Catalytic Conversion using a Sheet Silicate: Hydrogen Exchange between Hydrocarbons on a Synthetic Hectorite

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Summary 1,1-Diphenylethylene and 9,10-dihydroanthracene react smoothly over a synthetic hectorite catalyst to give anthracene and diphenylethane.

THE catalytic activity of sheet silicates has been abundantly demonstrated most particularly in relation to acid-catalysed processes.[1,2] However examples of other types of catalytic action have been observed in the formation of aniline from diaminostilbene[3] and in the formation of both benzophenone and diphenylethane from diphenylethylene.[4] Most conversions studied to date have involved interaction of a single substrate molecule with acid sites on the clay or with the hydration shell water surrounding the interlamellar cation, and it was of interest to explore the possibility that the reaction between two different substrate molecules could be catalysed by a sheet silicate. Such reactions could be highly selective since one member of a potential reactant pair might displace the other from the interlamellar space. Successful catalysis of esterification reactions by montmorillonite catalysts[2] demonstrates that mixed molecule catalysis is possible. The occurrence of hydrogen exchange between two molecules of 1,1-diphenylethylene over a fluorohectorite catalyst has already been reported[4] and hence 9,10-dihydroanthracene was treated with 1,1-diphenylethylene in refluxing octane over the same catalyst under nitrogen. A smooth conversion into anthracene and diphenylethane was observed (the reaction was 50% complete in 1·5 h), the progress of the reaction was monitored by n.m.r. spectroscopy and no side reactions could be detected. A slower conversion was achieved in refluxing hexane. The catalyst was prepared by the method of Barrer[5] and exchanged with ferric solutions to give ferric ion as the interlamellar cation (exchange capacity 22 mol equiv. per 100 g). It was demonstrated in separate experiments that both substrates entered the inter-lamellar space (to give nearly the same *d*-spacings) and thus, though there is no direct demonstration that the reaction is truly interlamellar it is highly probable that this is so. The selective nature of the process is borne out by the fact that 9,10-dihydroanthracene does not reduce *cis*- or *trans*-stilbene, diphenylacetylene, anethole, or iso-homogenol (the last two compounds are derivatives of propenylbenzene) under comparable conditions. Hydrogen exchange reactions on an alumina surface, with alcohols as hydrogen donor, have been observed,[6] but this is the first example of hydrogen exchange between hydrocarbons other than at a catalytic metal surface. The use of alcohols as hydrogen donors with sheet silicate catalysts is of course precluded since they are rapidly dehydrated by them.

We thank the S.R.C. for an Advanced Course Studentship (to S. E. D.).

(*Received*, 14*th March* 1979; *Com.* 257.)

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