Translated from *Uspekhi Khimii*, 50, 460-484 (1981) U.D.C. 541.67+547.245+547.246

The α-Effect in Organic Compounds of Group IVB Elements

V.P.Feshin, L.S.Romanenko, and M.G.Voronkov

A critical and systematic account is given of the results of studies of the α-effect by physical and chemical methods. The nature of the α-effect, its characteristic features, and its influence on the structure and properties of the corresponding organic compounds of Group IVB elements are discussed.
The bibliography includes 160 references.

CONTENTS

I. Introduction 248
II. Chemical manifestations of the α-effect 248
III. Investigation of the α-effect by physical methods 250
IV. The nature of the α-effect 255

I. INTRODUCTION

The mutual influence of the atoms X and E in organic molecules containing the triatomic group $X-\overset{|}{\underset{|}{C}}-E$ does not correspond to their electronegativities and to the inductive effect of the constituents (the geminal interaction effect)[1-5]. Such an effect is shown in virtually all compounds and the atoms E and X can have both unshared electron pairs and vacant orbitals. This non-inductive interaction is usually observed when one compares the properties of the above compounds with isostructural compounds in which E = C or with homologues of type XCH_2CH_2M. We have called[5-8] the non-inductive geminal interaction of a given atom X with an atom E having vacant *d* orbitals in the $X-\overset{|}{\underset{|}{C}}-E$ system the α-effect†. At the present time the problem of the α-effect in an organic compound of Group IVB elements has attracted the attention of many investigators[9] and numerous publications have been devoted to it. Nevertheless the views on the nature of the α-effect and on the very possibility of its occurrence, based on studies using a wide variety of different physical and chemical methods, are extremely contradictory. The methods employed make it possible to observe the geminal interaction effect and to investigate its characteristics, but the majority do not permit the determination of the mechanism of the effect. Therefore almost all the existing hypotheses concerning the nature of the α-effect do not have a serious basis.

Some investigators (see below) base their views on individual experimental data which are consistent with ideas concerning the dominant inductive interaction of the atoms E and X and the problem of the occurrence of the intramolecular non-inductive interaction of geminal atoms is still regarded as controversial. There also exists a view that the α-effect is not shown in all the compounds containing the $X-\overset{|}{\underset{|}{C}}-E$ group but only in certain molecules of this type.

This indefinite state of the problem of the α-effect led us to write the present review.

†The term "α-effect" sometimes has another significance. For example, it is used in the interpretation of the anomalous reactivity of hydrazine derivatives (see, for example, Edwards and Pearson[10] and Grekov and Veselov[11]).

II. CHEMICAL MANIFESTATIONS OF THE α-EFFECT

The anomalous (i.e. inconsistent with the inductive influence of the atom E or a substituent in which it is included) properties of compounds containing the group $\overset{|}{\underset{|}{X-C-E}}$ were observed a long time ago. Thus, as early as the 1950's, it was noted that chloromethyltrimethylsilane is much more reactive in nucleophilic substitution reactions than its carbon analogue, while it is inert with respect to electrophiles (see, for example, George et al.[12] and Andrianov and Petrashko[13]). This was explained by the steric characteristics of the group $CH_2Si(CH_3)_3$ and its comparatively pronounced electron-accepting properties[14]. The electronegativity (EN) of this group, determined by the Kharash method, proved to be higher than that of the alkyl groups $n-C_6H_{13}$, CH_3, and $CH_2C(CH_3)_3$ but lower than that of the phenyl group. The expectedly high electronegativity of this group was attributed to the electronic unsaturation of the silicon atom[14]. The unusual influence of the silicon atom in compounds of the type $XCH_2Si(CH_3)_3$ (X = Cl or I) on their reactivity has been called the "α-silicon effect".[14]

In contrast to β- and γ-chloroalkylchlorosilanes, chloromethylchlorosilanes undergo the Friedel–Crafts reaction with difficulty[15-21], which indicates a reduced electron density at the chlorine atom in the group $ClCH_2Si\lesssim$. The replacement of the chlorine atom linked to the silicon atom by an alkyl group as a rule increases the reactivity of the compound. For example, $ClCH_2(CH_3)SiCl_2$ is more reactive in this reaction than $ClCH_2SiCl_3$.[21].

The relatively high reactivity of $ClCH_2Si(CH_3)_3$ in the reaction with KI (higher by a factor of 16 than for $n-C_4H_9Cl$, by a factor of 15 than for $n-C_3H_7Cl$, and by a factor of 8 than for C_2H_5Cl) was explained by the stabilisation of the transition state as a result of the interaction of the approaching iodide ion with the vacant 3*d* orbitals of the silicon atom and with the carbon atom[22-24]. It has been suggested that the leaving chloride atom thus interacts with the Si and C atoms[22,25-27]:

$$ClCH_2Si(CH_3)_3 + {}^{-}I \rightleftarrows CH_2\begin{matrix}\diagup Cl\\ \\ \diagdown I\end{matrix}Si(CH_3)_3 \rightleftarrows ICH_2Si(CH_3)_3 + Cl^{-}.$$

An analogous mechanism has been postulated for the reaction of chloromethyltrimethylsilane with the SCN^- ion in acetone and with the $C_2H_5O^-$ ion in ethanol[22,25,28]. The reactivity of $ClCH_2Si(CH_3)_3$ with respect to the $C_2H_5O^-$ ion is somewhat lower than that of $n-C_4H_9Cl$. However, it

would be lower still were it not for the possibility of the coordination interaction of the type indicated above[25,29]. It has been shown that $ICH_2Si(CH_3)_3$ is less reactive in the exchange with the I^- ion in ethanol than $n\text{-}C_3H_7I$.[14,25]. In the absence of coordination interaction, one would expect that iodomethyltrimethylsilane is still less reactive[25].

In bimolecular nucleophilic substitution reactions with KI and KSCN the chlorine atom in chloromethyltrimethylsilane is much more mobile than in γ-chloropropyltrimethylsilane[12,30], which is consistent with the electron-accepting properties of the trimethylsilyl group. On the other hand, in the interaction of chloromethyl- and γ-chloropropyl-trichlorosilanes with alcoholic alkali, the chlorine atom in the γ-position with respect to the silicon atom is much more mobile[31]. The discrepancy between these results has been explained by the fact that alcoholic alkali is not a reagent characterising the reactivity of the chlorine atom in the C–Cl bond in reactions of organosilicon compounds, because under the influence of alkali on chloromethyltrichlorosilane the reaction involves only the Si–C bond, while the reaction with γ-chloropropyltrichlorosilane involves both the Si–C and the Si–Cl bonds[30].

The exchange reactions between the chloromethyltrimethylgermane and KSCN, $HN(C_2H_5)_2$, and KI are faster than the analogous reactions of chloromethyltrimethylsilane, which shows that the $CH_2Ge(CH_3)_3$ group is more electronegative than $CH_2Si(CH_3)_3$. This is consistent also with the lower basicity constant of $(C_2H_5)_2NCH_2Ge(CH_3)_3$ compared with $(C_2H_5)_2NCH_2Si(CH_3)_3$.[32] The reactivity of chloromethyltrimethylstannane (in reactions of the S_N2 type) with respect to I^- and $C_2H_5O^-$ ions is higher still than those of chloromethyltrimethylsilane and chloromethyltrimethylgermane[25]. On the other hand, the electron-donating properties of the $-E(CH_3)_3$ groups become more pronounced as a function of E in the following sequence: Si < Ge < Sn.[33,34]. Consequently the observed sequence in the variation of the reactivity of compounds of the $ClCH_2E(CH_3)_3$ series (E = C, Si, Ge, or Sn) does not correspond to the inductive effect of the groups $-E(CH_3)_3$. This was explained by the fact that the nucleophilic substitution reactions involving these compounds proceed via the "bridge mechanism" described above, which is most marked in the case of chloromethyltrimethylstannane. In conformity with this, the tin atom exhibits a greater tendency than silicon and germanium atoms to expand its coordination number with formation of pentacoordinate and hexacoordinate complexes[35] and exhibits the smallest steric hindrance to nucleophilic attack because of its large atomic radius[25].

The rate constants for the reaction of chloromethyltrimethylsilane with sodium in the gas phase are greater than for neopentyl chloride and γ-chloropropyltrimethylsilane almost by factors of 15 and 5 respectively, which shows that the negative charge on the chlorine atom in chloromethyltrimethylsilane is smaller than in the compounds with which it has been compared[36].

In the reaction with 80% aqueous ethanol α-halogenoisopropyltrimethylsilanes $X(CH_3)_2CSi(CH_3)_3$ (X = Cl or Br) are much less reactive than their carbon analogues $X(CH_3)_2 .CC(CH_3)_3$ and $XC(CH_3)_3$. This has been explained[37] by the enhanced electron-donating properties of the CH_3 and $C(CH_3)_3$ groups owing to the ability of their C–H and C–C bonds to participate in hyperconjugation (and not by the reduced electron-donating capacity of the trimethylsilyl group). It has also been suggested[37] that the lower reactivity of $Br(CH_3)_2CSi(CH_3)_3$ with respect to aqueous alcohol relative to $Br(CH_3)_2CH$ is caused by steric hindrance to solvation. A greater electron-accepting effect of the $Si(CH_3)_3$ group, compared with hydrogen, which would lead to the observed ratios of the rates of solvolysis of the above compounds is thought to be unlikely[37].

The rate constants for the acid-catalysed hydrolysis of triorganylsilanes $HSiR_3$ are correlated with the inductive Taft constants of the constituents R. However, the rate constant for the hydrolysis of chloromethyldimethylsilane deviates from this correlation, which has been explained[38] by the interaction of the unshared electron pair of the chlorine atom with the vacant *d* orbitals of silicon, described by the resonance structure $Cl^+CH_2=SiR_3$.

The enthalpies of the protonation reactions of the compounds $X(CH_2)_nEH_3$ (E = C or Si; X = Cl or F), calculated by the LCAO-MO method in the CNDO/2 approximation (with and without inclusion in the calculation of the vacant *d* orbitals of silicon), depend greatly on the molecular conformation for E = Si, but are insensitive to conformational changes for E = C. This indicates the occurrence of an intermolecular interaction in organosilicon compounds containing the $X-CH_2-Si$ group which is not characteristic of their organic analogues[39].

The reactivity of fluoromethyltrimethylsilane in the reaction with ethylmagnesium bromide is higher, as for the corresponding chloro-derivative, than that of γ-fluoropropyltrimethylsilane. In both compounds the fluorine atom is more mobile than in n-heptyl fluoride. It has been suggested[40] that this is caused by the "positive inductive influence" of the trimethylsilyl group, which has been shown most markedly in fluoromethyltrimethylsilane. The inertness of the fluorine atom in neopentyl fluoride has been attributed to the steric effect of the t-butyl group[40].

The numerous rearrangements involving the cleavage of the E–C bond and the migration of the substituent X from the carbon atom to the E atom have been explained by the intramolecular interaction between the E and X atoms in the molecules containing the group $X-\overset{|}{\underset{|}{C}}-E$ (E = Si, Ge, or Sn):

$$X-\overset{|}{\underset{|}{C}}-E- \rightarrow X-E+:C\overset{|}{\underset{|}{\ }}.$$

Reactions of this type are observed, for example, in the pyrolysis of organosilicon compounds containing the group $X-\overset{|}{\underset{|}{C}}-Si$ (X = halogen)[41–43]. A similar rearrangement with formation of a carbene takes place in the case of halogenomethylsilanes:

$$XCH_2SiH_3 \rightarrow XSiH_3 + :CH_2 \ (X = F, Cl, I)^{44}.$$

The cleavage of the Si–C bond with migration of the fluorine atom from the α-carbon atom to the silicon atom in the compound $F_2CHCF_2SiX_3$ takes place in the vapour phase at 130–210 °C (X = F) or at 310–370 °C ($X = CH_3$):[45]

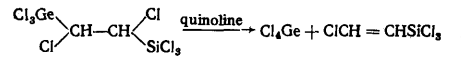
$$F_2CHCF_2SiX_3 \rightarrow \left[F_2CHCF\overset{F}{\diagdown\!\!\diagup}SiX_2\right] \rightarrow FSiX_3 + :CFCHF_2 .$$

The α-decomposition of perhalogeno-derivatives of ethylchlorosilanes at 185 °C proceeds much more readily than the very common β-elimination[46–48]:

$$Cl_3SiCF_2CFCl_2 \begin{cases} \xrightarrow{\alpha} Cl_3SiF + :CFCFCl_2 \rightarrow CFCl=CFCl & (80\%) \\ \xrightarrow{\beta} Cl_3SiF + F_2C=CCl_2 & (7\%) . \end{cases}$$

The pyrolysis of perfluoroalkyltrifluorosilanes proceeds similarly[49]. Similar reactions with liberation of dichlorocarbene are observed in the pyrolysis of Cl_3CSiCl_3 [24,47,50] and Cl_3CSiF_3.[51]

When 1,2-dichloro-2-trichlorogermyl-1-trichlorosilylethane is treated with quinoline, $GeCl_4$ is split off and not HCl. The explanation is that the germanium compounds exhibit a greater tendency towards β-decomposition than their silicon analogues[45]:



The α-elimination process is responsible for the thermal instability not only of α-fluoroalkylsilanes but also of α-fluoroalkylsiloxanes. For example, $(HF_2CCF_2SiO_{1.5})_n$ is rapidly converted into a polyfluorosesquioxane at 180–200 °C:[52]

$$(HF_2CCF_2SiO_{1.5})_n \rightarrow (FSiO_{1.5})_n + :CFCHF_2 \rightarrow CF_2=CHF \ .$$

α-Decomposition is also observed in the interaction of α-chloroalkyltrialkylsilanes with quinoline[50]:

$$RCHSiR_3 \xrightarrow{\text{quinoline}} ClSiR_3 \ .$$
$$\quad\ |$$
$$\quad Cl$$

In the presence of aluminium chloride trialkylchloromethylsilanes undergo an intramolecular rearrangement[53]:

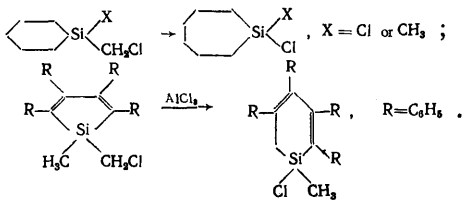
$$ClCH_2SiR_2R' \xrightarrow{AlCl_3} ClSi(CH_2R')R_2 \ .$$

The relative ability of compounds of this type to rearrange increases in the following sequence based on varying R′:

$$CH(CH_3)_2, CH_2Cl < CH_3 < CH_2CH_3 < (CH_3)_2CH_3 \ .$$

The rearrangement proceeds via a transition state in which both substituents, R′ and Cl, are coordinated to silicon and carbon atoms[54].

A special case of a rearrangement of this type is the expansion of the silacycloalkane ring[55] and also of the silacyclopentadiene ring[56]:



Aluminium chloride causes not a rearrangement but α-decomposition of α-chloroethylsilanes $CH_3CHClSiR_3$:[23,57]

$$CH_3CHClSi(C_2H_5)_2Cl \xrightarrow{AlCl_3} Cl_2Si(C_2H_5)_2 + H_2C=CH_2 \ .$$

The rearrangement of trialkyldichloromethylsilanes in the presence of $AlCl_3$ proceeds via the mechanism[23,57]

$$Cl_2CHSi(CH_3)_2 \rightarrow CH_2CHClSi(CH_3)_2Cl \rightarrow Cl_2Si(CH_3)_2 + H_2C=CH_2 \ .$$

1- and 2-dichloromethylheptamethyltrisilanes also undergo a rearrangement in the presence of $AlCl_3$ with rupture of the Si–Si bond and the migration of chlorine atoms to the silicon atom[59]:

$$(CH_3)_3SiSi(CH_3)_2Si(CH_3)_2CHCl_2 \xrightarrow{AlCl_3} (CH_3)_3SiSi(CH_3)_2CHClSi(CH_3)_2Cl \longrightarrow$$
$$\xrightarrow{AlCl_3} [Cl(CH_3)_2Si]_2CHSi(CH_3)_3 \xrightarrow{AlCl_3} [(CH_3)_3Si]_2CH + [Cl(CH_3)_2Si]_2CH +$$
$$+ [(CH_3)_3Si]_2CHSi(CH_3)_2Cl + [Cl(CH_3)_2Si]_2CHSi(CH_3)_3 \ .$$

The decomposition of $F_3CSn(CH_3)_3$ with formation of difluorocarbene[60–62] is apparently due to the coordination interaction between the fluorine and tin atoms. The reactivity of the chlorine atom in trialkylchloromethylstannanes[32,60,63,64], which is higher than in the carbon, silicon, and germanium analogues, has been explained by the intramolecular coordination between the Sn and Cl atoms.

Under the influence of bases, trialkylsilylmethanols are very readily converted into the isomeric ethers[65–69]:

$$R_3SiC(OH)R'_2 \xrightarrow{B} R_3SiOCHR'_2 \ ;$$

R = alkyl, aryl; R′ = alkyl, aryl, H; B = Na/K, Na, NaH, RLi, $(C_2H_5)_2NH$, $(C_2H_5)_3N$.

It has been suggested that this rearrangement takes place with formation of a bond between the silicon and oxygen atoms in the transition state; the silicon atom then becomes sp^3d-hybridised. Electron-accepting substituents at the silicon atom facilitate the rearrangement, since they promote the delocalisation of the negative charge in the three-membered transition state formed[65]. Such rearrangements are not observed for β- and γ-trialkylsilylalkanols $HO(CH_2)_n \cdot SiR_3$ ($n = 2$ or 3).[70] The thermal rearrangement of alkyl esters of α-trialkylsilylalkanecarboxylic acids, which has no analogy in organic chemistry, has been explained by a similar three-membered cyclic transition state[71].

In the pyrolysis of compounds containing the O–C–Si group the oxygen-containing group migrates from the carbon atom to the silicon atom and a carbene is evolved[72,73]:

$$(CH_3O)_2CHSi(OCH_3)_3 \longrightarrow CH_3OCH: + Si(OCH_3)_4 \ ;$$
$$C_6H_5C(OCH_3)_2SiR_3 \longrightarrow CH_3OSiR_3 + C_6H_5\ddot{C}OCH_3 \ .$$

$(C_6H_5)_2C(OCH_3)SiR_3$ is cleaved similarly[73].

The reactivity of organosilicon and organogermanium compounds of the type XCH_2ER_3 (X = O or S; E = Si or Ge) is largely consistent with the inductive influence of the ER_3 group. Thus, in a reaction with an electrophile (phenyl isocyanate) trimethylsilylmethanol is 6 times more reactive than neopentyl alcohol[74,75], more than 4 times more reactive than butanol[76], and 2.5–3 times more reactive# than methanol[74,75,77]. In its interaction with keten, trimethylsilylmethanol is 3 times more reactive than butanol[76]. The reactivity of trimethylgermylmethanol in these reactions is also significantly higher than those of neopentyl alcohol, methanol, and butanol[78]. The reactivity of alcohols of the $HO(CH_2)_nE(CH_3)_3$ series (E = Si or Ge; $n = 1–4$) in reactions with phenyl isocyanate and keten falls with increase of the number of methylene groups n and, when $n = 3$ and 4, becomes the same as that of butanol[76,78]

In the reaction with phenyl isocyanate[79] the reactivity of trimethylsilylmethanethiol is higher than that of the remaining thiols of the $HS(CH_2)_nSi(CH_3)_3$ ($n = 1–4$) series and butanol.

All these data can be accounted for by the enhanced electron-donating inductive influence of the trimethylsilyl or trimethylgermyl group which decays with increase of the number n.[76,78,79] The decrease of the nucleophilic properties of the thiyl group in mercaptans of the $HS(CH_2)_nSiR_3$ series with increase of n from 1 to 3, observed in the study of the vinylation of these compounds and confirmed by the results of potentiometric titration studies[80], can also be explained by the electron-donating influence of the trialkylsilyl group[80].

III. INVESTIGATION OF THE α-EFFECT BY PHYSICAL METHODS

The vast majority of studies on compounds containing the

$$X–\overset{|}{\underset{|}{C}}–E$$

(E = Si, Ge, or Sn group) by various physical

#The high reactivity of trimethylsilylmethanol in this reaction has also been explained[75] by the electron-accepting properties of the $CH_2Si(CH_3)_3$ group.

methods indicate the anomalous nature of their properties due to the non-inductive influence of the substituents X and E. Nevertheless some of the physical properties of these compounds are consistent with the inductive influence of the E atom (E = Si, Ge, or Sn) or more correctly of the group ER_3 incorporating it on the X atom.

On decrease of the electronegativity of the halogen atom in the sequence X = Cl, Br, I in molecules of the type XCH_2SiH_3, one should expect a decrease of their dipole moments, but in reality the dipole moments of all compounds of this type remain virtually constant. This has been explained[81] by the $(p-d)_\sigma$ or $(p-d)_\pi$ interaction of Si and X atoms not linked directly[81]. The dipole moment of the C–X bond in molecules of the type XCH_2EH_3 for E = Si is much smaller than for E = C. The difference between these dipole moments diminishes on passing from X = Cl to X = Br and I. It has been suggested[81] that this corresponds to a weakening of the interaction of the silicon and halogen atoms with decrease of the electronegativity of the halogen. Accordingly, if it is assumed that the dipole moments of the C–X bond in the XCH_2SiH_3 and XCH_2CH_3 molecules are the same, the calculated dipole moment of the SiH_3 group proves to depend on the nature of the halogen atom X.[81]

According to NMR data, the ^{29}Si atom in chloromethyltrimethylsilane is less shielded than in tetramethylsilane, which is consistent with the -I effect of the $ClCH_2$ group[82]. However, if electron-accepting substituents Y (Y = F, Cl, OR, or OCOR) are linked to the silicon atom instead of the methyl groups, the shielding of the silicon atom in compounds of the $ClCH_2SiY_n(CH_3)_{3-n}$ series proves to be greater than in the corresponding $Y_nSi(CH_3)_{4-n}$ molecules[82,83]. One of the possible explanations of the anomalous influence of the chloromethyl group on the shielding of the silicon atom in these compounds is the increase of its $(p-d)_\pi$ conjugation with the heteroatom of the substituent Y under the influence of the electron-accepting chloromethyl group[83].

According to ^1H NMR data[84], the substituents SiX_3 in molecules of the $ClCH_2SiX_3$ series influence the hydrogen atoms of the $ClCH_2$ group only via the inductive mechanism. This conclusion was reached on the basis of the ratio of the coefficients ($\rho/\rho' = 2.7$) in the correlation equations $\delta(CH_2Cl) = \delta_0 + \rho\sigma^*(SiX_3)$ for molecules of the $ClCH_2SiX_3$ (four compounds) and $ClCH_2CH_2SiX_3$ (two compounds) series, which is equal to the coefficient of the decay of the inductive influence of the substituents via the methylene group. However, it is quite evident that the small amount of experimental data makes these conclusions illegitimate.

The ^{19}F NMR spectra show that the electron density at the fluorine atom in the compounds $FCH_2Si(CH_3)_3$ is higher than in the isostructural molecules $FCH_2C(CH_3)_3$ and members of the $F(CH_2)_nSiR_3$ (R = CH_3, C_2H_5, OC_2H_5, or Cl; $n > 1$) series. These data are inconsistent with the existence of the α-effect in the fluoromethyltrimethylsilane molecule and are consistent only with the manifestation of a strong *+I* effect of the $CH_2Si(CH_3)_3$ group[85]. On the other hand, the order in which the ^{19}F NMR chemical shifts of compounds of the $Cl_nCH_{3-n}SiF_3$ series change as *n* is varied is the opposite of that expected on the basis of the inductive effect of the chlorine atoms, which has been explained by the *+M* effect of the latter[86].

The occurrence of two stretching vibration frequencies of the Si–H bond in the infrared spectra of the compounds $ClCH_2SiHRR'$ (in heptane) has been explained by the presence in solution of both molecules with intramolecular coordination between the unshared electron pair of the chlorine atom and the vacant *d* orbital of the silicon atom [the low-frequency ν(Si–H) band belongs to them] and molecules without such coordination[87]. Judging from the splitting of the ν(Si–H) line in the infrared spectra of compounds of the type $ClCH_2SiR_3$, the α-effect weakens with enhancement of the electron-accepting properties of the substituents R.[87] The steric influence of the substituents R affects to some extent the magnitude of the α-effect. The state of aggregation and the nature of the solvent also influence significantly the α-effect. It is a maximum in the gaseous state of the substance and is a minimum in the liquid state owing to its competition with the intermolecular interaction involving the vacant *3d* orbitals of the silicon atom[87].

Two bands are observed in the infrared spectra of gaseous $ClCH_2SiH(CH_3)_2$ and $BrCH_2SiH(CH_3)_2$ as well as their solutions in polar and non-polar solvents[88]. However, in this case the presence of two ν(Si–H) frequencies was explained by the existence of two rotational isomers (formed by the rotation of the $ClCH_2$ group about the Si–C bond) in which the dipole–dipole and steric interaction differ somewhat[88].

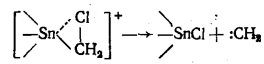
The authors own and the available literature data for the infrared and NMR spectra as well as the dipole moments of compounds of the X_3SiCH_2Y (Y = halogen) series have been analysed[89]. It was concluded that these data are consistent with an intramolecular interaction between the halogen and silicon atoms (α-effect) in halogenomethylsilanes.

It has been shown[90] that the relative basicity of the oxygen atom in the compounds $XX'X''SiOC_2H_5$, determined from the shift Δν(OH) of the stretching vibration frequency of phenol when the latter interacts with these compounds, is correlated with the sum of the Taft inductive constants of the substituents X, X', and X''. However, compounds in which one of the substituents is the chloromethyl group deviate from this correlation owing to the manifestation of the α-effect. The constant $\sigma^* = 0.54-0.57$ of the $ClCH_2$ group, calculated from Δν(OH) by means of a correlation equation, is appreciably lower than the standard value $\sigma^*_{(CH_2Cl)} = 1.05$.[84] Thus the α-effect in molecules of this type can be estimated as amounting to −0.5 of a unit on the scale of the inductive constants σ*.

The ratio of the intensities of the two lines in the ^{35}Cl NQR spectrum of the compound $ClCH_2SnCl_3$ due to the chlorine atoms in the $SnCl_3$ group is 1 : 2 and their splitting (~6%) greatly exceeds the limiting crystal [field?] splitting (1.5–2%).[91] The authors[91] attempted to explain such large splitting by the coordination interaction $Cl\overset{\frown}{-}CH_2\overset{\rightarrow}{-}Sn\lessdot$, leading to the asymmetrisation of the tin atom, which in its turn induces the non-equivalence of the Sn–Cl bonds. Nor can one rule out the possibility of an intermolecular interaction being responsible for this non-equivalence[91]. Later preference was given to the latter explanation[92]. However, the cryoscopic distribution of the molecular weights of $ClCH_2SnCl_3$ in benzene shows that this compound is not associated[93].

It has been suggested that the intramolecular coordination interaction of the X and Sn atoms in the molecules $XCH_2SnRR'R''$ is shown in those cases where the tin atom is linked to electronegative substituents R, "capable of exciting the vacant orbitals of tin".[94,95] This interaction is weakened by the competing π-complex formation with participation of the tin atom[94]. Thus, with increase of the number *n* of electronegative substituents at the tin atom in the compounds $(ClCH_2)_{4-n}SnCl_n$ ($n = 0-4$) and $(ClCH_2)_n \cdot Sn(CH_3)_{4-n}$ ($n = 1$ or 2), a downfield shift of the proton signal of the $ClCH_2$ group is observed. The magnitude of this shift in benzene is smaller than in CCl_4, which has been explained[94] by the formation of π-complexes of the type $C_6H_6 \rightarrow SnR_4$.[94]

Rearranged fragments formed via the mechanism[94]



have been detected in the mass spectra of compounds of the $ClCH_2SnRR'R''$ series.

The broadening of the lines in the Mössbauer spectrum of the compound $ClCH_2Sn(CH_3)_3$ can be caused by the unresolved quadrupole splitting[95], in agreement with intramolecular interaction between the chlorine and tin atoms in this molecule.

The intramolecular interaction of atoms not linked directly is manifested more strongly in the solid state of a given substance, where the thermal vibrations of the molecules are considerably weakened[93]. In conformity with this, according to gas electron diffraction data and ^{35}Cl NQR spectra (at 77 K), the mutual influence of the atoms in the $ClCH_2$ group of the $ClCH_2SnCl_3$ molecule in the gaseous and solid states is not the same. Thus in the gas phase all the Sn–Cl bonds are equivalent, while the NQR spectrum of solid $ClCH_2SnCl_3$ demonstrates their significant non-equivalence (see above).

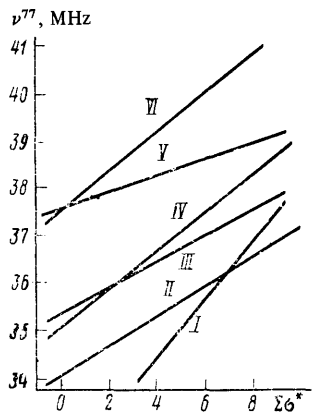


Figure 1. Correlation of the ^{35}Cl NQR frequencies (ν^{77}) of compounds of different series [*I*) $ClCH_2CRR'R''$; *II*) $ClCH_2SiRR'R''$; *III*) $Cl_2CHSiRR'R''$; *IV*) $Cl_2CHCRR'R''$; *V*) $Cl_3CSiRR'R''$; *VI*) $Cl_3CCRR'R''$] with the sum of the Taft inductive constants ($\Sigma\sigma^*$) of the substituents R, R', and R''.

The ^{35}Cl NQR frequencies of compounds of the $ClCH_2ERR'R''$ series with E = Si, Ge, or Sn are higher than for the corresponding organic analogues (E = C) [1–8,96–99] (Fig. 1). The points corresponding to the organoelemental compounds $ClCH_2E(CH_3)_3$ lie appreciably above the $\nu^{77} = f(\Sigma\sigma^*_R)$ correlation straight lines plotted for compounds of the ClR and $ClCH_2R$ series[6,100]. Bearing in mind the appreciably greater electronegativity of the carbon atom compared with silicon, germanium, and tin atoms, the opposite ratio of the NQR frequencies of the corresponding organic and organoelemental compounds was to be expected. In the ^{35}Cl NQR spectra of compounds of the $Cl(CH_2)_nERR'R''$ (E = C, $n = 0$, 2, or 3 but not $n = 1$) series the NQR frequency is higher, as expected, than for the corresponding compounds with E = Si, Ge, or Sn. This also applies to the NQR frequencies of compounds of the $ClC \equiv CE(CH_3)_3$ series.

The anomalously high ^{35}Cl NQR frequencies of compounds of the $ClCH_2ERR'R''$ (E = Si, Ge, or Sn) series compared with organic analogues (E = C) are due to the intramolecular interaction between the Cl and E atoms, which we call the α-effect[1–8,96–99]. The possibility of the interaction between the chlorine atoms involved in the C–Cl bond and the silicon atom is also confirmed by a comparison of the relations between the NQR frequencies of these chlorine atoms and their number *n* in molecules of the $Cl_3CC^{35}Cl_nH_{3-n}$ and $Cl_3SiC^{35}Cl_nH_{3-n}$ series (Fig. 2). Evidently, as a consequence of this interaction, the increase of the NQR frequencies with increasing number *n* in the spectra of the organosilicon compounds is much smaller than for their carbon analogues (the slope of the correlation straight line II in Fig. 2 is smaller than that of line I). The replacement of the CCl_3 group in the $Cl_3CCCl_nH_{3-n}$ molecules by $SiCl_3$ leads to a significant alteration of the mutual influence of the atoms in the $Cl_n.CH_{3-n}$ group. As the chlorine atoms accumulate in this group, each becomes a weaker electron acceptor for E = Si than in the corresponding organic molecules (E = C).[101]

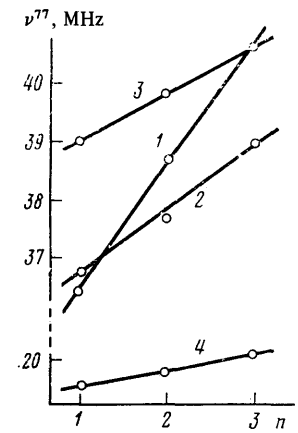


Figure 2. Relation between the ^{35}Cl NQR frequencies (ν^{77}) of compounds of the $Cl_3ECCl_nH_{3-n}$ (E = C or Si) series and the number of chlorine atoms *n*: *1*) for the chlorine atoms in the CCl_nH_{3-n} group with E = C; *2*) for the chlorine atoms in the same group with E = Si; *3*) for the chlorine atoms in the Cl_3C group; *4*) for the chlorine atoms in the Cl_3Si group.

The NQR frequencies of the chlorine atoms linked to silicon in compounds of the $Cl_3SiCCl_nH_{3-n}$ series are satisfactorily consistent with the general relation between the NQR frequencies of compounds of the Cl_2SiRR' series and the sum of the σ* constants of the substituents R. The suggested interaction between the Si atoms and the Cl atoms of the CCl_nH_{3-n} group in the $Cl_3SiCCl_nH_{3-n}$ molecules is shown only by a decrease of the sensitivity of the chlorine atoms of the Cl_3Si group to a change in the number of *n* compared with the organic analogues $Cl_3CCCl_nH_{3-n}$ (the slope of straight line IV in Fig. 2 is smaller than that of line III).[101]

Analysis of the ^{35}Cl NQR frequencies of compounds of the $Cl_nCH_{3-n}SiRR'R''$ and $Cl_nCR_{3-n}SiRR'R''$ series as well as the compound $Cl(CH_3)_2SiSi(CH_3)_2Cl$ led[102] to the conclusion that the α-effect is possible only in molecules where the Cl and Si

atoms are separated by the CH_2 or $Si(CH_3)_2$ groups, because only in these cases are the NQR frequencies of the organosilicon compounds higher than those of the corresponding organic derivatives. In reality this conclusion is incorrect.

Further study of the ^{35}Cl NQR spectra of compounds of the $ClCH_2SiRR'R''$, $Cl_2CHSiRR'R''$, and $Cl_3CSiRR'R''$ series showed[5,98,99] that the ratio of the NQR frequencies in the spectra of organic and organosilicon compounds of this type is not always anomalous. For example, the $ClCH_2SiF_3$ frequency is appreciably lower than that of $ClCH_2CF_3$, as was to be expected from the ratio of the electronegativities of the C and Si atoms. The NQR frequencies of compounds of these series are satisfactorily correlated with the sum of the σ^* constants of the substituents R, R', and R'' (Fig.1). For $\Sigma\sigma^* < 7.04$, the NQR frequencies of the organosilicon compounds $ClCH_2SiRR'R''$ are higher than for the corresponding organic analogues $ClCH_2CRR'R''$, i.e. an anomalous ratio of their NQR frequencies is observed. On the other hand, for $\Sigma\sigma^* > 7.04$, the NQR frequencies of the organosilicon compounds are lower than those of the organic derivatives. This is consistent with the ratio of the electronegativities of the Si and C atoms and the inductive effect of the substituents incorporating them. The value of $\Sigma\sigma^*$ for which the ratio of the ^{35}Cl NQR frequencies of the organic and organosilicon compounds $Cl_nCH_{3-n}ERR'R''$ is reversed, decreases sharply with increase of the number of electron-accepting chlorine atoms in molecules of the given series (7.04, 1.67, and 0.25 for $n = 1$, 2, and 3 respectively).

However, the different kinds of ratios of the NQR frequencies of these compounds do not imply that there is no α-effect in the $Cl_nCH_{3-n}SiRR'R''$ molecules for some values of $\Sigma\sigma^*$, while for others the effect does exist. The mechanism of the interaction of atoms in these series of compounds must be the same for all R, because there is a satisfactory linear correlation between their ^{35}Cl NQR frequencies and the sum of the inductive constants σ^* of the substituents. These data show that the α-effect occurs in all molecules containing the $Cl-\overset{|}{\underset{|}{C}}-E$ (or $X-\overset{|}{\underset{|}{C}}-E$) group. However, its manifestation depends on the nature of the substituents linked to the atoms E and C and also on the ratio of the abilities to transmit their electronic influence in organic and organoelemental molecules. Thus the unequal manifestations of the α-effect in the organosilicon compounds $Cl_nCH_{3-n}SiRR'R''$ for different n, R, R', and R'' is caused by their appreciably lower ability to transmit the electronic influence of substituents to the chlorine atom compared with their organic analogues. The ^{35}Cl NQR frequencies of compounds of the $ClCH_2ERR'R''$ (E = Ge or Sn) series are higher than for the corresponding organic derivatives (E = C), because the abilities of these compounds (E = C, Ge, or Sn) to transmit the electronic influence of substituents to the chlorine atom are similar in magnitude (the coefficients ρ in the correlation equation $\nu^{77} = \nu_0 + \rho\Sigma\sigma^*$ are 0.58, 0.43, and 0.46 for E = C, Ge, and Sn respectively[5,99]).

Data concerning the occurrence of an intramolecular noninductive interaction in molecules containing the $X-\overset{|}{\underset{|}{C}}-E$ group (E = Si, Ge, or Sn and X = N, O, or S), obtained by infrared spectroscopy, are extremely contradictory. The nature of the variation of the basicity of the oxygen atom in molecules of the $CH_3O(CH_2)_nSi(CH_3)_3$ [103] and $CH_3O(CH_2)_nC(CH_3)_3$ series with n is the same—the basicity diminishes with increasing n.[103] The increased basicity of the oxygen atom in organic and organosilicon compounds with $n = 2$ has been explained by the effect of hyperconjugation. For compounds of the type $CH_3O(CH_2)_n \cdot Si(CH_3)_3$, the increase of basicity observed on passing from $n = 0$ to $n = 1$ and 3 is consistent with the inductive influence of the trimethylsilyl group. The basicity of the oxygen atom in the $CH_3O(CH_2)_nSiX_3$ (X = H or Cl) molecules proves to be a minimum for $n = 1$, which has been accounted for by the interaction of the oxygen and silicon atoms[103,104]. The smaller basicity of the oxygen atom in $CH_3OCH_2Si(CH_3)_3$ compared with the carbon analogue has also been explained in the same way[105]. Such interaction is manifested most effectively when there are electron-accepting chlorine atoms at the silicon atom[103].

The experimental basicity of the oxygen atom in the $[(CH_3)_3SiCH_2]_2O$ molecules proved to be smaller than was to be expected from the electron-donating properties of the trimethylsilyl group; this is caused by the superposition of the α-effect. Comparison of the basicities of the oxygen atoms shows that the α-effect in $CH_3CH_2OCH_2Si(CH_3)_3$ is stronger than in $[(CH_3)_3SiCH_2]_2O$.[106]

The lower stretching vibration frequency $\nu(C-O)$ in the infrared spectra of the compounds $XO(CH_2)_nSiR_3$ with $n = 1$ compared with their homologues ($n = 2$ or 3) and also with their organic analogues $XOCH_2CR_3$ (X = H, alkyl, or $COCH_3$) is evidently caused by the intramolecular interaction between the oxygen and silicon atoms[107].

On passing from $n = 1$ to $n = 2$ and 3, the basicity of the oxygen atom in compounds of the $(CH_3)_3Si(CH_2)_nOSi(CH_3)_3$ series diminishes. For $n = 2$ and 3, it is virtually the same and close to the basicity in $(CH_3)_3C(CH_2)_nOSi(CH_3)_3$, while for $n = 1$ it is somewhat lower than might have been expected from the electron-donating properties of the trimethylsilyl group. The latter has been explained[108] by an interaction of the type $-O-CH_2-Si$. According to other data[109] the basicity of the oxygen atom in $(CH_3)_3SiCH_2OSi(CH_3)_3$ is consistent with the inductive influence of the $(CH_3)_3SiCH_2$ group ($\sigma^* = -0.26$).

The interpretation of the infrared spectra of compounds of the $ROCOCH_3$ series and of their temperature variation led to the conclusion that the electron-donating capacity of the $R = X_3SiCH_2$ groups is reduced due to the α-effect. This effect leads to a deviation of the frequencies $\nu(C=O)$ and $\nu(C-O-C)$ for $(CH_3)_3SiCH_2OCOCH_3$ from the linear correlation of these quantities with the inductive constants σ^* of the substituents R in compounds of the $ROCOCH_3$ series and to a decrease of the frequencies $\nu(C-O-C)$ for the compounds $H_3COCOCH_2E(CH_3)_2R$ (R = CH_3, C_2H_5, or C_6H_5; E = Si or Ge) compared with $H_3COCO(CH_2)_nE(CH_3)_3$ for $n > 1$ or with $H_3COCO(CH_2)_nR$ [R = $(CH_3)_3C$ or CH_3; $n = 1-4$].[110] The acetoxy-group in compounds of the $H_3COCOCH_2Si(CH_3)_{3-n}R_n$ (R = OC_2H_5 or $OCOCH_3$) series increases the shielding of the silicon atom compared with the compounds $R_nSi(CH_3)_{4-n}$. On the other hand, according to its inductive effect, deshielding of the silicon atom would have been expected[111].

The basicity of the oxygen atom in the $H_3COCH_2EH_3$ (E = Si or Ge) molecules is lower than in the carbon analogue (E = C), which is inconsistent with the electron-donating properties of the EH_3 groups for E = Si or Ge and has been explained[112,113] by the $(p-d)_\pi$ interaction between O and E (E = Si or Ge) atoms separated by the CH_2 group.

The frequencies $\nu(C-O-R)$ and $\nu(OH)$ in the infrared spectra of the compounds $RO(CH_2)_nGe(CH_3)_3$ [R = H or $Si(CH_3)_3$; $n = 1-4$] for $n = 1$ are lower than for $n = 2-4$ and are also lower than for the carbon analogues $RO(CH_2)_n \cdot C(CH_3)_3$. This has been explained by the lability of the C–O bond caused by the α-effect. The relative basicities of the oxygen atom in molecules of the $(CH_3)_3E(CH_2)_n \cdot OSi(CH_3)_3$ (E = C or Ge; $n = 1-4$) series are consistent

with the electron-donating properties of the $(CH_2)_nGe(CH_3)_3$ groups. For $n = 1$ and 2, the basicity is higher than for $n = 3$ and 4.[114]

The relative basicities of the alcohols HOR, determined from the shift of the stretching vibration frequency ν(OH) of phenol, are correlated with the inductive constants σ^* of the substituents R. The basicities of the compounds $HO(CH_2)_nSi(CH_3)_3$ with $n = 1$ and 2 also obey this correlation. The relative acidities of the latter likewise obey a linear correlation between the acidity of the alcohols HOR [determined from the shift of ν(OH) in the infrared spectra of their mixtures with tetrahydrofuran] and the σ^* constants of the substituents R. These data are inconsistent with an interaction between the silicon and oxygen atoms in organosilicon compounds containing the $-O-\overset{|}{\underset{|}{C}}-Si<$ group[115].

The ^{29}Si NMR chemical shifts of compounds of the $ROSi(CH_3)_3$ series are correlated with the inductive constants σ^* of the substituents R. Compounds with $R = CH_2Cl$ and $CH_2Si(CH_3)_3$ do not obey this correlation. The ^{29}Si NMR data show that the $CH_2Si(CH_3)_3$ group has a weaker electron-accepting activity when it is linked to an oxygen atom. The constant $\sigma^*[CH_2Si(CH_3)_3]$, calculated[109] from the correlation equation on the basis of the experimental quantity δ(Si) in the $(CH_3)_3SiCH_2OSi(CH_3)_3$ spectrum, is 0.15 ± 0.05.

The acidity of alcohols of the $HO(CH_2)_nSi(C_6H_5)_3$ series increases on passing from $n = 1$ to $n = 2$, the increase being particularly pronounced for $n = 0$. The acidity of isostructural organogermanium alcohols $HO(CH_2)_nGe(C_6H_5)_3$ increases on passing from $n = 2$ to $n = 1$ and further to $n = 0$. This sequence in the variation of the acidities of organoelemental alcohols is inconsistent with the electron-donating inductive effects of the triphenylsilyl and triphenylgermyl groups and can be explained by the $(p-d)_\pi$ interaction between the oxygen atom and the silicon or germanium atom via the methylene group. It has been suggested that such interaction is responsible also for the decrease of acidity on passing from E = Ge to E = Si and further to E = C in molecules of the $HOCH_2E(C_6H_5)_3$ series[116].

The basicity of the nitrogen atom in trimethylsilylmethylamine is higher than in its carbon analogue (by a factor of 5.69) or in γ-trimethylsilylpropylamine (by a factor of 1.5),[117] which agrees with the electron-donating effect of the trimethylsilyl group.

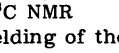
The basicity of compounds of the $H_2N(CH_2)_nSi(OC_2H_5)_m.(CH_3)_{3-m}$ ($m = 0-3$) series, determined spectroscopically, is much lower for $n = 1$ than for $n = 2-4$. This has been explained by the effect of hyperconjugation, which exceeds, when $n = 1$, the opposite inductive effect of the silyl group[118].

Compounds of the $H_2N(CH_2)_nSi(OC_2H_5)_m(CH_3)_{3-m}$ series have also been studied by the ^{29}Si, ^{14}N, and ^{13}C NMR methods[119]. The observed increase of the shielding of the silicon atom in these compounds for $n = 1$ and 2 relative to compounds of the $H(CH_2)_nSi(OC_2H_5)_m(CH_3)_{3-m}$ series has been explained by the intensification of the $(p-d)_\pi$ interaction between the silicon and oxygen atoms (in the ethoxy-group) under the influence of the electronegative group NH_2. This inductive influence decays for $n \geq 3$. It has been suggested that the more pronounced shielding of the nitrogen atom in the aminomethyl derivatives (which is almost independent of the number m) compared with other members of this series ($n \geq 2$) is inconsistent with the interaction between the silicon and nitrogen atoms in these molecules[119]. However, on the basis of NMR data, one can hardly draw inferences about this interaction, because the ^{14}N, ^{29}Si, etc. NMR shifts are not direct characteristics of the electron density of the indicator atom. This is evident also from the ^{14}N NMR spectra of compounds of the type $H_2N(CH_2)_n.Si(OC_2H_5)_m(CH_3)_{3-m}$ investigated. For example, a change in the number m for $n = 1$ does not affect δ_N and the chemical shift of the ^{14}N NMR signal in the spectrum of aminomethyltriethoxysilane differs by only 1 p.p.m. from δ for methylamine, etc.

The basicity of the amines $H_2C(CH_2)_mN(CH_2)_nSiR_3$ ($m = 3-5$) for $n = 1$ is lower than for $n = 2$,[120-122] which is due to the α-effect in the molecules with $n = 1$. The determination of the relative acidities of the hydrogen atom linked to the nitrogen atom in compounds containing the $RNHCH_2Si$ group by infrared spectroscopy[123] showed that they exhibit the α-effect. The magnitude of this effect depends on the nature of the substituent R linked to the nitrogen atom and is a maximum for R = alkyl. For $R = C_6H_5$, the α-effect is reduced owing to competition with p, π conjugation involving the aromatic ring. For $R = CH_3OC(O)$, there is no α-effect[123].

In molecules of the $R_2NCH_2E(CH_3)_3$ series, the basicity of the nitrogen atom for E = Ge is somewhat lower[32] and for E = Sn is lower by 4 orders of magnitude than for E = C.[124] The appreciably reduced basic properties of the nitrogen atom in trialkylaminomethylstannanes have been explained by the increase of the coordination number of the tin atom due to the formation of an intramolecular coordinate bond with the nitrogen atom, i.e. by the transfer of the unshared electron pair of the nitrogen atom to the vacant orbital of the tin atom with partial sp^3d character[124]. The upper limit to the strength of the intramolecular coordinate bond N → Sn ($\Delta\Delta H \cong 5.5$ kcal mol^{-1}) was estimated from the decrease of basicity by means of the relations $k_1/k_2 = \exp(-\Delta\Delta E/RT)$ and $\Delta\Delta F = \Delta\Delta H - T\Delta\Delta S^0$, neglecting the change in the entropy term[124]. Later[125] the authors admitted that these data and the hypothesis of the intramolecular coordination of the tin and nitrogen atoms based on them are erroneous. They found that the basicity of the amines containing the $>N-\overset{|}{\underset{|}{C}}-E<$ group increases in the following sequence of different E: C > Ge > Sn > Si.

The intramolecular coordination interaction between nitrogen and tin atoms is indicated by the retardation of the inversion of nitrogen in trialkyl(*N*-aziridinomethyl)stannanes; apart from overcoming the inversion barrier, a change in the configuration of these compounds requires the rupture of the N → Sn bond.[124]

In contrast to tetra-alkylstannanes, the ultraviolet spectra of trialkyl(aminomethyl)stannanes exhibit a slight bathochromic shift and an appreciable increase of the extinction coefficient[124], which is consistent with the N → Sn coordination. The absence of an intermolecular interaction in this case is confirmed, for example, by cryoscopic and electrothermic studies of the compound .[124,126]

The absence of quadrupole splitting and the small changes in the chemical shifts in the Mössbauer spectra of compounds of the XCH_2SnR_3 (X = H_2N, $R_3\overset{+}{N}$, RO, F, or Cl) series[95,127] are inconsistent with intramolecular coordination in these molecules[95,128]. This may be caused by the inadequate sensitivity of the method[124].

Certain examples of the anomalous influence of the groups ER_3 (E = Si, Ge, or Sn), which are inconsistent with their inductive effect on the atom X in molecules containing the $X-\overset{|}{\underset{|}{C}}-ER_3$ fragment, have also been quoted in reviews[125-131]. This anomalous influence is usually explained by the interaction between the unshared electron pair of the atom X and the vacant *d* orbitals of the atom E.[129,131].

Thus the results presented below show that data concerning the existence of the α-effect in molecules containing the X–C–E (E = Si, Ge, or Sn) group are at present contradictory. However, one must bear in mind that many theoretical conclusions are insufficiently well-founded. Data derived by certain research methods, on the basis of which the α-effect is accepted or rejected, do not permit inferences concerning the nature of the distribution of electron density at the E and X atoms, because such data are determined by contributions from several uncontrolled factors. This applies primarily to ^{14}N, ^{29}Si, etc. NMR spectra. Furthermore, the contradictory nature of the conclusions concerning the existence of the α-effect is caused by the fact that the nature of its manifestation in molecules containing the X–C–E group depends on the electron-accepting properties of substituents linked to the C and E atoms and also on the ratio of the abilities to transmit the inductive influence of substituents to the atom X in organic (E = C) and organoelemental (E = Si, Ge, or Sn) compounds. These characteristics of the manifestation of the α-effect have usually been disregarded. The conclusions concerning the existence of the α-effect, based on a comparison of the results of studies of individual pairs of organic and organoelemental compounds, cannot therefore be regarded as reliable.

The vast majority of the available experimental data indicate a non-inductive interaction between the atoms X and E in molecules containing the X–C–E group. Systematic study of ^{35}Cl NQR spectra of compounds containing this group (E = C, Si, Ge, or Sn) showed that the α-effect exists in all these molecules but is not manifested in the same way. By analogy with these data and also bearing in mind the results obtained by other research methods, one can assume that the α-effect exists in all molecules containing the X–C–E group.

IV. THE NATURE OF THE α-EFFECT

Views concerning the nature of the α-effect in molecules containing the X–C–E group are contradictory and the majority of them do not have a convincing basis. They are based on the analysis of data obtained in the study of the corresponding compounds by physical methods which are unsuitable for the investigation of the mechanism of the mutual influence of atoms in molecules. The quantum-mechanical calculations carried out on certain molecules to elucidate the nature of the α-effect also failed to solve the problem of the mechanism of this interaction. The anomalous (inconsistent with the inductive effect of the geminal substituent) physical and chemical properties of compounds containing the X–C–E group are usually explained by the coordination interaction between the atoms X and E with transfer of electron density from the atom X to the atom E. The commonest mechanism of this transfer is $(p-d)_\pi$ conjugation of the unshared electron pair of the atom X with the *d* orbitals of the atom E through space[81,112,113,116]. The principal arguments in support of this interaction—the anomalous nature of the properties of these compounds and the possibility, in principle, of the involvement of the unshared electron pairs and vacant *d* orbitals of the corresponding atoms in the formation of chemical bonds—are merely speculative.

If the intramolecular coordination interaction in the group X–C–E does indeed occur, it is to be expected that the ECX angle should be smaller than the tetrahedral value, that the non-bonding E...X distance should approach the sum of the covalent radii of these atoms, and that the E–C and C–X bond lengths should have anomalous values. However, the experimental geometry of the $ClCH_2SiH_3$ molecule[132] does not confirm this hypothesis. The ClCSi angle in this molecule is 109.3°, the Si–C and C–Cl bond length have the "normal" values (1.88 and 1.788 Å respectively), and the distance between the Si and Cl atoms is 3.0 Å, i.e. appreciably greater than the sum of their covalent radii.

According to gas electron diffraction data[93], the $ClCH_2.SnCl_3$ molecule has the structure of a somewhat distorted tetrahedron. All the Sn–Cl bonds have the same "normal" length (2.34 Å), which is less than the sum of the covalent radii (2.39 Å). The Sn–C bond length (2.23 Å) is somewhat greater than the sum of the covalent radii of the tin and carbon atoms (2.17 Å) and the length of the Sn–C bonds in other organic derivatives of tin. The C–Cl bond (1.74 Å) is shorter than in saturated organic compounds and its length is close to that of a C–Cl bond adjoining a double bond, for example in $Cl_2C=CCl_2$ (1.72 Å). The ClCSn angle (113°) is somewhat greater than the tetrahedral value and the non-valent Sn...Cl distance (3.31 Å) is greater than the sum of the covalent radii (2.39 Å) but smaller than the sum of the van der Waals radii (3.95 Å) of tin and chlorine atoms. Although this distance is sufficient for coordination interaction between the Sn and Cl atoms, nevertheless there is no direct evidence for such coordination.

It has been suggested that the characteristics of the changes in the basicity of the oxygen atom in molecules of the $[(CH_3)_3Si(CH_2)_n]_2O$ ($n = 1-4$) series[106] and the low stretching vibration frequencies ν(C–O) and ν(HO) [107] in the compounds $XOCH_2Si(CH_3)_3$ compared with their organic analogues and other members of the $XO(CH_2)_nSi(CH_3)_3$ [X = H or $Si(CH_3)_3$] series are caused by the $(p-d)_\sigma$, $\sigma_{OC} \rightarrow d$, or $\sigma_{OH} \rightarrow d$ interactions[106,107]. The last interaction has also been postulated in the $HOCH_2Ge(CH_3)_3$ molecule[107]. The α-effect in the molecules of acetoxysilanes $H_3COCOCH_2.Si(CH_3)_2X$ has been interpreted as $\sigma_{C(O)-O} \rightarrow d$, $\sigma_{C(O)-O} \rightarrow \sigma^*_{(O)C-Si}$, or $\sigma_{C(Si)-O} \rightarrow d$ interaction[110]. The shielding of the protons of the methylene group $XCH_2Sn\lesssim$ in the molecules $XCH_2Sn(C_2H_5)_2Cl$, which is smaller than expected on the basis of the electronegativity of the tin atom, has been explained by the partial transfer of the σ-electrons of the CH_2–X bond (X = Cl or OCH_3) to the vacant 5*d* orbitals of the tin atom ($\sigma-d$ conjugation).[133]

Analysis of the orbital interactions of the α-carbofunctional silanes XCH_2SiH_3 (X = NH_2, OH, or F) and the corresponding carbon analogues, based on the calculation of the wave functions in terms of the CNDO/2 approximation and the Mulliken analysis of the orbital populations, led to the conclusion that there exist two mechanisms of the electron-accepting influence of the second atom on the geminal heteroatom (two mechanisms of the α-effect)[134,135]: (1) interaction through space between the upper occupied molecular orbitals and low-lying antibonding orbitals ($n - \sigma + \sigma^*$), which

is reflected by the resonance structure $^{+}X-CH_2\ H-SiH_2$; the extent of this interaction diminishes in the following sequence of X: $H_2N > OH > F$; (2) interaction via bonds, which is most marked for X = F.

The sequence of the changes in the calculated (in terms of the CNDO/2 approximation without taking into account the *d* orbitals of the silicon atom) enthalpy of the reversible acid–base interaction ΔH for the compounds $X(CH_2)_nEH_3$ (E = C or Si; X = HO or H_2N; $n = 0-3$) is consistent with the sequence in the variation of the experimental basicities or acidities of these compounds determined in the gas phase. The enthalpy was calculated as the difference between the total energies E: $\Delta H = E_{(ROH)} - E_{(RO^-)}$ for the reaction $RO^- + H^+ \rightarrow ROH$ and $\Delta H = E_{(RNH_3^+)} - E_{(RNH_2)}$ for the reaction $RNH_2 + H^+ \rightarrow RNH_3^+$.

The basicity of the amine $H_2NCH_2Si(CH_3)_3$ is lower than for other members of the $H_2N(CH_2)_nSi(CH_3)_3$ series. On the other hand, the basicity of the alcohols $HO(CH_2)_nSi(CH_3)_3$ diminishes successively with increase of *n*. On the basis of the analysis of the orbital interactions, the unequal influences of the $(CH_3)_3Si$ group on the basicity of $H_2NCH_2Si(CH_3)_3$ and $HOCH_2Si(CH_3)_3$ have been explained by the stronger interaction of the unshared electron pair of the nitrogen atom with the Si–C bond compared with the oxygen atom, which leads to a decrease of the energy of the $n-\sigma$ orbital when the latter interacts with the antibonding σ^*_{Si-C} or σ^*_{Si-H} orbital[135]. It has been suggested[134] that the α-effect is a consequence of the high polarisability of the silicon atom, which is responsible for the existence of low-lying antibonding orbitals.

The inclusion of the vacant *d* orbitals of the silicon atom in the calculation on the XCH_2SiH_3 molecules reduces somewhat the total energy of these molecules and the energies of the individual orbitals. However, this does not alter qualitatively the tendency towards a distribution of the charges on the silicon atom and particularly on the heteroatoms of the substituents X when the latter are varied[134]. An analogous conclusion had been reached earlier[136] on the basis of *ab initio* non-empirical calculations with a contracted Gaussian basis. Furthermore, the contribution of the antibonding orbital σ^*_{Si-H} to the energy of a low-lying vacant molecular orbital is much greater than the contribution of the *d* orbitals[134].

The problem of the involvement of the vacant *d* orbitals of the atoms of non-transition elements in the formation of chemical bonds has attracted the attention of many investigators for a long time. Numerous quantum-mechanical calculations, including non-empirical calculations, have been carried out for its solution. The view (based on these calculations) that the presence of vacant *d* orbitals in the valence shells of atoms of non-transition elements hardly influences the properties of compounds incorporating them, because these orbitals are energetically so unfavourable and so diffuse that they are incapable of interacting in any way appreciably with the other valence orbitals, is nowadays gaining increasing currency (see, for example, Bochvar et al.[137] and Korol'kov[138]). In this connection it is evident that the α-effect can also be accounted for without taking into account the contribution of the vacant *d* orbitals of the atom E (E = Si, Ge, or Sn).

The α-effect in compounds containing the $X-\overset{|}{\underset{|}{C}}-E$ group is caused by the interaction of quite definite orbitals of the atoms E and X (see above). The occurrence of this non-inductive interaction between atoms and its nature can be established only with the aid of physical methods whereby one can follow the populations of these particular orbitals. One of these few methods is nuclear quadrupole resonance, which yields information about the spatial distribution of the electron density of the indicator atom. Other physical methods used to investigate the α-effect (see above) do not provide such information. The results of quantum-mechanical calculations also do not permit the elucidation of the nature of the α-effect.

According to ^{35}Cl NQR spectroscopic data for compounds of the $ClCH_2ERR'R''$ (E = C, Si, Ge, or Sn) series, the p_σ electrons of the chlorine atom, i.e. the electrons of the C–Cl bond, are involved in the interaction with the E atom of these molecules[1-8,97,139]. This follows from the higher ^{35}Cl NQR frequencies of the organoelemental compounds (E = Si, Ge, or Sn) compared with organic analogues (E = C) (see the previous Section).

The NQR frequency ν or the quadrupole coupling constant of the molecule e^2Qq are related to the number of unbalanced electrons of the chlorine atom V_p as follows (see, for example, Refs.92, 140–142):

$$e^2Qq_{mol} = e^2Qq_0 \cdot V_p = e^2Qq_0\left(\frac{N_x + N_y}{2} - N_z\right),$$

where e^2Qq_0 is the atomic quadrupole coupling constant and N_x, N_y, and N_z are the populations of the p_x, p_y, and p_z orbitals of the chlorine atom. Hence it is seen that the quantity e^2Qq can increase either with decrease of the population of the chlorine p_σ orbital (p_z orbital), involved in the formation of the C–Cl bond, or with increase of the population of the orbitals of its unshared electron pairs (p_x or p_y orbitals). The hypothesis that the populations of the $3p_x$ and $3p_y$ orbitals of the chlorine atom in organoelemental molecules are higher than in the isostructural organic molecules, where the populations of the p_x and p_y orbitals are virtually equal to 2, is unrealistic. Therefore the increase of the ^{35}Cl NQR frequency for compounds of the $ClCH_2ERR'R''$ series having E = Si, Ge, or Sn compared with organic analogues (E = C) as well as other anomalous properties of the compounds containing the $Cl-\overset{|}{\underset{|}{C}}-E$ or $X-\overset{|}{\underset{|}{C}}-E$ (E = Si, Ge, or Sn) group are caused by the decrease of the population of the p_σ orbital of the chlorine (or X) atom, i.e. by the involvement in the interaction with the E atom of the electrons of the C–Cl (C–X) bond[1-8,97,139]. This is an experimentally established fact. The participation of the p_σ electrons of the chlorine atom in this interaction is also confirmed by the comparatively low parameter of the asymmetry of the electric field gradient η at the location of the atomic nucleus of chlorine in chloromethylsilane $ClCH_2SiH_3$ ($\eta = 0.048$), which is close to the asymmetry parameter for $ClCH_2CH_3$ ($\eta = 0.035$). Consequently the hypothesis of the coordination interaction between the E and X atoms in the $X-\overset{|}{\underset{|}{C}}-E$ group with participation of the unshared electron pair of the X atom has not been confirmed experimentally.

One can only speculate in what way the E atom is involved in this interaction. According to the generally accepted view, the atoms E = Si, Ge, or Sn possess electron-accepting properties by virtue of their vacant *d* orbitals (see, for example, Refs.23, 131, 143, and 144). On this basis, one can assume that the p_σ electrons of the C–Cl (C–X) bond pass to the vacant *d* orbitals of the E atom and an electron-deficient three-centre bond is therefore formed between the

E, C, and Cl atoms[1-3]. The possibility of the formation of a three-centre bond as a result of the sharing of a single electron pair by three atomic nuclei was pointed out a long time ago by Longuett–Higgins[145]. The presence of such hypervalent bonds has been postulated in diborane[145-148], carbaboranes[149], etc. (see, for example, Refs,147, 148, and 150), but the existence of such bonds has not so far been confirmed experimentally.

In molecules containing the X–C–E group the C–X bond can also be polarised under the influence of the E atom, which should lead to a decrease of the p_σ electron density of the X atom[3]. This model of the intramolecular interaction does not conflict with the steric structure of molecules of the XCH_2ER_3 series established by gas electron diffraction[93] and microwave spectroscopy[132], since it does not require a decrease of the XCE angle relative to the tetrahedral value[2,3].

Analysis of the experimental data established a unique anomalous relation between the ^{35}Cl NQR frequencies of all compounds containing the Cl–C–E group and the charge (or, to a first approximation, the electronegativity) of the E atom[1-5]: with increase of the electronegativity (negative charge) of the E atom, the NQR frequencies of such compounds diminish (the p_σ-electron of the chlorine atom increases) and, conversely, with decrease of the electronegativity of the E atom, the NQR frequencies increase (the p_σ-electron density of the chlorine atom diminishes). Compounds with an E atom having unshared electron pairs (E = N, O, F, etc.), vacant *d* orbitals (E = Si, Ge, Sn, etc.), as well as atoms lacking either feature (E = H or C) obey this relation. The relation has been confirmed by the correlation analysis of the ^{35}Cl NQR frequencies of, for example, compounds of the $ClCH_2E^nR_{n-1}$ (*n* is the valence of the E atom) series[4]. The NQR frequencies of compounds of the $ClCH_2CR_3$ series are correlated with the inductive constants σ^* of the substituent CR_3. For $E \neq C$, such a correlation does not hold. The deviations of the NQR frequencies $\Delta\nu$ of compounds with $E \neq C$ from the above correlation are in their turn satisfactorily correlated with the electronegativity of the E atom (according to Pauling). The last correlation is obeyed by the deviations $\Delta\nu$ both for compounds with an E atom having unshared electron pairs or vacant *d* orbitals and for compounds with E = H as well as the average value of $\Delta\nu$ ($\Delta\nu_{av} = 0$) for compounds with $E^nR_{n-1} = CR_3$.

An analogous anomalous relation is shown also in the case of other physical and chemical methods for the investigation of compounds containing the X–C–E group. The anomalous properties of all these compounds (whatever the E) are due to the interaction of the E atom with the electron cloud of the C–X (C–Cl) bond, which follows from their ^{35}Cl NQR spectra. Bearing this in mind as well as the general anomalous dependence of the distribution of electron density at the X atom in the X–C–E group on the nature of the E atom, one can assume that the anomalous relation is caused by the same mechanism of the interaction of the X and E atoms whatever the E. This general mechanism can involve the electrostatic interaction of the charge of the E atom, directly through the field, with the electron cloud of the C–Cl (C–X) bond, because this interaction is almost independent of the presence of unshared electron pairs or vacant *d* orbitals in the E atom[2,4,5,139,153]. Furthermore, the electrostatic mechanism of the geminal interaction is indicated by the finding that virtually all interactions in the molecules are in fact electrostatic, the E atom influences all the C–X bonds in the given molecule in the geminal position with respect to it to virtually the same extent, etc.[5,153] The interaction of the E and Cl atoms in these molecules directly through the field has been confirmed by the ^{35}Cl NQR spectra of compounds of the $Cl_nCH_{3-n}CHClOR$ series[154,155], in which the resonance frequency of the β-chlorine atom corresponds to the inductive influence of the OR group on the latter, while the frequency of the α-atom is anomalously low. The interaction of the α- and β-chlorine atoms with the oxygen atom along the chemical bonds, the nature of the changes in their NQR frequencies would be the same. In the linear molecules Cl–C ≡ E the intramolecular interaction of the geminal Cl and E atoms takes place only along chemical bonds. The E atoms therefore influence the NQR frequency (or the quadrupole coupling constant) of these compounds in conformity with the inductive effect of the E atoms or the substituents incorporating them[4,5,139,153].

The calculated contribution $\Delta\nu$ to the ^{35}Cl NQR frequency of the interaction of the charge of the E atom with the electron cloud of the C–Cl bond directly through the field for certain molecules of the $ClCH_2E$ series agrees well with the experimental data and the quantum-chemical calculation of the charges on the E atoms in these molecules[156-158]. For example, the quantity $\Delta\nu = 4.2$–6.3 MHz (for different amounts of ionic character of the C–Cl bond, for different charges on the oxygen atom calculated for different parametrisations in terms of the CNDO approximation taking into account the error of the experimental determination of the Stark shift used in the calculation, etc.), calculated for the chloromethyl ether $ClCH_2OCH_3$, agrees satisfactorily with the deviation of the experimental NQR frequency of this ether from the linear correlation between the ^{35}Cl NQR frequencies of compounds of the $ClCH_2CR_3$ series and the inductive constants σ^* of the substituents CR_3 ($\Delta\nu_E = 4.9$ MHz). For $ClCH_2Si(CH_3)_3$, the quantities $\Delta\nu$ and $\Delta\nu_E$ are respectively 3.72 and 3.56 or 2.50 MHz, etc.[157]

The ^{35}CL NQR frequencies of compounds containing the Cl–Z–E and Cl–Z–E groups (Z = C, Si, Ge, P, etc.) obey the anomalous relation which holds for compounds containing the Cl–C–E group[2,4,5,98,139,153,159,160]. The contribution $\Delta\nu$ of the geminal interaction between the Cl and E atoms in the molecules ClZ(OR)XX′ (Z = C, Si, or Ge) is inversely related to the bulk of the central atom Z, i.e. to the distance between the E = O atom and the centre of the electron cloud of the Z–Cl bond[159]. An analogous relation has been observed also for compounds of the ClZ(OR)X series with Z = P or As.[159]. These data are also in good agreement with the electrostatic mechanism of the interaction of the Cl and E atoms in molecules containing the Cl–C–E (X–C–E) group and therefore with the electrostatic mechanism of the α-effect, which is a special case (for E = Si, Ge, Sn, etc.) of the general electrostatic effect of the geminal interaction.

The above data, obtained in the study by physical and chemical methods of compounds of Group IVB elements containing the X–C–E fragment (E = Si, Ge, or Sn; X = halogen, O, N, or S), show that in the vast majority of

cases the E atoms influence the substituent X not in conformity with the electronegativity of the E atom and the inductive effect of the group incorporating it. This non-inductive interaction of the X and E atoms has been called the α-effect. There exist most contradictory views concerning the existence of the α-effect and its nature. However, systematic studies of the ^{35}Cl NQR spectra of organosilicon compounds containing the Cl–C–Si group have shown that the α-effect occurs in all molecules of this type and that the conflicting conclusions concerning its existence arose from the fact that they were usually based on a comparison of data obtained in the study by some method of individual pairs of isostructural organoelemental and organic compounds or short series of compounds.

On the other hand, the nature of the manifestation of the α-effect depends significantly on the electron-accepting properties of the substituents linked to the C and E atoms and on the ability to transmit the inductive influence of the substituents to the indicator E atom in organic and organoelemental compounds and on the research technique employed, which may not reflect adequately the nature of the distribution of the electron density at the E and X atoms. The nature of the α-effect is usually inferred solely on the basis of the postulated possibility, in principle, that specific orbitals of the E and X atoms are involved in the formation of chemical bonds, without any experimental evidence for this hypothesis. Quantum-mechanical calculations also fail to provide a convincing explanation of the α-effect.

The ^{35}Cl NQR spectra of compounds containing the Cl–C–E (E = C, Si, Ge, or Sn) group indicate unambiguously the involvement of the p_σ electrons of the chlorine atom (the electrons of the C–Cl bond) in the interaction with the E atom. Systematic study of the ^{35}Cl NQR spectra of compounds of this type, in which the E atom has unshared electron pairs, vacant *d* orbitals, or neither one nor the other showed that their anomalous properties are caused by the electrostatic interaction directly through the field due to the charge of the E atom with the electron cloud of the C–Cl (C–X) bond, i.e. by the polarisation of the C–Cl (C–X) bond under the influence of the electric field generated by the charge of the E atom, and not by the coordination interaction between the E and Cl (or X) atoms, presupposing the transfer of electron density from the X atom to the E atom. The α-effect is only a special case of such electrostatic interaction. It is quite natural that the charge of the X atom interacts in the same way with the electron cloud of the C–E bond.

REFERENCES

1. M.G.Voronkov, V.P.Feshin, P.A.Nikitin, and N.I.Berestennikov, "Abstracts. II International Symposium on NQR Spectroscopy", CNR, Italy, 1973, p.61.
2. M.G.Voronkov, V.P.Feshin, P.A.Nikitin, and N.I.Berestennikov, "Proceedings of the IInd International Symposium on NQR Spectroscopy", A.Vallerini Publ., Pisa, Italy, 1973, p.207.
3. V.P.Feshin and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **209**, 400 (1973).
4. V.P.Feshin and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **229**, 398 (1976).
5. M.G.Voronkov and V.P.Feshin, Org.Magn.Res., **9**, 665 (1977).
6. M.G.Voronkov, V.P.Feshin, V.F.Mironov, S.A.Mikhailyanits, and T.K.Gar, Zhur.Obshch. Khim., **41**, 2211 (1971).
7. M.G.Voronkov and V.P.Feshin, "V Mezhdunarodnyi Kongress po Metalloorganicheskoi Khimii, Tezisy Dokladov" (The Vth International Congress on Organometallic Chemistry. Abstracts of Reports), Moscow, 1971, Vol.1, p.13.
8. M.G.Voronkov and V.P.Feshin, "Tezisy Dokladov Soveshchaniya 'Vliyanie Vysshikh Atomnykh Orbitalei na Fizicheskie i Khimicheskie Svoistva Soedinenii Neperekhodnykh Elementov' " (Abstracts of Reports at the Conference on 'The Influence of Higher Atomic Orbitals on Physical and Chemical Properties of Compounds of Non-Transition Elements'), Izd.Zinatne, Riga, 1971, p.87.
9. E.Lukevics and R.Ya.Sturkovich, Izv.Akad.Nauk Latv.SSR, **9**, 29 (1977).
10. J.Edwards and R.Pearson, J.Amer.Chem.Soc., **84**, 16 (1962).
11. A.P.Grekov and V.F.Veselov, Zhur.Org.Khim., **13**, 571 (1977).
12. P.D.George, M.Prober, and J.R.Elliott, Chem.Rev., **56**, 1065 (1956).
13. K.A.Andrianov and A.I.Petrashko, Uspekhi Khim., **38**, 408 (1969)[Russ.Chem.Rev., No.3 (1969)].
14. F.G.Whitmore and L.H.Sommer, J.Amer.Chem.Soc., **68**, 481 (1946).
15. V.B.Miller, M.B.Neiman, A.V.Savitskii, and V.F.Mironov, Dokl.Akad.Nauk SSSR, **101**, 495 (1955).
16. A.D.Petrov, E.A.Chernyshev, and M.E.Dolgaya, Zhur.Obshch.Khim., **25**, 2469 (1955).
17. E.A.Chernyshev and M.E.Dolgaya, Zhur.Obshch. Khim., **27**, 48 (1957).
18. E.A.Chernyshev, M.E.Dolgaya, and Yu.P.Egorov, Zhur.Obshch.Khim., **27**, 2676 (1957).
19. E.A.Chernyshev, M.E.Dolgaya, Yu.P.Egorov, L.V.Semenov, and A.D.Petrov, Zhur.Obshch.Khim., **28**, 613 (1958).
20. E.A.Chernyshev, M.E.Dolgaya, and Yu.P.Egorov, Zhur.Obshch.Khim., **28**, 2829 (1958).
21. E.A.Chernyshev and M.E.Dolgaya, Zhur.Obshch. Khim., **29**, 1850 (1959).
22. G.D.Cooper and M.Prober, J.Amer.Chem.Soc., **76**, 3943 (1954).
23. C.Eaborn, "Organosilicon Compounds", Butterworth, London, 1960.
24. R.N.Haszeldine and W.I.Bewan, US P.3233000 (1966); Chem.Abs., **64**, 15770 (1966).
25. R.W.Bott, C.Eaborn, and T.W.Swaddle, J.Organomet. Chem., **5**, 233 (1966).
26. C.A.Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom", Elsevier, Amsterdam, 1963.
27. R.W.Bott, C.Eaborn, and B.M.Rushton, J.Organomet.Chem., **3**, 455 (1964).
28. C.Eaborn and J.C.Jeffrey, J.Chem.Soc., 4266 (1954).
29. C.Eaborn and J.C.Jeffrey, J.Chem.Soc., 137 (1957).
30. V.F.Mironov, Dokl.Akad.Nauk SSSR, **108**, 266 (1956).
31. L.H.Sommer, E.Doreman, G.M.Goldberg, and F.G.Whitmore, J.Amer.Chem.Soc., **68**, 488 (1946).
32. V.F.Mironov and A.P.Kravchesko, Izv.Akad.Nauk SSSR, Ser.Khim., 1563 (1963).
33. R.W.Bott, C.Eaborn, H.C.Pande, and T.W.Swaddle, J.Chem.Soc., 1217 (1962).

34. R.W.Bott, C.Eaborn, and D.R.M.Walton, J.Organomet. Chem., **2**, 154 (1964).
35. I.R.Beattie, Quart.Rev., **17**, 382 (1963).
36. D.C.Boak and B.G.Gowenlock, J.Organomet.Chem., **29**, 385 (1971).
37. M.A.Cook, C.Eaborn, and D.R.M.Walton, J.Organomet.Chem., **29**, 389 (1971).
38. O.W.Steward and O.R.Piers, J.Amer.Chem.Soc., **83**, 4932 (1961).
39. R.Ponek, L.Deimek, and V.Chvalovsky, Coll.Czech. Chem.Comm., **42**, 1859 (1977).
40. I.Vcelak, L.Roman, and V.Chvalovsky, Coll.Czech. Chem.Comm., **41**, 2708 (1976).
41. C.Eaborn and R.W.Bott, "Organometallic Compounds of the Group IV Elements" (Edited by A.G.MacDiarmid), M.Dekker, New York, 1968, Vol.1, Part 1, p.105.
42. R.W.Bott, Organomet.Chem.Rev., **B7**, 1 (1971).
43. M.S.Newlands, Organomet.Chem.Rev., **B7**, 175 (1971).
44. J.M.Bellama and A.G.MacDiarmid, J.Organomet. Chem., **18**, 275 (1969).
45. V.F.Mironov and T.K.Gar, "Organicheskie Soedineniya Germaniya" (Organic Compounds of Germanium), Izd.Nauka, Moscow, 1967.
46. R.N.Haszeldine and J.C.Young, J.Chem.Soc., 4503 (1960).
47. W.I.Bevan, R.N.Haszeldine, and J.C.Young, Chem.Ind.(London), 789 (1961).
48. R.N.Haszeldine and J.C.Young, Proc.Chem.Soc., 334 (1959).
49. K.G.Sharp and T.D.Coyle, Inorg.Chem., **11**, 1259 (1972).
50. G.V.Motsarev and V.K.Rozenberg, Zhur.Prikl. Khim., **37**, 747 (1964).
51. J.M.Birchall, R.N.Haszeldine, and D.N.Roberts, Chem.Comm., 287 (1967).
52. T.N.Bell, R.N.Haszeldine, N.J.Newlands, and J.B.Plumb, J.Chem.Soc., 2107 (1965).
53. R.J.Fessenden and J.S.Fessenden, J.Org.Chem., **28**, 3490 (1963).
54. O.W.Steward, W.J.Uhl, and B.W.Sands, J.Organomet.Chem., **15**, 329 (1968).
55. N.S.Nametkin, V.M.Vdovin, K.S.Pushchevaya, and A.N.Egorochkin, Izv.Akad.Nauk SSSR, Ser.Khim., 2530 (1967).
56. V.Hagen and K.Puhlman, Z.Chem., **9**, 309 (1969).
57. L.H.Sommer, D.L.Bailey, J.R.Gould, and F.G.Whitmore, J.Amer.Chem.Soc., **76**, 801 (1954).
58. F.J.Harigton and D.H.O'Brien, J.Organomet.Chem., **23**, C41 (1970).
59. H.Sakurai, H.Yamamori, and M.Kumada, J.Org. Chem., **33**, 1527 (1968).
60. R.G.Kostyanovskii and A.K.Prokof'ev, Dokl.Akad. Nauk SSSR, **164**, 1054 (1965).
61. D.Seyferth and J.Jick-Pui Mui, J.Amer.Chem.Soc., **87**, 681 (1965).
62. H.C.Clark, in "Uspekhi Khimii Ftora" (Advances in Fluorine Chemistry) [Stacey, Tatlow and Sharpe (Editors), Butterworth, 1963], Izd.Khimiya, Leningrad, 1970, Vols.3 and 4, p.35.
63. R.G.Kostyanovskii and A.K.Prokof'ev, Izv.Akad. Nauk SSSR, Ser.Khim., 175 (1965).
64. V.F.Mironov, A.D.Petrov, and N.A.Pogonkina, Izv.Akad.Nauk SSSR, Ser.Khim., 768 (1955).
65. A.G.Brook, C.E.LeGrow, and D.M.MacRae, Canad. J.Chem., **45**, 239 (1967).
66. G.J.Peddle and I.E.H.Ward, J.Organomet.Chem., **13**, 269 (1968).
67. A.G.Brook, C.M.Warner, and M.E.McGriskin, J.Amer.Chem.Soc., **81**, 981 (1959).
68. L.H.Sommer, "Stereochemistry, Mechanism and Silicon", McGraw-Hill, New York, 1965.
69. A.G.Brook, Pure Appl.Chem., **13**, 215 (1966).
70. A.G.Brook and J.B.Pierce, Canad.J.Chem., **42**, 298 (1964).
71. A.G.Brook and R.J.Mauris, J.Amer.Chem.Soc., **79**, 971 (1957).
72. W.H.Atwell, D.R.Weynberg, and J.G.Uhlman, J.Amer.Chem.Soc., **91**, 2025 (1969).
73. A.G.Brook and P.F.Jones, J.Chem.Soc.D, 1524 (1969).
74. J.L.Speier, B.F.Daubert, and R.R.McGregor, J.Amer.Chem.Soc., **70**, 1117 (1948).
75. M.F.Shostakovskii and I.A.Shikhiev, Uspekhi Khim., **26**, 1087 (1957).
76. J.Pola, V.Bazant, and V.Chvalovsky, Coll.Czech. Chem.Comm., **37**, 3885 (1972).
77. V.F.Mironov and N.A.Pogonkina, Izv.Akad.Nauk SSSR, Ser.Khim., 1998 (1960).
78. M.Krumpole, V.Bazant, and V.Chvalovsky, Coll. Czech.Chem.Comm., **38**, 711 (1973).
79. J.Hetflejs, L.Svoboda, M.Jakoubkova, and V.Chvalovsky, Coll.Czech.Chem.Comm., **38**, 717 (1973).
80. M.F.Shostakovskii, N.V.Komarov, and N.N.Vlasova, Zhur.Obshch.Khim., **37**, 1151 (1967).
81. J.M.Bellama and A.G.MacDiarmid, J.Organomet. Chem., **24**, 91 (1970).
82. E.Lippmaa, M.Magi, G.Engelgardt, H.Janke, V.Chvalovsky, and J.Schraml, Coll.Czech.Chem. Comm., **39**, 1041 (1970).
83. J.Schraml, J.Vcelak, and V.Chvalovsky, Coll.Czech. Chem.Comm., **39**, 267 (1971).
84. J.Pola and V.Chvalovsky, Coll.Czech.Chem.Comm., **42**, 3581 (1977).
85. J.Vcelak, V.Chvalovsky, M.G.Voronkov, V.B.Pukhnarevich, and V.A.Pestunovich, Coll.Czech.Chem.Comm., **41**, 386 (1976).
86. J.Duer and J.Lee, Spectrochim.Acta, **26A**, 1045 (1970).
87.].Ya.Khorshev, A.N.Egorochkin, E.I.Sevast'yanova, N.S.Ostasheva, and O.V.Kuz'min, Zhur.Obshch. Khim., **46**, 1801 (1976).
88. J.Pola, M.Jakoubkova, and V.Chvalovsky, Coll. Czech.Chem.Comm., **42**, 2914 (1977).
89. J.Pola and V.Chvalovsky, Coll.Czech.Chem.Comm., **43**, 3192 (1978).
90. V.P.Mileshkevich, G.A.Nikolaev, A.Yu.Karlin, and L.E.Parshina, Reakts.Sposobn.Org.Soed., **9**, 805 (1972).
91. G.K.Semin, T.A.Babushkina, A.K.Prokof'ev, and R.G.Kostyanovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1401 (1968).
92. G.K.Semin, T.A.Babushkina, and G.G.Yakobson, "Primenenie YaKR v Khimii" (Chemical Applications of Nuclear Quadrupole Resonance), Izd.Khimiya, Leningrad, 1972.
93. I.A.Ronova, N.A.Sinitsina, Yu.T.Struchkov, O.Yu.Okhlobystin, and A.K.Prokof'ev, Zhur. Strukt.Khim., **13**, 15 (1972).
94. R.G.Kostyanovskii and A.K.Prokof'ev, Izv.Akad. Nauk SSSR, Ser.Khim., 275 (1968).
95. V.V.Khrapov, V.I.Gol'danskii, A.K.Prokof'ev, V.Ya.Rochev, and R.G.Kostyanovskii, Izv.Akad. Nauk SSSR, Ser.Khim., 1261 (1968).

96. M.G.Voronkov and V.P.Feshin, "International Symposium on Nuclear Quadrupole Resonance Spectroscopy, London, 1972", p.A1.
97. M.G.Voronkov and V.P.Feshin, in "Determination of Organic Structure by Physical Methods" (Edited by F.C.Nachad and J.J.Zuckerman), Acad.Press, N.Y.–London, 1973, Vol.5, pp.169, 323.
98. V.P.Feshin, M.G.Voronkov, J.Pola, L.S.Romanenko, N.I.Berestennikov, and V.Chvalovsky, "IV Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii Tezisy Dokladov" (The IVth International Symposium on the Chemistry of Organosilicon Compounds. Abstracts of Reports), Izd.NIITEKhIM, Moscow, 1975, p.5.
99. M.G.Voronkov, V.P.Feshin, L.S.Romanenko, J.Pola, and V.Chvalovsky, Coll.Czech.Chem.Comm., **41**, 2718 (1976).
100. I.P.Birjukov and M.G.Voronkov, Coll.Czech.Chem. Comm., **32**, 830 (1967).
101. V.P.Feshin, M.G.Voronkov, V.O.Reikhsfel'd, and L.S.Romanenko, Zhur.Obshch.Khim., **44**, 126 (1974).
102. G.Wulfsberg, "The IIIrd International Symposium on NQR Spectroscopy, Tampa, Florida, 1975", p.77.
103. J.M.Bellama and J.B.Davidson, Inorg.Chem., **14**, 3119 (1975).
104. J.M.Bellama and L.L.Gerchman, Inorg.Chem., **14**, 1618 (1975).
105. E.W.Abel, D.A.Armitage, and S.P.Typfield, J.Chem.Soc.A, 554 (1967).
106. J.Pola, J.Schraml, and V.Chvalovsky, Coll.Czech. Chem.Comm., **38**, 3158 (1973).
107. J.Pola, Z.Papouskova, and V.Chvalovsky, Coll. Czech.Chem.Comm., **38**, 3163 (1973).
108. J.Pola and V.Chvalovsky, Coll.Czech.Chem.Comm., **38**, 1674 (1973).
109. J.Pola, L.Papouskova, and V.Chvalovsky, Coll. Czech.Chem.Comm., **41**, 239 (1976).
110. J.Pola, L.Papouskova, and V.Chvalovsky, Coll. Czech.Chem.Comm., **40**, 2487 (1975).
111. J.Schraml, J.Pola, V.Chvalovsky, M.Magi, and E.Lippmaa, J.Organomet.Chem., **49**, C19 (1973).
112. G.A.Gibbon, J.T.Wang, and C.H.VanDyke, Inorg. Chem., **6**, 1989 (1967).
113. J.T.Wang and C.H.VanDyke, Inorg.Chem., **6**, 1741 (1967).
114. J.Pola, M.Jakoubkova, and V.Chvalovsky, Coll. Czech.Chem.Comm., **39**, 2651 (1974).
115. J.Pola, M.Jakoubkova, and V.Chvalovsky, Coll. Czech.Chem.Comm., **40**, 2063 (1975).
116. G.I.Peddle, R.I.Woznov, and S.C.McGeachin, J.Organomet.Chem., **17**, 331 (1969).
117. L.H.Sommer and J.Rockett. J.Amer.Chem.Soc., **73**, 5130 (1951).
118. V.Fialova, V.Bazant, and V.Chvalovsky, Coll. Czech.Chem.Comm., **38**, 3837 (1973).
119. J.Schraml, Nguen-Duc-Chuy, V.Chvalovsky, M.Magi, and E.Lippmaa, Org.Magn.Res., **7**, 379 (1975).
120. E.Lukevics, M.G.Voronkov, E.E.Shestakov, and A.E.Pestunovich, Zhur.Obshch.Khim., **41**, 2218 (1971).
121. M.G.Voronkov, T.V.Kashik, E.Deriglazova, E.Lukevics, A.E.Pestunovich, and R.Ya.Sturkovich, Zhur.Obshch.Khim., **46**, 1522 (1976).
122. M.G.Voronkov, T.V.Kashik, E.Lukevics, E.S.Deriglazova, A.E.Pestunovich, and R.Ya.Moskovich, Zhur.Obshch.Khim., **46**, 778 (1976).
123. A.N.Egorochkin, S.E.Skobeleva, E.I.Sevast'yanova, I.G.Kosolapova, V.D.Sheludyakov, E.S.Rodionov, and A.K.Kirillin, Zhur.Obshch.Khim., **46**, 1795 (1976).
124. R.G.Kostyanovskii and A.K.Prokof'ev, Dokl.Akad. Nauk SSSR, **164**, 1054 (1965).
125. A.K.Prokof'ev, Uspekhi Khim., **45**, 1028 (1976)[Russ. Chem.Rev., No.6 (1976)].
126. J.J.Neumayer, Anal.Chim.Acta, **20**, 519 (1959).
127. V.V.Khrapov, Doctoral Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1965.
128. A.K.Prokof'ev, V.P.Nechiporenko, and R.G.Kostyanovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 794 (1967).
129. W.P.Jarvie, Organometal.Chem.Rev., **A6**, 153 (1970).
130. A.K.Prokof'ev, V.I.Bregadze, and O.Yu.Okhlobystin, Uspekhi Khim., **39**, 412 (1970) [Russ.Chem.Rev., No.3 (1970)].
131. A.N.Egorochkin, N.S.Vyazankin, and S.Ya.Khorshev, Uspekhi Khim., **41**, 828 (1972) [Russ.Chem.Rev., No.5 (1972)].
132. R.H.Schwendeman and G.D.Jacobs, J.Chem.Phys., **36**, 1251 (1962).
133. V.G.Chernova, E.O.Tsetlina, and V.A.Pestunovich, Zhur.Obshch.Khim., **44**, 2169 (1974).
134. R.Ponek and V.Chvalovsky, Coll.Czech.Chem. Comm., **40**, 2309 (1975).
135. R.Ponek and V.Chvalovsky, Coll.Czech.Chem. Comm., **40**, 2480 (1975).
136. D.L.Wilthie and L.Spialter, J.Amer.Chem.Soc., **95**, 2100 (1973).
137. D.A.Bochvar, N.P.Gambaryan, and L.M.Epshtein, Uspekhi Khim., **45**, 1316 (1976)[Russ.Chem.Rev., No.7 (1976)].
138. D.V.Korol'kov, Symposium, "Razvitie Ucheniya o Valentnotsi" (Development of the Science of Valence), Izd.Khimiya, Moscow, 1977, p.194.
139. V.P.Feshin and M.G.Voronkov, Symposium, "Fundamental'nye Issledovaniya (Khimicheskie Nauki)" [Fundamental Research (Chemical Sciences)], Izd.Sibir.Otd.Akad.Nauk SSSR, Izd. Nauka, Novosibirsk, 1977, p.179.
140. E.A.C.Lucken, "Nuclear Quadrupole Coupling Constants", Acad.Press, London–New York, 1969.
141. C.H.Townes and B.P.Dailey, J.Chem.Phys., **17**, 782 (1949).
142. V.S.Grechishkin, "Yadernye Kvadrupol'nye Vzaimodeistviya v Tverdykh Telakh" (Nuclear Quadrupole Interactions in Solids), Izd.Nauka, Moscow, 1973.
143. E.A.V.Ebsworth, in "Organometallic Compounds of the Group IV Elements" (Edited by A.G.MacDiarmid), M.Dekker, New York, 1968, Vol.1, Part 1, p.1.
144. I.B.Repinskaya, Symposium, "Sovremennye Problemy Organicheskoi Khimii" (Modern Problems of Organic Chemistry), Izd.Leningrad, Gos.Univ., Leningrad, 1969, p.66.
145. H.C.Longuett–Higgins, J.Chim.Phys., **46**, 268 (1949).
146. W.H.Eberhardt, B.Growford, and W.N.Lipscomb, J.Chem.Phys., **22**, 989 (1954).
147. M.J.S.Dewar, "The Molecular Orbital Theory of Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972.
148. M.J.S.Dewar, "The PMO Theory of Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1977.

149. E.M.Shustorovich, Zhur.Vses.Khim.Obshch.im. Mendeleeva, **17**, 243 (1972).
150. M.J.S.Dewar, D.B.Patterson, and W.I.Simpson, J.Chem.Soc., Dalton Trans., 2381 (1973).
151. M.G.Voronkov, V.P.Feshin, E.A.Chernyshev, V.I.Savushkina, P.A.Nikitin, and V.A.Kotikov, Dokl.Akad.Nauk SSSR, **212**, 395 (1973).
152. V.V.Makarskii, M.G.Voronkov, V.P.Feshin, N.I.Berestennikov, E.F.Shibanova, and L.I.Volkova, Dokl.Akad.Nauk SSSR, **220**, 101 (1975).
153. V.P.Feshin and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **236**, 1166 (1977).
154. M.G.Voronkov, V.P.Feshin, A.M.Volkov, A.N.Khudyakova, N.I.Berestennikov, and P.A.Nikitin, Teor.Eksper.Khim., **10**, 538 (1974).
155. V.P.Feshin, M.G.Voronkov, P.A.Nikitin, M.A.Vasil'eva, A.Kh.Filippova, T.I.Bychkova, and A.V.Kalabina, Dokl.Akad.Nauk SSSR, **239**, 1381 (1978).
156. V.P.Feshin, P.A.Nikitin, and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **238**, 1404 (1978).
157. V.P.Feshin, P.A.Nikitin, M.G.Voronkov, and V.B.Kobychev, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, 159 (1979).
158. V.P.Feshin, M.G.Voronkov, P.A.Nikitin, G.M.Gavrilova, and V.B.Kobychev, Zhur.Obshch. Khim., **49**, 2496 (1979).
159. V.P.Feshin, M.G.Voronkov, G.Ya.Zueva, L.S.Romanenko, and G.V.Lipatova, Dokl.Akad. Nauk SSSR, **232**, 1370 (1977).
160. J.Pola, V.P.Feshin, M.G.Voronkov, L.S.Romanenko, and V.Chvalovsky, Coll.Czech.Chem.Comm., **41**, 3771 (1976).

Institute of Organic Chemistry,
Siberian Division of the USSR Academy of Sciences, Irkutsk