TRIOXANE AS A SOURCE OF FORMALDEHYDE

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Trioxane, the relatively stable, cyclic polymer of formaldehyde, possesses unique properties which give it value as a special form of formaldehyde for use in chemical syntheses. Since its use as a source of formaldehyde is dependent upon the rate at which it can be depolymerized, a study of trioxane depolymerization has been made in aqueous and nonaqueous solvents. Results demonstrate that depolymerization is a first-order reaction. In aqueous solutions relatively high concentrations of strong acids are required, whereas much smaller concentrations are equally effective in nonaqueous media. The kinetics of phenol-trioxane reactions have been studied. A study of synthetic reactions indicates that trioxane is of value in chloromethyations, production of formals, condensations with phenols and amides, and the Mannich synthesis.

The unique properties of trioxane, the cyclic trimer of formaldehyde, were briefly summarized by Walker and Carlisle. This polymer is quite unlike aqueous formaldehyde or the hydrous polymer, paraformaldehyde, since it is a colorless crystalline compound melting at 61-62 C. and boiling without decomposition at 115 C. It has a pleasant chloroformlike odor and is readily soluble in common organic solvents. In the molten state it is an excellent solvent. Recent physiological tests have shown that it does not appear highly toxic to rats when given by mouth or when inhaled. Patch tests show that there does not appear to be much risk of its causing dermatitis in humans.

One of the most obvious uses for trioxane is as a special source of formaldehyde in chemical reactions. For this purpose it possesses four advantages over aqueous formaldehyde and paraformaldehyde: (1) It is soluble in most organic solvents and reagents. (2) Its rate of reaction as formaldehyde can be controlled by the use of acid depolymerization catalysts. (3) It is a completely anhydrous form of formaldehyde. (4) It has a pleasant, nonirritating odor and, therefore, does not create special ventilating problems. Therefore, although trioxane is more expensive than present commercial forms of formaldehyde, it has value for uses in which these forms cannot be readily employed or prove less efficient. Since utilization of trioxane for this purpose requires a thorough knowledge of the conditions under which it may be converted to formaldehyde, a study was made of its rate of depolymerization in various solvents and with various acidic catalysts.

DEPOLYMERIZATION IN AQUEOUS SOLUTION

Trioxane is stable in neutral and alkaline solutions but is depolymerized by strong acids. To determine the rate of depolymerization, this reaction was followed by keeping acidified 3% trioxane solutions in a constant temperature bath and titrating samples at intervals for free formaldehyde by the iodometric method. Since the acid concentration does not change during the reaction, good first-order rate constants were obtained, an indication that the reaction velocity at any given temperature and acidity is a function only of the trioxane concentration. This agrees with the work of Skrabal, Stockmair, and Schreiner, who determined constants for trioxane depolymerization at 35, 45, and 55 C. by 0.5 M toluenesulfonic acid.

First-order constants were calculated from experimental data by the following equation:

\[ k = \frac{1}{t} \ln \frac{a}{a - x} \]

where \( a \) = initial trioxane concentration \( x \) = amount depolymerized in time \( t \) \( k \) = first-order rate constant

Table I shows the data for a typical reaction. Constant \( k \) varies with acid strength and temperature. A series of constants was determined for varying sulfuric acid concentrations at 20, 40, 70, and 95 C. using 3% trioxane. The results are shown in Figure 1, where the logarithm of the first-order constants is plotted against the normality of the acid used. For solutions containing 12 and 20% trioxane, the rate of depolymerization was
found to be substantially identical to that obtained for the 3% solution. However, with higher concentrations the rate increased rapidly. The percentage of trioxane depolymerized in one hour at 75°C for solutions which had a normality of 1 with respect to hydrochloric acid for a 20% trioxane solution was 23%. For solutions containing 40 and 60% trioxane, depolymerization was 40 and 65%, respectively. Pure trioxane was more than 90% depolymerized under the same conditions, but in this case the monomeric formaldehyde polymerized rapidly to polyoxymethylene. These findings indicate a deviation from first-order kinetics for highly concentrated trioxane solutions.

The time necessary for the depolymerization of any given percentage of the trioxane may be readily calculated with the following equation, where $t_v$ is the time necessary for the depolymerization of $x\%$ trioxane:

$$t_v = \frac{1}{k} \ln \frac{100}{100 - x}$$

Table II gives the time required for depolymerization of 10, 50, 75, and 99% of the trioxane at various temperatures and acidities as calculated from the first-order rate constants taken from the curves of Figure 1.

Experiments were also carried out to show the catalytic effect of different acids. As Table III shows, hydrochloric acid is more active than sulfuric acid of the same normality; the difference becoming greater at higher acidities. Phosphoric acid is less active even when it is considered as a monobasic acid. A value based on Skrabal"s work is included in Table III for comparison.

By use of the Arrhenius equation, the activation energy for the reaction was found to be $26 = 3$ kg.-cal. per mole.

**TABLE I.** DEPOLYMERIZATION OF 3% TRIOXANE IN 3.84 N SULFURIC ACID AT 40°C

<table>
<thead>
<tr>
<th>Time, Sec.</th>
<th>$\text{CrO}_3 \times 10^5$</th>
<th>$x$</th>
<th>$\text{S}_x$</th>
<th>$a - x$</th>
<th>$k \times 10^9$ for Interval 0 to 6, Sec. $^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>3.000</td>
<td></td>
<td>3.000</td>
<td>3.42</td>
</tr>
<tr>
<td>300</td>
<td>0.073</td>
<td>2.927</td>
<td></td>
<td>2.927</td>
<td>3.42</td>
</tr>
<tr>
<td>774</td>
<td>0.175</td>
<td>2.825</td>
<td></td>
<td>2.825</td>
<td>3.35</td>
</tr>
<tr>
<td>163</td>
<td>0.369</td>
<td>2.309</td>
<td></td>
<td>2.309</td>
<td>3.38</td>
</tr>
<tr>
<td>448</td>
<td>1.262</td>
<td>1.744</td>
<td></td>
<td>1.744</td>
<td>3.28</td>
</tr>
<tr>
<td>702</td>
<td>2.428</td>
<td>0.968</td>
<td></td>
<td>0.968</td>
<td>3.71</td>
</tr>
</tbody>
</table>

**TABLE II.** RATE OF TRIOXANE DEPOLYMERIZATION AT VARIOUS TEMPERATURES WITH SULFURIC ACID AS CATALYST

<table>
<thead>
<tr>
<th>Normality of $\text{H}_2\text{SO}_4$</th>
<th>Time of Liberation of Following Percentage Formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10%</td>
</tr>
<tr>
<td>8</td>
<td>12.3 hr.</td>
</tr>
<tr>
<td>12</td>
<td>35 min.</td>
</tr>
<tr>
<td>16</td>
<td>4.4 min.</td>
</tr>
<tr>
<td>20</td>
<td>22 sec.</td>
</tr>
<tr>
<td></td>
<td>12.3 hr.</td>
</tr>
<tr>
<td>1</td>
<td>3.0 days</td>
</tr>
<tr>
<td>3</td>
<td>29 hr.</td>
</tr>
<tr>
<td>4</td>
<td>6.5 hr.</td>
</tr>
<tr>
<td>8</td>
<td>31 min.</td>
</tr>
<tr>
<td>12</td>
<td>3.6 min.</td>
</tr>
<tr>
<td>16</td>
<td>25 sec.</td>
</tr>
<tr>
<td></td>
<td>12.3 hr.</td>
</tr>
<tr>
<td>0.5</td>
<td>41 hr.</td>
</tr>
<tr>
<td>1</td>
<td>7.9 hr.</td>
</tr>
<tr>
<td>2</td>
<td>10.1 hr.</td>
</tr>
<tr>
<td>4</td>
<td>66 sec.</td>
</tr>
<tr>
<td>8</td>
<td>10.7 sec.</td>
</tr>
<tr>
<td></td>
<td>12.3 hr.</td>
</tr>
<tr>
<td>0.1</td>
<td>11.3 days</td>
</tr>
<tr>
<td>0.25</td>
<td>38 min.</td>
</tr>
<tr>
<td>0.5</td>
<td>17.3 min.</td>
</tr>
<tr>
<td>1</td>
<td>7.4 min.</td>
</tr>
<tr>
<td>2</td>
<td>2.4 min.</td>
</tr>
<tr>
<td>4</td>
<td>45 sec.</td>
</tr>
<tr>
<td>8</td>
<td>11.6 sec.</td>
</tr>
</tbody>
</table>

**Figure 1.** Effect of Sulfuric Acid Concentration on Rate of Trioxane Depolymerization

**DEPOLYMERIZATION IN GLACIAL ACETIC ACID**

The rates of depolymerization of trioxane in glacial acetic acid using sulfuric acid as a catalyst were determined by the same method used for the aqueous reactions. However, in acetic acid solutions, the free formaldehyde concentration never reached the theoretical end value because some of it was converted to polyoxy-methylene acetates which do not show up as formaldehyde in the analysis used. This effect was greater for the higher concentrations of sulfuric acid. As this caused the values obtained for the constant to drop rapidly toward the end of the reaction, the figure obtained during the initial period was taken as the true constant. Therefore, these constants are not so accurate as those obtained for aqueous depolymerization. The results show that sulfuric acid is a much more effective catalyst in acetic acid than in water; the reaction with a given acid concentration was of the order of a thousand times faster in the former solvent. At 95°C, depolymerization proceeded at a measurable rate in glacial acetic acid with no added catalyst. Experiments with zinc chloride showed that this catalyst is much less effective than sulfuric acid.

**DEPOLYMERIZATION IN OTHER ORGANIC SOLVENTS**

As a preliminary to this study, the solubility of trioxane in a few organic solvents was determined as follows for temperatures below the melting point of trioxane:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Trioxane Solv., Grams/100 G. Soln.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>40</td>
</tr>
<tr>
<td>Benzene</td>
<td>40</td>
</tr>
<tr>
<td>Toluene</td>
<td>40</td>
</tr>
<tr>
<td>Trichloroethylen</td>
<td>23</td>
</tr>
</tbody>
</table>

Formaldehyde itself is nearly insoluble in solvents like toluene and trichloroethylene. Therefore, when trioxane is depolymerized in these solvents, most of the liberated formaldehyde polymerizes rapidly to paraformdehyde or polyoxymethylene which collects on any cool surface in the reaction vessel. To measure
The depolymerization in these solutions, it was necessary to determine both the small amount of dissolved formaldehyde and the amount which had polymerized. The sodium sulfite method (5) was used for this determination.

The first-order rate constant for depolymerization of 3% trioxane in toluene solution catalyzed by 0.05 N trichloroacetic acid at 75°C was found to be about $2 \times 10^{-6}$ sec.$^{-1}$. The constant appeared to be dropping during the course of the reaction, but, as in the case of the reaction in acetic acid, this was probably due to side reactions which decreased the acidity of the solution and lowered the concentration of free formaldehyde by converting it to derivatives or polymers.

A series of tests was made to compare the effects of different catalysts in trichloroethylene and toluene solution. Samples were heated at 75°C for 2 hours and then titrated. The most rapid depolymerization was obtained with a mixture of trichloroacetic acid and zinc chloride. The rates obtainable with mineral acids are limited by the solubility of the acids in the solvents used. Zinc chloride, apparently, did not accelerate the sulfuric acid-catalyzed reaction, but some of the liberated formaldehyde may have reacted with the toluene since zinc chloride is a good catalyst for the reaction of aromatic hydrocarbons with formaldehyde. Ferric chloride by itself was more effective than either zinc chloride or aluminum chloride, probably because it is a little more soluble. Ferric chloride and zinc chloride in combination with acetic acid catalyze the depolymerization at a moderate rate, but no quantitative data were obtained for these combinations. An experiment was tried with stannic chloride in each solvent, but black, resinous products separated at the bottom of the reaction mixture so that no rate measurements could be made. With all the catalysts tried, depolymerization took place more rapidly in toluene than in trichloroethylene. Table V lists the results.

The depolymerization of trioxane in alcohols was studied briefly but because formaldehyde reacts with the alcohol as fast as trioxane is depolymerized, no quantitative data were obtained. In acetone solution some free formaldehyde is liberated, but a large proportion reacts with the solvent to form condensation products.

### REACTION WITH PHENOL

Phenol is very soluble in trioxane; a mixture of 1 mole of phenol with trioxane equivalent to 1 or 2 moles of formaldehyde is liquid at room temperature. Solution takes place with pronounced absorption of heat on mixing the crystalline reagents. When acid catalysts are added to these phenol-trioxane solutions, resins are formed. The rate of reaction and the nature of the resinous product depend on the amount of catalyst used. The resin formation can be stopped at any desired point by neutralizing the catalyst.

Addition of 0.25% hydrochloric or sulfuric acid initiated an exothermic reaction at room temperature. When this mixture was allowed to warm itself, the reaction accelerated gradually until the temperature reached 70-80°C. Then the mixture boiled violently, the temperature rising to 180°C in 20-30 seconds. The product was a light pink, brittle resin. If external cooling was applied so that the temperature did not rise above 40-50°C, a
Table IV. Rate of Trioxane Depolymerization in Glacial Acetic Acid

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Molar Conc.</th>
<th>Time of Depolymerization of Following Percentage Trioxane</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10% 50% 75% 90%</td>
<td>40°C</td>
</tr>
<tr>
<td>H2SO4 0.5</td>
<td>8 x 10^-4</td>
<td>2 min 14 min 28 min 38 min</td>
<td>Depolymerization at 40°C.</td>
</tr>
<tr>
<td>H2SO4 1</td>
<td>2 x 10^-4</td>
<td>1 min 6 min 12 min 25 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Depolymerization at 70°C.</td>
<td></td>
</tr>
<tr>
<td>H2SO4 0.025</td>
<td>2 x 10^-4</td>
<td>10 min 1 hr 2 hr 6 hr</td>
<td></td>
</tr>
<tr>
<td>H2SO4 0.027</td>
<td>4 x 10^-4</td>
<td>10 min 1 hr 2 hr 6 hr</td>
<td></td>
</tr>
<tr>
<td>H2SO4 0.035</td>
<td>8 x 10^-4</td>
<td>1 min 6 min 12 min 25 min</td>
<td></td>
</tr>
<tr>
<td>ZnCl2 0.075%</td>
<td>5 x 10^-4</td>
<td>6 hr 16 days 3 days 10 days</td>
<td></td>
</tr>
<tr>
<td>ZnCl2 0.15%</td>
<td>3 x 10^-4</td>
<td>5 min 6 hr 11 hr 15 days</td>
<td></td>
</tr>
<tr>
<td>ZnCl2 0.30%</td>
<td>2 x 10^-4</td>
<td>3 min 3 hr 7 hr 1 day</td>
<td></td>
</tr>
</tbody>
</table>

Table V. Decomposition of 3% Trioxane in Toluene and in Trichloroethylene

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Catalyst</th>
<th>Concentration</th>
<th>Time of Depolymerization of Following Percentage Trioxane</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>H2SO4</td>
<td>0.01 M</td>
<td>28 sec 1 min 2 min 4 min</td>
<td>Depolymerization at 75°C.</td>
</tr>
<tr>
<td></td>
<td>ZnCl2</td>
<td>0.005 M + 0.045 M</td>
<td>20 sec 1 min 2 min 4 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trichloroacetic acid</td>
<td>1.0 M</td>
<td>35 sec 1 min 2 min 4 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trichloroacetic acid + ZnCl2</td>
<td>1.0 M + 0.0015 M</td>
<td>35 sec 1 min 2 min 4 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dioxalonic acid</td>
<td>1.0 M</td>
<td>35 sec 1 min 2 min 4 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Toluenesulfonic acid</td>
<td>0.009 M</td>
<td>2 sec</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FeCl3</td>
<td>&lt; 0.1%</td>
<td>22 sec 2 min 4 min 8 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnCl2</td>
<td>&lt; 0.1%</td>
<td>10 sec 2 min 4 min 8 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AlCl3</td>
<td>&lt; 0.1%</td>
<td>0 sec 2 min 4 min 8 min</td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>H2SO4</td>
<td>0.002 M</td>
<td>0 sec</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trichloroacetic acid</td>
<td>0.04 M</td>
<td>10 sec 2 min 4 min 8 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dioxalonic acid</td>
<td>1.0 M</td>
<td>10 sec 2 min 4 min 8 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Toluenesulfonic acid</td>
<td>0.009 M</td>
<td>0.8 sec</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FeCl3</td>
<td>&lt; 0.1%</td>
<td>10 sec 2 min 4 min 8 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnCl2</td>
<td>&lt; 0.1%</td>
<td>0 sec 2 min 4 min 8 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AlCl3</td>
<td>&lt; 0.1%</td>
<td>0 sec 2 min 4 min 8 min</td>
<td></td>
</tr>
</tbody>
</table>

Reactions 1, 2, and 3 show the combined effects of steps 1 and 2. A good interpretation of the curves can be made without more study of the reaction.

**ORGANIC SYNTHESSES**

Trioxane is most useful in organic syntheses involving compounds which are extremely reactive with the usual forms of formaldehyde (8). In these cases, the reaction is dependent upon the rate at which trioxane is converted to formaldehyde. Since this rate is determined by the catalyst concentration, conditions are ideal for chemical control. The solubility and compatibility of trioxane with organic reagents give a homogeneous medium in which unreacted trioxane functions as a subsidiary solvent. Reactions involving compounds which react slowly with formaldehyde are less satisfactory since the monomeric formaldehyde may polymerize to polyoxyethylene before reaction if the reaction medium does not function as a formaldehyde solvent. The condensation of tolunene with formaldehyde to form dimethylmethane is an example of the latter type. Anisole, on the contrary, reacts rapidly so that dialdehyde can be readily prepared by reaction with trioxane.

Trioxane was found to give better results in a number of chloromethylation reactions involving alcohols and aromatic hydrocarbons. A 98% yield of o-tolyl chloromethyl ether was obtained by passing anhydrous hydrogen chloride into a solution of trioxane in o-tolylene alcohol. It can also be used advantageously in the preparation of formals by reaction with alcohols and glycols.

Trioxane can be employed successfully in the Mannich synthesis. A synthesis of this type involving piperidine hydrochloride and acetophenone gave good results without addition of a solvent; trioxane has sufficient solvent action itself to form a clear initial solution. As reaction progressed, the mixture solidified to the solid reaction product, phenyl-β-piperidinoethyl ketone hydrochloride. Reaction of trioxane with amines is illustrated by the precipitation of polyvinylamines when hydrochloric acid is added to a molten solution of urea in trioxane.

**LITERATURE CITED**

1. Haskell Lab. of Industrial Toxicology. Unpub. results.
2. Nordlander, B. W., Unpub. work reprinted at Polytechnic Inst. of Brooklyn, Mar. 30, 1945.