Russian Journal of General Chemistry, Vol. 72, No. 3, 2002, pp. 394–397. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 3, 2002, pp. 423–426.
Original Russian Text Copyright © 2002 by Shcherbakov, Basova, Khorshev, Malysheva, Domrachev.

Synthesis and Thermolysis of Tris(triethoxysiloxy)aluminum and Its Complexes with Potassium and Sodium Triethoxysilanolates

V. I. Shcherbakov, G. V. Basova, S. Ya. Khorshev, I. P. Malysheva, and G. A. Domrachev

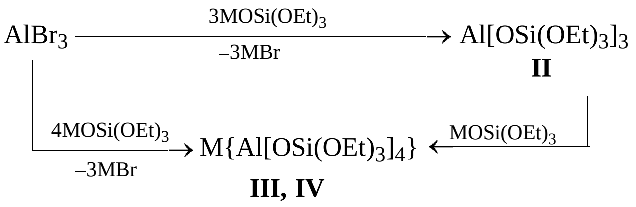
Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhni Novgorod, Russia

Received July 14, 2000

Abstract—Reaction of potassium (or sodium) triethoxysilanolate with $AlBr_3$ in benzene in a 3 : 1 or 4 : 1 ratio yields, respectively, tris(triethoxysiloxy)aluminum $Al[OSi(OEt)_3]_3$ or potassium (or sodium) tetrakis(triethoxysiloxy)aluminate $M\{Al[OSi(OEt)_3]_4\}$ (M = K, Na). Single-stage thermolysis of tris(triethoxysiloxy)aluminum (200°C) and potassium tetrakis(triethoxysiloxy)aluminate (300°C), followed by annealing of the solid residues at 1000–1250°C, yields ceramic materials, which were examined by X-ray diffraction. The crystalline phase obtained from tris(triethoxysiloxy)aluminum is aluminum metasilicate $Al_6Si_2O_{13}$ (mullite), and the product obtained from potassium tetrakis(triethoxysiloxy)aluminate is a mixture of aluminum orthosilicate Al_2SiO_5 (kyanite) and feldspar aluminosilicate $KAlSi_3O_8$ (microcline).

Direct thermolysis of mixed aluminum and silicon alkoxides $(RO)_2AlOSi(OR')_3$ (**I**) is a route to alumina–silica ceramic composites [1]. As a continuation of our works [1, 2] on synthesis and study of such dialkoxyaluminosiloxanes, we report in this paper the synthesis and thermolysis of tris(triethoxysiloxy)aluminum $Al[OSi(OEt)_3]_3$ (**II**) and its complexes with potassium and sodium triethoxysilanolates: potassium ($K\{Al[OSi(OEt)_3]_4\}$, **III**) and sodium ($Na\{Al[OSi \cdot (OEt)_3]_4\}$, **IV**) tetrakis(triethoxysiloxy)aluminates.

Previously [1, 2], aluminosiloxanes **I** and $R_2AlO \cdot Si(OR)_3$ were prepared by exchange of aluminum bromide $(EtO)_2AlBr$ or *i*-Bu_2AlBr with potassium (or sodium) triethoxysilanolate. A similar reaction of $AlBr_3$ with alkali metal triethoxysilanolate in a 1 : 3 ratio yields **II**. At a 1 : 4 ratio, complexes **III** and **IV** are obtained in one stage. These complexes can also be prepared by addition of an equimolar amount of potassium (or sodium) triethoxysilanolate to aluminosiloxane **II**. The scheme of the reactions is shown below.



M = K (**III**), Na (**IV**).

Complexes **III** and **IV** are solid nonmelting substances, in contrast to aluminosiloxanes **I** [2] and **II** which are very viscous liquids. Their IR spectra are practically identical and give little information. They contain a set of the same characteristic bands originating from vibrations of the EtO group (as in tetraethoxysilane) and a strong broad absorption band of the SiOAl group (in the range of SiOSi vibrations); for assignments, see [3–6].

We found previously [1] that dialkoxyaluminosiloxanes **I** start to decompose at 180–200°C; therefore, thermolysis of aluminosiloxane **II** was also performed at 200°C, with removal of volatiles in an evacuated system. In a cooled trap we collected and identified the following compounds (moles per mole of **II**): ethylene (1.11), ethanol (1.38), tetraethoxysilane (0.30), diethyl ether (0.27), and water (0.16). The dark solid residue formed after such treatment, according to the elemental analysis and the results of hydrolysis, still contained alkoxy groups and therefore was subjected to further thermolysis at 300°C. The following compounds were additionally collected (moles per mole of **II**): ethylene (0.49), ethanol (1.84), and water (1.72). Also, we obtained a dark powdered residue **IIa** in an amount of 44 wt % relative to **II**.

Similarly, in thermolysis of **III** at 300°C, we collected and identified the following compounds (moles per mole of **III**): ethylene (2.20), tetraethoxysilane (0.85), ethanol (2.63), and water (0.18). The amount of the dark solid residue **IIIa** was 53 wt % relative to **III**.

1070-3632/02/7203-0394 \$27.00 © 2002 MAIK “Nauka/Interperiodica”

Amorphous powdered residues **IIa** and **IIIa** were annealed in air at 1000 and 1250°C for 1 h, and the resulting crystalline phases were identified by X-ray phase analysis. After annealing of **IIa** at 1000°C, a dark powder **IIb** was obtained. The Debye pattern of **IIb** exhibits a set of well-defined reflections corresponding to $Al_6Si_2O_{13}$ (mullite). Residue **IIIa**, when annealed at 1000°C, undergoes caking and remains dark. No phases can be identified in its Debye pattern. On annealing at a higher temperature, 1250°C, a colorless fused ceramics **IIIb** is obtained. In its Debye pattern, three phases can be identified: mullite, aluminum orthosilicate Al_2SiO_5 (kyanite modification), and potassium-containing feldspar aluminosilicate $KAlSi_3O_8$ (microcline modification). The two latter phases are detected by several most intense rings, characteristic for each phase, in the complex diffraction pattern.

The colorless cake **IIIb** obtained by direct thermolysis of **III** with subsequent annealing of the residue at 1200–1250°C shows a very strong adhesion to the ceramic support. Presumably, with the sodium analog **IV** the annealing temperature required for preparing a ceramic material will be lower, because the melting point of the sodium-containing feldspar aluminosilicate is lower. Thus, compounds **II**–**IV** can be considered as possible precursors for one-stage preparation of ceramic materials by thermolysis in air.

Alkali metal triethoxysilanolates used for synthesizing **II**–**IV** were prepared in solution of tetraethoxysilane taken in a slight excess, with subsequent vacuum evaporation of the solvent at room temperature and drying of the residue in a vacuum at 35–40°C. It should be noted that at temperatures higher by only 20–30°C potassium triethoxysilanolate decomposes with release (moles per mole of the initial compound) of tetraethoxysilane (0.23) and small amounts of ethanol (0.06) and ethylene (0.01), and the powdered residue **V** is insoluble in tetraethoxysilane. The IR spectrum of the residue in the range of OEt absorption undergoes significant changes: the bands at 1160 and 940 cm^{-1} disappear, and a strong band at 760 cm^{-1} characteristic of potassium triethoxysilanolate is split in two very weak broad bands at 760 and 700 cm^{-1}. This means that the decomposition product **V** contains no $(EtO)_3Si$ groups but can contain $(EtO)_2Si$ groups. Its hydrolysis yields ethanol, and the balance with respect to EtO groups between the initial compound and decomposition products is 98%. It could be expected that thermolysis of potassium triethoxysilanolate would be accompanied by disproportionation to tetraethoxysilane and potassium diethoxysilanediolate $(EtO)_2Si(OK)_2$ (**Va**). However, the amount of the released tetraethoxysilane (~1 mol per 4 mol of the starting compound) is too low, and the analytical data for **V** are also inconsistent with the composition of **Va**. The number of KO groups in **V** determined by acid titration was also only 80% of the amount calculated for **Va**. Apparently, the composition of **V** is more complex, and at present we cannot identify this product.

EXPERIMENTAL

We used absolute ethanol, dry solvents [7], and freshly distilled tetraethoxysilane. All manipulations with aluminum bromide (analytically pure grade) were performed in a glove box with a dry atmosphere. The compositions and yields of the gaseous and liquid products of the thermal reactions were determined by GLC on a Tsvet-104 chromatograph (thermal conductivity detector, carrier gas helium, steel columns 3 mm in diameter). Gaseous products were determined at 50°C on a 2-m column packed with silica gel S-3. Tetraethoxysilane and ethanol were determined at 70°C on a 2-m column packed with Chromaton-N + 15% Reoplex-400. Water and ethanol were separated at 100°C on a 1-m column packed with Polysorb-1. The IR spectra were taken on a Perkin–Elmer-577 spectrometer (mineral oil, KBr). The X-ray phase analysis of annealed powders was performed on an IRIS-1 device equipped with a Debye camera; CuK_α radiation. The crystalline phases were identified by comparing the Debye patterns of the samples with the reference data from the ASTM data-base. Analysis of **II**–**IV** and solid residues **IIa** and **IIIa** for C and H by combustion in an oxygen flow was performed in the presence of PbO.

Potassium and sodium triethoxysilanolates. Tetraethoxysilane (4.5 ml) was added in portions with vigorous stirring to 0.5 g of powdered KOH, and the resulting mixture was heated at 35–40°C, avoiding agglutination of the precipitate, until KOH dissolved completely. Excess tetraethoxysilane and the released ethanol were vacuum-evaporated to dryness, and the solid residue was dried in a vacuum at 35–40°C to constant weight. Potassium triethoxysilanolate, 1.97 g, was obtained. IR spectrum, ν, cm^{-1}: 1160, 930, 760 (EtO); 1080, 470 (SiOC). Sodium triethoxysilanolate was prepared similarly using powdered NaOH.

Thermolysis of potassium triethoxysilanolate. A 1.57-g portion of potassium triethoxysilanolate was heated in an evacuated system at 80°C for 3 h. The volatile decomposition products were condensed in a trap cooled with liquid nitrogen. Noncondensable gases were virtually absent. The liquid phase (0.37 g) consisted of tetraethoxysilane (92.0%), ethanol (5.3%), and dissolved ethylene (2.7%). The residue was a colorless amorphous powder (1.2 g). IR spectrum, ν, cm^{-1}: 1040, 460 (SiOC); 760, 700 (EtO). Found, %: C 29.75; H 5.03. Calculated for potassuim diethoxysilanediolate, $C_4H_{10}K_2O_4Si$, %: C 21.04; H 4.41. A 0.9-g portion of the solid residue was hydrolyzed in an evacuated sealed glass ampule (1 ml) with acidified water (pH ~4) at 100°C for 1 h. In the hydrolysis products, 0.47 g of ethanol was detected by GLC, which corresponds to 0.62 g of ethanol in the whole amount of the residue.

Tris(triethoxysiloxy)aluminum (II). A solution of 1.25 g of $AlBr_3$ in 5 ml of benzene was added in a vacuum with vigorous stirring to a solution of sodium triethoxysilanolate, prepared as described above from 0.56 g of NaOH, in 10 ml of benzene. After heat evolution ceased, the ampule was sealed, and the mixture was heated at 40°C for 30 min with intermittent shaking. Then the mixture was centrifuged, and the transparent benzene solution was separated by decanting and vacuum-evaporated to leave 2.6 g (98%) of compound **II** as a viscous liquid hydrolyzing in air. IR spectrum, ν, cm^{-1}: 1100–1070 (AlOSi); 1150, 950, 780, 470 (EtO). Found, %: C 36.51; H 8.6; Al 4.80; Si 14.89. $C_{18}H_{45}AlO_{12}Si_3$. Calculated, %: C 38.28; H 8.03; Al 4.78; Si 14.92. The precipitate was washed with benzene (3 × 5 ml) and dried in air; it was identified as sodium bromide (1.42 g, 98%).

Potassium (III) and sodium (IV) tetrakis(triethoxysiloxy)aluminates. *a*. A solution of potassium triethoxysilanolate, prepared from 1.07 g of KOH, in 20 ml of benzene was placed in a three-necked flask equipped with a stirrer, a dropping funnel, and a reflux condenser. A solution of 1.28 g of $AlBr_3$ in 10 ml of benzene was added dropwise over a period of 15 min with vigorous stirring to the solution of potassium triethoxysilanolate, and the mixture was refluxed for 7 h. Then the mixture was placed in an ampule and centrifuged to separate KBr, and the colorless benzene solution was decanted and vacuum-evaporated; 3.32 g (88%) of $K\{Al[OSi(OEt)_3]_4\}$ (**III**) was obtained as a solid substance hydrolyzing in air. The product does not melt when heated to 300°C. Its IR spectrum is identical to that of **II**. Found, %: C 37.50; H 7.70; Al 3.55; K 5.13; Si 14.80. $C_{24}H_{60}\cdot AlKO_{16}Si_4$. Calculated, %: C 36.80; H 7.72; Al 3.44; K 4.99; Si 14.35. The precipitate was washed with benzene (4 × 5 ml) and dried in air; it was identified as potassium bromide (1.65 g, 96%).

b. A solution of 0.89 g of potassium triethoxysilanolate in 10 ml of benzene was added in small portions in a vacuum with stirring to a solution of 2.32 g of tris(triethoxysiloxy)aluminum in 20 ml of benzene, prepared in a glass ampule as described above. The ampule was sealed, and the solution was heated at 70°C for 10 h, after which the solvent was vacuum-evaporated at room temperature. Evacuation was continued until the residue became solid. Compound **III** was obtained; yield 3.1 g (96%). The product characteristics are identical to those of the sample prepared by procedure *a*.

c. Similarly, from 2.18 g of tris(triethoxysiloxy)aluminum and 0.78 g of sodium triethoxysilanolate, we prepared 2.89 g (98%) of $Na\{Al[OSi(OEt)_3]_4\}$ (**IV**) as a colorless solid. The product does not melt when heated to 300°C. Its IR spectrum is similar to that of **III**. Found, %: C 36.84; H 7.20; Al 3.58; Na 3.05; Si 14.92. $C_{24}H_{60}AlNaO_{16}Si_4$. Calculated, %: C 37.58; H 7.88; Al 3.52; Na 3.00; Si 14.65.

Thermolysis of tris(triethoxysiloxy)aluminum (II). A 2.0-g portion of tris(triethoxysiloxy)aluminum was heated for 2 h in an evacuated system at 200°C. The volatile decomposition products were condensed in a trap cooled with liquid nitrogen. Ethylene (88 ml) and a liquid fraction (0.52 g) were obtained; the latter consisted of ethanol (43.2%), tetraethoxysilane (43.1%), diethyl ether (13.6%), and water (2.0%). The residue (1.38 g) was a dark powder containing 13.58% C and 1.74% H. This substance was heated at 300°C for 1 h. Ethylene (39 ml) and a liquid fraction (0.41 g) were obtained; the latter consisted of ethanol (73.2%) and water (26.8%). The residue (0.88 g, **IIa**) was a black powder. Its annealing at 1000°C for 1 h gave a dark powdered ceramics **IIb**; the weight loss was 7% relative to **IIa**. Annealing of **IIb** at 1250°C for 1 h does not result in sintering, decolorization, or weight loss.

Thermolysis of potassium tetrakis(triethoxysiloxy)aluminate (III). A 1.90-g portion of **III** was heated in an evacuated system at 300°C for 2 h. The gas phase (119 ml) consisted of ethylene, and the liquid phase (0.73 g), of tetraethoxysilane (58.8%), ethanol (40.1%), and water (1.1%). The solid residue (1.01 g, **IIIa**) was a black powder. Found, %: C 3.97; H 1.10. Annealing of **IIIa** at 1000°C for 1 h gave a weakly sintered black product; its repeated annealing at 1250°C for 1 h gave a colorless ceramic cake **IIIb**. The weight loss relative to **IIIa** was 7.4%.

ACKNOWLEDGMENTS

The authors are grateful to I.L. Vasilevskaya for X-ray diffraction measurements.

REFERENCES

1. Domrachev, G.A., Shcherbakov, V.I., Basova, G.V., Malysheva, I.P., Matveev, A.P., and Vasilevskaya, I.L., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 9, pp. 1466–1469.

2. Shcherbakov, V.I., Basova, G.V., Stepovik, L.P., and Domrachev, G.A., *Zh. Obshch. Khim.*, 1995, vol. 65, no. 4, pp. 612–615.
3. Borisov, S.N., Voronkov, M.G., and Lukevics, E.J., *Kremneelementoorganicheskie soedineniya* (Organometallic Silicon Compounds), Leningrad: Khimiya, 1966, pp. 266–267.
4. Voronkov, M.G., Maletina, E.A., and Roman, V.K., *Geterosiloksany* (Heterosiloxanes), Novosibirsk: Nauka, 1984, pp. 110–111.
5. Korneev, N.N., Shcherbakova, G.I., Bochkarev, V.N., Belokon’, V.M., Kisin, A.V., and Apal’kova, G.M., *Zh. Obshch. Khim.*, 1985, vol. 55, no. 3, pp. 589–593.
6. Korneev, N.N., Shcherbakova, G.I., Kolesov, V.S., Sakharovskaya, G.V., Shevchenko, E.I., Nikitin, V.S., Bazhenova, L.N., and Nikishina, I.S., *Zh. Obshch. Khim.*, 1987, vol. 57, no. 2, pp. 330–335.
7. *Organic Solvents. Physical Properties and Methods of Purification*, Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., Eds., New York: Interscience, 1955.