

Heterogeneous Catalysis of Nucleophilic Substitution

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The opening of an epoxide ring by attack of a nucleophile can be catalysed by the heterogeneous catalyst, crystalline polymeric zirconium phosphate.

Reactions taking place on surfaces usually proceed either by rearrangement of a substrate adsorbed on the surface, or by reaction on the surface of two adsorbed molecules. The reaction of cyclohexene oxide with nucleophiles, catalysed by crystalline polymeric zirconium phosphate¹ does not fit into either of these classes.

We have found that cyclohexene oxide is unaffected by crystalline polymeric zirconium phosphate in solvents such as toluene, 1,4-dioxane, cyclohexane or dichloromethane even on refluxing, though the neat epoxide reacts with the polymer on refluxing.² In nucleophilic solvents such as methanol and acetic acid, reaction of the epoxide is complete within two days at room temperature. The products of reaction are typical products of bimolecular nucleophilic attack on this epoxide.³ Thus methanol yields *trans*-2-methoxycyclohexanol as the sole product, and acetic acid yields only *trans*-2-acetoxycyclohexanol. Reaction of 1-methylcyclohexene oxide with polymeric zirconium phosphate in methanol yields only 1-methyl-1-methoxycyclohexan-2-ol. Clearly, the reaction is under similar stereochemical control to the proton catalysed reaction.

On adding 5% of a nucleophile, water, to 1,4-dioxane, reaction took place at room temp. over a period of two days, yielding *trans*-cyclohexane-1,2-diol.

Evidence that the reaction is catalysed by surface protons rather than by the surface itself was obtained by exchanging the catalyst surface protons for caesium ions. This destroyed the catalyst activity.

Two possible reaction mechanisms may be put forward on the basis of these results. The reaction could take place entirely on the surface, or protonation could take place on the surface, followed by separation of the protonated substrate, which then undergoes reaction. However, if the substrate could be protonated and then separated from the catalyst, this process would take place even more readily with the more basic solvent, methanol, and an equilibrium would be set up between MeOH and MeOH₂⁺. Protonation of the substrate would occur *via* MeOH₂⁺ as well as *via* the catalyst, with the former route dominating, so that the catalyst would act in exactly the same way as a soluble acid, that is, as a proton source. The proton and polymer catalysed reactions would then be identical.

The reactions are similar in terms of products, but reaction rates differ widely. Using a single batch of crystalline zirconium phosphate polymer as catalyst, variation of reaction rate with catalyst sample was found to be small, as has been reported earlier;⁴ a typical reaction of polymer (0.2 g) with cyclohexene oxide (0.5 g) in methanol (25 ml) had a half life of around 20 minutes at 25 °C. Under similar conditions, using polymer from the same recrystallisation, 1-methylcyclohexene oxide reacted more *slowly* by a factor of 150, while α -pinene oxide did not react. In contrast, the relative rates of reaction with toluene-*p*-sulfonic acid catalyst⁵ in aqueous 80% ethanol are cyclohexene oxide, 1; methyl cyclohexene oxide, 300; and α -pinene oxide, 820. These results do not fit the second mechanism; they require a mechanism in which steric hindrance is important in the rate-determining step. Since protonation in solution is fast and reversible,⁶ this clearly favours reaction taking place entirely on the surface.

While the main effect on the rate of the polymer-catalysed reaction is steric, we cannot entirely exclude an electronic effect. The more highly substituted epoxides, on reaction under acid conditions, usually react *via* a carbocation.³ Formation of a carbocation under our conditions would not be favoured, since the developing carbocation would be destabilised by the proximity of the acidic surface.

We envisage the reaction as consisting of a rapid reversible adsorption of epoxide onto the polymer surface, with the oxygen atom bonding to protons on the surface of the polymer. This is followed by attack of a nucleophile on the epoxide carbon atom, breaking a C–O bond, and yielding products with the observed *trans*-stereochemistry.

Although the stereochemistry of the reaction is similar to that of the proton catalysed reaction, the steric effects cause large changes in the rate of reaction relative to the rates of reaction with soluble acids, thus providing a useful means of controlling the selectivity of reactions of epoxides.

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