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REARRANGEMENT OF 1,3-BROMOCHLOROPROPANE ON ACTIVATED ALUMINA

Kiyonori SHINODA and Kensei YASUDA
Toyama Technical College, Hongo, Toyama 930-11

The rearrangement of 1,3-bromochloropropane (BCP) on activated alumina was carried out at 160 - 280°C. This reaction proceeded as follows. $Br(CH_2)_3Cl \rightleftharpoons Br(CH_2)_3Br + Cl(CH_2)_3Cl$ It was suggested that the acidic sites of alumina played an important role in the rearrangement of halogen atom.

The transformation and isomerization of chlorobenzenes have been extensively studied by Erykalov and his co-workers.$^{1-5)}$ It has been reported that BCP was disproportionated into 1,3-dibromopropane (DBP) and 1,3-dichloropropane (DCP) in such an aprotic solvent as DMF.$^{6)}$ However, there has been no report on the catalytic transformation of aliphatic halides on solid acids or bases. In the present study, it was found that BCP was transformed on activated alumina into DBP and DCP, and a possible reaction mechanism was postulated. The reaction was carried out with a flow type reaction system as described elsewhere.$^{7)}$ Activated alumina as catalyst (KHD-24) was supplied by the Sumitomo Chemical Co. and the particle diameter was in a range of 2 to 4 mm. 20 g of catalyst was placed in the middle of the reactor and the reaction temperature was measured with a thermocouple in a thermowell placed in the catalyst bed. The reaction temperature was varied, the time factor being kept constant at 394.5 (g of catalyst/g-mol of BCP/h). The analysis of reaction products was performed by means of gas-chromatography (Shimadzu GC-5A, PEG 6000). The product distributions in the catalytic reactions at various temperatures are shown in Table 1. The conversion of BCP increased with increasing temperature, but the temperature effect was not large. Allyl bromide (AB) and allyl chloride (AC) are formed by the ordinary pyrolysis of BCP. 1,2-Dibromopropane and 1,2-dichloropropane might be formed by hydrohalogenation of allyl halides on activated alumina, according to the Markownikoff rule. However, the amounts of these compounds in the products were very small and hence the hydrohalogenation does not seem to be the main reaction. On the other hand,

Table 1. The effect of the reaction temperature on the product distribution

Reaction temperature	Product composition (mol %)						
(^{o}C)	AC	AB	$CH_2ClCHClCH_3$	DCP	$CH_2BrCHBrCH_3$	BCP	DBP
160	0.03	0.39	0.10	14.98	0.10	78.23	6.17
190	0.17	0.35	0.08	20.53	-	65.51	13.36
220	0.30	0.85	0.09	24.45	0.09	51.83	22.39
250	0.44	0.96	0.11	22.89	0.07	50.33	25.20
280	1.48	1.23	0.24	20.21	0.11	49.64	27.09

DBP and DCP were formed in large amounts on activated alumina. When a mixture of DBP and DCP was passed over activated alumina, BCP was formed to a considerable extent. It was observed that DCP and AB were formed from a mixture of BCP and AC, and DBP and AC were formed from a mixture of BCP and AB under the same reaction conditions. In addition, the presence of 1,1,2,2-tetrachloroethane had no effect on the rearrangement of BCP on activated alumina. Therefore, it is possible to exclude the possibility that the dehydrohalogenation of BCP followed by the hydrohalogenation yields DBP and DCP. As the halogen of BCP on activated alumina showed the same behaviors as one of allyl halide, it is supposed that the acidic sites of activated alumina play an important role in the rearrangement of halogen atom. BCP may be dissociated into a carbonium ion and a halogen anion on the acidic sites of alumina. It seems reasonable that the halogen anion attacks the carbonium ion according to S_N1 reaction mechanism.

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