

Pyrolysis of aromatic acetals over γ -alumina

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Abstract. When aromatic acetals in vapour phase were passed over alumina (γ - Al_2O_3), the product mixture was found to contain ester, ether and aldehyde of aromatic nature. Activated γ - Al_2O_3 exhibits Lewis acid-base properties at elevated temperatures. Possible mechanisms for the formation of the above products, consistent with experimental observation have been suggested.

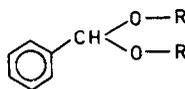
Keywords. Aromatic acetal; pyrolysis; γ -alumina.

1. Introduction

A lot of work dealing with pyrolysis of aliphatic acetals over alumina maintained at elevated temperatures has been reported in literature (McElain *et al* 1951; Hugh *et al* 1957; Michitoshi *et al* 1967; Robert and Ting 1973) and the major products were aldehyde and unsaturated ether. However, little attention has been paid to the aromatic analogues. We have studied in detail the reactions of various aromatic acetals over activated γ - Al_2O_3 kept at different constant temperatures. It was hoped that these investigations might throw light on the mechanism of the formation of various products in particular and the catalytic nature of γ - Al_2O_3 in general. The rearrangement studies of aliphatic and aromatic acetals in solution catalysed by Lewis acids such as TiCl_4 , SnCl_4 , SbCl_5 and FeCl_3 have been well established (Mastagli and Gnanadickam 1962; Arulraj 1971; Antony 1980; Alphonse 1981). The present paper concerns with the effect of Lewis acid and Lewis base active sites (Pines and Pillai 1961; Watanabe *et al* 1962; Mannassen and Pines 1965) of γ - Al_2O_3 on aromatic acetals.

2. Experimental

The following aromatic acetals were prepared by standard methods (Fischer and Baer 1935; Adkins and Nissen 1941).



R = ethyl, n-propyl, n-butyl,
isobutyl, n-amyl, isoamyl

Scheme 1

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The experimental set-up for the study was similar to that described by Brown *et al* (1977) except for the vertical mounting of the furnace. In a typical experiment the acetal was heated to boiling and the vapour diluted with nitrogen was passed through a pyrex tube (inner diameter of 1.5 cm and length of 30 cm) packed with activated granular $\gamma\text{-Al}_2\text{O}_3$ up to a height of 15 cm and kept at constant temperature (in the range 200–350°C). The acetal was fed at a rate of 12 ml/hr. Gentle suction was applied to get the products collected in an ice-cold trap. The product mixture was separated by column chromatography and TLC. The neatly separated components were characterized by IR and NMR spectral data. The relative percentage of the products present in the mixture was determined by GLC analyses.

All chemicals used were of analar grade. The tablet or granular form of activated $\gamma\text{-Al}_2\text{O}_3$ (Sarada Chemicals, Calcutta or ACC Ltd., Thane, India) was crushed into particles of 20–25, ASTM mesh was used for the reactions. Silica gels for column and TLC were supplied by BDH or Acme synthetic chemicals. The IR spectra were recorded on a Perkin–Elmer 599 or Perkin–Elmer 781 spectrophotometer and the ^1H NMR spectra on a Varian T-60 or Varian HA-100D spectrometer. The GLC analyses were carried out on a Toshniwal, India (type RL 04) chromatograph (5% SE 30 column of 8 ft length).

3. Characterization of the catalyst

The catalyst was characterized by the following studies.

3.1 XRD studies

Powder method was employed for XRD measurements. It was recorded on a horizontal goniometer PW 1380 Philips, Holland, using Cu as target. The characteristic x-ray intensity measurements and the *d*-values for the alumina used in our system were in good agreement with the standard values of the γ -alumina (Rooksby 1951). The values are presented in table 1.

3.2 Surface area and porosity measurements

Surface area was measured in Micromeritics, rapid surface area analyzer, USA 2205. The surface area of the alumina was 253 m²/g and the pore volume 0.61 cc/g. The experimentally determined values for the alumina employed conform to those of standard grade γ -alumina. By solution methods, the acidity of the alumina was found to be nil.

Table 1. The characteristic intensities and *d*-values of the standard $\gamma\text{-Al}_2\text{O}_3$ ($\gamma\text{-Al}_2\text{O}_3_{\text{Std}}$) and the Al_2O_3 used in the present work ($\text{Al}_2\text{O}_3_{\text{Expt.}}$).

<i>I</i> / <i>I</i> ₁		<i>d</i> -values	
$\gamma\text{-Al}_2\text{O}_3_{\text{Std}}$	$\text{Al}_2\text{O}_3_{\text{Expt}}$	$\gamma\text{-Al}_2\text{O}_3_{\text{Std}}$	$\text{Al}_2\text{O}_3_{\text{Expt.}}$
100	100	1.98	1.99
100	95	1.40	1.41
80	80	2.39	2.39
40	42	4.56	4.57

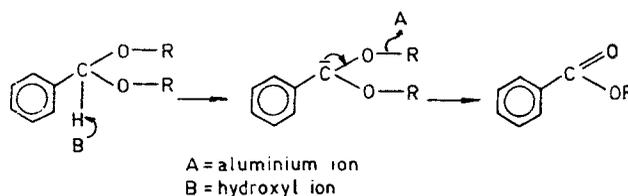
4. Results and discussion

The reactions of aromatic acetals over γ - Al_2O_3 catalyst were carried out at different constant temperatures in the range of 200–350°C. Above 400°C, decomposition occurred which led to carbonisation and darkening of the catalyst. It was observed by GLC analyses that at about 200°C the major product was the corresponding aromatic ester, while the corresponding ether was a minor product. As the temperature was raised, the ether predominated over ester. Benzaldehyde was also present in considerable amount in the product mixture, the amount of which varied with the nature of the alkyl group present in the substrate. It was also noted that the high temperature facilitated the aldehyde formation. The percentage conversion of the acetal increased from 70% at 200°C to 98% at 350°C. These observations may be due to the fact that more and more number of active sites were produced by desorption, which adsorbed more number of molecules of acetal as the temperature was increased, resulting in a different product distribution apart from increased net conversion.

Studies by Peri (1965) have presented a clear picture about the surface of partially dehydrated catalytic γ - Al_2O_3 . On the basis of his model, the following interpretation was made by Flockhart *et al* (1969) for the dehydration process. At activation temperature around 200°C, the surface sites on the partially dehydrated alumina are occupied mainly by bare unsolvated hydroxyl ions, since most of the surface water molecules have been removed. Above 250°C, combination of hydroxyl ions with formation and desorption of water proceeds rapidly leaving vacant sites on the surface. These sites expose aluminium ions, which in Peri's view exhibit the character of Lewis acid. Spectral studies (Hirota 1962; Hall *et al* 1963) supported the above view. In the range of activation temperatures up to 350°C, the reducing species (Lewis bases) are probably hydroxyl ions (Flockhart *et al* 1969; Hosaka *et al* 1971; Meguro and Esumi 1978).

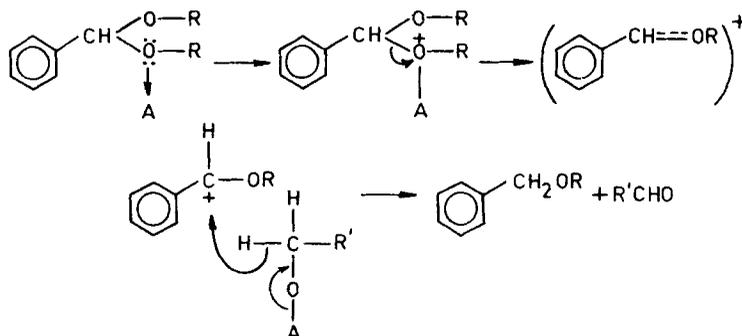
Keeping in view the above facts, the following possible mechanistic pathways could be assigned for the product formation in the present study. It has been proved that at 200°C, though the γ - Al_2O_3 surface possesses relatively a small number of exposed aluminium ions (Lunsford *et al* 1975) the catalyst chiefly exhibits the Lewis basic character due to the surface hydroxyl ions (Flockhart *et al* 1969). The basic hydroxyl groups may get protonated (Williams and Hipps 1982) probably by the benzylic protons of the acetal and pumped off as water, leaving exposed aluminium ion active sites on the surface. These ions can hold electron rich alkyl groups (Flockhart *et al* 1966; Larson and Hall 1965; Hirota *et al* 1962) originated from the acetal resulting in the formation of ester.

As the temperature is raised, the vacant site formation is increased. The exposed aluminium ions can then coordinate with the lone pair of alkoxy oxygen of acetal



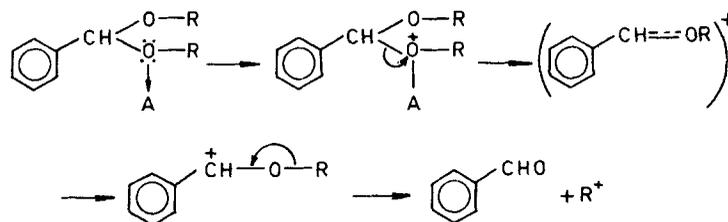
Scheme 2

(Mannassen and Pines 1965; Hair 1967; Williams and Hipps 1982) facilitating the cleavage of the alkoxy group from the acetal. The resulting aluminium alkoxide (Turner *et al* 1981; Williams and Hipps 1982; Brown *et al* 1982) would probably serve as the source of hydride ion required for the MPV type of reduction forming ether.



Scheme 3

The presence of aliphatic aldehyde in the product mixture was confirmed by GLC. The probable mechanism for the formation of aromatic aldehyde could be explained from the alkoxide oxonium ion as shown below.



Scheme 4

The alkyl carbonium ion may lose a proton and form alkene. The proton probably has two sites for abstraction; the one as described earlier, may result in the formation of water with surface hydroxyl ion (Williams and Hipps 1982) leaving an exposed active site of Al^{3+} and the other possibility may be the formation of the hydroxyl ion with surface oxide (Peri 1966) which is coordinated to aluminium ion.

The above mechanistic approach for the rearrangement of acetals was further supported by the following catalytic poisoning and kinetic studies.

5. Specific poisoning of the catalyst

In an attempt to relate the role of the active sites with the nature of products formation; NH_3 , CO_2 and H_2S poisoning studies were carried out. NH_3 poisoning was done as described by Peri (1965) and CO_2 and H_2S poisoning by the method described in

Lunsford *et al* (1975). Benzaldehyde di-*n*-butyl acetal was employed as reference to study the poisoning effect. The results obtained and the most probable reasons for the observed facts are discussed below.

5.1 NH_3 poisoning

Ammonia-poisoned alumina catalyst gave traces of ester at low temperatures ($\leq 200^\circ C$) and slightly higher amount of ester along with traces of ether at higher temperatures ($\sim 300^\circ C$).

These results could very well be explained by the adsorption study of NH_3 on alumina proposed by Peri (1965). NH_3 could be strongly held by coordination to Al^{3+} ion or by strong hydrogen bonding at oxide defects. Moreover, the preexisting hydroxyl groups are strongly affected, and new hydroxyl groups are formed. So, the catalytic surface as a whole would be disturbed by NH_3 adsorption and as expected the yield of the desired products was very low. Traces of ester formed at low or high temperatures may be attributed to the loosely bonded hydroxyl groups, which could easily be removed as water by the benzylic proton as described in the above proposed mechanism. At higher temperatures, few exposed Al^{3+} active sites would be formed under these conditions due to desorption (Peri 1965), which could be the most probable factor to account for the low yield of ether.

5.2 CO_2 poisoning

CO_2 adsorption over alumina surface has some effect over its catalytic behaviour (Lunsford *et al* 1975). This effect was also felt in the present studies. At lower temperatures ($\leq 200^\circ C$) ester was formed but in traces and as the temperature was raised besides ester, ether was formed and its yield increases to some extent on further elevation in temperature ($> 300^\circ C$).

The hydroxyl groups and oxide sites are much disturbed by CO_2 poisoning. Traces of ester at lower temperature may be due to the loosely bonded hydroxyl groups as described earlier. Though the most probable sites for the adsorption of CO_2 are exposed Al^{3+} ions, it can be removed by brief evacuation even at $25^\circ C$ (Lunsford *et al* 1975). Hence, the ether formation is favoured at higher temperatures. However, the adsorption of CO_2 probably would have affected the original nature of the alumina surface and as a result the yield of ether was lower than the expected one.

5.3 H_2S poisoning

Alumina poisoned by H_2S gas gave only a small amount of ester at the experimental temperature conditions. This striking feature may be attributed to the selective adsorption of H_2S on exposed Al^{3+} sites (Lunsford *et al* 1975). Further by ^{27}Al hyperfine structure in nitric oxide spectrum De Russet (1962) confirmed that the H_2S or possibly a dissociation product of H_2S was tenaciously adsorbed over exposed Al^{3+} ion. So, the responsible site for the ether formation was completely poisoned and hence ether formation was almost nil even at elevated temperatures. The desorption of easily removable hydroxyl ions would have occurred with the aid of the benzylic proton resulting in ester formation. The low yield of ester may be due to the complexity of the neighbouring groups which would have affected the existing hydroxyl groups.

6. Kinetic studies (for benzaldehyde di-*n*-butyl acetal)

The flow rate of the acetal vapour over alumina kept at two different constant temperature was varied and the product mixture in each case was analysed by GLC. It was observed that as the flow rate decreased (from 24 ml/hr to 6 ml/hr) the total conversion of acetal increased and the quantity of aldehyde formed decreased. When the flow rate was kept at the minimum there was formation of a number of secondary compounds in the form of charred material. The observed results are tabulated in table 2.

At higher flow rate the possibility of the decomposition of acetal to aldehyde is greater as the time allowed may not be sufficient for the acetal molecules to get themselves adsorbed on active sites and to undergo subsequent rearrangement. However, at the minimum flow rate (6 ml/hr) the time allowed may be sufficient for the products to undergo further changes to give a number of undesired secondary compounds in the form of charred material.

The pyrolytic study of the ester (*n*-butyl benzoate) was separately carried out to verify whether, the ether and aldehyde were formed by the decomposition of the ester or directly from the acetal. The GLC analyses showed the absence of ether and aldehyde confirming the fact that the ester does not undergo further reaction to give the former products. This evidently shows that the ether and aldehyde form directly from the acetal.

The net conversion and the relative percentage of the product distribution found out by the GLC analyses are presented in table 3. The results reveal some important aspects regarding the product distribution. The higher alkyl groups in acetals would behave as better leaving groups favouring the formation of benzaldehyde at elevated temperatures. One more distinct feature observed is the lower yield of ester for benzaldehyde di-isobutyl acetal. This anomaly in the series could be explained by the fact that the aluminium ions lie beneath a layer of surface oxide ions and hence the adsorption of the alkyl group over aluminium ion is hindered by the steric crowding offered by the closeness of the branched secondary carbon with the oxide surface. Such a factor may be expected to be much less with isoamyl group in which the bulky branched secondary carbon is farther away from the active centre.

Further study with substituted aromatic acetals is well underway to investigate the substituents effects on the reaction course.

Table 2. Flow rate and product distribution for the pyrolysis of benzaldehyde di-*n*-butyl acetal over γ -Al₂O₃.

Temp.	Flow rate ml/hr	Net conversion	Product distribution in %			
			Es	Et	Al	Charred products
at 200°C	24	52	33	8	59	—
	12	70	75	14	11	—
	6	92	58	11	10	21
at 300°C	24	76	10	19	71	—
	12	91	18	59	23	—
	6	100	9	32	16	43

Table 3. Percentage of pyrolysis products of various acetals at different temperatures.

Acetal	Net conversion 70% at 200°C			Net conversion 82% at 250°C			Net conversion 91% at 300°C			Net conversion 98% at 350°C		
	% in net conversion			% in net conversion			% in net conversion			% in net conversion		
	Es	Et	Al									
Et. A	83	10	7	57	31	12	21	62	17	11	70	19
<i>n</i> -Pr. A	79	14	7	52	37	11	20	61	19	12	67	21
<i>n</i> -Bu. A	75	14	11	45	39	16	18	59	23	7	66	27
Iso-Bu. A	33	36	31	16	48	36	9	54	37	3	56	41
<i>n</i> -Am. A	70	18	12	40	39	21	16	56	28	7	63	30
Iso-Am. A	66	18	16	38	36	26	16	53	31	8	58	34

Es = corresponding benzoic ester; Et = corresponding benzyl ether; Al = benzaldehyde; Et. A = benzaldehyde di-ethyl acetal; *n*-Pr. A = benzaldehyde di-*n*-propyl acetal; *n*-Bu. A = benzaldehyde di-*n*-butyl acetal; Iso-Bu. A = benzaldehyde di-iso-butyl acetal; *n*-Am. A = benzaldehyde di-*n*-amyl acetal; Iso-Am. A = benzaldehyde di-iso-amyl acetal.

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