251. Synthesis of Pure $Al^{35}Cl_3$ and $Al^{37}Cl_3$

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Summary

Chemically and isotopically pure $Al^{35}Cl_3$ and $Al^{37}Cl_3$ are synthesized from Al (s) and HCl (g). The yield is quantitative and no measurable decrease in isotopic content from HCl to $AlCl_3$ takes place.

1. For the study of gas phase complexes by IR.-, Raman- or microwave spectroscopy isotope substitution is a great help or a necessity for the assignment of vibrational/rotational transitions. Two groups active in the field of volatile chlorocomplexes and high temperature transport reactions have asked us to provide high purity $Al^{35}Cl_3$ and $Al^{37}Cl_3$ for their investigations[2]). We communicate our results since aluminium chloride is an important reagent and no synthesis of its ^{35}Cl or ^{37}Cl labelled species has been found in the literature.

2. It is easy to obtain 99.999% aluminium[3]). Chlorine isotopes are commercially available, *e.g.* in the form of Na*Cl with a content of either isotope of max. 85%[4]). This is not sufficient for the above mentioned applications. From an earlier preparation of $>99.9997\%$ ^{38}Ar spike for potassium/argon geochronology by thermal diffusion in a special composition of $H^{35}Cl/H^{37}Cl$ auxiliary gas [1] we have a small stock of $\geqslant 99\%$ ^{37}Cl and $>99.9\%$ ^{35}Cl. HCl is an excellent starting material, since the reaction

$$\begin{aligned}&Al(s)+3\ HCl(g)\rightarrow AlCl_3(s)+1.5\ H_2(g) \quad \Delta G^\circ_{298}=-82.29\ \text{kcal/mol}\\ \text{or}\\ &Al(s)+3\ HCl(g)\rightarrow AlCl_3(g)^{5)}+1.5\ H_2(g) \quad \Delta G^\circ_{700}=-60.30\ \text{kcal/mol}\end{aligned} \tag{1}$$

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[2]) *W. Schläpfer, F.P. Emmenegger & A. v. Zelewsky*, Fribourg (Switzerland) and Dr. *E. Rytter*, Trondheim (Norway).

[3]) Supplied by Alusuisse, Neuhausen (Switzerland).

[4]) Now commercially available from *Oak Ridge National Laboratory* in 99.35% ^{35}Cl isotope purity.

[5]) All equations are for $AlCl_3$(g) only. Of course the monomer/dimer equilibrium should be included for a precise discussion.

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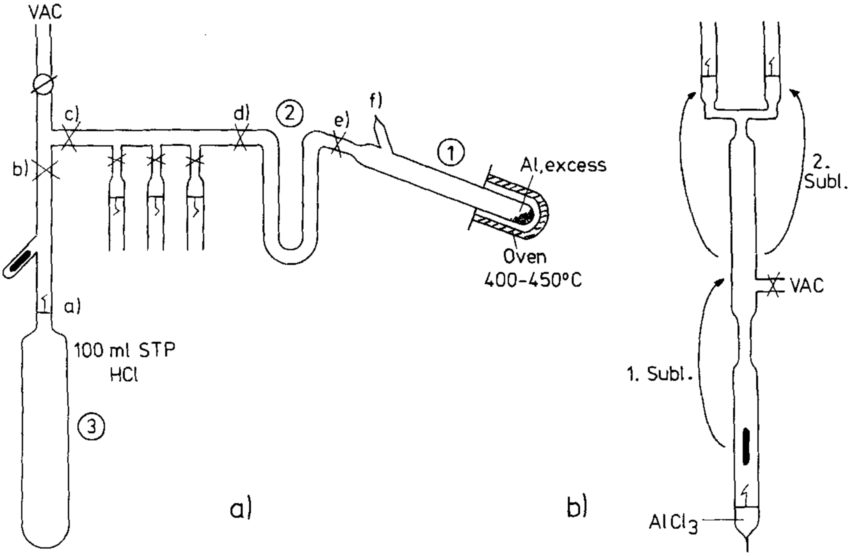

Fig. 1. *First version of synthesis:* 1a) ① Pyrex ampoule. Side tube sealed off at f) after introduction of Al-chips. ② Liquid nitrogen trap. ③ H*Cl-ampoule; a) breakseal; b), c), d), e) prepared vacuum seals. 1b) Final distillation of the $AlCl_3$ into breakseal ampoules.

goes to completion⁶). However, with pure dry HCl-gas it is not spontaneous at room temperature, contrary to the more exothermic reaction with Cl_2-gas

$$\begin{aligned} &Al(s) + 1.5\,Cl_2(g) \rightarrow AlCl_3(s) \quad \Delta G^\circ_{298} = -150.61 \text{ kcal/mol} \\ &Al(s) + 1.5\,Cl_2(g) \rightarrow AlCl_3(g) \quad \Delta G^\circ_{700} = -131.10 \text{ kcal/mol.} \end{aligned} \tag{2}$$

It is not easy to prepare small amounts of isotopic Cl_2-gas from chloride in a high yield. As it is true for many syntheses of labelled compounds, none of the well known syntheses⁷) is useful, the best probably being the microelectrolysis of an HCl-solution as elaborated by *Stuke & Schäfer* [4].

An alternative [5] to the method with HCl described below, and preferable if NaCl is the starting material, contains two steps:

$$\begin{aligned} &Cl^{\ominus} \rightarrow \{AgCl\} \text{ (dry and shielded from light)} \\ &Al(s) + 3\,AgCl(s) \xrightarrow{450^\circ} AlCl_3(g) + 3\,Ag(s) \quad \Delta G^\circ_{700} = -67.44 \text{ kcal/mol.} \end{aligned} \tag{3}$$

The reaction has to be conducted in a quartz tube and is rather violent⁸).

3. Since the thermal diffusion experiment yields H*Cl-gas we chose reaction (1). With chips of very pure aluminium and 100 ml STP (standard pressure and

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⁶) All thermodynamic data from [2].

⁷) See *e.g.* [3].

⁸) Unpublished work of *E. S.*

temperature: 0°, 1 atm) H*Cl in a 200 ml pyrex ampoule H_2-evolution starts between 400° and 450° depending on whether the Al-chips have or do not have an oxide surface. While the details are given in the experimental part, two versions of the preparation are summarized here: The apparatus in *Figure 1* creates a convective gas circulation above the oven which deposits the generated $AlCl_3$ on the upper side of the cold part (room temperature) of the reaction tube ① and transports unreacted HCl to the excess Al. The evolved H_2 is pumped through the U-tube ② at liquid-nitrogen temperature 20 min after the onset of the reaction in

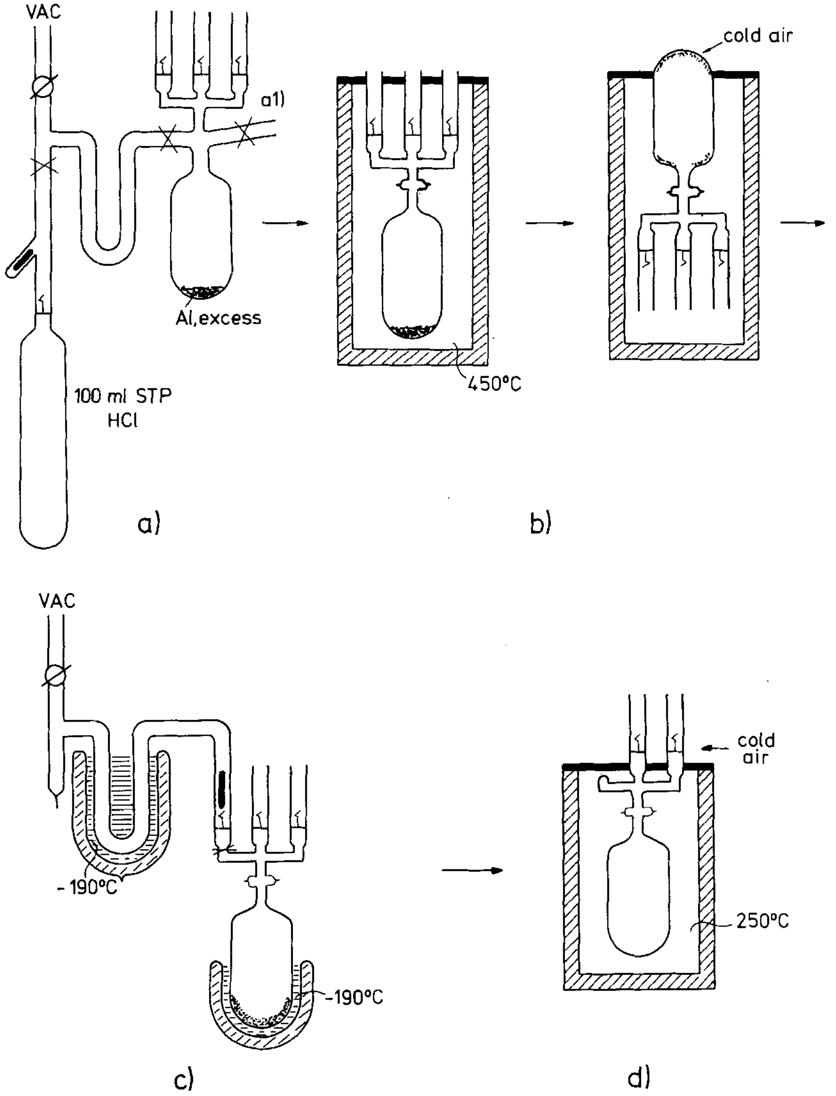

Fig. 2. *Second version of synthesis:* 2a) Filling of reactants. 2b) Synthesis and condensation. 2c) Removal of excess HCl and of H_2. 2d) Final distillation into breakseal ampoules.

order to trap unreacted HCl. No measurable amount of HCl (*i.e.* partial pressure $< 10^{-3}$ Torr) can be detected. However, during sublimation of the $AlCl_3$ from ① into ② small amounts of additional H_2 are produced, either by hydrolysis of $AlCl_3$ on surface hydroxyl groups, evolution of HCl and reaction with Al or by dissociation of the weak $HAlCl_4(s)$ complex. Since all glass surfaces have been baked near 500° *in vacuo* before the experiment we believe that the second source of additional HCl is responsible for the hydrogen. In order to prevent this complication and minimizing the glass surfaces, the simpler apparatus in *Figure 2* has been used for the final preparations. During the synthesis the $AlCl_3$ is kept in the gas phase of the ampoule which is completely immersed in an oven at 440°. After 40 min the ampoule is turned around and put back into the oven. Its lower end sticks out and is air cooled, whereby $AlCl_3$ crystallizes on the wall. Then one of the break-seals is blown to the vacuum line, the ampoule is cooled with liquid N_2, the seal broken and H_2 pumped away through the U-tube. Afterwards the vacuum connection is sealed off and the ampoule immersed again in the oven at 200–250°. Then the two remaining break seal tubes are raised and air cooled to collect the $AlCl_3$ in them. After completion of this process the two sample tubes are sealed off. No additional H_2 production can be observed in this version.

Both versions produce a quantitative yield of crystallized colourless Al^*Cl_3 with no measurable decrease of the isotopic purity from starting to final product.

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Experimental Part

1. Ingots of 99.999% Al are put into a glove bag which is carefully filled with 99.99% argon. About 2 g of chips are drilled by an electrical drill. The chips from the surface are discarded, those from the inside collected and sealed under argon.

3. $AlCl_3$ synthesis, version *Figure 1:* about 0.5 g of the Al chips are filled under argon into the reaction tube ① which is sealed off at f). Immediately the system is evacuated to $< 10^{-3}$ Torr and baked by torch almost to the glass transition point of pyrex. Then tube ① and ampoule ③ are frozen with liquid N_2, breakseal a) is opened, 100 ml STP H^*Cl condensed into ①, and b) sealed off. The oven is heated to 400° when the reaction sets in. $AlCl_3$ sublimes and condenses on the upper side of the tube ①. After 20 min (= average diffusion time for mixing of the contents of the apparatus), trap ② is put into liquid N_2 and H_2 pumped away. $AlCl_3$ is then sublimed by a hot hair drier or blow torch from ① into ②, the latter now at $-80°$, whereby small amounts of H_2 are periodically pumped away. It is necessary to heat all those parts of the apparatus simultaneously, where condensation of $AlCl_3$ is unwanted. For the last sublimation steps c) and e) are sealed off. About 1 mg of $AlCl_3$ each is trapped in two of the breakseal tubes (for isotope analysis) and the product is collected in the third. This material is twice sublimed under vacuum in the glass apparatus 1b).

4. $AlCl_3$ synthesis, version *Figure 2:* the first steps are similar to the above. The filled and closed reaction tube *Figure 2a)* is heated to approx. 450°, *Figure 2b*, when the reaction starts with Al-chips which have been transferred from the argon atmosphere into the reaction tube at 1a) with a short exposure to air. After 40 min the reaction tube is reversed and the $AlCl_3$ condensed by a cold air jet. In the step at *Figure 2c)* H_2 is evacuated and the apparatus sealed off again. Finally, at 2d) $AlCl_3$ is sublimed into the two remaining breakseal tubes which are closed off.

5. The yield of the reaction has been determined during a run with ordinary HCl. $AlCl_3$ is hydrolyzed with water, the solution/suspension neutralized with $\{NaHCO_3\}$, put to dryness and

flashed to red heat. Then NaCl is extracted and $Cl^{\ominus}$ determined by titration with $Ag^{\oplus}$. Checks of the yield are given by the observation of traces of unreacted HCl after the pumping off of H_2. No excess HCl has been detected.

6. Isotope analysis: the starting $H^{35}Cl$ and $H^{37}Cl$ are transformed into CH_3Cl with the reaction $(CH_3)_2SO_4 + 2\,HCl \rightarrow H_2SO_4 + 2\,CH_3Cl$ in the presence of traces of CH_3OH [6]. The procedures for a reproducible conversion have been carefully investigated⁸). For mass analysis in a mass-spectrometer *Varian* MAT CH_4, the ratios of *m/z* 52 to 50 and 50/48 have been used. Careful calibration with CH_3Cl formed from HCl with natural isotopic composition has been used.

A more precise method [7] uses thermal ionization of NaCl and measurement of the *m/z* 83/81 ratio of the Na_2Cl^+-ions: $AlCl_3$ is hydrolyzed, neutralized with $NaHCO_3$, and put to dryness. A drop of the extracted NaCl-solution is placed onto one ribbon of a two ribbon surface ionization source. After evaporation of the solvent and a short flash to red heat in air (in order to oxidize the rhenium surface) the MS. of the Na_2Cl^+ is measured. The analyses prove that no measurable decrease (*i.e.* $< \pm 0.1\%$) of the isotopic purity of the H^*Cl exists in the products $Al^{35}Cl_3$ or $Al^{37}Cl_3$.

REFERENCES

[1] *E. Schumacher*, Chimia *29*, 441 (1975).

[2] *I. Barin & O. Knacke*, in 'Thermochemical Properties of Inorganic Substances', Springer-Verlag, Berlin/Heidelberg/New York 1973.

[3] *Gmelin*, Vol. 'Chlorine', 1968 part A, 1968 part B, No. 1, 1969 part B, No. 2.

[4] *M. Stuke & F.P. Schäfer*, Chem. Phys. Lett. *48*, 271 (1977), and M. Stuke, Dissertation, Marburg/Lahn 1977.

[5] *C.H. Wallace & J.E. Willard*, J. Am. Chem. Soc. *72*, 5275 (1950).

[6] *H.R. Owen & O.A. Schaeffer*, J. Am. Chem. Soc. *77*, 898 (1955).

[7] *R.J. Hayden*, Phys. Rev. *74*, 650 (1948).