

CLEAVAGE OF ANISOLE BY HYDROGEN CHLORIDE IN NON-AQUEOUS MEDIA IN PRESENCE OF INORGANIC CATALYSTS

By S. P. WALVEKAR* and A. B. HALGERI*

[Manuscript received 31 August 1972]

Abstract

Anisole is cleaved and rearranged with HCl and Al₂O₃ or Cr₂O₃ catalysts, but is rearranged without cleavage by HCl-SiO₂ or by catalysts alone. A mechanism is proposed.

The mechanism of cleavage of anisole by hydrogen chloride in non-aqueous media in presence of Al₂O₃-SiO₂ catalyst has already been reported by us elsewhere.¹ The object of the present work is to investigate the catalytic effect of some other inorganic catalysts (Al₂O₃, SiO₂, Cr₂O₃) on the cleavage of anisole in the presence or absence of HCl in non-aqueous media, and also to support the validity of the mechanism proposed earlier.¹

Experimental

Materials

Anisole and other solvents of Analar quality were further purified by distillation. Hydrogen chloride was prepared from conc. H₂SO₄ and pure ammonium chloride, and dried by passing through conc. H₂SO₄.

Alumina, silica, and chromia catalysts were prepared from AnalaR chemicals by standard procedures.^{2,3}

Measurement of Surface Acidity and Basicity

For the quantitative measurement of acidity the amine titration method developed by Benesi⁴ was used. The surface basicity was measured by the trichloroacetic acid adsorption method.⁵

Procedure and Analysis

Anisole solution in non-aqueous media was made to react with dry hydrogen chloride in presence of metal oxide catalysts. The reaction was carried out in sealed tubes at 140 or 200°C,

* Department of Chemistry, Central College, Bangalore University, Bangalore-560001, India.

¹ Walvekar, S. P., and Halgeri, A. B., *Tetrahedron Lett.*, 1971, **28**, 2663.

² Dzisko, V. A., Kolovertnova, M., and Kotsarenko, K., *Kinet. Katal.*, 1966, **7**, 508.

³ Selwood, P. W., and Lyon, L., *Discuss. Faraday Soc.*, 1950, **8**, 222.

⁴ Benesi, H. A., *J. phys. Chem.*, 1957, **61**, 970.

⁵ Walvekar, S. P., and Halgeri, A. B., *J. Res. Inst. Catalysis Hokkaido Univ.*, 1973, **20**, 212.

for 7 hr. The technique adopted was that described by earlier workers.^{6,7} The final products were analysed by chemical methods,⁸ and the results were confirmed by infrared spectroscopy and gas chromatographic analysis.

Results and Discussion

The results obtained for the cleavage of anisole by HCl in non-aqueous media in presence of Al₂O₃, Cr₂O₃, and SiO₂ and those obtained without HCl in presence of these oxide catalysts are presented in Table 1. It is observed from these values that the reaction is nearly complete at 140°C and raising the reaction temperature to 200°C does not appreciably alter the percentage of cleavage.

TABLE 1
CLEAVAGE OF ANISOLE BY HCl (0.5M) IN NON-AQUEOUS MEDIA IN PRESENCE OF THE CATALYST AND IN PRESENCE OF THE CATALYST ALONE WITHOUT HCl
Anisole 0.5M, catalyst 1 g

Catalyst	Solvent	Temp. (°C)	With HCl		Catalyst only	
			Phenol (%)	Cresols (%)	Phenol (%)	Cresols (%)
Alumina	C ₆ H ₆	140	15	21	—	21
		200	18	18	—	19
	n-C ₆ H ₁₄	140	17	21	—	21
		200	18	21	—	21
	CCl ₄	140	16	30	—	30
		200	22	42	—	42
Silica	C ₆ H ₆	140	—	21	—	21
		200	1	21	—	24
	n-C ₆ H ₁₄	140	—	21	—	21
		200	2	18	—	21
	CCl ₄	140	—	21	—	24
		200	1	21	—	21
Chromia	C ₆ H ₆	140	4	12	—	12
		200	5	12	—	15
	n-C ₆ H ₁₄	140	2	15	—	12
		200	5	12	—	12
	CCl ₄	140	3	15	—	12
		200	5	12	—	15

Examination of the results in Table 1 indicates that HCl in presence of Al₂O₃, Cr₂O₃ can bring about cleavage and rearrangement of anisole to form phenol and (*ortho* and *para*) cresols, but in the case of SiO₂ mostly cresols are formed, with little phenol. When reactions were carried out in presence of catalysts alone without HCl, only rearrangement took place to form cresols and no phenol was formed. The amounts of cresols formed with HCl and these catalysts and with catalysts alone are the same (see Table 1).

It appears that acidic sites on the catalyst surface bring about rearrangement in a way similar to the rearrangement brought about by AlCl₃.⁹ It is observed that

⁶ Walvekar, S. P., Phalnikar, N. L., and Bhide, B. V., *J. Indian chem. Soc.*, 1943, **20**, 131.

⁷ Drummond, A. Y., and Eastham, A. M., *J. Am. chem. Soc.*, 1957, **79**, 3689.

⁸ Tarbell, D. S., and Petropoulos, J. C., *J. Am. chem. Soc.*, 1952, **74**, 244.

⁹ Dewar, M. J. S., and Puttnam, N. A., *J. chem. Soc.*, 1959, 4080.

Al_2O_3 ,¹⁰ SiO_2 ,¹¹ and Cr_2O_3 ,¹² which have acidic sites on their surface, bring about rearrangement of anisole to form *o*- and *p*-cresols.

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.⁶ The adsorbed HCl attacks the anisole in solution and brings about cleavage. It is observed that Al_2O_3 ^{10,13} and Cr_2O_3 which have basic sites on their surface bring about cleavage of anisole to form phenol in presence of HCl. Cleavage of anisole does not take place in the case of SiO_2 as this catalyst has no basic sites on its surface.¹³

It appears that cleavage and rearrangement are directly proportional to the basicity and acidity of the catalyst surface. The values of acidity and basicity calculated from the rearrangement and cleavage results (Table 1) agree very well with the actually measured values of acidity and basicity which are presented in Table 2.

TABLE 2
ACIDITY AND BASICITY VALUES CALCULATED FROM CLEAVAGE EXPERIMENTS
AND MEASURED EXPERIMENTAL VALUES

Catalyst	Acidity (mmol/g)		Basicity (mmol/g)	
	Calc.	Exptl	Calc.	Exptl
Al_2O_3	0.58	0.55	0.41	0.48
Cr_2O_3	0.30	0.28	0.10	0.10
SiO_2	0.55	0.56	nil	nil

These results agree with the results of cleavage of anisole by Al_2O_3 - SiO_2 catalyst¹ and therefore the same mechanism¹ holds in the case of these catalysts also.

It is further observed from the results of the reactions conducted in CCl_4 that the percentage of *o*- and *p*-cresol formation is much higher in the presence of Al_2O_3 than in that of Cr_2O_3 and SiO_2 . This probably is because Al_2O_3 reacts with CCl_4 , converting some of the acidic sites into Al-Cl bonds^{14,15} which are more reactive and generally give higher results for the cresol formation.

Acknowledgments

The authors wish to express their thanks to Professors M. Shadaksharaswamy and T. D. Bhaskar for discussions, and to the Indian Institute of Science, Bangalore, for providing i.r. and g.l.c. facilities.

¹⁰ Jain, J. R., and Pillai, C. N., *J. Catal.*, 1967, 9, 322.

¹¹ Shibata, K., Kiyoura, T., and Hayashi, Y., *J. Res. Inst. Catalysis Hokkaido Univ.*, 1971, 19, 29.

¹² Voltz, S. E., Hirschler, A. E., and Smith, A. J., *J. phys. Chem.*, 1960, 64, 1594.

¹³ Tanaka, M., and Ogasarawa, I., *J. Catal.*, 1970, 16, 157.

¹⁴ Basset, J., Mathieu, M. V., and Prettre, M., *J. Chim. phys.*, 1969, 66, 1264.

¹⁵ Rideal, E. K., "Concepts in Catalysis," p. 154 (Academic Press: New York 1968).