

## Effect of Hydrogen Bonding on Properties of Hexafluorosilicates with Heterocyclic Cations

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**Abstract**—The known data regarding the effects of interionic hydrogen bonding on properties of onium hexafluorosilicates with heterocyclic cations are summarized. Thermal stability parameters and water solubilities for this type of salts are shown to correlate with the number of strong and medium-strength hydrogen bonds or the number of hydrogen donors in the salt structure.

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Over the last few decades, researchers have been focused on various aspects of the coordination and supramolecular chemistry of anions [1–3]. One reason behind this is the important role played by anions in biological systems and engineering processes. The specifics of the coordination chemistry of anions consists in that, although various types of interactions may potentially exist in a cation–anion system [4], the structures of salts of anions with synthetic receptors (such as protonated forms of amines) are formed mostly via interionic hydrogen bonding, as well as Coulomb electrostatic and van-der-Waals interactions [3]. Electrostatic interactions are not oriented; hence, hydrogen bond systems play the major role in structural organization of anion complexes [3, 5]. Fluoride ion is the strongest hydrogen acceptor among the anions; while hexafluorosilicate anion is the strongest one in the series of complex fluoro anions of *p*-elements  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ , and  $\text{SiF}_6^{2-}$  [6], and this gives grounds for regarding onium hexafluorosilicates as convenient models to elucidate the effect of interionic hydrogen bonding on the structural characteristics and properties of these salts [7, 8]. The last is rather topical due to the diverse use of onium hexafluorosilicates and materials based on these compounds [8]. This report is aimed at summarizing the known data illustrating the effect of interionic hydrogen bonding on properties of hexafluorosilicates with heterocyclic cations.

**Thermal stability.** The concept of the stabilizing effect of hydrogen bonding has been repeatedly used in literature in discussing the thermal properties of onium hexafluorosilicates [8–12]. In particular, a decrease in thermal stability of hexafluorosilicates in the series  $(\text{RNH}_3)_2\text{SiF}_6 > (\text{R}_2\text{NH}_2)_2\text{SiF}_6 > (\text{R}_3\text{NH})_2\text{SiF}_6$  was attributed to the decrease in stabilizing effect of  $\text{NH}\cdots\text{F}$  interionic hydrogen bonds caused by a decrease in number of hydrogen-donating centers in the corresponding alkylammonium cations [9]. In

turn, the failure to find candidate ionic liquids among the 1-methyl-3-propylimidazolium, methylammonium, piperidinium, 2,2,6,6-tetramethylpiperidinium, and quinolinium hexafluorosilicates (all these salts are characterized by high melting temperatures) [11, 12] was interpreted in light of X-ray diffraction data, which indicated the stabilization of complex structures by  $\text{CH}\cdots\text{F}$  interactions and  $\text{NH}\cdots\text{F}$  hydrogen bonds.

As mentioned in [12], the thermal stability of carboxypyridinium hexafluorosilicates  $[n\text{-HO(O)CC}_5\text{H}_4\text{NH}]_2\text{SiF}_6$  ( $n = 2, 3, 4$ ) is somewhat higher than that of salts  $(\text{C}_5\text{H}_5\text{NH})_2\text{SiF}_6$  and  $(n\text{-CH}_3\text{C}_5\text{H}_4\text{NH})_2\text{SiF}_6$  ( $n = 2, 3, \text{ or } 4$ ) [13] regardless of the higher basicity index  $\text{p}K_a$  of pyridine and isomeric picolines. A hypothesis has been put forward [12] that the relative stabilization of carboxypyridinium salts as compared to  $(\text{C}_5\text{H}_5\text{NH})_2\text{SiF}_6$  and  $(n\text{-CH}_3\text{C}_5\text{H}_4\text{NH})_2\text{SiF}_6$  is due to additional  $\text{OH}\cdots\text{F}$  interionic hydrogen bonds [12, 14, 15] that are not observed in the structures of pyridinium and picolinium salts.

It is clear that, in the first approximation, the thermal stability of a complex (the onset thermolysis temperature  $T_0$  being typically used as a measure of it) can be related to the number of hydrogen bonds in the structure. However, the hydrogen bonds in the crystal structures of complexes may be considerably differentiated in terms of their energy characteristics [6, 16] and include so-called “weak” hydrogen bonds (where the donor–acceptor distance  $> 3.2 \text{ \AA}$ ) whose contribution can be neglected. Therefore, the parameter  $h$  proposed in [17] is a more adequate parameter for a comparative assessment of the effect of hydrogen bonding on physicochemical characteristics of onium hexafluorosilicates. This parameter takes into account the strength characteristics of hydrogen bonding:

$$h = n/d(\text{D}\cdots\text{A})_{\text{avg}}, \quad (1)$$

**Table 1.** Starting thermolysis temperatures of pyridinium hexafluorosilicates,  $h$  values, and basicities of the corresponding pyridines

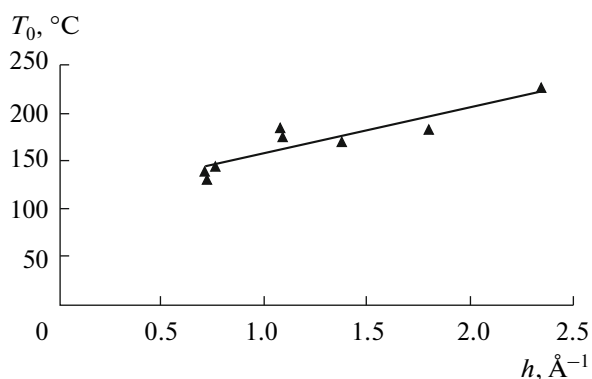
Compound	$T_0$ , °C*	$h$ , Å <sup>-1</sup>	$pK_aL$ [18, 19]	Source
[2-CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> NH] <sub>2</sub> SiF <sub>6</sub>	140	0.71	5.96	[20]
[2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> NH] <sub>2</sub> SiF <sub>6</sub>	130	0.72	6.47	[20]
[2-HO(O)CC <sub>5</sub> H <sub>4</sub> NH] <sub>2</sub> SiF <sub>6</sub>	145	0.76	1.04	[14]
[3-HO(O)CC <sub>5</sub> H <sub>4</sub> NH] <sub>2</sub> SiF <sub>6</sub>	175	1.09	2.05	[15]
[4-HO(O)CC <sub>5</sub> H <sub>4</sub> NH] <sub>2</sub> SiF <sub>6</sub>	185	1.08	1.75	[12]
[4-H <sub>3</sub> NHN(O)CC <sub>5</sub> H <sub>4</sub> NH] <sub>2</sub> SiF <sub>6</sub>	185	1.80	1.82	[21]
[2-H <sub>2</sub> NC <sub>5</sub> H <sub>4</sub> NH] <sub>2</sub> SiF <sub>6</sub>	170	1.38	6.86	[17]
[2,6-(H <sub>2</sub> N) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> NH] <sub>2</sub> SiF <sub>6</sub>	230	2.35	6.48	[17]

\* Sources: [12, 13, 22].

where  $n$  is the number of strong and medium-strength hydrogen bonds ( $D\cdots A \leq 3.2$  Å according to classification [16]) and  $d(D\cdots A)_{\text{avg}}$  is the average donor–acceptor distance in the complex.

Table 1 lists the onset thermal decomposition temperatures for pyridinium hexafluorosilicates and the  $h$  and  $pK_a$  parameters of the corresponding pyridines. The relationship between  $T_0$  and  $h$  is shown in Fig. 1 [22]. Noteworthy, these findings demonstrate the absence of a generally expected symbatic correlation between the  $pK_a$  values of pyridines and the  $T_0$  values of the corresponding hexafluorosilicates, which in particular was observed in the series of hexafluorosilicates of para-substituted anilinium derivatives [23]. Meanwhile, the data in Table 1 and Fig. 1 show a clear correlation between  $T_0$  and  $h$ : an increase in  $h$ , representing the increase in the effect of interionic hydrogen interactions, is accompanied by a linear rise in the onset decomposition temperatures of hexafluorosilicates.

If no structural data are available, the number of potential hydrogen donors ( $N_H$ ) within cations can be used as a variable that allows one to estimate the relationship between the effects of hydrogen bonds and



**Fig. 1.** Relationship between the starting thermolysis temperature  $T_0$  and parameter  $h$ .

the properties of onium hexafluorosilicates. This follows from numerous X-ray diffraction data (see [7, 8] and references therein), which point to the fact that either all or most of the possible hydrogen donors of the cation typically participate in hydrogen bonding. The use of the numbers  $N_H$  as a measure of the effect of hydrogen bonding is a rather raw approximation, since it does not allow for the strength of hydrogen bonds, as opposed to parameter  $h$ . We believe that this allowance could be indirectly provided by using parameter  $h'$  [24]:

$$h' = N_H/pK_aL, \quad (2)$$

where  $pK_aL$  is the basicity constant of ligand L within the corresponding onium cation. Noteworthy, parameter  $h'$  preserves the meaning of  $h$  to a certain extent:  $n$  (the number of hydrogen bonds) and  $N_H$  values change in a symbatic manner, as well as  $d(D\cdots A)_{\text{avg}}$  and  $pK_aL$  (an increase in  $pK_aL$  is accompanied by a decrease in the hydrogen donating ability of the cation and, therefore, an increase in the  $D\cdots A$  distances).

Table 2 lists the onset temperatures of thermal decomposition of pyridinium hexafluorosilicates,  $N_H$  and  $h'$  values. As follows from the data in Table 2 and Fig. 2 (which demonstrate the correlation between the  $T_0$  and  $h'$  values), this correlation is linear and similar to the above-discussed correlation between  $T_0$  and  $h$ .

**Water solubility.** Water solubility, along with thermal stability, is a key macroscopic property of a compound. It is well known that the calculation methods (e.g., the QSPR model and the related approaches [25–27] that are widely used to quantitatively assess water solubilities of organic compounds with molecular structure) cannot be used for ionic compounds, thus making the search for empirical relationships between the structure and solubility of onium hexafluorosilicates a rather topical task. The effect of interionic hydrogen bonds on the solubility of hexafluorosilicates was first demonstrated for salts with substituted pyridinium cations that contain hydrogen-donating groups:  $-\text{COOH}$ ,  $-\text{CONHNH}_2$ ,  $-\text{CONH}_2$ ,