tetroxide in 1,4-dioxane there is no tendency toward polymerization. In the range up to 0.1 molal, X is equal to unity ±10%. The very slight upward trend at the two higher concentrations reflects the fact that as the concentration of dinitrogen tetroxide increases an appreciable partial pressure of dinitrogen tetroxide above the solution develops. This fact in addition to the general limitations of cryoscopy for molecular weight determinations limited our measurements to dilute solutions.

On the basis of the cryoscopic and viscosimetric data reported herein we may conclude that there is little basis for postulating a polymeric, chain-type structure for the compound $N_2O_4 \cdot 1,4\text{-}O(CH_2CH_2)_2O$.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

Some Reactions of the Etherate of Aluminum Triethyl[1]

BY EVELYN BLUST BAKER AND HARRY H. SISLER

RECEIVED JUNE 19, 1953

The preparation of sodium aluminum tetraethyl and lithium aluminum tetraethyl by the reaction of the corresponding alkali metal alkyl with the etherate of aluminum triethyl has been carried out. The reactions of this etherate with pyridine to give the compound $Al(Et)_3 \cdot C_5H_5N$, and with sulfur dioxide to give the aluminum salt of ethylsulfinic acid were studied. It was also found that the etherate of aluminum triethyl reacts with dinitrogen tetroxide to give a product which upon hydrolysis yields N,N-diethylhydroxylamine; with nitric oxide to give a product which is believed to hydrolyze to ethylnitrosohydroxylamine; and gives little, if any, reaction with carbon dioxide.

Though the compound aluminum triethyl has been known for almost a century, literature concerning its chemistry is rather sparse, presumably because of its extreme reactivity. The etherate of this compound, first prepared about thirty years ago,[2] is also very reactive but is less so than aluminum triethyl itself. We were interested, therefore, in observing some of the reactions of the etherate to see if it gives the same sort of reactions as would be expected for free aluminum triethyl.

Furthermore, no synthetic details for the compounds lithium aluminum tetraethyl and sodium aluminum tetraethyl have ever been published,[3] and in view of the current interest in alkyl derivatives of aluminum and boron it seemed desirable to us to investigate the synthesis of these compounds.

The present report includes the results of the investigation of the reactions of the etherate of aluminum triethyl with lithium ethyl, sodium ethyl, sulfur dioxide, dinitrogen tetroxide, nitric oxide, carbon dioxide and pyridine.

Experimental

General Precautions.—Since the alkali metal alkyls, the etherate of aluminum triethyl, and many of reaction products of these compounds react rapidly with water and air, these materials were prepared, purified, stored and sampled in a dry, inert atmosphere, usually nitrogen, except in the case of lithium ethyl where helium was used. The nitrogen and helium were purified and dried by passing successively through Fieser's solution, lead acetate solution, concd. sulfuric acid, Ascarite, Drierite and a phosphorus (V) oxide–sand mixture. Because of the reactivity of metal alkyls toward organic matter, all-glass equipment was used in these experiments, lubricated very sparingly with Silicone high-vacuum stopcock grease.

Preparation of the Etherate of Aluminum Triethyl.—This compound was prepared by the procedure of Kraus and Wendt[2] and of Hurd[4] in which anhydrous aluminum chloride is caused to react with ethylmagnesium bromide in ether solution and the product distilled under vacuum. A good yield of halide-free product having the composition $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$[5] was obtained.

Preparation and Properties of Sodium Aluminum Tetraethyl.—Sodium ethyl prepared[6,7] from 10 g. of sodium and 20 g. of mercury diethyl in 150 ml. of petroleum ether (65–100° fraction) was cooled in an ice-bath, and 41 ml. (a slight excess) of the etherate of aluminum triethyl was added dropwise with stirring. The funnel was rinsed with 50 ml. of petroleum ether and stirring continued for three hours. The solution was then filtered and the residue washed with 150 ml. of petroleum ether. The solvents were distilled off, using an oil-bath to heat the flask, and the bath temperature was kept at 110° for 10 min. after distillation had stopped. The contents were then heated under vacuum for 30 min. with the bath at 110°. This additional heating seemed necessary to remove the ethyl ether from the sodium aluminum tetraethyl. The mixture was then cooled, 150 ml. of benzene added, the mixture refluxed for one hour and filtered while hot. The benzene was then distilled off until approximately 100 ml. of the solution remained. As the solution was allowed to stand, crystals separated. Crystallization sometimes was slow, several days being required. The mixture was then cooled to 10° and filtered, washed twice with 15-ml. portions of benzene and twice with 15-ml. portions of petroleum ether and dried under vacuum. If the crystals were yellow they were recrystallized again from benzene. The yield after two recrystallizations was about 10 g., or 40% of theory.

Sodium aluminum tetraethyl is a white, crystalline solid which reacts violently with water, decomposing to oxide and hydroxide with gas evolution. It is highly soluble in diethyl ether, much less soluble in benzene, and still less soluble in petroleum ether. It melts, without sublimation, *in vacuo* at about 125°. Two preparations were analyzed for aluminum as the 8-hydroxyquinolate and for sodium as the sulfate. Calcd. for $NaAl(C_2H_5)_4$: Na, 13.84; Al, 16.23. Found: Na, 13.89, 14.02; Al, 16.11, 16.18.

Preparation and Properties of Lithium Aluminum Tetraethyl.—Lithium ethyl was prepared[8] in 350 ml. of petroleum ether (30–60° fraction) from 4.5 g. of lithium sand and 15 ml. of ether-free ethyl bromide. To this was added dropwise, with stirring, 41 ml. of the etherate of aluminum triethyl. The funnel was rinsed with 50 ml. of petroleum ether. Three hundred ml. of benzene was then added and

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[1] Taken from the Ph.D. dissertation of E. B. Baker, The Ohio State University, 1953.

[2] E. Krause and B. Wendt, *Ber.*, **56B**, 466 (1923).

[3] Grosse and Mavity reported at the 96th Meeting of the American Chemical Society, September, 1938, that they had prepared $LiAlEt_4$, $NaAlEt_4$ and $KAlEt_4$ by the reaction of $Al(Et)_3$ with either the alkali metal or the alkali metal alkyl, but gave few experimental details and the work has not yet been published.

[4] D. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

[5] E. B. Baker and H. H. Sisler, THIS JOURNAL, **75**, 4828 (1953).

[6] F. Whitmore and H. Zook, *ibid.*, **64**, 1783 (1942).

[7] H. Gilman and R. Young, *J. Org. Chem.*, **1**, 315 (1936).

[8] T. Perrine and H. Rapoport, *Anal. Chem.*, **20**, 635 (1948).

all of the petroleum ether distilled off. The solution was filtered while hot. Benzene was distilled off until about 75 ml. of solution remained. The solution was cooled to about 10° and the benzene was filtered from the crystals. The crystals were washed three times with 50-ml. portions of cold petroleum ether and dried under vacuum. The yield was about 9 g. or 35% of theory.

Lithium aluminum tetraethyl as prepared above is a white solid, which forms needle-like crystals, radiating from a central point and appearing under the microscope as smooth, round rods. It is similar in properties and solubility to the sodium compound except that it melts with sublimation *in vacuo* at about 160°. Three preparations were analyzed for aluminum as the 8-hydroxyquinolate, and for lithium as the sulfate. Calcd. for $LiAl(C_2H_5)_4$: Li, 4.62; Al, 17.96. Found: Li, 4.48, 4.66, 4.69; Al, 17.42, 17.42, 17.86.

Reaction of $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$ with Pyridine.—Approximately 5 ml. of the etherate of aluminum triethyl was distilled under vacuum into a flask containing a magnetic stirring bar and cooled to about −75°. Fifty ml. of pyridine was added with stirring. The reaction mixture was allowed to warm to room temperature and the excess pyridine distilled off under vacuum at room temperature until the residue in the flask was losing weight at a constant and very slow rate. The product was an amber colored liquid which decomposed, becoming bright red and precipitating a solid, before boiling under atmospheric pressure. The freezing point was found to be around −40°. Aluminum was determined as the 8-hydroxyquinolate, and pyridine by distillation from a highly alkaline solution into excess standard acid and back-titration with standard base, using a *p*H meter to detect the equivalence point. Calcd. for $Al(C_2H_5)_3 \cdot C_5H_5N$: Al, 13.96; C_5H_5N, 40.93. Found: Al, 14.24; C_5H_5N, 40.2.

Reaction of $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$ with Sulfur Dioxide.—An excess of dry sulfur dioxide was condensed at about −75° on a small amount of the etherate of aluminum triethyl which was stirred by a magnetic stirring bar. A greenish-yellow crystalline solid formed. The excess sulfur dioxide was vaporized by allowing the flask to warm to room temperature. No liquid remained. Dry nitrogen was passed over the solid product until no noticeable odor remained. The product was then dried overnight under vacuum. The product is white, crystalline, soluble in water, and rapidly gains weight in air. Calcd. for $Al(O_2SC_2H_5)_3$: Al, 8.80; S, 31.40; C, 23.52; H, 4.94. Found: Al, 8.80, 9.02; S, 31.51, 31.12; C, 23.38, 23.42; H, 4.99, 4.94.

Diethyl sulfone ($C_2H_5SO_2C_2H_5$) and 1,2-di-(ethylsulfonyl)-ethane ($C_2H_5SO_2C_2H_4SO_2C_2H_5$) were made from the product using a modification of Allen's procedure.[9] Attempts to use the aluminum salt in *n*-butyl alcohol or *n*-propyl alcohol were unsuccessful. However, after conversion to the sodium salt successful preparations of the derivatives were obtained in ethyl alcohol. The melting point of the diethyl sulfone was 71° and of the 1,2-di-(ethylsulfonyl)-ethane was 136° which are within one degree of literature values.

Reaction of $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$ with Dinitrogen Tetroxide.—A flask containing 25 g. of the etherate of aluminum triethyl and 250 ml. of diethyl ether was cooled to about −75° and, while stirring with a magnetic stirrer, approximately 5 g. of purified[10] dinitrogen tetroxide was condensed in the solution. At times a white solid collected on the cool sides of the flask. When this solid was warmed with the fingers, white fumes appeared. Occasionally, a bluish-green solid appeared on the sides and once the entire solution became bluish-green, but this color quickly disappeared. The solution was yellow-brown at the end of the run. The flask was allowed to warm to room temperature open to the air through a drying tube. It then was cooled in an ice-bath and the excess etherate hydrolyzed, using a minimum amount of water. The paste which resulted was made strongly basic with potassium hydroxide and extracted with diethyl ether in a continuous extractor. The ether extract was dried several days over barium oxide, the barium oxide filtered out, and the ether distilled off. Approximately 5 g. of crude product remained. This was vacuum-distilled, the receiver being cooled to −75°.

The product was identified as N,N-diethylhydroxylamine. It was a clear, colorless liquid, b.p. 132–134° (lit. 130–134°), m.p. −8 to −15° (lit. *ca.* −10°). The compound was soluble in ether and soluble in water to give a slightly alkaline solution. It reduced ammoniacal silver nitrate. *Anal.* Calcd. for $(C_2H_5)_2NOH$: C, 53.89; H, 12.44; N, 15.72. Found: C, 53.72, 53.93; H, 11.82, 11.89; N, 14.70, 14.93. The oxalate derivative was prepared and was found to have a m.p. of 135–138° (lit. 137–139°). Some of the analytical values are poor because it was not realized at the time that the material had partly decomposed from standing. Therefore to verify the identification some N,N-diethylhydroxylamine was prepared from diethylamine and hydrogen peroxide and the infrared spectra of the two preparations compared. The spectra were essentially the same, but each sample contained a small amount of impurity not present in the other.

Reaction of $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$ with Nitric Oxide.—Purified nitric oxide[11] was bubbled through 20 ml. of the etherate of aluminum triethyl in 200 ml. of ether. It was found that the reaction was very slow. In the most successful run, nitric oxide (0.6 mole) was bubbled through for 7.5 hr. and the mixture allowed to stand overnight, and even in this case, all the starting material had not reacted. The reaction mixture, after standing, was diluted with ether, cooled in an ice-bath, hydrolyzed with ice-water, acidified with 1:1 sulfuric acid, and extracted with ether. Since it was suspected that ethylnitrosohydroxylamine is produced in this reaction, a small amount of the ether extract was tested for nitroso groups by the Liebermann nitroso test. A positive test was obtained but it lasted only a few seconds.

Treatment of the ether extract or of a benzene extract of the original reaction mixture with freshly precipitated hydrous cupric oxide yielded purple, needle-like crystals of a copper derivative which was extremely soluble in benzene, less soluble in ether and even less soluble in water, and which decomposed when warmed. After recrystallizing from water, the substance was subjected to micro-combustion analysis, the copper being estimated from the ash left from the ignition. One old report[12] in the literature lists this copper salt of ethylnitrosohydroxylamine as containing one-half mole of water of crystallization when crystallized from water. Calcd. for $Cu[O(ON)NC_2H_5]_2$: C, 19.87; H, 4.17; N, 23.18; Cu, 26.30. Calcd. for $Cu[O(ON)NC_2H_5]_2 \cdot {}^1/_2H_2O$: C, 19.16; H, 4.42; N, 22.34; Cu, 25.35. Found: C, 20.04; H, 4.18; N, 23.09; Cu, 25.62. It thus appears likely, but is not conclusive, that the etherate of aluminum triethyl slowly reacts with nitric oxide to yield a solution which undergoes hydrolysis to yield the rather unstable compound ethylnitrosohydroxylamine.

Reaction of $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$ with Carbon Dioxide.—Pure, dry carbon dioxide was bubbled through liquid $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$ at temperatures between 25 and 100° for periods of time up to several days. In every case a small amount of solid formed about the inlet tube, but most of the etherate remained unchanged. The solid appeared, upon acidification, to yield acetic acid, but the quantities of material involved were so small as to make the distinction between acetate and other possible products, as *e.g.*, propionate, very difficult.

Discussion

The reactions of the etherate of aluminum triethyl with lithium ethyl, sodium ethyl and with pyridine can be interpreted simply as the displacement of the base ethyl ether from its union with the acid aluminum triethyl by the stronger bases ethide ion and pyridine

$$(C_2H_5)_3Al{:}O(C_2H_5)_2 + {:}C_2H_5^- \longrightarrow Al(C_2H_5)_4^- + (C_2H_5)_2O$$

$$(C_2H_5)_3Al{:}O(C_2H_5)_2 + C_5H_5N{:} \longrightarrow (C_2H_5)_3Al{:}NC_5H_5 + (C_2H_5)_2O$$

The reaction of the etherate with sulfur dioxide is quite analogous to the reaction of a Grignard reagent with sulfur dioxide. In this connection, it seems somewhat strange that the etherate of aluminum triethyl should show such a pronounced reluctance to react with carbon dioxide.

In its reactions with nitric oxide and dinitrogen

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[9] P. Allen, Jr., *J. Org. Chem.*, **7**, 23 (1942).

[10] W. Giauque and J. Kemp, *J. Chem. Phys.*, **6**, 10 (1938).

[11] H. Johnston and W. Giauque, THIS JOURNAL, **51**, 3194 (1929).

[12] E. Frankland, *Ann.*, **99**, 345 (1856).

tetroxide, the etherate of aluminum triethyl exhibits the reducing properties which are characteristic of metal hydrides and alkyls.

The general trend of the results reported herein indicates that the etherate of aluminum triethyl should be a convenient substitute for the free aluminum triethyl, since the etherate behaves in a manner to be expected for metal alkyls, but is less difficult to handle.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHEASTERN UNIVERSITY]

Acids and Bases. IX. Conductance of Aluminum Bromide and Stannic Chloride in Thionyl Chloride on Addition of Pyridine and Quinoline[1]

BY LEON E. D. PEASE, JR., AND W. F. LUDER

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Conductance curves are presented for the addition of the bases pyridine and quinoline to the acids aluminum bromide and stannic chloride dissolved in thionyl chloride. Explanations for the differing shapes of the curves are suggested.

I. Introduction

In an earlier paper of this series[2] the behavior of aluminum chloride, ferric chloride and stannic chloride as acid catalysts in the reaction of metals with thionyl chloride according to the electronic theory of acids and bases[3] was described. This paper reports additional properties of two aprotic acids in the same aprotic solvent, as determined by the methods of Van Dyke and Kraus.[4]

II. Experimental

Materials.—C.P. aluminum bromide and stannic chloride were distilled into weighed, fragile bulbs, employing the technique of Kraus and Nelson.[5] Pyridine was purified according to the method of Burgess and Kraus.[6] Quinoline was fractionated off aluminum oxide. Thionyl chloride was purified as in the previous paper.[2] The specific conductance of that used in runs was between 5×10^{-8} and 12×10^{-8} mho.

Apparatus.—The bridge has been described previously.[7] The cell was constructed from a 250-ml. erlenmeyer flask employing the method of Hnizda and Kraus.[8] It was fitted with a ground cap, into which a 5-ml. micro-buret was sealed. A side arm was attached, through which the cell could be evacuated and filled with dry nitrogen. The cell constant was 0.3926. An oil thermostat was employed to maintain the temperature of the cell at $25 \pm 0.01°$.

Procedure.—After the estimated amount of thionyl chloride for a concentration between 0.05 and 0.2 molal was weighed in the cell, a fragile bulb containing a weighed amount of acid was dropped in. Usually the bulb broke with the impact; if it did not, it was crushed with a glass tube. Because considerable heat was evolved during the solution of aluminum bromide, the cell was cooled in ice before the ampule was added. A tube from a source of dry nitrogen was attached to the side arm, so that whenever the cell was open a slow stream of nitrogen flowed out the top.

The micro-buret, filled with liquid base through the tip, was then attached to the cell. After the cell had been in the thermostat for 10 minutes the first increment of base was added. For 30 seconds, the cell was agitated to mix the solution without removing from the thermostat. The final resistance reading was taken four minutes from the time the base was added.

III. Results

Although many more runs were made, typical results obtained by this procedure are shown in Figs. 1–4.

Early in the investigation it was noted that the resistances on the far acid side (left) of the break-point shown in the figures changed slowly with time, although they became constant close to the break-point and were constant on the basic side. Therefore several time runs were made using a fixed concentration of either acid or base alone in the solvent. The resistance of the basic solutions remained constant. The resistances of the acid solutions decreased about 100% over a period of several hours before coming to a constant value.

Several addition runs were then made over different time intervals, some as rapidly as possible and others over periods of 12 hours or more. In all the runs the break occurred at the same mole ratio for a given pair.

Apparently, a slow reaction occurs between the acid and the solvent. The slowness of this reaction is not entirely unexpected, because of the high acidity of the solvent, as indicated by the curves in Figs. 1–4 and by the previous investigation.[2] However, the fact that the same break is obtained and that the resistances become constant as the break is approached and remain so on the basic side indicates that the reaction between the acid and the base takes precedence over the reaction of the acid with the solvent, as is to be expected. Consequently, when readings are taken at similar time intervals for a given acid and base, rapid runs can be made, from which smooth curves, all showing a break at the same ratio, are obtained.

When aluminum bromide is added to thionyl chloride a deep red color is produced, which disappears as the break-point is approached at a 1–1 molal ratio of base to acid. No precipitate is formed during the addition of base. On the other hand, when either base is added to stannic chloride solution a white precipitate is formed.

IV. Conclusion

The shape of the curves in Fig. 1 may be explained as follows. Addition of pyridine to the aluminum bromide solution first forms the addition

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[1] Abstracted from a thesis submitted by Leon E. D. Pease, Jr., to the faculty of Northeastern University in partial fulfillment of the requirements for the M.S. degree, June, 1952.

[2] R. A. Hubbard, Jr., and W. F. Luder, THIS JOURNAL, **73**, 1327 (1951).

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[4] R. E. Van Dyke and H. E. Crawford, THIS JOURNAL, **73**, 2022 (1951), and the preceding papers in the series.

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[6] D. S. Burgess and C. A. Kraus, *ibid.*, **70**, 706 (1948).

[7] W. F. Luder, *Rev. Sci. Instruments*, **14**, 1 (1943).

[8] V. F. Hnizda and C. A. Kraus, THIS JOURNAL, **71**, 1565 (1949).