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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 20(3), 212-218
Issue Date	1972-12
Doc URL	https://hdl.handle.net/2115/24944
Type	departmental bulletin paper
File Information	20(3)_P212-218.pdf



CLEAVAGE OF PHENETOLE BY HYDROGEN CHLORIDE IN NONAQUEOUS MEDIA IN PRESENCE OF MIXED OXIDE CATALYSTS

By

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(Received August 29, 1972)

Abstract

Cleavage of phenetole has been studied in presence of HCl and the mixed-oxide catalysts and the catalyst alone without HCl. Cleavage takes place in case of $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{Al}_2\text{O}_3\text{-MoO}_3$, $\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{SiO}_2\text{-ZrO}_2$ and $\text{SiO}_2\text{-TiO}_2$ catalysts in the presence of HCl in non-aqueous media. In addition to cleavage, rearrangement also takes place in all the above cases giving *o*-, *p*-ethylphenols along with phenol in the reaction mixture. This has been confirmed by IR studies, gas chromatography and chemical analysis of the reaction product. Since the above mixed-oxide catalysts have dual sites (acidic and basic sites) on the surface, reactions were also carried out with phenetole solutions in benzene and n-hexane in the presence of these catalysts without HCl. It was observed that only rearrangement took place giving only *o*-, *p*-ethylphenols and no phenol was formed in all cases. This clearly proves that the catalyst is responsible for rearrangement. The cleavage is brought about by the HCl adsorbed on the catalyst surface. Taking advantage of the existence of the dual sites (acidic and basic sites) present on the surface of catalysts, a mechanism for the reaction has been proposed.

The agreement between the acidity and basicity values calculated from our cleavage results and those from measured values supports the mechanism proposed by us, *i. e.*, basic sites (in the presence of HCl) are responsible for the cleavage of phenetole and acid centres are responsible for re-arrangement of phenetole and this holds good in general for aromatic ethers.

Introduction

We have previously proposed¹⁾ the mechanism of cleavage of anisole by hydrogen chloride in nonaqueous media in presence of silica-alumina catalyst. Taking advantage of the existence of dual sites (acidic and basic sites) present on the surface of the catalyst, the mechanism for the reaction has been proposed. The present work has been extended to investigate the effects of other mixed oxide catalysts in the study of cleavage of phenetole and to

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support the validity of the mechanism proposed earlier.

Experimental

Catalysts and Reagents

The binary oxides were prepared from A. R. quality chemicals by the precipitation and coprecipitation technique²⁾. The mixtures of the precipitated hydroxides were digested for several hours and then filtered, washed and dried at 110°C for 20 hours. The samples thus obtained were powdered and only such samples collected between 100 and 150 mesh sieves were used. The powders were subjected to heat treatment to the required temperature for 6 hours in an electrical muffle furnace with temperature control arrangement. The samples after heat treatment were cooled in a desiccator and preserved in glass tubes, under vacuum.

Phenetole and the solvents were of analar quality and were further purified by careful distillation. Hydrogen chloride gas was prepared by the action of concentrated H₂SO₄ on pure ammonium chloride. The gas was dried by passing through concentrated H₂SO₄.

Measurement of surface acidity and basicity

The quantitative measurement of the acidity has been made by using the amine titration method³⁾ using neutral red (pK_a = +6.8) as indicator. The surface basicity was measured by the trichloroacetic acid adsorption method⁴⁾. For this purpose 0.5 g of the catalyst was suspended in 50 ml solution of 0.025M trichloroacetic acid in dry benzene for two hours. During this period the mixture was kept stirred. After this the mixture was kept aside for 24 hours. The suspension was filtered off and 5 ml of the solution was titrated against 0.02M n-butylamine solution in dry benzene using bromthymol blue as indicator. The basicity of the mixed oxide surface was calculated from the decrease in trichloroacetic acid concentration in benzene.

Procedure and analysis

Phenetole solution in benzene and n-hexane (0.1M) was made to react with dry hydrogen chloride in presence of mixed oxide catalysts. The reaction was carried out at 160°C, for a period of seven hours in sealed tubes. The technique adopted was essentially the same as described by earlier workers^{6,8)}. The final products were analysed by chemical methods⁵⁾ and the results were confirmed by infrared (using Perkin-Elmer spectrometer) and also by gas chromatographic analysis.

Results and discussion

The results obtained for the cleavage of phenetole by HCl in non-aqueous media in presence of mixed oxide catalysts are presented in Table 1. It is clear from these results that in presence of mixed oxides, HCl can bring about cleavage of phenetole. It has been pointed out earlier⁶⁾ that HCl by itself cannot bring about cleavage in nonpolar solvents. From this it is clear that the cleavage is brought about by the adsorbed HCl and not the HCl molecule. Since the mixed oxides are having acid sites⁷⁾, it was thought that this acidity may be responsible in bringing about the cleavage of phenetole. Reactions were tried in sealed tubes with phenetole solutions in nonpolar solvents in presence of mixed oxides without HCl. The results obtained are given in Table 2.

A reference to the results in Table 1 clearly shows that both phenol and *o*-, *p*-ethylphenols are formed in case of all mixed oxide catalysts. From the results in Table 2 for all these mixed oxides, it is seen that only *o*-, *p*-ethylphenols are formed and no phenol is formed. These results are confirmed by the IR spectra of the products. From these two observations it is clear that HCl in presence of mixed oxide catalysts can bring about

TABLE 1 Cleavage of phenetole by HCl in non aqueous solvent in presence of mixed oxide catalysts

Ether-phenetole (0.1M) Reagent-HCl (0.5M) Temperature of reaction 160°C						Catalyst-1g
Sl. No.	Catalyst	Temperature of heat treatment of catalyst °C	Solvent	% of phenol	% of <i>o</i> -, <i>p</i> -ethyl phenols	
1	Al ₂ O ₃ -ZrO ₂ (80%-20%)	500	Benzene	28	24	
	Al ₂ O ₃ -ZrO ₂ (80%-20%)	500	n-Hexane	30	24	
2	Al ₂ O ₃ -MoO ₃ (74%-26%)	450	Benzene	13	30	
	Al ₂ O ₃ -MoO ₃ (74%-26%)	450	n-Hexane	11	30	
3	SiO ₂ -TiO ₂ (87%-13%)	550	Benzene	18	21	
	SiO ₂ -TiO ₂ (87%-13%)	550	n-Hexane	19	21	
4	Al ₂ O ₂ -SiO ₃ (13%-87%)	600	Benzene	20	30	
	Al ₂ O ₃ -SiO ₂ (13%-87%)	600	n-Hexane	19	33	
5	SiO ₂ -ZrO ₂ (89%-11%)	500	Benzene	23	27	
	SiO ₂ -ZrO ₂ (89%-11%)	500	n-Hexane	19	30	

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TABLE 2 Cleavage of phenetole in non aqueous media in presence of mixed-oxide catalysts alone without HCl.

Ether-phenetole (0.1 M)
 Reagent-Nil
 Temperature of reaction 160°C

Sl. No.	Catalyst	Solvent	% of phenol	% of <i>o</i> -, <i>p</i> -ethyl phenols
1	Al ₂ O ₃ -ZrO ₂	Benzene	—	18
	Al ₂ O ₃ -ZrO ₂	n-Hexane	—	24
2	Al ₂ O ₃ -MoO ₃	Benzene	—	30
	Al ₂ O ₃ -MoO ₃	n-Hexane	—	33
3	SiO ₂ -TiO ₂	Benzene	—	21
	SiO ₂ -TiO ₂	n-Hexane	—	24
4	Al ₂ O ₃ -SiO ₂	Benzene	—	33
	Al ₂ O ₃ -SiO ₂	n-Hexane	—	30
5	SiO ₂ -ZrO ₂	Benzene	—	27
	SiO ₂ -ZrO ₂	n-Hexane	—	24

cleavage of phenetole forming phenol. Similarly it is observed that the catalyst alone without HCl can bring about rearrangement forming *o*-, *p*-ethylphenols.

It has been observed by DEWAR and PUTTNAM⁸⁾ that strong acids like AlCl₃ and AlBr₃ bring about rearrangement in an aromatic ether molecule. It appears that the rearrangement brought about in our experiments to give *o*-, *p*-ethylphenols must be due to the acidic sites on the catalyst surfaces. Alumina-silica³⁾ and other mixed oxides⁷⁾ have strong and large quantity of acid sites on their surfaces. If these catalysts are used for rearrangement of phenetole, the rearrangement should be maximum in case of alumina-silica and less in case of other mixed oxides as the acidity decreases. This is confirmed by the results obtained for *o*-, *p*-ethylphenol formation in Tables 1 and 2. It is also observed that the values for the *o*-, *p*-ethylphenol formation in case of each catalyst as presented in Table 1 as well as Table 2 are the same. This confirms that acidic sites bring about rearrangement of phenetole to give *o*-, *p*-ethyl phenols.

It has been shown by WALVEKAR *et al.*⁶⁾ that addition of little quantity of an organic base like pyridine to the mixture of anisole and HCl brings about the cleavage of the ether. Similarly it can be concluded that addition of the catalyst to the phenetole and HCl brings about cleavage in the same

manner as in case of pyridine. The catalyst surface behaves very much similar to pyridine. Pyridine is a base and hence the catalyst's surface must have basic centres. It has been pointed out by TANABE *et al.*⁹⁾ that alumina-silica has basic centres on its surface and this value is 0.58 mmoles/g. Similarly it has been established by us⁴⁾ that the other mixed-oxide catalysts have basic sites on their surface.

In the light of the observations made above it is clear that $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{Al}_2\text{O}_3\text{-MoO}_3$, $\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{SiO}_2\text{-TiO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ catalysts which have basic centres on their surface should bring about cleavage of phenetole to form phenol in presence of HCl. From the results in Table 1, it is clear that these catalysts bring about cleavage of phenetole giving phenol as one of the products.

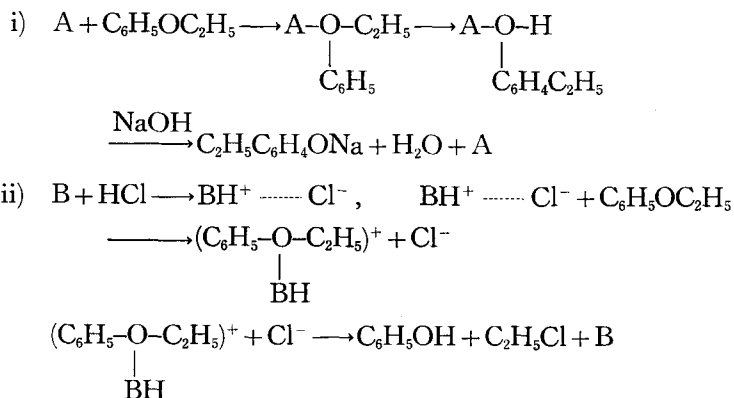
The cleavage is greater for alumina-zirconia, and is less for alumina-silica and still less in case of other mixed oxide catalysts as the basicity decreases. It appears that cleavage is directly proportional to the basicity of the catalyst surface and rearrangement is proportional to the acidity of the catalyst surface. The values of acidity and basicity calculated from the rearrangement and cleavage (Tables 1 and 2) agree very well with the actually measured values of acidity and basicity, which are presented in Table 3. This observation agrees with our earlier observation in case of cleavage of anisole by alumina-silica¹⁾.

On the basis of our conclusions that acidic centres on the catalyst surface bring about rearrangement and basic centres on the catalyst surface in presence of HCl bring about cleavage of ethers, a mechanism for rearrangement by acidic sites and cleavage by HCl in presence of basic sites as proposed earlier by the authors¹⁾ holds good in this case also and is given below.

TABLE 3 Acidity and basicity values calculated from the cleavage experiments and actually measured.

Catalyst	Acidity (m. moles/g)		Basicity (m. moles/g)	
	From our experiments	measured	From our experiments	measured
1. $\text{Al}_2\text{O}_3\text{-ZrO}_2$	0.60	0.58	0.72	0.68
2. $\text{Al}_2\text{O}_3\text{-MoO}_3$	0.80	0.76	0.30	0.30
3. $\text{SiO}_2\text{-TiO}_2$	0.56	0.55	0.45	0.45
4. $\text{Al}_2\text{O}_3\text{-SiO}_2$	0.80	0.75	0.50	0.58
5. $\text{SiO}_2\text{-ZrO}_2$	0.67	0.68	0.52	0.58

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i) The phenetole is adsorbed on the acidic sites. Rearrangement takes place in these adsorbed molecules giving the products *o*- and *p*-ethylphenols. The acidic sites on the catalyst surface brings about rearrangement in a way similar to the rearrangement brought about by AlCl_3 .⁸⁾

ii) The HCl adsorbed on the basic sites behaves just like ionised HCl. The catalyst surface functions in a way similar to that of pyridine in the cleavage of anisole in nonpolar solvents in presence of HCl.⁶⁾ The adsorbed HCl attacks the phenetole in the solution and brings about cleavage. It is indicated in the mechanism (i) above that *o*-, *p*-ethylphenols are formed after the phenetole is adsorbed on the surface and the adsorbed ethylphenols are extracted by heating the catalyst with NaOH. Similarly it is indicated in mechanism (ii) above that the adsorbed HCl attacks the phenetole in the solution and brings about the cleavage. In all the above experiments the *o*-, *p*-ethylphenols should be in the adsorbed condition and the phenol should be present in the solution. In every cleavage reaction the results for which have been presented in Tables 1 and 2, the supernatant liquid was examined by I. R. absorption spectra, gas chromatography method and by chemical analysis. It was found that the supernatant liquid contained only phenol and there was not a trace of *o*-, *p*-ethylphenols present in the supernatant liquid. This observation supports our earlier observation mentioned in mechanism (ii) above. The quantities of phenol formed were the same as given in Table 1 for each of the catalysts.

Similarly the *o*-, *p*-ethylphenols and phenol adsorbed on the catalyst surface were extracted with NaOH as indicated in mechanism (i) above and analysed with the help of I. R. spectra, gas chromatography and by chemical methods described earlier. The NaOH extract when acidified with HCl showed the presence of *o*- and *p*-ethylphenols and did not show the presence

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of phenol. This shows that only *o*-, *p*-ethylphenols are formed. The quantities of ethylphenols formed were the same as shown in Tables 1 and 2 for each of the catalysts.

Acknowledgements

The authors wish to express their thanks to Dr. M. SHADAKSHAR-ASWAMY and Prof. T. D. BHASKAR for their keen interest in the present work and to the Indian Institute of Science, Bangalore, for providing facilities in the study of infrared spectroscopy and analysis by gas chromatography.

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