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KINETICS AND MECHANISM OF OXIDATION OF ORGANOELEMENT COMPOUNDS BY OZONE

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SUMMARY

The mechanism of ozonization of organic derivatives of the silicon subgroup elements has been examined. The quantitative trends of the influence of the nature of the heteroatom, the substituents, non-specific solvation and electron-donating ligands on the reactivity of organoelement compounds toward ozone have been established.

CONTENTS

INTRODUCTION

The interaction of ozone with organic derivatives of the silicon subgroup elements (tetraalkyl derivatives (1-12), bielementoxanes (12-14), alkoxy and hydroxy derivatives (11,12,14), chlorine substituted derivatives (14-17) and hydrides of organoelements (11,12, 18-22)) in the case when the organic fragment has a normal structure follows a bimolecular heterolytic mechanism (14,23,24) which may be presented as a series of the following stages:

1. Coordination of ozone to the heteroatom of the organoelement compound due to interaction of the vacant d-orbitals of the heteroatom and the electron cloud of the nucleophilic ozone center.

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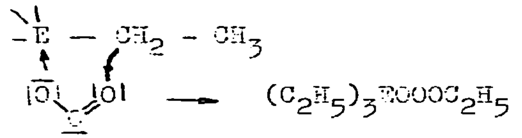
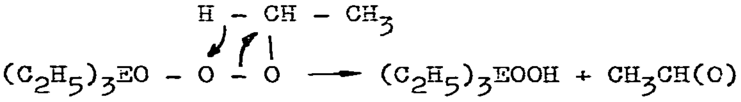
2. Electrophilic attack on the element-carbon bond by coordinated ozone to form an intermediate trioxide.

3. Rearrangement of the trioxide with hydrogen migration from the α-carbon atom to the central oxygen of the trioxide.

$$(C_2H_5)_4E + O_3 \longrightarrow (C_2H_5)_4E{\cdot}O_3 \qquad (1)$$



$$\longrightarrow (C_2H_5)_3EOOOC_2H_5 \qquad (2)$$



$$(C_2H_5)_3EO - O - O \longrightarrow (C_2H_5)_3EOOH + CH_3CH(O) \qquad (3)$$

A quantum-chemical investigation of the reaction of ozone with SiH_4 has been carried out (25). The most energetically advantageous directions of attack of the ozone molecule on SiH_4 are at the Si atom and grouped near the C_2 symmetry axis of SiH_4 with orientation of the ozone molecule towards SiH_4 by the terminal atoms. The attack causes (without activation) formation of a labile intermediate complex of donor-acceptor type (the donor is the ozone molecule; electron transfer 0.1 e). The estimated value of the heat of formation of the complex is 20-30 kcal/mol. The complex which has a low activation barrier rearranges into the trioxide $H_3SiOOOH$.

Organobielement compounds (12,26) interact with ozone through the element-element bond to form hexaalkyl- (12) or hexaaryldielement oxanes (26)

$$(C_6H_5)_3PbPb(C_6H_5)_3 + O_3 \longrightarrow (C_6H_5)_3PbOPb(C_6H_5)_3 + O_2 \qquad (4)$$

The authors (26) presume that at low temperature (-100°C) the organobielement compounds react with ozone to form intermediate trioxides

$$(C_2H_5)_3SnSn(C_2H_5)_3 + O_3 \longrightarrow (C_2H_5)_3SnOOOSn(C_2H_5)_3 \qquad (5)$$

which are further consumed according to the reaction:

$$(C_2H_5)_3SnOOOSn(C_2H_5)_3 + (C_2H_5)_3SnSn(C_2H_5)_3 \longrightarrow$$

$$(C_2H_5)_3SnOOSn(C_2H_5)_3 + (C_2H_5)_3SnOSn(C_2H_5)_3 \qquad (6)$$

When the temperature rises the organoelement trioxide decomposes according to the equation (27):

$$(C_2H_5)_3SnOOOSn(C_2H_5)_3 \longrightarrow (C_2H_5)_3SnOSn(C_2H_5)_3 + O_2 \qquad (7)$$

Interaction of ozone with organoelement compounds having several element-element bonds also occurs mainly through these bonds. Thus it has been shown (28) that oxidation of octa-tert-butyltetrastannocyclobutane requires 4 moles of ozone. The stoichiometry of the reaction corresponds to the following equation:

$$(\text{tert-}C_4H_9)_8Sn_4 + 4O_3 \longrightarrow 4(\text{tert-}C_4H_9)_2SnO + 4O_2 \qquad (8)$$

The above stated data have been basically generalized (29-31). The results of investigations of the mechanism and kinetics of reactions of organoelement compounds with ozone, the most successfully studied in recent years, have been systematized and discussed in this review.

MECHANISM OF OZONIZATION OF ORGANOELEMENT COMPOUNDS

The mechanism of oxidation of organoelement compounds by ozone has been suggested on the basis of experimental data obtained from the ozonization of a comparatively small number of compounds (14,30), in which an ethyl radical played the role of the organic fragment. One of the stages of the supposed mechanism is a stage (3) of transformation of the proposed intermediate trioxide, occuring with migration of the α-hydrogen atom (relative to the OEC heteroatom) of the organic radical to the oxygen atom to form a carbonyl compound and an organoelement hydroperoxide (30). In this connection the study of ozonization of such compounds, of which the organic radical has no α-hydrogen atoms is of interest. For this purpose ozonization of dichloro- and dimethyl(ditert-butyl)stannanes has been investigated in CCl_4 at 0°C (32). It has been established that the organoelement compounds studied react readily with ozone, acetone and tert-butyl alcohol being identified as organic reaction products. Ditert-butylstannane dichloride reacts with ozone with a markedly lesser rate in comparison with dimethyl(ditert-butyl)stannane. The stoichiometry of ditert-butylstannane dichloride ozonization is close to two. When the conversion degree is small ($<20\%$), 1 mole of acetone and about 0.1 mole of tert-butyl alcohol form per mole of the initial substance. The main organotin product of ditertbutylstannane ozonization is a white microcrystalline powder, with a composition $C_2H_6O_4SnCl_2$, containing active oxygen sparingly soluble in hydrocarbons and highly soluble in methanol.

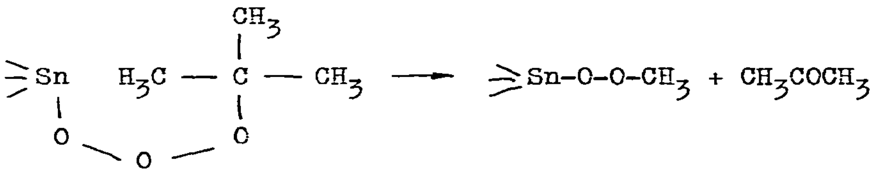
Dimethyl(ditert-butyl)stannane interacts with ozone in a 1:1 ratio to give up to 60% conversion of the initial compound. As a result about 1 mole of acetone and a much smaller quantity (about 0.2 moles at conversion degree not more than 40%) of tert-butyl alcohol form per mole of the initial compound reacted.

Besides the above-stated compounds the product of incomplete oxidation of dimethyl(ditert-butyl)stannane has been found. A significant quantity of the product of incomplete oxidation of the initial organoelement compound was observed at a practically complete oxidation of initial $(tert\text{-}C_4H_9)_2Sn(CH_3)_2$ according to chromatographic data, indicating consecutive oxidation of Sn-C bonds and a relatively low reactivity of the intermediate compound formed toward ozone in comparison with the initial compound. Further oxidation of the intermediate products by ozone also leads to formation of acetone and tert-butyl alcohol; however, the acetone:alcohol ratio, in this case close to 1:2, differs markedly from the ratio of the same products obtained at low conversion degrees of initial $(tert\text{-}C_4H_9)_2$ $Sn(CH_3)_2$ (1:0.2).

The final organoelement product of dimethyl(ditert-butyl)stannane ozonization was a white powdery sudstance containing traces of active oxygen. IR spectroscopy indicated the presence of Sn-O, O-C and $Sn\text{-}CH_3$ bonds in the product. This product reacts readily with HCl in diethyl ether to form dimethylstannane dichloride.

It should be mentioned that a decrease of the temperature of dimethyl(ditert-butyl)stannane ozonization to -68°C does not result in the formation of a peroxide.

On the basis of the above data (32), and considering the known mechanism of OEC ozonization (14,30), one can assume that the intermediate trioxide under conditions of the hindered migration of the alkyl radical (in comparison with the more mobile α-hydrogen atom) may undergo conversion in two directions: a heterolytic one , associated with a methyl group migration leading to formation of a peroxide product and a ketone:



$$\geqslant Sn\text{-}O\text{-}O\text{-}O\text{-}C(CH_3)_2\text{-}CH_3 \longrightarrow \geqslant Sn\text{-}O\text{-}O\text{-}CH_3 + CH_3COCH_3 \qquad (9)$$

and a homolytic one, followed by cleavage of the C-O bond:

$$\geqslant Sn\text{-}O\text{-}O\text{-}O\text{-}C(CH_3)_3 \longrightarrow \geqslant Sn\text{-}O\text{-}O^{\bullet} + {}^{\bullet}OC(CH_3)_3 \qquad (10)$$

The substituents situated at the heteroatom of the organoelement compound affect the direction of the process significantly. Thus, in the case of dimethyl(ditert-butyl)stannane ozonization the process mainly occurs heterolytically, and in the case of ozonization of its intermediate product the process takes place for the most part homolytically (equation 10).

The further development of the homolytic process may be expressed by the following scheme (32):

$$(CH_3)_3CO^\bullet + SH \longrightarrow (CH_3)_3COH + S^\bullet$$

$$\geqslant Sn{-}O{-}O^\bullet + SH \longrightarrow \geqslant SnOOH + S^\bullet$$

with further decomposition of the hydroperoxide (33):

$$\geqslant Sn{-}O{-}OH \longrightarrow \geqslant SnOH + \tfrac{1}{2}O_2$$

It should be pointed out that the conversion of organoelement hydroperoxides may occur in some other way. For instance, the organoelement hydroperoxide obtained as a result of trialkylchlorostannane ozonization forms a complex with the initial compound (34):

$$R_3SnCl \cdot R_2ClSnOOH \qquad (R = C_2H_5,\ n{-}C_4H_9)$$

This complex decomposes on heating for the most part heterolytically according to the equation (35):

$$(C_2H_5)_3SnCl \cdot (C_2H_5)_2ClSnOOH \longrightarrow (C_2H_5)_2ClSnOSnCl(C_2H_5)_2 + OCHCH_3$$

The low efficiency of initiation (0.04) by this complex of the reaction of methylmethacrylate polymerization (35) is indicative of its partial decomposition into radicals. Unlike the corresponding chlorides, iodine-substituted trialkyl- and dialkylstannanes react with ozone through the tin-iodine bond. Due to the high oxidation potential of ozone (36) iodine oxidizes in this case to form corresponding iodates (37):

$$\geqslant Sn{-}I + 3O_3 \longrightarrow \geqslant SnIO_3 + 3O_2$$

REACTIVITY OF ORGANOELEMENT COMPOUNDS TO OZONE

Influence of the nature of the heteroatom

The kinetics of $(C_2H_5)_4E$ (38-50), $(C_6H_5)_4E$ (51-52) and $(C_2H_5)_3E$-$E(C_2H_5)_3$ (43-46,50,53-57) ozonization, (where E is an element of the silicon subgroup) in CCl_4 in the temperature range of 0-20°C (Table 1) has been investigated. The results of the investigation point to a first order reaction for ozone and a first order reaction for the initial organoelement compound. The dependence of the rate constant k on the temperature of ozonization for all organoelement compounds studied may be satisfactorily expressed by the Arrenius equation.

It should be noted that k values of hexaethyldisiloxane, hexaethyldigermanoxane and hexaethyldistannoxane ozonization (Table 1, compounds IX-XI), which can be chosen as model reaction products of the appropriate organoelement compounds (28), are substantially lower for the most reactive ones toward ozone than the k values for the ozonization of the initial compounds.

TABLE 1

The influence of the nature of the heteroatom on the reactivity of organoelement compounds toward ozone (28,52,53)

No	Compound	k,20°C (l/mol sec)	$\lg k_o$	E (kJ/mol)	α ± 0.01
I	$(C_2H_5)_4Si$	2.4×10^{-2}	4.1	31.8	3.583
II	$(C_2H_5)_4Ge$	1.2×10^{-1}	7.3	46.0	3.574
III	$(C_2H_5)_4Sn$	96	6.7	26.4	3.563
IV	$(C_2H_5)_4Pb$	1300	8.5	29.3	3.559
V	$(C_2H_5)_6Si_2$	0.7	6.5	37.7	3.573
VI	$(C_2H_5)_6Ge_2$	2.1	6.0	31.4	3.567
VII	$(C_2H_5)_6Sn_2$	300	8.0	31.4	3.549
VIII	$(C_2H_5)_6Pb_2$	1650	-	-	3.542
IX	$[(C_2H_5)_3Si]_2O$	1×10^{-2}	-	-	-
X	$[(C_2H_5)_3Ge]_2O$	4×10^{-2}	-	-	-
XI	$[(C_2H_5)_3Sn]_2O$	40	7.1	31.4	-
XII	$(C_6H_5)_4Si$	0.33	6.8	35.1	-
XIII	$(C_6H_5)_4Ge$	0.36	6.3	37.7	-
XIV	$(C_6H_5)_4Sn$	1.82	9.2	50.2	-
XV	$(C_6H_5)_4Pb$	5.90	7.5	37.7	-

Thus, the obtained ozonization rate constants for compounds I–VIII (Table 1) may be considered rather precisely to be ones referring to the primary process.

In the studied series of compounds $(C_2H_5)_4E$, $(C_6H_5)_4E$ and $[(C_2H_5)_3E]_2O$ which are equivalent from the point of view of influence of organic groups, steric hindrances and availability of vacancies in the coordination sphere of the heteroatom, there is a considerable difference in electronegativity values of their heteroatoms. It has been shown (43,45,51,52) that the ozonization k values at 20°C of $(C_2H_5)_4E$, $(C_6H_5)_4E$ and $(C_2H_5)_6E_2$ correlate satisfactorily with the values of the effective electronegativity of the heteroatom in these compounds. The measure of the effective heteroatom electronegativity was expressed by the value of their "stability ratios" (α), which were calculated on the basis of the values of electronegativity obtained following the Gordy system (58):

for $(C_2H_5)_4E$, $\lg k = 709-198.4\alpha$

for $(C_2H_5)_6E_2$, $\lg k = 389-109\alpha$

This result is indicative of a symbatic change of the organoelement compound reactivity toward ozone with changing heteroatom nucleophility. With regard to the mechanism of reaction of ozone with organic derivatives of the elements of the silicon subgroup that has been suggested (14,31,32), the results obtained are indicative of a limitation of the bimolecular reaction of these compounds with ozone by the electrophilic attack on the E-C or E-E bonds by ozone.

The influence of substituents at the heteroatom

a)Full organic derivatives and halogenides of organoelements. Proceeding from the ozonization of some tetraalkyl derivatives of tin in CCl_4 (42) the influence of inductive effect of organic substituents in alkyl derivatives of Group IV elements has been studied. Interaction of these compounds with ozone is of a general second order nature; the temperature dependence may be satisfactorily expressed by the Arrenius equation (Table 2). It has been shown (28) that the obtained k values of ozonization may be referred to the interaction of R_4Sn with ozone with an adequate degree of precision, i.e. the kinetics of ozonization of the initial organotin compounds is not complicated by secondary reactions or by any influence of the products. The comparison of kinetic parameters of the reaction of R_4Sn with ozone (Table 2, compounds II-VII) with the sum of Taft induction constants for the organic fragments (59) demonstrates that the difference in the values of the +I-substituent effect has very little influence upon the reactivity of R_4E toward ozone.

In the case of substitution of ethyl groups in tetraethylstannane (germane) by substituents having strong -I-effects (Br,Cl,OH) the reactivity of the compounds decreases markedly (Table 3) (41,43,46, 49,50,60).

TABLE 2

Influence of the organic radical upon the rate of ozonization of organotin compounds in CCl_4 (32,42) ($[\text{compound}] = 10^{-3} - 10^{-5}$ mol/l , $[O_3] = 10^{-4} - 10^{-7}$ mol/l)

No	Compound	k, 0°C (l/mol sec)	$\lg k_o$	E (kJ/mol)	$-\Sigma\sigma^*$
I	$(CH_3)_4Sn$	$2.8x10^{-2}$	5	34.3	0
II	$(C_2H_5)_4Sn$	46	6.7	26.4	0.40
III	$(n\text{-}C_3H_7)_4Sn$	18	7	30.5	0.46
IV	$(n\text{-}C_4H_9)_4Sn$	17	7	30.1	0.52
V	$(iso\text{-}C_4H_9)_4Sn$	16	7	30.1	0.50
VI	$(n\text{-}C_5H_{11})_4Sn$	16	6.3	26.8	0.65
VII	$(tert\text{-}C_4H_9)_2(CH_3)_2Sn$	4.7	6.1	28.5	0.6

Proceeding from the relationship $\lg k = f(\Sigma\sigma^*)$ (Table 3) the authors (28,60) suggest that in this case at least two effects probably affect the reaction rate. The first is strong inductive effect of the chlorine, bromine or hydroxyl group which favours decrease of electron density on the carbon atoms next to the tin atom, which causes hindrance of electrophilic attack upon the tin-carbon bond by ozone.

TABLE 3
Influence of I-effect of the substituent on the rate of ozonization of organoelement compounds in CCl_4 (60) ($[\text{compound}] = 10^{-2} - 10^{-5}$ mol/l, $[O_3] = 10^{-4} - 10^{-7}$ mol/l)

No	Compound	k,10°C (l/mol sec)	$\lg k_o$	E (kJ/mol)	$\Sigma\sigma^{*50}$
I	$(C_2H_5)_4Ge$	1.2×10^{-1}	7.3	46.0	- 0.40
II	$(C_2H_5)_3GeBr$	1.5×10^{-2}	3	26.4	2.6
III	$(C_2H_5)_4Sn$	96	6.7	26.4	-0.40
IV	$(C_2H_5)_3SnCl$	1.34	5.3	27.6	2.7
V	$(C_2H_5)_2SnCl_2$	6.5×10^{-2}	3.8	27.6	5.7
VI	$(C_2H_5)SnCl_3$	2×10^{-2}	-	-	8.7
VII	$(C_2H_5)_3SnCH$	3	-	-	1.35
VIII	$(C_2H_5)_3SnBr$	1.6	-	-	2.6

The second one is d_π-p_π- conjugation of p-electrons of the chlorine with vacant d-orbitals of tin. This effect is the reverse of the inductive one, and it favours the electrophilic attack of ozone on the tin-carbon bond. It should be noted that the presence of d_π-p_π-conjugation in the silicon compounds is convincingly supported by independent physical methods (61).

b)<u>Organosilanes.</u> It has been noted (22,62) that interaction of organosilanes with ozone may be described by a kinetic equation of the second order type. For the ozonization of monohydrosilanes (63) the existence of an isotopic effect has been established, and on the basis of this fact the conclusion about participation of the $\geqslant$Si-H bond in the rate limiting stage of the process has been drawn.

Relative constants of the ozonization rate have been correlated with stretching vibration frequency of the valent ν Si-H bond or with Hammet and Taft inductive constants for the group of silanes (22,62,64,65). These correlations were established proceeding from the assumption of the predominant influence of inductive effects on ν_{Si-H} (66) and on the rate constant for ozonization, but resonance effects were not taken into account, which is not correct (61).

The authors (67-69) have used a sufficiently large series of trisubstituted organosilicon hydrides for the investigation of the influence of substituents at silicon on the rate of interaction of silanes with ozone. The reaction of organosilanes with ozone is a more convenient model for the study of this problem, since the interaction of organosilicon hydrides with ozone is of bimolecular character and proceeds only through the silicon-hydrogen bond. The products of these reactions are the corresponding silanols (12,62-65), which do not take any noticeable part in the reaction, just as organic solvents (hydrocarbons,halogenhydrocarbons et al.).

The k values of ozonization of 16 organosilanes have been found (67) (Table 4). In the case of ozonization of each silane it has been established that all of them interact readily with ozone at room temperature. A 5-10 fold change of initial concentration of ozone or silane does not influence the k values. The reaction stoichiometry is close to 1:1. This indicates that ozone and the initial organosilane participate in a first order reaction. The equation for k reads as follows:

$$k(1/\text{mol sec}) = k_0 \exp(-E/RT)$$

The values of k_0 and E are given in Table 4.

The organosilanes studied may be subdivided into three groups (Table 4). The first group (compounds I-VI) is expected to show just inductive influence of the substituents, the second (compounds VII-IX) an additional $d_\pi - p_\pi$ interaction with the heteroatom. The third group of organosilanes (compounds X-XIV and XV,XVI) is of interest in comparison with the first and the second groups,because the effect of σ,σ-conjugation in methyl groups is much stronger than that of alkyl or aryl radicals (59).

It has been established (67) that in the case of organosilane ozonization the dependence of k values on the sum of inductive constants of the organic substituents may be expressed by the Hammet-Taft equation ($\lg k = \rho \sum \sigma^* + \text{const}$), which is illustrated by Fig.1. In the case of the first group of organosilanes this equation at 20°C reads as follows:

$$\lg k = -0.696 \sum \sigma^* + 1.7114 \qquad (11)$$

It should be pointed out that the ratio of the sensitivity of the organosilane reactivity (i.e. slope ρ) in the reaction of interest

TABLE 4

Influence of $\Sigma\sigma^*$ substituents on the rate constant of silane ozonization in CCl_4 at 20°C (67)

No	Silanes	$\Sigma\sigma^*$	k_{exp}	k_{calc}	$\Delta \lg k$	E (kJ/mol)	$10^{-7}k_o$ (1/mol s)
I	$(C_5H_{11})_3SiH$	-0.486	107	-	-	32.2	6.3
II	$(C_4H_9)_3SiH$	-0.390	100	-	-	31.8	5
III	$(C_3H_7)_3SiH$	-0.345	94.5	-	-	32.2	4
IV	$(C_2H_5)_3SiH$	-0.300	80	-	-	33.5	6.3
V	$(C_2H_5)(C_6H_5CH_2)_2SiH$	0.330	30	-	-	-	-
VI	$(C_6H_5CH_2)_3SiH$	0.645	18.5	-	-	38.1	10
VII	$(C_2H_5)_2(C_6H_5)SiH$	0.400	53	27.1	0.29	28.5	0.63
VIII	$(C_2H_5)(C_6H_5)_2SiH$	1.100	40	8.8	0.65	33.9	4
IX	$(C_6H_5)_3SiH$	1.800	30.5	2.9	1.03	42.7	100
X	$(CH_3)(C_5H_{11})_2SiH$	-0.324	63	86.5	-0.13	31.4	2
XI	$(CH_3)(C_4H_9)_2SiH$	-0.260	60	78.05	-0.11	31.4	2
XII	$(CH_3)(C_3H_7)_2SiH$	-0.230	56	74.4	-0.12	27.2	0.31
XIII	$(CH_3)(C_2H_5)_2SiH$	-0.200	50.5	70.9	-0.15	31.8	2
XIV	$(CH_3)(C_6H_5CH_2)_2SiH$	0.430	21.5	25.8	-0.08	33.5	2
XV	$(CH_3)(C_6H_5)_2SiH$	1.200	29.5	7.5	0.60	29.7	0.5
XVI	$(CH_3)_2(C_6H_5)SiH$	0.600	35	19.7	0.25	33.5	2.5

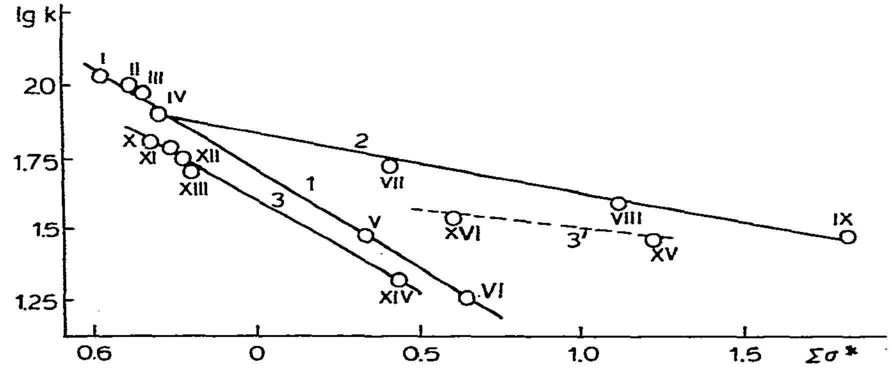


Fig.1. Dependence of lg k on $\Sigma\sigma^*$ for reaction of ozone with organosilanes in CCl_4 at 20°C; straight lines 1,2,3 and 3^* are for the silanes of group 1,2 and 3, respectively.

to the value of $\Sigma\sigma^*$ is practically independent of the temperature (Table 5). The negative value of ρ confirms the proposed mechanism of the simple reaction of organic compounds of Group IV ele-

TABLE 5
The ρ values at different ozonization temperatures of group one organosilanes in CCl_4 (67)

t (°C)	ρ	r
20	-0.696	0.998
15	-0.735	0.980
10	-0.787	0.996
5	-0.672	0.995
0	-0.762	0.995

ments with ozone as a consecutive coordination of ozone to the heteroatom of the organoelement compound followed by electrophilic attack on the heteroatom-carbon bond or the heteroatom-hydrogen by ozone (depending on the nature of organoelement compound). Proceeding from this idea, the reactivity of compounds differing from each other only in the total inductive substituent effect towards ozone should increase with decreasing $\Sigma\sigma^*$ value. The experimental data obtained (67) correspond quantitatively to this relationship.

The dependence of lg k on $\Sigma\sigma^*$ for organosilanes of the second and third groups cannot be expressed by the equation 11 as seen in Fig.1. In this case the k values of the ozonization of organosilanes calculated from equation 11 in accordance with the values of organic substituents of these compounds ($k_{calc.}$) are lower than those found experimentally ($k_{exp.}$) for organosilanes of the second group and larger for the third group of organosilanes (Table 4, compounds X-XIV). This fact, observed with organosilanes of the second group, was explained (67) by the effect of d_π-p_π interaction of the phenyl fragments with silicon, which is opposite to the negative inductive effect of this group. As for the silanes of the third group difference may be explained by σ,σ-conjugation of the methyl group.

The assignment of the differences between the values of $k_{exp.}$ and $k_{calc.}$ for the second group of organosilanes only to the effect of d_π-p_π interaction is supported by the linear relationship (Fig.2) between $\Delta \lg k = \lg k_{exp.} - \lg k_{calc.}$ for compounds VII-IX (Table 4) and the values of $\Delta\nu_{Si-H}$ taken from the literature (70) ($\Delta\nu_{Si-H}$ denotes the contribution to the change of the stretching vibration frequency of the Si-H bond occurring due to d_π-p_π interaction between silicon and phenyl substituents.

Quantitative comparison of the contributions of σ,σ-conjugation to the reactivity of the third group of organosilanes (compounds X-XIV) have not been carried out because of the very small differen-

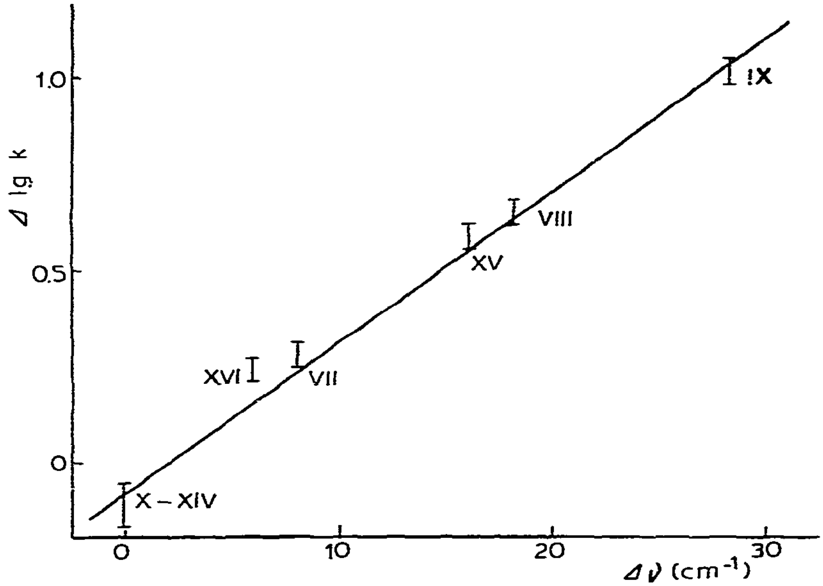


Fig.2. Relationship between $\Delta \lg k$ and $\Delta\nu$ for organosilanes.

cies in $\Delta\nu_{Si-H}$ values for these compounds (61). However "the point" in Fig.2, corresponding to these organosilanes with "unresolved" values of $\Delta\nu_{Si-H}$ falls satisfactorily on the common straight line.

The additivity of the influence of d_π-p_π interaction effects and σ,σ-conjugation on organosilane reactivity towards ozone is supported by a good agreement of the obtained linear relationship between $\Delta \lg k$ and $\Delta\nu_{Si-H}$ (Fig.2) with analogous experimental data for methyl(diphenyl)silane and dimethyl(phenyl)silane (Table 4, compounds XV and XVI), for which the $\Delta\nu$ values have been also taken from literature (61,70).

The comparison of ozonization rate constants of a number of organosilicon and organotin compounds with the electron density dis-

TABLE 6
The results of the calculation of the charge and the index τ_c/β of the reactivity of some organotin compounds (here and below the charge quantities are given in terms of the electron charge (48,49))

Compound	q_{Sn}	q_C	τ_c/β	Compound	q_{Sn}	q_C	τ_c/β
$(C_2H_5)SnCl_3$	0.78	-0.05	4.05	$(C_2H_5)_3SnCl$	0.68	-0.16	4.16
$(C_2H_5)_2SnCl_2$	0.73	-0.11	4.11	$(C_2H_5)_4Sn^*$	0.63	-0.21	4.21

* For $(n\text{-}C_3H_7)_4Sn$, $(n\text{-}C_4H_9)_4Sn$, $(n\text{-}C_5H_{11})_4Sn$, $(iso\text{-}C_4H_9)_4Sn$ the values of q_{Sn}, q_C and τ_c/β are the same as those for $(C_2H_5)_4Sn$.

tribution in these compounds results in very interesting conclusions (48,49) (Table 6). For all the calculated compounds the tin atom charge has the highest positive value, whereas the charge on the carbon atoms next to the heteroatom has the highest negative value in comparison with other carbon atoms of the same molecule, and consequently τ_c/β has the highest positive value. The comparison of the calculated values of the reaction center charges of the organoelement compounds with the values of relative ozonization rate constants of these compounds (k/k_0, where k_0 is the ozonization rate constant of the tetraethyltin, see Table 5) leads to derivation of a semilogarithmic relationship which is completely linear (Fig.3). In this case ratio k/k_0 increases with increasing negative charge on the carbon atom of the reaction center. These results agree with the above-mentioned heterolytical mechanism of organoelement compound ozonization. The deviation from linearity is likely associated with d_π-p_π interaction of the chlorine atom with the tin atom (which has been neglected), because such interaction results in increase of negative charge on the carbon atom.

Analogous calculation of electron density distribution for a number of silanes (methyl(diethyl)silane, methyl(di-n-propyl)silane, me-

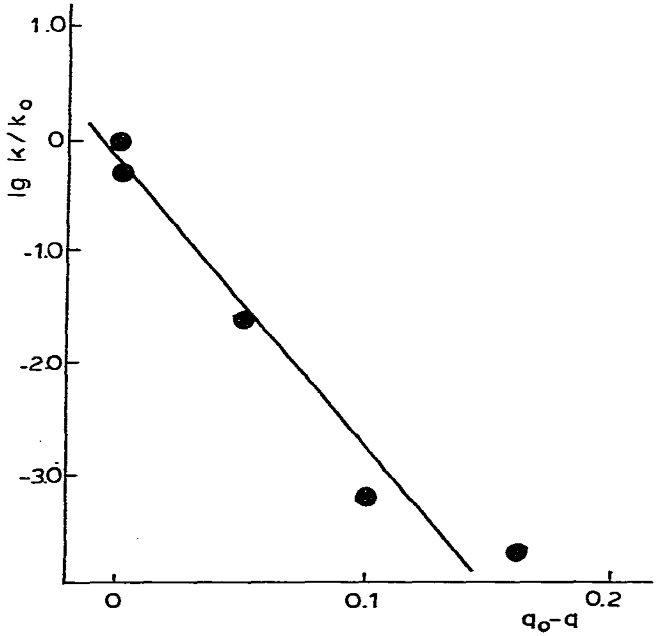


Fig.3. Dependence of the logarithm of relative rate of ozonization for organotin compounds on the change of charge of the reaction center.

thyl(di-n-butyl)silane, methyl(di-n-amyl)silane, triethylsilane, tri-n-propylsilane, tri-n-butylsilane (58)) gives practically equal charge densities on the atoms of silicon (q_{Si} = 0.33), hydrogen ($q_{H(Si)}$ = -0.15 - -0.16) and also on carbon at silicon ($q_{C(Si)}$ =-0.07- - 0.09). This result points to a disadvantage of the empirical calculation (Del Re method) employed by the authors (48,49), which did not allow in case of silanes resilution of the differencies in their electronic structure. However, the high electron density on hydrogen in comparison with the carbon atom (at silicon) is of interest. The latter agrees with the fact that in the case of silane ozonization the attack of coordinated ozone is directed to the silicon-hydrogen bond, but not to the silicon-carbon bond (11,12).

Influence of non-specific solvation. The influence of non-specific solvation on the reactivity of organic derivatives of the silicon subgroup elements toward ozone has been studied in a number of works (47,51,52,55-57,71). In reference (57) two organosilanes (tribenzylsilane and triethylsilane) and also two organobielement derivatives (hexaethyldisilane and hexaethyldigermane) were chosen as the object of investigation. In each of these pairs the compouds differ sufficiently in their reactivity towards ozone (See part II). CCl_4 and 1,1,2,2-tetrachlorethane were chosen as solvents having comparatively small values of dielectric permeability (ε) and no functional groups, which would provide for specific solvation of the compounds under investigation.

In the course of the study it was established (57) that at 25°C the k values of ozonization of compounds depend on ε of the medium; in the case of a mixed solvent the value of ε was calculated from equation

$$\lg \varepsilon = N_1 \lg \varepsilon_1 + N_2 \lg \varepsilon_2,$$

where N_1 and ε_1 denote the mole fraction and dielectric permeability of the mixed solvent component, respectively. k may be expressed by the Kirkwood equation:

$$\lg k = A + B(\varepsilon - 1)/(2\varepsilon + 1), \qquad (12)$$

the coefficients of which have the following values:

Compound	Triethylsilane	Tribenzylsilane	Hexaethyldigermane	Hexaethyldisilane
A	1.72	1.24	-0.45	-0.63
B	1.15	1.11	3.87	2.32

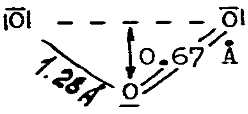
(I > r > 0.99 from the least squares method).

The data obtained testify to the fact that non-specific solvation of organoelement compounds and ozone increases their reactivity in the course of interaction. In this case each pair of the compounds has the higher sensitivity towards non-specific solvation effects the higher is their reactivity toward ozone. Such a result agrees with the heterolytic mechanism of the ozonization of organic derivatives of the silicon subgroup elements (14,31,32).

Valence electrons of the heteroatom in the activated "compound-ozone" complex are, evidently, in the sp^3d state, that is influenced by ozone coordination to the tetravalent silicon atom (or germanium). Such hybridization seems to be unlikely in the case of solvation of the studied compounds by a solvent in the CCl_4-1,1,2,2,-tetrachlorethane system. Hence one may not take into account "diffusion pair" formation, when discussing the medium effect, and should explain the data obtained by a higher polarity of activated "compound-ozone" complex in comparison with the initial reagent. Thus, the angular coefficient (B) in equation 12 is related to the dipole moment and effective radius of the activated complex ($\mu^{\#}$, $r^{\ddagger}$) and also to the corresponding values for the initial reagents (μ_1, r_1 for the organoelement compound, μ_2, r_2 for ozone) by the well-known relationship (72):

$$B = - \frac{1}{2{,}3kT}\left(\frac{\mu_1^2}{r_1^3} + \frac{\mu_2^2}{r_2^3} - \frac{\mu^{*2}}{r^{*2}}\right) \qquad (13)$$

Equation 13 has been used for the estimation of dipole moment values of the activated compound-ozone complex and of relative charge values (q) on the organoelement compound heteroatom. When carrying out the calculations the authors assumed $\mu_2 = 0.53$ D (73) and when choosing r_2 and r^* proceeding from the assumption that the heterolytic mechanism of organosilane interaction with ozone results in formation of an activated complex of ozone of zwitterionic form, where the nucleophilic center is bound with the compound heteroatom by a coordinative bond. In this connection $r^{\#}$ was assumed to be $r_{Si-O} = 1.64$ Å (74) for silanes and hexaethyldisilane and $r_{Ge-O} = 1.85$ Å (74) for hexaethyldigermane, and for r_2 the values of 1.28 and 0.67Å were assumed taking into account various spatial arrangements of the ozone molecule toward the attacked bond (75).



For triethylsilane and tribenzylsilane $r_1 = 1.47$ Å (75), and μ_1 =

1.54 D and 1.31 D, respectively. For hexaethyldisilane and hexaethyldigermane r_1 was assumed to be equal to 2.34 Å and 2.41 Å (75) and the values of μ_1 were equated to zero (74). Proceeding from the afore-mentioned data, $\mu^{\neq}$ and q for activated "compound-ozone" complex in the case of ozonization of the organoelement compounds studied have been calculated. It can be seen from Table 7 that the value of q at r_2 = 1.28 Å correlates satisfactorily with the q value obtained by other investigators on the basis of spectroscopic data (76). This fact allows one to conclude (57) in the ozonization of these compounds the value of r_2 = 1.28 Å is more probable than r_2 = 0.67 Å. Hence it is preferable to present the dipolar ozone molecule reacting with the organoelement compound as a zwitterionic form, in which the nucleophilic center is localized mainly on one oxygen atom.

An analogous investigation has been carried out using different solvents (56) which differ significantly in their nature and values of ε : carbon tetrachloride (2.23), chloroform (4.72), 1,2-dichlorethane (10.16), 1,1,2,2-tetrachlorethane (8.03), propionic acid (3.2), acetic acid (6.2) and acetic anhydride (20.5). The authors chose to investigate the following compounds: methyl(di-n-propyl)silane,tribenzylsilane, hexaethyldisilane and hexaethyldigermane.

TABLE 7

Calculation of $\mu^{\neq}$ and q for the ozonization of organoelement compounds at 25°C (57) (the values of q are expressed in terms of an electron charge)

Compound	$\mu^{\neq}$	q	$\mu^{\neq}$	q	q (76)
	r_2=1.28 Å		r_2=0.67 Å		
$(C_2H_5)_3SiH$	2.08	0.26	2.84	0.36	0.22
$(C_6H_5CH_2)_3SiH$	1.85	0.24	2.55	0.32	0.18
$(C_2H_5)_6Ge_2$	1.78	0.20	2.87	0.32	-
$(C_2H_5)_6Si_2$	1.25	0.16	2.26	0.29	-

The investigation allowed them to establish that the dependence of k of ozonization of these compounds on ε of the solvent may be also expressed by the Kirkwood equation, which is indicative of non-specific solvation of substrates in the solvents employed.

The quantitatively established dependences (6) have the following coefficients at 0°C (56):

Compound	Methyl(di-n-propyl)-silane	Tribenzyl-silane	Hexaethyl-digermane	Hexaethyl-disilane
A	0.91	0.44	-0.60	-1.09
B	1.88	1.35	2.50	1.45

(from least squares method, $0.90<r<0.99$).

The nature of the established dependences agrees with the results of the investigation carried out in binary mixtures like carbon tetrachloride-1,1,2,2-tetrachlorethane. Using equation 13 and the same initial data for $r^{\#}$, r_1, r_2,μ_1 and μ_2 as in the previous case, the values of $\mu^{\#}$ and q for the activated compound-ozone complex have been calculated. The calculated values of $\mu^{\#}$ and q agree satisfactorily with the results obtained in case of binary mixtures employed as solvents (Table 8). The reactivity of $(C_6H_5)_4E$ toward ozone, as in the case of the alkyl analogs, increases with increasing dielectric permeability of the medium (51,52).

TABLE 8

$\mu^{\#}$ and q values of activated compound-ozone complexes at 0°C (r_2=1.28 Å) (56)

Compound	$\mu^{\#}$	q	Compound	$\mu^{\#}$	q
$(CH_3)(C_3H_7)_2SiH$	2.24	0.32	$(C_2H_5)_6Si_2$	1.08	0.14
$(C_6H_5CH_2)_3SiH$	2.10	0.30	$(C_2H_5)_6Ge_2$	1.49	0.20

The sensitivity of interaction of $(C_6H_5)_4E$ with ozone to the medium polarity is symbatic to their reactivity and is in the same order as the analogous interrelations of the rate constants of ozone interaction with alkyl derivatives of the above-mentioned elements (56,57).

It should be noted that the increase of the rate constant of ozonization with increasing ε is also observed (55) at other temperatures (Fig.4); however, the value of the angular coefficient B in the Kirkwood equation (20) decreases with temperature increase. Since B characterizes the transition state polarity, and the higher the polar molecule solvation the higher is their polarity, the decrease of coefficient B (Fig.4) may be explained by partial desolvation of the activated complex at higher temperatures.

It has been established (55) that kinetic and activation parameters of ozonization of the organoelement compounds studied change significantly depending on ε values of the solvent. However, for each compound in all the solvents studied their $\Delta G^{\#}$ values are very

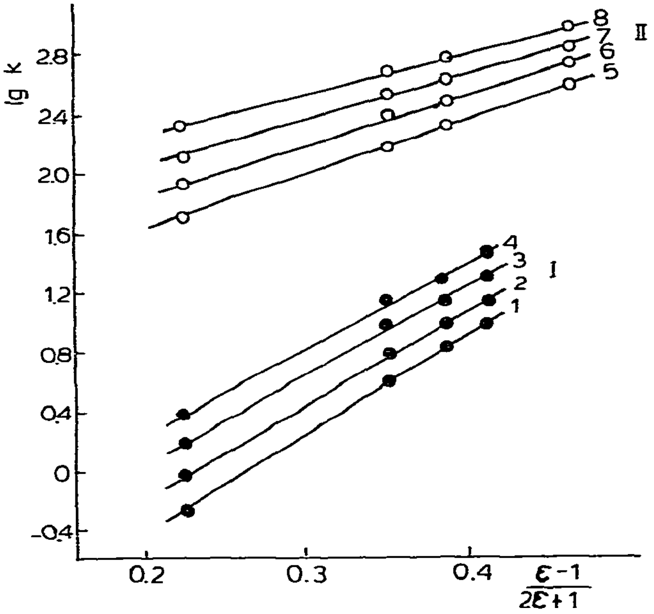


Fig.4. Dependence of ozonization rate constant of hexaethyldisilane (1-4) and methyl(di-n-propyl)silane (5-8) upon dielectric permeability of the medium. 1-4 and 5-8 refer to 20,30,40 and 50°C, respectively.

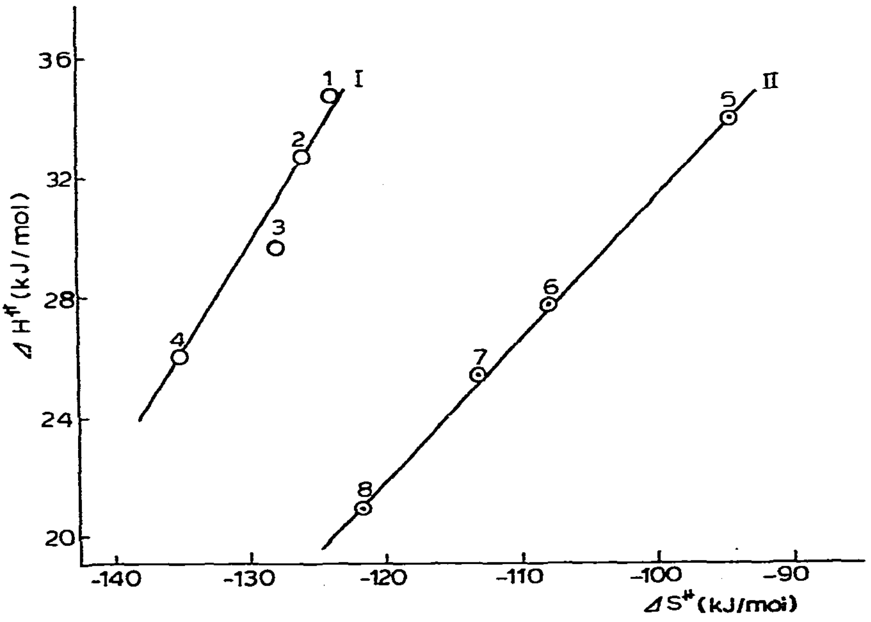


Fig.5. Relationship between $\Delta H^{\#}$ and $\Delta S^{\#}$ for ozonization of hexaethyldisilane (I) and methyl(di-n-propyl)silane (II).

close to each other. Similar values of $\Delta G^{\#}$, as well as the linear relationship $\Delta H^{\#}=f(\Delta S^{\#})$ (Fig.5), are indicative of a compensation effect.

The analytical terms of dependence of $\Delta H^{\#}$ on $\Delta S^{\#}$ calculated from the data of Fig.5 read as follows:

$\Delta H^{\#} = 0.712\Delta S^{\#} + 122.3$ for $(C_2H_5)_3SiSi(C_2H_5)_3$,

$\Delta H^{\#} = 0.454\Delta S^{\#} + 76.6$ for $CH_3(n\text{-}C_3H_7)_2SiH$
(correlation coefficient $r > 0.96$).

The presence of compensation effect is confirmed by the method described (77,78). The values of the isokinetic temperature (T_i) for hexaethyldisilane (673°K) and for methyl(di-n-propyl)silane (467°K) have been calculated from the following equation:

$T_i = [T_1T_2(b-1)]/(bT_1-T_2)$,

where $T_1 > T_2$; b is the tangent of the slope angle of the straight lines in the coordinates of $\lg k_{T_1} = f(\lg k_{T_2})$ (Fig.5b), which agrees satisfactorily with the corresponding values (670°K and 460°K) found by the cross-point of Arrenius straight lines (Fig.5c).

TABLE 9

Kinetic and activation parameters for the ozonization of hexaethyldisilane and methyl(di-n-propyl)silane[*] (55)

No	Compound	Solvent	ε	k, 20°C, (l·mol⁻¹ s⁻¹)	E (kJ/mol)	lg A	$\Delta G^{\#}$ (kJ/mol)
1.	$(C_2H_5)_3SiSi(C_2H_5)_3$	CCl_4	2.23	1.34	37.6	6.7	71.1
2.		CCl_4+TCE[**]	4.57	4.8	35.4	7.0	69.4
3.		CH_3COOH	6.2	7.3	32.0	6.5	67.3
4.		TCE	8.8	11.4	28.4	6.2	65.6
5.	$CH_3(C_3H_7)_2SiH$	CCl_4	2.23	65	36.4	8.3	61.4
6.		CCl_4+TCE	4.57	191	30.1	7.6	58.9
7.		CH_3COOH	6.2	263	27.8	7.3	58.5
8.		$(CH_3CO)_2O$	20.5	450	23.4	6.8	56.9

[*] The numbers of Fig.5 correspond to ordinal numbers of the systems presented in Table 9.

[**] 1,1,2,2-Tetrachlorethane.

From the point of view of the two series of uniform reactions studied, the compensation effect indicates (79) that the solvent nature does not influence the reaction mechanism.

The considerable difference observed in the values of the isokinetic temperature for hexaethyldisilane and methyl(di-n-propyl)silane (670 and 460°K, respectively) is of obvious interest. From the point of view of the Barkley-Butler empiric rule (80) the difference in the values of T_i is indicative of a more energetic interaction between methyl(di-n-propyl)silane and the solvent in comparison with that of hexaethyldisilane, in which case dispersion forces dominate. An indirect support of this conclusion is presented by the higher dipole moment of methyl(di-n-propyl)silane (1.54 D) in comparison with that of hexaethyldisilane (0).

The interaction of organoelement compounds with ozone in the gas phase (47,81) follows kinetic rules, analogous to those for liquid phase. The reaction products do not influence much the rate of gas-phase oxidation of organoelement compounds by ozone. The data from an investigation (81) of the kinetics of gas-phase oxidation of organoelement compound mixtures indicate a lack of influence of the reaction products on the kinetics of the process. It has been established that the oxidation rate of organoelement compound mixtures by ozone consists of an additive sum of the rates for each compound until a certain limit of the reaction is reached. Hence, the kinetic characteristics of gas-phase oxidation of organoelement compounds by ozone may be referred directly to those of the bimolecular reactions of these compounds with ozone.

The dependence of the obtained values of the rate constant (k, $l\cdot mol^{-1}sec^{-1}$) of the gas-phase oxidation on the temperature may be expressed satisfactorily by the Arrenius equation, and the full form of these values is the following (81):

$k=10^{5.4}\exp\{-5800/RT\}$ for $(C_2H_5)_3SiH$
$k-10^{3.6}\exp\{-3700/RT\}$ for $CH_3(n\text{-}C_3H_7)_2SiH$
$k=10^{4.9}\exp\{-8600/RT\}$ for $(CH_3)_4Sn$
$k=10^{2.8}\exp\{-3200/RT\}$ for $(CH_3)_4Pb$
$k=10^{3.6}\exp\{-4000/RT\}$ for $CH_3(C_2H_5)_2SiH$

The rate constant of organoelement compound interaction with ozone in the gas phase is much lower than the rate constant of this reaction in an organic solvent, e.g. CCl_4 (Table 10).

The increases of the values of the bimolecular reaction rate constant in going from the gas phase to the liquid one are similar and are the consequence of the appearance of cohesion interaction when the substance transfers from the gas state to the liquid one (80). In accordance with this the experimental value of the rate constant of the gas-phase reaction of organoelement compounds with ozone (k_g) may be lower compared with the value of the rate constant found by extrapolation of the Kirkwood dependence of k_1 on $\frac{\varepsilon-1}{2\varepsilon+1}$ to the value of zero, corresponding to the value of $\frac{\varepsilon-1}{2\varepsilon+1}$ for gas phase (Fig.6).

TABLE 10
The values of the rate constants of reactions of some organoelement compounds with ozone in the gas phase and in CCl_4 at 20°C (k_g and k_1 ($l \cdot mol^{-1} sec^{-1}$), respectively (81))

Compound	k_g	k_1
$(CH_3)_4Sn$	2.2×10^{-2}	7.6×10^{-2}
$(CH_3)(C_3H_7)_2SiH$	17.3	57
$(CH_3)(C_2H_5)_2SiH$	3.9	50.5
$(C_2H_5)_3SiH$	11.1	80
$(CH_3)_4Pb$	2.86	25

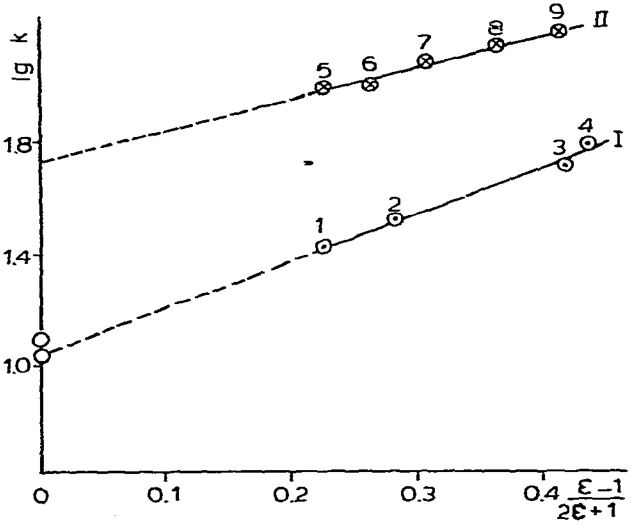


Fig.6. Dependence of reactivity of methyl(di-n-propyl)silane at 0°C (I) and triethylsilane at 25°C (II) toward ozone on the medium dielectric permeability: 1,5-CCl_4; 2-CH_3CH_2COOH; 3,9-1,1,2,2-tetrachlorethane (TCE); 4-1,2-dichlorethane; 6-CCl_4 + TCE(14%); 7-CCl_4 + + TCE(35%); 8-CCl_4 + TCE(58%).

Influence of specific solvation. The influence of specific solvation on ozonization of organoelement compounds has been investigated for the first time (82) while studying the reaction of triethylstannane chloride with ozone in CCl_4 in presence of dimethylformamide

(DMFA), which solvates specifically the initial compound. It has been established (82) that the course of the reaction practically does not change in the presence of DMFA. However, k in this case depends significantly on the concentration of DMFA (Table 11).

TABLE 11
Influence of DMFA additives ($N=[D_0]/[A_0]$) on the rate of oxidation of triethylstannane chloride by ozone in CCl_4 ($[O_3]=2\times10^{-4}$ mol/l, c=concentration of Et_3SnCl in mol/l) (82)

N	k (l/mol sec)	N	k (l/mol sec)	N	k (l/mol sec)
-17°C	$c=4.23\times10^{-3}$	0°C	$c=2.82\times10^{-3}$	20°C	$c=1.41\times10^{-3}$
0	0.110	0	0.42	0	1.34
5.2	0.184	5.2	0.53	2.7	1.38
8.7	0.250	7.0	0.62	5.4	1.44
12.2	0.300	13.1	0.76	8.0	1.62
15.2	0.320	18.3	0.91	13.5	1.50
20.8	0.380	23.5	0.93	20.0	1.39
29.6	0.390	31.3	0.93	27.0	2.18
		39.2	0.93	40.0	2.17

The moderate kinetic effect found (82) may be explained by a specific solvation of triethylstannane chloride in DMFA by analogy with well-known complexes of alkylstannane halogenides with many ligands (amides, ketones etc. (83)). The authors (82) carried out calorimetric and spectroscopic measurements to check this assumption. Calorimetric measurements of thermal effects occuring as a result of mixing triethyltin chloride with DMFA in the 1:2 proportion, accomplished at 20°C, gave a value of the complexing enthalpy equal to -5±0.5 kcal/mol. The IR spectra of triethyltin chloride mixed with DMFA in the proportion 1:20 indicated a considerable shift of the stretching vibration frequency of the C=O bond ($\nu_{C=O}$) toward lower frequencies (18 cm^{-1} lower) in comparison with $\nu_{C=O}$ of pure DMFA (1680 cm^{-1}) which was assumed as evidence of complexing of triethylstannane chloride and DMFA via the unshared electron pair of the carbonyl oxygen of the amide molecule. Evidence for specific solvation of triethylstannane chloride in DMFA was also obtained (82) in the course of the analysis of UV spectra of this organoelement compound.

The degree of charge transfer in the complex triethylstannane-DMFA was 5-7% per donor-acceptor bond. The estimation of this value was carried out according to the known correlation (83) of complexing enthalpy with the value of charge transfer. From the data obtained the authors (82) assume that the increase of the reaction rate in case of interaction between triethylstannane chloride and ozone in the presence of DMFA is associated with formation of a complex that is more reactive toward ozone than the initial organoelement compound. On the basis of this assumption the analysis of kinetic measurement results has been carried out. Denoting triethylstannane chloride, DMFA, ozone and reaction products with A, D, C and P, respectively, the scheme of the process may be presented as follows:

$$A + C \xrightarrow{k_1} P$$

$$A + D \underset{k_{-2}^{(1)}}{\overset{k_2^{(1)}}{\rightleftharpoons}} AD \qquad (14_1)$$

$$AD + D \underset{k_{-2}^{(2)}}{\overset{k_2^{(2)}}{\rightleftharpoons}} AD_2 \qquad (14_2)$$

....

$$AD_{n-1} + D \underset{k_{-2}^{(n)}}{\overset{k_2^{(n)}}{\rightleftharpoons}} AD_n \qquad (14_n)$$

$$AD + C \xrightarrow{k_3^{(1)}} P$$

$$AD_2 + C \xrightarrow{k_3^{(2)}} P$$

....

$$AD_n + C \xrightarrow{k_3^{(n)}} P$$

In this case the reaction rate can be expressed by the following equation:

$$W = k_1[A][C] + \sum_{i=1}^{n} k_3^{(i)}[AD_i][C]$$

When the extent of oxidation of triethylstannane chloride is small we have

$$[A] = [A]_o - \sum_{i=1}^{n} [AD_i]$$

$$k_{exp} = \frac{W}{[A]_o[C]} = k_1 + \frac{\sum_{i=1}^{n} k_3^{(i)}[AD_i] - k_1 \sum_{i=1}^{n} [AD_i]}{[A]_o} \qquad (15)$$

We have suggested (82) that the reactivities of the complexes formed according to equations 14_1-14_n should differ significantly and therefore (for the sake of simplification of mathematical treatment) we take into account only the complex of arbitrary composition, AD_n, the most active one toward ozone.

In this connection, in the case of $[D]_o \gg n[AD_n]$ equation 15 will have the following form:

$$k_{exp} = k_1 + (k_3^{(n)} - k_1)\frac{N^n}{N^n + \frac{1}{K[A]_o^n}}, \qquad (16)$$

where $N=[D]_o/[A]_o$, K is the equilibrium constant of the total process, expressed by equations 14_1–14_n, denoting its stages. Having made use of the experimental data (Table 11) the authors (82) used equation 16 to determine the minimum value of the root-mean-square deviation for each temperature studied in the range of n=0.5–3 with steps equal to 0.5 and for optimum values of k, estimated by the value of the root-mean-square deviation of the calculated values from the experimental ones. It appeared that the optimum value of n=2 and the experimental data, obtained at −17°C (Table 11) may be satisfactorily expressed by the following equation:

$$k_{exp} = (k_1 + k_{max} - k_1)\frac{N^2}{N^2 + 70} \qquad (17)$$

(the root-mean-square deviation does not exceed 3%).

The good correlation between the k values of triethylstannane chloride ozonization in the presence of DMFA, found experimentally at −17°C and calculated from equation 17 (Fig.7) confirms the formation Of a 1:2 complex triethylstannane chloride-DMFA.

The influence of electron-donor compounds on the kinetics of ozonization is also observed when triethylchloroplumbane (84-86) is oxidized by ozone in n-heptane and acetone at −78°C. Triphenylphosphine and N,N-dimethylformamide were used as samples of electron-donor compounds, in quantities which practically do not change the medium polarity. It has been established that the kinetics of triethylchloroplumbane interaction with ozone in a wide range of concentrations of ozone and $(C_2H_5)_3PbCl$ (1×10^{-4}–5×10^{-4} mol/l and 6×10^{-4}–3×10^{-3} mol/l, respectively) may be expressed by a first order equation for each of the initial reagents, and in the case of introduction of additives of the electron-donor compounds triphenylphosphine (n-heptane solvent) and N,N-dimethylformamide (DMFA) (acetone solvent) is of a complicated nature as in case of trimethylstannane chloride.

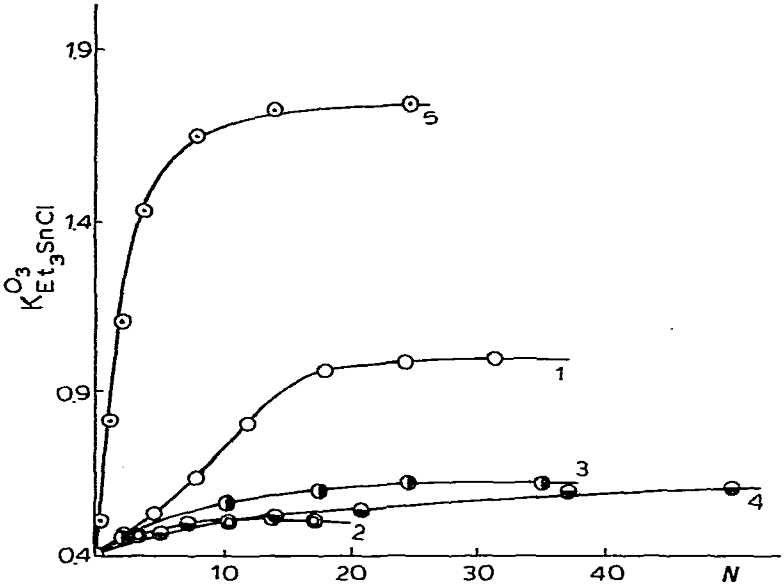


Fig.7. Influence of additives of some organic compounds on the reactivity of triethyltin chloride toward ozone: 1-dimethylformamide, 2-acetophenone, 3-benzophenone, 4-tris(chloroethyl)phosphine, 5-tripropylphosphine oxide (for curves 1 and 5 the dots correspond to experimental values, the solid line is calculated on the basis of equations 17 and 24, respectively).

The kinetic effect mentioned (86) may be due to solvation of the initial organoelement compound or ozone, or by simultaneous solvation of initial reagents by the introduced complexing compound.

The influence of electron-donor and electron-acceptor additives upon ozone solubility has been determined (84-86) in order to learn whether the complexing compounds influence ozone solvation or not. It should be noted in this case that if ozone underwent noticeable specific solvation, it would cause an increase of the ozone solubility coefficient (α) or an additional absorption of ozone on introduction of additive compounds which are difficult to oxidize under the conditions of experiment (continuous bubbling of ozone-oxygen mixture at -78°C) (Table 12).

The data of Table 12 indicate that specific solvation of ozone by the studied compounds practically does not exist. Proceeding from this statement, the authors (84,85) have assumed that the kinetic effect observed is due to the formation of a "organoelement compound-ligand" complex, a more reactive one than the initial triethylchloroplumbane, as occurs in case of triethylchlorostannane ozonization in the presence of ligands (82).

TABLE 12

Influence of additives of complexing compounds (D) on additional absorption of ozone (86)

Solvent	D	t(°C)	$\frac{[D]_o}{[O_3]_o}$	Solubility coefficient of ozone, α
Methylacetate	$(C_2H_5)_2SnCl_2$	-78	200	*
-"-	$(C_2H_5)_3SnCl$	-"-	32	22.6
-"-	-	-"-	0	23.0
n-Heptane	$SnCl_4$	-78	130	*
	$(C_2H_5)_3SnCl$	-"-	8000	*
	$TiCl_4$	-"-	60	*
	N,N-dimethylformamide	-"-	10	*
	acetone	-"-	130	*
	methylacetate	-"-	140	*
	acetophenone	-"-	15	*
	benzophenone	-"-	12	*
CCl_4	acetophenone	0	600	*
	benzophenone	-"-	1000	*
	acetone	-"-	8000	*
	N,N-dimethylformamide	0	600	*

*When adding ligands into the reactor with solvents no additional absorption of ozone was observed.

It is known that triphenylphosphine reacts readily with ozone (87), and the only product of its ozonization at low temperatures is the ozonide of the initial organophosphorus compound, which is stable under these conditions and decomposes at elevated temperatures to release singlet oxygen and to form triphenylphosphine oxide. It should be mentioned that addition of triphenylphosphine oxide did not influence the rate of oxidation of $(C_2H_5)_3PbCl$ by ozone.

The data reported (84,86) suggest that triphenylphosphine ozonide is indeed the catalyst in triethylchloroplumbane ozonization. Mathematical treatment of the kinetic data on ozonization of $(C_2H_5)_3PbCl$ in the presence of dimethylformamide and $(C_6H_5)_3PO_3$ carried out according to the scheme suggested (82) has shown that the reactivity of $(C_2H_5)_3PbCl$ toward ozone at -78°C may be satisfactorily expressed by the following equations :

for $(C_6H_5)_3P$ $$k_{exp} = 0.90 + 1.1\frac{N^2}{N^2 + 270} \qquad (18)$$

for DMFA $$k_{exp} = 0.80 + 0.33\left[3.08 + N - \sqrt{(3.08 + N)^2 - 4N}\right] \qquad (19)$$

(the root-mean-square relative deviation is 2%, Fig.7).

The data (84,86) and equations 18 and 19 give a basis for the conclusion that triethylchloroplumbane forms complexes with diethylformamide and triphenylphosphine ozonide of 1:1 and 1:2 ratios, respectively.

In ref.(87) the nature of the influence of ligand electron-donor properties on their catalytic activity in the reaction of triethyltin chloride with ozone is reported for acetophenone, benzophenone and a number of organophosphorus compounds (D). All compounds D used as ligands are much less reactive than triethyltin chloride toward ozone (Table 13). Just as in case of DMFA (82), on addition of compounds D the ozonization rate constant of the organoelement compound increases, reaching a certain (depending on D) maximum value (Fig.7). Taking into consideration the fact that when studying ozonization of triethyltin chloride both in the presence of compounds D and in the presence of DMFA no change of the reaction mechanism was observed, the above mentioned kinetic effect was interpreted by the authors (88) from the point of view of a specific solvation of the initial organoelement compound by compounds D.

Compounds D show a difference in catalytic effect and, accordingly, a decrease of stretching vibration frequency of C=O (DMFA, acetophenone, benzophenone) or P=O (organophosphorus compounds) bonds in the triethyltin chloride D system is different in comparison to that for individual compounds D. It is known (83) that a decrease of stretching vibration frequency of C=O (or P=O) bonds may be considered a measure of donor ability of compound D toward the initial organoelement compound.

The authors (88) have shown by their experiment with organophosphorus compounds (Fig.8) that the increase in relative catalytic activity of the additive ($\Delta \lg k = \lg k_1 - \lg k_2$, where k_1 and k_2 are rate constants of ozonization of organoelement compound and complex of that compound with D, respectively) correlated satisfactorily with the decrease of vibration frequency of P=O and the sum of Taft inductive constants ($\sum\sigma^*$) of the substituents at phosphorus atom in compounds D.

The results obtained indicate that specific solvation of triethyltin chloride by the organophosphorus compounds employed is in fact

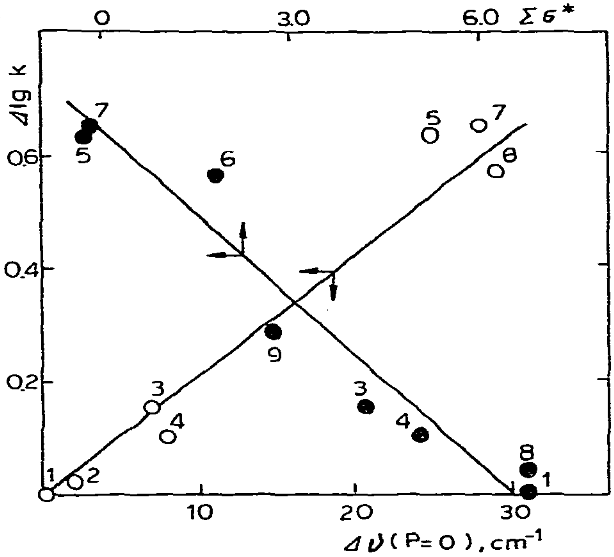


Fig.8. Dependence of ligand catalytic activity ($\Delta \lg k$) on the value of shift of vibration frequency of P=O bond $[\Delta\nu$ (P=O)$]$ and the sum of Taft inductive constants for substituents in organophosphorus compounds (the dot numbering corresponds to Table13).

a donor-acceptor interaction of the organoelement compound and compound D with the participation of the oxygen unshared electron pair of P=O, a fragment of a compound D. The rate of oxidation of organoelement compound by ozone is directly related to the strength of the donor-acceptor interaction. Hence, it is possible to estimate the ligand donor-acceptor ability by its variation.

Specific solvation of organoelement compound A by ligands D may result in the formation of complexes with various compositions (AD_1, AD_2... AD_n...). It has been shown previously (82) that the effective rate constant for the most active complex (AD_n) may be expressed by equation 15, from which one can derive

$$k_{exp} = k_1 + (k_2 - k_1)\frac{[AD_n]}{[A]_0} \qquad (20)$$

The maximum catalytic influence of some organophosphorus compounds (for instance, influence of tri-n-propylphosphine oxide Fig.7, curve 5) in the reaction studied is realized at comparatively low values of $N=[D]_0/[A]_0$, when it is not possible to assume that $[D] \cong [D]_0$. The equilibrium constant of total complexing process

$$A + nD \overset{k_p}{\rightleftharpoons} AD_n \qquad (21)$$

may be expressed by the following equation

$$k_p[A]_o^n = \frac{[AD_n]/[A]_0}{(1-[AD_n]/[A]_o)(N-n[AD_n]/[A]_o^n)} \qquad (22)$$

Analysis of expressions 20 and 22 allows one to determine the composition of the "organoelement compound-ligand" complex, i.e. by finding the value of "n" in the donor molecules in AD_n. Calculation has shown that for tri-n-propylphosphine oxide - one of the most active ligands - n is equal to 1 (88).

TABLE 13

Effective rate constants (k) of ozonization of some organic and organophosphorus compounds in CCl_4 at 0°C ($[O_3]_o$ 1×10^{-4} mol/l) (88)

No	Compound	k(l/mol sec)	$\Sigma\sigma^*_{R_1R_2R_3}$
1.	Triphenylphosphine	3×10^{-2}	7.04 (89)
2.	Tris(chloropropyl)phosphine	$<1\times10^{-3}$	
3.	Tris(chloroethyl)phosphine	$<1\times10^{-3}$	
4.	Tributylphosphine	$<1\times10^{-3}$	5.04 (90)
5.	Tri-n-propylphosphine oxide	$<1\times10^{-3}$	-0.345(90)
6.	Triphenylphosphine oxide	1.3×10^{-3}	1.80 (90)
7.	Tri-n-amylphosphine oxide	1.7×10^{-2}	-0.492(90)
8.	Diethyl ether of methylphosphonic acid	$<1\times10^{-3}$	2.732(89)
9.	Tris(perfluoropropyl)phosphine oxide	$<1\times10^{-3}$	-
10.	Dimethylformamide	7×10^{-3}	-
11.	Benzophenone	1×10^{-2}	-
12.	Acetophenone	1.5×10^{-2}	-
13.	Triethyltin chloride	4.2×10^{-1}	-

It is natural to suppose that the rest of the organophosphorus compounds from the studied series, being similar to each other in composition and having not a stronger catalytic effect than that of tri-n-propylphosphine will also form complexes with composition ratio 1:1.

Thus, expression 20 can be written in the following form:

$$k_{exp} = k_1+\tfrac{1}{2}(k_2^{(n)}-k_1)\left\{1+N+\frac{1}{k_p[A]_o} - \sqrt{(1+N+1/k_p[A]_o)^2-4N}\right\} \qquad (23)$$

and in particular, for tri-n-propylphosphine oxide (87)

$$k_{exp}= 0.42+0.7\left\{2.22+N- \sqrt{(2.22+N)^2-4N}\right\} \qquad (24)$$

(the root-mean-square deviation does not exceed 4%).

The agreement of the experimental data with those calculated from equation 24 is shown in Fig.7.

The spectra of mixtures of OEC and tri-n-propylphosphine oxide with different mole ratios of components at 240 nm have been recorded to check the correctness of the calculations. The presence of a break on the curve (Fig.9) when OEC:ligand = 1:1, confirms the above stated data on formation of complex with such a composition.

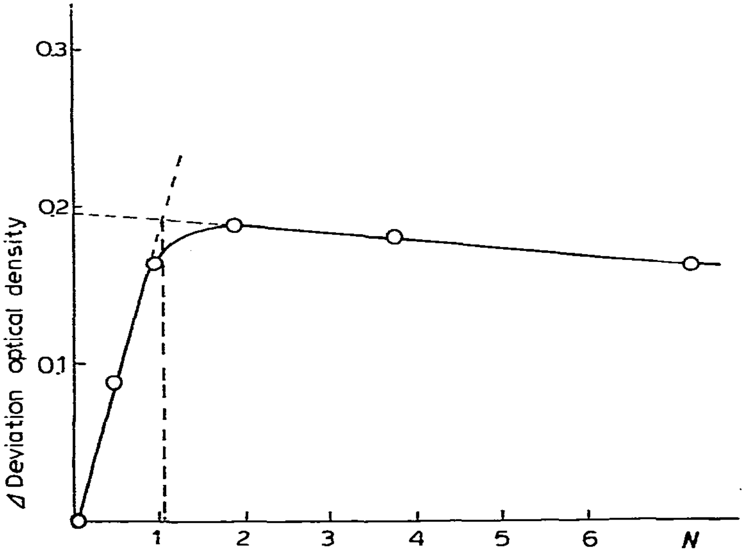


Fig.9. Dependence of the deviation of optical density of $(C_2H_5)_3SnCl$ and $(C_3H_7)_3PO$ mixtures on additive (Δ D) at different values of N.

CONCLUSION

The data summarized on oxidation of organic derivatives of silicon subgroup elements by ozone on the element-carbon bond allows to us present the mechanism of the process as a series of stages consisting of coordination of ozone to heteroatom, formation of an intermediate trioxide followed by its conversion, both heterolytically and homolytically.

The reactivity of organoelement compounds toward ozone is significantly influenced by the heteroatom nature, organic substituents, medium polarity and electron-donor ligands, forming donor-acceptor complexes with the initial organoelement compounds.

The dependence of the catalytic activity of the ligand on their donor ability has been established.

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