these measurements as well as the general properties of the metal solutions we have written the "solvated electron" in equation 1 in a paired state instead of in an unpaired state as previously written for the moderately dilute region.[1]

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BOSTON UNIVERSITY
BOSTON 15, MASSACHUSETTS

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The Compressibility of Trimethylamine

BY H. O. DAY[1] WITH W. A. FELSING

Recently the authors determined[2] the critical constants of pure trimethylamine by the method of determining numerous isotherms very near, above and below, the critical temperature. Since these determinations involved the use of the dead-weight piston gage[3] of this Laboratory, it was decided to extend the measurements to include compressibility determinations for the temperature range +80 to 275°, since no such data could be located in the literature.

Apparatus and Material.—The dead-weight piston gage, its accessories and its operation, have been described previously.[3] Thermostat temperatures were measured with a platinum resistance thermometer, calibrated by the National Bureau of Standards, and these temperatures were held constant by means of this same resistance thermometer system in conjunction with a photoelectric cell relay.

The trimethylamine was prepared from highly purified trimethylamine hydrochloride, dried, stored, and transferred as described by Day and Felsing.[2] The purity was estimated to be 99.9 mole per cent.

The Experimental Data.—The compressibility data[4] at nine temperatures are presented graphically in Fig. 1; the accuracy of these data is from 0.1 to 0.2% over the entire range of temperature.

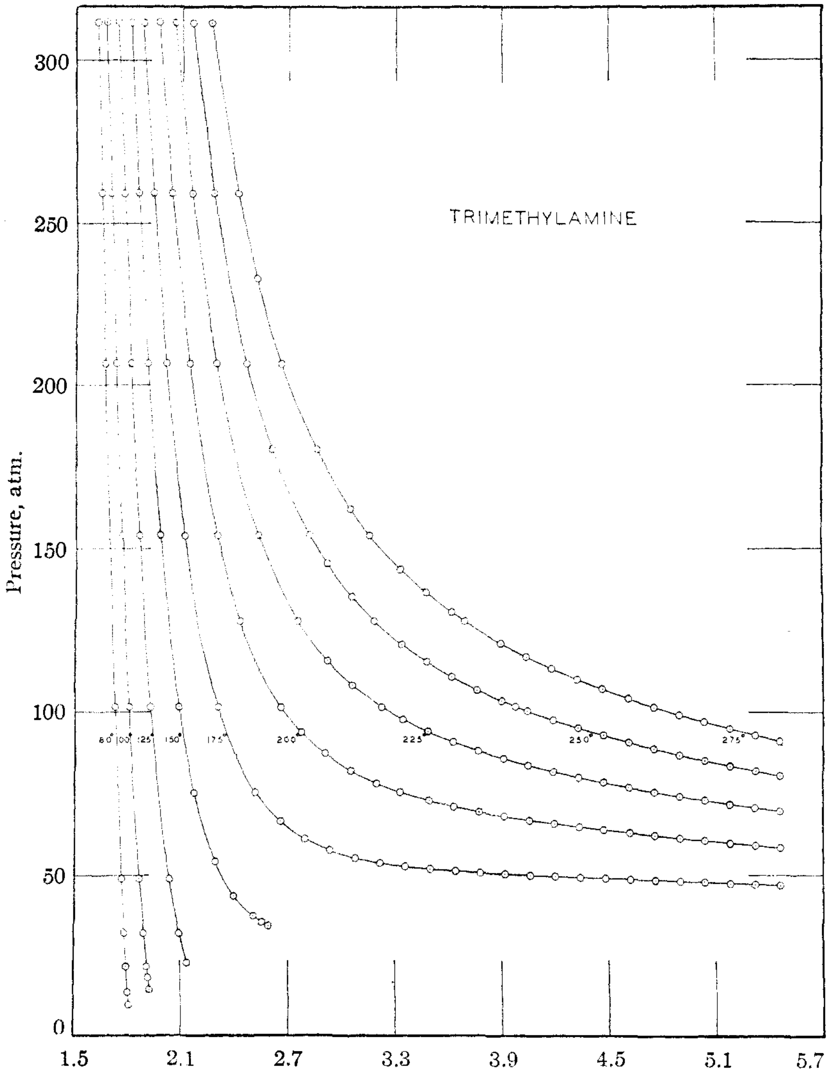

Fig. 1.

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(1) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(2) Day with Felsing, THIS JOURNAL, **72**, 1698 (1950).

(3) Kelso with Felsing, *ibid.*, **62**, 3132 (1940); *Ind. Eng. Chem.*, **34**, 161 (1942).

(4) For tables supplementary to this article, order Document 3333 from American Documentation Institute, 1719 N. Street, N. W., Washington, D. C., remitting $1.00 for microfilm (images one inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

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DEPARTMENT OF CHEMISTRY
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The Reaction of 1,3-Butadiene with Formaldehyde

BY O. C. DERMER, LEON KOHN AND WILLIAM J. NELSON

Whereas Gresham and Steadman[1] were unable to condense formaldehyde with 1,3-butadiene without a catalyst, the acid-catalyzed reaction has been reported to yield 4-vinyl-1,3-dioxane[2] (I), 5-vinyl-1,3-dioxane[3] (II), 5,6-dihydro-2H-pyran[2,3] (III) (predicted[4] as a product of the uncatalyzed reaction), 3-hydroxy-4-hydroxymethyltetrahydro-2H-pyran[2] (IV) or possibly the 3-hydroxymethyl-4-hydroxy isomer thereof, and the cyclic formal[2,3] (V) of the dihydroxy compound, presumably hexahydro-2H-pyrano[3,4]*m*-dioxin. However, II is an unexpected product for which no proof of structure was given; the only description of the III obtained "boiling point about 80°") does not agree well with the literature[4]; and analytical data were given only for IV. We are therefore recording work which was completed before the appearance of these patents and which confirms and extends their disclosures. I has been converted by catalytic hydrogenation into 4-ethyl-1,3-dioxane, by bromination into 4-(1,2-dibromoethyl)-1,3-dioxane, and by oxidation with hydrogen peroxide and formic acid[5] into 4-(1,2-dihydroxyethyl)-1,3-dioxane.

Experimental

4-Vinyl-1,3-dioxane (I).—The reaction of 1,3-butadiene and formaldehyde was effected at 0–30° and one atmosphere, with diethyl ether or glacial acetic acid as solvent and concentrated sulfuric acid (15–35% by volume) as catalyst. Anhydrous aluminum chloride proved ineffective as a catalyst. Paraformaldehyde suspended in a solution of the catalyst by stirring was treated with gaseous 1,3-butadiene until the desired gain in weight had occurred. After three to 16 hours the mixture was made basic with sodium hydroxide, refluxed therewith to destroy sulfuric esters, extracted with ether, and distilled. Yields of the formal (V) were inferior in all cases to those previously reported,[2,3] but 30% of the formaldehyde was found convertible to I by using 1.6 moles of diene per mole of aldehyde in ether.

The I obtained had the following constants: b.p. 144°, n^{20}_{D} 1.4439, d^{20}_{4} 1.00. An approximate determination of the heat of combustion[6] gave the value −844 ± 3 kcal./mole.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.1; H, 8.83; bromine number, 140; mol. wt., 114; *M*D, 30.3. Found: C, 63.3; H, 8.93; bromine number, 143; mol. wt. (in freezing benzene), 111; *M*D, 30.3.

We believe this product, evidently identical with that reported in the patents, is 4-vinyl-1,3-dioxane rather than the 5-vinyl isomer, not only because normal orientation in the Prins reaction calls for the former but because the compound is appreciably reactive at its boiling point toward sodium. This behavior is indicative of an allyl ether structure, present in I but not in II.

5,6-Dihydro-2H-pyran (III).—Treatment of 100 g. of paraformaldehyde in 200 ml. of anhydrous ether and 30 ml. of concentrated sulfuric acid with 60 g. of 1,3-butadiene during nine hours at 20–30° produced 36.6 g. of I (29% based on the diene), 20.8 g. of V (13%), and about 4 g. of a forerun material shown to be III by its properties. Found: b.p. 94–96°; $d^{28.5}_{4}$ 0.943; n^{20}_{D} 1.4451; bromine number, 184. Literature[4]: b.p. 93–94°; d^{19}_{4} 0.940; n^{19}_{D} 1.4477; bromine number (calcd.), 190.

3-Hydroxy-4-hydroxymethyltetrahydro-2H-pyran (IV).—A run in glacial acetic acid, including saponification of esters, gave not only IV, b.p. 128–133° at 2 mm., but an impure unsaturated alcohol, b.p. 93–102° at 2 mm., bromine number 140–146°, believed to be either 4-pentene-1,3-diol or 2-pentene-1,5-diol,[3] b.p. 85° at 5 mm., bromine number 157.

4-Ethyl-1,3-dioxane.—The hydrogenation of 11.4 g. of I in 150 ml. of ethanol at room temperature and 3 atmospheres pressure, with Raney nickel[7] catalyst, required about 45 minutes. Distillation gave a practically quantitative yield of 4-ethyl-1,3-dioxane, b.p. 140–142°, n^{32}_{D} 1.4176, d^{32}_{4} 0.949.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.1; H, 10.3; *M*D 31.0. Found: C, 62.4; H, 10.5; *M*D, 30.8.

4-(1,2-Dibromoethyl)-1,3-dioxane.—A solution of bromine in carbon tetrachloride was added to 10 g. of I until the color of bromine persisted. Fractional distillation gave a pale-colored liquid, b.p. 159–160° at 28 mm., n^{30}_{D} 1.5332, d^{30}_{4} 1.85.

Anal. Calcd. for $C_6H_{10}O_2Br_2$: C, 26.3; H, 3.65; Br, 58.4; *M*D, 46.5. Found: C, 26.1; H, 3.56; Br, 58.1; *M*D, 45.9.

4-(1,2-Dihydroxyethyl)-1,3-dioxane.—Twenty grams of I was added to 26 ml. of 30% hydrogen peroxide in 109 ml. of 90% formic acid and the mixture worked up by the method of Roebuck and Adkins.[5] Only 0.7 g. (2.7%) of 4-(1,2-dihydroxyethyl)-1,3-dioxane was obtained by repeated recrystallization from ethyl acetate and then isopropyl ether, m.p. 96–98°.

Anal. Calcd. for $C_6H_{12}O_4$: C, 48.6; H, 8.2. Found: C, 48.1; H, 8.2.

No 1,3-dioxane-4-carboxylic acid could be isolated from the reaction mixture of I and the theoretical amount of hot aqueous alkaline potassium permanganate. I showed no noticeable tendency to be polymerized by benzoyl peroxide or stannic chloride.

Hexahydro-2H-pyrano[3,4-*d*]*m*-dioxin (V).—This compound had m.p. 52° (from benzene or ligroin), b.p. 212–213° (distilled from sodium), n^{26}_{D} 1.4670 (supercooled), d^{26}_{4} 1.139 (supercooled).

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.3; H, 8.3; *M*D, 35.05. Found: C, 58.2; H, 8.4; *M*D, 35.1.

Reaction of V with excess 2,4-dinitrophenylhydrazine in 3 *N* hydrochloric acid unaccountably gave only 70–85% of the theoretical amount of formaldehyde 2,4-dinitrophenylhydrazone. Methanolysis[8] in boiling methanol failed, no methylal being produced. Hydrolysis with boiling 10% sulfuric acid and removal of formaldehyde as methylal gave an unpurified residual glycol that responded to the periodate test for hydroxyl groups on adjacent carbon atoms. This suggests (*via* opening of the pyran ring) that IV has the structure named and not that of the isomeric 3-hydroxymethyl-4-hydroxytetrahydro-2H-pyran.

Acetolysis of V by the method of Senkus[9] gave what appeared to be a pure compound, b.p. 196–197° at 30 mm., n^{20}_{D} 1.4535, d^{20}_{4} 1.16, but no reasonable structure has been devised for it.

Anal. Found: C, 50.6, 50.7; H, 6.9, 7.1; equiv. wt. by saponification, 123.

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