Thermal Decomposition of Aluminum Alkoxides[1]

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Received August 9, 1962

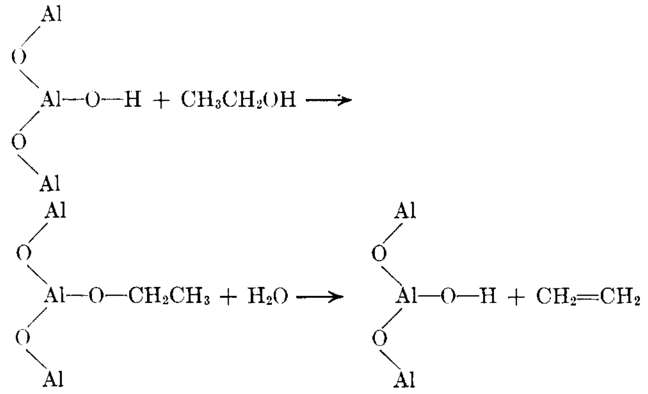
The rates of thermal decomposition of aluminum ethoxide, aluminum isopropoxide, and aluminum *t*-butoxide have been determined in the temperature range, 166–265°. At lower temperatures, the rates are relatively independent of structure or temperature, diffusion of water vapor into the system being rate-controlling for decomposition by hydrolysis. At higher temperatures, olefins are formed with a linear Arrhenius temperature dependence. For the series ethoxide–isopropoxide–*t*-butoxide, activation energies are 17.2 ± 2.6, 21.7 ± 0.4, 26.5 ± 5.8 kcal., and 7.3 ± 5, 17.8 ± 1, 34 ± 12 e.u., respectively. A number of alkoxides were prepared by alcohol interchange, then pyrolyzed. Analysis of the olefin mixtures produced shows a similarity between this reaction and dehydration of alcohols over alumina. Primary alcohols give 66–82% terminal olefins, with some rearrangement.

Introduction

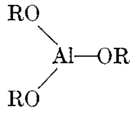
The thermal decomposition of metal alkoxides has been the subject of previous investigations.[4] Alkali metal salts of the simple alcohols usually react by loss of a β-hydrogen to form olefin and a hydroxide, but potassium *t*-butoxide[5] and more highly branched alcohols[4] undergo transformation which is effectively reversal of a Grignard reaction, forming, for example, acetone and methane from the *t*-butoxide.

There has been relatively little investigation of the thermal stability of trivalent metal alkoxides. Dialkoxyaluminum halides form mixtures of olefins, alkyl halides, alcohols, and ethers.[6] Perhaps because they can be distilled at reduced pressure, aluminum alkoxides frequently are considered to be relatively stable at elevated temperatures. Thus, a standard inorganic treatise[7] stages that "They are solids which melt and then distil at rather high temperature without decomposition," then cites boiling points of 320° for aluminum ethoxide and 242° at 10 mm. for the isopropoxides. We have observed decomposition of these salts on heating for a few minutes at temperatures from 200–265°.

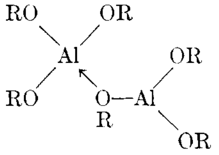
The dehydration of alcohols on alumina catalysts apparently involves preliminary formation of a surface alkoxide,[8] which then decomposes to olefin.



An aluminum alkoxide possesses a structure resembling that of the surface compound,



or considering the polymeric nature of the alkoxides,



This investigation was undertaken with the anticipation that a relationship might be shown between dehydration of alcohols over alumina and the pyrolysis of alumina alkoxides. Were this the case, the alkoxides would serve as model compounds for study of dehydration in homogeneous systems. A second potential relationship exists; considering the amphoteric nature of aluminum, aluminum alkoxides might also be considered as esters of aluminic acid, and therefore, to resemble other esters, particularly borates, in undergoing a unimolecular elimination reaction. Following the observation that olefins were indeed produced by pyrolysis of aluminum alkoxides, an attempt to ascertain directive effects was made, using both primary alcohols of varying chain length and the various five-carbon alcohols. When preliminary results demonstrated similarity between this reaction and dehydration over alumina, a kinetic study was conducted to check for autocatalysis and to supply further information regarding the nature of the relationship.

Experimental

Preparation of Reagents.—Aluminum ethoxide was prepared from absolute ethanol and aluminum foil by the method of Vogel.[9] Fresh bottles of aluminum isopropoxide and aluminum *t*-butoxide were used. 3-Methyl-2-butanol was prepared by a Grignard reaction of isopropyl bromide and acetaldehyde. The other alcohols were commercially available reagents, and were checked gas chromatographically for purity.

Preparation and Pyrolysis of Aluminum Alkoxides.—A mixture of 0.5 ml. of an alcohol and 0.3 g. of aluminum ethoxide was placed in a side-arm test tube, heated in a boiling water bath for 5 min., then connected to a vacuum. When the liquid had evaporated, the stopcock at the mouth of the tube was closed and

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[1] (a) Supported by a grant from the Research Corporation; (b) presented at the American Chemical Society Southeast–Southwest Regional Meeting, New Orleans, La., December 6–8, 1961; (c) we wish to thank Mr. Thomas Harris for his competent assistance in a part of this work.

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TABLE I

PYROLYSIS OF ALUMINUM PENTYL OXIDES

Alcohol	Relative percentage of olefin				
	C=C—C—C—C	C—C=C—C—C	C—$\overset{\text{C}}{\text{C}}$—C=C	C—$\overset{\text{C}}{\text{C}}$=C—C	C=$\overset{\text{C}}{\text{C}}$—C—C
1-Pentanol	74–82	18–26			
2-Pentanol	35	65			
3-Pentanol	1.5	98.5			
3-Methyl-1-butanol			38	34	28
3-Methyl-2-butanol			33	47	20
2-Methyl-2-butanol			1	51	48
2-Methyl-1-butanol			1	46	43

TABLE II

PYROLYSIS OF ALUMINUM *n*-ALKOXIDES

Alcohol	Relative percentage of olefins Terminal	Internal
1-Hexanol	81	19
1-Heptanol	76	24
1-Dodecanol	*a*	
1-Hexadecanol	*b*	

[a] Six olefin peaks, presumably the six isomeric dodecenes. [b] Eight olefin peaks.

a 5-ml. hypodermic syringe, the plunger lightly greased with silicone grease, was inserted into the side arm through a rubber stopper bored about 3/4 of its length. The test tube was heated in a flame until the syringe filled with gas; then the heating was stopped and the contents of the syringe were injected into a gas chromatograph. Occasionally a second sample was gathered by re-inserting the syringe and heating again. Results are summarized in Table I.

A mixture of 0.1 mole of alcohol and 5.4 g. of aluminum ethoxide was placed in a micro-distillation apparatus. The material was heated until distillation ceased; then the distillate was analyzed gas chromatographically. Results are summarized in Table II.

A 0.3-g. portion of aluminum ethoxide was decomposed in the side-arm test tube. The first 5-ml. sample consisted primarily (76%) of ethanol, 15% of acetaldehyde, 5% of one unidentified component, 1% of another, and 3% of a third (possibly ethyl ether). The second 5-ml. sample consisted of 97.3% gases (air and ethylene), 2.7% of ethanol and a trace of acetaldehyde, representative of product composition after hydrolytically produced alcohol is removed.

A 12.2-g. portion of aluminum *t*-butoxide was placed in the micro-distillation apparatus and heated until distillation ceased. A gas, identified chromatographically as isobutylene, escaped. The condensate, b.p. 81–83°, weighed 4.3 g. (*t*-butyl alcohol). The aluminum *t*-butoxide had partially hydrolyzed so that 12.2 g. contained at least 2.7 g. of *t*-butyl alcohol and 1.0 g. of aluminum hydroxide (from kinetic data below). Therefore, 8.5 g. of aluminum *t*-butoxide gave at most 1.6 g. or 21% of *t*-butyl alcohol, and presumably 79% of isobutylene.

Rearrangement of 1-Pentene.—A sample of aluminum isopropoxide was heated until decomposition had begun, then 1 g. of 99.9% 1-pentene (from *n*-amyl acetate) was added. The tube was sealed and heated in an oil bath at 200° for 15 min. The 1-pentene/2-pentene ratio of the product was 98.5/1.5.

Analysis of Olefin Mixtures.—A Beckman GC-2 gas chromatograph with an 8-ft. column containing benzyl ether on firebrick was used for analysis of the pentenes and methylbutenes. Products were identified by retention time. A reference sample of 1-pentene was prepared by pyrolysis of *n*-amyl acetate. The major (98.5%) constituent of the mixture obtained from 3-pentanol was used to identify 2-pentene. 3-Methyl-1-butene was prepared by pyrolysis of isoamyl acetate. The predominant olefin from reaction of *t*-amyl chloride with sodium methoxide was considered to be 2-methyl-2-butene, the minor constituent to be 2-methyl-1-butene. The column was found to separate olefins in the order of their boiling points.

A 6-ft. silicone column was used for higher boiling olefins. It also gave a boiling point separation. Commercial samples of 1-hexene and 3-heptene were used as reference materials. Closely grouped peaks of lower retention time than dodecanol and hexadecanol were considered to be dodecenes and hexadecenes.

Rate of Decomposition of Aluminum Alkoxides.—A constant temperature bath for use at elevated temperatures was constructed of a 4-l. resin kettle placed in a Glas-col heating mantle supplied with electricity through a 26-amp. constant voltage transformer and a variable transformer. An intermittent heater with a manual switch was immersed in a sulfuric acid bath[10] through one of the ground joints, a glass stirrer with Teflon paddle was inserted through another, and a thermometer through a third.

Two reaction vessels, constructed of 8-mm. tubing sealed to 24/40 joints (effectively, a thermometer well) were used simultaneously, being inserted through the remaining joints. The temperature could always be maintained at least to 0.5°, and when the line voltage was stable, variation as small as 0.1° was achieved. After weighing approximately 0.8-g. samples into the tubes, they were placed in the bath. The tubes were withdrawn, washed with acetone, and immediately weighed at the end of the desired time.

A semilogarithmic graph of weight *vs.* time showed an immediate drop, due to evaporation of hydrolytically produced alcohol, followed by a linear section. Extrapolation to zero time and subtraction of the weight of hydrolytic aluminum hydroxide gave the initial weight of aluminum alkoxide. A linear plot of the logarithm of the weight of alkoxide remaining *vs.* time resulted, taking weight lost as olefin, except for the reactions of aluminum ethoxide and aluminum isopropoxide at 177°, in which cases linear plots resulted from the assumption that weight lost was alcohol. Rate constants were determined from the slope of the curves, (Δ log wt./ΔT), and energies and entropies of activation calculated using the following equations.

$$E_a = \frac{2.303\ RT_1T_2}{T_2 - T_1} \log (K_2/K_1)$$

$$\Delta S\ddagger = \frac{(Ea - RT_1) + 2.303\ RT_1 \log (K_1h/K_bT_1)}{T_1}$$

Data are summarized in Table III. Linear Arrhenius temperature dependence within the range of accurate data (200–250° for ethoxide and isopropoxide, 166–200° for *t*-butoxide)[11] was noted.

TABLE III

KINETICS OF ALKOXIDE PYROLYSIS

Alkyl group	Temp., °C.	k, sec.$^{-1}$ $\times 10^5$	E_a, kcal.	$\Delta S\ddagger$, e.u.	Average
Ethyl	177	2.7			
	200	2.4	14.6	7.6	
	224	5.10	18.8	7.0	7.3 ± 5
	250	12.9		7.3	
	265	64.6			
Isopropyl	177	2.6			
	200	2.73	21.4	16.9	
	224	8.08	22.1	16.5	17.8 ± 1
	250	24.0		20.1	
t-Butyl	166	23.5	32.7	35.1	
	185	108.5	20.7	31.2	34 ± 12
	203	255		35.3	
	228	472			

A 1.002-g. sample of aluminum *t*-butoxide was left in the bath at 166° for 23 hr. The final weight was 0.321 g. [theoretical for $Al(OH)_3$, 0.318 g.]. After 1.737 g. of *t*-butyl alcohol was added, the tube was returned to the bath. Following an initial rapid evaporation, 0.127 g. of chemisorbed alcohol remained. The rate constant for dehydration of the chemisorbed alcohol was 5.26×10^{-5} sec.$^{-1}$.

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(10) Mercury thermoregulators were unsatisfactory because evaporation of the mercury at 250–260° was sufficient to prevent maintenance of a constant temperature. A vegetable oil bath decomposed to tar within 12 hr. at 250°.

(11) The data for pyrolysis of aluminum *t*-butoxide is relatively inaccurate because the reaction proceeded so rapidly that heating and cooling times were appreciable compared to reaction time. At 265°, temperature control was poor. The data are included for order of magnitude comparison.

Discussion

Considering only the over-all process, a number of reactions may be considered possible. The alkoxide might decompose to aluminum oxide, water, and olefin (1). More likely, if this were the case, water would react hydrolytically with the alkoxide, leading to alcohol formation (2). Alternatively, the alkoxide could decompose to aluminum hydroxide and olefin (3). Finally hydrolysis of the alkoxide might lead to aluminum hydroxide and alcohol (4) followed by a catalytic dehydration of the alcohol (5). An analogous pathway has been shown to operate for zirconium alkoxides, even with rigorous exclusion of water.[12]

$$2Al(OR)_3 \longrightarrow Al_2O_3 + 3H_2O + 6\text{ olefin} \tag{1}$$

$$2Al(OR)_3 \longrightarrow Al_2O_3 + 3ROH + 3\text{ olefin} \tag{2}$$

$$Al(OR)_3 \longrightarrow Al(OH)_3 + 3\text{ olefin} \tag{3}$$

$$Al(OR)_3 + 3H_2O \longrightarrow Al(OH)_3 + 3ROH \tag{4}$$

$$ROH \longrightarrow H_2O + \text{olefin} \tag{5}$$

$$2Al(OH)_2 \longrightarrow Al_2O_3 + 3H_2O \tag{6}$$

The reaction actually follows the stoichiometry of 3 most closely. Heating of aluminum *t*-butoxide at 166° for 24 hr. to ensure complete decomposition gives a residue with the weight calculated for aluminum hydroxide. No water can be detected gas chromatographically. Aluminum ethoxide gives only 2.7% of ethanol, with a preponderance of ethylene and a trace of acetaldehyde. Moreover, the rate data yield straight line pseudo-first-order plots when weight loss is taken to be olefin. Finally, the rate of decomposition of aluminum *t*-butoxide is greater than that for dehydration of the alcohol. The small amounts of alcohol formed at higher temperatures may be due to hydrolysis (4) following dehydration of aluminum hydroxide (6). At low temperatures (177° for aluminum ethoxide and isopropoxide) rate data were erratic, and no olefin could be detected gas chromatographically. The controlling factor in this case seems to be diffusion of water vapor into the system, in the absence of an outgoing stream of olefin gas, resulting in hydrolysis (4).

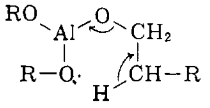
While no precise temperature control was applied during pyrolysis of the higher primary alkoxides (Table II), the temperature at which pyrolysis begins in each case should be approximately the same (intermediate between the boiling point of the olefin and of the alkoxide) for homologous compounds. Minor differences in the terminal to internal olefin ratio therefore probably are not a reflection of differences in the pyrolysis temperature. Each of the alkoxides used in the kinetic study was chosen because it can form only a single olefin (neglecting thermodynamically unfavorable rearrangement of the *t*-butyl group).

At the time this work was begun, it seemed probable that comparison of olefin mixtures formed by alkoxide pyrolysis with those reported in the literature for alumina catalyzed dehydration would prove fruitful in establishing a relationship between the two reactions. Recent articles by Pines and co-workers[13] have demonstrated that basicity of the catalyst and the method of preparation markedly affect the composition of the olefin mixtures produced. No data are presently available for alumina from alkoxide pyrolysis; a completely conclusive comparison must be deferred until such data are secured. It is a reasonable assumption that results will not differ too much from those obtained using alumina from alkoxide hydrolysis. A number of striking similarities may be noted.

The ratio of terminal to internal olefins formed from primary alcohols has been the subject of several investigations.[13a,14] In general, the unrearranged olefin predominates. For the unbranched five to seven carbon alkoxides, the ratio of internal to terminal olefins formed varied from 18:82 to 24:76 (Tables I and II). It is obvious that 18–24% rearrangement occurred. Since 1-pentene only rearranged to 1–2% of 2-pentene on heating at 200° for 15 min. with partially decomposed aluminum isopropoxide, rearrangement must have occurred during reaction. Aluminum 2-methyl-1-butoxide forms 66% of terminal olefins, 38% 3-methyl-1-butene and 28% 2-methyl-1-butene. Since the equilibrium mixture (Table IV) of 2-methyl-2-butene to 2-methyl-1-butene is 3.1/1, migration of the double bond down the chain cannot account for the rearranged product. Migration of a methyl group must, therefore, have occurred, presumably *via* a carbonium ion. Evidence for carbonium ion formation in alumina catalyzed dehydration includes formation of dimethylcyclopropanes.[13] Small amounts (< 1%) of unidentified low boiling products were usually observed on the gas chromatograms. It is tempting to assume that they were dimethylcyclopropanes, but no effort was made to identify them.

A second point of similarity between the pyrolysis and catalytic dehydration was observed with secondary alcohols. For example, 2-pentanol on alumina gives 34% of 1-pentene, 3-pentanol 2.5–5.8%; aluminum 2-pentoxide gives 35% of 1-pentene, aluminum 3-pentoxide 1.5%. Finally, the activation energy for ethanol dehydration[8] is 14.5 kcal., compared to 14.6–18.8 kcal. for pyrolysis of aluminum ethoxide. The possibility remains that the reactions are related by virtue of a two-step hydrolysis–dehydration mechanism as proposed for zirconium alkoxides,[9] but since the kinetic data show no autocatalysis and a faster rate for *t*-butoxide pyrolysis, it must be considered remote.

From the information presently available, some tentative conclusions regarding the nature of the transition stage for alkoxide pyrolysis can be drawn. The entropy of activation is positive, but shows a marked variation with structure, ranging from 34 e.u. for aluminum *t*-butoxide to 18 e.u. for the isopropoxide to 7 e.u. for the ethoxide, strongly suggesting a transition state less organized than the initial molecule. A positive entropy



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change apparently is not consistent with a cyclic mechanism (see the mechanism in col. 2, p. 909) involving basic attack by oxygen on a β-hydrogen, nor with a similar bimolecular process. It is consistent with an ionic mechanism involving formation of a free carbonium ion. However, the limited extent of rearrangement discourages consideration of the latter as a unique pathway.

A more appealing explanation is that polymeric alkoxides tend to dissociate in a rate determining step, followed by a relatively rapid cyclic elimination reaction. Alkoxides with bulkier alkyl groups should form less stable polymers, with a greater degree of dissociation in the transition state. Freeing an electron pair of the oxygen atom from a bond with aluminum should greatly augment the basicity of the oxygen atom and facilitate cyclic elimination.

Alkali metal alkoxides are not able to undergo elimination unimolecularly through a five- to six-member ring. Since the oxygens are bonded covalently to one aluminum atom and are coördinated with a second in the polymeric alkoxide, aluminum alkoxides must be somewhat weaker bases then the corresponding sodium or potassium alkoxides. In accordance with this lessened basicity, the aluminum alkoxide is less likely to displace a carbanion, and reversal of the Grignard reaction does not take place, at least in the case of the *t*-butoxide, as contrasted to the formation of acetone from potassium *t*-butoxide.

The combination of these two factors, the greater ease of cyclic olefinic elimination from aluminum alkoxides and the greater basicity of alkali metal alkoxides, must lead to formation of olefin uncontaminated with aldehyde or ketone.

Transmission of Electronic Effects by the Cyclopropane Ring. Rates of Alkaline Hydrolysis of Ethyl *cis*- and *trans*-2-Phenylcyclopropanecarboxylates

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Received December 5, 1961

The rates of alkaline hydrolysis of a series of *m*- and *p*-substituted ethyl β-phenylpropionates and of ethyl *trans*- and *cis*-2-(substituted phenyl)cyclopropanecarboxylates in 87.8% ethanol at 30° have been measured. A comparison of Hammett ρ-values for these series, ethyl *cis* and *trans* cinnamates, and ethyl phenylpropiolates indicates that the influence of substituents on the reactivity increases in the six ester series in the order listed.

The relative abilities of the cyclopropane ring and the saturated dimethylene group ($-CH_2CH_2-$) to transmit electronic effects has been a continued subject of controversy. The chemical and physical evidence available in 1958 has been summarized in an article[1b] reporting the ionization constants of a series of β-phenylpropionic and *trans*-2-phenylcyclopropanecarboxylic acids. This work suggested that the three-membered ring is no better than the dimethylene group in transmitting electronic effects, in agreement with certain earlier evidence, but opposing other information. More recent information has also supported both sides of the question. The lack of hydrogen exchange and carbanion addition reactions involving diethyl 2-methylcyclopropane-1,1-dicarboxylate[2] led to the conclusion that the cyclopropane ring is poor in transmitting electronic effects to a methyl substituent β to electron withdrawing groups. In the solvolysis of *cis*- and *trans*-2-phenylcyclopropylcarbinyl β-naphthalenesulfonates and cyclopropylcarbinyl β-naphthalenesulfonate[3] rate differences were found to be fairly small, and it was concluded that little positive charge is dispersed in the transition state.

Evidence supporting the conjugative properties of the cyclopropane ring has been obtained from Raman line intensities,[4] and from the solvolysis of some cyclopropylisopropylcarbinyl *p*-nitrobenzoates,[5] wherein the three-membered ring has a strong rate-enhancing effect. Stabilization of the transition state due to the considerable π-bond character of the cyclopropane ring has been cited as the reason for the high rate of solvolysis of *p*-cyclopropyl-α,α-dimethylbenzyl chloride compared to other *p*-cycloalkyl substituted compounds.[6] Conjugation of the cyclopropane ring with the carbon–carbon double bond of α-cyclopropylstyrene apparently accounts for the 1,5 conjugate addition of maleic anhydride.[7] Recent measurements in this laboratory of the ionization constants of a series of *m*- and *p*-substituted β-phenylpropionic, *cis*- and *trans*-2-phenylcyclopropanecarboxylic acids[8] in 50% ethanol are in disagreement with Trachtenberg's earlier measurements[1b] in water; the ionization constants of the latter two acids are appreciably more affected by substituent changes than is the former, thus supporting the transmitting ability of the cyclopropane ring. A preliminary report[9] of the rates of hydrolysis of a series of ethyl *trans*-2-phenylcyclopropanecarboxylates indicated that in this case, also, the cyclopropane ring is superior to the dimethylene group. In the present paper the complete results of this investigation are reported along with similar data for the *cis* compounds and a series of ethyl β-phenylpropionates.

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