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NEW METHODS OF INORGANIC SYNTHESIS

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NEW METHODS OF INORGANIC SYNTHESIS

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NEW METHODS OF INORGANIC SYNTHESIS

V. I. Mikhéyeva, Doctor of Chemical Sciences

The most characteristic feature of contemporary inorganic chemistry is the rapid progress in the regions of synthesis of new compounds, especially nonmetals, the simplest and the complex.

This rise to a significant degree is connected with the development of contemporary directions in technology: atomic power engineering, altitude aviation and preparation for space flights. Elementary boron and borides, for instance, are the basis of creation of new heat-resistant materials; hydrides and fluorine compounds are long-term components of fuels on a purely inorganic basis, polymeric compounds of phosphorus and boron can be heat-resistant plastic substances. The practical significance of these directions of inorganic chemistry promoted the fact that after unparalleled short periods (calculated by several years), many compounds, until recently little or quite unknown, were studied from all sides and began to be produced on an industrial scale.

Chemistry was enriched by the highest oxygen compounds of metals (superoxides and ozonides), nonmetals (acyl perchlorates), new types of complex compounds with atoms of boron, chlorine, and bromine as a central atom, complex compounds of transition metals with hydrogen hydride as addenda, cyclical compounds with atoms of nitrogen, phosphorus, boron, oxygen, and sulfur in cycles and others. A study...
of the structure and properties of a new type of compounds significantly expanded presentations about the reaction ability of atoms and molecules.

Special advances have been achieved in the chemistry of electronegative hydrogen -- in the synthesis of new hydrides, until recently with comparatively rare exhibits in laboratories. In recent years many hydrides began to be produced on an industrial scale both here and abroad. Unknown hydrides of magnesium, beryllium and aluminum were synthesized formerly. With the works of G. Shlezinger a new chapter of inorganic synthesis was opened -- complex boro-and alumohydrides and their derivatives.

The biggest difficulties in the practical use of hydrides, their hygroscopicity and inflammability, are surmounted in two ways. On the one hand, substances (such as sodium and potassium hydrides), energetically reacting with moisture and air which are used in the form of solid solutions in hydroxides or chlorides of alkali metals, acquire great thermal and chemical stability.* These solid solutions, easily obtained by hydrogenation of a mixture of salts and alkali metals, represent ideal reducing agents for the majority of metallic oxides (their application is especially long-term for the surface deoxidation of metallic articles).

Another direction of stabilization of unstable and inflammable hydrides is complexing.** Simple hydrides, which ignite easily and react violently with water, for instance sodium and potassium hydrides, diborane, aluminum hydride and others, owing to the formation of complex anions with boron and aluminum as a central atom turn into complicated hydrides LiBH₄, NaBH₄, LiAlH₄, NaAlH₄, which are thermally stable up to 250--500°. Sodium and potassium borohydrides are even melted without decomposition respectively at temperatures of 510° and 620°.


Some complex hydrides, for instance LiAlH$_4$ and LiBH$_4$, are dissolved well in organic substances and are ideal selective reducing agents for reactions proceeding in anhydrous solutions. Borohydrides of the alkali metals NaBH$_4$ and KBH$_4$ on the contrary are dissolved well in water without decomposition and behave in aqueous solutions like the usual salts, preserving at the same time all the properties of powerful reducing agents for reactions proceeding in aqueous solutions.

Aqueous solutions of borohydrides in essence are labile and only the forces of complexing and stabilizing additions to water of alkalis retain the electronegative hydrogen of the borohydride anion from the reactions with the electropositive ion of water according to the general equation: NaBH$_4$ + 2H$_2$O $\rightarrow$ NaBO$_2$ + 4H$_2$ ↑.

Sometimes this reaction especially is initiated by the use of catalysts -- salts of the transition metals -- and then complex boro- and alumohydrides are the most effective gas-formers. One kilogram of LiAlH$_4$, NaBH$_4$, and LiBH$_4$ gives respectively during the reaction with water 2.36, 2.37 and 4.13 m$^3$ of hydrogen.

If the first grams of these compounds were obtained by the reactions of organometallic compounds with diborane and were very expensive now the synthesis of them is in the stage of radical improvement. Sodium borohydride for instance can be obtained by the reduction of natural boro-containing minerals with metallic sodium in the presence of hydrogen, alumohydrides of alkali metals by direct synthesis from metallic aluminum and alkali metal in the presence of compressed hydrogen.

With the help of the exchange reactions of boro- and alumolithium hydrides and sodium with salts of the other metals the synthesis of complex hydrides of all the metals of the periodic system is possible in principle. However, its realization requires a high level of experimental technology.

The theory of exchange reactions developed by N. S. Kurnakov on aqueous-salt systems suitable for the use of natural salt resources receives further development being transferred to the synthesis of complicated hydrides in a medium of organic solvent according to a reaction of the type:
where \( \text{Me}^\text{I} \) is an atom of the alkali metal and \( \text{Me}^{\text{III}} \) is boron, aluminum or their analogies.

The obtaining of crystalsolvates of borohydrides of alkali earth metals -- \( \text{M}_2(\text{BH}_4)_2 \), \( \text{Ca}(\text{BH}_4)_2 \) -- and aluminum/uranium alumohydrides -- \( \text{U}(\text{AlH}_4)_3 \), cerium -- \( \text{Ce}(\text{AlH}_4)_3 \) and several other transition metals is accomplished by reactions of a similar kind. The principal importance of these compounds is determined not only by their properties, hydrogen-carriers and hydrogen generators, but also by the possibility of pyrolytic decomposition with the formation of metallic compounds in a state of the highest purity with a strictly stoichiometrical composition.

Among hydrogen compounds the biggest puzzle until recently was the chemical nature of the hydrides of variable composition of the transition metals, for instance: titanium \( \text{TiH}_{1.75} \), vanadium \( \text{VH}_{0.9} \), cerium \( \text{CeH}_{2.7} \) and others, or, as they are frequently called, metallic hydrides, inasmuch as to change the property of these hydrides in a wide range of compositions without disturbing the homogeneity the first quantitatively were studied for metallic phases. Recent works* showed that within the limits of homogeneity of these phases a continuous transition of the atoms of the transition metal from one valence to another is carried out, controlled by external conditions. For cerium, for instance, the transformation within the limits of the hydride phase is reflected by the formula \( \text{Ce}^{\text{III}_{1-x}}\text{Ce}^{\text{II}_{x}} \), where \( x \) passes through all values from 0 to 1.

A study of the chemical nature and properties of hydrides of variable composition is the scientific basis of the search for hydrogenation catalysts. The high thermal

stability, for instance of hydrides of rare-earth metals creates prospects of their use as decontaminators, reducing and deoxidizing agents.

Penetration into the chemical essence of hydride phases of variable composition also opens a way of understanding of the chemical nature of a huge region of phases of variable composition -- daltonides and berthollides. The value of the study of the chemistry of phases of variable composition hardly can be reevaluated, taking into account the principal importance of the problem of interconnection of the chemical compounds and solutions and the fact that phases of variable composition are such substances as natural minerals, ores, silicates, semiconductor materials, a large part of catalysts and others.

The chemistry of boron has achieved significant successes*. The number of systematically studied simplest and complex compounds of it, in particular boron hydrides and their derivatives, grew vigorously.

Mastering the methods of obtaining technically pure and purest boron and borides of almost all metals -- this is the basis on which the technology of heat-resistant alloys and semiconductors for work at increased temperatures is constructed. At the same time the exchange reactions of borohydrides with metallic salts in aqueous solutions allow us to obtain borides in states of increased activity with clearly expressed catalyst characteristics.

The most interesting property of boron hydrides is their mutual transformation as a result of the quasiequilibrium reaction of thermal decomposition, for instance:

\[ \begin{align*}
B_4H_6 & \rightarrow 2BH_3 \\
B_5H_7 & \rightarrow BH_3 + BH_4 \\
B_6H_15 & \rightarrow 2B_3H_5 + 2BH_3 \\
(BH)_8 & \rightarrow 3BH_4 
\end{align*} \]

---

In conditions of weak heating or electrodischarge these reactions lead to regrouping of the radicals and obtaining of new representatives of the class of boron hydrides. On the other hand, the equilibrium character of transformations of boron hydrides opens a way of synthesis of new substances. During the reaction of boron hydrides with nitrogen-containing bases -- amines, amides and nitriles -- owing to the detachment of the boron hydride radicals additive products can be obtained, which easily pass into polymeric compounds* with cycles or chains of alternated atoms of boron and nitrogen $\text{B}=\text{N} \text{B}=\text{N} \text{B}=\text{N}$. At the same time hydrogen to a significant degree loses its own hydride character, i.e. the ability to react violently with water with the liberation of hydrogen, which allows us to obtain materials with increased thermal stability and less sensitive to moisture and air.

One of the most urgent directions of inorganic chemistry is the creation of a new form of sources of active oxygen -- a necessary element for the majority of industries, transport and aviation.

A brilliant page of new inorganic synthesis was the discovery of superoxides and ozonides $\text{NaO}_2$, $\text{KO}_2$, $\text{NaO}_3$, $\text{K}O_3$**, the technology of obtaining which has improved significantly of late.***

However, a not less interesting oxygen-carrier is chloric acid and its derivatives -- perchlorates.****

In the gaseous state chloric acid exists in the form of molecules of $\text{HClO}_3$, but in the liquid, from the viewpoint of molecular composition, it is possible to consider it as an equilibrium

$$3\text{HClO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{ClO}_4^- + \text{ClO}_3^-.$$  


The appearance in the liquid phase of an unstable compound -- chloric anhydride -- makes 100% chloric acid an explosive substance and limits the region of its use. Chloric acid, a salt for instance perchlorates of lithium, calcium and barium -- LiClO₄, Ca(ClO₄)₂, Ba(ClO₄)₂ are safer as oxidizers. They yield during decomposition respectively 1024, 1080 and 1018 liters of oxygen from one liter of salt melt, i.e. more than liquid oxygen (811 1/2). Thus, "chemical compression" within the limits of the perchlorate molecule is more effective from the viewpoint of economy of volume, than liquefaction of oxygen.

Enumeration of the most rapidly developing directions of inorganic synthesis will be incomplete, if we do not mention the advances in the region of the chemistry of inorganic fluorine compounds**.

Methods of increasing stability developed for the stabilization and modification of properties of unstable compounds of the formerly described classes, begin to be used with success in "taming" this element, still being "the pole of inaccessibility" in the practice of preparative works. Together with compounds of the GF₃, GF₅, and GF₇ type, where the halide can be chlorine, bromine and iodine, is opened the class of halogenofluorides -- complex compounds of the general formula MeGF₄, for instance KCIF₄, Ba(ClO₄)₂, NaClO₄. These compounds are incomparably less dangerous in circulation than fluorine itself and its simplest compounds with other halogens. Some of them can even be combined with organic solvents.

The synthesis and study of those or other classes of compounds, as can be seen analyzing the separate stages of development of general and inorganic chemistry,
always were accompanied by translational motion in the region of theory and methods of study of the substance.

With what kind of theoretical directions is the development of new inorganic synthesis connected?

Data of a study of the valence possibilities of atoms and molecules on the basis of existing theories of a chemical bond undoubtedly have first priority in the selection of the direction of synthesis and even more important, the atoms of nonmetals (in view of the more complicated structure of the orbital electron shell) possess a large variety of manifestation of chemical activity as compared with typical metals.

The above-cited examples confirm also that the theory and method physico-chemical analysis (during the study of phases of variable composition and complicated phase equilibriums) and the theory of complex compounds (in questions of the modification of properties and the stabilization of compounds) are very important for the determination of ways of synthesis of new compounds.

But there is something new also in the actual placement of synthetic works in the region of such high-reaction substances as the typical nonmetals and their compounds. This is the dynamic nature in conducting the reactions themselves, incomparably larger than during synthetic preparative and methods of physico-chemical analysis in their classical form.

The nonreversible character and many possible directions of the reaction of typical nonmetals and their compounds require studies of the reactions in wide ranges of the changes of various factors: the concentration of the parent substances, the temperature, the pressure, and the application of neutral and chemically-active solvents.

Only on the basis of the manifestation of all possible directions of the reaction in the given system does the selection of the conditions of realization of the given direction of synthesis and the suppression of all the secondary directions become possible.
A necessary additional condition for the realization of synthesis and the obtaining of substances in a state should be systematic work on the search for new solvents as media for conducting reactions and refining products. It is sufficient to indicate that the synthesis of that or another of the complex hydrides with exchange reactions is solved by the use of solvents, only recently accessible — diethylene glycol tetrahydrofuran, methylformamide and others.

On the other hand, the creation on the basis of freshly synthesized and formerly known compounds of materials, directly utilized in technology — heat-resisting articles, regulated sources of hydrogen and oxygen — requires studies of the phase composition of individual compounds and their mutual combinations at various temperatures, studies of the boundaries of propagation of phases of variable composition and the establishment of conditions of stable existence of little-durable and easily decomposed compounds.

Finally, obtaining new compounds and the characteristic of their properties is inconceivable at present without a study of their crystal and molecular structure by contemporary experimental methods: X-ray spectroscopy, mass spectroscopy, gas chromatography and electronography and others.

The specific properties of the majority of freshly synthesized compounds (hydroscopicity, toxicity and sometimes explosiveness) require special shaping equipment for conducting synthesis and for the study of their properties. In recent years the role of the synthesis and study of the properties of compounds with the use of compressed gases — hydrogen, oxygen, and ammonia — at various temperatures has increased. Direct synthesis, for instance of magnesium hydride and alumohydrides of alkali metals is impossible without the combination of the technology of high pressures of hydrogen and the intense dispersion of reaction mixtures. However, here researchers meet with definite difficulties, caused by the fact that inorganic chemistry in the Academy of Sciences is still not provided with the necessary equipment.

In conclusion one should say that the directions of inorganic synthesis mon-
do not exhaust its interesting aspects in the theoretical and practical relation. It is desirable to show the expediency of intensifying synthetic work in the sphere of inorganic compounds of sulfur and its analogies — elements, especially prone to the formation of linear and cyclic polymers, mixed carbonyl-hydrogen derivatives of the light transition metals, compounds with special physical properties — ferromagnetic substances, superconductors, and semi-conductors on a base of regulated pyrolysis of volatile compounds of metals and nonmetals, new catalysts, simple and complex nitrides, phosphides, carbides, silicides and others.
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