Tetrahedron Letters No. 28, pp. 2663-2666, 1971. Pergamon Press. Printed in Great Britain.

MECHANISM OF CLEAVAGE OF AROMATIC ETHERS BY HALOGEN ACIDS IN NON-AQUEOUS MEDIA - IN PRESENCE OF INORGANIC CATALYSTS.

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(Received in UK 3 June 1971; accepted in UK for publication 15 June 1971)

Anisole solutions in benzene, n-hexane and carbon tetrachloride (0.1 M) was made to react with dry hydrogen chloride in presence of alumina-silica catalyst (activated by heating to 600°C.) containing 13% alumina. The reaction was carried out at two temperatures i.e. 140°C and 200°C. The mixture was kept at the above temperatures for a period of seven hours in sealed tubes. The final product was analysed by chemical methods and the results were confirmed by studying the IR spectra. The typical results obtained are given in table I.

TABLE I.

Concentration of HCl 0.5 M, Concentration of anisole 0.1 M.

Temperature of reaction	Solvent	% Phenol formed	% o- & p-Cresol formed
140°C	C_6H_6	18	30
200°C	C_6H_6	19	30
140°C	n-Hexane	19	29
200°C	n-Hexane	20	29
140°C	CCl_4	18	41
200°C	CCl_4	30	44

It is clear from the above results that in presence of a catalyst like alumina-silica, HCl can bring about cleavage of anisole. It has been pointed out earlier[1] that HCl by itself cannot bring about cleavage in non-polar solvents. From this it is clear that the cleavage is brought about by the adsorbed HCl and not the HCl molecules in the solution.

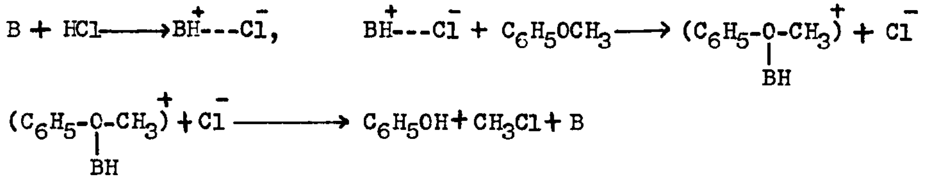
Alumina-silica is a catalyst with dual sites i.e. acid sites as well as basic sites[2]. Since the catalyst is having acid sites, it was thought that this acidity may be responsible in bringing about the cleavage of anisole. Reactions were tried in sealed tubes with anisole solutions in benzene, n-hexane and carbon tetrachloride in presence of the catalyst alumina-silica and without HCl. The results obtained are given in table II.

TABLE II.

Concentration of HCl - nil, Concentration of anisole 0.1 M.

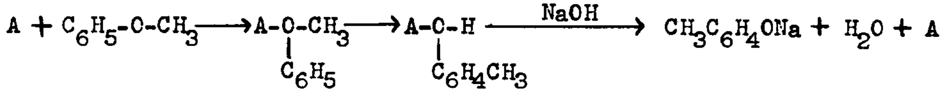
Temperature of reaction	Solvent	% Phenol formed	% o- & p-Cresol formed
140°C	C_6H_6	nil	30
200°C	C_6H_6	nil	29
140°C	n-Hexane	nil	30
200°C	n-Hexane	nil	30
140°C	CCl_4	nil	41
200°C	CCl_4	nil	43

A reference to results in table II shows that only re-arrangement takes place to form o- and p-cresols. Cleavage of anisole to form phenol does not take place. A reference to results in table I and II shows that the amount of cresols formed in both the cases is nearly the same. This clearly proves that the catalyst is responsible for the re-arrangement and the product formed is a mixture of o- and p-cresols. The cleavage is brought about by the HCl adsorbed on the catalyst surface. Taking advantage of the existance of the dual sites (acid sites and basic sites) present on the surface of alumina-silica the following mechanism has been proposed for (1) the cleavage and (2) the re-arrangement in case of anisole in particular and aromatic ethers in general. (In the following reactions B stands for the basic sites on the catalyst surface and A stands for the acid sites on the catalyst surface.)

1.


$$B + HCl \longrightarrow B\overset{+}{H}---\overset{-}{Cl}, \qquad B\overset{+}{H}---\overset{-}{Cl} + C_6H_5OCH_3 \longrightarrow (C_6H_5-\underset{\overset{|}{BH}}{O}-CH_3)^{+} + Cl^{-}$$

$$(C_6H_5-\underset{\overset{|}{BH}}{O}-CH_3)^{+} + Cl^{-} \longrightarrow C_6H_5OH + CH_3Cl + B$$

2.


$$A + C_6H_5-O-CH_3 \longrightarrow A-\underset{\overset{|}{C_6H_5}}{O}-CH_3 \longrightarrow A-\underset{\overset{|}{C_6H_4CH_3}}{O}-H \xrightarrow{NaOH} CH_3C_6H_4ONa + H_2O + A$$

1. The HCl adsorbed on the basic sites behaves just like ionised HCl. The catalytic surface functions in a way similar to that of pyridine in the cleavage of anisole in non-polar **solvents** in presence of HCl[1]. This adsorbed HCl attacks the anisole in the solution and brings about cleavage.

2. The anisole is adsorbed on the acidic sites. Re-arrangement takes place in these adsorbed anisole molecules giving the products o- and p-cresols. The acidic sites on the catalyst surface bring about re-arrangement in a way similar to the re-arrangement brought about by $AlCl_3$[3]. The acidic sites on alumina-silica are much weaker than those of $AlCl_3$.

In case of the cleavage reactions shown in the 1st mechanism the phenol and methyl chloride formed are present in the solution. In case of the re-arrangement reactions shown in the 2nd mechanism the cresol remains adsorbed to the catalyst surface and is extracted only when the catalyst is warmed with NaOH solution. To prove this the supernatant liquid in the 1st case was analysed for the presence of phenol and the cresols. It was found that this liquid contained only phenol and the amount of phenol present was 20 per cent, a figure that agrees with the figures for phenol formation in table I. Similarly the amount of phenol and cresol adsorbed on the catalyst surface were also analysed in this case. It was found that only cresols were present in the adsorbed condition and the amount of cresols present was 30 per cent, a figure that agrees with the figures for cresol formation in tables I and II. These results support the mechanism proposed for the cleavage reaction and for the re-arrangement reaction.

Since the amount of cresols formed in both the cases (results in tables I and II) is the same, it appears that the acid sites which are mostly Lewis type acid sites are completely utilised for bringing about re-arrangement to form cresols. The phenol formed at 140°C and 200°C is the same (table I) except in case of CCl_4. This shows that the basic sites are completely utilised for the adsorption of HCl and hence for the cleavage of anisole.

Reactions were carried out without HCl and in presence of the catalyst. The amount of the phenol or cresol present in the supernatant solution and that in the adsorbed condition were estimated. It was found that there was no phenol formed either in the solution or on the surface of the catalyst. But cresol was formed and it was present only in the adsorbed condition and it was 30 per cent. This result agrees with the results for the cresol formation in both the cases. This observation supports our mechanism.

Attempts were made to calculate the basicity and the acidity of alumina-silica from the cleavage and the re-arrangement results obtained in our experiments. The results obtained by us and those available from literature[2] are given in table III.

TABLE III.

Acidity results from-		Basicity results from-	
Literature.	Present work.	Literature.	Present work.
0.72 mili moles/g	0.75 mili moles/g	0.58 mili moles/g	0.50 mili moles/g

The agreement between our results and those from literature supports the mechanism proposed by us i.e. basic sites (in presence of HCl) are responsible for the cleavage of anisole and the acid sites are responsible for the re-arrangement of anisole. CCl_4 since it reacts with alumina, gives higher results[4]. Similar results were obtained for anisole and phenetole with alumina, chromia and silica.

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