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Some Properties of Anhydrous Formaldehyde

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In the present paper are discussed some of the physical and chemical properties of liquid formaldehyde, the anhydrous polymer which is obtained from it, and solutions of formaldehyde in organic solvents. A simplified procedure for the preparation of liquid formaldehyde is also described.

Liquid Formaldehyde.—Liquid formaldehyde was prepared by the condensation of the vapors of alkali-precipitated polyoxymethylene obtained by vaporizing this polymer in a stream of dry nitrogen. The crude liquid was purified by distilling it alone or over phosphorus pentoxide.

The liquid aldehyde is a colorless, mobile fluid boiling at approximately $-21°$. If pure it is comparatively stable at temperatures below $-30°$ and can be kept for at least four hours without showing signs of polymerization. It is comparatively inert chemically and does not appear to react with phosphorus pentoxide, potassium hydroxide, or elemental sodium. It does not even react with ice to any observable extent and may be distilled from it unchanged except for a slight amount of polymerization. This is of particular interest because the anhydrous gas reacts rapidly with water, forming methylene glycol or the polymethylene glycols (paraformaldehydes). Even the smallest trace of water will cause the polymerization of the gas.

The liquid may be handled most conveniently for chemical work in its non-aqueous solutions. Inert solvents which do not contain hydroxyl groups or other active radicals must be chosen for this work. Liquid formaldehyde is completely miscible with ether, methylal, acetal, ethyl acetate, ethyl carbonate, chloroform, carbon tetrachloride and toluene. Solutions of formaldehyde in ether and methylal were used extensively in this work and were found to be much more stable than the pure liquid. Liquid formaldehyde is not miscible with petroleum ether or *p*-cymene. Gases such as carbon dioxide, ethylene oxide and acetylene dissolve in it readily.

Alcoholic Solutions of Formaldehyde.—Delépine[1] has pointed out that formaldehyde dissolves in methanol but that the solution differs from solutions in inert solvents. It does not give up its formaldehyde on warming and boils at a temperature much above the boiling point of the pure alcohol. Such solutions are obtained with all solvents containing hydroxyl groups. These solutions are also characterized by the fact that considerable heat is evolved when they are formed. According to Staud-

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(1) Delépine, *Ann. chim.*, [7] **15**, 554 (1898).

inger and others the solutions of formaldehyde in methanol contain formaldehyde in the form of methoxy methylene glycols such as CH_3OCH_2OH and $CH_3O(CH_2O)_nCH_2OH$.

We have found that when pure dry methanol is added to liquid formaldehyde at about −80°, a clear mobile solution is obtained without noticeable heat evolution. On standing, however, a violent reaction takes place and the solution solidifies. On warming to room temperature the solid melts and a clear liquid is obtained. Apparently the low reactivity of the cold liquid allows the formation of a true solution whose components later react to form the usual type of "solution."

To secure better knowledge of alcoholic solutions of formaldehyde, the approximate heats of solution for dry formaldehyde gas in methanol, *n*-propanol and *n*-butanol were determined. For comparison, the heat of solution of the gas in water was also measured. Delépine[2] formerly determined this figure to be 15 large calories and our value was found to be in accord with this figure. The heats of solution obtained for the three alcohols were approximately the same as the value obtained for water. The heat of polymerization of formaldehyde as determined by Delépine[3] is also 15 large calories. These findings seem to indicate that in all of the above cases there is some common happening which determines the amount of energy set free. This happening is probably the saturation of the formaldehyde molecule.

Formaldehyde Polymerization Catalysts.—Liquid formaldehyde is easily polymerized by impurities and many chemicals cause this polymerization to proceed with rapidity. We have found that the normal aliphatic amines are powerful polymerizing agents. When a trace of one of these compounds is added to a 33% solution of liquid formaldehyde in dry ether at −80°, polymerization takes place at once. One part of *n*-butylamine per 60,000 parts of anhydrous formaldehyde is sufficient. Isoamylamine and *n*-ethylamine seem to be approximately equal to *n*-butylamine in this respect. Tri-*n*-butylamine is much less effective. In a recent publication Staudinger has pointed out[4] that trimethylamine is a formaldehyde polymerizing agent. Ammonia, however, when added to an ether solution of formaldehyde in small quantities does not cause polymerization.

In order to study the action of aromatic amines on liquid formaldehyde, aniline and dimethylaniline were tested. Dimethylaniline was found to be a weak polymerizing agent whereas aniline reacted with liquid formaldehyde but did not cause it to polymerize. The products of the aniline reaction were water and a micro-crystalline colorless compound melting at 172–180°. This product dissolved in hot toluene and appeared to crystallize out when the solution was cooled. The crystals, however, were

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(2) Delépine, *Compt. rend.*, **124**, 816 (1897).

(3) Ref. 2, p. 1528.

(4) Staudinger, "Die hochmolekularen organischen Verbindungen," 1932, p. 286.

found to melt at 139–140° and by means of a mixed melting point were found to be identical with the trimeric methyleneaniline which is usually obtained when formaldehyde reacts with aniline. The original product of the reaction is probably a higher polymeride of this compound.

The Anhydrous Polymer of Formaldehyde.—In our work on the properties of liquid formaldehyde, a study was made of the anhydrous polymer that is obtained when it polymerizes. Since then Staudinger[5] has published an account of this compound and its relation to his theories of polymerization. We prepared this polymer by warming a 33% solution of liquid formaldehyde in dry ether to 0° or room temperature in sealed glass tubes. The powder-like polymer thus obtained, in general, resembled the anhydrous polymer described by Staudinger. It possessed, however, a definite melting point at 170–172° at which temperature it went over to a clear viscous boiling liquid. It was also found to absorb water from the air and could not be dried again even by vacuum desiccation over phosphorus pentoxide. This fact might indicate that the polymer reacts with moisture in the air to form a polymethylene glycol but it may also be a case of adsorption. The polymer dissolved in dilute alkali although it did not dissolve as rapidly as α-polyoxymethylene.

We have found that for practical purposes formaldehyde polymers may be best classified by a comparison of their melting points and their rates of solution in water. Since the polymers must depolymerize to react or dissolve in water, the rate at which they dissolve is also a measure of their reactivity. When the paraformaldehydes, the acid- or alkali-precipitated polyoxymethylenes and the anhydrous polymer are classified in this way, they fall rather sharply into two groups which we have designated as the paraformaldehyde and polyoxymethylene groups. The members of the first group have a melting point of 120–130° or lower, and show a high rate of solution in water. The members of the latter group melt in the range 170–175°, and have a slow rate of solution in water.

It is of importance to observe in this connection that paraformaldehyde can be changed to a polyoxymethylene-like polymer by heating it in a sealed tube. This was first observed qualitatively by Auerbach[6] and later Brown and Hrubesky[7] made the observation that on heating paraformaldeyde at 100°, it became less reactive. We have found that when a 96.1% paraformaldehyde is heated for twenty minutes at 178°, its melting point is changed from 119–122° to 175–178°, and its rate of solution in water is greatly decreased. It is still soluble in dilute alkali. Since it has been heated in a sealed tube it still contains water but this water is probably no longer chemically combined, since polymers which have been thus heated lose water on merely standing in the air until their formaldehyde

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(5) Ref. 4, pp. 255–263, 280–287.

(6) Auerbach, *Arb. kais. Gesundh.*, **27**, 19 (1907).

(7) Brown and Hrubesky, *Ind. Eng. Chem.*, **19**, 217 (1927).

content is 98% or higher. That this polymer should form in the presence of hot water vapor would seem to indicate that the change is irreversible and may be more than a simple change to a higher polymer of the same type.

All these observations seem to indicate that the acid- and alkali-precipitated polyoxymethylenes and the anhydrous polymer are chemically of the same type whereas paraformaldehyde is a radically different type of polymer. The polyoxymethylene type of polymer probably has a cyclic structure and possesses the type formula $(CH_2O)_n$, the only possible formula for the anhydrous polymer. Staudinger has proved that paraformaldehyde is a polymethylene glycol. He also believes, however, that all the higher formaldehyde polymers have chain formulas and possess end groups like the hydroxyl groups in paraformaldehyde. In the case of the anhydrous polymer, he assumes the presence of end groups although he admits that it is impossible to say just how they are formed. He believes that the precipitated polyoxymethylenes contain hydroxyl groups like paraformaldehyde but differ in having a higher degree of polymerization. The fact that they cannot be freed completely of water by desiccation is considered to be evidence of combined water. However, we have found that the anhydrous polymer absorbs water from the air which cannot be removed by desiccation and one is hence not surprised that the polymers prepared from aqueous solutions cannot be freed of every trace of water. The fact that precipitated polyoxymethylenes dissolve in dilute alkali is believed to indicate that they contain hydroxyl groups. However, the anhydrous polymer also dissolves in dilute alkali and Schweitzer[8] was unable to methylate α-polyoxymethylene although he was able to methylate the hydroxyl groups in paraformaldehyde by the same procedure. Ott's x-ray studies[9] have not proved either the presence or absence of end-groups in polyoxymethylenes. Our knowledge of the exact chemical structure of the higher polymers of formaldehyde is still incomplete. The theory that the polyoxymethylene type of polymer does not contain combined water, however, is compatible with the facts and helps to correlate observations that are not otherwise adequately explained.

Experimental Part

Preparation of Liquid Formaldehyde.—The apparatus used in preparing liquid formaldehyde is shown in the drawing. The freezing mixture used to condense the gas consisted of solid carbon dioxide and methanol. The vaporizing tube was charged with 20 g. of alkali-precipitated polyoxymethylene[10] and a slow current of dry nitrogen was passed through the apparatus. The oil-bath was heated to 150° and the temperature

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[8] Schweitzer, "Über Polyoxymethylene und Polyëthylenoxyde," Inaugural Dissertation, pp. 18, 46–47.

[9] Ott, *Z. physik. Chem.*, **9**, 378–400 (1930).

[10] Staudinger and co-workers, *Ber.*, **64B**, 398–405 (1931).

was then gradually raised until all the polymer had vaporized. It was found that better yields of liquid could be obtained if the tubes leading from the vaporizer to the condensing tube were kept hot. This was done by winding them with resistance wire and heating with electricity. The crude liquid product was purified by distilling in a stream of dry nitrogen alone or over phosphorus pentoxide. Approximately 10 to 12 cc. of pure liquid formaldehyde was obtained from 20 g. of polymer.

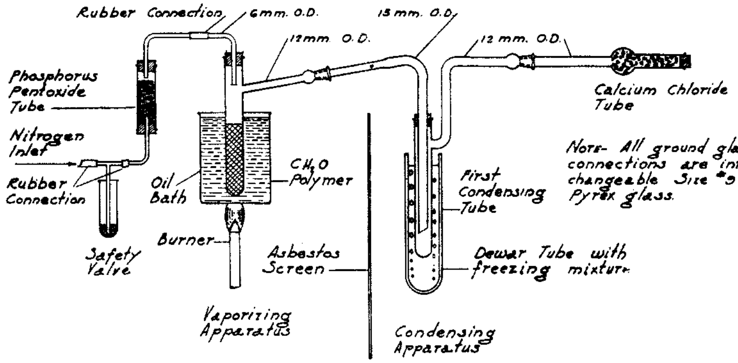

Fig. 1.

Preparation of Anhydrous Polymer.—The powder-like form of this polymer was prepared by mixing one volume of liquid formaldehyde with two volumes of dry ether and sealing nine to ten cc. batches of this solution in small Pyrex tubes. Each tube was then placed in a small capped iron pipe. After four hours the sealed tubes were opened and the paste of polymer and ether was removed and vacuum dried. In some experiments the Pyrex tubes containing the ether–formaldehyde solution were immersed in an ice and water bath and allowed to polymerize at 0°.

Samples of the polymer were analyzed by heating on the steam-bath for twenty-four hours with 50-cc. amounts of a 2 N chromic acid solution containing approx. 10 g. of sulfuric acid for each gram of chromic acid. The solutions were then diluted to 1000 cc. in a volumetric flask and 50-cc. aliquots were titrated with $N/10$ thiosulfate solution. This titer subtracted from a blank titer gives the quantity of thiosulfate equivalent to one-twentieth of the sample (1 cc. of $N/10$ thiosulfate $\approx$ 0.7502 mg. of CH_2O).

Anal. Subs. 0.4278 g., 0.4676 g.; titers, 29.40, 32.10 cc. of 0.09690 N thiosulfate for one-twentieth aliquot of samples. Oxidizables calculated as CH_2O, 100.0, 99.9%.

A sample of polymer which had been exposed to the air in a loosely stoppered bottle for several months was vacuum desiccated over phosphorus pentoxide for two weeks and then analyzed. It was found to contain only 98.0% formaldehyde, having taken up 2.0% of water.

Anal. Subs., 0.4977 g.; titer, 32.59 cc. of 0.09972 N thiosulfate for one-twentieth aliquot of sample. Oxidizables calculated as CH_2O, 98.0%.

Solubility and Melting Points of Polymers.—The table shows the melting point and solubility rate figures for samples of the anhydrous polymer, acid- and alkali-precipitated α-polyoxymethylene and paraformaldehyde. The solubility figure was obtained by agitating 5 g. of polymer with 25 cc. of water at room temperature for one hour and filtering. The undissolved polymer was washed with 10 cc. of water and the washings added to the original filtrate. The filtrate was then analyzed for formaldehyde by the sodium sulfite procedure using aurine as an indicator.

Polymer	Melting point, °C.	Solubility figure (G. of CH_2O per 100 cc. of water)
Anhydrous polymer	170–172	0.017
α-Polyoxymethylene (alkali-precipitated)	170–172	.02
α-Polyoxymethylene (acid-precipitated)[a]	172–173	.00
Paraformaldehyde	121–123	.24

[a] Prepared according to Staudinger's directions, *Ann.*, **474**, 251 (1929).

All solubility figures were determined simultaneously under identical conditions.

Determination of the Heats of Solution of Formaldehyde Gas in Water and Alcohols.—A weighed quantity of the liquid (approx. 100 cc.) was placed in a calorimeter consisting of a silvered Dewar flask whose water equivalent had been previously determined. Pure dry formaldehyde gas mixed with a little dry nitrogen was then passed into the liquid. This formaldehyde gas was generated by vaporizing two grams of anhydrous polymer in a nitrogen stream maintained at a fixed rate (about 10 cc. per minute). The mixed gases were always passed through a −20° condenser to remove any impurities. The quantity of formaldehyde which dissolved in the liquid in the calorimeter was determined by means of the alkaline peroxide procedure. Suitable blank analyses were always carried out on samples of the original liquid. The nitrogen current being slow, no correction was necessary for solvent evaporation except in the case of methanol and even here the correction was very small. The data and results are shown.

Solvent	Solvent, g.	CH_2O dissolved, g.	ΔT, °C.	Av. calorim. temp., °C.	Heat capacity of solv. at av. cal. temp.	ΔH in kg.-cal. per mole of CH_2O
Water	99.41	2.71	12.1	21	0.999	14.8
Methanol	78.93	1.82	15.6	23	.605[a]	15.0
n-Propanol	79.85	1.78	14.6	23	.588[a]	14.2
n-Butanol	80.31	1.68	15.0	23	.560[a]	14.9

[a] Francis, *Ind. Eng. Chem.*, **20**, 283–285 (1928).

Water equivalent of calorimeter, 10.7 g. cal. per degree.

Summary

1. The chemical and physical properties of liquid formaldehyde and the anhydrous polymer obtained from this liquid have been described.

2. The heats of solution of formaldehyde in water, methanol, *n*-propanol, *n*-butanol, and its heat of polymerization have been found to be approximately equal. The heat evolved in these cases is probably the heat of saturation of the formaldehyde molecule.

3. The primary amines have been found to be powerful polymerizing agents for liquid formaldehyde. Tertiary amines are less active. Ammonia does not cause polymerization when added in small quantities. Aniline reacts with the liquid instead of causing polymerization.

4. A practical method for classifying formaldehyde polymers has been described.

5. Paraformaldehyde has been shown to go over to a polyoxymethylene when heated in a sealed tube.

6. A simple procedure for the preparation of pure liquid formaldehyde has been described.

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