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Alumina-Catalyzed Cleavage of Ethers and Thermal Decomposition of Aluminum Alkoxides

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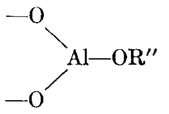
A relation between the pyrolysis of aluminum alkoxides and the alumina-catalyzed decomposition of alcohols or ethers is shown by a comparison of products obtained from the reactions. Results of comparative studies with alcohols, ethers, and alkoxides that do not contain beta hydrogen atoms provide evidence for alcohol and ether decomposing over alumina via intermediate surface alkoxides. Kinetic results indicate that the decomposition of the intermediate alkoxide proceeds via a cyclic transition state.

INTRODUCTION

The alumina-catalyzed dehydration of alcohols and cleavage of ethers have been the subject of numerous investigations (*1–3*) but the nature of the active catalytic sites and their mechanistic role in bringing about the reaction has not been fully understood. Though alumina is not an active catalyst for hydrocarbon conversions it has been proposed (*2*) that the active sites are acidic in nature and that the dehydration of alcohols or the cleavage of ethers proceeds through an oxonium–carbonium ion sequence analogous to the general type of acid-catalyzed dehydration. A very different view, however, has been stated recently (*3*) and the opinion was expressed "that the dehydration of alcohols on alumina involves the formation of a surface alkoxide of the general type,



Evidence gathered from spectroscopic studies about the nature of the active sites on alumina has not been less controversial. In one instance (*4*) it has been pointed out that the hydroxyl groups on alumina detected by infrared spectra were not acidic and were not involved in the chemisorption or isomerization of olefins such as butene-1. A later investigation (*5*), however, showed that chemisorbed olefins such as ethylene undergo slow interaction with the hydroxyl groups on alumina surfaces and are transformed to ethyl groups as illustrated by infrared spectra.

The present investigation was undertaken to throw light on the nature of the active sites and their role in the cleavage of ethers or alcohols. It was anticipated that if indeed alumina-catalyzed reactions of alcohols or ethers do proceed through the initial formation of surface aluminum alkoxides, then a relationship might be established between the pyrolysis of aluminum alkoxides and the cleavage of alcohols or ethers over alumina.

In order to avoid complications that could result from secondary hydrolytic reactions of eliminated water, the study was restricted to ethers and alcohols with no beta hydrogen atoms. A kinetic study was also conducted to supply information regarding the nature of the transition state during the course of the reaction.

METHODS

Materials

The alumina used in this study was Harshaw Al-0104 in the form of ⅛-inch pellets. Aluminum benzyl oxide was prepared following the procedure of Meerwein and Bersin (*6*), m.p. 59–60°. Aluminum methoxide was prepared by allowing pure aluminum powder to react with excess anhydrous methanol under reflux for 24 hr. Undissolved aluminum was filtered off and excess methanol was removed under high vacuum at 125°. Benzyl methyl ether was prepared from benzyl bromide and sodium methoxide, b.p. 170–172°. Dibenzyl ether was prepared from benzyl bromide and sodium benzyl oxide, b.p. 295–298°.

Procedure

Decomposition of aluminum alkoxides. In a typical experiment 10 g of the alkoxide was placed in a 25-ml Claisen flask heated in a Woods metal bath and the temperature controlled to ±3° (temperature ranges were from 300°to 380°). The decomposition products were condensed successively in an ice-cooled trap and a Dry Ice trap. The noncondensable gases were collected in a gas burette and their rate of evolution was followed. The noncondensable gases were analyzed by mass spectrometry and the liquid products were analyzed by vapor phase chromatography using a silicone-rubber-packed column. In the kinetic runs with aluminum methoxide, a linear plot was obtained from comparing the logarithm of the volume of gas evolved $(V_\infty - V)$ against time. Rate constants were determined from the slope of the curve $(\Delta \log V/\Delta T)$. The activation energy was obtained from the slope of the curve of rates plotted against reciprocal absolute temperatures. Entropy of activation was calculated using the reported equation (*7*).

Decomposition of ethers or alcohols over alumina. In a typical run 10 g of ⅛-inch pellets of alumina was placed in a ¾ × 12-inch Vycor reactor fitted with an inside thermowell and heated by external wire and regulated by a Variac. The reactants were introduced through a syringe needle from a constant drive syringe pump (JKM Instrument Co., Durham, Penna.) at contact times between 10 and 20 sec. The reaction products were collected in a series of air-cooled and ice-cooled receivers and the noncondensed gases were measured using a wet test meter. The liquid and gaseous products were analyzed as previously described.

RESULTS

Thermal Decomposition

Aluminum methoxide. The principal products obtained above 300° from the thermal decomposition of aluminum methoxide were dimethyl ether, methane, hydrogen, and carbon monoxide. A small amount of ethylene and propylene were also observed. Below 300° considerable yields of dimethyl ether were obtained. In no case was water detected.

Methanol and dimethyl ether underwent similar decomposition over alumina and gave closely related product distributions. The over-all activation energy of the decomposition of aluminum methoxide was calculated to be 23 kcal/mole. This low activation energy rules out the possibility that there is a free radical decomposition of intermediate dimethyl ether. Rice and Herzfeld (*8*) have determined the over-all activation energy for the gas-phase free radical decomposition of dimethyl ether and have reported a value of 62.5 kcal/mole.

The kinetics for the aluminum methoxide decomposition are presented in Table 1 and a comparison of products from this decomposition with those from methanol or dimethyl ether are given in Table 2.

TABLE 1
KINETICS OF THE THERMAL DECOMPOSITION OF ALUMINUM METHOXIDE

Temp. (°C)	K_1 (sec^{-1})	E_a (kcal)	$\Delta S^\dagger$ (e.u.)
325 ± 2	8.1×10^{-6}	—	–
347 ± 3	16.3×10^{-6}	23	−47
385 ± 3	46.6×10^{-6}	—	—

TABLE 2
DECOMPOSITION OF METHYL DERIVATIVES

Product	$Al(OCH_3)_3$ at 385° (mole %)	CH_3OH over alumina at 450°, LHSV of 0.5 (Relative quantity)	$(CH_3)_2O$ over alumina at 450°, LHSV of 0.5 (Relative quantity)
CH_4	22.5	Major	Major
H_2	35.2	Major	Major
CO	31.1	Major	Major
C_2H_4	1.3	Minor	Minor
C_3H_6	2.5	Minor	Minor
$(CH_3)_2O$	7.1	Major	Major
Other	0.3	Minor	Minor

Aluminum benzyl oxide. Aluminum benzyl oxide underwent smooth thermal decomposition at 310° and the principal products were toluene, benzaldehyde, and dibenzyl ether. At higher temperatures some decomposition of the benzaldehyde to benzene and carbon monoxide was observed. Very similar spectra and distribution of products were also observed from the alumina-catalyzed decomposition of benzyl alcohol or dibenzyl ether as shown in Tables 3–5. Conducting the reactions at various temperatures, though influencing the rate of reaction, did not change the relative distribution of products. Identical blank runs were made using quartz as a substitute for alumina, and as can be seen in Tables 6 and 7, very little decomposition was observed.

TABLE 3
THERMAL DECOMPOSITION OF ALUMINUM BENZYL OXIDE

Product	$Al(OCH_2Ph)_3$ at 310° (mole %)
$PhCH_3$	22.5
PhCHO	25.3
$(PhCH_2)_2O$	42.0
Ph_2CH_2	4.0
$PhCH_2CH_2Ph$	3.8
PhCH=CHPh	
PhC≡CPh	
Other	2.4
$PhCH_3$/PhCHO	0.9

TABLE 4
DECOMPOSITION OF BENZYL ALCOHOL

Product (mole %)	Over Al_2O_3 at LHSV of 0.64		
	300°C	350°C	400°C
$PhCH_3$	8.14	16.56	30.78
PhCHO	6.25	17.45	34.45
$(PhCH_2)_2O$	30.18	35.28	14.81
Ph_2CH_2	0.10	0.38	0.96
$(PhCH_2)_2$	0.49	1.06	2.25
Other	0.15	—	—
$PhCH_2OH$	54.69	29.27	16.72

TABLE 5
DECOMPOSITION OF DIBENZYL ETHER

Product	Over Al_2O_3, LHSV = 0.64 (mole %)		
	300°C	350°C	400°C
$PhCH_3$	14.01	14.08	36.20
PhCHO	10.51	15.48	29.98
Ph_2CH_2	0.41	0.34	0.92
$(PhCH_2)_2$	2.74	1.90	3.51
PhCH=CHPh	—	0.61	0.85
Other	0.07	1.80	1.72
$(PhCH_2)_2O$	72.26	65.79	25.82

The relative composition of the products obtained over quartz was quite different from that obtained over alumina. At all of the temperatures studied, bibenzyl and stilbene constituted about 50% of the total

TABLE 6
DECOMPOSITION OF BENZYL ALCOHOL

Product (mole %)	Over quartz at LHSV of 0.64		
	300°C	350°C	400°C
$PhCH_3$	0.04	0.81	2.39
PhCHO	0.21	0.54	1.31
$(PhCH_2)_2O$	—	—	—
Ph_2CH_2	—	—	—
$(PhCH_2)_2$	0.10	0.76	1.06
Other	—	—	0.17
$PhCH_2OH$	99.65	97.89	95.17

TABLE 7
DECOMPOSITION OF DIBENZYL ETHER

Product	Over quartz, LHSV = 0.64 (mole %)		
	300°C	350°C	400°C
$PhCH_3$	0.55	1.15	1.92
PhCHO	0.88	0.88	1.72
Ph_2CH_2	—	—	—
$(PhCH_2)_2$	1.53	1.51	1.90
PhCH=CHPh	1.06	0.82	0.68
$(PhCH_2)_2O$	95.98	95.64	93.78

reaction products. Bibenzyl and stilbene are products reminiscent of free radical reactions. The change of the composition of products over quartz compared with those over alumina and the considerable difference in the over-all reaction rate does not support the possibility of homolytic cleavage over alumina.

Benzyl methyl ether. The decomposition of benzyl methyl ether was studied over alumina in the temperature range of 240° to 430° and the results are listed in Table 8 and Fig. 1. At lower temperatures, where relatively little decomposition took place, the ether disproportionated, in part, into dimethyl ether and dibenzyl ether. This ether disproportionation went through a maximum conversion and then declined above 380°. This is also evident from the data plotted in Fig. 1, which shows that benzaldehyde formation rises and then levels off. Benzaldehyde is a product from the cleavage of dibenzyl ether which appears to decompose more readily than dimethyl ether. Toluene, one of the major decomposition fragments from benzyl methyl ether, showed a comparable sudden increase in yield above 360°.

The appearance of dibenzyl ether and dimethyl ether support the concept of the reversibility of the initial interaction of alcohols or ethers with alumina. It indi-

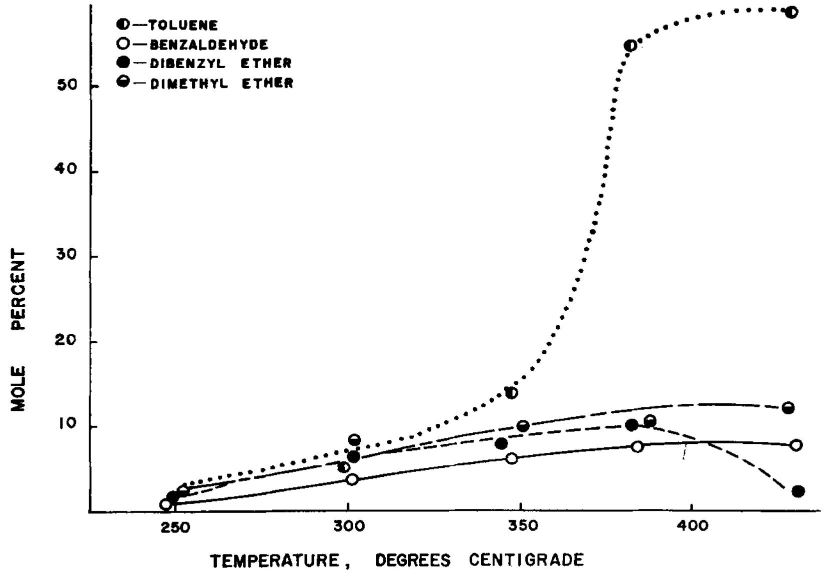


Fig. 1. Decomposition of benzyl methyl ether over alumina.

TABLE 8
Decomposition of Benzyl Methyl Ether

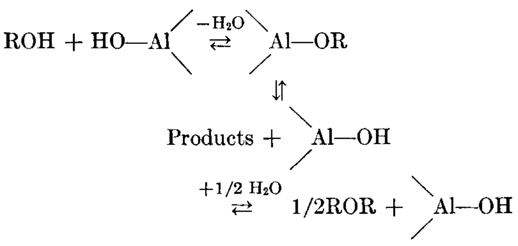
	Over Al_2O_3, LHSV = 0.64 (mole %)				
Product	240°C	300°C	340°C	380°C	430°C
$(CH_3)_2O$	1.13	8.35	9.36	10.22	15.05
CH_2O	2.14	1.90	2.86	5.69	3.15
$PhCH_2OCH_3$	92.84	73.68	57.20	13.25	6.63
$PhCH_3$	1.48	4.37	14.56	45.40	60.14
PhCHO	0.92	3.87	6.70	7.80	8.27
Ph_2CH_2	—	0.05	0.22	1.13	1.13
$(PhCH_2)_2$	—	0.03	0.73	3.40	2.57
$(PhCH_2)_2O$	1.49	7.75	8.37	13.11	3.06

cates that the initial reaction of ethers over alumina involves a dissociative chemisorption resulting in the cleavage of the C–O bond. This process is reversible at low temperature but the surface compound can undergo further decomposition at higher temperatures.

There was little reaction from benzyl methyl ether over quartz at this same temperature range. No ether disproportionation products were observed and below 400° only a trace of products reminiscent of free radical reactions was noted.

DISCUSSION

Among the plausible mechanisms that have been proposed for the dehydration of alcohols over alumina are those (*3*) that propose that the dehydration involves preliminary formation of surface oxides which then decompose to olefin.



$$\mathrm{ROH} + \mathrm{HO{-}Al} \overset{-H_2O}{\rightleftarrows} \mathrm{Al{-}OR}$$
$$\downarrow\uparrow$$
$$\mathrm{Products} + \mathrm{Al{-}OH}$$
$$\overset{+1/2\,H_2O}{\rightleftarrows} \ 1/2\mathrm{ROR} + \mathrm{Al{-}OH}$$

In this connection we were of the opinion that comparison of over-all rates and products from alkoxide pyrolyses with those obtained from cleavage of ethers or alcohols over alumina would prove fruitful in establishing a relationship. In our studies we limited ourselves to the so-called neutral alumina (i.e., not active for hydrocarbon conversion though effective for dehydration) since it had been demonstrated by Pines and co-workers (*2*) that acidic alumina promotes secondary hydrocarbon reactions. Our studies were limited to ethers and alcohols that do not possess beta hydrogen atoms. Each of the alkoxides used in the kinetic study was chosen because it could undergo decomposition to other products without the necessity of eliminating water.

Our data, presented in Tables 2–5, point out great similarity between the decomposition of alcohols or ethers over alumina as compared to the decomposition of aluminum alkoxides. The following significant points were also noted: 1. Ethers were found to be significant products from the alkoxide decompositions. At about the same temperature at which alkoxides undergo decomposition, ethers were found to undergo decomposition over alumina to give the same products. 2. Mixed ethers, e.g. benzyl methyl ether, disproportionate at low temperatures over alumina and yield the symmetrical ethers as well as other reaction products. This clearly demonstrates that the initial interaction of ethers over alumina is a reversible process and could involve C–O bond cleavage. 3. The similarity and the equimolar ratio of the cleavage products from alcohols or from ethers indicate that the nature of the surface compounds with alumina are the same whether alcohols or ethers are the starting materials.

All of these points support the suggestion that alcohols or ethers decompose through initial interaction with active centers in alumina, forming an unstable chemical surface compound of the alkoxide type. Subsequent decomposition of this compound yields the observed products.

It may be argued that the products from alcohols and ethers can also be explained using familiar free radical reaction patterns. Thus, if alumina removes one hydrogen atom from dimethyl ether,

$\cdot CH_2{-}O{-}CH_3 \rightarrow HCHO + CH_3\cdot$

$HCHO \rightarrow CO + H_2$

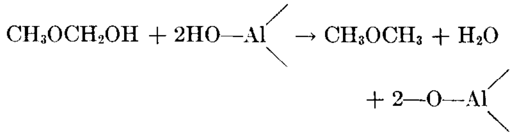
$CH_3\cdot + CH_3{-}O{-}CH_3 \rightarrow CH_4 + \cdot CH_2{-}O{-}CH_3$

Final major products: CH_4, CO, H_2

Similarly, if alumina removes a hydrogen atom from methanol,

$\cdot CH_2OH \rightarrow HCHO + H\cdot$

$CH_3O\cdot + \cdot CH_2OH \rightarrow CH_3OCH_2OH$



$$CH_3OCH_2OH + 2HO{-}Al \rightarrow CH_3OCH_3 + H_2O + 2{-}O{-}Al$$

Proceed as above to CH_4, CO, H_2 from dimethyl ether.

Our experimental results utilizing unreactive solids including quartz at 200° to 450°, demonstrate that such radical reactions play a negligible role in the reaction mechanism.

Concerning the structure in the transition state for the decomposition of alkoxides, our kinetic results are informative and certain conclusions can be drawn. The linear plot that resulted from plotting the logarithm of the weight of alkoxide remaining against time suggests that alumina, a product of the pyrolysis, does not interfere with the over-all decomposition. The entropy of activation is negative, contrary to what has been claimed (*9*). A negative entropy suggests a transition state more organized than the starting molecule. Thus a cyclic transition state is attractive to account for the major decomposition products.

Concerning relative reactivities, aluminum benzyl oxide decomposed more readily than aluminum methoxide and dibenzyl ether was more reactive over alumina than was dimethyl ether. In view of the lack of evidence supporting a free radical mechanism, these results point to cleavage of the carbon–oxygen bond as a process with some polar character. Hence the preference in the direction of cleavage and the order of reactivity.

A plausible explanation of our results is that the rate-determining step is the heterolysis of the oxygen–carbon bond where the flow of electrons is towards the aluminum and hence the residual positive charge on carbon should facilitate a hydride ion transfer. As we propose that the cleavage of alcohols or ethers over alumina proceed along the same path, we are in accord with the concept that reactions of alcohols or ethers over alumina are *p*-type reactions (*10*). The negative entropies indicate that the heterolysis is followed by a rapid hydride ion transfer and that the breaking of the carbon–hydrogen bond is nearly complete in the transition state.

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