Journal of Thermal Analysis, Vol. 5 (1973) 475–482

REACTION OF ALKALI AND AMMONIUM BIFLUORIDES WITH ALUMINIUM AND SILICON

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(Received March 7, 1972)

The reactions of alkali and ammonium bifluorides with aluminium and silicon were studied by DTA. Reaction temperatures were determined and reaction products identified. The reaction mechanism of the fluorinating reaction was established. Hydrofluorides appear very promising fluorinating agents.

The fluorinating actions of elemental fluorine, halogen fluorides and hydrogen fluoride are well known and these compounds are widely applied for synthetizing inorganic fluorides [1]. Lately, however, interest in solid fluorinating agents has continually grown, since they possess many advantages. By way of example, silver difluoride [2], cobalt and manganese trifluorides [3–5], xenon fluoride [6] and alkali fluorohalogenates [7] can be mentioned.

Much attention has been paid to ammonium bifluoride as a potential fluorinating agent, because the melting and evaporation temperatures of this compound are relatively low. The reactivity of $NH_4F \cdot HF$ is close to that of anhydrous hydrofluoric acid and the compound can be successfully applied as a fluorinating agent in many reactions [1, 8–10]. It is obvious that other bifluorides are also suited for such purposes.

In the present paper we wish to report studies on the reaction of alkali and ammonium bifluorides with aluminium and silicon. The method used was differential thermal analysis and the reaction products were identified by X-ray phase analysis and thermal analysis. In reactions of metals with bifluorides, the thermal properties of the latter are very important. The thermal stabilities and decomposition kinetics of hydrofluorides were earlier studied by thermogravimetry [11, 12]. It was found that lithium and sodium bifluorides are decomposed before melting, whereas potassium, rubidium and caesium bifluorides first undergo polymorphous transformation on heating, and subsequently melt without perceptible decomposition. On further heating, hydrogen fluoride is evolved from the melt [12]. Ammonium bifluoride too melts without perceptible decomposition, and on further heating decomposes, hydrogen fluoride being split off.

Experimental

Alkali and ammonium bifluorides were synthetized according to data on the $HF-MF-H_2O$ systems, and identified by methods of chemical, X-ray phase and thermal analysis [12]. Aluminium and silicon were used in the form of finely dispersed powders.

Mixtures with different ratios of the constituents were prepared in platinum crucibles. The samples were heated at a rate of 10 – 12°C.min^{-1}, starting from room temperature. Pt – Pt/Rh thermocouples were used for temperature measurement.

PTFE vessels, metallic aluminium and silicon reference standards and filtered copper radiation were used to obtain the X-ray diffractions of the starting materials and reaction products.

Results

The principal experimental data on the reaction of bifluorides with aluminium and silicon, together with data on the thermal properties of these bifluorides [12, 13] are summarized in Table 1.

Up to the temperature of complete decomposition sodium bifluoride does not react with metallic aluminium and silicon.

Table 1

Thermal properties of alkali and ammonium bifluorides

Compound	Temperature of polymorphous transformation, °C	Melting temperature, °C	Decomposition temperature, °C	ΔH°_{298}, kcal.mole^{-1}		Temperature of reaction with metals, °C	
				decomposition	formation	Al	Si
$LiF \cdot HF$	—	—	151	13.4—13.7	224.2	—	—
$NaF \cdot HF$	—	—	268	17.9	216.6	—	—
$KF \cdot HF$	196	238.7	280—490	21.1—21.3	220.0	270	210
$RbF \cdot HF$	176	205	280—520	21.8	217.3	210	180
$CsF \cdot HF$	61	176	240—500	25.0	216.1	190	170
$NH_4F \cdot HF$	—	126.3	130—260	51.1—51.9	191.4	120	80

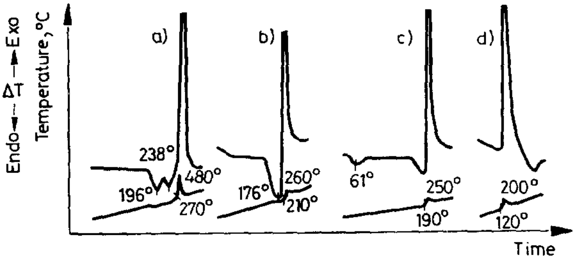

Fig. 1. DTA curves of the mixtures $Al + KF \cdot HF$ (a), $Al + RbF \cdot HF$ (b), $Al + CsF \cdot HF$ (c) and $Al + NH_4F \cdot HF$ (d)

The thermal analysis of mixtures of K, Rb, Cs or NH_4 bifluoride with aluminium indicates that reaction takes place. This is accompanied by a substantial temperature increase and by vigorous gas evolution. The flare of the evolved gas indicates the presence of hydrogen. The endothermic effects in the DTA curves of mixtures of K, Rb or Cs bifluoride with aluminium (Fig. 1) correspond to the polymorphous transformation and melting of the bifluoride. The exothermic effect corresponding to the reaction with aluminium starts immediately after the melting of the bifluoride. In the case of ammonium bifluoride (Fig. 1d), the temperature of the reaction with aluminium is practically identical with the melting point of NH_4HF_2.

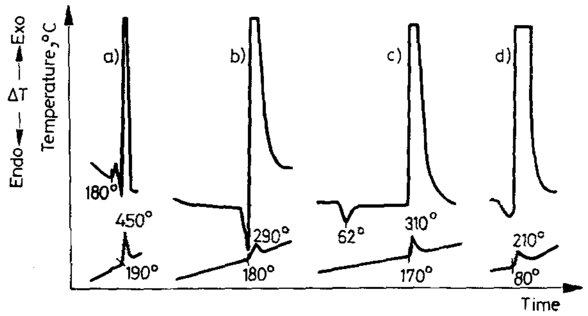

Fig. 2. DTA curves of the mixture Si + KF · HF (a), Si+RbF · HF (b), Si+CsF · HF (c) and Si+NH_4F · HF (d)

Metallic silicon reacts equally actively with the above bifluorides, accompanied by hydrogen evolution. However, the reactions proceed at lower temperatures (Fig. 2).

For both aluminium and silicon, the exothermic peak temperatures corresponding to the reaction with the bifluoride increase from caesium to potassium (cf. Table 1).

In order to elucidate the reaction mechanism, the reaction products were identified. Since the reaction type is obviously similar for all the investigated bifluorides, a more detailed study was limited to the reactions of potassium bifluoride and ammonium bifluoride with aluminium and silicon.

Al + KF · HF

X-ray phase analysis of the reaction product indicated that the main reaction product for the stoichiometric ratio KF · HF : Al = 3 : 1 is potassium hexafluoroaluminate K_3AlF_6 in the tetragonal modification. In the case of excess potassium bifluoride, reflections characterizing a mixture of K_3AlF_6 and KF appear in the diffractogram of the reaction product, owing to the formation of KF in the thermal decomposition of the excess KF · HF (Fig. 3). This phase composition is confirmed by the thermal analysis of the reaction product (Fig. 4) and the comparison of these data with the phase diagram of the KF$-$AlF$_3$ system [14]. The endothermic effect recorded on the DTA curve at ~300° corresponds to the polymorphous transformation of the tetragonal modification to the cubic modification. Further heating results in the melting of the mixture. The temperature of this endothermic effect (825°) is in good agreement with the temperature of the solidus line in the KF$-$AlF$_2$ system of the corresponding composition.

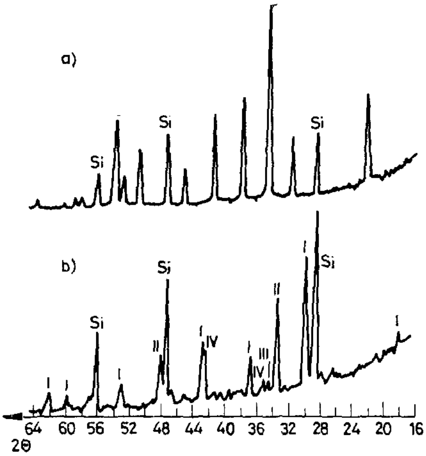

Fig. 3. Diffraction patterns of KF · HF (a) and of the product of the reaction Al+KF · HF (b); I $-$ K$_3$AlF$_6$, II $-$ KF, III $-$ KF · HF, IV $-$ KF · 2H$_2$O

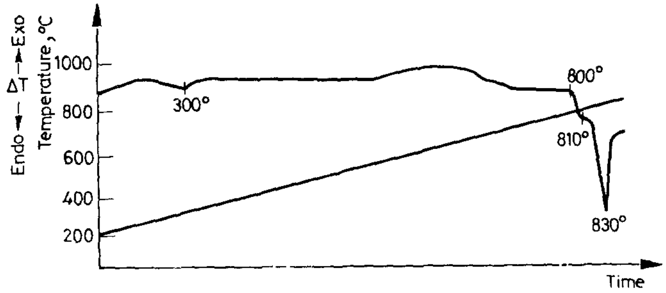

Fig. 4. DTA curve of the product of the reaction Al+KF · HF

The phase composition of the reaction product did not change on heating to 900°, as shown by the identity of the diffractograms. This fact indicates that under our experimental conditions the reaction between potassium bifluoride and aluminium proceeds completely.

Different reaction mechanisms could be assumed leading to the formation of potassium hexafluoroaluminate. Thus, for example, fluorination of metallic aluminium could proceed by hydrogen fluoride, the latter being formed by the thermal decomposition of KF · HF. The further reaction would then consist of the reaction of AlF_3 with KF, yielding K_3AlF_6. However, at the temperatures in question, fluorination of aluminium by hydrogen fluoride proceeds to only a very slight extent [15]. In addition, no interaction between AlF_3 and KF would occur at such low temperatures. This is confirmed by our data on a 1 : 1 mixture of aluminium fluoride and potassium fluoride (Fig. 5), indicating that their interaction starts only immediately before melting: the endothermic effect appears at 570°.

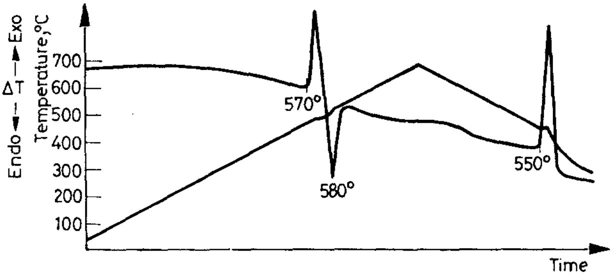

Fig. 5. DTA curve of a mixture of KF and AlF_3 (1 : 1)

Another reaction mechanism, therefore, appears to be correct. As shown above, the reaction between potassium bifluoride and aluminium starts after the melting of KF · HF. Alkali metal bifluorides being ionic compounds, their melts dissociate according to the scheme [13]

$$MF \cdot HF \rightleftharpoons M^+ + HF_2^-$$

and therefore it can be assumed that the reaction between potassium bifluoride and aluminium proceeds according to the following equation:

$$3\,K^+ + 3\,HF_2^- + Al \rightarrow 3\,K^+ + AlF_6^{3+} + 1.5\,H_2^{\uparrow}$$

$Al + NH_4F \cdot HF$

X-ray phase analysis of the reaction products indicates that ammonium hexafluoroaluminate is formed. This is in full agreement with the proposed reaction mechanism. Ammonium bifluoride dissociates in the melt analogously to alkali bifluorides [13] and therefore the formation of the hexafluoroaluminate ion proceeds similarly to the case of potassium bifluoride:

$$3\,NH_4^+ + 3\,HF_2^- + Al \rightarrow 3\,NH_4^+ + AlF_6^{3-} + 1.5\,H_2^{\uparrow}$$

The diffractogram of the reaction product (Fig. 6) indicates the presence of NH_4AlF_4 and AlF_3 besides $(NH_4)_3AlF_6$. This can be explained by the fact that

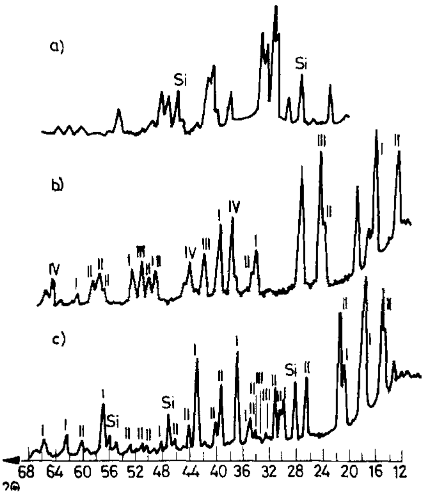

Fig. 6. Diffraction patterns of $NH_4F \cdot HF$ (a), of the product of the reaction $Al + NH_4F \cdot HF$ (b) and of the product of the reaction $Si + NH_4F \cdot HF$ (c); in (b): I – $(NH_4)_3AlF_6$, II – NH_4AlF_4, III – AlF_3, IV – Al, in (c): I – $(NH_4)_2SiF_6$, II – $(NH_4)_2SiF_6 \cdot NH_4F$, III – $NH_4F \cdot HF$

the ammonium hexafluoroaluminate formed is stable only up to 100° and begins to decompose at higher temperatures, yielding first NH_4AlF_4 and subsequently AlF_3 [15]. Ammonium fluoride was not found among the reaction products, since under the given experimental conditions it is thermally unstable.

Si + KF · HF

The reaction between potassium bifluoride and silicon proceeds very vigorously. The diffractogram of the obtained reaction product reveals the presence of only one new phase, potassium fluoride. Thus, no fluorocomplexes are formed in this reaction, in contrast to the reaction of potassium bifluoride with aluminium. Fluorination of silicon yields gaseous SiF_4:

$$4\,KF \cdot HF + Si \rightarrow 4\,KF + SiF_4^{\uparrow} + 2H_2^{\uparrow}$$

Si + NH_4F · HF

The diffractogram of the reaction product reveals the presence of two new phases: ammonium hexafluorosilicate $(NH_4)_2SiF_6$ and a binary salt $(NH_4)_2SiF_6$ NH_4F (Fig. 6). The reaction therefore proceeds in the following way:

$$8\,NH_4F \cdot HF + 2\,Si \rightarrow (NH_4)_2SiF_6 + (NH_4)_2SiF_6 \cdot NH_4F + 3\,NH_4F + 4\,H_2^{\uparrow}$$

The distinctive characteristic of this reaction as compared to the reaction between potassium bifluoride and silicon is the well-known ability of ammonium fluoride to form complexes, resulting in the coordination of SiF_4.

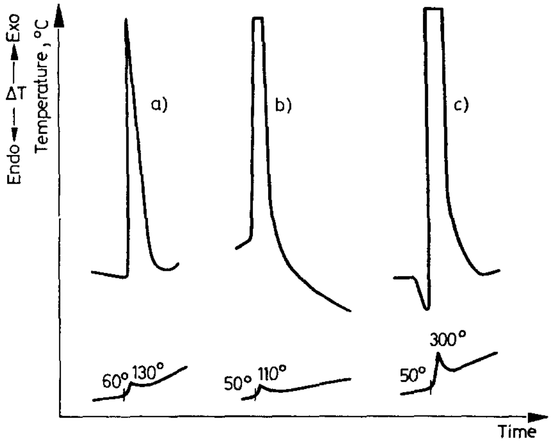

Fig. 7. DTA curves of the mixtures $Al + KF \cdot 2HF$ (a), $Al + RbF \cdot 2HF$ (b) and $Al + CsF \cdot 2HF$ (c)

The results of our work indicate that alkali and ammonium bifluorides are suitable fluorinating agents. The fluorinating reactions proceed at fairly low temperatures and yield fluorocomplexes of binary fluorides.

A further decrease in the reaction temperature can be obtained by using polyhydrofluorides $MF \cdot nHF$ ($n > 1$). Their melting temperatures are lower [13] and they contain a higher percentage of active fluorine. Fig. 7 shows data on the reactions of $MF \cdot 2HF$ ($M = K, Rb, Cs$) with aluminium. The melting points of these polyhydrofluorides are 71.7, 51.7 and 50.2 respectively. Their reaction temperatures with aluminium are very close to their melting points.

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Résumé — On a étudié par ATD les réactions données par les hydrogénofluorures alcalins et d'ammonium avec l'aluminium et la silice. On a déterminé les températures des réactions et identifié les produits de réaction. On a établi le mécanisme de la réaction de fluoration. Les hydrogénofluorures semblent être des réactifs de fluoration très prometteurs.

Zusammenfassung — Die Reaktionen von Alkali- und Ammoniumbifluoriden mit Aluminium und Silicium wurden mittels DTA studiert. Die Reaktionstemperaturen wurden bestimmt und die Reaktionsprodukte identifiziert. Der Reaktionsmechamismus der Fluoridierungsreaktion wurde ermittelt. Die Hydrofluoride erwiesen sich als vielverheißende Fluoridierungsreagenzien.

Резюме — Исследовано взаимодействие бифторидов щелочных металлов и аммония с алюминием и кремнием методом дифференциально-термического анализа. Определена температура взаимодействия, идентифицированы продукты реакции. Установлена схема протекания реакций фторирования металлов. Отмечается перспективность использования гидрофторидов в качестве фторирующих агентов.