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Radiation Effects in the Chemistry of Group IVB Elements (Silicon, Germanium, Tin, and Lead)

N.V.Fomina, N.I.Sheverdina (deceased), and K.A.Kocheshkov (deceased)

Data concerning the effect of ionising radiation on the principal reactions in organometallic synthesis involving Group IVB elements are considered: radiolysis of organometallic compounds of Group IVB elements, addition to the C=C bond, redistribution of radicals, reactions leading to the substitution of functional groups or organic substituents at the metal atom, reactions involving the organic group, and direct synthesis of organometallic compounds from the metal and alkyl halides.
The bibliography includes 104 references.

CONTENTS

I.	Introduction	238
II.	Radiation stability of compounds containing silicon, germanium, tin, and lead atoms	238
III.	Radiation-chemical hydrometallation	239
IV.	Direct synthesis in the field of ionising radiation	241
V.	The effect of radiation on the radical redistribution reaction	242
VI.	Reactions under the influence of ionising radiation not involving the metal-carbon bond	242

I. INTRODUCTION

Physical methods for the stimulation of chemical processes have been acquiring increasing importance in synthetic chemistry. Together with methods whose application dates back to the XIXth century (electrochemistry and photochemistry), various types of radiation (laser, ultrahigh-frequency, and γ-radiation) have found fairly extensive applications during recent decades[1].

This review is devoted to the experience gained in the use of γ-radiation in reactions of Group IVB elements. There are many reviews in the literature demonstrating the wide scope of the application of ionising radiation in organic synthesis; however, the reactions of Group IVB elements have been described fragmentarily (for example, direct synthesis has been described for tin and hydrometallation for silicon)[2-13]. The influence of ionising radiation on reactions of Group IVB elements has not been considered systematically, although extensive data have accumulated in the literature on this problem.

II. RADIATION STABILITY OF COMPOUNDS CONTAINING SILICON, GERMANIUM, TIN, AND LEAD ATOMS

In the study of the influence of radiation on chemical reactions the main task was to discover whether radiation-chemical synthesis is possible. From the standpoint of the utilisation of substances in radiation-chemical synthesis, data on radiation stability and pathways leading to the decomposition of molecules under the influence of high-energy radiation are very important.

Brinskman et al.[14] investigated the mode of dissociation of chemical bonds in organometallic compounds of Group IVB elements and showed (by ESR) that for low energies the decomposition involves mainly the M-C bond, while for high energies the situation becomes more complicated.

It was found for trichloromethylgermane at -196° C that the primary radiolysis products are the $CH_3^{\cdot}$ and $GeCl_3^{\cdot}$ radicals, which enter into secondary reactions via two pathways:

$$CH_3GeCl_3 \xrightarrow{h\nu} CH_3^{\cdot} + GeCl_3^{\cdot},$$

$$GeCl_3^{\cdot} + CH_3GeCl_3 \xrightarrow{1} HGeCl_3 + Cl_3GeCH_2^{\cdot}$$

$$\xrightarrow{2} GeCl_4 + CH_3GeCl_2^{\cdot}.$$

The secondary processes proceed mainly via pathway 2.

The decomposition of silicon compounds under the influence of temperature and an electron beam has been most widely investigated (in connection with the development of the method for the preparation of semiconducting silicon films)[15,16]. The decomposition is usually carried out in the gas phase at elevated temperatures (150-200° C) and electron energies in the range 250-800 eV. (We may note that the thermal decomposition of organosilicon compounds begins above 500° C.) A study of the decomposition of triethylvinylsilane under the influence of an electron beam showed that the rate and mode of decomposition of organosilicon compounds depend less on electron energy and more on the temperature of the support and the vapour pressure of the organosilicon compound. Below 100° C and at a high vapour pressure, polymers are formed, while at higher temperatures elemental silicon is produced[17]. The radiolysis of tetrasubstituted organosilicon compounds proceeds in different ways depending on the phase state of the substance. The gas-phase radiolysis of tetramethylsilane leads ultimately to a complex mixture of products[18,19]: H_2 ($G = 8.56$), C_2H_6 ($G = 4.23$), CH_4 ($G = 1.28$), $C_2H_5Si(CH_3)_3$ ($G = 4.52$), and $(CH_3)_6Si_2$ ($G = 1.4$), where G is the radiation-chemical yield (mol./100 eV). A more detailed study of the mechanism of the radiolysis using the O_2 and NO radical trapping agents established that the majority of the products are formed as a result of

secondary processes. The primary stages in the radiolysis are reactions involving the elimination of a hydrogen atom from the organic group:

$$(CH_3)_4Si \rightsquigarrow (CH_3)_3SiCH_2^{\cdot} + H^{\cdot}$$

or the elimination of the methyl radical

$$(CH_3)_4Si \rightsquigarrow (CH_3)_3Si^{+} + CH_3^{\cdot} + e^{-} \quad .$$

Hydrogen and methane are formed as a result of atomic reactions and molecular elimination reactions, while ethane is produced as a result of the recombination of methyl radicals.

The study of the radiolysis of tetramethylsilane by ESR[20] in the solid phase permitted certain comparisons between hydrocarbons and organosilicon compounds. It was shown that the yield of free radicals in alkyl- and aryl-substituted organosilicon compounds hardly differs from that observed in hydrocarbons ($G \simeq 5$), which is consistent with the comparable Si–C and C–C bond dissociation energies. The ESR spectra of irradiated (77 K) alkylchlorsilanes[2] indicate the dissociation of the C–H, Si–C, and Si–Cl bonds, while free radicals are formed from the corresponding carbon compounds mainly as a result of the dissociation of the C–Cl bond. The yield of radicals in the radiolysis of unsaturated organosilicon compounds has been determined[22].

In contrast to the gas phase[18], the radiolysis of tetramethylsilane in the liquid phase[23] is characterised by an increase of the contribution of reactions involving the abstraction of hydrogen by methyl radicals from tetramethylsilane molecules and an increased yield of methane (G_{CH_4} = 4.8 mol./100 eV, while in the gas phase G_{CH_4} = 1.28 mol./100 eV). The yield of bis(trimethylsilyl)ethane and bis(trimethylsilyl)methane also increases with a corresponding decrease of the yield of ethane and ethyltrimethylsilane. The yield of "intrinsic" radical trapping agents—C_2H_4, C_2H_2, and C_3H_6—decreases by a factor of 50–100.

The thermal decomposition of organogermanium compounds, like that of organosilicon compounds, has been thoroughly investigated in connection with the necessity to prepare films of semiconducting germanium[15]. We may note that the thermal decomposition of organogermanium compounds is observed only above 350° C.

The available information about the radiation-thermal decomposition of organogermanium compounds is very scanty. Brinskman et al.[14] and Duval[24] disagree as regards the determination of the principal pathway in the decomposition of organogermanium molecules under the influence of radiation. Duval suggests that, even in the photochemical decomposition, the reaction involves the C–H bond and not the Ge–C bond, as claimed previously by Brinskman et al.[14] Magat and coworkers[25,26] demonstrated the formation of the $GeCl_3^{\cdot}$ radical and possibly also $GeCl^{\cdot}$ and the Cl_2^{-} ion ($G \simeq 0.5$) in the radiolysis of inorganic germanium halides.

In the determination of the radiation stability of tetraalkyl compounds of germanium it was shown[27] that an appreciable yield of the final radiolysis products is not observed in the field of ^{60}Co γ-radiation at 200° C over a period of 24 h: a germanium mirror is formed on the walls of the vessel at 250° C. Germanium tetrahalides do not undergo significant changes under analogous conditions.

The thermal decomposition of organotin compounds and their decomposition under the influence of electrons has been described in detail in a review[15]. The authors[15] note that the thermal decomposition of the majority of the organotin compounds investigated begins at ~ 300° C. Metallic tin is produced at an appreciable rate from an organotin compound at 200° C in the field of γ-radiation[27].

Dunn and Oldfield[28] investigated the radiolysis products of organotin compounds in benzene, hexane, and pentafluorobenzene. They showed that the radiolysis leads to the formation of traces of stepwise decomposition products:

$$R_3SnCl \rightsquigarrow R_4Sn + R_2SnCl_2 \quad ,$$
$$R_2SnCl_2 \rightsquigarrow R_4Sn + R_3SnCl + SnCl_4 \quad ,$$
$$RSnCl_3 \rightsquigarrow \text{residue} \quad ,$$
$$R_3SnOSnR_3 \rightsquigarrow R_2SnO.$$

The action of radiation on ethyltrimethylstannane and tetramethylstannane results in the formation of mainly the trialkylstannyl radical. The radiolysis of tetrabutylstannane in pentafluorobenzene leads to the formation of dibutyldifluorostannane (0.1%) and tributylfluorostannane (7.8%). The preferential formation of the trialkylstannyl radical during radiolysis is consistent with mass-spectrometric data for the elimination of alkyl groups from alkyl compounds of tin[29]. Irradiation of tetramethylstannane at 77 K also leads to the dissociation of the C–H bond and the formation of the $CH_3Sn{-}CH_2^{\cdot}$ radical. Prolonged irradiation results in the formation of species with an average number of tin atoms less than unity (in contrast to photolysis). Metallic tin is not produced during radiolysis[30-32].

As regards organolead compounds, it is known only that, in contrast to tetramethylstannane, irradiation of tetramethylplumbane at low temperature is accompanied by the liberation of metallic lead[33] and that its radiolysis in the gas phase leads to a complex mixture of products[34,35].

The available data on the radiolysis of organometallic compounds of Group IVB elements show that the dissociation of the element–carbon bond is one of the main pathways to the decomposition of the molecule under the influence of high-energy radiation. This suggests that the use of radiation methods in organometallic synthesis is desirable.

III. RADIATION-CHEMICAL HYDROMETALLATION

Reactions involving addition to a carbon–carbon double bond proceed in high yields via a radical-chain mechanism. Many examples of the initiation of such reactions by ultraviolet light are known[36]. The overall mechanism of reactions involving addition to a double bond can be represented by a series of consecutive or parallel stages[6].

(1) The generation of a free radical as a result of the action of ionising radiation on the molecule of the substance undergoing addition (the addend):

$$M \rightsquigarrow R^{\cdot} \quad , \qquad (1)$$

where $R^{\cdot}$ is the chain propagating radical. The efficiency of the action of radiation depends to a large extent on the ability of the addend to decompose in the field of radiation with formation of free radicals.

(2) Initiation of the chain reaction as a result of the addition of the carrier radical to the double bond:

$$R^{\cdot} + R_1CH{=}CHR_2 \rightarrow R_1CHR{-}CHR_2^{\cdot} \quad . \qquad (2)$$

The rate of the second stage must be high, slow addition resulting in the formation of short chains and the possibility of dimerisation. The rate of reaction (2) is influenced by the structures of both the addend and the olefin. In the

general case the rate of addition decreases on passing from ethylene to aromatic olefins in the sequence ethylene > substituted ethylenes > higher aliphatic alkenes > cycloalkenes > aromatic alkenes. Substitution by polar groups, for example halogens, lowers the reactivity of the double bond, but perhalogeno-compounds nevertheless react comparatively effectively. A terminal double bond is more reactive than an inner double bond. The $R^{\cdot}$ radical can in principle add to any carbon atom of a substituted ethylene, giving a mixture of isomeric products, but in each specific case the problem of the mode of addition requires special consideration[6].

(3) The complex radical $R_1CHR-CHR_2^{\cdot}$, formed in reaction (2), can in principle react in two ways: with the olefin or with an addend molecule. If the addend molecule is attacked by the carrier radical, we have the "normal" propagation of the chain reaction:

$$R_1CHR-CHR_2^{\cdot}+M\rightarrow R_1CHRCH_2R_2+R^{\cdot}\quad , \qquad (3)$$

etc.

(4) The radical formed in reaction (2) attacks an olefin molecule

$$R_1CHRCHR_2^{\cdot}+\underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}}\rightarrow R_1CHRCHR_2-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}^{\cdot} \quad . \qquad (4)$$

The reaction results in the formation of polymeric products.

(5) The radical formed via reaction (4) may attack an addend molecule with formation of a chain-propagating radical (a carrier radical) and a 1 : 2 adduct (a telomerisation reaction). Adducts with compositions corresponding to a ratio greater than 1 : 3 are rarely encountered.

A mechanism agreeing with the general scheme[37,38] has been demonstrated in many instances for compounds of Group IVB elements.

Chain initiation:

$$HSiCl_3\rightsquigarrow H^{\cdot}+SiCl_3^{\cdot}\quad , \qquad (1')$$

$$SiCl_3^{\cdot}+CF_2=CF_2\rightarrow CF_2-CF_2SiCl_3^{\cdot}\quad . \qquad (2')$$

Chain transfer:

$$CF_2CF_2SiCl_3^{\cdot}+HSiCl_3\rightarrow CHF_2CF_2SiCl_3+SiCl_3^{\cdot}\quad . \qquad (3')$$

Chain termination:

$$CF_2CF_2SiCl_3^{\cdot}+H^{\cdot}\rightarrow CHF_2-CF_2SiCl_3 \qquad (4')$$

Telomerisation:

$$CF_2CF_2SiCl_3^{\cdot}+CF_2=CF_2\rightarrow CF_2CF_2CF_2CF_2SiCl_3^{\cdot}\quad .$$

The reaction mechanism for alk-1-enes can be represented similarly[38]:

$$HSiCl_3\rightsquigarrow H^{\cdot}+SiCl_3^{\cdot}\quad ; \qquad (1'')$$

$$SiCl_3^{\cdot}+RCH=CH_2\rightarrow RCHCH_2SiCl_3^{\cdot}\quad ; \qquad (2'')$$

$$RCHCH_2SiCl_3^{\cdot}+HSiCl_3\rightarrow RCH_2CH_2SiCl_3+SiCl_3^{\cdot}\quad . \qquad (3'')$$

Stage (3) is rate-determining for the reactions of simple olefins. Stage (4′) plays a major role when more complex unsaturated compounds, such as allyl chloride, allyl acetate, and *cis*-1,2-dichloroethylene, are involved in the reaction. It leads to the formation of 1 : 2 adducts and high-boiling compounds[38].

Radical-chain mechanisms of the type quoted above describe satisfactorily the majority of reactions of silicon compounds with olefins, but Lampe et al.[39] believe that an ionic mechanism operates in the addition reactions of unsubstituted silanes:

$$SiH_4\rightsquigarrow SiH_3^{+}+H^{\mp}+e\quad ,$$

$$CH_2=CH_2+SiH_3^{+}\rightarrow CH_2-CH_2SiH_3^{+}\quad ,$$

$$CH_2-CH_2SiH_3^{+}+SiH_4\rightarrow CH_3CH_2SiH_3+SiH_3^{+}\quad ,$$

etc.

The literature data for the interaction of silicon compounds with olefins in the field of ionising radiation are fairly extensive. Studies by various workers have made it clear that the structure of the silane undergoing addition has a decisive influence on the result of the reaction. It is essential to distinguish the following main cases: unsubstituted silanes of the type SiH_4; silanes substituted only by organic groups (alkylsilanes of the type R_nSiH_{4-n}); silanes substituted by halogens as well as organic groups (alkylchlorosilanes); silanes substituted by halogens only; finally, silanes without a hydrogen atom, for example, tetrachlorosilane. The reactivity of many aliphatic silicon compounds increases with respect to the double bond in the sequence

$$R_3SiH < R_2SiHCl < RSiHCl_2 < HSiCl_3\quad .$$

This can be accounted for by a decrease in the above sequence of the hydride character of the hydrogen atom, which facilitates the homolysis of the Si–H bond under the influence of radiation.

An increase of the rate of reaction of aromatic compounds has been observed[40] on passing from dichlorophenylsilane to chlorodiphenylsilane and triphenylsilane. Apart from the unusual addition mechanism postulated by Lampe et al.,[39] the possibility of stepwise addition with formation of products having the structure $CH_3CH_2SiH_2CH_2CH_3$ together with 1 : 1 and 1 : 2 adducts should be noted for unsubstituted silanes[41]. Methylsilane and dimethylsilane mixed with ethylene (in proportions of 1 : 3 or 1 : 5) react in the gas phase[39,42] at 50° C to give a 1 : 1 adduct with the radiation-chemical yield G = 38 mol./100 eV and a 1 : 2 adduct with a yield of 15 mol./100 eV. Triphenylsilane adds to cyclohexene and oct-1-ene[43] under the conditions of γ-irradiation to give low yields of cyclohexyltriphenylsilane and octyltriphenylsilane. A comparatively high yield of nonyltriphenylsilane (radiation-chemical yield G = 200 mol./100 eV and a chemical yield of 66%) was obtained in the reaction with non-1-ene[44].

Under analogous conditions, naphthenes give very low yields, while alk-2-enes hardly react at all. The addition of alkylsilanes to vinylsilanes is of interest[45]:

$$(C_6H_5)_3SiH+(C_6H_5)_3SiCH=CH_2\rightsquigarrow$$
$$\rightsquigarrow(C_6H_5)_3SiCH_2CH_2Si(C_6H_5)_3\quad .$$

Very small yields have been obtained, but an increase of the latter may be expected when sources with a higher power are used.

Silanes containing chlorine atoms together with organic substituents react more vigorously. A radiation-chemical yield of ~ 200 mol./100 eV is reached in many reactions, the chemical yield amounting to ~ 50% under these conditions (80% for high doses). A large number of organosilicon compounds have been obtained by the radiation-chemical addition of alkylchlorosilanes to olefins with different structures (ethylene, propene, hexafluoropropene, cyclopentene)[30,40,46,47]. The main studies in this field have been carried out by Zimin and coworkers[47]. The authors found that the yields of products in reactions with unsaturated hydrocarbons vary appreciably with temperature, while those of reactions with fluoro-olefins are independent of temperature.

Among silicon compounds, trichlorosilanes are the most reactive in relation to olefins. The yield reaches 10^3 mol./100 eV in the radiation-initiated addition to olefins. The addition of trichlorosilane to ethylene, isobutene, C_5–C_8 alk-1-enes, certain alk-2-enes, cyclopentene, cyclohexene, allyl chloride, allyl acetate, 1,2-dichloroethylene, and polyfluoroalkenes has been described[38,40,46,47].

On the basis of the mechanism of the addition reaction described, one may assume that silicon compounds without hydrogen atoms are incapable of adding to olefins. On the other hand, it is known that the halides of certain elements, for example phosphorus[48,49], do add to olefins under the influence of ionising radiation. The data available at the present time do not allow an unambiguous answer to the question concerning the possibility of the addition to olefins of organosilicon halides without a hydrogen atom.

In the radiolysis of a mixture of tetrachlorosilane with methyl methacrylate and styrene[50], addition products were not isolated and only polymerisation of the above monomers was initiated. Shostenko et al.[51] attempted to add tetrachlorosilane and tetrachlorogermane to alk-1-enes. The addition products were isolated but the radiation-chemical yield proved to be very low (~ 1 mol./100 eV) and the process was complicated by many side reactions.

The nature of the addend plays a decisive role in radiation-chemical hydrosilylation reactions, but the nature of the olefin in many cases also alters the course of the reaction significantly. Thus γ-irradiation of a mixture of trichlorosilane and vinyl acetate leads to the formation of ethyl 2-trichlorosilyl ether apart from the 1 : 1 and 1 : 2 adducts. By selecting the reactant ratio, it is possible to make the reduction of the carbonyl group to the methylene group the main process[52]. The reaction of allyl derivatives is complicated by the formation of telomers[41,46] of the type $CH_3CH(X)CH(X)CH_2Y$, where $X=CH_2Cl$ or CH_2OOCH_3 and $Y=SiCl_3$ or $SiCl_2CH_3$. It was noted in a study of the hydrosilylation of polychlorofluorocyclobutene, polyfluorocyclobutene, and cyclopentene initiated by γ-radiation that the presence of an organic substituent at the silicon atom greatly retards the reaction[53,54]. Apart from the expected addition products, reduction products were obtained as a result of the exchange of Cl atoms for hydrogen atoms. The reactivity decreases on passing from butenes to pentenes[53,54].

The addition of germanium compounds to olefins in the field of ionising radiation has been scarcely investigated; this problem is merely touched on in the study mentioned above[51].

Liquid-phase hydrostannylation takes place with a high radiation-chemical yield at room temperature[55,56]. Kocheshkov and coworkers[57] developed a method for the radiation-chemical hydrostannylation in order to synthesise many organotin compounds, including those which are difficult to obtain or which have been described for the first time. The authors showed that, in contrast to hydrosilylation, radiation-chemical hydrostannylation takes place at room temperature. Low reaction temperatures are responsible for the specific reaction pathway leading to the formation of products of the "normal" addition to the double bond. Side products or products of the polymerisation of the initial olefins have scarcely been detected. The reaction has been carried out for olefins having different structures: hex-1-ene, hept-1-ene, oct-1-ene, styrene, allyl alcohol, etc; the radiation yield is ~ 10^3 mol./100 eV in all cases.

A study of radiation-chemical hydrostannylation[58] using triethylstannane and hept-1-ene as a model showed that the rate of reaction is described by S-shaped kinetic curves, which are typical of branched-chain processes. The activation energy (1.5 kcal $mole^{-1}$) shows that the role of temperature as a factor increasing the rate of the process is in this case small. The relation between the rate of reaction and the dose rate is quadratic; the induction period observed at low dose rates (2 h for 5 rad s^{-1}) diminishes with increasing dose rate; when irradiation is interrupted, the reaction stops.

IV. DIRECT SYNTHESIS IN THE FIELD OF IONISING RADIATION

The interaction of metals with alkyl halides (direct synthesis) is an important method for the preparation of organometallic compounds:

$$M + RHal \rightarrow RMHal,$$

where M is the metal, R the organic group, and Hal the halogen. Group IVB elements react with alkyl halides under severe temperature conditions, which differ strongly depending on the nature of the metal and the halogen atom and the reaction temperature is frequently above the limit corresponding to the pyrolytic decomposition of alkyl halides. For example Rochow's method, used nowadays for germanium, consists in passing the alkyl halide vapour over a germanium–copper mixture heated to 300–350° C; alkyl halides containing more than four carbon atoms decompose under these conditions. It is necessary to carry out special studies in order to intensify the direct synthesis and to find milder reaction conditions.

The usefulness of radiation in direct synthetic reactions is based on the following considerations. It follows from studies of the mechanism of the direct synthesis in recent years that electron transfer from the metal atom to the molecule of the organic halide is the most important stage of the reaction of the metal with the alkyl halide, responsible for the formation of the M–C bond[59-63]. Electron transfer results in the formation of active radical species. (The ideas about the mechanism of the direct synthesis of organosilicon and organogermanium compounds are developing mainly in relation to catalytic gas-phase processes involving copper[64,65].) It is appropriate to mention here that the formation of organic radicals (for example by irradiation) promotes a more vigorous direct synthesis. The formation of radicals in the radiolysis of alkyl halides has been frequently observed even in early investigations[66,67]; subsequently it was shown that, with increase of temperature, radiation-induced processes in liquid alkyl halides (isomerisation) may take place quantitatively[68].

The influence of γ-irradiation on the direct synthesis was investigated for the first time by Kocheshkov and coworkers[69,70] in the reaction between powdered tin and butyl bromide. They showed that, in the absence of irradiation, tin does not react with boiling butyl bromide, while on irradiation with ^{60}Co γ-rays the reaction proceeds at an appreciable rate even at room temperature. The radiation-chemical yield is 50–58 mol./100 eV. The lack of thermal experiments under comparable conditions precludes the consideration of the magnitude of the effect of irradiation, but in this instance any decrease of reaction temperature below the boiling point of the alkyl halide is of great practical importance: the necessity for employing an excess pressure during the reaction is obviated.

Subsequently research on the radiation-chemical synthesis of organotin compounds was developed in order to devise an experimental industrial plant[71-82]. The study of the process over a wide temperature range showed that the radiation-chemical yield may be increased to 10^3 mol./100 eV.

The interaction of metallic tin and alkyl halides is an extremely complex process, the rate and direction of which depend significantly on many factors: the nature of the initial reactants and their mass ratio, temperature, dose

rate, rate of stirring of the reaction mixture, and the presence of impurities. It has been shown that the reaction is to a large extent specific, with formation of dibromodibutylstannane and a certain amount of bromotributylstannane[69,70]. An increase of temperature accelerates the reaction[71], the optimum temperature of the synthesis of dibromodibutylstannane being 95° C; a further increase of temperature leads to a decrease of the reactivity of tin, probably owing to its aggregation. Temperature also influences the proportions of the final products: when the temperature is reduced, the content of tribromobutylstannane increases. According to Vereshchinskii and coworkers[72], the effective activation energy is 12 kcal mole^{-1}, while according to Fentiman and coworkers[81,82] it is 35 kcal mole^{-1} at 95° C and shows a tendency to vary with temperature. By varying the irradiation dose rate from 0.7 to 220 rad s^{-1}, it has been shown that the rate of reaction is proportional, other conditions being equal, to the square root of the absorbed dose rate. In the synthesis of dibromodibutylstannane under optimum conditions the radiation-chemical yield is 1600–2100 mol./100 eV. The radiation-chemical yield varies with the length of the carbon chain in the alkyl halide, decreasing with increase in chain length.

Vereshchinskii and coworkers[78] and Fentiman and coworkers[81,82] noted an appreciable induction period in the reaction and discussed various methods for eliminating it[79,81]. The preparation of the tin surface, the particle size, and the method of obtaining tin affect both the rate of the process and the proportions of the reaction products[71,72,81].

It is noteworthy that the nature of the halogen in the alkyl halide is very important. Alkyl chlorides do not react[82]. The effect of irradiation in the reaction of alkyl halides with a mobile halogen atom, for example, allyl bromide, is manifested by a decrease of the induction period[83].

The effectiveness of the influence of γ-radiation on the direct synthesis of organotin compounds stimulated research on the role of γ-radiation in the direct synthesis of organogermanium compounds. The influence of radiation and the reaction between germanium and alkyl bromides has been studied by Kocheshkov and coworkers[84,85]. It has been shown that γ-radiation has different effects on the direct synthesis of organogermanium compounds in the liquid and gas phases. Under steady-state conditions, gaseous butyl bromide reacts with germanium powder at 240° C over a period of 13 h only to an extent of 10–12%, while on γ-irradiation (at a dose rate of 100 rad s^{-1}) the extent of the reaction is 20–25% even at 160° C, i.e. the temperature of the onset of the reaction under irradiation conditions is reduced by 100° C. At 220–230° C the germanium charge has been consumed to an extent of 80–85%, i.e. almost quantitatively. The radiation-chemical consumption of germanium (at 200° C) after 13 h amounts to 5×10^2 mol./100 eV, which indicates a chain mechanism of the process. In the liquid phase the influence of γ-radiation is much weaker: the temperature thresholds of the reactions of germanium with butyl bromide and hexyl bromide are reduced by only 20° C. The temperature dependence of the degree of reaction also shows that the thermal stage plays an important role in the liquid phase. The radiation-chemical consumption of germanium in the liquid phase is ~ 50 mol./100 eV.

The quantitative compositions of the products obtained under the influence of γ-radiation in the gas and liquid phases are different. In the liquid-phase reaction the main product is tribromobutylgermane, as in the experiments without irradiation. A mixture of tribromobutylgermane and germanium tetrabromide in proportions of 1 : 3 is obtained in the gas phase. The radiation-chemical yields of tribromobutylgermane in the liquid and gas phases are approximately the same, amounting to 50 mol./100 eV under the following conditions: 200° C, reaction time 13 h. Thus γ-radiation makes it possible to reduce appreciably the temperature of the reaction of germanium with gaseous alkyl halides, but it leads to the formation of an undesirable product—germanium tetrabromide. The process occurring in the gas phase under the influence of γ-radiation can be driven towards the formation of organogermanium compounds by adding copper. In the presence of copper, the content of germanium tetrabromide in the reaction mixture decreases and the yield of tribromobutylgermane increases[84,85].

V. THE EFFECT OF RADIATION ON THE RADICAL REDISTRIBUTION REACTION

If it is assumed that the rate of the radical redistribution reaction

$$R_4M + MX_4 \rightleftarrows \Sigma R_nM_{4-n}$$

depends on the M–C bond strength, one may postulate a stimulating effect of γ-radiation since the molecules of the initial organometallic compounds decompose in the field of ionising radiation at the M–C bond[23–26,29].

Kocheshkov et al.[86] found that the reaction between tetra-alkylstannane and germanium tetrahalide in the field of γ-radiation can be carried out at room temperature. In the absence of radiation the analogous reaction takes place above 200° C.[87,88]

The reaction between tetra-alkylstannane and germanium tetrahalide takes place with transfer of only one organic group regardless of the initial reactant ratio, in contrast to the analogous reaction between tetra-alkylstannane and tin halides. Under the joint influence of radiation and an increased temperature, the abstraction of a second organic group from tetra-alkylstannane is observed, but only monosubstituted organogermanium compounds are formed[27]. The reaction proceeds in accordance with the equation

$$R_4Sn + 2GeHal_4 \rightarrow R_2SnHal_2 + 2RGeHal_3 \ .$$

The thermal radical redistribution reaction between tetra-alkylstannane and germanium tetrahalides takes place only in the presence of a catalyst. Under the influence of radiation, the reaction may be carried out at 200° C with transfer of a single organic group[89].

VI. REACTIONS UNDER THE INFLUENCE OF IONISING RADIATION NOT INVOLVING THE METAL–CARBON BOND

Chlorination, oxidation, and polymerisation reactions, which are fairly well known in the radiation-chemical synthesis of organic compounds, can be in principle initiated by irradiation of the organic group[2–4]. However, there are few experimental data concerning Group IVB elements. Dzhagatspanyan and coworkers[90–93] investigated the radiation-chemical chlorination of organochlorosilanes. The radiolysis of a mixture of chlorine and dichlorodimethylsilane leads to the formation of a 30% yield of a monochloro-substituted product with traces of a dichloro-product. The composition of the chlorination products is

independent of temperature and the yield is only slightly temperature dependent. The yield is also independent of the dose rate, but decreases significantly in the presence of oxygen. In the reactions of dichloromethylphenylsilane and trichlorophenylsilane the result depends significantly on temperature. Vigorous incorporation of chlorine in the benzene ring, analogous to that in photochemical chlorination, is observed in the range 0–20°C, but above 100°C ring substitution begins; both processes take place simultaneously at intermediate temperatures. Oxygen does not inhibit the reaction at 100–150°C, which suggests an ionic reaction mechanism. Substitution in the methyl group was not observed under the conditions of radiation-chemical chlorination.

Table 1. Radiation-induced reactions of silicon, germanium, tin, and lead compounds.

Compound	Irradiation conditions	Radiolysis products	Radiation-chemical yield, mol./100 eV	References
R_4Si	electron-beam decomposition gas phase, 150°C	Si	—	15, 16
	X-rays, gas phase, 4.2×10^{17} eV ml^{-1}	H_2, C_2H_6, CH_4, $C_2H_5Si(CH_3)_3$, $(CH_3)_6Si_2$	>10	18, 19
	γ-rays, solid phase, −130–−180°C	—	~5	20–22
	liquid phase, 25°C	CH_4, $(CH_3)_3Si-CH_2CH_2-Si(CH_3)_3$, $(CH_3)_3Si-CH_2-Si(CH_3)_3$	>10	23
R_4Ge	γ-rays, 24 h, 100 rad s^{-1}	Ge	—	27
$RGeCl_3$	solid phase, −196°C	$HGeCl_3$, $GeCl_4$	—	14
$GeCl_4$	solid phase	—	0.5	25, 26
R_4Sn	γ(^{60}Co), solid phase, 200°C, 100 rad s^{-1}	Sn	—	27
	X-rays, liquid and solid phases	$R_3Sn^{\cdot}$, $R_3SnCH_2^{\cdot}$	—	28–31
R_3SnCl	γ(^{60}Co), solvent, 25°C	R_4Sn, R_2SnCl_2, $SnCl_4$, R_2SnO	—	28
R_4Pb	γ(^{60}Co), solid, liquid, and gas phases	Pb	—	33–35

Table 2. The influence of irradiation on the reactions of free radicals with alkyl halides (direct synthesis).

Reactants	Reaction conditions	Radiation-chemical yield, mol./100eV	Chemical yield, %	Reaction products	References
Sn + RBr	γ(^{60}Co), liquid phase, 25–100°C	~10^3	80 (w.r.t. Sn charge)	R_2SnBr_2, R_3SnBr, $SnBr_2$	70–82
Sn+CH_2=CH−CH_2Br	γ(^{60}Co), 25°C)	—	—	$(CH_2=CH-CH_2)_2SnBr_2$, $[(CH_2=CH-CH_2)_2SnBr_2]_n$	83
Ge + RBr	γ(^{60}Co), liquid phase, 100 rad s^{-1}, 250°C	~10^1	50 (w.r.t. Ge charge)	$RGeBr_3$	84–85
Ge + RBr	γ(^{60}Co), gas phase, 150–200°C	~10^2	50 (w.r.t. Ge charge)	$RGeBr_3$, $GeBr_4$	85

Table 3. The influence of irradiation on reactions leading to the replacement of an organic substituent or a functional group at the metal atom.

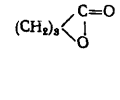
Reactants	Reaction products	Irradiation conditions	Radiation chemical yield, mol./100 eV	Chemical yield, %	Refs.
$R_4Sn + GeCl_4$	R_3SnCl, $RGeCl_3$	γ(^{60}Co), 20 Mrad, 25°C	—	50–90	86
$R_4Ge + GeBr_4$	R_2GeBr $RGeBr_3$	γ(^{60}Co), 10 h, 100 rad s^{-1}, 250°C	200	70–80	27, 89
$R'Cl + R_kHSiCl_{4-(k+1)}$	$R'R_kSiCl_{4-(k+1)}$	50–150°C	100–600	60–80	99, 103
 $+HSiCl_3$	$Cl_3SiOSiCl_2$, 	γ(^{60}Co), 0.185 Mrad h^{-1} 25°C	—	33–81	104

Table 4. The influence of irradiation on the hydrometallation reaction.

A	Reaction products	Chemical yield, %	Radiation-chemical yield, eV mol./100 eV
$(C_2H_5)_3SnH$ + A [25°C, γ (^{60}Co), 2 × 10^6 rad] (Refs.56–58)			
CH_2=CHC_6H_{11}	$(C_6H_{11})_3SnC_2H_5$	74.5	1000
CH_2=CHC_6H_{13}	$(C_6H_{13})_3SnC_2H_5$	77	1000
CH_2=CHC_8H_{17}	$(C_8H_{17})_3SnC_2H_5$	96	1000
C_6H_5CH=CH_2	$(C_2H_5)_3SnCH_2CH_2C_6H_5$	50	700
C_6H_5C≡CC_6H_5	$(C_6H_5)_3SnC_6H_5C$=CHC_6H_5	70	800
C_6H_5C≡CH	$(C_2H_5)_3SnCH$=CHC_6H_5	87.5	1200
CH_2=$CHCH_2OH$	$(C_2H_5)_3SnCH_2CH_2CH_2OH$	92.7	1500
CH_2=$CHOC_6H_5$	$(C_2H_5)_3SnCH_2CH_2OC_6H_5$	80	1300
CH_2=$CHOC_4H_9$	$(C_2H_5)_3SnCH_2CH_2OC_4H_9$	88	1300
CH_2=$CHCOOCH_3$	$(C_2H_5)_3SnCH_2CH_2COOCH_3$	74	1200
$(C_4H_9)_3SnH$ + A (25° C, 2 × 10^6 rad) (Ref.56–58)			
CH_2=CHC_6H_{11}	$(C_6H_{11})_3SnC_2H_5$	85.9	960
CH_2=CHC_6H_{13}	$(C_6H_{13})_3SnC_2H_5$	70	750
C_6H_5CH=CH_2	$(C_6H_5)_3SnCH_2CH_2C_6H_5$	97	2100
C_6H_5C≡CC_6H_5	$(C_6H_5)_3SnC_6H_5C$=CHC_6H_5	80	720
CH_2=$CHCH_2OH$	$(C_4H_9)_3SnCH_2CH_2CH_2OH$	84	2000
CH_2=$CHOC_6H_5$	$(C_4H_9)_3SnCH_2CH_2OC_6H_5$	92	1300
CH_2=$CHOC_4H_9$	$(C_4H_9)_3SnCH_2CH_2OC_4H_9$	99	1100
CH_2=$C(CH_3)COOCH_3$	$(C_4H_9)_3SnCH_2CH(CH_3)COOCH_3$	90.7	1000
CH_2=$CHCONH_2$	$(C_4H_9)_3SnCH_2CH_2CONH_2$	75	950
$(C_6H_{13})_3SnH$ + A (25° C, 2 × 10^6 rad) (Refs.56–58)			
CH_2=CHC_6H_{13}	$(C_6H_{13})_3SnCH_2CH_2C_6H_{13}$	73.6	700
CH_2=$CHCH_2OH$	$(C_6H_{13})_3SnCH_2CH_2CH_2OH$	80	1200
$HSiCl_3$ + A [25°C, γ (^{60}Co), 3–9 Mrad] (Refs.38,46,47,52)			
ClCH=CHCl	$CH_2ClCHClSiCl_3$	27	—
CF_2=CF_2	$CHF_2CF_2SiCl_3$	11	—
CH_2–CH_2–CH_2CH=CH	$C_4H_9SiCl_3$	96	—
CF_2CF=CF_2	$(C_3HF_6)SiCl_3$	95	—
CH_2=$CH-CF_2CF_2$	$C_3F_5(CH_2)_2SiCl_3$	—	—
CH_2=$CH-CF_2-CF_2-CF_3$	$C_3F_7(CH_2)_2SiCl_3$	52	—
H_2C=$C(CH_3)-CF_2-CF_3$	$C_3F_7CH(CH_3)CH_2SiCl_3$	11	—
CH_2=$CH-CH_2Cl$	$ClCH_2(CH_2)_2SiCl_3$	40	—
	$H(CH_2ClCHCH_2)_2SiCl_3$	34	—
CH_2=$CH-CH_2-COO-CH_3$	$CH_3COO(CH_2)_2SiCl_3$	22	—
	$H(CH_3COOCH_2CHCH_2)_2SiCl_3$	71	—
CH_2–$CH(CH_2CH$=$CH_2)$–CH_2–CH=CH	$C_6H_{10}(CH_3)SiCl_3$	92	—
CH_2=$CH-OCOCH_3$	$Cl_3SiCH_2CH_2OCH_2CH_3$	—	—
	$Cl_3SiCH_2CH_2OCOCH_3$	—	—
	$Cl_3SiOSiCl_3$	—	—
$F_3C-(R)C$=$CCl-CF_3$	$Cl_3Si(R)C-CHCl-CF_2-CF_3$	12.8	—
	$Cl_3Si(R)C-CF_2-CH_2-CF_3$	—	—
RCl_2SiH + A [25°C, γ (^{60}Co)] (Refs. 38,46,47,53,54)			
CH_2-CH=$CH-CH_3$	$C_2H_4CH(CH_3)SiRCl_2$	57	—
$CH_2-C(CH_3)$=$CH-CH_3$		30	—
CF_2-CF=CF_2	$(C_3HF_4)SiRCl_2$	85	—
CH_2=$CH-CF_2-CF_2-CF_3$	$C_3F_7(CH_2)_2SiRCl_2$	23	—
CH_2=$CH-CH_2Cl$	$ClCH_2(CH_2)_2SiRCl_2$	4	—
CH_2–CH=$CH-CH_2$–CH_3	$C_6H_5SiRCl_2$	20	—
CF_2-CF_2-CCl=CR	$RCl_2Si(R)CCF_2-CF_2-CHCl$	12.8	—
R_nSiH_{4-n} + A [50°C, γ (^{60}Co), gas phase] (Refs.39,41,42)			
CH_2=CH_2	$(R_nSiH_{3-n})CH_2-CH_3$	—	—
$(C_6H_5)_3SiH$ + A [γ(^{60}Co)] (Refs.43–45)			
CH=$CH-CH_2-CH_2-CH_2-CH_3$	$(C_6H_5)_3Si-CH-CH_2-CH_2-CH_2CH_3$	66	200
RCH=CH_2	$RCH_2-CH_2Si(C_6H_5)_3$	—	—
CH_2=$CH-Si(C_6H_5)_3$	$(C_6H_5)_3SiCH_2-CH_2-Si(C_6H_5)_3$	20	—

Irradiation of triethylvinyl-, trimethoxyvinyl-, triethoxyvinyl-, diethylvinyl-, dichloromethylvinyl-, and trichlorovinyl-silanes with ^{60}Co γ-rays leads to the formation of a viscous polymer with a radiation-chemical yield ranging from 20 to 320 mol./100 eV.[94,95] Both γ-initiated polymerisation and polymerisation under the influence of

β-rays have been investigated for allyl derivatives of silicon[96]. Triethylvinylstannane and triphenylvinylstannane polymerise[97] in the field of γ-radiation at 80°C with a radiation-chemical yield of 140–220 mol./100 eV. The polymerisation product consists mainly of dimers and trimers.

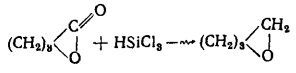
Certain reactions leading to a change in the mobile groups at the metal atom in the field of radiation have been described. The homolytic reduction of organic halides by silicon hydrides in the field of ^{60}Co radiation or in a stream of accelerated electrons, observed in early investigations[98], takes place under comparatively mild conditions:

$$RCl + HSiR'_3 \rightsquigarrow R'_3RSi + HCl \quad .$$

The reaction has been studied in a series of investigations by Zimin and coworkers[99–103]. The authors showed that, under the most severe conditions of synthesis, the temperature does not exceed 300°C, i.e. is less than the temperature of the radiation-chemical decomposition of organochlorosilanes. Fluorinated organic halides react at a lower temperature (100–120°C) than the non-fluorinated compounds (170–180°C), which has been shown for chlorobenzene and pentafluorobenzene. The activation energies for the reactions are respectively 2–4 and 12–13 kcal mole^{-1}. The average radiation-chemical yield is 600 mol./100 eV and a quadratic relation has been observed between the radiation-chemical yield and the dose rate.

The authors[99–103] concluded that the radiation-chemical reduction of organic halides by silicon hydrides is of interest as a convenient method for synthesising organosilicon compounds. The data obtained are sufficient to design an enlarged radiation-chemical plant for the synthesis of organochlorosilanes[102].

Inorganic silanes may be used for the radiation-chemical reduction of organic compounds: the quantitative synthesis of cyclic ethers from lactones has been described[104]:



In conclusion we may note that ionising radiation has a significant influence in many instances (Tables 1–4)† on the chemical reactions of the elements under consideration. This factor can be used successfully in practical synthesis.

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†In the tables R stands for aliphatic radical and $\gamma(^{60}Co)$ for γ radiation from a ^{60}Co source. As in the original reports, the tables list the maximum yields.

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Karpov Physicochemical Institute,
Moscow