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ABILITY OF ELEMENTS TO FORM POLYMERS WITH INORGANIC CHAIN MOLECULES

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The chemistry of organoelemental compounds is being intensively developed as an independent branch of chemistry in the direction of studying the general regularities of the formation and transformation reactions of the organoelemental compounds, the investigation of the reactivitv of various compounds, and also in the field of the synthesis and study of the properties of high-molecular-weight compounds.

The development of the chemistry of high-molecular--weight organoelemental compounds is linked not only with the study of the transformation reactions of the monomeric compounds into polymers, but also with the investigation of the possible uses of various elements and their compounds for the synthesis of polymers. The synthesis of organoelemental polymers is complicated by the variety, not only of monomeric compounds, but also of elements whose monomeric compounds can be used for this purpose. Therefore we consider some aspects of the theory which characterise the ability of various elements to form homo- and hetero--chain polymers. Polymers which do not contain carbon atoms in the chain are known as polymers with inorganic main-chain molecules, framed‡ by various organic, inorganic, and organoelemental groups.

At present the general principles which determine the formation of inorganic chains of molecules of various elements have been insufficiently worked out, and the known reactions for the synthesis of polymers, for example, polyorganosiloxanes, are always accompanied by the formation of cyclic compounds, which serve as "monomers" for the synthesis of high-molecular-weight compounds.

The use of inorganic cyclic compounds framed by organic groups for the production of polymers is also linked with the fact that unsaturated compounds of the general formulae $R_nE{=}O$ and $R_nE{=}ER_n$, capable of polymerising through the double bonds, as in the synthesis of organic homo- and hetero-chain polymers[1-3], have not yet been obtained.

An attempt will be made here to establish the most important factors which determine the ability of elements to form inorganic rings and chain molecules, framed by organic and organoelemental groups. It is evident that the routes to the formation of inorganic rings and chain molecules are extremely varied, not only on account of the large number of elements which can be used to construct these chains, but also on account of the diverse types of chemical bonds which may be used in the formation of cyclic and chain polymeric compounds.

Two types of chemical bonds play an important part in the formation of polymers with inorganic chain molecules: covalent and coordination. They can be the basis for the formation of large molecules of various structures. Aggregates, consisting of a large number of ionic particles bound to one another by ionic bonds, for example, ionic crystals, cannot be considered as proper molecules, and such structures are not true polymers, although they consist of a large number of structural units. It is true that covalent bonds between elements with different electronegativities have polar character, or, in other words, are partly ionic, preventing the strict demarcation of polymers with inorganic chain molecules from ionic aggregates (crystals). Usually ionic aggregates have a three-dimensional structure, whereas for polymers there is greater interest in chains of linear, branched, or network type of molecular structure. The present review considers mainly polymers with chain molecules of such structure, for otherwise we would have to consider a large number of inorganic compounds going beyond the bounds of polymer

‡ Not considered in the text of the review.

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‡ The term "framed" presumably means having side-groups of the type mentioned (Ed. of Translation).

chemistry (for example, borides, silicides, silicates, and phosphides), although in broad conception they can be classified as high-molecular-weight compounds. Coordination polymers will also not be considered here. Polymers with inorganic chain molecules can also be formed using multicentric bonds, characteristic, in particular, of the boron hydrides [4-6]. However, such compounds have low stability, oxidise and hydrolyse readily, and also will not be considered here. Hence this article considers the ability of elements to form polymers with inorganic chain molecules framed by organic and organoelemental groups of the covalent and ionic type of chain structure.

General consideration of the experimental material both on homocyclic compounds and on compounds with chain molecules shows that unlike organic chemistry homo-rings play a lesser part and homo-chain molecules with a high degree of polymerisation are not formed. This is the result of the essential difference between the properties of carbon and those of other elements (and even of the non-metals of Periodic Group IV), in terms of ability to form stable chains or cyclic compounds consisting of the same atoms.

On the one hand, the energy of the C–C bond is greater than the E–E bond of other elements (Table 1), and on the other hand the C–C bond is chemically more inert than the E–E bond of other elements.

Carbon forms various types of chain molecules based on the C–C bond: linear, branch, network, cyclic. For other elements – either non-metals or metals – the formation of homo-chain molecules with a significant degree of polymerisation is not characteristic. Only compounds containing short E–E chains are known. For example, silicon forms long chains in the molecule $Si_{25}Cl_{52}$ where 25 atoms of silicon are directly linked [10], but this compound is unique and in other homologous series the highest terms are $Si_{10}F_{22}$,[11] Si_4Br_{10},[12] Si_6H_{14}.[13] The longest Si–Si chain with organic side-groups is the molecule $Si_9(C_6H_5)_{16}(CH_3)_4$, where nine silicon atoms are directly linked [14]. Recently a series of polymeric compounds with P–P bonds has been described [15], but a very large degree of polymerisation was not attained.

On the contrary, the possibility of forming organoelemental hetero-chain molecules is much wider than in carbon chemistry, but the realisation of such possibilities is not always clear, since they are linked with the properties of various elements to form stable cyclic and chain molecules with one another. The tendency of various elements to form cyclic compounds and chain molecules depends on the chemical properties of the elements and, in particular, their electronic structure. We consider that an important factor determining the ability of an element to form hetero-chain polymeric molecules is its electronegativity and the electronic hybridisation of its atoms [16].

TABLE 1. E–E bond energies.

Bond	Bond energies			Bond	Bond energies		
	Ref. 7	Ref. 8	Ref. 9		Ref. 7	Ref. 8	Ref 9
C–C	83.1	66.2	64	As–As	32.1	35	38
Si–Si	42.2	45	50	Sb–Sb	30.2	29	34
Ge–Ge	37.6	45	40	S–S	50.9	54	50
N–N	38.4	21	32	Se–Se	44.0	41	42
P–P	51.3	48	50				

TABLE 2. Electronegativities of the elements, after Pauling [7].

Li 1.0	Be 1.5	B 2.0											C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5											Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.8	Zn 1.9	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.8	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.8	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.5	U 1.7	Np–Po 1.3										

Consideration of the electronegativity of various elements (Table 2) shows that carbon occupies a central position between the most electronegative element, fluorine ($x_F = 4.0$) and the most electropositive element, caesium ($x_{Cs} = 0.8$).

Therefore carbon has the least tendency to donate or receive electrons, that is, to form positive or negative ions and less to submit to electrophilic or nucleophilic attack. This is one of the reasons for the stability of carbon chain molecules. Other elements possessing electronegativity close to carbon, for example, sulphur and selenium, are also characterised by an ability to form long chains of similar atoms, S–S or Se–Se. This explains also why other elements form less stable homo-chain structures.

If an element has an electronegativity greater than that of carbon, the homo-chain is of low stability on account of the tendency to produce electrons. Therefore long chains or rings consisting of N–N or O–O bonds are unstable. If the electronegativity of an element is less than that of carbon, the stability of the E–E bond is diminished, on account of the tendency to yield electrons. Hence B–B, Si–Si, P–P, As–As, and Ge–Ge bonds are readily oxidised and are less stable than the C–C bond.

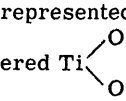
The great stability of bonds between atoms of elements of different electronegativities (greater and less than for carbon) is probably linked with the compensations of opposite tendencies of the atoms which form the chain to give and receive electrons. Comparison of the mean electronegativities of the interconnected elements shows that for many pairs of elements the mean value is close to the electronegativity of carbon. Inorganic hetero-rings and polymers with organic side-groups, formed by alternation of two interconnected elements, have mean electronegativities differing from that of carbon by 0.35–0.40 units [17]. The following pairs of elements, for example, fall within this interval:

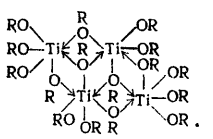
B–N	Al–N	Si–N	Ge–N	Ti–N	Sn–N	(Pb–N)
B–O	Al–O	Si–O	Ge–O	Ti–O	Sn–O	Pb–O
B–S	(Al–S)	Si–S	Ge–S	(Ti–S)	Sn–S	Pb–S
P–N	As–N	(Sb–N)	S–N	Se–N	—	—
P–O	As–O	Sb–O	—	Se–O	Mo–O	W–O
P–S	As–S	Sb–S	S–S	Se–S	—	—

For all these pairs, except those in parentheses, inorganic rings [16,18] and some polymers [3,4,19] have been described. It should be noted that the concept of electronegativity relates to a simple bond of the interconnected elements and does not take into account that in molecules it

is possible for additional donor–acceptor bonds to be formed, unshared electron pairs to be delocalised, multicentric bonds to be formed, induction effects to operate, etc.[20]

An important factor, determining the ability of an element to form hetero-rings or hetero-chains, with organic side-groups, is the characteristic hybridisation of the electron cloud of the elements. It is determined by the number and direction of the chemical bonds, the presence or absence of unshared electron pairs and free orbitals, and also by the coordination number of the elements. Of course, the coordination number, that is, the number of atoms of one element with which the atoms of another element can be bound, is determined by steric factors (that is, the relation between the dimensions of the given atoms) as well as by electronic hybridisation.

Fundamentally, the coordination number (c.n.) of elements of the second period of the Periodic System is not greater than four. With elements of the third period the c.n. can reach 6, but the corresponding configuration is unstable. With elements of the fourth and fifth periods a higher c.n. is easily effected. The elements of these periods form octahedral structural units (at c.n. = 6), which readily unite to form monocyclic compounds and linear polymers and often form polymers with other types of structures, in particular, polycyclic coordination polymers. For example, the tetramer tetraethoxytitanium $[Ti(OC_2H_5)_4]_4$ is not a monocyclic coordination compound, as might be expected, and its molecule consists of four octahedra with Ti atoms at the centre, joined at the vertices[21], which can be represented by a structural formula containing four-membered TiTi rings:



Inorganic rings and chain molecules are formed by alternation of two elements of different electronegativity, therefore it is important to consider, on the one hand, elements having an electronegativity greater than that of carbon (that is, oxygen and nitrogen) and, on the other, elements having an electronegativity less than that of carbon, in particular the non-transition elements: boron, aluminium, silicon, germanium, tin, lead, titanium, phosphorus, arsenic, and antimony. Sulphur and selenium, which have an electronegativity close to that of carbon, occupy an intermediate position.

The electronegative elements, oxygen and nitrogen, have the following structure of the valency electron shells:

$$\text{oxygen} - 2s^2\ 2p_x^2p_y^1p_z^1,$$

$$\text{nitrogen} - 2s^2\ 2p_x^1p_y^1p_z^1,$$

and form chemical bonds by virtue of the p orbital. Covalent bonds, using p orbitals, are separated by an angle of 90°. Both oxygen and nitrogen retain unshared electron pairs. They can form additional coordinate bonds or be delocalised intramolecularly into free orbitals of the element bonded with the oxygen or nitrogen. This means, in other words, the participation of the unshared pair of electrons in electronic hybridisation with the p orbitals which leads to a change in the valence angle of oxygen or nitrogen from 90° to greater values. Therefore the angle of the N< or O< bonds can indicate the delocalisation of the unshared electron pairs or their partial participation in hybridisation with the p orbitals. In inorganic hetero-rings there is the same phenomenon: the angles of the R–N< and O< bonds vary widely, depending on the elements with which they are connected.

Thus the valence angle of oxygen in a ring varies from 112° ± 4° in trimethylboroxole[22] to 142.5° in octamethylcyclotetrasiloxane[23]. The valence angle of nitrogen in a ring varies from 91.7° ± 2° in *N*-bis(trimethylsilyl)tetramethylcyclodisilazane[24] to 131° in octachlorocyclotetraphosphazene[25] and octamethylcyclotetraphosphazene[26].

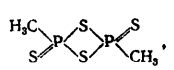
Since the valence angle can change over a wide range, oxygen, nitrogen, and sulphur have a great possibility of forming heterocyclic and hetero-chain polymeric compounds with many less electronegative elements.

Sulphur, as the electronegative element of a hetero-ring, is usually bivalent. The same can be said about selenium. The valence electrons of sulphur and selenium are disposed thus in the outer shell:

$$S^{II} \text{ and } Se^{II};\ s^2;\ p_x^1p_y^1p_z^1.$$

Evidently sulphur and selenium in the divalent state form p^2 bonds with a valence angle of 90°. This value is also observed in hydrogen sulphide, SH_2, but in the homo-ring S_8 it even acquires the value 107°.[27,28] The valence angles of sulphur in inorganic hetero-rings also vary over a wide range — from 75° in tetramethylcyclodisilthiane[29] to 138° in tribromoborosulphone[30].

However, sulphur has a tendency to form bonds of small angles: in the compound:



the valence angle of the sulphur in the ring is 84°,[31] but in hexamethylcyclotrisilthiane it is 110°.[29] In this connection the valence angle in tribromoborosulphone seems excessively large. Sulphur easily forms valence angles less than 90°, which facilitates the formation of four-membered rings with boron, silicon, and phosphorus, whereas not a single oxygen-containing four-membered ring is known (excepting coordination rings) and only one nitrogen-containing four-membered ring (S_2N_2). Hence the conclusion that the valence angles of nitrogen, sulphur, and oxygen are not the decisive influence on the formation of inorganic rings since they can be varied over a wide range of values and probably will not impede cyclisation with any less electronegative partner-element. However, they can determine the number of groups of interbonded elements in the hetero-ring and facilitate the formation of only one or two more sterically favourable hetero-rings from a whole series of possible ones. For example, 6-, 8-, 10-, and 12-membered hetero-rings, etc., with Si–O bonds are known, but Si_2O_2 hetero-rings are unknown. The hetero-rings Si_2N_2, Si_3N_3, Si_4N_4 are known, but the hetero-rings Si_5N_5 and Si_6N_6 are not known, although their oxygen analogues have been obtained[18].

There are now experimental data which show that combination of an element with oxygen leads to the formation of long E–O–E–O– chains more easily than combination of the element with nitrogen or with sulphur. In the case of

E–N and E–S alternations the tendency to ring formation is more sharply expressed and this probably explains why long E–N–E–N or E–S–E–S chains have not yet been obtained and why attempts to prepare them result only in derivatives of the corresponding rings. An exception is provided by the phosphazenes, but in such derivatives the valence angle of the nitrogen is greater and reaches values characteristic for oxygen. Evidently a small valence angle for an electronegative element facilitates cyclisation and hinders the formation of long chains. Hence the conclusion not only about the significance of steric factors but also that oxygen-containing inorganic polymeric chains are capable of reaching a high degree of polymerisation.

The value of the bond angle of an electronegative element is also determined by the number of atoms in an inorganic hetero-ring. For example, comparing the known hetero--rings of silicon formed by alternation of silicon with oxygen, nitrogen, and sulphur:

$$\underline{Si_2O_2}\ \underline{Si_4O_4}\ Si_5O_5\ Si_6O_6\ \ldots\ Si_nO_n$$
$$Si_2N_2\ \underline{Si_3N_3}\ \underline{Si_4N_4}$$
$$\underline{Si_2S_2}\ \underline{Si_3S_3}\ Si_4S_4$$

(rings which are formed readily are underlined), we can conclude that on passing from oxygen-containing to nitrogen- and sulphur-containing cyclic compounds of silicon the tendency towards formation of lower-molecular-weight rings grows simultaneously with a decrease in the valence angle of the electronegative element.

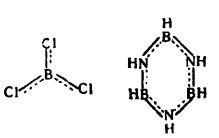
Let us now consider the hybridisation of elements more electropositive than carbon.

The atoms of Group III of the Periodic System (main subgroup): boron, aluminium, gallium, indium, thallium, are characterised in their compounds by sp^2 and sp^3 hybridisation: the latter is observed in the formation of an additional coordinate bond.

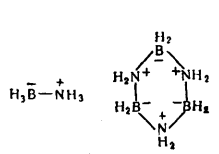
For boron sp^2 hybridisation is particularly characteristic. It determines the planar distribution of the bonds at an angle of 120°. This explain the planar structure of such molecules as $B(CH_3)_3$, BF_3, BCl_3, and the comparative ease of formation of B_3N_3 and B_3O_3 planar hetero-rings.

The elements of Group III have a free p orbital which can be used by an unshared pair of electrons. With boron this can take place in two ways:

1. Intramolecular delocalisation of unshared electron pairs of an element bonded to boron (the formation of additional π bonds between boron and the element bonded to it):



2. The formation of coordinated monomeric and cyclic compounds of boron (with sp^3 hybridisation of σ bonds between boron and the element bonded to it):



In this case the bonds to boron are tetrahedrally directed, as in the carbon atom.

The advantageous valence angle of boron (120°) and the possibility of using its vacant p orbital can evidently explain the fact that in all the reactions the formation of only 6-membered B_3N_3 and B_3O_3 rings is observed.

The formation of an 8-membered B_4N_4 ring [32] or the linear chain B–N–B–N– (with a low degree of polymerisation) [33] is observed only when the formation of a six-membered ring is sterically hindered.

With aluminium, gallium, indium, and thallium the tendency to use free p orbitals is still greater than with boron, which leads to the formation of compounds with coordination number 4 or even 6 (since these elements can use the d orbital). This leads, in particular, to the formation of coordinated rings and polymeric chains of aluminium, gallium, etc.

The elements of Group IV of the Periodic System have four electrons in the valency shell and with carbon three types of hybridisation are possible:

sp^3 four σ bonds (tetrahedral direction);
sp^3 three σ bonds (triangular direction) + one π bond;
sp two σ bonds (linear direction) + two π bonds.

Carbon does not possess d orbitals. Hence in any hybrid state a carbon atom uses all its valency electrons and orbitals, that is, carbon has neither unshared electron pairs nor vacant orbitals.

The remaining elements of the principal subgroup of Group IV — silicon, germanium, tin, and lead (in the quadrivalent state) — possess empty d orbitals. Usually four valency electrons participate in sp^3 hybridisation while the d orbital remains vacant. Hence the structure of most of the compounds of these elements comprises a few united tetrahedra. The tendency to form p_π bonds is quite insignificant for these elements and therefore the elements Si, Ge, Sn, and Pb do not form stable monomeric compounds with double bonds of the type Si=E, Ge=E, Sn=E, and Pb=E. The hybrid states sp and sp^2 are uncharacteristic for these elements and they always change into the sp^3 hybrid state. This is important in the chemistry of inorganic rings and polymers with inorganic chain molecules, for thanks to the instability of the sp and sp^2 hybrid states, the derivatives of silicon, germanium, tin, and lead, which from their composition should possess multiple bonds, polymerise to form rings or polymeric chains of various structures. For example, all compounds with the general formulae R_2SiO_2, R_2SiNR', and R_2SiS are polymerised with the formation of cyclic or polymeric structures [1-3,18].

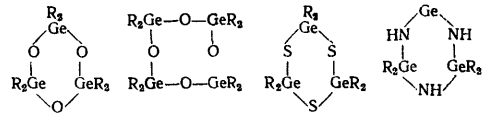
The existence of five vacant d orbitals of silicon would in principle permit the formation of another five coordination bonds by filling them with unshared electron pairs of another element, but this is almost impossible sterically. The c.n. of silicon reaches six in the anion $[SiF_6]^{2-}$ and in certain complexes of SiF_4 with amines, which becomes possible owing to the small dimensions of the fluorine atom. With increase in the dimensions of the ligand the c.n. of silicon diminishes: the ion $[SiCl_6]^{2-}$ is unstable and the similar ion with bromine is generally not formed.

In relation to oxygen, silicon usually exhibits c.n. = 4, but some examples are known in which the silicon is linked with six oxygen atoms, for example, in an acetylacetonato--complex [34]. Silicon with c.n. = 5 is formed in an intermediate complex in several chemical reactions [35]. This is important in the chemistry of inorganic rings and polymers based on silicon, since such intermediate complexes appear

in the reactions of ring opening, telomerisation, and polymerisation by both electrophilic and nucleophilic reagents [3,18].

The presence of the empty *d* orbitals of the silicon atom brings about intramolecular delocalisation of the unshared electron pairs from atoms of oxygen, nitrogen, and chlorine bonded to the silicon. This leads to the appearance of double-bonding between such elements as Si–O, Si–N, and Si–Cl. In the chemistry of inorganic rings and polymeric chains this plays a determinative role and is probably one of the factors affecting the thermal stability of these compounds.

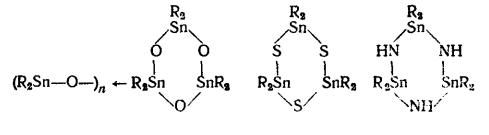
Similar conclusions can be drawn for germanium, tin, and lead. Germanium compounds of type R_2GeO, R_2GeNR', and R_2GeS are not monomeric. Cyclic and polymeric diorganogermoxanes [36] and trimeric organogermathianes $[R_2GeS]_3$ [37] have been described. It is interesting to note that the molecular weight of R_2GeNH ($R = C_2H_5$) is close to that of a trimer [38] which indicates a cyclic structure:



$(R_2GeO)_3$ $(R_2GeO)_4$ $(R_2GeS)_3$ $(R_2GeNH)_3$

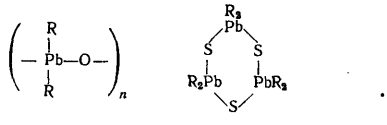
The molecular weight of the polymer $(R_2GeO)_n$ [36] is unknown.

Tin derivatives of the type R_2SnO, R_2SnS, and R_2SnNR' are also polymeric. Oxygen derivatives of tin compounds are described as linear polymers [39] and as cyclic trimers [40]. Sulphur-containing derivatives [41] and nitrogenous derivatives [42] are cyclic trimers:

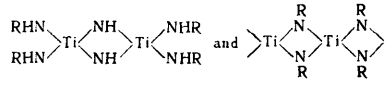


$(R_2SnO)_3$ $(R_2SnS)_3$ $(R_2SnNH)_3$

The lead derivatives of the types R_2PbO, R_2PbS, and R_2PbNR' have been little studied. The oxygen derivatives are described as linear polymers [39] and the sulphur derivatives have a tripled molecular weight [43] indicating a cyclic structure:



Titanium, zirconium, and hafnium are transition elements of the fourth group and the *d* orbitals play an important part in their electronic structure. The value c.n. = 6 is characteristic for these elements and in the case of Zr and Hf even reaches c.n. = 8. Therefore the chemistry of polymeric compounds with inorganic chain molecules takes another form for these elements and the monocyclic compounds of these elements are not formed as a rule. Here, coordination polymers predominate. Titanium, for which c.n. = 4 and 6, exhibits great possibilities for the formation of rings and polymers. Compounds of the type:

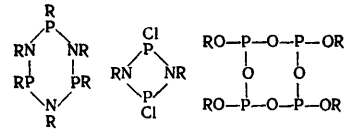


were recently described [44], reminiscent of silicon compounds with an analogous structure. When titanium has c.n. = 6, it forms polycyclic coordination compounds.

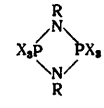
The elements of Group V have five valency electrons. Their valency is variable, and, depending on the distribution of the valency electrons in the orbitals, can be either three or five. In the case of phosphorus, arsenic, and antimony the following hybrid states are possible:

$$p^{III} - p^3;\ p^V - sp^3,\ sp^3d,\ \text{and}\ sp^3d^2.$$

The hybrid state p^3 plays a small part in the chemistry of inorganic rings and polymers. Only a few rings with tervalent phosphorus [43,45,46] are known:



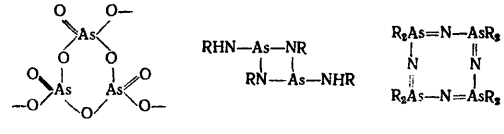
The hybrid state sp^3d is also rarely encountered in the chemistry of phosphorus and only a few cyclic compounds of this type [47,48]:



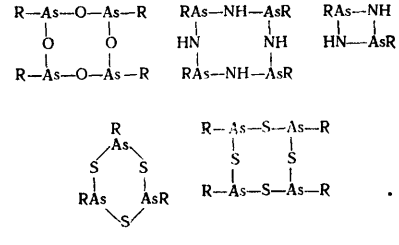
are known.

The most characteristic hybrid state of phosphorus is sp^3, which corresponds with the tetrahedral direction of the phosphorus bonds [49]. This hybrid state is encountered in all polymeric and cyclic compounds of phosphorus: in metaphosphates [49,50], phosphazene derivatives [51,52,53], and in phosphorus–sulphur compounds [54]. It is worth noting that phosphorus readily forms both cyclic and linear polymeric high-molecular chains.

In its compounds arsenic also usually displays the hybrid states p^3 (tervalent arsenic) and sp^3 (quinquevalent arsenic). A few cyclic arsenic compounds [55–57] and high-molecular-weight polyarsenates [4] have been described:



Compounds of the type RAsO, RAsNR', and RAsS are also known. Their molecular weights do not correspond to monomeric forms: RAsO [58] and RAsNH [59] are tetramers and RAsS trimers [58] and tetramers [60], which corresponds to the following cyclic compounds [61,62]:

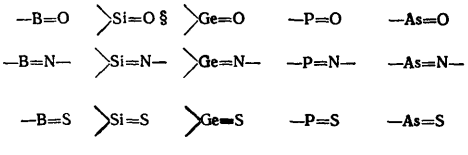


The elements of Group VI possess six valency electrons and exhibit the valencies 2, 4, and 6. Bivalent sulphur and selenium participate in inorganic rings and polymers as the electronegative element. As electronegative components sulphur and selenium enter inorganic rings and polymeric chains in the quadrivalent or sexivalent states respectively with p^3 (or sp^2) and sp^3 hybridisation. Cyclic compounds of sulphur with oxygen — for example $(SO_3)_x$ [63] — and nitrogen [64,65] are also now known. The non-transition elements under consideration can be divided into the following types: elements which after hybridisation have neither free orbitals nor unshared electron pairs (carbon); elements which after hybridisation have unshared pairs of electrons (nitrogen and oxygen); elements which after hybridisation have free orbitals [boron and aluminium (p orbitals), silicon and germanium (d orbitals)]; elements which after hybridisation have both unshared electron pairs and vacant orbitals (phosphorus, arsenic, antimony, sulphur, selenium, and tellurium).

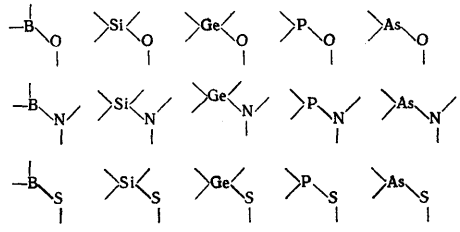
All transition elements have vacant orbitals, therefore they have a tendency to form mainly coordination rings and polymers.

As this classification indicates, carbon differs from all other elements (apart from hydrogen) in exhibiting neither free orbitals nor unshared electron pairs. In addition to its electronegativity, this property explains the especial stability of homo-chain structures with C–C bonds. Homo--rings and homo-chains of other elements, having an electronegativity close to that of carbon (for example, sulphur and selenium) enter into various reactions with electrophilic and nucleophilic reagents, on account of the existence of unshared electron pairs or vacant orbitals; therefore their reactivity is greater than for carbon chains.

As the examples given show, each element enters into the composition of an inorganic ring or polymeric chain in the hybrid state most stable and most characteristic for it. This explains the instability of the multiple bonds of some elements with oxygen, nitrogen, and sulphur. Not a single compound containing one of the following multiple bonds:

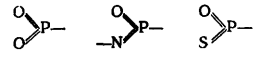


has yet been obtained. In such bonds boron, phosphorus(III), and arsenic(III) would have the hybrid state sp or p^2, which are uncharacteristic for them. Silicon and germanium would also have the sp^2 hybrid state, which is uncharacteristic of them. Therefore such monomeric compounds with multiple bonds, if they are formed, would probably be labile and consequently difficult to isolate. In all the reactions in which the formation of monomers with such bonds could be expected, only cyclic or polymeric compounds with the following structural units are always obtained:

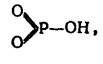


In such groups every element exhibits its stable hybridisation: boron sp^2, silicon sp^3, germanium sp^3, phosphorus(III) p^3, arsenic(III) p^3. Therefore, many compounds which in the initial period of development of organoelemental chemistry were considered monomers were shown by subsequent investigation to be cyclic or polymeric compounds. And now the literature contains descriptions of many compounds which are considered to be monomers with double bonds of the above type (in particular, in the chemistry of phosphorus, arsenic, and antimony), but the structure of these compounds was not studied and actually they are probably cyclic or polymeric compounds. The same can be expected of compounds of the types R_nEO, R_nENR', and R_nES, where E = Al, Ga, In, Sn, or Pb.

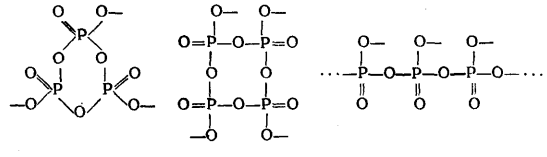
Electronic hybridisation also provides an explanation for the instability of the groupings:



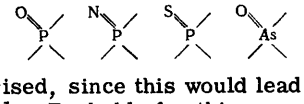
in which the phosphorus atoms have the sp^2 hybrid state, uncharacteristic of it. By polymerisation of such monomers phosphorus effects sp^3 hybridisation, which is more stable and characteristic of its quinquevalent state. Therefore, for example, metaphosphoric acid and its salts do not exist in the monomeric form:



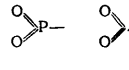
but only as cyclic or linear polymers:



On the basis of hybridisation it is possible to understand why other compounds which contain the same multiple bonds P=O, P=N, P=S (and also As=O, As=N–, and As=S–) are not polymerised. This occurs in those compounds in which the phosphorus(V) or arsenic(V) atom has a hybrid state most characteristic for it (sp^3). Compounds containing the grouping:



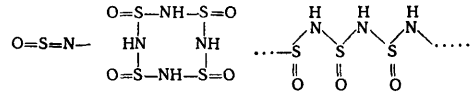
are not polymerised, since this would lead to the less stable hybrid state sp^3d. Probably for this reason compounds containing the groupings:



§ In mass-spectrographic investigations of polyorganosiloxane [66] the species $R_2Si{=}O$ were observed. They are formed in the depolymerisation of polyorganosiloxanes but cannot exist for any considerable time.

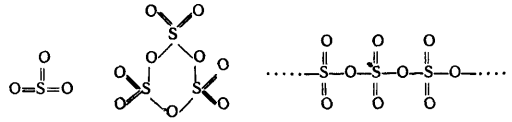
are polymerised only on account of one of the double bonds, which produces the hybrid state sp^3.

In the case of sulphur and selenium, the various hybridisations which are able to appear in a definite valency state, either monomeric compounds with multiple bonds or the corresponding cyclic and polymeric analogues can exist. For example, for quadrivalent sulphur the following compounds are known [65]:



although the hybrid states of sulphur in the monomer and in the polymers are different.

In the case of sexivalent sulphur the sp^3 hybrid state is more stable than the sp^2 hybrid state, therefore sulphur trioxide polymerises with formation of a cyclic trimer and a linear polymer [63]:



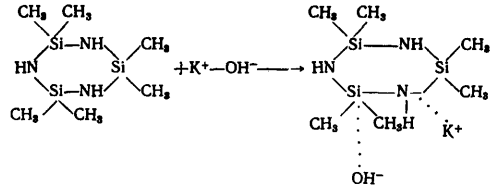
The stability of the sp^3 hybrid state of sexivalent sulphur explains why the sulphones R_2SO_2 do not polymerise, despite the presence of two double bonds in the molecule.

On the basis of the above review we can draw the following conclusions about the paths for obtaining inorganic rings and polymers with inorganic main-chain molecules with organic and organoelemental side-groups. In our opinion the most important direction of the synthesis of polymers with inorganic main-chain molecules is that which ensures the formation of chain molecules constructed from atoms of two or more elements alternating in the main chain. In choosing the elements for constructing the chains of large molecules it is necessary to take into account which type of hybridisation is most stable for these elements and also the electronegativity of the elements forming the chain. The alternation of elements in the chain of the molecule should be selected so that one element would be more electronegative and the other less electronegative than carbon. In this case the difference in the electronegativity of the elements leads to a polar type of bonds for the interlinked elements A–B (or to its partially ionic character), which increases the bond energy (Dp_{AB}) in comparison with the hypothetically pure covalent bond ($Dnp_A + Dnp_B$) in accordance with the formula:

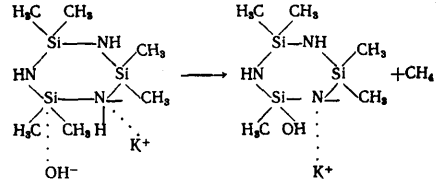
$$Dp_{AB} = Dnp_A + Dnp_B + 23.06\,(X_A - X_B)^2,$$

where Dp_{AB} is the energy of the polar bond AB, Dnp_A and Dnp_B are the "non-polar contribution" of the corresponding elements A and B to the bond energy, and X_A, X_B are the electronegativities of elements A and B on the Pauling scale.

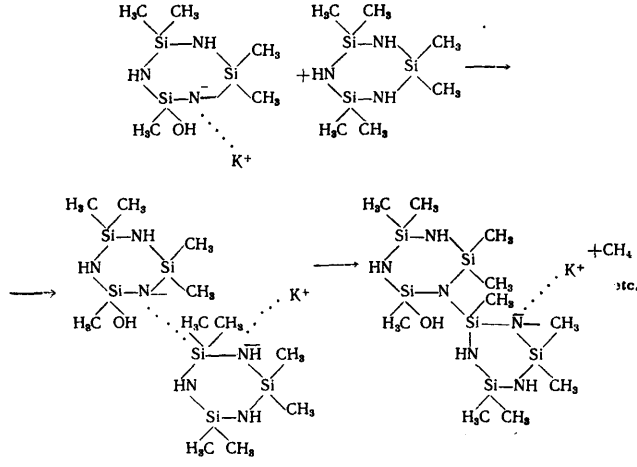
As examples illustrating this thesis we can quote the synthesis of polymers with silicon–nitrogen bonds obtained recently by catalytic polymerisation of dimethylcyclosilazanes [67]. The polymerisation of these rings with the aid of catalytic quantities of alkalis takes place not with cleavage of the ring, as occurs in the case of the alkaline polymerisation of dimethylcyclosiloxanes, but by detachment of a methyl group from the silicon atom and hydrogen from nitrogen, with formation of methane:



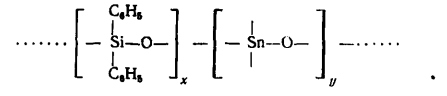
In the transitional complex formed as a result of redistribution of the electronic density one of the Si–C bonds is weakened and methane is detached with formation of a negatively charged ion:



Subsequently the process proceeds through coordination of the ions of cyclosilazanes by the reaction:



Several polymers have been obtained with chain molecules, including both Si–O and Sn–O bonds. Such polymers are obtained from the disodium salt of diphenyldihydroxysilane and tin chloride [68]. These organostannosilicon polymers have the following structure:



Organostannosiloxane oligomers were obtained in an analogous way from difunctional organotin monomers and the sodium salts of dialkyl(aryl)dihydroxysilanes [69], and polyorganostannosiloxanes by the polycondensation of diethoxydimethylsilane with tin diacetate and with diacetoxydiisobutyltin [70].

The possibility of preparing polyorganostannosiloxanes of linear structure by the polycondensation of dialkoxy--derivatives of tin with organosilicon hydroxyl derivatives has been described [71].

In the formation of the main chains of large molecules steric hindrance can become an unsurmountable difficulty, for even when the hybrid state characteristic for the elements concerned is maintained and the electronegativity of the elements is correctly chosen the formation of the main chain of a large molecule is unsuccessful. This shows that in choosing the direction for the synthesis of polymers with inorganic chain molecules account should be taken of all the factors considered above.

In the present article an attempt has been made to evaluate the ability of various elements to form the chains of large molecules, and general consideration has been given to the trends for the preparation of polymers with inorganic chain molecules. The authors do not pretend to have given a complete exposition of these problems, but hope that the article will be of assistance to those who are working in the field of the synthesis and investigation of organoelemental compounds.

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METHODS OF STEPWISE SYNTHESIS OF THE SPECIFIC $C_{3'}$–$C_{5'}$ INTERNUCLEOTIDE BOND

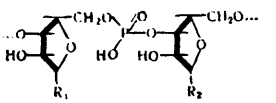
S. M. Zhenodarova

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I. INTRODUCTION

The considerable advances in the elucidation of the role of nucleic acids in the biosynthesis of protein[1] have led to increasing interest in synthetic polynucleotides which serve as models in the investigation of the chemical, biochemical, and biological properties of nucleic acids. There is particular interest in the methods of preparation of nucleotides with a known sequence of nucleotide residues in the polynucleotide chain. One of such methods is the stepwise synthesis of the specific internucleotide bond which consists of a phosphodiester unit joined to the $C_{3'}$ atom† of one nucleotide and the $C_{5'}$ atom of another[2]:



In developing methods of synthesis of the specific $C_{3'}$–$C_{5'}$ internucleotide bond it is necessary to solve two principal problems: (1) to find ways of protecting the functional groups present in nucleoside and nucleotide molecules (the hydroxy-group of the sugar and the amino-groups of purine and pyrimidine bases) and thus obtain derivatives of the nucleosides and nucleotides with only one reactive group; (2) to achieve the condensation of these residues in such a way that only the $C_{3'}$–$C_{5'}$ phosphodiester linkage is formed. In both cases it is necessary to bear in mind the low stability of the $C_{3'}$–$C_{5'}$ linkage which is hydrolysed by acids[4] and alkalis[5] and isomerises to the $C_{2'}$–$C_{5'}$ linkage in an acid medium[6,7]. All these factors restrict the choice of protective groups, since their subsequent complete or selective removal often requires fairly severe conditions.

II. METHODS OF SPECIFIC PROTECTION OF FUNCTIONAL GROUPS IN NUCLEOSIDES AND NUCLEOTIDES

The synthesis of the $C_{3'}$–$C_{5'}$ linkage may be achieved in two ways: (1) a nucleoside-3′ phosphate is condensed with a nucleoside having a free hydroxy-group in position $C_{5'}$ (5′-OH); (2) a nucleoside-5′ phosphate is condensed with a nucleoside having a free hydroxy-group in position $C_{3'}$ (3′-OH). Thus for the synthesis of the $C_{3'}$–$C_{5'}$ internucleotide bond it is necessary to have nucleosides with free 3′-OH and 5′-OH groups (nucleoside components) and nucleotides with a phosphate residue in position $C_{3'}$ or $C_{5'}$ with the remaining functional groups completely protected (nucleotide component).

1. Protection of Hydroxy-Groups in Deoxyribonucleosides and Deoxyribonucleotides

The preparation of protected deoxyribonucleosides and deoxyribonucleotides does not present great difficulties because there is no hydroxy-group in position $C_{2'}$ and the 3′-OH and 5′-OH groups are known to differ in their reactivity. The use of triphenylmethyl chloride (trityl chloride) for the protection of the 5′-OH group is based on this difference: trityl chloride reacts much more rapidly with the primary hydroxyl[8–12]. Although the trityl group is most often used for the protection of the 5′-OH group in deoxyribonucleosides[13] and deoxyribonucleotides[14], the acetyl group[15] and the di-(*p*-anisyl)phenylmethyl group (di-*p*-APM group) are employed for this purpose too[16,17]. The acetyl group has also been used for the protection of

† The numbering of the atoms in the base and sugar residues of nucleic acids is based on that given by Kochetkov *et al.*[3].