Zachariasen, "Theory of X-Ray Diffraction in Crystals," John Wiley and Sons, Inc., New York, N. Y., 1945, p. 213.

(6) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1949, p. 189.

calculated on the assumption of molecules with spherical symmetry on the average.

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### The Reaction between Calcium Hydroxide and Uranyl Nitrate Solutions<sup>1</sup>

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Tridot<sup>5</sup> has shown recently that the precipitates obtained from uranyl salt solutions by the addition of ammonia, sodium hydroxide or potassium hydroxide solutions have many points in common including the following: (1) the hydroxide is precipitated only after addition of 1.5 to 1.6 moles of base per mole of uranium; (2) the initial precipitate is  $\text{UO}_3 \cdot x\text{H}_2\text{O}$ ; (3) this precipitate reacts with additional base to form a di-uranate such as  $2\text{UO}_3 \cdot \text{K}_2\text{O}$ ; (4) in an excess of base, the mono-uranate,  $\text{UO}_3 \cdot \text{Na}_2\text{O}$ , can be prepared, but on washing with water this loses alkali until it reaches the composition of the di-uranate.

These results of Tridot are consistent with observations we made in 1945 while investigating the reaction between calcium hydroxide and uranyl salt solutions. As shown in Table I, considerably more than one equivalent of hydroxyl ion per mole of uranium must be added to stoichiometric uranyl nitrate solutions before a precipitate is obtained. In agreement with Tridot, we found the color of a solution of uranyl salt to deepen as the base is added even though no precipitate has appeared. Thus, between pH 4.1 and 5.5 the optical density at 4300  $\text{\AA}$ . of a 0.00685 *M* uranyl nitrate solution to which dilute  $\text{Ca}(\text{OH})_2$  solution was being added increased about 2.5-fold.

TABLE I  
FORMATION OF INITIAL PRECIPITATE BY ADDITION OF 0.02 *M*  $\text{Ca}(\text{OH})_2$  TO URANYL NITRATE SOLUTIONS

U concn. at turbidity point	Equiv. OH <sup>-</sup> /mole U at turbidity point
0.00187	1.92
.00442	1.64
.00716	1.68
.0173	1.60

Also, the initial precipitates contained very little calcium; the atomic ratio U/Ca was found to lie between 36 and 64.

Table II summarizes experiments on the dependence of the pH of precipitation on the uranium concentration; the pH decreases as the uranium concentration increases. The table also indicates that equilibrium in the precipitation is attained slowly, for after the initial precipitate is observed, the pH decreases in 24 hours by 0.8 to 1.1 pH units.

(1) Done under contract W-7401-eng-23 for the Manhattan Project by Tennessee-Eastman Corporation at Oak Ridge, Tennessee in 1945.

(2) Department of Chemistry, State University of Iowa, Iowa City, Iowa.

(3) Thomas A. Edison, Inc., West Orange, New Jersey.

(4) Division of Chemistry, University of California, Davis, California.

(5) G. Tridot, *Ann. Chem.*, [12] 5, 358 (1950).