

THERMAL STABILITY OF ALKALI METAL BIFLUORIDES

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The thermal stability and non-isothermal kinetics of the decomposition of alkali metal bifluorides were studied using a derivatograph. The removal of hydrogen fluoride from $\text{LiF} \cdot \text{HF}$ and $\text{NaF} \cdot \text{HF}$ takes place before melting and their decomposition occurs in a single stage; however, potassium, rubidium and cesium bifluorides at first undergo polymorphous transformation and melting on heating, and their decomposition proceeds stepwise. The thermal stability of alkali metal bifluorides has been found to increase with increasing ionic radius of the cation, reflecting its correlation with the hydrogen bond strength in these compounds.

Of the presently known hydrofluorides the alkali metal bifluorides $\text{MF} \cdot \text{HF}$ (MHF_2) are the most stable thermally. The thermal stability of these compounds is important from the point of view of their practical application. However, the literature data on this point are sometimes contradictory. For lithium bifluoride, for example, the following decomposition temperatures have been given: 210° [1], 105° [2], 27° [3], and 129.5° [4]. The values of the "rapid decomposition temperature" for $\text{RbF} \cdot \text{HF}$ and $\text{CsF} \cdot \text{HF}$, $500-600^\circ$ and $550-670^\circ$ respectively [1], are also in doubt. The thermal stability of sodium and potassium bifluorides has been studied more thoroughly. The dissociation pressure of $\text{NaF} \cdot \text{HF}$ was determined within different temperature ranges [5–9] and the decomposition temperature found to be 278° [5]. The dissociation pressure of $\text{KF} \cdot \text{HF}$ has been measured in the ranges 196 to 238.8° [10] and 230.5 to 347.5° [11], and the data given by different authors on the temperature of decomposition of potassium bifluoride differ significantly: $310-440^\circ$ [1], $400-504^\circ$ [12], $600-620^\circ$ [13]. The variety of methods used by the authors of the works mentioned above makes the comparison of the results difficult as they often differ greatly. The insufficient purity of the studied substances, especially in the early works, also gave rise to inaccuracies. The kinetics of the decomposition of bifluorides has not been studied at all. In the present work the thermal stability and non-isothermal kinetics of the decomposition of alkali metal bifluorides were studied by thermogravimetry.

Lithium bifluoride was obtained by crystallization from a saturated solution of lithium fluoride (analytical grade) in hydrofluoric acid of special purity [3]. The crystals obtained were washed several times with anhydrous hydrogen fluoride to remove water, and then excess HF was exhausted in a vacuum desiccator

at room temperature. Bifluorides of sodium, rubidium and cesium were prepared from the fluorides of sodium (special purity), rubidium and cesium (analytical grade) and hydrofluoric acid, using the data on HF – MF – H₂O systems [14, 15]. Potassium bifluoride (analytical grade) was recrystallized the aqueous solution. The compounds obtained, MF · HF (M = Na, K, Rb, Cs), were washed with ethanol, dried and analysed for metal by the sulphate method and for hydrogen fluoride by titration with standard alkali solution (Table 1).

The thermal curves were recorded by means of a Paulik – Paulik – Erdey derivatograph. 0.2–0.7 g samples were heated at rates of 3 to 10°/min in a platinum crucible. The peak temperatures shifted by less than 5° on varying the heating rate. The weight loss during heating corresponded within the limits of error to the hydrogen fluoride content of the bifluorides (Table 1).

Table 1
Chemical composition of bifluorides

Compound	M content, weight %		HF content, weight %		Weight loss on heating
	Calculated	Found	Calculated	Found	
LiF · HF	15.11	15.15	43.53	43.58	43.00
NaF · HF	37.10	37.15	32.26	32.23	32.09
KF · HF	50.06	50.00	25.61	25.55	25.90
RbF · HF	68.67	68.63	16.07	16.07	15.86
CsF · HF	77.31	77.37	11.63	11.82	11.57

The bifluorides of lithium and sodium decompose before melting, hydrogen fluoride removal occurs in a single stage and the curves of both of these compounds show an endothermic peak. The decomposition temperature was determined on the thermogravimetric curves at the moment of maximum reaction rate (maximum on the DTG curve). The values for LiF · HF and NaF · HF were 151° and 268°, respectively. The data [1–3] on the decomposition temperature of LiF · HF are very different and are suspect, the more so as they have no strict experimental basis. The value of the temperature at the maximum reaction rate found by us for LiF · HF is close to the value of 129.5° obtained by the extrapolation of dissociation pressure data for LiF · HF over the temperature range 36 to 118° [4]. The difference of the determined temperature of sodium bifluoride decomposition from the one found by the extrapolation of dissociation pressure data of NaF · HF (100–250°) [5] is probably due to the inaccuracy of the experimental data, since the enthalpy of sodium bifluoride decomposition calculated in [5] differs significantly from the data of other authors [6–9].

The decompositions of lithium and sodium bifluorides follow the scheme: $\text{MF} \cdot \text{HF}_{\text{solid}} \rightarrow \text{MF}_{\text{solid}} + \text{HF}_{\text{gas}}$, and it was possible to determine the kinetic parameters of these reactions. We used the method of Horowitz and Metzger [16] for calculation, the applicability of which has been shown by us on alkaline earth

metal hydrofluorides [17, 18]. The errors in the activation energy values have been calculated as the deviation of individual values from the arithmetical mean. The effective values of reaction order, the activation energy and frequency factor obtained by averaging over the series of experiments are given in Table 2. They allow the calculation of the rate constants of the decomposition reactions of $\text{LiF} \cdot \text{HF}$ and $\text{NaF} \cdot \text{HF}$ within the temperature ranges 100 to 151° and 180 to 270°, respectively.

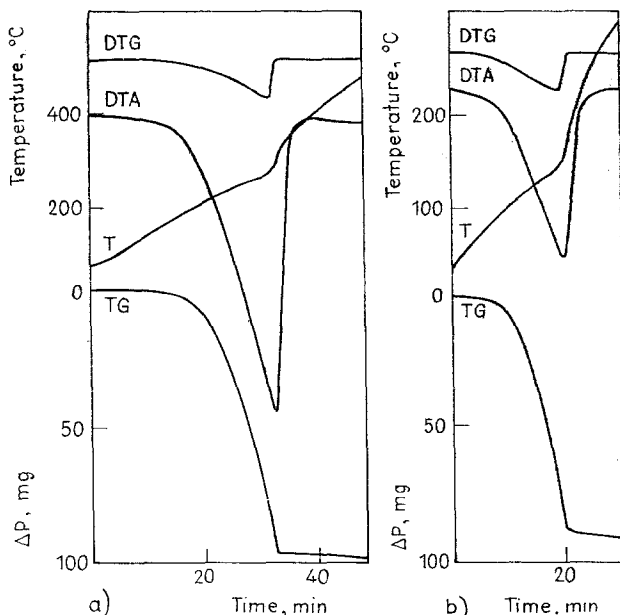


Fig. 1. Derivatograms of a) $\text{LiF} \cdot \text{HF}$ and b) $\text{NaF} \cdot \text{HF}$

Table 2

Kinetic parameters of the decomposition of lithium and sodium bifluorides

Compound	Temperature of maximum reaction rate, °C	Reaction order	Activation energy kcal/mole	Frequency factor mole ^{0.9} min ⁻¹
$\text{LiF} \cdot \text{HF}$	151	0.10	17.5 ± 0.4	4×10^6
$\text{NaF} \cdot \text{HF}$	268	0.10	18.3 ± 0.4	1×10^9

The thermal behaviour of potassium, rubidium and cesium bifluorides differs significantly from that of lithium and sodium bifluorides (see Table 3). Their heating leads first to the polymorphous transformation of the tetragonal modification into the cubic one (first endothermic peak), and then to melting without

appreciable decomposition (second endothermic peak). The temperatures of these endothermic peaks are in good agreement with literature data for the temperatures of the polymorphous transformation [19] and melting of these compounds [4, 20–22]. Further temperature increase leads to their decomposition, so that the removal of hydrogen fluoride occurs in this case from the melt, and the corresponding endothermic peaks are of a complex form. Weight loss curves

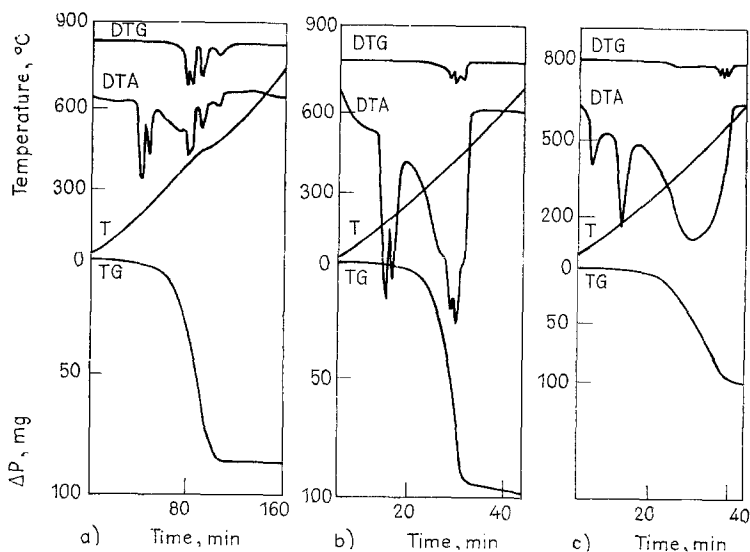


Fig. 2. Derivatograms of a) $\text{KF} \cdot \text{HF}$, b) $\text{RbF} \cdot \text{HF}$ and c) $\text{CsF} \cdot \text{HF}$

for potassium, rubidium and cesium bifluorides are characterized by the occurrence of several sections differing in the decomposition rate (it is especially seen on the DTG curve), which indicates a stepwise removal of hydrogen fluoride from the $\text{MF} \cdot \text{HF}$ melt. However, it cannot be related to the formation of new phases as intermediates, as in the case of alkaline earth metal hydrofluorides [18, 19], because the results of the study of $\text{HF} - \text{MF}$ systems [20–22] show that no intermediate compounds are formed. The results obtained confirm the earlier statement on the irregularity of the process of HF removal from potassium bifluoride on heating [12, 13]; however, the decomposition temperatures of $\text{MF} \cdot \text{HF}$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) given in [1, 12, 13] should be considered as erroneous.

Comparison of the decomposition temperatures of bifluorides shows the increase of their thermal stability with the increase of the ionic radius of the cation, in parallel with the regular change of the decomposition enthalpies of these compounds [4]. The thermal stability increases strongly from lithium to sodium and potassium, while the thermal behaviours of potassium, rubidium and cesium are very similar.

Table 3
Thermal properties of alkali metal bifluorides

Compound	Temperature, °C				
	Polymorphous transformation	Melting	Start of decomposition	Maximum rate of reaction	End of decomposition
LiF · HF	—	—	90	151	170
NaF · HF	—	—	150	268	300
KF · HF	196	236	280	450	490
RbF · HF	177	205	280	450	520
CsF · HF	62	175	240	450	600

The regularities observed can be explained as follows. It is known that anions HF_2^- are formed in the structure of bifluorides $\text{MF} \cdot \text{HF}$ as a result of hydrogen bonding [19, 23, 24]. The results of studies on hydrogen bonding in these compounds [25–27] show that its strength increases from lithium to cesium, but for the isostructural potassium, rubidium and cesium [19] bifluorides the hydrogen bond strengths differ only insignificantly. Decomposition of bifluorides leads to the rupture of hydrogen bonds in their structure and to the breakage of the bifluoride ion. Therefore, it is obvious that the thermal stability of bifluorides is determined mainly by the strength of the hydrogen bonds in them.

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RÉSUMÉ — Etude thermogravimétrique de la stabilité thermique de fluorhydrates de métaux alcalins et de la cinétique de leur décomposition en conditions non isothermes. Dans le cas de $\text{LiF} \cdot \text{HF}$ et de $\text{NaF} \cdot \text{HF}$, le départ de l'acide fluorhydrique se produit avant la fusion et la décomposition s'effectue en une seule étape. Par contre, les fluorhydrates de potassium, rubidium et césium subissent une transition cristalline et une fusion avant de se décomposer. On observe que la stabilité thermique des fluorhydrates de métaux alcalins augmente avec le rayon ionique du cation et l'on montre qu'elle peut être reliée à la force de la liaison hydrogène dans ces composés.

ZUSAMMENFASSUNG — Es wurde die thermische Stabilität und die nichtisotherme Kinetik der Zersetzung der Alkalibifluoride thermogravimetrisch untersucht. HF entweicht aus $\text{LiF} \cdot \text{HF}$ und $\text{NaF} \cdot \text{HF}$ vor dem Schmelzen in einer Stufe. Bei den entsprechenden Salzen des Kaliums, Rubidiums und Cäsiums erfolgt zuerst eine polymorphe Umwandlung, danach das Schmelzen, wobei die Zersetzung in mehreren Stufen vor sich geht. Die thermische Stabilität der Verbindungen wächst mit zunehmenden Ionenradien, was auf die entsprechende Stärke der Wasserstoffbindung zurückgeführt werden kann.

Резюме — Методом термогравиметрического анализа изучена термическая устойчивость и неизотермическая кинетика разложения бифторидов щелочных металлов. Отщепление фтористого водорода от $\text{LiF} \cdot \text{HF}$ и $\text{NaF} \cdot \text{HF}$ происходит до плавления и процесс их разложения протекает в одну стадию, тогда как бифториды калия, рубидия и цезия при нагревании сначала претерпевают полиморфный переход и плавятся, и их разложение протекает ступенчато. Установлено, что термическая устойчивость бифторидов щелочных металлов повышается с ростом ионного радиуса катиона, что указывает на ее корреляцию с силой водородной связи в этих соединениях.