REARRANGEMENT OF SUBSTITUTED AROMATIC ACETALS CATALYSED BY y-ALUMINA

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Abstract Aromatic acetals over γ -alumina undergo rearrangement to give the corresponding esters (b) and ethers (c) in good yield. The product distribution varied unusually over the range of reaction temperatures. The effect of substituents has also been felt much in the study. Probable mechanisms have been suggested for the reaction. The catalyst has been characterized by various studies and the specific poisoning of the catalyst has been done with NH₃, CO₂ and H₂S.

Literature survey reveals very few references to reactions of aromatic acetals in heterogeneous catalysts system. In 1925, Meerwein and Schmidt¹ reported for the first time the decomposition of benzaldehyde diethylacetal over ThO₂, but they did not pay much attention to the mechanistic aspects. Recently Morris Don² has disclosed some features regarding the reactions of aromatic cyclic acetals over Pt/C type of catalysts. However no attempt has been made to investigate in detail the reactions of aromatic acetals catalysed by solid acids. Similar studies with acetals of aliphatic aldehydes have been extensively investigated by various authors³⁻⁵ with a series of such catalysts. Most of these acetals yielded synthetically important α,β -unsaturated ethers as the major products. The above results prompted us to study the reactions concerning aromatic acetals over heterogeneous catalysts. In this paper we wish to disclose some of the aspects observed in the title study. Alumina is an excellent and widely used catalyst for a variety of reactions such as dehydration,6,7 isomerization,8,9 rearrangement^{10,11} and dealkylation.¹² Of various crystallographically distinct forms of alumina, y- $Al_2O_3^{13}$ is of greatest catalytic interest. Hence we prefer to use the same catalyst in our system.

Ten acetals 1a 10a were used in the present study (Scheme 1). The product distribution determined by GLC is presented in Table 1.

As seen from Table 1 both ester and ether were obtained in all cases as compared to the isolation of either ether¹ or ester² as reported earlier. One more striking feature observed in the present experiment was the dependence of product distribution on reaction temperatures. At low temperatures, the ester was the major product while the ether was a minor one, and at elevated temperatures, the latter yield predominated over the former. This trend led us further to look into the mechanistic aspects of the reaction course.

The catalytic activity of alumina has been attributed to the surface active sites, which exhibit Lewis acid and base character.^{6,13,14} The nature of active sites vary with activation temperatures. At low temperature basic character is exhibited more due to the surface hydroxy ions. High temperature would favour the desorption of hydroxyl ions, which leave exposed Al^{3+} ions on the surface, as a result the alumina shows





pronounced acidic character. Probably this varying nature of the surface active sites would alter the course of the reaction and hence the unusual product variation.

The above facts were also supported by the dehydration studies of alcohol.¹⁵ It has been suggested that concerted E_2 mechanism is preferred at low temperatures due to the presence of Lewis basic and weak acidic sites. At elevated temperatures carbonium ion intermediate, E_1 mechanism is facilitated, since both strong acid sites and high temperature would activate C O bond breaking. The selectivity variation observed in these dehydration studies evidently proves the operation of two different mechanisms as described above.

In the light of the above proposals probable mechanisms have been suggested in the present study. Active acid-base sites would promote concerted elimination by the adsorption of alkyl groups^{13,16} on Lewis acid sites and the hydrogen on the base sites¹⁵ leading to ester formation as shown in Scheme 2.



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	Net conversion 68% at 200°			Net conversion 81% at 250°			Net conversion – 90%, at 300°			Net conversion 98% at 350°		
Acetai	ь	c	đ	ь	C	đ	Ъ	c	đ	ь	c	d
1.	42	12	46	29	22	49	14	28	58	6	32	62
2#	68	13	19	43	36	21	19	57	24	11	58	31
34	62	14	24	41	28	31	17	42	41	6	46	48
54	67	19	14	44	36	20	21	55	24	10	65	25
68	58	24	18	30	46	24	12	62	26	6	70	24
80	53	12	35	39	21	40	18	30	52	9	39	52
9 a	32		68	21	****	79	9		91			100
10a	75	14	11	45	39	16	18	59	23	7	66	27

Table 1. Percentage of rearranged products of acetals

GLC yields were corrected for detector response factor and are the average of at least three injections. The experimental reproducibility in the study was approximately 5%.

Temperature was maintained constant within $\pm 5^{\circ}$.



At higher temperatures, strong Lewis acid sites would initiate the carbonium ion intermediate mechanism. The aluminium alkoxide^{17,18} formed during the cleavage of acetal would probably serve as the source of hydride ion¹⁹ required for the MPV type of reduction forming ether (Scheme 3). The presence of aliphatic aldehyde has been confirmed by GLC, coinjection with authentic sample and its yield corresponds to the yield of ether (c).

The aromatic aldehyde could be formed from the carbonium ion (V) as shown in Scheme 4. A similar mechanism has been proposed for aldehyde formation from acetal in the presence of Lewis acids.²⁰

The alkyl carbonium ion (VII) formed may eliminate a proton resulting in alkene. The proton probably has two sites for abstraction; the one is the surface hydroxyl ion with which water is eliminated exposing Al^{3+} ion in the surface;²¹ the other would be the surface oxide at which hydroxyl ion is formed.²² GLC confirms the presence of olefin and its yield varies with parent aldehyde formation.

The above mechanistic approach for the rearranged products was further supported by the following catalytic poisoning and kinetic studies.

Poisoning study. In an attempt to relate the role of active sites with the nature of product formation the catalyst was poisoned with NH_3 , CO_2 and H_2S independently and the reactions were carried out as usual. In addition to the normal compounds (b, c, d) various undesired products were formed. Since the poisoning study itself is a very complicated process²³ the present discussion is confined to the effect of poisoning on the variation of the desired products. The results obtained by GLC are presented in Table 2.

The ester formation at low temperature may be attributed to the presence of relatively few acid-base active sites. At elevated temperature (250°) the number



Table 2. Relative percentage of product distribution on poisoned catalyst

	Net conversion 70%, at 200°			Net conversion-82% at 250°			Net conversion-91% at 300"			Net conversion98% at 350°						
Catalyst	ь	c	d	Oth	ь	c	d	Oth	ь	c	đ	Oth	b	¢	d	Oth
Al ₂ O ₃ poisoned with NH,	9	2	30	57	13	7	42	38	7	15	46	34	4	19	51	26
Al ₂ O ₃ poisoned with CO ₂	14	4	39	44	19	12	46	33	9	19	51	31	5	23	56	26
Al ₂ O ₃ poisoned with H ₂ S	7	_	36	57	11	-	48	41	6	siemin	54	40	3		56	41

0th-undesired products.

Temperature	Flow rate	Net	Product distribution in %					
· · · · · · · · · · · · · · · · · · ·	ml/min	conversion	ъ	c	ď	Oth		
ana ana danaka ka sa	1/2.5	52	38	8	59			
200	1/5	70	75	14	11			
	1/10	92	58	11	10	21		
	1/2.5	76	10	19	71			
300	1/5	91	18	59	23			
	1/10	100	9	32	16	42		

Table 3. Product distribution at different flow-rates

of such sites may increase on desorption of poisoning species. The formation of aluminium alkoxide which is necessary for hydride transfer process might have been suppressed by the poisoning effect and hence the low yield of ether. The absence of ether in the case of H_2S poisoning study may be ascribed to the tenacious adsorption of H_2S on Al^{3+} sites and the complex interaction with the surface²⁴ which may inhibit the alkoxide formation. The interaction of the substrate with preadsorbed poisoning species may lead to the formation of undesired products.²³

Kinetic study. This study was carried out with a view to relate the flow-rate with the nature of product formation. The results are given in Table 3.

The marked observation in Table 3 is the peculiar increase in the yield of aromatic aldehyde at higher flow-rates. Two different possibilities may be formulated for the above observation. At the reaction temperatures, the desorbed water in presence of active acid sites may hydrolyze the acetal to give aldehyde and alcohol. This explanation may be ruled out for the following two reasons.

1. In the experiment, before sending acetal, the reaction column was sufficiently flushed with N_2 , during which water molecules if present would have been expelled.

2. Irrespective of the flow-rates, corresponding to the amount of desorbed water, the same quantity of aldehyde is expected at a particular temperature. But, as different quantities of aldehyde are formed, the above proposal may not fit in suitably. The other probable explanation offered would be that the formation of carbonium ion (V) was the invariable intermediate irrespective of the flow-rates. At medium and lower flow-rates carbonium ion has sufficient time to interact with the alkoxide at the catalyst surface in an intermolecular way to give ether in better yields. In addition, at lower flow-rates, the contact time may be long enough for the formed products to undergo further reactions to give a number of undesired products in the form of resinous or charred materials.

At higher flow-rates, the carbonium ion may not have sufficient time to interact with the alkoxide, as a result it undergoes some intra-molecular rearrangement to get itself stabilized in the form of aldehyde. This fact has been supported by the proposal that the production of aldehyde was favoured at shorter contact time on Ag catalyst.²⁵ In addition, for the hydride transfer process, proper orientation of the molecules would be an essential factor, for which sufficient time lag is expected. As this would be deprived of at higher flow-rates ether formation is contained.

The influence of substituents on product formation is

felt much with acetals having substituents at the ortho and para positions. In general, the activating groups enhance the yield of desired products, while the deactivating groups lower it. As expected no significant variation is observed with the meta substituents.

Acetals 4a and 7a fail to yield the desired products ether and ester. It is not regarded as surprising, since the steric factor may be felt acutely with these compounds.²⁶ Even in solution, they behave abnormally due to steric hindrance²⁷ and such effect may be more pronounced in heterogeneous system.²⁸ Hence, we are deprived of the expected compounds. However, 1a yields the normal products but in low yield, which implies that halide group offer less steric hindrance.²⁹ The more pronounced deactivating ability of NO₂ group at the para position would destabilise³⁰ the intermediate carbonium ion as a result 9e is not formed with 9a acetal. This observation may be considered as additional evidence in favour of carbonium ion intermediate mechanism for ether formation.

The product mixture obtained in the experiment is simpler than those from aliphatic acetals. This observation is in agreement with the suggestion made by Fleming³¹ that the products derived from aliphatic acetals are very reactive and hence they undergo further reactions to give a number of secondary products.

To verify whether the ether and aldehyde were formed at the expense of ester or directly from acetal, the experiment was repeated using the ester 10b. GLC showed the absence of ether and aldehyde. Further, the reaction was performed with a mixture of 1:2 molar ratio of aldehyde 10d and n-butyl alcohol, to find out whether the former reacts with the latter to give ester and ether. The product analysis showed the absence of these products. The above observations evidently prove that the products **b**, c and **d** are formed directly from acetals.

EXPERIMENTAL

Characterization of the catalyst. The characteristic X-ray intensities and the d-values for the alumina used in our system were in agreement with the standard values³² of γ -alumina. The values are given in Table 4.

The surface area of the catalyst was found to be $253 \text{ m}^2/\text{g}$ and the pore volume 0.61 ml/g. The acid amount of alumina was measured to be 0.642, 0.751 and 0.891 mmol/g at H₀'s, + 3.3, + 4.8 and + 6.8 respectively. Water content of alumina was found to be 0.19, 0.16, 0.11 and 0.07 gm in 1 gm of the sample at 200, 250, 300 and 350° respectively.

IR spectra were obtained on a Perkin-Elmer 599 or Perkin-Elmer 781 spectrometer. ¹H-NMR were recorded on a Varian T-60 or Varian HA-100D with Me₄Si as internal standard and CCl₄ or CDCl₃ as solvent. GLC was performed on a Toshniwal RLO4, $3 \text{ mm} \times 2.5 \text{ m SS}$ column packed with 5% SE

Table 4. X-ray intensities and d-values of the standard γ -Al₂O_{3(sid)} and the Al₂O_{3(rept)} used in the present work

L1,		d-values				
y-Al2O3(and)	Al2O3(expt)	y-Al2O3isidi	Al ₂ O _{3(espi)}			
100	100	1.98	1.98			
100	95	1.4	1.41			
80	80	2.39	2.38			
40	42	4.56	4.57			

30 on chromosorb W-HP. The X-ray powder diffraction pattern of the alumina sample was recorded on a Philips PW 1380 diffractometer, Horizontal Goniometer using Cu K α radiation with Nickel filter. The surface area of the catalyst was measured on a Micromeritics, Rapid surface area analyzer USA 2205 and the pore volume by benzene adsorption method.³³ Acidity measurement was done with nbutylamine³⁴ using Hammett indicators dimethyl yellow (+3.3), methyl red (+4.8) and neutral red (+6.8).

Acetals were prepared by the described procedures^{35,36} and characterized by IR and NMR spectral data. B.p. and refractive index were also compared with reported values.

The experimental set-up was similar to that developed by Brown et al., except for the vertical mounting of the reaction column. In a typical experiment the acetal vapour in presence of a stream of N_2 (acetal: $N_2 = 1:4$) was fed (1 ml/5 min) through a Pyrex tube (300 mm length, 15 mm inner diam) packed with about 15 g of catalyst kept at constant temp in the range of 200-350°. Gentle suction was applied to get the products collected in an ice-cold trap. The products obtained were separated by column chromatography and TLC and characterized by IR and NMR spectral data. By GLC the compounds were assigned, coinjection with authentic samples and the relative percentage of the products distribution were determined.

 γ -Al₂O₃ (ACC Ltd., Bombay) sieved particles of 20–35 mesh ASTM was used in the experiments. Before use, Al₂O₃ was given a pretreatment which consisted of the following steps. First, Al₂O₃ was outgassed at 300° for 2 hr. It was then contacted with 200 mm of O₂ and the temp was raised to 500° for 1 hr. After 30 min, evacuated at 500°, another 200 mm charge of O₂ was admitted and allowed to stand for 2 hr at the same temp. After that, it was evacuated at 500° for 3 hr. The catalyst was then cooled to room temp and stored in a desiccator. Fresh sample was used in each experiment and it was kept in the reaction temp for an hour in the reaction column. A stream of N₂ was flushed before the passage of acetal. In the experiment 10 ml of acetal was passed for 50 min.

All chemicals used were of analar grade. Column chromatography and TLC were performed with silica gels supplied by BDH or Acme Synthetic Chemicals.

Kinetic and poisoning studies were carried out using 10a acetal as a reference. NH_3 poisoning was done as described by $Peri^{38}$ and CO_2 and H_2S poisoning as per Lunsford's procedure.²⁴

Above 400[°] decomposition occurred which led to carbonization and darkening of the catalyst. The temperatures and flow-rates were so chosen to avoid secondary reaction products that could complicate the study of the mechanism of the process.

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