Mechanism of the Esterification Catalysis by Graphite Hydrogen Sulfate

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Graphite Hydrogen Sulfate

Reduction\(^{1}\), oxidation\(^{2}\) and catalysis\(^{3}\) by lamellar graphite intercalation compounds have received considerable attention within the last few years. One reason for this is that graphite intercalation compounds of highly reactive reagents (e.g., AlCl\(_3\) and SbCl\(_5\)-graphite which are commercially available\(^4\)) may be handled easier than the free reagents. Moreover, the reaction with an intercalated substance may yield products different from those of the reaction with the corresponding free substance. This change in reactivity may be related to steric effects\(^1\) or to different chemical behaviour of intercalated molecules\(^2\).

Graphite hydrogen sulfate (GHS), with the "idealized" composition \(\text{C}_{24}\text{H}_2\text{S}_4\cdot 2\text{H}_2\text{SO}_4\)\(^\) was proposed as catalyst superior to sulfuric acid for the esterification of carboxylic acids with alcohols in cyclohexane. The reaction was supposed to occur at the solid phase via a reactive species formed from the carboxylic acid with GHS\(^5\).

The results presented in this paper indicate a catalysis by sulfuric acid released only after disintegration of GHS.

As GHS is a hygroscopic compound and tends to self-decomposition, we tried to replace it by anodically formed lamellar "graphite oxide" (empirical formula \(\text{C}_{4.6}\cdot 0.75\text{H}_2\text{O}\)\(^\) which can be stored being even stable to atmosphere. This "graphite oxide" absorbs large amounts of sulfuric acid and an \textit{in situ} formation of GHS via the equilibrium

\[
\text{C}_n\text{OH} + \text{H}_2\text{SO}_4 \rightarrow \text{C}_n\text{HSO}_4 + \text{H}_2\text{O}
\]  

\(1\)

can be expected\(^7\).

Comparative experiments on the acetylation of cyclohexanol were performed at 30 °C with I) GHS, II) sulfuric acid absorbed in "graphite oxide" and III) pure sulfuric acid, using the conditions given by BERTIN, KAGAN, LUCHE and SETTON\(^8\) (8.5 mmol acetic acid, 8.5 mmol cyclohexanol, 15 ml dried cyclohexane, stirred solution). The concentrations of cyclohexanol and cyclohexyl acetate were followed by GLC (silicone oil, 140 °C), those of acetic acid and sulfuric acid by potentiometric titrations. Graphite compounds were characterized by X-ray powder diagrams. GHS (\(\text{C}_{24}\) stage) was prepared by anodic oxidation of graphite foil and natural graphite, and the total of intercalated and adherent sulfuric acid was weighed.

Fig. 1 shows typical values of the time dependence of the cyclohexanol and cyclohexyl acetate concentration in presence of sulfuric acid and GHS, respectively. Common attribute is the fast decrease of the cyclohexanol concentration which exceeds the rate of acetylation and gives evidence for cyclohexyl sulfate formation. The start of cyclohexanol esterification is delayed if GHS is used instead of sulfuric acid; this delay decreases with decreasing particle size. With sulfuric acid absorbed in "graphite oxide" the progress of esterification is even more retarded. This fits in the model of an esterification rate depending only on the availability of free sulfuric acid.

**Fig. 1.** Esterification of 8.5 mmol cyclohexanol with 8.5 mmol acetic acid in 15 ml cyclohexane at 30 °C. Catalyst a) 3 mmol \(\text{H}_2\text{SO}_4\), b) graphite hydrogen sulfate containing 3 mmol \(\text{H}_2\text{SO}_4\).

The final concentration of cyclohexyl acetate was determined after the reaction mixture was allowed to stand for three weeks at room temperature. Values of approx. 90% of theory were obtained without significant influence of the type of catalyst used.

Since GHS removes acetic acid from cyclohexane solution and shows different colour and EPR signal after this reaction, an activated species of acetic acid being tightly bound to the solid support was assumed to exist\(^9\). As pure sulfuric acid also removes acetic acid from cyclohexane solution, this acetic acid species is likely to be acetic anhydride which is insoluble in cyclohexane. The observed changes of GHS must not be attributed to the existence of a
solid acetic acid compound. They are rather to be expected because of a hydrolysis of GHS (Eq. (1)) by the water released during the acetic anhydride formation. X-ray powder diagrams of GHS after a 15 h contact with cyclohexanol or equimolar cyclohexanol plus acetic acid in cyclohexane, respectively, revealed the formation of graphite, i.e. the release of sulfuric acid. As GHS is a strong oxidant its reduction is not unexpected and obviously consumes alcohol as it was not observed if only acetic acid was present.

Moreover, a self-decomposition of GHS yielding graphite and oxygen was reported to be initiated even by small amounts of water. Thus, a dehydrating influence of hydrophilic "graphite oxides" which was supposed to shift the esterification equilibrium to completion seems not to be effective in the final stage of the reaction. The only additional water consuming reaction of GHS as compared to sulfuric acid is its hydrolysis corresponding to Eq. (1).

GHS in contact with reducing agents and water represents a very complex system, and indeed there are some interesting aspects with regard to the stereochemistry and electronic theory of catalytic reactions. On the other hand, large surface area graphite compounds continuously releasing their "encapsulated" catalyst may offer some synthetic advantage.

However, there is no conclusive experimental proof for any specific influence of GHS on esterification of carboxylic acids compared with that of sulfuric acid alone.

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4 "Graphimets", Alfa Chemicals.