Chemical and Physical Properties

In this section, we discuss the safety aspects of the chemical and physical properties of organometallics. Aluminum alkyls are used as representative of many highly reactive organometallic alkyls in commercial use. While these alkyls have many chemical properties which are described in detail in the literature, here we describe only those properties which are essential for safe handling: their reaction with air and water, and their behavior under thermal stress.

Reactivity towards air

When aluminum alkyls come into contact with air, vigorous oxidation and decomposition reactions immediately take place. The heat of reaction is so high for the lower aluminum alkyls, with 1 to 6 carbon atoms per alkyl group, that self-ignition usually takes place.

The heat released during the combustion of aluminum alkylsis similar to that released during the combustion of hydrocarbons. In this reaction aluminum trialkyls and dialkylaluminum hydrides produce aluminum oxide, water and carbon dioxide. In addition to these products, hydrogen chloride is formed on the combustion of alkylaluminum chlorides. which dissolves in water to give hydrochloric acid.

$(C_2H_5)_3Al$	$+ 10.5\ O_2$	$\rightarrow 0.5\ Al_2O_3$	$+ 7.5\ H_2O$	$+ 6\ CO_2$	
$(i\text{-}C_4H_9)_2AlH$	$+ 13.5\ O_2$	$\rightarrow 0.5\ Al_2O_3$	$+ 9.5\ H_2O$	$+ 8\ CO_2$	
$(C_2H_5)_{32}AlCl$	$+ 7.0\ O_2$	$\rightarrow 0.5\ Al_2O_3$	$+ 4.5\ H_2O$	$+ 4\ CO_2$	$+HCl$

The violence of the oxidation reaction can be reduced by diluting with an inert solvent. Under controlled conditions the oxidation can be guided in a way that the reactions do not proceed beyond the alkoxide stage.

R_3Al	$+ 1.5\ O_2$	$\rightarrow (RO)_3Al$	
$2\ R_2AlH$	$+ 2.5\ O_2$	$\rightarrow [(RO)_2Al]\ _2O$	$+ H_2$
R_2AlCl	$+ 1.0\ O_2$	$\rightarrow (RO)_2AlCl$	

The oxidation reactions proceed stepwise and only partially if the available oxygen is limited.

R_3Al	$+ 0.5\ O_2$	$\rightarrow R_2AlOR$	
$2\ R_2AlH$	$+ 0.5\ O_2$	$\rightarrow (R_2Al)_2O$	$+ H_2$
R_2AlCl	$+ 0.5\ O_2$	$\rightarrow RAL(OR)Cl$	

Due to the high reactivity of aluminum alkyls, inert aromatic or saturated aliphatic hydrocarbons are typically used as solvents. The danger associated with hydrocarbons is further increased by dissolved aluminum alkyl, because the heat given off by the oxidation when a leak occurs will increase solvent evaporation. Even highly diluted aluminum alkyl solutions must be handled under inert gas, in order to prevent oxidation in air and the resultant loss in quality of the product.

Reactivity towards water

Aluminum alkyls react even more vigorously with water than with air. The extremely violent and highly exothermic decomposition of the lower aluminum alkyls releases a large quantity of highly flammable gases immediately. As the temperature increases further decomposition reactions take place.

The violence of the hydrolysis reaction can also be reduced by diluting with an inert solvent. Under controlled conditions aluminum trialkyls give aluminum hydroxide and the corresponding alkane; dialkyl aluminum hydrides hydrogen is liberated as well. Alkyl aluminum chlorides are hydrolyzed to alkanes and aluminum chlorides. The latter react at increased temperature to form hydrochloric acid and aluminum hydroxide.

R_3Al	$+ 3\ H_2O$	$\rightarrow Al(OH)_3$	$+ 3\ RH$	
R_2AlH	$+ 3\ H_2O$	$\rightarrow Al(OH)_3$	$+ 2\ RH$	$+ H_2$
R_2AlCl	$+ 3\ H_2O$	$\rightarrow Al(OH)_3$	$+ 2\ RH$	$+ HCl$

As with oxidation, hydrolysis takes place in distinct steps, and is only partial with small amounts of water.

$2\ R_3Al$	$+ H_2O$	$\rightarrow (R_2Al)_2O$	$+ 2\ RH$
$2\ R_2AlH$	$+ H_2O$	$\rightarrow (R_2Al)_2O$	$+ 2\ H_2$
$2\ R_2AlCl$	$+ H_2O$	$\rightarrow (RClAl)_2O$	$+ 2\ RH$

Commercially available aluminum alkyls are stable at normal storage temperatures when stored in tightly closed, special containers under inert gas. We use nitrogen as the inert gas for transporting aluminum alkyls.

If aluminum alkyls contain carbon atoms in the β-position withhydrogen, olefins can be split off via intra molecular β-hydride elimination at elevated temperatures. The temperature at which this process begins - defined by us as the “thermal limit of product grade" - depends on the particular alkyl. Triisobutylaluminum is particularly sensitive to temperature, decomposing at about 60° C with the loss of isobutene to give diisobutylaluminum hydride.

$$(i\text{-}C_4H_9)_3Al \rightleftarrows (i\text{-}C_4H_9)_2AlH + i\text{-}C_4H_8$$

In aluminum alkyls with non-branched hydrocarbon chains elimination usually does not take place until higher temperatures are reached. However, this limit temperature drops as the chain length of the alkyl groups increases. Triethylaluminum does not eliminate olefin until 120° C, tributylaluminum at 100° C, and trioctylaluminum is only about 80 ° C.

Even at elevated temperatures this elimination reaction proceeds in a controllable manner.

If triisobutylaluminum is heated in a closed container so that no isobutene can escape, methane are other products are formed. If dialkylaluminum hydrides are subjected to heat, they decompose, releasing hydrogen and generating aluminum. Diisobutylaluminum hydride begins to decompose at a temperature of about 120 ° C. This decomposition proceeds rapidly at temperatures over 200° C at atmospheric pressure.

$$(i\text{-}C_4H_9)_2AlH \rightarrow Al + 1.5\ H_2 + 2i\text{-}C_4H_8$$

Alkylaluminum chlorides are thermally more stable. Diethylaluminum chloride does not begin to decompose until a temperature of about 170 ° C is reached; ethylaluminum dichloride at about 140 ° C.

Decomposition reactions of aluminum alkyls can be catalyzed by impurities. This can cause a considerable reduction in the decomposition temperature. This catalytic effect is well known from the chemistry of finely divided metals, from aluminum or titanium, and from metallic salts.

Health Hazards

Aluminum alkyls cause severe burns when allowed to come into contact with skin. This effect is reduced with increased dilution in an inert solvent, but even highly diluted solutions can be hazardous. The harmful effect of the solvent should also be taken into account. Poisoning through adsorption of aluminum alkyls is highly improbable.

During burning of trialkylaluminums, dialkylaluminum hydrides, or their solutions, fumes containing aluminum oxide are produced. These fumes can cause irritation and inflammation of the respiratory tract, sometimes called “metal fume fever.”

The fumes produced from alkylaluminum halides or their solutions contain aluminum oxyhalides and hydrogenhalides which are particularly dangerous. Hydrogen bromide and particularly hydrogen iodide decompose partly into the elements even at moderately high temperature. The fumes which are produced by the decomposition reaction of aluminum alkyls in air, without burning taking place, are as hazardous as smoke from a fire. Furthermore, fumes resulting from the decomposition of aluminum solutions also contain solvent vapor.

References

Descriptions of the reactivity of aluminum alkyls can be found in greater detail in the following literature:

H.Lehmkuhl, K. Ziegler and H.G.Gellert: Methoden zur Herstellung und Umwandling von Organischen Aluminum-Verbindungen, in Methoden der Organischen Chemie (Houben-Weyl), Volume XIII/4, pp. 1 -314, Georg Thieme Verlag, Stuttgart (1970)

T.Mohle and E.A.Jeffrey Organoaluminum Compounds, Elsevier Publishing Company, Amsterdam-London-New York (1972)

K.H.Müller: Organische Aluminum-Verbindungen, in Ullmanns Encyklopädie der technischen Chemie, Volume 7, pp. 343 -350, Verlag Chemie, Weinheim (1973)

J.J. Ligi and D.B.Malpass: Aluminum Alkyls, in Encyclopoedia of Chemical Processing and Design, Volume 3, pp. 1-56, Marcel Dekker, New York and Basel (1977)

D.B.Malpass, L.W.Fannin, J.J.Liggi: Organometallics, Aluminum, in Kirk-Othmer, Encyclopoedia of Chemical Technology, Third Edition, Volume 16, pp. 565 -572, Jon Wiley & Sons, New York-Chichester-Brisbane-Toronto-Singapore (1981)

J.J.Eisch: Aluminum, in Comprehensive Organometallic Chemistry, Volume 1 , pp. 555 - 682, Pergamon Press, Oxford-New York-Toronto-Sydney-Paris-Frankfurt (1982)

J.R.Zietz, Jr., G.C.Robinson and K:L:Lindsay: Compounds of Aluminum in Organic Synthesis, in Comprehensive Organometallic Chemistry, Volume 7, pp. 365-464, Pergamon Press, Oxford-New York-Toronto-Sydney-Paris-Frankfurt (1982)

J.R.Zietz, Jr.: Aluminum Compounds, Organic, in Ullmann's Encyclopoedia of Industrial Chemistry, Volume A 1, pp. 543-556, VCH-Verlagsgesellschaft, Weinheim-Deerfield Beach-Base