

Interaction of Fluosilicic Acid with *N*-*tert*-Butyl-Substituted Urea. Crystal Structure of *N,N*-Di-*tert*-butylurea

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Abstract—Fluosilicic acid reacts with solutions of *N,N*-di-*tert*-butylurea (DTBU) in methanol or acetone to form crystalline compounds $2\text{DTBU} \cdot \text{H}_2\text{SiF}_6$ and $2\text{DTBU} \cdot \text{H}_2\text{SiF}_6 \cdot \text{Me}_2\text{CO}$, which were characterized by the IR and ^{19}F NMR spectra and mass spectroscopy supplemented by theoretical calculations. According to the data of IR and ^{19}F NMR spectra, the complexes are hexafluorosilicates of O-protonated DTBU. They undergo hydrolysis in organic media with water traces; their solubility in water is very low (0.10 and 0.14 wt %, respectively). In the DTBU structure, two independent ligand molecules are joined by hydrogen bonds $\text{NH}\cdots\text{O}$ ($\text{N}\cdots\text{O}$) 2.888(5)–2.944(5) Å.

INTRODUCTION

The products of reaction between fluosilicic acid (FSA) and N,O- and N,S-ambidentate organic bases have been earlier studied systematically [1]. In the framework of these studies, we have synthesized and characterized FSA compounds with urea and a series of its N-substituted derivatives using different physicochemical methods [2–4]. According to the data of IR spectroscopy and X-ray diffraction analysis [1, 5], these compounds are hexafluorosilicates of O-protonated forms of bases. The complexes with *N*-mono- and *N,N*- and *N,N*-dialkyl-substituted derivatives of urea (in particular, methylurea) are rather highly soluble in water. However, FSA compounds with a low solubility are of interest for analytical and technological purposes.

In this work, we studied the conditions of preparation and some properties of the products of FSA reaction with *N-tert*-butyl-substituted derivatives of urea containing the bulky hydrophobic alkyl substituents.

EXPERIMENTAL

Synthesis. Commercial 45% FSA solution (analytical grade) was used. *N-tert*-butylurea (TBU) and *N,N*-di-*tert*-butylurea (DTBU) were synthesized by the alkylation of urea with *tert*-butanol according to a described procedure [6].

X-ray diffraction analysis of a single crystal of DTBU (0.464 × 0.067 × 0.028 mm) was carried out on an Stoe IPDS diffractometer with an image plate detector (180 K, MoK_α radiation, $2\theta_{\text{max}} = 51.94^\circ$, index range $-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-20 \leq l \leq 22$). The crystals are orthorhombic (FW = 172.27): $a = 9.4579(14)$, $b = 13.823(2)$, $c = 17.9603(18)$ Å, $V = 2348.1(5)$ Å³,

$F(000) = 768$, $\rho_{\text{calcd}} = 0.975$ g/cm³, $\mu = 0.064$ mm⁻¹, $Z = 8$, and space group $\text{P}2_12_12_1$.

The structure was solved by direct methods followed by Fourier syntheses. Hydrogen atoms were fixed in the calculated positions. The least-squares refinement on 4596 reflections was carried out in the anisotropic approximation for all non-hydrogen atoms (SHELXL97) [7]. The final R factor was 0.0400 for reflections with $I > 2\sigma(I)$, $wR_2 = 0.1272$, GOOF (for F^2) = 0.524, $\Delta\rho_{\text{min}} = -0.105$, and $\Delta\rho_{\text{max}} = 0.114$ eÅ⁻³.

The crystallographic data were deposited with the Cambridge Structural Database as an additional publication CCDC-202935. The data on the structural factors are available from the authors.

The coordinates of atoms and thermal parameters are presented in Table 1. The bond lengths and bond angles are given in Table 2. The parameters of hydrogen bonds are listed in Table 3. A brief description of the structural parameters of DTBU is given in [8].

IR absorption spectra were recorded on a Specord 75IR spectrophotometer in a region of 4000–400 cm⁻¹ (suspensions in Nujol and KRS-5 glasses). ^{19}F NMR spectra were obtained on a Bruker AC-200P radiospectrometer (the working frequency was 188.3 MHz, Fourier mode, CFCl_3 as an external standard). Mass spectra were recorded on an MX-1321 instrument (direct sample injection into the source, the energy of ionizing electrons was 70 eV). The charge distributions and geometry were calculated by the AM1 method (HYPERCHEM program package).

Table 1. Atomic coordinates and thermal parameters $U_{\text{equiv/iso}}$ in the structure of DTBU

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equiv/iso}}, \text{\AA}^2$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equiv/iso}}, \text{\AA}^2$
O(1)	0.3017(4)	0.5505(3)	0.09227(19)	0.0600(11)	H(18C)	0.256	0.797	0.052	0.11
O(2)	0.3040(4)	0.5484(3)	-0.1662(2)	0.0632(12)	C(19)	0.0761(6)	0.7442(4)	-0.0583(3)	0.0719(19)
N(11)	0.4143(4)	0.5108(3)	-0.0162(2)	0.0508(12)	H(19A)	0.1553	0.7811	-0.079	0.11
H(11)	0.425	0.527	-0.063	0.06	H(19B)	0.0001	0.789	-0.044	0.11
N(12)	0.2422(4)	0.6260(3)	-0.0170(2)	0.0480(12)	H(19C)	0.041	0.699	-0.096	0.11
H(12)	0.266	0.632	-0.064	0.06	C(21)	0.2765(7)	0.5224(4)	-0.2309(3)	0.0601(18)
N(21)	0.1746(6)	0.4569(4)	-0.2475(3)	0.0809(18)	C(22)	0.0813(8)	0.4079(5)	-0.1975(4)	0.072(2)
H(21)	0.165	0.443	-0.295	0.10	C(23)	-0.0149(10)	0.4802(7)	-0.1630(6)	0.197(6)
N(22)	0.3469(5)	0.5579(4)	-0.2916(2)	0.0664(15)	H(23A)	0.041	0.528	-0.135	0.30
H(22)	0.318	0.539	-0.336	0.08	H(23B)	-0.080	0.447	-0.129	0.30
C(11)	0.3168(6)	0.5605(4)	0.0238(3)	0.0498(14)	H(23C)	-0.069	0.513	-0.202	0.30
C(12)	0.5056(7)	0.4309(4)	0.0117(4)	0.0664(18)	C(24)	0.1674(11)	0.3540(8)	-0.1409(6)	0.237(8)
C(13)	0.4123(6)	0.3465(4)	0.0376(4)	0.084(2)	H(24A)	0.253	0.329	-0.165	0.36
H(13A)	0.344	0.370	0.074	0.13	H(24B)	0.112	0.300	-0.121	0.36
H(13B)	0.472	0.296	0.060	0.13	H(24C)	0.193	0.398	-0.100	0.36
H(13C)	0.362	0.3194	-0.003	0.13	C(25)	-0.0099(9)	0.3390(5)	-0.2416(4)	0.119(3)
C(14)	0.5997(6)	0.4677(4)	0.0747(4)	0.093(2)	H(25A)	-0.067	0.376	-0.277	0.18
H(14A)	0.6541	0.524	0.057	0.14	H(25B)	-0.072	0.303	-0.208	0.18
H(14B)	0.665	0.416	0.090	0.14	H(25C)	0.051	0.293	-0.269	0.18
H(14C)	0.541	0.487	0.117	0.14	C(26)	0.4670(7)	0.6248(4)	-0.2887(3)	0.0568(17)
C(15)	0.5956(6)	0.3990(4)	-0.0534(4)	0.087(2)	C(27)	0.4223(7)	0.7201(4)	-0.2543(4)	0.085(2)
H(15A)	0.534	0.376	-0.094	0.13	H(27A)	0.3411	0.746	-0.282	0.13
H(15B)	0.658	0.346	-0.038	0.13	H(27B)	0.501	0.766	-0.257	0.13
H(15C)	0.653	0.454	-0.071	0.13	H(27C)	0.396	0.710	-0.202	0.13
C(16)	0.1260(6)	0.6881(4)	0.0104(4)	0.0579(17)	C(28)	0.5923(7)	0.5811(4)	-0.2484(3)	0.076(2)
C(17)	0.0048(6)	0.6248(4)	0.0398(4)	0.074(2)	H(28A)	0.565	0.565	-0.197	0.11
H(17A)	-0.024	0.579	0.001	0.11	H(28B)	0.670	0.628	-0.247	0.11
H(17B)	-0.076	0.666	0.053	0.11	H(28C)	0.623	0.523	-0.275	0.11
H(17C)	0.037	0.589	0.084	0.11	C(29)	0.5071(7)	0.6419(4)	-0.3709(3)	0.075(2)
C(18)	0.1787(6)	0.7575(4)	0.0714(3)	0.0725(19)	H(29A)	0.540	0.581	-0.3930	0.11
H(18A)	0.213	0.720	0.114	0.11	H(29B)	0.583	0.690	-0.374	0.11
H(18B)	0.101	0.800	0.087	0.11	H(29C)	0.424	0.665	-0.398	0.11

RESULTS AND DISCUSSION

Single crystals of DTBU as thin colorless needles were obtained in an attempt to isolate the product of the DTBU reaction with FSA from a water–methanol solution (the molar ratio FSA : DTBU = 3 : 1). The crystal structure of DTBU is shown in the figure. Two independent DTBU molecules in an asymmetric unit form dimers due to intermolecular hydrogen bonds NH...O (N...O 2.888(5)–2.944(5) Å). The C=O bond lengths for two independent DTBU molecules are 1.245(6) and 1.244(6) Å, and the C–N bond length is 1.363(6)–1.489(6) Å. In the W(VI) complex with O-bonded DTBU [9], the C=O distance is elongated to 1.257(5) Å,

while the C–N distances, on the contrary, are shortened to 1.340(8) and 1.316(1) Å due to the coordination effect. The standard deviation of the atoms from the plane of amide group conjugation is 0.036 and 0.019 Å for two independent DTBU molecules **A** and **B**, respectively. The dihedral A/B angle is 86.9°. The thermal vibrations of the *tert*-butyl groups of molecules **A** and **B** differ significantly.

The interaction of FSA with a methanolic solution of DTBU (the molar ratio FSA : DTBU = 6 : 1) followed by the isothermal evaporation of the reaction solution at room temperature resulted in the crystallization of a colorless compound, whose composition was found from the data of elemental analysis.

For 2DTBU · H₂SiF₆ (**I**) anal. calcd. (%): Si, 5.73; N, 11.46.

Found (%): Si, 5.94; N, 10.83.

Mass spectrum of **I**: M⁺_{DTBU} (*m/z* = 172, *I* = 5%), SiF₃⁺ (*m/z* = 85, *I* = 8%), C₄H₁₀⁺ (*m/z* = 58, *I* = 100%).

The product of FSA reaction with a solution of DTBU in acetone (the molar ratio FSA : DTBU = 3 : 1) was isolated similarly to compound **I** and represents a solvate 2DTBU · H₂SiF₆ · Me₂CO (**II**).

For 2DTBU · H₂SiF₆ · Me₂CO (**II**) anal. calcd. (%): Si, 5.15; N, 10.33.

Found (%): Si, 5.02; N, 10.63.

Mass spectrum of M⁺_{DTBU} (*m/z* = 172, *I* = 3%), SiF₃⁺ (*m/z* = 85, *I* = 2%), C₄H₁₀⁺ (*m/z* = 58, *I* = 100%).

No solid products of the reaction of FSA with TBU were isolated.

The data of IR spectroscopy (Table 4) confirm that compound **II** contains an acetone molecule. The spectrum of the acetone solvate exhibits an intense band at 1625 cm⁻¹ corresponding to ν(C=O) vibrations. This band is absent from the IR spectrum of compound **I**. The other features of the IR spectra of compounds **I** and **II** are similar. The appearance of new medium-intensity bands at 2730 and 2650 cm⁻¹ and an intense band at 1765 cm⁻¹ attributed to ν(OH) and δ(COH) vibrations, respectively [2, 3, 10], indicates the O-protonation of DTBU in the salt structures.

In this case, the ν(C=O) band, which is observed in the IR spectrum of DTBU at 1620 cm⁻¹, undergoes the low-frequency shift to 1590 cm⁻¹ in the spectra of compounds **I** and **II**. The fact of DTBU O-protonation is indirectly confirmed by the calculations of charge distribution in a base molecule, indicating the localization of a maximum negative charge on the oxygen atom of the carbonyl group (-0.335), whereas the charges on the nitrogen atoms are -0.135 and -0.305. The ν(SiF) vibrations that characterize the SiF₆²⁻ anions appear in the IR spectra of compounds **I** and **II** as an intense absorption band at 730–735 cm⁻¹, including the δ(CH₃) vibrations as well. In the spectrum of compound **I**, the δ(SiF₂) vibrations appear as a doublet (in the spectrum of compound **II**, as a triplet) absorption band with maxima at 475, 455 and 475, 460, 430 cm⁻¹, respectively.

According to the ¹⁹F NMR data, salt **I** is stable in anhydrous chloroform: the spectrum of the solution at room temperature contains an intense narrow singlet signal of the SiF₆²⁻ anion (δ_F = -127.6 ppm). The appearance of a low-intensity signal of the BF₄⁻ anion (δ_F = -148.0 ppm) [11] can be due to the manipulation with the samples in glassware. The dissolution of compound **I** in methanol and acetone, which were not dehy-

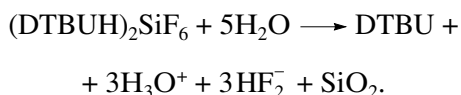
Table 2. Bond lengths and bond angles in the structure of DTBU

Bond	<i>d</i> , Å	
	molecule A	molecule B
O–C(1)	1.245(6)	1.244(6)
N(1)–C(1)	1.356(6)	1.356(7)
N(1)–C(2)	1.489(6)	1.430(7)
N(2)–C(1)	1.363(6)	1.368(6)
N(2)–C(6)	1.479(6)	1.466(6)
C(2)–C(3)	1.535(7)	1.486(10)
C(2)–C(4)	1.528(7)	1.500(9)
C(2)–C(5)	1.512(8)	1.509(8)
C(6)–C(7)	1.536(7)	1.515(7)
C(6)–C(8)	1.539(7)	1.514(7)
C(6)–C(9)	1.530(7)	1.542(7)
Angles	ω, deg	
OC(1)N(1)	123.0(5)	123.2(6)
OC(1)N(2)	123.1(5)	122.6(6)
N(1)C(1)N(2)	113.8(5)	114.2(5)
C(1)N(1)C(2)	126.3(5)	128.1(5)
C(1)N(2)C(6)	126.2(5)	125.1(5)
N(1)C(2)C(3)	109.4(5)	108.7(7)
N(1)C(2)C(4)	109.9(5)	109.0(6)
N(1)C(2)C(5)	106.4(5)	108.8(6)
N(2)C(6)C(7)	109.8(4)	110.3(5)
N(2)C(6)C(8)	111.0(5)	111.8(5)
N(2)C(6)C(9)	104.8(5)	104.7(5)
CCC (in <i>t</i> -Bu)	109.6(5)–111.3(5)	107.1(7)–112.6(8)
Torsion angles	τ, deg	
C(2)N(1)C(1)O	7.2(9)	1.0(11)
C(2)N(1)C(1)N(2)	-176.2(5)	-178.9(6)
C(6)N(2)C(1)O	-5.7(9)	4.0(10)
C(6)N(2)C(1)N(1)	177.7(5)	-176.1(5)
C(1)N(1)C(2)C(3)	61.5(7)	66.0(10)
C(1)N(1)C(2)C(4)	-61.1(7)	-57.1(10)
C(1)N(1)C(2)C(5)	179.9(5)	-177.8(7)
C(1)N(2)C(6)C(7)	-60.1(7)	-62.9(8)
C(1)N(2)C(6)C(8)	62.4(7)	62.1(8)
C(1)N(2)C(6)C(9)	-177.7(5)	179.9(6)

Table 3. Selected hydrogen bond geometry in the structure of DTBU

Bond D–H...A	Distance, Å			Angle D–H...A, deg
	D–H	H...A	D...A	
N(11)–H(11)...O(2)	0.88	2.19	2.936(6)	142
N(12)–H(12)...O(2)	0.88	2.19	2.944(5)	143
N(21)–H(21)...O(1)	0.88	2.05	2.888(5)	158
N(22)–H(22)...O(1)	0.88	2.12	2.928(6)	153

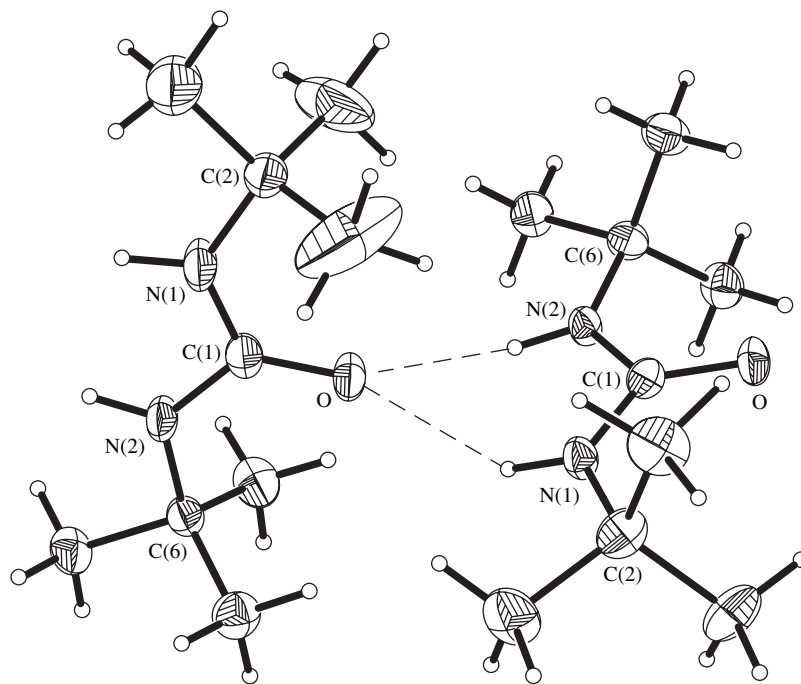
drated and contained up to several wt % of water, is accompanied by salt hydrolysis



This process is reflected in the change in the ^{19}F NMR spectrum: the appearance of a broadened signal of the hydrodifluoride anion ($\delta_{\text{F}} = -139.3 \dots -142.4$ ppm) [12, 13]. The behavior of compound **II** in a medium of the above-discussed solvents is similar. Evidently, the hydrolytic instability of compounds **I** and **II** is mainly determined by the properties of DTBU as a very weak base (hydrolysis of the cation). The hydrolytic decomposition of the SiF_6^{2-} anions can be stimulated by a substantial weakening (elongation) of some Si–F bonds induced by the involvement of the corresponding fluorine ligands into the strong hydrogen bonds OH...F. This disproportionation of the Si–F bond lengths was

found in the structure of the urea complex $[(\text{H}_2\text{N})_2\text{COH}]_2\text{SiF}_6$ [5] and confirmed by the results of simulation of the geometry of compound **I**: in this compound, a strong hydrogen bond OH...F (O...F 2.03 Å) is formed between one of the $[(t\text{-BuNH})_2\text{COH}]^+$ cations and the SiF_6^{2-} anion, which elongates one Si–F bond (1.76 Å) as compared with the other five Si–F bonds (1.64–1.66 Å). A dependence between the relative weakening of the Si–F bonds in organopentafluorosilicates due to H-bonding and the affinity of the RSiF_5^{2-} anions to hydrolysis in aqueous solutions was discussed in [14].

Complexes **I** and **II** show very low solubility in water: 0.10 and 0.14 wt %, respectively, at 25°C. Note, for comparison, that the solubility of the salt Na_2SiF_6 , in the form of which FSA is usually precipitated in technological practice, is 0.72 wt % [15]. Evidently, the relative solubility of the FSA compounds with N-alkyl(aryl)-substituted derivatives of urea should be determined mainly by the base nature, namely, by the balance of the hydrophilic parameters of the amide fragment and hydrophobic alkyl substituents; comparatively soluble salts correspond to more soluble bases. In this respect, the following order of solubility decrease for the FSA compounds with the urea derivatives with the general formula $2\text{L} \cdot \text{H}_2\text{SiF}_6$ seems quite expected (solubility of the base in water in wt % at 25°C is given in parentheses): *N,N*-dimethylurea (43.11, our data) > *N,N*-dimethylurea (22.97 [4]) > *N*-phenylurea (1.35 [16]) > DTBU (0.10). The solubility of the *N,N*-



Molecular structure of DTBU (the 20% probability ellipsoids are shown; molecule **A** is on the right, and molecule **B** is on the left).

Table 4. Wave numbers (cm⁻¹) of absorption band maxima in the IR spectra of DTBU, **I**, and **II**

DTBU	I	II	Assignment
	3550 m		v(NH)
3420 m			
3335 s	3340 m	3330 s	
3170 m			v(COH)
	3050 s	3045 m	
2725 sh	2730 m	2730 m	δ(COH)
	2650 m	2655 m	
	1765 v.s	1760 v.s	v(CO)
1655 sh			
1620 s		1625 s	δ(CNH), v(CN)
	1590 s	1590 m	
1565 sh			v _{as} (N-C(CH ₃) ₃), ρ(CNH) δ(NCN)
1540 s	1525 s	1520 s	
1500 sh	1500 m	1500 sh	
	1405 m	1405 s	v _s (N-C(CH ₃) ₃), ρ(CNH), τ(CNH), τ(CH ₃)
1280 m	1280 m	1275 m	
1220 m	1220 m		ρ(CNH), δ(CH ₃), v(SiF)
1200 m	1180 m	1180 m	
955 m	965 m	965 m	δ(NCO), δ(NCN)
	935 sh		
915 m	915 m	905 m	δ(SiF ₂)
	855 m	850 m	
775 sh	785 s	785 s	
720 m	735 v.s	715 s	
	655 s	655 c	
640 m	635 sh	620 s	
610 sh			
530 w	530 w	530 w	
	510 w	510 m	
	475 s	475 s	
	455 m	460 m	
		430 m	

dimethylurea complex (*sym*-DMU), which is the most hydrophilic of the urea derivatives studied) is very high, such that a solid phase 2*sym*-DMU · H₂SiF₆ cannot be isolated in the FSA-*sym*-DMU-H₂O system at 25°C.

Thus, the reaction of FSA with N,O-ambidentate DTBU affords hexafluorosilicates of the O-protonated

form of the base. These compounds exhibit hydrolytic instability and very low solubility in water. The crystal structure of DTBU was determined. A correlation between the solubilities of the urea derivatives and their compounds with FSA was observed.

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