SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS
PART VI. FORMALDEHYDE-d_2 AND FORMALDEHYDE-d[1]

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ABSTRACT

Formaldehyde-d_2 was prepared in 62.5% over-all yield from 1,2-dibromoethane-d_4 via the corresponding glycol diacetate and glycol. Formaldehyde-d was prepared by the same method from sym-1,2-dibromoethane-d_2. From the high isotopic purity of the deuterated formaldehydes obtained, it has been definitely established that it is a pair of hydrogen atoms from the hydroxylic groups of the glycols that generates acetic acid during dialdehyde fission with lead tetraacetate. The densities and refractive indices of the deuterated ethylene glycol diacetates and ethylene glycols used as intermediates in the synthesis of the deuterated formaldehydes have been determined.

INTRODUCTION

This investigation was undertaken to obtain a quantity of formaldehyde-d_2 which was required by Steacie and co-workers (25) for use in the study of hydrogen abstraction reactions. A synthetic method was required which would provide formaldehyde-d_2 of maximum deuterium content in a physical state from which the monomer could be readily generated for use in photochemical reactions. Further, it was desirable that the over-all yield be high, that the starting material be readily available in a high state of isotopic purity, and that intermediates should not be prone to loss of deuterium by exchange reactions during manipulation.

In 1938 Ebers and Nielsen (7) prepared formaldehyde-d_2 by irradiating a mixture of carbon monoxide and deuterium in a quartz mercury arc, but gave no experimental details. The formaldehyde-d_2 thus obtained was contaminated with glyoxal and required considerable purification before it could be used in spectroscopic studies (7). It was therefore considered that this method of preparation would not be suitable for the present investigation.

It was reported by Klar (17) that both hydrogen atoms in formaldehyde are readily exchangeable by the reaction shown in Equation 1.

$$CH_2O + D_2O \rightleftarrows CD_2O + H_2O \qquad [1]$$
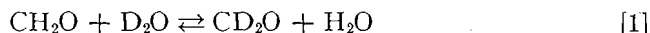
Subsequently, Wirtz and Bonhoeffer (31) found that this exchange process does not occur even in the presence of acidic or alkaline catalysts after several months' equilibration. The latter results were confirmed by Waters (30) who obtained α-polyoxymethylene containing no deuterium by polymerization of formaldehyde in deuterium oxide under either acidic or alkaline conditions.

The availability of paraformaldehyde by the catalytic oxidation of methanol (27, pp. 1–17) has made unnecessary, heretofore, the development of laboratory methods for the direct synthesis of anhydrous formaldehyde. Application of the catalytic method to the preparation of formaldehyde-d_2 was excluded because the necessary deuteromethanol is not readily available.

The thermal decomposition of metallic formates to either methanol or formaldehyde was extensively studied before the successful application of the high pressure methanol synthesis (21). The best yield of formaldehyde was obtained from stannous formate which decomposed at 180° C. according to Equation 2 (9).

$$3(H-\overset{O}{\overset{||}{C}}-O)_2Sn \xrightarrow{\Delta} CH_2O + HCOOCH_3 + 3SnO + 3CO_2 \qquad [2]$$

Some formaldehyde-d_2 was obtained by this method in the present work. However, yields were not sufficiently high to warrant a detailed study because, according to Equation 2, at least two-thirds of the deuterium initially employed would be converted to methyl-d_3 formate-d.

Some interest has recently arisen in the synthesis of formaldehyde-C^{14}. Jones and Skraba (15) subjected methanol-C^{14} to acetylation with acetyl chloride to form methyl-C^{14} acetate. Chlorination and hydrolysis of the latter substance followed by dilution with carrier formalin gave, on distillation, paraformaldehyde containing paraformaldehyde-C^{14}. Cox and Warne (3) have more recently prepared formaldehyde-C^{14} in aqueous solution by oxidative fission of ethylene-C^{14} glycol with sodium bismuthate.

A serious objection to the application of the two foregoing methods is that the formaldehyde-C^{14} is obtained as a dilute aqueous solution. According to Walker (27, pp. 58–63), the isolation of monomeric formaldehyde from aqueous solutions by distillation is not realizable in practice, although it is theoretically possible. Under the best conditions of formaldehyde recovery, the end product is paraformaldehyde containing 7% combined water (13). Isolation via derivatives might be helpful in effecting concentration without substantial loss but regeneration of the formaldehyde by hydrolysis would still necessitate isolation as paraformaldehyde. To obtain good yields of anhydrous formaldehyde it would first be necessary to prepare alkali-precipitated α-polyoxymethylene from the paraformaldehyde (28). The yield in this step is, at best, only 58% of theoretical (24). The conversion of alkali-precipitated α-polyoxymethylene to anhydrous monomeric or polymeric formaldehyde has been elaborated by Walker (28). These considerations made any synthetic method in which formaldehyde-d_2 is generated in aqueous solution appear most unattractive and expensive. It was, therefore, considered essential to develop a method which would produce directly formaldehyde in an anhydrous condition.

The cleavage of ethylene glycol to two moles of formaldehyde can be carried out nearly quantitatively. Reagents which must be used in aqueous solution, such as periodic acid (14, 19), sodium bismuthate (10, 22, 3), the unstable trivalent silver ion (10), and chromyl chloride (23), were ignored because of the difficulty of obtaining a good yield of anhydrous formaldehyde from the resulting solution (see above). Hence attention was centered on the use of lead tetraacetate in organic solvents (4, 5).
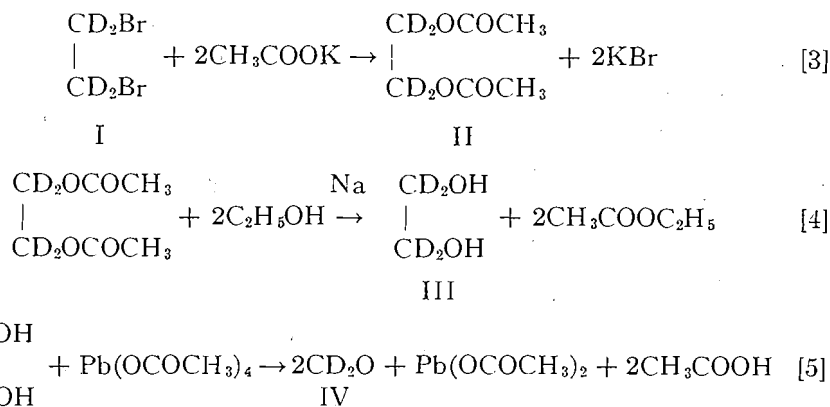
In a recent patent, Drewitt (6) claims to have obtained almost quantitative yields of formaldehyde by mixing red lead, glacial acetic acid, and ethylene glycol

at room temperature, followed by heating at 60–70° C. with vigorous stirring until the red lead dissolved. Experiments were performed according to Drewitt's directions but in no case was monomeric formaldehyde isolated by heating the resultant solution under reflux with adequate facilities for condensing volatile effluent gases. It was possible to isolate small amounts of formaldehyde polymer on fractionation of the solution, but the yields were too low (15%) to warrant further study of the method. Drewitt's claim (6) must refer to the yield of formaldehyde in solution, available for reaction, but not isolable as anhydrous formaldehyde.

Hockett and co-workers (12) obtained formaldehyde from the carbohydrate "arlitan" by a technique in which the carbohydrate, dissolved in a small quantity of glacial acetic acid, was added to dry lead tetraacetate. The formaldehyde was swept out of the reaction system by heating the mixture under reflux in a slow current of dry air. The effluent gases were adsorbed in an acidic 2,4-dinitrophenylhydrazine solution, and the quantity of formaldehyde evolved estimated as the 2,4-dinitrophenylhydrazone. By this method 62% of the theoretical yield of formaldehyde was obtained. Control experiments were also performed using ethylene glycol as substrate. The yield of formaldehyde was not reported in this instance but the authors state that the procedure and apparatus are not wholly satisfactory (12). Acetic acid is known to form loose addition compounds with formaldehyde which are probably monoesters of methylene and polyoxymethylene glycols (27, p. 191). Furthermore, solutions of formaldehyde in hydroxylic solvents do not evolve formaldehyde quantitatively on heating (28). However, solutions of formaldehyde in nonhydroxylic solvents evolve monomeric formaldehyde gas almost quantitatively on warming to room temperature (27, p. 28). Evidently, maximum yields of formaldehyde from ethylene glycol by oxidative cleavage with lead tetraacetate would most probably be realized in a nonhydroxylic solvent. Benzene was selected as solvent because it can be readily dried and dissolves lead tetraacetate more readily than most other nonhydroxylic solvents (5).

Glycol cleavage with lead tetraacetate proceeds only if the hydroxyl groups of the glycol are unsubstituted (5). It was logical to conclude from this observation that the two hydrogen atoms lost from the glycol during dialdehyde cleavage, which appear ultimately as acetic acid, are hydrogen atoms originally bound to oxygen rather than to carbon. This view is in agreement with that of Waters (29), who considers that primary attack by the lead tetraacetate is at a hydroxylic and not a carbon-bound hydrogen atom. It was therefore not considered necessary to prepare ethylene-d_4 glycol-d_2 as starting material for the synthesis of formaldehyde-d_2, because two deuterium atoms would merely be lost as acetic acid-d during dialdehyde cleavage. Attention was therefore turned to the synthesis of ethylene-d_4 glycol.

1,2-Dibromoethane-d_4 (I) was chosen as starting material for the preparation of ethylene-d_4 glycol, since it was readily available in a high state of isotopic purity by the method of Leitch and Morse (18). The synthetic scheme is shown in Equations 3, 4, and 5.

$$\begin{matrix} CD_2Br \\ | \\ CD_2Br \end{matrix} + 2CH_3COOK \rightarrow \begin{matrix} CD_2OCOCH_3 \\ | \\ CD_2OCOCH_3 \end{matrix} + 2KBr \qquad [3]$$

$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$

$$\begin{matrix} CD_2OCOCH_3 \\ | \\ CD_2OCOCH_3 \end{matrix} + 2C_2H_5OH \xrightarrow{Na} \begin{matrix} CD_2OH \\ | \\ CD_2OH \end{matrix} + 2CH_3COOC_2H_5 \qquad [4]$$

$$\text{III}$$

$$\begin{matrix} CD_2OH \\ | \\ CD_2OH \end{matrix} + Pb(OCOCH_3)_4 \rightarrow 2CD_2O + Pb(OCOCH_3)_2 + 2CH_3COOH \quad [5]$$

$$\text{IV}$$

Pilot experiments were first performed with undeuterated substances to establish the range of yields to be expected for the syntheses with deuterated compounds to be undertaken later.

Ethylene glycol diacetate was prepared in 88.5% yield by the action of fused potassium acetate on 1,2-dibromoethane, using a modification of the method of Henry and Henry (11). The use of silver acetate in this reaction gave greatly reduced yields (32). Ethylene glycol diacetate was converted to ethylene glycol in 93.0% yield by a modification of the transesterification procedure of Bainbridge (1). An attempt to obtain ethylene glycol from 1,2-dibromoethane by oxidation with silver oxide was unsuccessful. This result agrees with the previous observations of Beilstein and Wiegand (2). Formaldehyde was prepared in 80% yield by cleavage of the ethylene glycol with lead tetraacetate in benzene suspension heated under reflux. The product was obtained first as anhydrous gas which was condensed, distilled *in vacuo*, and redistilled *in vacuo* into anhydrous ether. The formaldehyde dissolved in the ether polymerized slowly to eu-polyoxymethylene on standing at 0° C. in a sealed tube for three days. The over-all yield of formaldehyde, based on 1,2-dibromoethane, was 66%.

Difficulty was at first experienced with the polymerization step and several explosions resulted by allowing the trap containing formaldehyde solution in ether to warm too rapidly (16). This hazard was at first overcome by conducting the polymerization in ether at −80° C. with addition of *n*-butylamine as polymerization catalyst (28). It was found, however, that the polymer thus obtained could not be depolymerized by heating *in vacuo*. Consequently, addition of the polymerization catalyst was omitted in subsequent preparations in favor of polymerization at 0° C.

In a similar manner *sym*-1,2-dibromoethane-d_2 was converted to *sym*-ethylene-d_2 glycol diacetate in 90.0% yield. Transesterification of the latter substance gave 81.5% of *sym*-ethylene-d_2 glycol, oxidative cleavage of which produced formaldehyde-*d* as anhydrous polymer in 76% yield.

1,2-Dibromoethane-d_4 (I) was converted to ethylene-d_4 glycol diacetate (II) in 94.0% yield, transesterification of which produced an 88.5% yield of ethyl-

ene-d_4 glycol (III). Oxidative cleavage of the latter substance produced a 75% yield of formaldehyde-d_2 (IV) as anhydrous polymer.

The fact that the yield of formaldehyde is not quantitative by the method elaborated in this paper may be readily explained by the assumption that some formaldehyde is retained in solution by the acetic acid which is generated in accordance with Equation 5. The lower yields which Hockett and co-workers obtained (12) seem to substantiate this view. It was noted that the residual benzene solution possessed a definite odor of formaldehyde even after prolonged boiling to the point where no further liquid formaldehyde was being condensed by the cooling system. The same phenomenon was observed in the unsuccessful attempts to evolve monomeric formaldehyde by oxidative fission in acetic acid media. A quantitative yield of monomer could only be realized by neutralizing the acetic acid as it is generated. The basic substance used for this purpose must not promote the irreversible polymerization of the monomer.

The isotopic purity of the deuterated 1,2-dibromoethanes used as starting materials was determined by mass spectrometer analysis, whereas the isotopic purity of the deuterated formaldehydes was established by conversion to deuterated methylene chlorides, followed by mass spectrometer analysis. Since the isotopic purity of the formaldehyde-d_2 exceeded 98%, it is evident that it is the hydroxylic hydrogen atoms of the glycol which are eliminated as acetic acid during oxidative fission with lead tetraacetate.

The deuterium content of the deuterated ethylene glycol diacetates and ethylene glycols could not be determined by their mass spectra. However, the densities and refractive indices of the deuterated substances in relation to the same physical constants for the undeuterated compounds should serve as an indication of isotopic purity. McLean and Adams (20) developed an equation by means of which the densities of deuterated organic compounds can be calculated if the extent of deuterium substitution and density of the ordinary compound are known. Table I shows the observed densities for the deuterated

TABLE I

DENSITIES AND REFRACTIVE INDICES OF ETHYLENE
GLYCOL DIACETATES AND ETHYLENE GLYCOLS

Compound	Refractive index, n_D^{20}	Density, d_4^{20}	
		Calculated	Found
Ethylene glycol diacetate	1.4154		1.1051; 1.1052
sym-Ethylene-d_2 glycol diacetate	1.4150	1.1204	1.1210; 1.1211
Ethylene-d_4 glycol diacetate	1.4147	1.1356	1.1372; 1.1371
Ethylene glycol	1.4313		1.1137; 1.1135
sym-Ethylene-d_2 glycol	1.4302	1.1496	1.1507; 1.1505
Ethylene-d_4 glycol	1.4293	1.1858	1.1895; 1.1894

ethylene glycol diacetates and ethylene glycols in relation to those calculated by McLean and Adams' equation. The refractive indices of the compounds are also given in this table.

In Table I it is noted, as would be expected, that the densities increase progressively as the degree of substitution of deuterium for hydrogen increases. The effect of deuterium substitution on the densities of the glycols is much greater per deuterium atom introduced than in the case of the glycol diacetates because of the much higher molecular weights of the latter substances.

The densities found agree well with the calculated values in the case of the d_2 compounds but not for the d_4 compounds. In all cases the observed densities exceed the calculated values. These results differ from those of McLean and Adams (20) who found that where the observed and calculated values were in poor agreement, the calculated always exceeded the observed. The discrepancies were attributed to one of two causes (20). Either the deuterated compounds were not of sufficiently high isotopic purity, or the fundamental assumption that the molecular volumes of hydrogen and deuterium in organic compounds are identical—made by McLean and Adams in developing their equation—was invalid, and that the molecular volumes of deuterated compounds must exceed those of nondeuterated compounds. In the light of the results of the present investigation both of these explanations appear inadequate since the error is in the wrong direction. It is certain, however, that such calculations cannot be relied upon as an absolute measure of isotopic purity, and further studies along this line are necessary to determine the cause of the discrepancies.

EXPERIMENTAL

Ethylene Glycol Diacetate

Sixty gm. (0.612 mole) of fused potassium acetate, 63.0 gm. (0.335 mole) of 1,2-dibromoethane, and 19 cc. of glacial acetic acid were mixed in a 500 cc. round-bottomed flask fitted with a reflux condenser protected by a calcium chloride drying-tube. The mixture was heated under reflux for three hours, after which the liquid portion was removed by distillation, first at atmospheric pressure (60 cc.) and finally at 20 mm. pressure (2 cc.). The distillate was transferred to a 500 cc. round-bottomed flask containing 80.0 gm. (0.816 mole) of fused potassium acetate and 60.0 gm. (0.309 mole) of 1,2-dibromoethane. The mixture was heated under reflux for three hours, following which the liquid portion was distilled as described above, yielding 100 cc. of distillate at atmospheric pressure and a further 3.7 cc. at 20 mm. pressure. The combined distillates were fractionated at atmospheric pressure and the fraction of b.p. 182–188° C. (mostly at 186–188° C.) was retained. The column and pot residue were extracted with anhydrous ether, and the extract combined with the above-mentioned fraction. The resultant solution was fractionated *in vacuo* yielding 84.5 gm. (88.5%) of colorless liquid, b.p. 91–93° C. at 23 mm.; n_D^{20} 1.4154; d_4^{20} 1.1051, 1.1052. Taylor and Rinkenbach (26) report the refractive index of ethylene glycol diacetate as n_D^{20} 1.4150.

sym-Ethylene-d_2 Glycol Diacetate

The procedure was the same as for the preparation of ethylene glycol diacetate except that 50.0 gm. (0.263 mole) of *sym*-1,2-dibromoethane-d_2, 59.0 gm. (0.602 mole) of fused potassium acetate, and 8 cc. of glacial acetic

acid were used. Ethylene-d_2 glycol diacetate was obtained as a colorless liquid (35.0 gm.; 90.0%) b.p. 185–188° C.; n_D^{20} 1.4150; d_4^{20} 1.1210, 1.1211. The *sym*-1,2-dibromoethane-d_2 used in this preparation was found to contain 95.5 mole % $C_2D_2H_2Br_2$ by mass spectrometer analysis.

Ethylene-d_4 Glycol Diacetate

The procedure was the same as for the preparation of ethylene glycol diacetate except that 51.0 gm. (0.265 mole) of 1,2-dibromoethane-d_4, 59.0 gm. (0.602 mole) of fused potassium acetate, and 8 cc. of glacial acetic acid were used. Ethylene-d_4 glycol diacetate was obtained as a colorless liquid (37.4 gm.; 94.0%), b.p. 186–188° C.; n_D^{20} 1.4147; d_4^{20} 1.1372, 1.1371. The 1,2-dibromoethane-d_4 used in this preparation was found to contain 97.9 mole % $C_2D_4Br_2$ by mass spectrometer analysis.

Ethylene Glycol

A sodium ethoxide solution was prepared—from 0.5 gm. of sodium and 200 cc. of absolute ethanol—in a 500 cc. round-bottomed flask equipped with a reflux condenser protected by a calcium chloride drying tube. A solution of 43.8 gm. (0.300 mole) of ethylene glycol diacetate in 100 cc. of absolute ethanol was added at room temperature to the sodium ethoxide solution, and the resultant solution heated under reflux for six hours. The ethyl acetate and most of the ethanol were removed by distillation at atmospheric pressure. The residue was transferred to a 50 cc. modified Claisen flask and fractionated *in vacuo* when 17.3 gm. (93.0%) of ethylene glycol was obtained as a colorless liquid; b.p. 99–104° C. at 22–23 mm.; n_D^{20} 1.4313; d_4^{20} 1.1137, 1.1135. Gallaugher
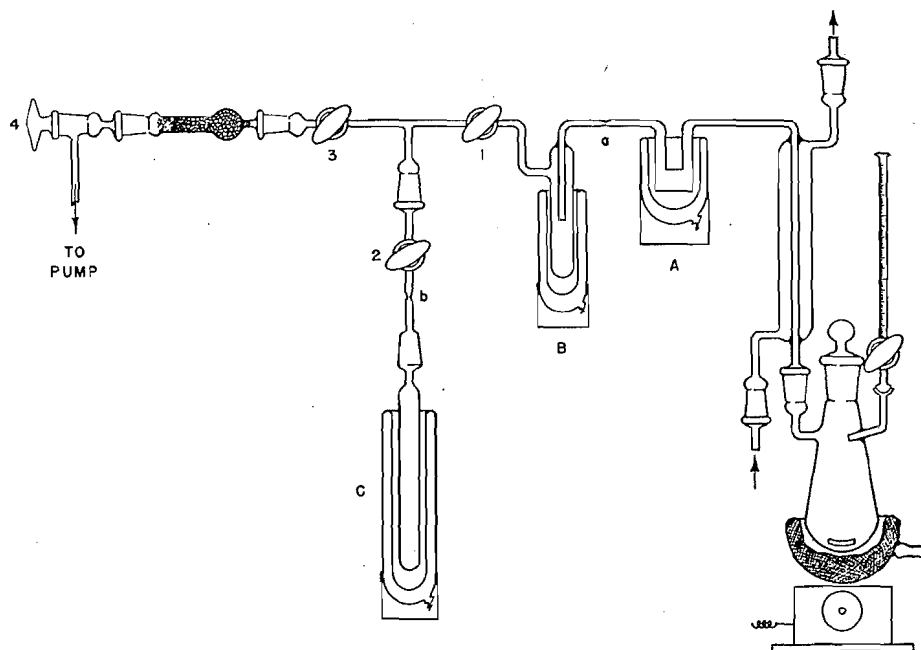

FIG. 1. Apparatus for preparation of formaldehyde-d and formaldehyde-d_2.

and Hibbert (8) report the refractive index of ethylene glycol as n_D^{20} 1.4314.

sym-Ethylene-d2 Glycol

The procedure was the same as for the preparation of ethylene glycol except that 29.0 gm. (0.196 mole) of sym-ethylene-d_2 glycol diacetate, 240 cc. of absolute ethanol, and 0.6 gm. of sodium were used. sym-Ethylene-d_2 glycol was obtained as a colorless liquid (10.2 gm.; 81.6%); b.p. 86–87° C. at 8 mm.; n_D^{20} 1.4302; d_4^{20} 1.1507; 1.1505.

Ethylene-d4 Glycol

The procedure was the same as for ethylene glycol except that 35.5 gm. (0.236 mole) of ethylene-d_4 glycol diacetate, 250 cc. of absolute ethanol, and 0.5 gm. of sodium were used. Ethylene-d_4 glycol was obtained as a colorless liquid (13.8 gm.; 88.5%) b.p. 86–87° C. at 8 mm.; n_D^{20} 1.4293; d_4^{20} 1.1895, 1.1894.

Formaldehyde

The apparatus was assembled as shown in Fig. 1. Lead tetraacetate, 56 gm. (0.12 mole) was placed in the reaction flask and the system evacuated to 0.05 mm. pressure for 30 min. while the apparatus was heated gently with a bare flame to remove moisture. Dry air was introduced through stopcock No. 4 and 200 cc. of anhydrous reagent benzene was added via the burette. Stirring was begun, water at 0° C. was circulated through the condenser, traps 1 and 2 were immersed in dry ice and acetone, and the mixture was heated under gentle reflux. Ethylene glycol, 6.2 gm. (0.10 mole), was added dropwise over a 15 min. period by means of the burette. During this period, the originally dark brown mixture became pale yellow and a white precipitate of lead diacetate separated. Simultaneously, liquid formaldehyde collected in trap A, and formaldehyde polymer appeared on the upper walls of the condenser and delivery tube leading to trap A. The burette was rinsed with 10 cc. of anhydrous reagent benzene, and the mixture was heated under reflux with stirring for a further hour. The reaction vessel was cooled in an ice bath, and the formaldehyde polymer which had formed on the upper walls of the flask depolymerized by gentle heating with a bare flame. The reaction flask was disconnected, the lower end of the condenser closed by means of a cap, trap B immersed in liquid nitrogen, and stopcock No. 1 shut. The system was evacuated to 0.1 mm. pressure, and stopcock No. 1 opened very slowly to minimize loss of formaldehyde during evacuation of the remainder of the system to 0.1 mm. pressure. Stopcock No. 1 was shut and the liquid formaldehyde distilled into trap B by allowing trap A to warm slowly after removal of the dry ice and acetone from the latter. The rate of distillation was controlled by occasional immersion of trap A in dry ice and acetone. After the liquid formaldehyde had distilled, the condenser jacket was heated with nitrobenzene under reflux to depolymerize the formaldehyde polymer which had collected on the walls. At the same time, trap A and the delivery tube leading to trap B was heated gently with a bare flame for the same purpose. Trap B was sealed off at constriction a. Trap C, containing 20 cc. of anhydrous reagent ether, was connected to the system, evacuated to 0.1 mm. pressure. Stopcock No. 3 was shut, the ether allowed to melt, then

trap C was cooled in dry ice and acetone. The formaldehyde was distilled into trap C after opening stopcock No. 1. Trap C was sealed off at constriction *b*. The trap was kept overnight in dry ice and acetone at −78° C., throughout the following day at −25 to −10° C., then for three days at 0° C. during which time the polymer separated as a white flocculent solid. The trap was cooled once more in dry ice and acetone, opened, inserted on a vacuum line and evacuated. The ether was distilled slowly from the polymer into another trap immersed in liquid nitrogen. Distillation of ether was continued until the trap containing the formaldehyde polymer was at 35° C. Formaldehyde, 4.8 gm. (80%), was thus obtained as a colorless polymeric powder. Found % CH_2O; 100.1; 99.8%.

Formaldehyde-d

sym-Ethylene-d_2 glycol (6.2 gm.; 0.10 mole) was oxidized in exactly the same manner. Formaldehyde-*d*, 4.65 gm. (75%), was obtained as colorless polymer, which on treatment with phosphorus pentachloride gave methylene-*d* chloride of the following composition, as determined by mass spectrometer analysis:

$$93.3 \pm 0.2 \text{ mole } \% \text{ } CHDCl_2.$$

These figures establish that the formaldehyde-*d* also contains 93.3 ± 0.2 mole % CHDO.

Formaldehyde-d_2

Formaldehyde-d_2 was prepared in 76% yield (4.8 gm.) from 6.5 gm. (0.098 mole) of ethylene-d_4 glycol by the same method as described for formaldehyde. The colorless polymer was converted into methylene-d_2 chloride. Mass spectrometer analysis of the chloro-compound gave the following composition: 97.0 mole % CD_2Cl_2; 2.7 mole % $CHDCl_2$. The formaldehyde-d_2 therefore contains 97.0 mole % CD_2O (98.3 atom % D).

ATTEMPTED ISOLATION OF FORMALDEHYDE MONOMER BY GLYCOL CLEAVAGE IN GLACIAL ACETIC ACID

Seventy-five gm. (0.11 mole) of red lead, 250 gm. of glacial acetic acid, and 6.2 gm. (0.10 mole) of ethylene glycol were mixed in the reaction flask of the formaldehyde generator shown in Fig. 1 and heated with mechanical stirring at 60–70° C. for 30 min. until the red lead had dissolved. The solution was heated under reflux for a further 30 min. but no liquid formaldehyde collected in the traps, and only an insignificant amount of polymeric formaldehyde collected at the lower end of the condenser. The solution possessed a strong odor of acetic acid, but the pungent odor of formaldehyde was also perceptible. The solution was fractionated at atmospheric pressure, but although the formaldehyde concentrated in the heads fraction of b.p. 101–115° C., as shown by the strong odor of formaldehyde which this fraction possessed, no separation of polymer occurred.

A second experiment was performed as described for the preceding experiment, except that 56.5 gm. (0.125 mole) of lead tetraacetate was used instead of the red lead, and the ethylene glycol was added dropwise. No liquid for-

maldehyde was obtained on heating the solution under reflux, but on fractionation of the solution, polymeric formaldehyde separated from the fraction of b.p. 100–114° C. on standing. The polymer was collected by filtration and washed with 25 cc. of anhydrous ether. Weight, 0.9 gm. (15.0%).

ACKNOWLEDGMENT

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