leveling of the chemical reactivity can also be observed rather reliably on going from nonviscous solutions to viscous solutions at a temperature higher than the glass transition temperature of the solvent. This implies that the leveling effect should be taken into account in constructing theoretical models of liquid-phase intramolecular processes.

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Experimental

The radicals studied in this work were prepared by the reaction of the corresponding organometallic derivatives with 3,6-di-*tert*-butylpyrocatechol in the presence of air followed by evacuation according to the previously described procedure.[4,7] Multiligand silicon-containing free radicals with pyrocatechol ligands were synthesized by the reaction of silicon bis-3,6-di-*tert*-butylpyrocatecholate with the corresponding radicals.[5] ESR spectra were recorded on a Varian E-12A spectrometer.

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Structure and thermal stability of difluoroamino compounds in the liquid state

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The kinetics of decomposition of 15 difluoroamino compounds with NF_2 groups at primary, secondary, and tertiary carbon atoms in the liquid state was investigated. Activation energies (E_a) for all of the compounds were in the interval 100—120 $kJ \cdot mol^{-1}$. The reaction rate does not depend on the electronic effects of the substituents and decreases only in the case of steric shielding of the NF_2 group. For *N*-difluorobenzylamine it was shown that the gas-phase elimination of HF is characterized by $E = 176$ $kJ \cdot mole^{-1}$, while the rate of decomposition in a solution depends on the dielectric constant of the medium. Based on the results obtained, a mechanism for liquid-phase decomposition, which involves heterolysis of the N—F bonds, is suggested.

Key words: difluoroamino compounds, thermal decomposition, reaction mechanism.

The most common type of organic compounds with an N—F bond are substances with NF_2 groups at the primary and secondary carbon atoms. Information on the thermal decomposition of these compounds is very limited. Some examples suggest that the gas-phase decomposition of these substances at moderate temperatures occurs as elimination of HF, and at higher temperatures (400—600 °C), the C—N bond cleaves.[1–3] For vicinal compounds, abstraction of N_2F_4 is also possible (see Ref. 4).

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Table 1. Kinetic parameters of the decomposition of difluoroamines in the liquid state

Compound	ΔV_∞ /cm^3 g^{-1}	Interval T/°C	E_a /kJ mol^{-1}	log$A$ /s^{-1}	ω*
1 $C_6H_5CH_2NF_2$	266	110—145	110.2	8.33	1.0
2 $(C_6H_5)_2CHNF_2$	122	110—150	118.2	9.55	1.3
3 $C_6H_5CH(NF_2)_2$ **	315	110—150	109.1	8.30	1.3
4 $C_6H_5CH(NF_2)CN$	160	110—150	108.9	8.50	2.1
5 $CH_3CH(NF_2)CH{=}CHCH_2NF_2$	303	110—145	100.8	6.88	0.7
6 $C_6H_5CH(NF_2)CH_2NF_2$	280	90—140	116.1	9.30	1.4
7 $F_2NCH(CH_2)_4CHNF_2$	334	100—145	112.7	8.55	0.8
8 $[F_2NCH_2CH(NF_2)CH_2{-}]_2$	310	100—140	119.8	9.35	0.5
9 $F_2NCH_2CH(NF_2)CH_2OOCC(CH_3)(NF_2)CH_2NF_2$	268	110—150	100.6	6.80	0.7
10 $F_2NCH_2(CHNF_2)_3CH_3$	332	107—157	106.4	8.00	1.6
11 $F_2NCH_2C(CH_3)(NF_2)CH(NF_2)CH_2NF_2$	211	107—157	111.5	8.60	1.2
12 $(CH_3)_2CHC(CH_3)(NF_2)CH_2NF_2$	268	90—140	128.2	9.80	0.1
13 $[F_2NCH_2C(CH_3)(NF_2)COOCH_2{-}]_2$	248	110—160	119.8	8.73	0.1
14 $CH_3COOC(CH_3)(NF_2)CH_2C(CH_3)(COOCH_3)CH_2NF_2$	180	110—160	129.4	9.60	0.05
15 $(CH_3)_2C(NF_2){-}C(NF_2)(CH_3)_2$	238	110—160	125.7	9.38	0.1

* Relative rate at 100 °C

** The data are taken from Ref. 5

Close analogs of the compounds under consideration, bis(difluoroamino) compounds, that do not contain α-hydrogen decompose in the liquid state by homolytic cleavage of the C—N bond with E_a > 180 kJ mol^{-1}, and those containing α-hydrogen decompose by an ionic mechanism with E_a of about 100 kJ mol^{-1} (see Ref. 5). Therefore, the role of α-hydrogen in the decomposition of monofunctional compounds also needs verification.

In the present work, we studied the liquid-phase decomposition of difluoroamines with NF_2 groups at the primary, secondary, and tertiary carbon atoms, both vicinal and separated by several atoms. Structures with various branchings at the α- and β-carbon atoms, which shield neighboring NF_2 groups, were specially chosen. The series of structures used makes it possible to determine the role of induction and steric effects, conjugation of the substituent with the reaction site, and the presence of a hydrogen atom in the α-position relative to the NF_2 group for the reaction. Two compounds, $PhCH_2NF_2$ (**1**) and Ph_2CHNF_2 (**2**), were taken for comparison with the previously[5] studied $PhCH(NF_2)_2$ (**3**). In particular, comparison of **1** with **3**, which has a higher acidity, enables one to determine immediately whether dissociation of a C—H bond is significant for decomposition.

Experimental

The compounds studied and the kinetic parameters of their liquid-phase decomposition are given in Table 1. The rates were measured by the manometric method. Rate constants were calculated from the time necessary for 1 % conversion, and the overall gas evolution used for calculating the degree of conversion was determined at low m/v values (10^{-4} g cm^{-3}) and high temperatures (180 °C) to diminish variations in the composition of products due to autocatalytic reactions. The accuracy of the manometric methods for compounds **1**, **2**, and **15** was confirmed by GLC in which the decrease in the amount of the starting compound was monitored. Decomposition of compound **1** in solution was also studied by this method. The conditions of the analysis have been described previously.[5] At 140 °C, the rate constants determined by the two methods coincide with an accuracy of 20 %.

When the gas-phase decomposition of difluoroamines **2**, **6**, **10**, and **15** was investigated, we found that at temperatures limited by the observed rate constant of 10^{-3} s^{-1} and at initial vapor pressure p_0 > 50 Torr, the reaction mostly occurs at the surface of the vessel in all of the cases, except for compound **1**. Decomposition of **1** above 280 °C obeys first-order kinetics and does not depend on either p_0, within the interval 30—300 Torr, or S/V for the vessel when S/V < 1 cm^{-1}. At lower temperatures and greater S/V, heterogeneous decomposition of **1** on the surface begins, and this type of decomposition gradually comes to prevail. PhCN, SiF_4, and H_2O were detected among the products of the homogeneous decomposition of **1**. The final gas evolution is poorly reproducible and varies over the range from 1.45 to 1.97 moles. A brown film of condensed products is deposited on the walls of the vessel.

Decomposition of 2 % solutions of compound **1** (the solvents are listed in Table 2) occurs according to a first-order reaction up to a substantial degree of conversion. Arrhenius parameters for the decomposition of **1** are given in Table 2. The rate constant depends on the polarity of the medium. From the data of Table 2 for 132 °C, a linear relationship was established:

$$\log k = -4.644 - 3.22/D.$$

Results and Discussion

The results obtained imply that the homogeneous gas-phase decomposition of **1** occurs through elimina-

Table 2. Kinetic parameters of the decomposition of *N*-benzyldifluoroamine

Medium	Interval T/°C	E_a /kJ mol^{-1}	lg(A/c)	$k \cdot 10^6$/s^{-1} at 132 °C
Gas phase	280—300	178.1	11.78	$6.96 \cdot 10^{-6}$
Liquid phase	110—145	110.2	8.33	1.37
Solution in				
CCl_4	170—190	106.4	7.61	0.78
C_6H_6	170—190	107.2	7.90	1.21
$CHCl_3$	132	—	—	5.20
CH_3CN	132	—	—	18.00
CH_3NO_2	132	—	—	22.00

tion of HF. The activation energy coincides with that (176 kJ mol^{-1}) for thermal abstraction of HF from CH_3NF_2 estimated from experiments with chemically activated CH_3NF_2 (see Ref. 1). Cleavage of the C—N bond in **1** may be excluded on the basis of the composition of the products and the bond dissociation energy, D(C—N) = 214 kJ mol^{-1} (see Ref. 6). The preexponential factor for C—N bond cleavage must be about $10^{14.5}$ s^{-1}, therefore this process would compete with elimination of HF at temperatures above 400 °C.

The products formed in the first stage, PhCH=NF and HF, do not affect the rate of decomposition due to their rapid decay: HF reacts with glass to give SiF_4 and H_2O, while PhCH=NF quickly decomposes to yield PhCN and HF and partly polymerizes on the surface. Due to polymerization, the total gas evolution (1.9 mol) is less than that following from the overall reaction.

$$\mathbf{1} \rightarrow PhCN + H_2O + 0.5\ SiF_4$$

The decomposition rate of compound **1** in the liquid phase is higher than that in the gas phase by 6 orders of magnitude. This attests to a change in the mechanism and accounts for a significant degree of the heterogeneous reaction in the decomposition of difluoroamine: in the layers adsorbed on the surface, rapid decomposition occurs, which is governed by liquid-phase laws, and the contribution of this process increases with the increase in the p_0/p_s ratio, where p_s is the saturated vapor pressure at the temperature of the experiment.

The decomposition rate of **1** in solution depends on the dielectric constant of the medium, which attests to the strongly polar character of the transition state.

The decomposition rates of compounds **1—11** in the liquid phase are practically identical. Undoubtedly, the mechanism of the decomposition of all of these compounds is the same. Small preexponential factors are not consistent with any of thee homolytic monomolecular mechanisms and are characteristic of E1-type ionic processes. The absence of electronic and resonance effects of the substituents on the reaction rate indicates that they are remote from the reaction site, *i.e.*, the latter may be located at the N atom rather than at the C atom. This is also supported by the fact that the rate does not depend on the polarity of the C—H bond, as can be seen from a comparison of compound **1** with compounds **2** and **3**.

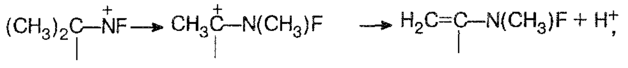
All of these facts can be unambiguously explained by assuming that the liquid-phase decomposition of fluoroamines occurs through ionic dissociation of the N—F bond according to the following scheme

$$RCH_2NF_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [RCH_2NF^+|F^-] \xrightarrow{k_3} RCH{=}NF + HF$$

The observed rate constants and activation energies are $k_0 = k_1k_3/k_2$ and $E_0 = E_1 + E_3 - E_2$.

Compounds **12—15**, having chain branchings at the α- and β-carbon atoms, decompose more slowly than the other compounds by an order of magnitude. This is also explained by steric hindrance to solvation of the ion pair from the side of the bulky substituents.

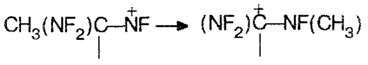
Decomposition of the NF_2 group at a tertiary carbon atom occurs at the same rate as the decomposition of $R_3CCH_2NF_2$ groups sterically shielded from the side of the β-atom. Thus, in multifunctional compounds the presence of an α-hydrogen atom is not a necessary condition for decomposition, in contrast to the case of *gem*-bis(difluoroamino) compounds.[5] It is likely that the cationic constituent of the ion pair containing a tertiary carbon atom undergoes rearrangement, which ends in the abstraction of H$^+$



$$(CH_3)_2C{-}\overset{+}{N}F \longrightarrow CH_3\overset{+}{C}{-}N(CH_3)F \longrightarrow H_2C{=}C{-}N(CH_3)F + H^+,$$

but in this case k_3 is smaller and E_3 is greater than those for direct elimination of H$^+$ from R_2CHN^+F.

It was found previously[5] that the decomposition of *gem*-bis(difluoroamino) compounds does not involve abstraction of HF if no hydrogen atom exists in the α-position. Apparently, the rearrangement of the cation



$$CH_3(NF_2)C{-}\overset{+}{N}F \longrightarrow (NF_2)\overset{+}{C}{-}NF(CH_3)$$

does not occur, since the electron-withdrawing NF_2 group destabilizes the positive charge at the α-carbon atom.

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Novel organosilicon betaines

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The structure of organosilicon betaines $R_3P^+CMe_2SiMe_2S^-$ (R = Ph and Me_2N) was determined by X-ray diffraction analysis.

Key words: organosilicon betaines, X-ray diffraction analysis.

The Wittig reaction is one of the fundamental reactions of organic chemistry. Interest in the study of this reaction for thiocarbonyl compounds has grown in recent years.[1,2] It has been assumed (without experimental verification) that in this case betaines $R_3P^+CR_2{}^1CR_2{}^2S^-$ (**1**) act as intermediates. Recently we prepared silicon-containing analogs of these betaines, $R_3P^+CR_2{}^1SiR_2{}^2S^-$ (**2**) (see Ref. 3). Their structures were assigned on the basis of high-resolution ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra. However, the spectral data did not completely exclude alternative structures, such as monomeric thiasilaphosphetanes or their oligomers $[R_3PCR_2{}^1SiR_2{}^2S]_x$. Taking into account the fact that precise data on the structure of type **2** betaines are of fundamental importance for subsequent investigations in this field, we carried out an X-ray structural study of two representatives of these compounds (R = Ph (**2a**) and Me_2N (**2b**), $R^1 = R^2 = Me$). It was shown that the PCSiS fragment in compounds **2a** and **2b** has an acyclic zwitter-ionic structure (Fig. 1). The details of the X-ray structural study of betaines **2** will be published elsewhere.

A characteristic feature of the betaines studied is the *gauche*-cisoid conformation at the C—Si bond of the main chain (the P—C—Si—S torsion angles are 56.1(2)° (**2a**), 46.8(7)° (an adduct of **2a** with Ph_3PS), and 50.4(2)° (**2b**)), which is obviously caused by Coulomb interaction between the charged sites of the molecule (P^+ and S^-). Consequently, the P and S atoms are brought together,

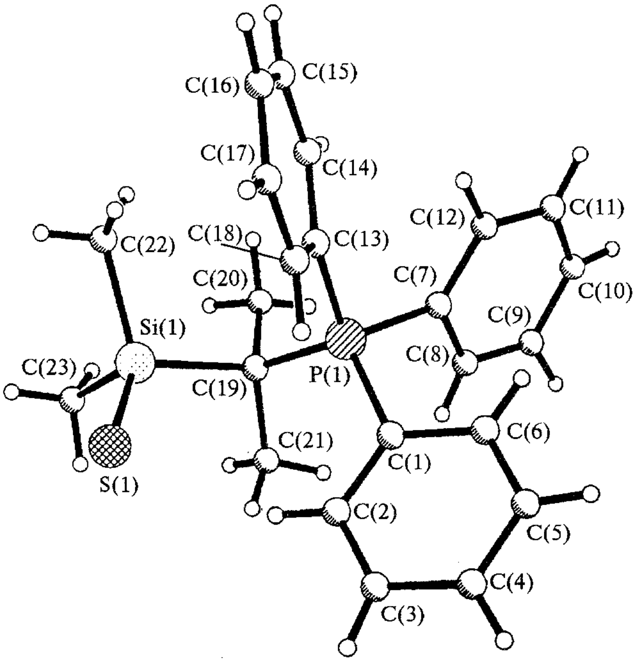

Fig. 1. General view of molecule **2a**.