# Reviews

## The nature of the super-electron-releasing inductive effect of the silatranyl group and its spectroscopic and chemical consequences

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The relationship between the structure of carbofunctionally substituted 1-methylsilatranes $XCH_2Si(OCHRCH_2)_3N$ (R = H, Me; X = $R'_2N$, R′S, Cl, *etc.*, R′ = Alk), the unusually high electron-releasing properties of the silatranyl group, and the enhanced chemical reactivity of the exocyclic $XCH_2$ substituent is discussed.

**Key words:** silatranes, silatranyl group, hydrogen bond, inductive constants, super-electron-releasing effect, IR, UV, photoelectron spectroscopy.

Organic derivatives of pentacoordinated silicon, 1-organylsilatranes of the general formula $RSi(OCHR'CH_2)_3N$ (R is organic substituent or halogen; R′ = H, Me), have been known for four decades.[1—4] Their structures have been extensively studied by X-ray diffraction analysis, NMR, NQR, IR, Raman, UV, and He(I) photoelectron spectroscopy, dielcometry, and other physicochemical methods.[1—3,5—7] However, many aspects related to their electronic structures and reactivity still remain debatable.

The purpose of this work is to study the nature of the super-electron-releasing inductive effect of the silatranyl group and its spectroscopic and chemical consequences, as a continuation of our research.

**Silatranes as chelates.** The presence of the donor-acceptor transannular N→Si bond in silatrane molecules allows them to be regarded as intramolecular electronic donor-acceptor (EDA) complexes.[8—12] The R—Si bond length in the molecules of 1-substituted silatranes (Table 1), as in intermolecular EDA complexes of the n—σ type,[8] is longer than this bond in the related

**Table 1.** Lengths of the R—Si and N→Si bonds ($r$) in 1-substituted silatranes $RSi(OCH_2CH_2)_3N$ and the corresponding derivatives of tetracoordinated silicon ($r_0$)

| R | $r$ | | $r_0$[a] | ξ[b] |
|---|---|---|---|---|
| | Å | | | |
| | R—Si | N→Si | R—Si | |
| Me[c] | 1.853 [14] | 2.453 [14] | 1.842 [15] | 0.71 |
| Me[d] | 1.870 [14] | 2.175 [14] | 1.842 [15] | 0.81 |
| $ClCH_2$[d] | 1.912 [16] | 2.120 [16] | 1.863 [13] | 0.83 |
| F[c] | 1.567 [17] | 2.318 [17] | 1.588 [13] | 0.74 |
| F[d] | 1.622 [18] | 2.042 [18] | 1.588 [13] | 0.87 |
| Cl[d] | 2.153 [19] | 2.022 [19] | 2.072 [13] | 0.89 |
| $CH_2$=CH[d] | 1.880 [20] | 2.150 [20] | 1.853 [21] | 0.82 |
| β-Ph[d] | 1.908 [22] | 2.156 [22] | 1.870 [23] | 0.82 |

[a] The N—Si bond length in tetracoordinated silicon compounds is 1.742 Å.[13]

[b] The parameter ξ characterizes the charge transfer from the donor to the A′—p bond.

[c] Gas.

[d] Crystal.

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compounds of tetracoordinated silicon ($r > r_0$). The N→Si interatomic distance in silatranes (1.95—2.45 Å) is much longer than the N—Si covalent bond (1.74 Å).

As in EDA complexes, the longer the R—Si bond in the silatrane molecule, the higher its dipole moment. The dipole moments of 1-substituted silatranes are normally in the range of 5—9 D,[1,2,24] while those of organyltrialkoxysilanes are much lower. For example, the dipole moments of 1-methylsilatrane in benzene and $CHCl_3$ are 5.30 and 7.57 D, respectively,[25] and the dipole moment of neat methyltrimethoxysilane is 1.78 D.[26] The increment of the dipole moment of 1-methylsilatrane $\Delta\mu/\Delta r$(R—Si) ≥ 4.7 D ($\Delta\mu$ is the gain in the dipole moment upon the increase in the coordination number of the Si atom from 4 to 5). The formation of n—σ-type EDA complexes is known to be accompanied by charge transfer from one molecule to the other[8]

$$A'{-}p + D \rightarrow A'{-}p...D \rightarrow A'^{-} + p^{+}{-}D, \qquad (1)$$

where A′—p is acceptor; D is donor; $A'^{-}$ is the negative ion formed from the acceptor molecule upon complete removal of the $p^+$ cation.

The charge transfer from the donor D to the A′—p bond is characterized quantitatively by the ξ value (see Table 1):[8]

$$\xi \equiv (r(A'{-}p)/r(p{-}D))(r_0(p^{+}{-}D)/r_0(A'{-}p)), \qquad (2)$$

where $r_0(A'{-}p)$ and $r_0(p^{+}{-}D)$ are the A′—p and $p^+$—D bond lengths, respectively.

The ξ value for silatranes occurs in the 0.7—0.9 range (see Table 1). According to the Mulliken classification, these compounds are weak EDA complexes of the n—σ-type.[10] This assignment is consistent with the relatively small charge transfer from the lone electron pair (LEP) of the nitrogen atom.[24,27] For example, when R = $C_6H_5$ and $C_6F_5$, the charge transfer is 0.07 and 0.10 e.u., respectively.[27] In this case, for R = Me, H, and EtO, the energies of the N→Si transannular bond are 54, 73, and 93, kJ $mol^{-1}$, respectively.[28] It is pertinent to compare these values with the energy of the OH...N hydrogen bond (37 kJ $mol^{-1}$ for the H-bond between triethylamine and phenol).[29] The ionization energies of the LEP of the nitrogen atom in trialkylamines occur in the range of 7.9—8.4 eV, while the half-widths of the corresponding peaks are 0.4—0.85 eV.[6,30—34] The presence of weak broad peaks in the region of 8.5—9.7 eV in the He(I) photoelectron spectra of 1-organylsilatranes (for R = Me, the half-width δ = 1.2 eV) is due to the ionization energy of the LEP of the endocyclic N atom. These peaks depend on the inductive constant of the substituent R, which also points to a chelate structure of silatrane molecules[35—38] (Fig. 1).

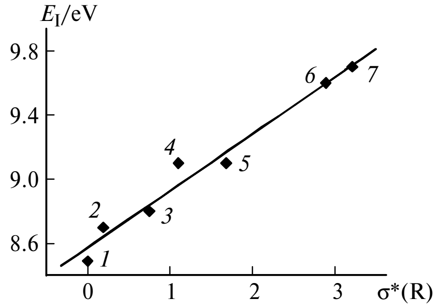

**Fig. 1.** Correlation between the ionization energy of the LEP of the endocyclic N atom ($E_I$)[35—38] and the Taft inductive constants σ* of the substituent R in compounds of the $RSi(OCH_2CH_2)_3N$ series: R = Me (*1*), $EtSCH_2CH_2$ (*2*), Ph (*3*), $ClCH_2$ (*4*), EtO (*5*), Cl (*6*), F (*7*). $E_I = 8.61 + 0.35\sigma^*$, $n = 7$, $r = 0.985$.

**Electron-releasing inductive effect of the $(CH_2)_nSi(OCHRCH_2)_3N$ ($n$ = 0—3) groups.** The formation of the EDA complex (see Eq. (1)) leads to the migration of the p fragment and an increase in the negative charge on the rest of the A′—p molecule.[8] The synthesis of ammonium salts of the $[R_{4-n}NH_n]^+Y^-$ type from Y—H (A′—p) and amine (D) is a classical example of formation of EDA complexes with proton transfer. The resulting $—N^+H_nR_{3-n}$ groups exhibit an abnormally high electron-withdrawing inductive effect (σ* = 3.7—4.5).[39] Conversely, the molecules of 1-substituted silatranes are weak EDA complexes with a slight charge transfer from the nitrogen LEP;[24,27] therefore, the nitrogen-containing fragment retains its electron-releasing properties. In combination with the unique structure of silatrane molecules, this accounts for the enhanced electron-releasing inductive effect of the $Si(OCHRCH_2)_3N$ group compared to the $Si(OEt)_3$ group. These considerations are in line with the fact that the oxygen atoms located in the equatorial position relative to the silatranyl group possess enhanced basicity due to hyperconjugation effects (through-bond interaction).[6,40,41]

The σ* Taft constant of the silatranyl group known by the beginning of our studies has not been determined precisely; the known values varied over wide limits (−1.2—−3.5).[42—44] The inductive constants found for other organosilicon substituents ($SiY_3$) were also substantially different, though.[45,46] For example, the σ* Taft constants of the $SiMe_3$ group varied from −0.72 to 1.38, while those for the $Si(OAlk)_3$ group ranged from −0.8 to 1.75.[39,42,45—48] It was believed that only the silatranyl group exhibits a variable electron-releasing effect due to the change in the N→Si transannular interaction depending on the nature of the substituent at the silicon atom, solvent, *etc.*[7,49]

Since it is difficult to determine the inductive constants of organosilicon substituents, we proposed to use the homologous series of substituents $(CH_2)_nSiY_3$ for this purpose.[43] The inductive effect of the $SiY_3$ groups attenuates with an increase in the number of methylene groups.[42,43,50—53] Therefore, the inductive constant of the silatranylmethyl group should be smaller than the inductive constant of the silatranyl group (−2.24 and −3.49, respectively), and the inductive constants of the

**Table 2.** Taft inductive constants (σ*) of the organosilicon substituents $(CH_2)_nSiY_3$ in compounds of the $X(CH_2)_nSiY_3$ series.

| X | $SiY_3$ | *n* | σ* |
|---|---|---|---|
| Ph | $Si(OCH_2CH_2)_3N$ | 0 | −3.49 [41,42] |
| $FC_6H_4$ | $Si(OCH_2CH_2)_3N$ | 1 | −2.24 [51] |
| NC | $Si(OCHMeCH_2)_3N$ | 2 | −1.48 [42] |
| $(CH_2)_5N$ | $Si(OCH_2CH_2)_3N$ | 3 | −0.32 [42] |
| $(CH_2)_5N$ | $MeSi(OCH_2CH_2)_2NMe$ | 0 | −2.0—−2.3 [53] |
| $(CH_2)_5N$ | $MeSi(OCH_2CH_2)_2NMe$ | 1 | −1.4—−1.6 [53] |
| NC | $MeSi(OCH_2CH_2)_2NMe$ | 2 | −0.87 [42] |
| $(CH_2)_5N$ | $MeSi(OCH_2CH_2)_2NMe$ | 3 | −0.1—−0.3 [53] |
| Ph | $Si(OEt)_3$ | 0 | −0.81 [41,42] |
| $FC_6H_4$ | $Si(OMe)_3$ | 1 | −0.62 [51] |
| NC | $Si(OEt)_3$ | 2 | −0.39 [42] |
| $(CH_2)_5N$ | $Si(OEt)_3$ | 3 | −0.13 [42] |
| $(CH_2)_5N$ | $SiMe(OEt)_2$ | 0 | −0.8 [53] |
| $(CH_2)_5N$ | $SiMe(OEt)_2$ | 1 | −0.56 [53] |
| NC | $SiMe(OEt)_2$ | 2 | −0.37 [52] |
| $(CH_2)_5N$ | $SiMe(OEt)_2$ | 3 | −0.13 [52] |

$(CH_2)_2Si(OCHRCH_2)_3N$ group cannot be higher than the Taft constant of the $Si(OCHRCH_2)_3N$ group. Thus, among the previously determined σ* constants of the silatranyl group, the values lower than −2.24 are incorrect. According to the values given in Table 2 and published data,[39,45,47,48] the $(CH_2)_nSi(OCHRCH_2)_3N$ group (*n* = 0, 1) is the most powerful electron donor. Moreover, regarding the magnitude of the +*I* effect, this group has no analogs; hence we have called it a super-electron-releasing group.

**Spectroscopic manifestations of the super-electron-releasing inductive effect of the silatranyl group.** The super-electron-releasing properties of the silatranyl and silatranylmethyl groups markedly influence the spectral parameters of silatranes. The stretching Si—H frequency in the IR spectra of 1-hydrosilatranes $HSi(OCHRCH_2)_3N$ (R = H, Me, $CF_3$) and 1-hydrosilatrane-3,7,10-trione $HSi(OCOCH_2)_3N$ is lower than those in the related compounds with tetracoordinated silicon (Fig. 2).[54—56] On passing from the crystalline state to solutions, this band in the spectra of 1-hydrosilatranes shifts to higher frequencies, especially with a decrease in the solvent polarity and an increase in the temperature of the solution.[12,54—57] As for n—σ-type EDA complexes, this is matched by shortening of the Si—H bond. Upon a pressure increase from 1 bar to 2 kbar, the Si—H stretching frequency in the IR spectra of $CCl_4$ solutions of 1-hydrosilatranes decreases to become equal or even lower than the corresponding frequency in the spectrum of the substances in the crystal.[58] For example, in the IR spectra of crystalline 1-hydro-3,7,10-trimethylsilatrane, the ν(Si—H) value is 2115 $cm^{-1}$, while those in $CCl_4$ solutions at pressures of 1 bar and 2 kbar are 2164 and 2087 $cm^{-1}$, respectively (Fig. 3). This attests to a substantial shortening of the N→Si bond upon the phase transition of $CCl_4$ (at a pressure of 1460 bar and 20 °C, $CCl_4$ transforms to the solid state).

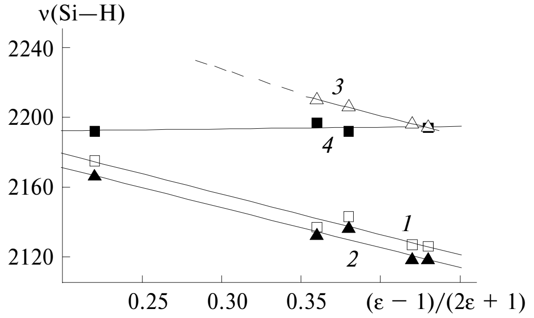

**Fig. 2.** Effect of the solvent polarity on the position of the absorption band of the Si—H stretching vibration in the IR spectra of compounds of the $HSi(OCHRCH_2)_3N$ series: R = H (*1*), Me (*2*), $CF_3$ (*3*), $HSi(OEt)_3$ (*4*).[54,55]

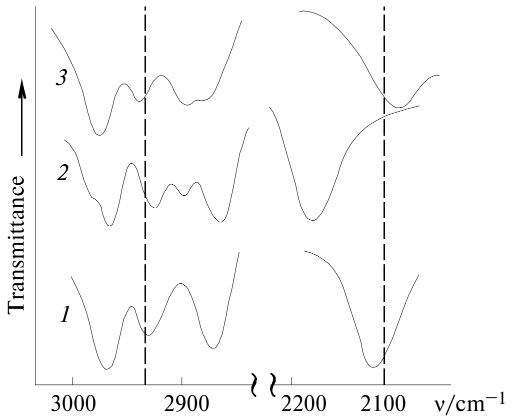

**Fig. 3.** IR spectra of $HSi(OCHMeCH_2)_3N$ in KBr pellets (*1*) and in solutions in $CCl_4$ at a pressure of 1 bar (*2*) and 2 kbar (*3*).[58]

As distinct from this, the changes in the parameters of the IR spectra of monocyclic and acyclic analogs of the silatranes $HSiR(OCHR'CH_2)_2NR''$ (R = Alk; R′ = H, Alk; R″ = H, Me, Ph) and $HSi(OEt)_3$ induced by variation of the solvent polarity, temperature, and pressure are largely determined by conformation effects.[59,60]

The IR spectra of ternary $RSi(OCHR'CH_2)_3N—PhOH—CCl_4$ systems at R = $ClCH_2$ and $CH_2{=}CHCH_2$ exhibit two associated maxima for the OH stretching vibration, which comply with the complexation of phenol involving not only the oxygen atom of the silatranyl group but also the chlorine atom or the double bond of the allyl group (Fig. 4).[40] In similar systems with R = $EtSCH_2$, the half-width of the associated band increases 1.5-fold, which also points to the presence of two basicity centers in the $EtSCH_2Si(OCHMeCH_2)_3N$ molecule, the sulfur atom being a more basic center than oxygen.[36] However, the IR spectra of phenol complexes with the corresponding Si-substituted triethoxysilanes contain only one associated absorption band due to the H-bond of the oxygen atom of the triethoxysilyl group.

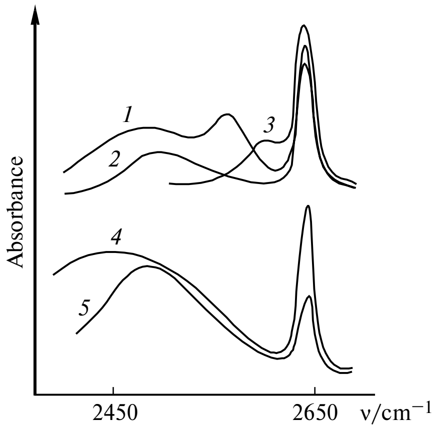

**Fig. 4.** IR spectra of solutions of ternary $XCH_2SiY_3$—PhOH—$CCl_4$ systems ([PhOH] = 0.01 mol $L^{-1}$).

| Curve | X | $SiY_3$ | $[XCH_2SiY_3]$/mol $L^{-1}$ |
|---|---|---|---|
| *1* | Cl | $Si(OCHMeCH_2)_3N$ | 0.05 |
| *2* | Cl | $Si(OEt)_3$ | 0.1 |
| *3* | — | $Me(CH_2)_3Cl$ | 0.5 |
| *4* | EtS | $Si(OCHMeCH_2)_3N$ | 0.05 |
| *5* | EtS | $Si(OEt)_3$ | 0.1 |

In the silatranes $(CH_2)_5NCH_2Si(OCH_2CH_2)_3N$ and $EtSCH_2Si(OCH_2CH_2)_3N$, the ionization energies of the lone electron pairs of the exocyclic N and S atoms are much lower than those in the related organyltrialkoxysilanes $(CH_2)_5NCH_2Si(OEt)_3$ or $EtSCH_2Si(OMe)_3$ (Table 3), *i.e.*, the exocyclic N and S atoms in these silatranes bear an increased electron density. Correspondingly, the equilibrium constant $K_{as}$ in the H-complex of phenol with 1-(piperidinomethyl)silatrane is an order of magnitude higher than that for the similar complex with piperidinomethyltriethoxysilane (1100 and 110 L mol$^{-1}$, respectively), and in the UV spectra of charge transfer complexes of 1-(ethylthiomethyl)silatrane with tetracyanoethylene, the charge transfer band is shifted to longer wavelengths with respect to that of (ethylthiomethyl)triethoxysilane ($\lambda$ = 548 and 515 nm, respectively).

**Table 3.** Parameters of the photoelectron and ultraviolet spectra of compounds of the $(CH_2)_5NCH_2SiY_3$ and $EtSCH_2SiY_3$ series[36,61]

| Compound | PES | UV | | |
|---|---|---|---|---|
| | $E_I$ | Δν* | $K_{as}^{20}$ | λ** |
| | /eV | /cm$^{-1}$ | /L mol$^{-1}$ | /nm |
| $(CH_2)_5NCH_2Si(OCHMeCH_2)_3N$ | 7.46 | 620 | 1100 | — |
| $(CH_2)_5NCH_2Si(OEt)_3$ | 7.92 | 440 | 110 | — |
| $EtSCH_2Si(OCHMeCH_2)_3N$ | 7.80 | — | — | 548 |
| $EtSCH_2Si(OMe)_3$ | 8.54 | — | — | 515 |

* Shift of the long-wavelength band for the π→π* transition of phenol upon the formation of an the PhOH...H bond.

** Charge transfer band.

Owing to the super-electron-releasing effect of the silatranyl group, the stretching vibration frequency of the carbonyl group in the IR spectrum of 1-(4-chlorobenzoyloxymethyl)silatrane $4\text{-}ClC_6H_4COOCH_2Si(OCH_2CH_2)_3N$ (1720 and 1742 cm$^{-1}$) is lower than in the spectrum of (4-chlorobenzoyloxymethyl)triethoxysilane (1740 and 1759 cm$^{-1}$).[62] Similarly, the frequency of the C=O stretching vibration in the spectrum of $MeC(O)NMeCH_2Si(OCH_2CH_2)_3N$ (1614 cm$^{-1}$) is lower than that in the IR spectrum of $MeC(O)NMeCH_2Si(OCH_2CH_3)_3$ (1643 cm$^{-1}$).[63] The long-wavelength absorption band for the π→π* transition in the UV spectrum of an acetonitrile solution of 8-(silatranylmethylthio)quinoline ($C_9H_6NSCH_2Si(OCH_2CH_2)_3N$) is shifted bathochromically by 12 nm relative to the corresponding band in the spectrum of a silane with a related structure, $C_9H_6NSCH_2Si(OMe)_3$.[64] In the $^{35}Cl$ NQR spectrum of 1-chloromethylsilatrane recorded at 77 K, the $\nu^{77}$ signal is located much lower than those in the spectrum of chloromethyltriethoxysilane (32.702 and 35.122 MHz, respectively).[44]

The linear correlations of spectral parameters (basicity Δν(OH), equilibrium constant $K_{as}$ for H-bonding with phenol, ionization energies $E_I$ for the LEP of the exocyclic N or S atoms in the $XCH_2Si(OCH_2CH_2)_3N$ molecules with X = $(CH_2)_5N$ and EtS) with the σ* value of the organosilicon substituent, including the silatranyl group, confirm the invariability of the super-electron-releasing inductive effect of this group (Fig. 5, 6).[36,52,53,61]

**The influence of the super-electron-releasing inductive effect of the $Si(OCH_2CH_2)_3N$ group on the reactivity of silatranes.** The reactions of carbofunctional 1-methylsilatrane derivatives $XCH_2Si(OCH_2CH_2)_3N$

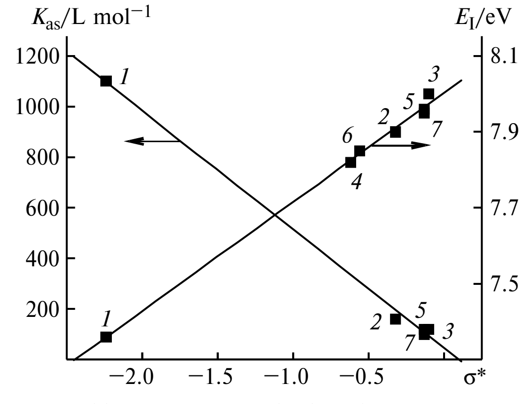

**Fig. 5.** Equilibrium constants ($K_{as}$) and ionization energies of the LEP of the exocyclic N atom ($E_I$) in compounds of the $R_2N(CH_2)_nSiY_3$ series *vs.* σ* Taft inductive constants of the $(CH_2)_nSiY_3$ groups. $SiY_3$ = $Si(OCHRCH_2)_3N$, R = Me, *n* = 1 (*1*), *n* = 3 (*2*); $SiY_3$ = $MeSi(OCH_2CH_2)_2NMe$, *n* = 3 (*3*); $SiY_3$ = $Si(OEt)_3$, *n* = 1 (*4*), *n* = 3 (*5*); $SiY_3$ = $MeSi(OEt)_2$, *n* = 1 (*6*), *n* = 3 (*7*).[53]

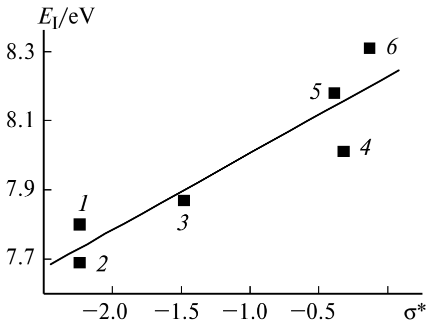

**Fig. 6.** Ionization energy ($E_I$) of the LEP of the S atom *vs.* σ* Taft inductive constants of the $(CH_2)_nSiY_3$ group in compounds of the $EtS(CH_2)_nSiY_3$ series. $SiY_3 = Si(OCHRCH_2)_3N$, R = Me, $n = 1$ (*1*); R = H (*2*); R = H, $n = 2$ (*3*); R = H, $n = 3$ (*4*); $SiY_3 = Si(OMe)_3$, $n = 2$ (*5*), $n = 3$ (*6*).[36]

($X = R_2N$, RS) involving the substituent heteroatom X are governed by the super-electron-releasing inductive effect of the silatranylmethyl group.[65—67] For instance, the reaction of 1-(dialkylaminomethyl)silatranes $R_2NCH_2Si(OCH_2CH_2)_3N$ ($R_2 = Me_2$, $(CH_2)_5$) with $CCl_4$ is characterized by an abnormally short induction period and a very short duration compared to reactions of other organosilicon amines such as $(CH_2)_5NCH_2Si(Me)(OCH_2CH_2)_2NMe$ and $(CH_2)_5NCH_2Si(OEt)_3$ or triethylamine (Table 4). The reactions of $CCl_4$ with organic amines are known to give initially charge transfer complexes.[68—73]

$$R_3N + CCl_4 \rightleftharpoons R_3N \cdot CCl_4, \qquad (3)$$

$$R_3N \cdot CCl_4 \longrightarrow R_3N^{\cdot +} \cdot CCl_4{}^{\cdot -}, \qquad (4)$$

$$R_3N^{\cdot +} \cdot CCl_4{}^{\cdot -} \longrightarrow \\ \longrightarrow R_2NC^{\cdot}HCH_2R' + {}^{\cdot}CCl_3 + HCl, \qquad (5)$$

$$R_2NC^{\cdot}HCH_2R' + {}^{\cdot}CCl_3 \longrightarrow \\ \longrightarrow R_2NCH{=}CH_2R' + CHCl_3, \qquad (6)$$

$$R_3N + HCl \longrightarrow R_3N^{+}H \cdot Cl^{-}, \qquad (7)$$

R = Alk; R′ = H, Me.

**Table 4.** Characteristics of the reaction of $CCl_4$ with organosilicon amines $(CH_2)_5NCH_2SiY_3$ and triethylamine in benzene.[65]

| $SiY_3$ | Illuminance/lx | Δτ* | τ** | Yield*** (%) |
|---|---|---|---|---|
| | | h | | |
| $Si(OCH_2CH_2)_3N$ | $18—20 \cdot 10^3$ | 0.2 | 20 | 44 |
| $Si(OCH_2CH_2)_3N$ | 250 | 12 | 32 | 28 |
| $SiMe(OCH_2CH_2)_2NMe$ | $18—20 \cdot 10^3$ | 96 | 116 | 8 |
| $Si(OEt)_3$ | $18—20 \cdot 10^3$ | 120 | 140 | Traces |
| $Et_3N$ | $18—20 \cdot 10^3$ | 144 | 164 | 0.5 |

* Induction period of the reaction.

** Reaction duration.

*** Yield of amine hydrochloride.

The final step of this process (7) affords a minor amount of amine hydrochloride. Meanwhile, the yield of the corresponding hydrochlorides in the reactions of $CCl_4$ with dialkylaminomethylsilatranes is nearly quantitative (see Table 4). When $CCl_4$ reacts with 1-(dialkylaminomethyl)silatranes, the super-electron-releasing properties of the exocyclic N atom determine the high concentration of the complexes with $CCl_4$ formed initially, which increases the rate of the subsequent steps. The abnormal behavior of these compounds is due to the superbasicity of the exocyclic N atom caused by the powerful +*I* effect of the silatranylmethyl group.

The 1-(organylthiomethyl)silatranes $RSCH_2Si(OCHR'CH_2)_3N$ possess an unusually high reactivity resulting from the enhanced electron density on the S atom. The reactions of these compounds with organyl halides lead to the formation of the corresponding sulfonium salts,[66] which are, in turn, readily oxidized to the corresponding sulfoxides.[67]

The super-electron-releasing effect of the silatranyl group promotes the formation of oxonium complexes in the reaction of 1-ethoxysilatrane with $CF_3SO_2OH$, $HBF_4$, $MeBF_4$, and $EtBF_4$ with participation of the exocyclic (rather than equatorial) oxygen atom.[74]

The ease of cleavage of the Si—C bond in 1-organylsilatranes on treatment with heavy metal salts,[75,76] bromine, and iodine monochloride[77] is also due to the strong +*I* effect of the silatranyl group.

The super-electron-releasing effect of the silatranyl group has a dramatic influence on the $Fe^{II}/Fe^{III}$ redox potential in mono- and disilatranyl derivatives of ferrocene.[78] Indeed, the presence of two trimethoxysilyl groups in the ferrocene molecule changes the iron redox potential from 0.40 to 0.56 V. Replacement of one or two of these groups by silatranyl groups shifts the redox potential to negative values down to −0.34 and −0.62 V, respectively. Thus, the silatranyl group attached to ferrocene exhibits a powerful electron-releasing effect, and the trimethoxysilyl group exerts an electron-withdrawing effect (*cf.* Refs. 79 and 80).

The reactions considered above convincingly demonstrate the substantial role of the super-electron-releasing inductive effect of the silatranyl group on the reactivity of silatranes.

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The unusual spectral and chemical properties of silatranes belonging to intramolecular EDA complexes are due to the super-electron-releasing inductive effect of the silatranyl group. The introduction of a silatranyl group in the molecules of organic and heteroorganic compounds opens up prospects for the preparation of compounds with unique physical and chemical properties and biological activities.

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