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Oxidation by Ozone of Hetero-organic Compounds of the Silicon Subgroup

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The kinetics and the reaction products are surveyed, and the mechanism is discussed. The reactivity of the compounds towards ozone depends on the nature of the heteroatom, the attached substituent, and non-specific and specific solvation. A list of 68 references is included.

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I. INTRODUCTION

The early publications devoted to the action of ozone on hetero-organic compounds[1-3] report only qualitative observations concerned to elucidate oxidisability. Thus Bailey et al.[1] noted that bubbling ozone through vinyltrichlorosilane in tetrachloromethane at 0°C gave a product whose hydrolysis with dilute aqueous hydrogen peroxide yielded silicon dioxide. It was suggested that an ozonide was formed as intermediate in the ozonolysis of vinyltrichlorosilane. A possible structure for the ozonide was not discussed[1]. Later Clasen[2] showed that under ordinary conditions diethylsilane is oxidised by ozone with cleavage of the alkyl–silicon bond. Barry and Beck[3] found that siloxanes are formed by the oxidation of organosilicon compounds.

More recently it has been reported that ozone is able to cleave the lead–lead bond in diplumbanes[4], which has been used to obtain triphenylplumbane hydroxide and acetate from hexaphenyldiplumbane. Enek'yanov et al.[5] utilised the high reactivity of tetraethylplumbane towards ozone in the application of this toxic organolead compound. Investigations on the ozonolysis of hetero-organic compounds of non-transition elements of Groups V and VI have been discussed in some detail[6].

Reactions of ozone with organic derivatives of transition and non-transition metals of other groups have remained almost uninvestigated. Only isolated studies have shown that ferrocene and its vinyl derivatives are readily oxidised by ozone[7,8], and that the main product of the ozonisation of phenylmagnesium bromide in an inert atmosphere at low temperatures (−78°C) is phenol[9], but products of the action of ozone on certain mercury-containing organic compounds[10,11] may be acids (if the organic group is of normal structure) or ketones and alcohols (if it is secondary or tertiary).

The ozonolysis of hetero-organic compounds of elements in the silicon subgroup has been investigated systematically since 1965 (by Spialter, Austin, Aleksandrov, et al.). The results were summarised in a review [12], but more than five years have elapsed since its publication, during which period a considerable number of

studies have been made, extending significantly our knowledge of the ozonolysis of hetero-organic compounds. This work will be surveyed in the present Review.

II. REACTION PRODUCTS AND MECHANISM

1. Fully Organic Derivatives of the Elements

Information has now been published on the ozonolysis of tetraethylsilicon[13-19], tetraethylgermanium[18], tetramethyltin[20], tetraethyltin[16-23], tetrapropyltin[20], tetrabutyltin[20], tetraisobutyltin[20], tetrapentyltin[20], tetraethyllead[23,24], tetrapropyl-lead[24], diethyldimethylsilane[14], methyltriethylsilane[14], and phenyltrimethylsilane[14]. All completely organic derivatives of elements in the silicon subgroup whose reactions with ozone have been investigated are usually extremely stable in air at room temperature[25]. However, they are readily oxidised by ozone under these conditions.

The rate of ozonolysis of the tetra-alkyl derivatives is described by a kinetic equation of the first order with respect to ozone and the first order with respect to the initial hetero-organic compound[19,20]. The example of tetraethyltin in n-nonane and in the absence of a solvent shows[22] that ozonolysis of a hetero-organic compound does not initiate oxidation of the solvent. The proportions of ozone and tetra-alkyl compound that react are nearly equimolecular[22]. The composition of the ozonolysis products indicates[13-17,21-24] that the heteroatom–carbon bond is attacked.

The ozonolysis of tetraethylsilane (up to 50% and more conversion of the initial organosilicon compound) yields as hetero-organic products a mixture[13,14] of various polyethylsiloxanes of linear or cyclic structure (hexaethyldisiloxane, hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, octaethyltrisiloxane). 1,1,3,3-Tetraethyl-1,3-dimethyldisiloxane has been detected as main product of the ozonolysis of methyltriethylsilane at room temperature, but under analogous conditions phenyltrimethylsilane gives hexamethyldisiloxane in theoretical yield[13]. Ozonolysis of tetraethylsilane involves formation in the early stages[15] of triethylsilyl hydroperoxide, bistriethylsilyl peroxide, hexaethyldisiloxane, hydrogen peroxide, water, acetaldehyde, and acetic acid.

A complicated mixture of products is formed by the ozonolysis of tetraethylstannane[22]: free acetaldehyde is accompanied by organotin compounds containing ethylidene, diethylstannylene, and terminal triethylstannyl groups linked by oxygen or a peroxide bond. Hydrolysis of these products gives acetaldehyde, diethyltin oxide, hydrogen peroxide, and triethylstannyl hydroxide in respective yields (hydrolysis of the reaction mixture after ozonolysis of tetraethylstannane in the absence of a solvent at 0°C) of 0.68, 0.70, 0.86, and 1.29 mole mole^{-1} active oxygen. It was also established[22] that the peroxide product present in the reaction mixture is an intermediate: its rate of accumulation diminishes with rise in temperature, but at a sufficient degree of conversion of the tetraethylstannane (ozonolysis in trichlorobenzene, tetrachloromethane, and 1,1,2,2-tetrachloroethane) the rate curves for the accumulation of active oxygen are extremal in character.

It was suggested[21] that the reactions of ozone with tetraethylsilane and with tetraethylstannane have the same mechanism, but that the latter process is complicated by secondary reactions of intermediate peroxy-compounds. The oxidation of tetraethylstannane by ozone was therefore investigated in the presence of a large excess of water, i.e. under conditions of controllable secondary reactions, when triethylstannyl hydroperoxide or peroxide, if formed, would undergo hydrolysis:

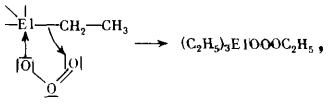
$$(C_2H_5)_3SnOOH + H_2O \rightarrow (C_2H_5)_3SnOH + H_2O_2,$$
$$(C_2H_5)_3SnOOSn(C_2H_5)_3 + 2H_2O \rightarrow 2(C_2H_5)_3SnOH + H_2O_2.$$

It would then be expected that equimolar quantities of acetaldehyde, hexaethyldistannoxane, and hydrogen peroxide would accumulate in the reaction mixture when tetraethylstannane undergoes ozonolysis in the presence of water. The main products were in fact hydrogen peroxide, acetaldehyde, and triethylstannyl hydroxide in nearly equimolecular quantities. It was shown further[21] that tetraethyldistannoxane dihydroxide is also formed, by ozonolysis of triethylstannyl hydroxide as intermediate.

Discussion of the mechanism of the ozonolysis of tetra-n-alkylated hetero-organic compounds[12,16,17] has led to the suggestion that reaction with ozone involves the sequence of stages—(1) coordination of ozone to the heteroatom by means of vacant *d* orbitals of the latter and the electron shell of the nucleophilic centre of ozone

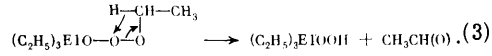
$$(C_2H_5)_4El + O_3 \longrightarrow (C_2H_5)_4El\cdot O_3, \qquad (1)$$

(2) electrophilic attack by the coordinated ozone on the heteroatom–carbon bond to form an intermediate trioxide



(2)

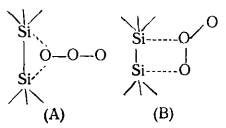
and (3) transformation of the trioxide with migration of hydrogen from the α-carbon atom to the middle oxygen atom of the trioxide



(3)

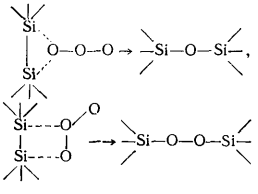
2. Bihetero-organic Compounds

Only three representatives of this class of compounds—hexamethyldisilane[14], hexaethyldistannane[26], and octa-t-butylstannetan[27]—have been examined. Spialter and Austin[14] showed that hexamethyldisilane reacts readily with ozone at room temperature, giving hexamethyldisiloxane as sole organosilicon product. Two possible mechanisms were discussed[14], involving intermediate formation of either a three-membered (A) or a four-membered (B) complex



(A) (B)

subsequent conversion of which would give either hexamethyldisiloxane or bistriethylsilyl peroxide:



From the composition of the products of ozonolysis it was supposed[14] that the action of ozone on hexamethyldisilane involves a three-membered intermediate complex:

$$(CH_3)_3SiSi(CH_3)_3 + O_3 \rightarrow (CH_3)_3SiOSi(CH_3)_3 + O_2 . \quad (4)$$

The ratio of hexaethyldistannoxane formed to the quantities of hexaethyldistannane and ozone that have reacted at room temperature also corresponds to the stoichiometry of reaction (4).[26] When hexaethyldistannane is treated in isopropyl chloride with excess of ozone at −100°C, however, hexaethyldistannoxane is accompanied by an almost equimolecular quantity of bistriethylstannyl peroxide. This was attributed[26] to a different reaction mechanism from the above[14], at least at temperatures considerably lower than 0°C. It was assumed[26] that formation of an intermediate trioxide

$$(C_2H_5)_3SnSn(C_2H_5)_3 + O_3 \rightarrow (C_2H_5)_3SnOOOSn(C_2H_5)_3$$

was followed by the reaction

$$(C_2H_5)_3SnOOOSn(C_2H_5)_3 + (C_2H_5)_3SnSn(C_2H_5)_3 \rightarrow (C_2H_5)_3SnOOSn(C_2H_5)_3 + (C_2H_5)_3SnOSn(C_2H_5)_3 .$$

Under these conditions (−100°C) the reaction of bistriethylstannyl peroxide with hexaethyldistannane, which occurs comparatively easily at room temperature[28], can play no significant part. On these views the observance of the stoichiometry of Eqn.(4) is attributed to the thermal instability of the trioxide at room temperature:

$$(C_2H_5)_3SnOOOSn(C_2H_5)_3 \rightarrow (C_2H_5)_3SnOSn(C_2H_5)_3 + O_2 .$$

The action of ozone on hetero-organic compounds containing several heteroatom–heteroatom bonds also takes place predominantly at these bonds. Thus the oxidation of octa-t-butylstannetan involves[27] ~4 moles of ozone, in conformity with the equation

$$(t\text{-}C_4H_9)_8Sn_4 + 4O_3 \rightarrow 4(t\text{-}C_4H_9)_2SnO + 4O_2 .$$

This result is consistent with the above mechanism for the action of ozone on the heteroatom–heteroatom bond[26].

3. Bihetero-oxanes, Alkoxy and Hydroxy-derivatives

Information on ozonolysis is available only for these derivatives of silicon and tin[13,14,16,17,21,29,30]. The main products of the oxidation of hexaethyldisiloxane by ozone at room temperature are acetic acid and a mixture of various polydiethylsiloxanes (hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, octaethyltrisiloxane)[14]. The ozonolysis of triethylsilyl hydroxide or ethoxytriethylsilane at room temperature[14] yields hexaethyldisiloxane as the main product, oxidation being more rapid with the second compound.

A detailed investigation of the ozonolysis of hexaethyldistannoxane by Aleksandrov and Sheyanov[29] showed that oxidation in n-decane at 10–60°C yields a polydiethylstannoxane $(C_2H_5)_3Sn.[O.Sn(C_2H_5)_2]_6.OSn(C_2H_5)_3$ together with acetaldehyde and triethylstannyl acetate. Estimation of the quantity of ozone consumed suggested that initiated oxidation of the initial organotin oxide either does not occur or plays no significant part in the ozonolysis of hexaethyldistannoxane.

The ozonolysis of triethylstannyl hydroxide in aqueous solution[21] is accompanied by the formation of acetaldehyde and tetraethyldistannoxane dihydroxide, whereas that of diethyldimethoxystannane in n-nonane yields acetaldehyde, acetic acid, and an organotin compound $(C_2H_5)_2Sn(OCH_3).OSn(OCH_3)_2C_2H_5$.[30] This work showed also[30] that diethyldimethoxystannane readily undergoes ozonolysis in n-decane at room temperature, but rise in temperature has little effect on the reaction velocity, as with hexaethyldistannoxane[29].

The mechanism of ozonolysis suggested earlier for tetraethyl derivatives of elements of the silicon subgroup is assumed to apply to the ethyl derivatives, alkoxides, and hydroxides of bihetero-oxanes[30,31].

4. Hetero-organic Halides and Hydrides

Information has been published on the ozonolysis of triethyltin chloride[16,17,30,32], diethyltin dichloride[16,17,30,33], triethyl-lead chloride[16,17,30,33], and organosilicon compounds containing various numbers of unsubstituted hydrogen atoms[13,14,34–41].

Ozone reacts readily with halides of organic derivatives of Group IV elements at room temperature and in the absence of illumination[16,17]. Under such conditions these compounds are extremely stable towards oxygen. Ozonolysis of triethylstannyl chloride in n-hexane at 0°C leads to the formation[32] of acetaldehyde and a solid product presumed to be $2(C_2H_5)_3SnCl.OSn(C_2H_5)Cl.O_3$. The same workers found[30,33] that the ozonolysis of triethylplumbyl chloride under similar conditions yields acetaldehyde, acetic acid, ethanol, and ethyl-lead chloride oxide $(C_2H_5ClPbO)n$. The yields of these products and the quantity of ozone that reacts correspond to the stoichiometric relation

$$(C_2H_5)_3PbCl + O_3 \rightarrow 0.9 \cdot C_2H_5ClPbO + 0.9 \cdot CH_3CHO + 0.24 \cdot CH_3COOH + 0.57 \cdot C_2H_5OH .$$

The oxidation of diethyldichlorostannane under the same conditions[30,33] gives acetaldehyde, acetic acid, and an organotin product $C_2H_5Sn(COH)Cl_2.(C_2H_5)_2SnCl_2$, in the respective yields 0.1, 0.33, and 0.46 mole mole^{-1} initial organotin compound.

The mechanism of the ozonolysis of hetero-organic chlorides is assumed[12] to be fundamentally the same as that of the reaction of ozone with fully organic derivatives of the elements.

Organosilicon compounds containing unsubstituted hydrogen atoms undergo ozonolysis at a silicon–hydrogen bond to form the corresponding silanols[13,14,34–41]. The mechanism is assumed[34,37,38] to involve formation of an intermediate trioxide:

$$R_3ElH + O_3 \rightarrow R_3ElOOOH \rightarrow R_3ElOH + O_2 .$$

III. REACTIVITY TOWARDS OZONE

1. Influence of Nature of Heteroatom

The kinetics of the ozonolysis of $(C_2H_5)_4El$[18,42,43] and $(C_2H_5)_3El.El(C_2H_5)_3$[44–46] (where El represents an element of the silicon subgroup) has been investigated in tetrachloromethane over the range 0–20°C. The results (Table 1) show that the reaction is first order with respect both to ozone and to the hetero-organic compound. The temperature dependence of the ozonolysis rate constant k is described satisfactorily by the Arrhenius equation for all the compounds investigated.

It is noteworthy that the ozonolysis rate constants for hexaethyldisiloxane, hexaethyldigermanoxane, and hexaethyldistannoxane (Nos. IX–XI), representing the most reactive (towards ozone) of the corresponding reaction products[16], are significantly smaller than those for

the initial compounds. For this reason the ozonolysis rate constants obtained for compounds I–VIII can be assigned quite accurately to the primary act.

Table 1. Influence of nature of heteroatom on reactivity towards ozone [27,46].

No.	Compound	$k_{20°C}$, $M^{-1}\,s^{-1}$	$\lg k_0$	E, kcal mole^{-1}	$\alpha \pm 0.01$
I	$(C_2H_5)_4Si$	$2.4\cdot10^{-2}$	4.1	7.6	3.583
II	$(C_2H_5)_4Ge$	$1.2\cdot10^{-1}$	7.3	11	3.574
III	$(C_2H_5)_4Sn$	96	6.7	6.3	3.563
IV	$(C_2H_5)_4Pd$	1300	8.5	7,0	3.559
V	$(C_2H_5)_6Si_2$	0,7	6.5	9.0	3.573
VI	$(C_2H_5)_6Ge_2$	2,1	6.0	7.5	3.567
VII	$(C_2H_5)_6Sn_2$	300	8.0	7,5	3.549
VIII	$(C_2H_5)_6Pb_2$	1650	—	—	3.542
IX	$[(C_2H_5)_3Si]_2O$	$1\cdot10^{-2}$	—	—	—
X	$[(C_2H_5)_3Ge]_2O$	$4\cdot10^{-2}$	—	—	—
XI	$[(C_2H_5)_3Sn]_2O$	40	7.1	7.5	—

In the series of compounds investigated—$(C_2H_5)_4El$, $(C_2H_5)_6El_2$, and $[(C_2H_5)_3El]_2O$—which are equivalent with respect to the influence of the organic groups, steric hindrance, and the presence of vacancies in the coordination capacity of the heteroatom, there is considerable variation in the electronegativity of the heteroatom. Ozonolysis rate constants for the first two series at 20°C correlate satisfactorily with the effective electronegativities of the heteroatoms in these compounds [27]. The latter were measured by the "stability ratios" α of the heteroatoms, calculated from the Gordy system of electronegativities [47]:

$$\text{for } (C_2H_5)_4El,\ \lg k = 709 - 198.4\cdot\alpha,$$
$$\text{for } (C_2H_5)_6El_2,\ \lg k = 389 - 109\cdot\alpha.$$

This result indicates parallel variation in the reactivity towards ozone with the nucleophilicity of the heteroatom. In view of the suggested mechanism [30,48,49] the results indicate that the bimolecular reaction of the hetero-organic compound with ozone is limited at the stage of electrophilic attack by ozone on a heteroatom–carbon or heteroatom–heteroatom bond.

2. Influence of Substituent attached to Heteroatom

(*a*) Fully organic derivatives and halides

The ozonolysis of several tetra-alkylstannanes in tetrachlorom ethane has been used [20] to investigate the influence of the inductive effect of the organic substituent in alkyl derivatives of Group IV elements. The reaction of these compounds with ozone is overall of second order, and the temperature dependence satisfies the Arrhenius equation (Table 2). The values obtained for the ozonolysis rate constant can be attributed quite accurately to reaction of the tetra-alkylstannanes with ozone [27]: i.e. the kinetics of ozonolysis of the initial compounds is not complicated by secondary reactions or by the products. Comparison of the kinetic parameters (Table 2, compounds II–VI) with the sum of the Taft inductive constants of the organic groups [50] indicates that differences in the $+I$ effects of the substituents have little influence on the reactivity of the tetra-alkyl derivative towards ozone.

When ethyl groups in tetraethylstannane and tetraethylgermane are replaced by substituents possessing powerful $-I$ effects (bromo, chloro, hydroxy), the reactivity of the compound is greatly diminished (Table 3) [51,52]. The dependence of $\lg k$ on $\Sigma\sigma^*$ (Table 3) had led to the suggestion [27,51] that in this case the reaction velocity is probably influenced by at least two effects: firstly the strong inductive effect of chlorine, bromine, or hydroxyl tends to diminish the electron density on the carbon atoms adjacent to the tin atom, which hinders electrophilic attack by ozone on the tin–carbon bond; secondly, $d_\pi - p_\pi$ conjugation of the p electrons of chlorine with vacant d orbitals of tin tends to oppose the inductive effect and to promote such electrophilic attack. It is noteworthy that the presence of $d_\pi - p_\pi$ conjugation in the corresponding silicon compounds is convincingly supported by independent physical methods [53].

Table 2. Effect of organic radical on rate of ozonolysis of organotin compounds ($\sim10^{-3}$–10^{-5} M) in tetrachloromethane [20] ($[O_3] = 10^{-4}$–10^{-7} M).

No.	Compound	$k_{0°C}$, $M^{-1}\,s^{-1}$	$\lg k_0$	E, kcal mole^{-1}	$\Sigma\sigma^*$
I	$(CH_3)_4Sn$	$2.8\cdot10^{-2}$	5	8.2	0
II	$(C_2H_5)_4Sn$	46	6.7	6.3	0.40
III	$(p\text{-}C_3H_7)_4Sn$	18	7	7.3	0.46
IV	$(p\text{-}C_4H_9)_4Sn$	17	7	7.2	0.52
V	$(iso\text{-}C_4H_9)_4Sn$	16	7	7.2	0.50
VI	$(p\text{-}C_5H_{11})_4Sn$	16	6.3	6.4	0.65

Table 3. Influence of $-I$ effect of substituent on rate of ozonolysis of hetero-organic compounds (10^{-2}–10^{-5} M) in tetrachloromethane [51] ($[O_3] = 10^{-4}$–10^{-7} M).

No.	Compound	$k_{20°C}$, $M^{-1}\,s^{-1}$	$\lg k_0$	E, kcal mole^{-1}	$\Sigma\sigma^*$ [50]
I	$(C_2H_5)_4Ge$	$1.2\cdot10^{-1}$	7.3	11	−0.40
II	$(C_2H_5)_3GeBr$	$1.5\cdot10^{-2}$	3	6.3	2.6
III	$(C_2H_5)_4Sn$	96	6.7	6.3	−0.40
IV	$(C_2H_5)_3SnCl$	1.34	5.3	6.6	2.7
V	$(C_2H_5)_2SnCl_2$	$6.5\cdot10^{-2}$	3.8	6.6	5.7
VI	$(C_2H_5)SnCl_3$	$2\cdot10^{-2}$	—	—	8.7
VII	$(C_2H_5)_3SnOH$	3	—	—	1.35
VIII	$(C_2H_5)_3SnBr$	1.6	—	—	2.6

(*b*) Organosilanes

A fairly long series of trisubstituted organosilicon derivatives has been used [54–56] to examine the influence of substituents attached to the heteroatom on the rate of reaction with ozone. Organosilanes provided a more convenient model to solve this problem because ozone acts bimolecularly on organosilicon hydrides and only at the silicon–hydrogen bond. The products are the corresponding silanols [13,14,34–41], which, like the organic solvents (hydrocarbons, halogenated hydrocarbons, etc.), have no appreciable chemical role in the reaction.

Relative ozonolysis rate constants for a considerable group of silanes have been correlated with the silicon–hydrogen stretching frequency ν_{Si-H} [35] or with the Hammett and Taft inductive constants [34,37–39]. These correlations were obtained on the assumption that inductive effects have a decisive influence on such frequencies [57]

and on the rate constants. Resonance effects ($d_\pi - p_\pi$ and σ,σ conjugation) were disregarded, which cannot be accepted as correct[53].

Table 4. Effect of $\Sigma\sigma^*$ of substituents on ozonolysis rate constants for silanes in tetrachloromethane at 20°C.[54]

No.	Silane	$\Sigma\sigma^*$	k_{exp}	k_{calc}	$\Delta \lg k$	E, cal mole^{-1}	$10^{-7} k_0$, $M^{-1} s^{-1}$
I	$(C_5H_{11})_3SiH$	−0.486	107	—	—	7 700	6.3
II	$(C_4H_9)_3SiH$	−0.390	100	—	—	7 600	5
III	$(C_3H_7)_3SiH$	−0.345	94.5	—	—	7 700	4
IV	$(C_2H_5)_3SiH$	−0.300	80	—	—	8 000	6.3
V	$(C_2H_5)(C_6H_5CH_2)_2SiH$	0.330	30	—	—	—	—
VI	$(C_6H_5CH_2)_3SiH$	0 645	18.5	—	—	9 100	10
VII	$(C_2H_5)_2(C_6H_5)SiH$	0.400	53	27.1	0.29	6 800	0.63
VIII	$(C_2H_5)(C_6H_5)_2SiH$	1.100	40	8.8	0.65	8 100	4
IX	$(C_6H_5)_3SiH$	1.800	30.5	2.9	1.03	10 200	100
X	$(CH_3)(C_5H_{11})_2SiH$	−0.324	63	86.5	−0.13	7 500	2
XI	$(CH_3)(C_4H_9)_2SiH$	−0.260	60	78.05	−0.11	7 500	2
XII	$(CH_3)(C_3H_7)_2SiH$	−0.230	56	74.4	−0.12	6 500	0.31
XIII	$(CH_3)(C_2H_5)_2SiH$	−0.200	50.5	70.9	−0.15	7 600	2
XIV	$(CH_3)(C_6H_5CH_2)_2SiH$	0.430	21.5	25.8	−0.08	8 000	2
XV	$(CH_3)(C_6H_5)_2SiH$	1.200	29.5	7.5	0.60	7 100	0.5
XVI	$(CH_3)_2(C_6H_5)SiH$	0.600	35	19.7	0.25	8 000	2.5

Determination of the ozonolysis rate constants for sixteen organosilanes (Table 4) has shown[54] that they all react readily with ozone at room temperature. Variation in the initial concentration of ozone or silane by factors of 5–10 has no effect on the rate constant. The stoichiometry is almost equimolecular, which indicates a first-order reaction with respect to ozone and to the initial organosilane. The equation for the rate constant is

$$M^{-1} s^{-1} = k_0 \exp(-E/RT).$$

Values of k_0 and E are included in Table 4.

The organosilanes investigated can be divided into three groups (Table 4). Only the inductive effect of the substituents can reasonably be expected to appear in the first group (compounds I–VI), but in the second group (VII–IX) this is supplemented by $d_\pi - p_\pi$ interaction with the heteroatom. The third group of organosilanes (X to XIV and XV, XVI) is of interest in comparison with the first and second groups respectively, since the σ,σ-conjugation effect of methyl exceeds considerably those of other alkyl and aralkyl radicals[50].

The dependence of the ozonolysis rate constants for the organosilanes on the sum of the inductive constants of the organic substituents is described[54] by the Hammett–Taft equation

$$(\lg k = \rho\Sigma\sigma^* + \text{const}),$$

as illustrated by Fig. 1. For organosilanes of the first group at 20°C the equation is

$$\lg k = -0.696\,\Sigma\sigma^* + 1{,}7114. \quad (5)$$

The sensitivity to $\Sigma\sigma^*$ of the reactivity of the organosilanes (i.e. the slope ρ) is almost independent of temperature (Table 5). The negative slope supports a mechanism of the primary reaction of an organic compound of a non-transition Group IV element with ozone as coordination of the latter to the heteroatom followed by electrophilic attack at a heteroatom–carbon or heteroatom–hydrogen bond (depending on the nature of the hetero-organic compound). According to these views, reactivity towards ozone in a series of such compounds differing only in the total inductive effect of the substituents should increase with decrease in $\Sigma\sigma^*$. This is quantitatively consistent with experimental results[54].

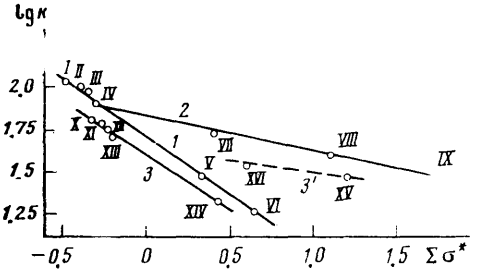


Figure 1. Dependence of $\lg k$ on $\Sigma\sigma^*$ for reaction of ozone with organosilanes in tetrachloromethane at 20°C: the numbering of the straight lines (1–3, 3′) corresponds to the groups of silanes.

Table 5. Values of ρ at various temperatures of ozonolysis of the first group of organosilanes in tetrachloromethane[54].

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

For organosilanes of the second and third groups the dependence of $\lg k$ on $\Sigma\sigma^*$ is not described by Eqn. (5), as is illustrated by Fig. 1. Rate constants k_{calc} calculated by means of formula (5) from values of $\Sigma\sigma^*$ are smaller than the experimental values k_{exp} for organosilanes of the second group, but larger in the third group (Table 4, compounds X–XIV). In the case of the second group this is attributed[54] to $d_\pi - p_\pi$ interaction of phenyl radicals with silicon, which opposes the negative inductive effect of this substituent and is formally equivalent to a decrease in its $-I$ effect; and for silanes of the third group to σ,σ conjugation of the methyl group.

The explanation of the difference between experimental and calculated rate constants for the second group of organosilanes solely by $d_\pi - p_\pi$ interaction is supported by the linear relation (Fig. 2) between $\Delta \lg k = \lg k_{exp} - \lg k_{calc}$ for compounds VII–IX (Table 4) and values[58] of $\Delta\nu$Si–H for these compounds (where $\Delta\nu$Si–H is the contribution to the change in the silicon–hydrogen stretching frequency due solely to the $d_\pi - p_\pi$ interaction between silicon and phenyl substituents).

Quantitative comparison of the contributions by σ,σ conjugation to the reactivity of the third group of organosilanes (X–XIV) could not be made[53] owing to the relatively minute differences in the values of $\Delta\nu$Si–H for these compounds. However, the "point" on Fig. 2 corresponding to the organosilanes with "unresolved" frequency differences lies satisfactorily on the general straight line.

The additivity of the effects of $d_\pi - p_\pi$ interaction and σ,σ conjugation on the reactivity of the organosilanes towards ozone is confirmed by the good agreement, with the linear relation obtained between $\Delta \lg k$ and $\Delta\nu$Si–H (Fig. 2), of analogous experimental data for methyldiphenylsilane and phenyldimethylsilane (XV and XVI in Table 4), values of $\Delta\nu$ for which have been taken also from Refs. 53 and 58.

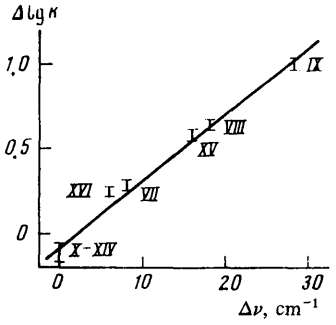


Figure 2. Relation between $\Delta \lg k$ and $\Delta\nu$ for organosilanes.

Table 6. Calculated charges and reactivity indices of reaction centre τ_C/β for certain organotin compounds (here and subsequently charges are given in units of the electronic charge).

ЭОС	q_{Sn}	q_C	τ_C/β	ЭОС	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

*The parameters q_{Sn}, q_C, and τ_C/β have the same values for $(n\text{-}C_3H_7)_4Sn$, $(n\text{-}C_4H_9)_4Sn$, $(n\text{-}C_5H_{11})_4Sn$, and $(iso\text{-}C_4H_9)_4Sn$ as for $(C_2H_5)_4Sn$.

Comparison of the ozonolysis rate constants with the distribution of electron density in several organotin (Table 6) and organosilicon compounds leads to extremely interesting conclusions[27,59]. The tin atom always bears the highest calculated positive charge, while the charge on the carbon atoms adjacent to the heteroatom is more negative than on the other carbon atoms, so that τ_C/β has its highest positive value. Comparison of the calculated charges on the reaction centre with the relative ozonolysis rate constants k/k_0, where k_0 is the rate constant for tetraethyltin (Table 3), leads to a dependence whose semilogarithmic form is almost linear (Fig. 3). The relative rate constant increases with the absolute value of the negative charge on the carbon atom of the reaction centre. These results are consistent with the above heterolytic mechanism of ozonolysis. Departure from linearity may be due to disregard of the $d_\pi - p_\pi$ interaction between chlorine and tin atoms, since such interaction tends to increase the negative charge on the carbon atom.

The analogous calculation of the distribution of electron density in a series of silanes—methyldiethyl, methyldi-n-propyl, methyldi-n-butyl, methyldi-n-pentyl, triethyl, tri-n-propyl, and tri-n-butyl—gives[27] almost the same charge density on silicon, *Si*-hydrogen, and *Si*-carbon atoms [qSi, qH(Si), and qC(Si) respectively +0.33, from −0.15 to −0.16, and from −0.07 to −0.09]. This result indicates that the empirical method of calculation used[27] (the Del Re method) is not sufficiently effective to "resolve" differences in the electronic structure of the silanes. However, the higher electron density on the hydrogen than on the carbon atom attached to silicon is of interest. It is consistent with the experimental observation in the ozonolysis of silanes that attack by the coordinated ozone is directed at the silicon–hydrogen bond, not at a silicon–carbon bond[13,14].

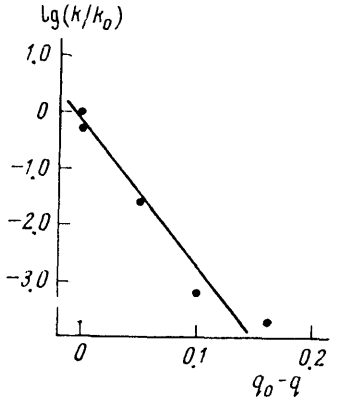


Figure 3. Dependence of logarithm of relative rate of ozonolysis of organotin compounds on variation in charge on reaction centre.

3. Effect of Non-specific Solvation

The influence of non-specific solvation on reactivity towards ozone has been investigated[60] on two organosilanes (tribenzyl and triethyl) and also on two biheteroorganic derivatives (hexaethyl-disilane and -digermane). Significant differences in reactivity towards ozone are present in both of these pairs of compounds (see subsection 1). In the choice of solvents preference was given to tetrachloromethane and 1,1,2,2-tetrachloroethane, which possess comparatively low dielectric constants ϵ and contain no functional groups that might have caused specific solvation of the test compounds.

The investigation has established[60] that at 25°C the dependence of the ozonolysis rate constant on the dielectric constant of the medium (for a mixed solvent the latter was calculated by means of the formula

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

where N_i and ϵ_i are the respective component mole fractions and dielectric constants) is described by Kirkwood's equation

$$\lg k = A + B(\varepsilon - 1)/(2\varepsilon + 1) \qquad (6)$$

with the coefficients listed in Table 7 ($1 > r$ (correlation coefficient) > 0.99, method of least squares). The results indicate that non-specific solvation of the heteroorganic compound and of ozone enhance their mutual reactivity. In each pair of compounds the sensitivity of

ozonolysis to non-specific solvation is greater the greater the reactivity towards ozone. Such a dependence is consistent with a heterolytic mechanism of ozonolysis [12,16,17].

Table 7.

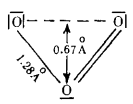
Compound	Triethylsilane	Tribenzylsilane	Hexaethyldigermane	Hexaethyldisilane
A	1.72	1.24	−0.45	−0.63
B	1.15	1.11	3.87	2.32

In the activated complex the valency electrons of the heteroatom are probably in an sp^3d state owing to coordination of ozone with the quadrivalent silicon (or germanium) atom. Such hybridisation seems improbable if the test compounds are solvated in the tetrachloromethane–1,1,2,2-tetrachloroethane system. In discussing the effect of the medium, therefore, we have grounds for ignoring the formation of "diffusion pairs", and interpreting the results in terms of the greater polarity of the activated complex than of the initial reactants. On this basis the slope B in Eqn.(6) is related to the dipole moment $\mu^{\ddagger}$ and the effective radius $r^{\ddagger}$ of the activated complex, as well as to the corresponding parameters of the initial reactants (μ_1 and r_1 for the hetero-organic compound, and μ_2 and r_2 for ozone), by the well known formula [61]

$$B = -\frac{1}{2{,}3\,kT}\left(\frac{\mu_1^2}{r_1^3} + \frac{\mu_2^2}{r_2^3} - \frac{\mu^{\ddagger 2}}{r^{\ddagger 3}}\right) \qquad (7)$$

which has been used to estimate the dipole moment of the activated complex and the relative charge q on the heteroatom.

For the calculations the value $\mu_2 = 0.53$ D [62] was adopted. The choice of r_2 and $r^{\ddagger}$ was governed by the amphiphilic nature of ozone, with its nucleophilic centre coordinated with the heteroatom, entailed in a heterolytic reaction mechanism. The latter was therefore taken to be $r^{\ddagger} = r_{Si-O} = 1.64$ Å [63] for silanes and hexaethyldisilane, and $r_{Ge-O} = 1.85$ Å [63] for hexaethyldigermane, while r_2 was given the values 1.28 and 0.67 Å depending on the different steric positions



For triethylsilane and tribenzylsilane $r_1 = 1.47$ Å, while μ_1 has the values 1.54 and 1.31 D respectively [65]; for hexaethyldisilane and hexaethyldigermane r_1 was taken to be 2.34 and 2.41 Å, while μ_1 was equated to zero [63]. The above data were used to calculate $\mu^{\ddagger}$ and q for the activated complex in the ozonolysis. Table 8 shows satisfactory agreement between the value of q with $r_2 = 1.28$ Å and the value obtained by other investigators from spectroscopic data [65], from which it can be concluded [60] that 1.28 Å is more probable than 0.67 Å for r_2 in the ozonolysis of the hetero-organic compounds investigated. Hence the dipolar ozone molecule entering into reaction is preferably regarded as an amphiphilic form with the nucleophilic centre localised mainly on a single oxygen atom.

An analogous investigation was made with individual solvents [66] differing essentially in nature (and dielectric constant)—tetrachloromethane (2.23), chloroform (4.72), 1,2-dichloroethane (10.16), 1,1,2,2-tetrachloroethane (8.08), propionic acid (3.2), acetic acid (6.2), and acetic anhydride (20.5)—the test compounds being methyldi-n-propylsilane, tribenzylsilane, hexaethyldisilane, and hexaethyldigermane. This established that the dependence of the ozonolysis rate constant on the dielectric constant was also described by Kirkwood's equation, which indicated non-specific solvation of the substrates in the solvents. The coefficients in the relations (6) established at 0°C are given in Table 9 [66] (method of least squares, $0.90 < r < 0.99$).

Table 8. Calculation of $\mu^{\ddagger}$ and q for ozonolysis at 25°C [60] (values of q in units of the electronic charge).

Compound	$\mu^{\ddagger}$	q	$\mu^{\ddagger}$	q	q^{lit}
	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	—

Table 9.

Compound	Methyldipropylsilane	Tribenzyl silane	Hexaethyldigermane	Hexaethyldisilane
A	0.91	0.44	−0.60	−1.09
B	1.88	1.35	2.50	1.45

Table 10. Values of $\mu^{\ddagger}$ and q for hetero-organic–ozone activated complex at 0°C ($r_2 = 1.28$ Å). [66]

Compound	$\mu^{\ddagger}$	q	Compound	$\mu^{\ddagger}$	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 type of relations established is consistent with the results obtained in binary mixtures of tetrachloromethane and 1,1,2,2-tetrachloroethane. Substitution in Eqn.(7) of the same values for $r^{\ddagger}$, r_1, r_2, μ_1, and μ_2 as in the preceding case yielded calculated values of $\mu^{\ddagger}$ and q for the activated complex agreeing satisfactorily with those obtained with use of the binary solvents (Table 10).

4. Effect of Specific Solvation

The first study of the effect of specific solvation on the ozonolysis has been made [67] on triethylstannyl chloride in tetrachloromethane in the presence of dimethylformamide, which solvates the initial hetero-organic compound specifically. The phenomenology of the reaction remains almost unchanged in the presence of dimethylformamide [67]. In this case, however, the rate constant depends significantly on its concentration (Table 11).

The observed [67] kinetic effect of the medium is explained by specific solvation of triethylstannyl chloride

by dimethylformamide, by analogy with the well known complexes formed by halides of alkylstannanes with many ligands (amides, ketones, etc.[68]). Calorimetric and spectroscopic measurements were made[67] to test this hypothesis. Determination of the heat of mixing of triethyltin chloride and dimethylformamide in the proportions 1 : 2 at 20°C gave for the enthalpy of formation of the complex the value -5 ± 0.5 kcal mole^{-1}. The infrared spectra of a 20 : 1 mixture showed a significant low-frequency shift (by 18 cm^{-1}) of the carbonyl-stretching frequency (for pure dimethylformamide $\nu C:O = 1680$ cm^{-1}), which was accepted as proof of complex formation through the lone pair on the carbonyl oxygen atom of the amide molecule. Proofs of the specific solvation of triethylstannyl chloride by dimethylformamide were obtained[67] also on analysing the infrared spectra of the former compound.

Table 11. Effect of additions of dimethylformamide ($N = [D_0]/[A_0]$) on rate of oxidation of triethylstannyl chloride (concentration c, M) by ozone (2×10^{-4} M) in tetrachloromethane.

N	k, M^{-1} s^{-1}	N	k, M^{-1} s^{-1}	N	k, M^{-1} s^{-1}
−17°C, $c=4.23\cdot10^{-3}$		0° C, $c=2.82\cdot10^{-3}$		20° C, $c=1.41\cdot10^{-3}$	
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	7.9	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	1.59
20.8	0.380	23.5	0.93	20.0	1.89
29.6	0.390	31.3	0.93	27.0	2.18
		39.2	0.93	40.0	2 17

The degree of charge transfer in the dimethylformamide complex of the hetero-organic compound was 5–7% estimated for one donor–acceptor bond from the correlation[68] of the enthalpy of complex formation with the transfer of charge. From the results it was assumed[67] that the increase in the rate of reaction of triethylstannyl chloride with ozone in the presence of dimethylformamide was due to formation of a complex that was more reactive towards ozone than was the original hetero-organic compound. To analyse the kinetic results we denote triethylstannyl chloride, dimethylformamide, ozone, and the reaction products by A, D, C, and P respectively, when the process can be written

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

$$A + D \underset{k_{-2}^{(1)}}{\overset{k_2^{(1)}}{\rightleftarrows}} AD, \qquad (8_1)$$

$$AD + D \underset{k_{-2}^{(2)}}{\overset{k_2^{(2)}}{\rightleftarrows}} AD_2, \qquad (8_2)$$

. . . . . .

$$AD_{n-1} + D \underset{k_{-2}^{(n)}}{\overset{k_2^{(n)}}{\rightleftarrows}} AD_n. \qquad (8_n)$$

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

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

. . . . . .

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

The reaction velocity will then be

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

When the extent of oxidation of triethylstannyl chloride is small,

$$[A] = [A]_0 - \sum_{i=1}^{n}[AD_i],$$

$$k_{exp} = \frac{w}{[A]_0[C]} = k_1 + \frac{\sum_{i=1}^{n} k_3^{(i)}[AD_i] - k_1\sum_{i=1}^{n}[AD_i]}{[A]_0}. \qquad (9)$$

On the hypothesis[67] that the complexes formed by reactions $(8_1)-(8_n)$ differed significantly in reactivity, the mathematics was simplified by considering only the most reactive complex towards ozone (of arbitrary composition AD_n). With $[D]_0 \gg n[AD_n]$ Eqn.(9) then becomes

$$k_{exp} = k_1 + (k_3^{(n)} - k_1)\frac{N^n}{N^n + \dfrac{1}{K[A]_0^n}}, \qquad (10)$$

where $N = [D]_0/[A]_0$ and K is the equilibrium constant of the overall process comprising stages $(8_1)-(8_n)$.

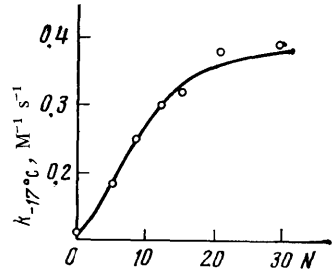


Figure 4. Agreement between ozonolysis rate constants k obtained experimentally (points) and calculated by means of Eqn.(11) (curve).

Experimental data (Table 11) were substituted in Eqn. (10) to find the minimum standard deviation, for each temperature investigated, over the range $n = 0.5-3$ in steps of 0.5 with optimum values of K estimated from the standard deviation between calculated and experimental values. The optimum value $n = 2$ was found, and the experimental results at −17°C (Table 11) were satisfactorily described by the equation

$$k_{exp} = k_1 + (k_{max} - k_1)\frac{N^2}{N^2 + 70} \qquad (11)$$

(standard deviation not exceeding 3%). Formation of a 1 : 2 complex of triethylstannyl chloride with dimethylformamide is confirmed by the good agreement between ozonolysis rate constants k in the presence of dimethylformamide determined experimentally at −17°C and calculated by means of formula (11) (Fig.4).

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