

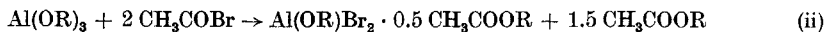
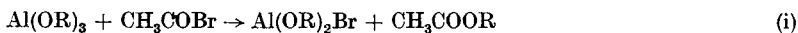
## Bromide Alkoxides of Aluminium

By R. C. MEHROTRA and R. K. MEHROTRA

### Summary

The reactions between aluminium alkoxides (methoxide, ethoxide, isopropoxide, n, sec. and tert. butoxides) and acetyl bromide has been studied and the compounds of the type:  $\text{AlBr}(\text{OR})_2$ ,  $\text{Al}(\text{OR})\text{Br}_2 \cdot 0.5 \text{CH}_3\text{COOR}$  and  $\text{AlBr}_3 \cdot 1.5 \text{CH}_3\text{COOR}$ , where OR is OMe, OEt, OPr<sup>t</sup>, n, sec. or tert. OBu, have been isolated. The reaction of aluminium tert. butoxide and acetyl bromide was found to be very slow in cold as well as in boiling condition. The above compounds were crystallised from their respective alcohols, wherever possible. The ease with which these compounds exchange their radicals has been demonstrated by the reaction between tri-bromide and mono-bromide di-isopropoxide, in isopropanol, whereby the di-bromide was crystallised out. These bromide alkoxides are not stable to heat, even under reduced pressure.

Considerable amount of work has been done on the preparation and properties of chloride alkoxides of aluminium<sup>1-3</sup>), but very little work appears to have been done on bromide derivatives of aluminium alkoxides. Only FUNK et al<sup>2</sup>) have reported a compound of the formula,  $\text{AlBr}_2(\text{OC}_2\text{H}_5) \cdot 2 \text{AlBr}_3 \cdot 15 \text{C}_2\text{H}_5\text{OH}$  prepared from the reaction of aluminium bromide and ethyl alcohol. Therefore, it was considered of interest to investigate some bromide derivatives of aluminium alkoxides. For this purpose, reactions of aluminium alkoxides (methoxide, ethoxide, isopropoxide, n, sec. and tert. butoxides) with acetyl bromide were studied and the products as indicated below, could be isolated, using stoichiometric amounts of the reactants:



The reactions were exothermic and were carried out in refluxing benzene. The products were obtained by removing the excess of benzene and acetyl bromide under reduced pressure at room temperature (25 to 30 °C). The mono-bromide di-alkoxides were found to be free of alkyl

<sup>1</sup>) Thomae G.m.b.H., Chemisch-pharmazeutische Fabrik. Brit., May 21, 795, 222 (1958).

<sup>2</sup>) H. FUNK, J. SCHROMULLER and W. HENSINGER, Z. anorg. Chem. **205**, 361 (1932).

<sup>3</sup>) R. K. MEHROTRA and R. C. MEHROTRA, Z. anorg. Chem. (in press), 1961.

acetate, but di and tri derivatives were found to retain 0.5 and 1.5 moles of alkyl acetate respectively. The greater tendency of donor bond acceptance from alkyl acetate molecule as the alkoxy radical is replaced by the more electronegative bromide radical in the above derivatives is easily understandable in view of the lower electron density round the aluminium atom. Similar observations for chloride zirconium alkoxides<sup>4)</sup> and boron tri-fluoride<sup>5)</sup> have been already made.

The reaction products of aluminium isopropoxide and acetyl bromide could be crystallised out from dry isopropanol, with isopropanol of addition; repeated attempts to crystallise the other alkoxy derivatives from their respective alcohols were not very successful. These bromide alkoxide derivatives are not stable to heat even under reduced pressure and hence they could not be distilled. On the distillation being attempted, a residue was left in every case, the analysis of which showed decomposition of the compounds. These properties are in sharp contrast to the bromide alkoxide derivatives of titanium<sup>6)</sup> and zirconium<sup>7)</sup><sup>8)</sup> where the lower bromide alkoxides could be distilled undecomposed.

Aluminium tert. butoxide showed a different behaviour in these reactions. The reactions with n and sec. butoxide were found to be completed stoichiometrically within a short time. The reaction of aluminium tert. butoxide with acetyl bromide was found to be very slow and even with excess of acetyl bromide the ratio of Br:Al could not be exceeded by more than about 0.7, neither in cold nor in boiling benzene.

As in the case of titanium<sup>6)</sup> and zirconium<sup>7)</sup> isopropoxide and acetyl bromide reaction, the stoichiometric nature of the products in the reactions, indicated that radical interchange might occur between bromide alkoxides of aluminium also. This has been confirmed by refluxing together aluminium tri-bromide and mono-bromide di-isopropoxide in the molar ratio 1:1 in dry isopropyl alcohol, when the di-bromide compound crystallised out on cooling.

## Experimental

### Apparatus

The reactions were carried out in an all glass apparatus with standard ground joints (Quick fit) and with complete exclusion of moisture. For fractionating, a long column packed with RACHIG rings was used.

<sup>4)</sup> D. C. BRADLEY, F. M. HALIM and W. WARDLAW, J. Chem. Soc. 3450 (1950).

<sup>5)</sup> H. J. EMELEUS and J. S. ANDERSON, „Modern Aspects of Inorganic Chemistry“, Routledge and Kegan Paul Ltd., London, 1960, p. 183.

<sup>6)</sup> I. D. VERMA and R. C. MEHROTRA, J. of the Less Common Metals, 1959, Vol. I, 263.

<sup>7)</sup> R. N. KAPOOR and R. C. MEHROTRA, J. of the Less Common Metals (in press), 1961.

<sup>8)</sup> R. C. MEHROTRA, J. Indian chem. Soc. **32**, 759 (1955).

### Materials

Aluminium methoxide, ethoxide, isopropoxide, *n*, *sec*, and *tert*. butoxides were prepared as described by MEHROTRA<sup>9)</sup>, and purified by distillation or sublimation under reduced pressure.

Acetyl bromide (B.D.H., analar) was fractionated carefully before use. Benzene was first dried by refluxing with sodium and finally by azeotropic distillation with ethanol. Isopropyl alcohol was dried by storing over quick lime and then fractionating over aluminium isopropoxide. Methyl, ethyl, *n*, *sec*., and *tert*. butyl alcohols were dried by distilling over corresponding sodium alkoxide.

### Analytical methods

Aluminium was estimated as oxinate and bromide as silver bromide gravimetrically.

#### 1. Reaction between aluminium methoxide and acetyl bromide (molar ratio 1:1)

Aluminium methoxide (1.1 g.) was dissolved in benzene (30–40 c. c.) by refluxing. Acetyl bromide (1.1 g.) was added to the solution and the mixture refluxed for 2 hours. Excess of solvents were removed by distillation and the residue dried at 25°/1 mm for 2 hours to give a powder with a light yellow tinge (1.5 g.).

Found: Al, 16.1; Br, 45.0%.

AlBr(OMe)<sub>2</sub> requires Al, 15.9; Br, 47.3%.

#### 2. Reaction between aluminium methoxide and acetyl bromide (molar ratio 1:2)

Aluminium methoxide (1.3 g.) was added to acetyl bromide (2.8 g.). A very strong exothermic reaction was observed causing the mixture to reflux. Benzene (25 c. c.) was added and the mixture was allowed to reflux for 4 hours. Solvents were distilled out under reduced pressure at 25° and the yellow residue dried at 25°/1 mm for 4 hours to give a yellow solid (3.0 g.).

Found: Al, 9.8; Br, 52.7%.

AlBr<sub>2</sub>(OMe) 1 CH<sub>3</sub>COOMe requires Al, 9.2; Br, 54.7%.

#### 3. Reaction between aluminium methoxide and acetyl bromide (molar ratio 1: > 3)

Aluminium methoxide (1.25 g.) was added to acetyl bromide (6.9 g.), causing a very strong exothermic reaction and resulting a yellow solution. Excess of acetyl bromide was removed at 25°/1 mm to give a yellow paste which was dried under reduced pressure to give a yellow solid, fuming in air and soluble in water.

Found: Al, 7.4; Br, 60.2%.

AlBr<sub>3</sub> · 1.5 CH<sub>3</sub>COOMe requires Al, 7.1; Br, 63.4%.

<sup>9)</sup> R. C. MEHROTRA, J. Indian chem. Soc. **30**, 585 (1953).

#### 4. Reaction of aluminium ethoxide and acetyl bromide (molar ratio 1:1)

Aluminium ethoxide (1.1 g.) was dissolved in benzene (30 c. c.) by refluxing. Acetyl bromide (0.82 g.) was added to it causing an exothermic reaction. The mixture was refluxed at bath temperature of 90° for 15–20 minutes. Excess of solvents were removed under reduced pressure and the residue was dried at 30°/.1 mm for 4 hours to give a light yellow powder which was soluble in water (1.3 g.).

Found: Al, 14.6; Br, 39.4%.

Calcd. for  $\text{AlBr}(\text{OEt})_2$ , Al, 13.7; Br, 40.6%.

#### 5. Reaction of aluminium ethoxide and acetyl bromide (molar ratio 1:2)

Aluminium ethoxide (1.1 g.) was dissolved by heating in benzene (30–40 c. c.). Acetyl bromide (1.9 g.) was added to it producing an exothermic reaction. The above mixture was refluxed at bath temperature of 90° for half hour. Solvents were distilled and the residue dried at 30°/.1 mm for 3 hours to give a yellow crystalline powder, soluble in water.

Found: Al, 10.5; Br, 55.9%.

Calcd. for  $\text{AlBr}_2(\text{OEt}) \cdot 0.5 \text{CH}_3\text{COOEt}$ , Al, 9.8; Br, 57.9%.

#### 6. Reaction of aluminium ethoxide and acetyl bromide (molar ratio 1: > 3)

Acetyl bromide (7.1 g.) was added to aluminium ethoxide (1.79 g.) causing an strong exothermic reaction and turning the mixture yellow. Excess of acetyl bromide was distilled at 30°/.1 mm and the residue was dried under reduced pressure for 3 hours yielding a yellow paste which fumed in air and had, a characteristic smell.

Found: Al, 7.1; Br, 57.5%; Br.: Al, 2.7.

Calcd. for  $\text{AlBr}_3 \cdot 1.5 \text{CH}_3\text{COOEt}$ , Al, 6.7; Br, 60.1%.

#### 7. Reaction of aluminium isopropoxide and acetyl bromide (molar ratio 1:1)

Aluminium isopropoxide (4.6 g.) was added to acetyl bromide (2.8 g.) producing considerable heat. After adding benzene (15 c. c.) the mixture was refluxed. After removing the solvents the residue was dried at 30°/.2 mm for 3 hours to give a yellow mobile paste, soluble in water. (5.1 g.).

Found: Al, 12.1; Br, 35.8%.

Calcd. for  $\text{AlBr}(\text{OPr}^i)_2$ , Al, 12.0; Br, 35.5%.

The above compound was dissolved in dry isopropanol to give a clear solution, which could not be crystallised even after standing for 20 hours. Solvents were removed under reduced pressure and the residue dried at 30°/.1 mm to give a yellow semi solid, soluble in water.

Found: Al, 10.4; Br, 31.0%.

Calcd. for,  $\text{AlBr}(\text{OPr}^i)_2 \cdot 0.5 \text{Pr}^i\text{OH}$ , Al, 10.5; Br, 31.3%.

#### 8. Reaction of aluminium isopropoxide with acetyl bromide (molar ratio 1:2)

Aluminium isopropoxide (2.8 g.) was added to acetyl bromide (3.5 g.), producing heat and giving a yellow solution. Benzene (20 c. c.) was added and the mixture refluxed for

half hour. Solvents were distilled and the residue dried at 30°. 3 mm for 4 hours to give a yellow solid (4.1 g). with a characteristic smell and soluble in water.

Found: for Al, 8.9; Br, 50.8%.

Calcd. for  $\text{AlBr}_2(\text{OPr}^t) \cdot 0.5 \text{CH}_3\text{COOPr}^t$ , Al, 9.0; Br, 53.8%.

To the above compound was added isopropanol (10 c. c.) and the mixture was heated to give a clear yellow solution, which on cooling gave yellow crystals. The mother liquor was decanted off and the crystals dried at 30°/.5 mm.

Found: Al, 6.7; Br, 42.8%.

Calcd. for  $\text{AlBr}_2(\text{OPr}^t) \cdot 2.5 \text{Pr}^t\text{OH}$ , Al, 6.8; Br, 40.4%.

### 9. Reaction of aluminium isopropoxide and acetyl bromide (molar ratio 1: > 3)

Aluminium isopropoxide (2.0 g.) was introduced to acetyl bromide (5.2 g.). A very strong exothermic reaction was noticed, with refluxing of the mixture. It was cooled, excess of acetyl bromide was removed and the residue dried at 30°/1 mm for 3 hours to give a yellow semi solid fuming in air having characteristic smell and soluble in water.

Found: Al, 6.9; Br, 56.8%

Calcd. for  $\text{AlBr}_3 \cdot 1.5 \text{CH}_3\text{COOPr}^t$ , Al, 6.4; Br, 57.1%.

### 10. Reaction between aluminium n butoxide and acetyl bromide (molar ratio 1: 1)

Aluminium n butoxide (2.8g.) was dissolved in benzene (20 c. c.), and acetyl bromide (1.4 g.) was added producing an exothermic reaction and resulting a pale yellow solution. This was refluxed at 90° for a and 1 hour then allowed to cool when a solid was found to separate. Solvents were removed and the residue dried under reduced pressure to give a white powder (2.9 g.).

Found: Al, 11.1; Br, 32.4%.

Calcd. for  $\text{AlBr}(\text{OBu}^n)_2$ , Al, 10.7; Br, 31.6%.

On attempting the compound could not be distilled even at bath temperature o 250°. 1 mm. A red shining residue was left in the distillation flask.

Found: Al, 19,1; Br, 31.8%; Br:Al, 0.55.

### 11. Reaction of aluminium n butoxide with acethyl bromide (molar ratio 1:2)

To a solution of aluminium n butoxide (2.6 g.) in benzene (20 c. c.) was added acetyl bromide (2.7 g.) causing evolution of heat and turning the mixture yellow. This was heated at bath of 90° for 1 hour. Solvents were removed under reduced pressure and the residue dierd at 60°/.05 mm for 2 hours to give a yellow mobile paste (3.4 g.).

Found: Al, 8.2; Br, 47.5%.

Calcd. for  $\text{AlBr}_2(\text{OBu}^n) \cdot 0.5 \text{CH}_3\text{COOBu}^n$ , Al, 8.4; Br, 50.3%.

On attempting, the above compound could not be distilled. A residue was left in the distilling flask.

Found: Al, 18.5; Br, 32.9%; Br: Al, 0.59.

### 12. Reaction between aluminium n butoxide and acetyl bromide (molar ratio 1: >3)

Acetyl bromide (5.1 g.) was added to aluminium n butoxide (1.5 g.) causing evolution of heat. The yellow mixture was refluxed at 90° for 1 hour to give a yellow solution. Excess of acetyl bromide was removed under reduced pressure and the residue dried at 30°/1 mm. to give a yellow mobile liquid with a characteristic smell, fuming in air and soluble in water.

Found: Al, 6.0; Br, 51.3%.

Calcd. for  $\text{AlBr}_3 \cdot 1.5 \text{CH}_3\text{COOBu}^n$ , Al, 6.1; Br, 54.4%.

### 13. Reaction of aluminium sec. butoxide and acetyl bromide (molar ratio 1:1)

Aluminium sec. butoxide (3.1 g.) was dissolved in benzene (20 c. c.) to give a clear solution. Acetyl bromide (1.64 g.) was added causing an moderate exothermic reaction. This mixture was refluxed at 90° for 1 hour to produce a light yellow mixture. Solvents were distilled under reduced pressure and the residue dried at 30°/1 mm to give light yellow paste (3.2 g.).

Found: Al, 10.7; Br, 32.5%.

Calcd. for  $\text{AlBr}(\text{OBu}^{\text{sec.}})_2$ , Al, 10.6; Br, 31.6%.

### 14. Reaction of aluminium sec. butoxide with acetyl bromide (molar ratio 1:2)

Acetyl bromide (2.6 g.) was introduced to a solution of aluminium sec. butoxide (2.6 g.) in benzene (20 c. c.) and the mixture refluxed at 90° for 1 hour to give a yellowish red solution. After removing the solvents the residue was dried at 30°/0.05 mm to give thick red paste having a characteristic odour, soluble in water.

Found: Al, 8.1; Br, 48.3%.

Calcd. for  $\text{AlBr}_2(\text{OBu}^{\text{sec.}})_2 \cdot 0.5 \text{CH}_3\text{COOBu}^{\text{sec.}}$ , Al, 8.4; Br, 50.3%.

On attempting to distil, a yellow solid residue was obtained.

Found: Al, 23.4; Br, 40.5%; Br: Al, 0.58.

### 15. Reaction between aluminium sec. butoxide and acetyl bromide (molar ratio 1: > 3)

Aluminium sec. butoxide (2.0 g.) was added to acetyl bromide (9.1 g.) causing a very strong exothermic reaction and producing a dark yellow solution. The mixture was allowed to cool. Excess of acetyl bromide was removed under reduced pressure and the residue dried at 30°/1 mm to give a red mobile paste having a characteristic smell, fuming in air and soluble in water.

Found: Al, 6.3; Br, 51.3%; Br: Al, 2.8.

Calcd. for  $\text{AlBr}_3 \cdot 1.5 \text{CH}_3\text{COOBu}^{\text{sec.}}$ , Al, 6.1; Br, 54.4%.

### 16. Reaction of aluminium tert. butoxide with acetyl bromide (molar ratio 1: > 3) (at 30 °C)

Aluminium tert. butoxide (1.1 g.) was dissolved in benzene (25 c. c.). Acetyl bromide (9.4 g.) was added causing evolution of a little heat. After removing the excess of acetyl bromide under reduced pressure the residue was dried at 30°/1 mm yielding a white powder (1.1 g.).

Found: Al, 10.5; Br, 21.5%; Br: Al, 0.69.

Calcd. for  $\text{Al}(\text{OBu}^{\text{tert.}})_3 \cdot 2.3 \text{Br}_{0.7}$ , Al, 10.7; Br, 22.3%.

**17. Reaction between aluminium tert. butoxide and acetyl bromide (molar ratio 1:>3) (at 100°C)**

Aluminium tert. butoxide (0.86 g.) was dissolved in benzene (15 c. c.). Acetyl bromide (9.7 g.) was added. On shaking some heat was evolved. The mixture was refluxed at 100° for half hour. After removing the excess of acetyl bromide the residue was dried at 30°, 1 mm to give a white powder (0.8 g.).

Found: Al, 10.5; Br, 15.4%; Br:Al, 0.5.

The analysis shows that on refluxing the product gets decomposed with lowering of bromide:aluminium ratio. Similar observations have been made for bromide tertiary alkoxides of titanium<sup>6</sup> and zirconium<sup>7</sup>).

**18. Reaction between  $\text{AlBr}_3 \cdot 1.5 \text{CH}_3\text{COOPr}^t$ ; and  $\text{AlBr}(\text{OPr}^t)_2 \cdot 0.5 \text{Pr}^t\text{OH}$  in equimolecular proportion**

A mixture of  $\text{AlBr}_3 \cdot 1.5 \text{CH}_3\text{COOPr}^t$  (0.6 g.) and  $\text{AlBr}(\text{OPr}^t)_2 \cdot 0.5 \text{Pr}^t\text{OH}$  (0.36 g.), on isopropanol (10 c. c.) was refluxed to get a clear solution. On cooling crystals were obtained which were dried under reduced pressure at room temperature.

Found: Al, 6.9; Br, 41.6%.

Calcd. for  $\text{AlBr}_2(\text{OPr}^t) \cdot 2 \text{Pr}^t\text{OH}$ , Al, 7.3; Br, 43.7%.

The authors are grateful to the Council of Scientific and Industrial Research, New Delhi for providing a fellowship to one of us (R.K.M.), during the tenure of which this work was carried out.

*Gorakhpur (India), Chemical Laboratories, University of Gorakhpur.*

Bei der Redaktion eingegangen am 12. Juli 1961.