

The Acid-Catalyzed Reaction of Acetic Anhydride with Some Oxocanes

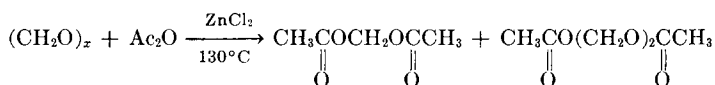
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Synopsis

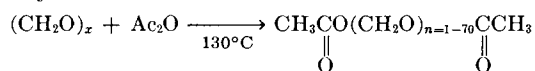
Three cyclic polymers of formaldehyde, namely, trioxane, 1,3,5,7-tetraoxocane, and 1,3,5,7,9-pentaoxocane, were reacted with acetic anhydride containing a catalytic amount of sulfuric acid. The progress of each reaction was followed by GLC. The cyclic compounds increased in reactivity with increasing molecular weight. The first step in each reaction was a ring opening, which produced a poly(oxymethylene diacetate) containing the same number of formaldehyde units as in the original cyclic compound. The poly(oxymethylene diacetate) then reacted with additional acetic anhydride to produce diacetates containing a smaller number of formaldehyde units. By controlling the time of reaction, the higher or lower molecular weight diacetates were made to predominate in the reaction mixture. Zinc chloride can be used in place of sulfuric acid as the catalyst for the conversion of oxocanes to poly(oxymethylene diacetates). The reaction with ZnCl₂ at room temperature is less vigorous and easier to control, yielding as the main product poly(oxymethylene diacetate) containing the same number of formaldehyde units as in the starting oxocane.

INTRODUCTION

In 1903, Descudé¹ reacted equimolar amounts of acetic anhydride and paraformaldehyde at 130°C using a trace of ZnCl₂ as catalyst. The product was a mixture of mono- and dioxymethylene diacetates:



In 1925, Staudinger² and his co-workers confirmed Descudé's work. They also showed that ZnCl₂ should not be used at 130°C if one wishes to prepare diacetates with higher molecular weights. The ZnCl₂ causes catalytic decomposition of these compounds. By not using ZnCl₂ and by increasing the ratio of moles of anhydride to moles of formaldehyde, Staudinger was able to obtain a mixture of diacetates that contained from 1 to 70 formaldehyde units:

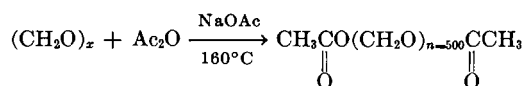


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In the 1925 paper, Staudinger concluded that low molecular weight diacetates could be converted to high molecular weight diacetates by heating them with paraformaldehyde.

In a reinvestigation of this reaction in 1929, Staudinger³ concluded that the high molecular weight diacetates are not produced by the addition of formaldehyde to low molecular weight diacetates. He believed that the low molecular weight diacetates decomposed to yield acetic anhydride. The acetic anhydride then reacted with paraformaldehyde to produce high molecular weight diacetates.

In 1960, Jenkins and Punderson⁴ obtained a patent on the use of sodium acetate as a catalyst for the production of acetal resins in which the number of formaldehyde units per diacetate molecule is about 500:

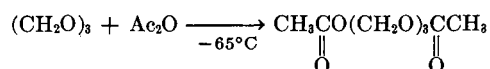


Evidently, the more acidic the catalyst, the lower the average molecular weight of the diacetate in the product.

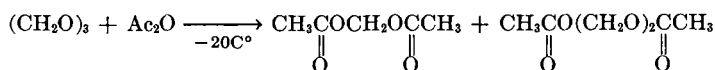
In his ACS monograph on formaldehyde, Walker⁵ stated that when trioxane is heated in a substantially anhydrous system in the presence of strong acids such as sulfuric acid or acidic materials such as ZnCl_2 , it is readily depolymerized to monomeric formaldehyde. The formaldehyde enters readily into combination if a compound capable of reacting with formaldehyde is present.

However, in 1962, Tomiska and Spousta⁶ and in 1963 Tomiska⁷ published papers on the preparation of low molecular weight poly(oxyethylene diacetates) from trioxane and acetic anhydride using a strong mineral acid as a catalyst. From 1 mole acetic anhydride, 0.22 mol trioxane, and 0.2 ml 60% perchloric acid, the following results were obtained:

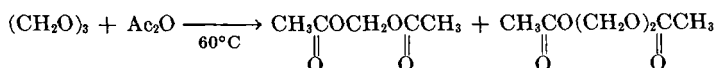
Below -65°C the product was mainly trioxymethylene diacetate:



Below -20°C and above -65°C , the product was mainly monoxy- and dioxymethylene diacetates:

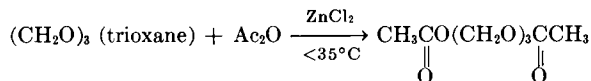


Some trioxy compound was also present. At 60°C , the product was an equimolar mixture of monoxy and dioxy compounds. The yield was 94%:



According to Tomiska and Spousta,⁶ the composition of the product remained constant (1 mole monoxy to 1 mole dioxy) over a wide range of concentrations and temperatures (from 0° to 100°C).

In 1965, Buchar,⁸ in a Czech patent, claimed that ZnCl_2 catalyzes the reaction of equimolar amounts of trioxane and acetic anhydride to yield trioxymethylene diacetate as the sole product if the temperature is kept below 35°C :



He obtained yields of 70–90%.

This paper extends the work on trioxane and shows how some additional oxocanes react with acetic anhydride in the presence of sulfuric acid and then in the presence of ZnCl_2 .

EXPERIMENTAL

Some of the work of Tomiska and Spousta⁸ was repeated. By reacting 0.22 mol trioxane (sample provided by Celanese Corporation of America) with 1 mole acetic anhydride plus 0.2 ml concentrated H_2SO_4 at 60°C to 70°C , an equimolar mixture of monoxy- and dioxymethylene diacetate was produced. Tomiska and Spousta obtained the same results.

However, when a similar reaction was run at 60°C and samples were withdrawn and injected into a gas chromatograph after 0, 0.25, 1.0, and 24 hr, it was found that trioxymethylene diacetate was present during the early stages of the reaction and gradually disappeared as the reaction proceeded.

All the chromatographic separations shown in Figure 1 were carried out on a 6-ft stainless steel column packed with silicone gum rubber SE 30 on Chromosorb-W. In each case, the column was kept at 75°C until the acetic anhydride had passed through. The column temperature was then raised as rapidly as possible to 165°C . In the 0-time chromatogram, the

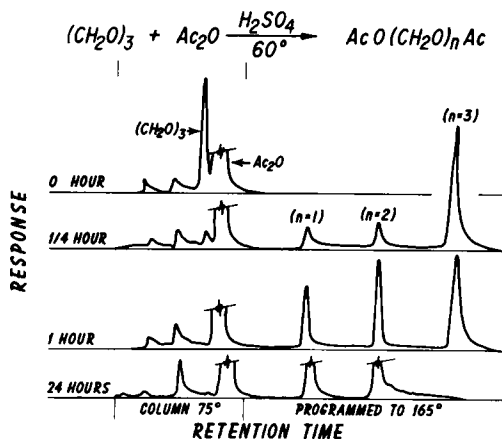


Fig. 1. Chromatograms of reaction mixture prepared from trioxane, acetic anhydride, and sulfuric acid at 60°C .

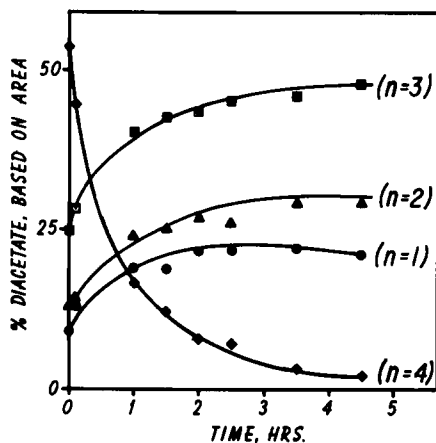
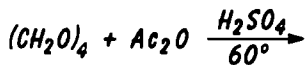
GLC ANALYSIS

Fig. 2. Percentages of monoxymethylene ($n = 1$), dioxymethylene ($n = 2$), trioxymethylene ($n = 3$), and tetraoxymethylene ($n = 4$) diacetates present after selected time intervals in the reaction of tetraoxocane with acetic anhydride in the presence of sulfuric acid at 60°C .

trioxane peak appeared just before the acetic anhydride peak with the column at 75°C . No other peaks appeared at 165°C . After $1/4$ hr had passed, most of the trioxane had been converted to the trioxymethylene diacetate, with some dioxy and monoxy as impurities. After 1 hr, the trioxane was gone. Even though the trioxymethylene diacetate is the major product, there were considerable amounts of dioxy and monoxy compounds. After 24 hr, the product was essentially an equimolar mixture of the monoxy- and dioxymethylene diacetates.

Although the final product was the same as that obtained by Tomiska,⁷ the gas chromatograms showed that Tomiska was incorrect when he stated that the final mixture of monoxy- and dioxymethylene diacetates cannot result from further splitting of initially formed trioxymethylene diacetates.

Next, the reaction of acetic anhydride, two parts by weight, and tetraoxocane (supplied by Mitsui Toatsu Chemicals, Inc.), one part by weight, with a catalytic amount of sulfuric acid was studied at 60°C . Samples were withdrawn from time to time and injected into the gas chromatograph with the silicone gum rubber column held constant at 165°C . The area under each diacetate peak was divided by the area under all four diacetate peaks to obtain an estimate of the percentage of each diacetate.

It can be seen from the curves in Figure 2 that the amount of the tetraoxymethylene compound fell off rapidly and the quantity of the trioxymethylene compound built up rapidly. The percentage of monoxy- and the per-

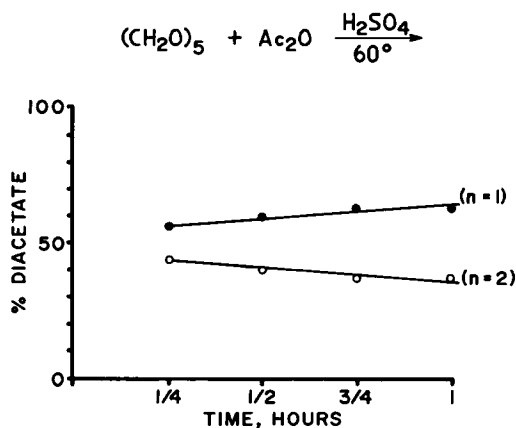


Fig. 3. Percentages of monoxymethylene ($n = 1$) and dioxymethylene ($n = 2$) diacetate present after selected intervals in the reaction of pentaoxocane with acetic anhydride in the presence of sulfuric acid at 60°C .

centage of dioxymethylene both climbed slowly. After $4\frac{1}{2}$ hr, the reaction more or less came to a standstill. This result suggested that the concentration of acetic anhydride was important; the higher the concentration of acetic anhydride, the more the reaction proceeded toward the mixture of the monoxy- and dioxymethylene diacetates. Perhaps the most surprising result here was the fact that a monoxymethylene diacetate was not produced each time a trioxymethylene diacetate was produced.

Pentaoxocane (supplied by Mitsui Toatsu Chemicals, Inc.) will not dissolve in acetic anhydride containing a catalytic amount of sulfuric acid. Apparently, the surface of the solid becomes coated with a covering of paraformaldehyde. To overcome this difficulty, some pentaoxocane was dissolved in acetic anhydride, and then additional acetic anhydride containing the catalyst was added. After being heated a short time at 60°C , the reaction product contained only monoxy- and dioxymethylene diacetate, as shown in Figure 3, and a white solid, which appeared to be paraformaldehyde. The strong odor of formaldehyde was apparent.

At 25°C , the changes occurring at the beginning of the reaction between pentaoxocane and acetic anhydride plus sulfuric acid were more easily followed. Pentaoxocane (66 mg) was dissolved in acetic anhydride ($47\ \mu\text{l}$). Acetic anhydride ($47\ \mu\text{l}$) containing sulfuric acid (94 ml Ac_2O -0.4 ml H_2SO_4) was then added. After 1 hr, pure acetic anhydride ($94\ \mu\text{l}$) was added to the reaction mixture (a white viscous mass). A sample was then withdrawn and injected into the gas chromatograph. As seen in Figure 4, a large part of the pentaoxocane was converted to the pentaoxymethylene diacetate. All of the low molecular weight diacetates were also present in the reaction mixture.

When Buchar's experiment⁸ was repeated using 0.025 mole ZnCl_2 as the catalyst for the reaction between 1 mole trioxane and 1 mole acetic anhydride at 35°C (or less), the yield of trioxymethylene diacetate was indeed

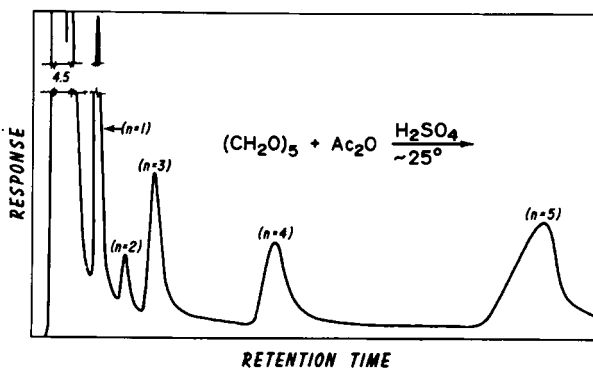


Fig. 4. Chromatogram showing that reaction between pentaoxocane and acetic anhydride can be made to yield pentaoxymethylene diacetate as major product.

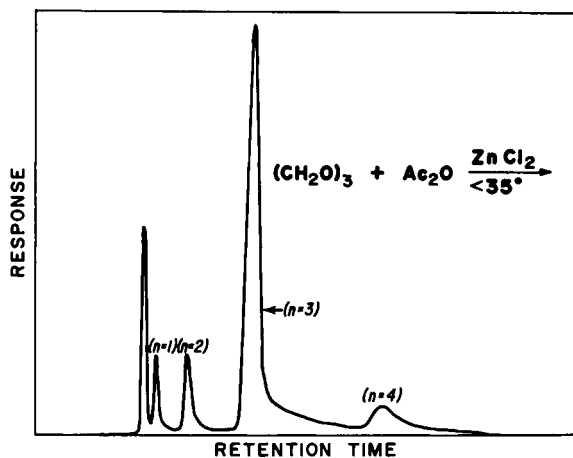


Fig. 5. Chromatogram showing that reaction between acetic anhydride and trioxane at room temperature with zinc chloride as catalyst yields trioxymethylene diacetate ($n = 3$) as major, but not the sole, poly(oxymethylene diacetate).

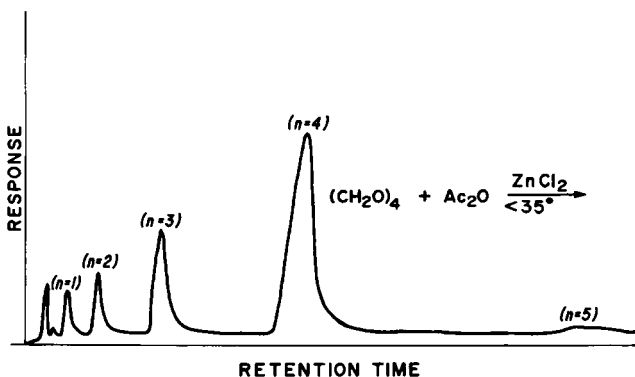


Fig. 6. Chromatogram showing that reaction between acetic anhydride and tetraoxocane at room temperature with zinc chloride as catalyst yields tetraoxymethylene diacetate ($n = 4$) as the major, but not the sole, poly(oxymethylene diacetate).

about 80% as claimed by Buchar. However, the gas chromatogram of the product washed with aqueous NaHCO_3 , extracted into ether and concentrated, showed the presence of some monoxy- and some dioxymethylene diacetate as impurities, as shown in Figure 5. It also unexpectedly showed the presence of some tetraoxymethylene diacetate. In any case, the procedure using ZnCl_2 is an excellent method for the preparation of trioxymethylene diacetate.

Buchar's method was applied to tetraoxocane for the preparation of tetraoxymethylene diacetate. Again, 1 mole tetraoxocane, 1 mole acetic anhydride, and 0.025 mole ZnCl_2 were mixed, and the temperature was kept below 35°C . After $3\frac{1}{2}$ hr, the reaction was stopped by the addition of aqueous NaHCO_3 . The organic layer was extracted into ether. After evaporation of the ether, the yield of crude tetraoxymethylene diacetate

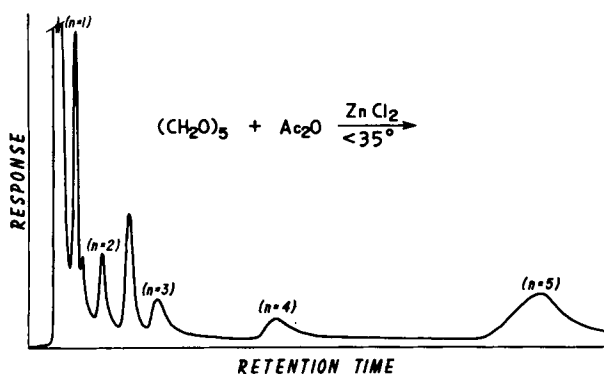


Fig. 7. Chromatogram showing that the reaction between acetic anhydride and pentaoxocane at room temperature with zinc chloride as the catalyst yields pentaoxymethylene diacetate ($n = 5$) as the major, but not the sole, poly(oxyethylene diacetate).

was 48%. The gas chromatogram of the product (Fig. 6) showed a significant amount of $\text{CH}_3\text{CO}(\text{CH}_2\text{O})_3\text{CCH}_3$, some $\text{CH}_3\text{COCH}_2\text{OCCH}_3$, $\text{CH}_3\text{CO}(\text{CH}_2\text{O})_2\text{CCH}_3$ and, rather remarkably, some $\text{CH}_3\text{CO}(\text{CH}_2\text{O})_5\text{CCH}_3$.

When Buchar's method was applied to pentaoxocane in acetic anhydride at the same mole ratios, but on a much smaller scale, the addition of the ZnCl_2 while stirring caused the formation of a precipitate almost at once. The reaction was allowed to continue for $3\frac{1}{2}$ hr, and then it was worked up in the usual way with aqueous NaHCO_3 and ether. The yield was 4.4%. A gas chromatogram of the final product (Fig. 7) showed the presence of all five of the possible diacetates in the mixture, with pentaoxymethylene diacetate as the major product.

CONCLUSIONS

Several precautions should be observed in converting an oxocane to a poly(oxymethylene diacetate) with minimum loss of formaldehyde from the chain:

1. Keep the amount of acetic anhydride to a minimum (not over 1 mole acetic anhydride per mole oxocane).
2. Use a mild acidic catalyst.
3. Avoid heating the reaction mixture.

Mention of a company or a product does not imply endorsement by the U.S. Department of Agriculture to the exclusion of others which may be equally suitable.

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