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Radiochemical Methods for the Preparation of Organic Derivatives of the Elements

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The review deals with the radiochemical procedures for the preparation of organic derivatives of the elements based on the carrier method and also processes occurring in the β-decay of the constituent atoms of the molecular systems.
These methods are particularly important for the synthesis and investigation of the properties of the organic derivatives of elements without stable and long-lived isotopes and also compounds of the inert gases.
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I. INTRODUCTION

The chemistry of organic derivatives of the elements, the "third chemistry"[1], is a branch of science on the borderline between inorganic and organic chemistry. At one time such compounds played an important role in the development of the concept of valence[2] and also in the development of the theory of the structure of organic compounds[3,4]. Nowadays compounds of this class have found wide application in science and engineering and are manufactured on an industrial scale.

The intense development of the chemistry of organic derivatives of various elements began in the USSR at the end of the 1920's. The development of theoretical and practical problems in this field is especially due to Nesmeyanov and his school[5-9]. The establishment of a relation between the ability of elements to form organic compounds and their position in the Periodic System[5,9] led to the discovery of the possible syntheses of organic derivatives of elements which had not been investigated in this respect. These include all the elements with atomic numbers greater than 83 (radioactive elements) and also the inert gases. The relation established by Nesmeyanov can be undoubtedly extended also to radioactive elements such as francium, radium, astatine, and polonium.

II. METHOD OF SPECIFIC CARRIERS

1. Characteristics of the Preparation and Investigation of Compounds of Radioactive Elements

For a long time organic derivatives of the above elements were not prepared because of a number of features encountered in syntheses of radioactive elements[10]. These include, on the one hand, the impossibility of obtaining weighable amounts of individual radioactive elements, even by the most modern methods of nuclear physics, because of their short lifetime (astatine, francium, radon). On the other hand, studies with large amounts of many radioactive elements inevitably involve intense radiation-chemical changes both in the substances themselves and in the surrounding medium. The latter make it impossible to secure

accurate information about the properties and the state of the elements and the nature of the compounds obtained[11,12].

These factors make it necessary to work with extremely small amounts of radioactive elements, which greatly complicates the syntheses in practice and also makes it impossible to establish the composition of the compounds prepared by direct analytical methods. For this reason, the so called method of specific carriers has played a special role in the usual chemical syntheses of compounds of radioactive elements[13-16].

The carrier method is based on the similarity of the properties and behaviour of similar elements and their compounds. Examination of the Periodic Table shows that all the radioactive elements up to element No. 115 inclusive have such close analogues. Therefore the basis of this method is extremely general.

Radiochemical experiments have shown that the data on the behaviour of radioactive elements obtained using submicroscopic amounts and similar elements as carriers adequately reflect the properties of the given radioactive element. Thus the numerous facts established by studies on the chemical behaviour of sometimes even individual atoms of radioactive elements were subsequently confirmed by experiments with macro-amounts of the substance[17,18]. The most striking example in this respect is provided by the design of nuclear manufacturing plant in which the technological isolation of plutonium was developed on the basis of radiochemical investigations of submicroscopic amounts of this element. The scaling-up coefficient on transition to the industrial process was 10^{10}.

The similarity of the properties and behaviour of similar organic derivatives of analogous elements should be even greater. This is because in complex derivatives of this kind the differences between the individual properties of the central atoms are largely obliterated.

Since it is impossible to establish by direct chemical analytical methods the composition of the compounds of the radioactive elements obtained, indirect methods, based on a comparison of the behaviour of the test substances with that of compounds of analogous elements, play a considerable role. In preliminary experiments, the behaviour of compounds of the analogous element is investigated and the data thus obtained constitute the basis for the identification and the determination of the yield of the analogous compound of the radioactive element. Chromatographic methods have proved particularly convenient for this purpose[19-26]. The study of the properties of compounds of radioactive elements based on a comparison with data on the chromatographic behaviour of compounds of analogous elements is widely employed at the present time. In this connection, one can show, for example, that the similar chromatographic behaviour of the trivalent cation of lanthanide and transuranic elements has played a very important role in the identification of americium, californium, and other "far" transuranic elements[27-36].

Numerous compounds of polonium and astatine have been synthesised by the method of carriers[25,37-46].

2. Preparation of Organopolonium Compounds by the Method of Carriers

In view of the position of polonium in the Periodic System and the electronic configuration of its atoms ($6s^26p^4$), it was expected that polonium would form both alkyl and aryl organic derivatives of the following types: R_2Po, R_2PoX_2, R_3PoX, and $RPoX_3$, where R is an organic group and X a halogen atom.

The first studies on the synthesis of organopolonium compounds of the type R_2Po were carried out by Khlopin and coworkers as early as the 1930's for methyl and benzyl derivatives[37-39]. The existence of polonium in the form of an organic compound was proved by the observation that in the recrystallisation of the dibenzyl derivative and in the distillation of dimethyl telluride, polonium behaves analogously to the corresponding tellurium compounds.

Further studies showed that not all the classical methods suitable for organotellurium compounds can be used to prepare organopolonium derivatives[40-42]. The lower thermal stability of fully organic derivatives of divalent polonium of the type R_2Po excluded synthetic methods involving elevated temperatures. For example, the reaction of metallic tellurium with diphenylmercury or the reaction of tellurium chloride with anisole, which give rise to the formation of high yields of tellurium compounds[47,48], gave only 1-5% of the analogous organic derivative in the case of polonium[49]. The tendency towards decreased thermal stability of similar fully organic derivatives with increasing atomic weight of the central atom is well known and has been observed for elements of other Groups[50].

Table 1. Organic compounds of polonium obtained by the carrier method.

R	Type of compound					
	R_2Po		R_2PoX_2		R_2PoX	
C_6H_5	R_2Po	[40]	R_2PoCl_2	[40]	R_2PoCl	[40]
					R_2PoI	[40]
	R_2Po	[41]	R_2PoF_2	[41]		
p-$CH_3C_6H_4$			R_2PoCl_2	[41]	R_2PoCl	[41]
			R_2PoBr_2	[41]		
			R_2PoI_2	[41]	R_2PoI	[41]
p-$CH_3OC_6H_4$	R_2Po	[25]	R_2PoF_2	[41]		
			R_2PoCl_2	[25]	R_2PoCl	[25]
					R_2PoBr	[25]
					R_2PoI	[25]
α-$C_{10}H_7$	R_2Po	[42, 42]	R_2PoF_2	[49]		
			R_2PoCl_2	[49]	R_2PoCl	[49]
			R_2PoBr_2	[49]	R_2PoBr	[49]
			R_2PoI_2	[49]	R_2PoI	[49]

Note. The numerals in the table denote references (Ed. of Translation).

An extremely convenient method for the preparation of aromatic derivatives of divalent polonium consists in the synthesis via a Grignard reagent in the presence of a 2-8-fold excess of the latter. The experiments were performed with amounts of polonium-210 of the order of 10^{-10} g using as carriers tellurium compounds labelled with radioactive tellurium-127.[25,40-42,49]. The use of labelled tellurium compounds as carriers is very convenient, since under these conditions radiometric analysis makes it possible to follow simultaneously the behaviour of both polonium and tellurium compounds. The yields of organic derivatives of divalent polonium were 65-80%. In many cases, by reducing the amount of the Grignard reagent, the relative yield of the organopolonium compounds was increased. Thus the yield of ditolylpolonium in the presence of a 2-3-fold excess of the Grignard reagent exceeded the yield of ditolyltellurium by a factor of 3-5.[41]

Triallylpolonium halides were obtained by the reaction of stoichiometric amounts of tellurium and polonium tetrachlorides with a Grignard reagent. A higher yield of the polonium compound was not observed in this case.

Diarylpolonium dichlorides were synthesised by chlorinating diarylpolonium. Gradual chlorination of a mixture of diarylpolonium and diaryltellurium showed that the latter is chlorinated much more slowly than the analogous polonium compound[49].

Despite the great similarity in the behaviour of the compounds of analogous elements, under certain conditions it is possible to find methods for their separation. In particular, the separation of organic derivatives of polonium and tellurium may be based on the difference between the oxidising properties of the compounds of divalent tellurium and polonium and also on the difference in the chromatographic behaviour of diaryl polonium and diaryltellurium dihalides in certain polar solvents. It has been shown[25,40-42,49] that in general the chromatographic behaviour of tellurium and polonium compounds is almost identical. However, in certain systems (for example, in a 3 : 2 methanol–water mixture) they are completely separated. Organic compounds of polonium obtained by the carrier method are listed in Table 1.

3. Preparation of Organoastatine Compounds

Astatine is immediately adjacent to polonium on the right-hand side in the Periodic System. Since the stability of organic derivatives of polyvalent halogens in Group VII of the Periodic System increases on going from fluorine to iodine, it was reasonable to suppose that astatine, the heaviest halogen, would form organic derivatives in which it would exhibit valence states analogous to those of iodine (III and V).

The most long-lived astatine isotope is astatine-210 with a half-life of 8.3 h. Such a short half-life intensifies the already considerable difficulties of synthesising organic derivatives of this element. The overall duration of synthetic operations must not exceed 3–4 h in this case. Organoastatine compounds were prepared on the basis of the following scheme[44,45,51]:

$$R_2ICl + KI(At) \rightarrow R_2I(At) \xrightarrow{170^\circ} RI(At) \xrightarrow{Cl_2} RI(At)Cl_2 \begin{cases} \xrightarrow{R_2Hg} R_2I(At)Cl \\ \xrightarrow{NaOCl} RI(At)O_2 \end{cases}$$

The astatine compounds were separated from the parent substances and analysed by paper and thin-layer chromatography.

III. METHOD OF STABILISATION AND FRAGMENTATION OF PRIMARY MOLECULAR IONS

1. Behaviour of Primary Molecular Species Formed in β^--Decay

A fundamentally new method for the preparation of organic derivatives of radioactive elements is based on the stabilisation and partial fragmentation of the so called primary molecular ions. These ions arise as a result of the β^--decay of the constituent atom in different kinds of molecule.

We shall consider briefly the processes which develop in the β^--conversion of the constituent atoms of molecular systems. The β^--decay of atoms yields isobars of the adjacent elements to the right in the Periodic System according to the following general scheme:

$$^{A}M_z \xrightarrow{\beta^-} {}^{A}N_{z+1} + e^- + \tilde{\nu} \ .$$

If the atom forms part of a neutral molecule or ion, then the initial instantaneous process is the generation of a primary molecular species containing the atom of the new element, for example:

$$C_6H_5{}^{133}I \xrightarrow{\beta^-} [C_6H_5{}^{133m}Xe]^+; \quad {}^{133}IO_3^- \xrightarrow{\beta^-} {}^{133m}XeO_3^* \rightarrow {}^{133m}XeO_3 \ .$$

The new molecular species containing the adjacent element which are produced in this stage have the same structures and electronic configurations as the initial molecule. Subsequent processes undergone by the primary molecular species are associated with the characteristic response of the electron cloud of the initial atom to the sudden change in nuclear charge as a result of the β^--decay (the electron cloud of the parent system is suddenly placed in the field of a nucleus with a new value of z). This inconsistency results in excitation, ionisation, and partial breakdown of some of the primary molecular species[52-66]. The fraction of primary molecular species which break down as a result of excitation and ionisation does not exceed 20%. Investigations have shown that in the case of organic derivatives of the elements this breakdown (fragmentation) involves the splitting off of the organic radical[19,22-24,26,67].

On the basis of a number of characteristic features of the β^--decay process (instantaneous change in nuclear charge and low probability of the interaction of the β^--particle with orbital electrons), an expression was obtained for the probability of the generation of new states of the daughter atom. This expression permits the calculation of the fraction of daughter atoms in excited and ionised states:

$$P_{mn} = \left| \int \psi_m^* \psi_n dv \right|^2 ,$$

where Ψ_m^* is the wave function of the parent atom in the state m and Ψ_n the wave function of the daughter atom in the state n.

According to the selection rules established by Migdal[53], transitions are possible only between levels differing solely in principal quantum numbers. The formula for the transition probability in the hydrogen-like approximation was obtained by Schwartz[54,63]. Carlson[57-59] and Skorobogatov[68] made the most detailed and thorough calculations of the excitation and ionisation probabilities. The results led to conclusions concerning the relation between the excitation and ionisation probabilities as a function of the valency and the charge state of the atom and also the position of the elements within the limits of the same Group or Period of Mendeleev's System.

According to theoretical considerations and experimental data, the results of calculations for isolated atoms can be extended to processes involving the constituent atoms of molecular systems. Thus, using an expression for the internal wave function of the molecule obtained as a product of the electronic and nuclear functions on the basis of the Born–Oppenheimer approximation (and neglecting, in accordance with the Franck–Condon principle, the dependence of the electronic wave function on the internuclear distance), Wolfsberg[64] obtained an expression for the probability of the transition of the molecular system from one state to another:

$$P_{A \rightarrow B} = P_{a \rightarrow \beta} P_{a \rightarrow b} \ ,$$

where $P_{\alpha \rightarrow \beta}$ is the overlap integral of the electronic wave

function of the initial and final states of the molecular system for the equilibrium internuclear distance in the initial molecule and $P_{a\to b}$ the probability of vibrational and rotational excitations under the action of the momentum of the radioactive recoil in the β-transition. The individual factors in this expression can be calculated independently. The factor $P_{\alpha\to\beta}$ for the molecular system differs little from the analogous factor for the isolated atom [68]. The numerical value of $P_{a\to b}$ can be calculated from the energy spectrum of the recoil atoms, the bond energy, and the rotational-vibrational factor.

If it is assumed that all the electronically excited and multiply ionised states are unstable, the fraction of the residual primary molecular species is determined by the probability of transitions to the ground electronic state and bound rotational-vibrational levels. Since the fraction of the latter corresponds to the transitions in which the recoil energy available for the dissociation of the bond is less than the energy of this bond, the calculations require a knowledge of the energy of the chemical bond involving the daughter atom in the primary molecular species†.

When β-decay leads to isotopes of stable elements, the bond energies can be found experimentally. The estimation of the bond energy in primary molecular species containing atoms of typically radioactive elements or elements of Group 0 may be based on the isoelectronic principle [69,70].

The processes discussed do in fact largely determine the behaviour of the primary molecular species produced in the β-decay of the constituent atoms of isolated molecules‡.

Theoretical and experimental studies on processes in the β-decay of the constituent atoms of molecules in the gas phase do not resolve the question of the fate of the primary molecular species if the molecules of the parent substances are present partly in the condensed phases. Then there is a possibility of a definite change in the electronic states of the parent molecules, of processes involving excitation energy transfer to the surrounding medium, etc., and finally of changes in the nature of the processes in which the primary molecular species take part. At the same time, in condensed phases many changes can be due to processes in which the primary molecular species and their fragments are neutralised by free electrons and the electrons of the surrounding species, by ion–molecule interactions, and by radiation-chemical processes.

It follows from the above that at the present time it is impossible to give a rigorous quantitative explanation of the changes observed in the β-breakdown of the constituent atoms of molecular systems in condensed phases. At the same time the processes occurring in β-conversions of the constituent atoms of molecular systems are of interest for a wide variety of branches of science, including molecular biology, genetics, the science of the origin of pre-biological formations, etc. [71-73] β-Decay processes are particularly important for the development of new research methods and new synthetic pathways.

† In the calculation of the contribution of the transitions leading to bound rotational-vibrational states, it is necessary to consider only breakdown processes of the primary molecular species requiring a minimum expenditure of energy.

‡ Since the lifetimes of the excited states in radiation-induced transitions exceed by 4–5 powers of ten the vibration periods of the atomic bonds, other processes (for example the transfer of excitation energy under conditions excluding intermolecular interaction) cannot play a significant role.

2. The Use of β-Decay Processes for the Development of New Research Techniques

From the standpoint of the development of new research methods, β-decay processes of halogen and tritium atoms, leading to the formation of the inert gas atoms [74-85], are of considerable interest. If these processes occur in molecular systems such as halogen derivatives (except iodine derivatives) and hydrocarbons, then the resulting molecular ions are unstable and their breakdown leads to the formation of free carbonium ions [82-85]. For example:

$$CH_3F \xrightarrow{\beta^-} CH_3Ne^+ \to Ne + CH_3^+ ,$$

$$CT_4 \xrightarrow{\beta^-} CT_3He^+ \to He + CT_3^+ .$$

In principle, these processes make it possible to obtain free carbonium ions of any composition and structure and with any initial localisation of the charge and also to investigate their reactions with substances of different kinds in the gaseous, liquid, and solid phases. The possibility of using β-decay processes to obtain carbonium ions in a free (non-solvated) state has a wide scope for the development of new research methods in organic chemistry. From this point of view, the most interesting is the breakdown of tritium in highly tritiated hydrocarbons, since it is then possible to investigate the reaction of free carbonium ions by radiochemical methods. These studies are at present being vigorously developed in the Department of Radiochemistry of Leningrad University.

3. The Use of β-Decay Processes for the Synthesis of Organic Derivatives of Elements

The β-decay method can be used to obtain and investigate the compounds of any elements the precursors of which are radioactive isotopes undergoing a short chain of β-transformations. For example: $^{125}Sb-^{125m}Te$, $^{210}Bi-^{210}Po$, $^{133}I-^{133m}Xe$, etc. [86-103]

A distinctive feature of the synthetic methods based on the stabilisation and fragmentation of primary molecular ions arising in the β-decay processes of the constituent atoms of molecular systems is the possibility of obtaining neutral and charged molecular species of the daughter element in the matrices of the crystal lattices of the parent substances. This may be of interest from the standpoint of the investigation of the phenomena which occur in molecular systems during β-transformations of atoms, and also from the standpoint of the investigation and preparation of unstable compounds such as di- and tetra-chlorides of zenon and the halides of krypton [104-107], etc. It is also significant that β-decay processes make it possible to obtain radioactive compounds of daughter elements without a carrier, which is important for the investigation of the behaviour of infinitesimal amounts of substances in processes of different kinds, including deep-purification processes.

The study of the processes in the β-transformation of bismuth isotopes in various aryl derivatives resulted in the preparation of all possible types of organic compounds of polonium, containing a wide variety of groups and an essentially new branch of chemistry was created—the chemistry of organic polonium compounds [19,20,22-24,26] (Table 2).

The use of synthetic methods based on β-decay processes is not restricted to typical organic derivatives of the elements. For example, it has been established that, in the β-decay of molybdenum-99 in the hexacarbonyl of this

element, a considerable proportion of the resulting technetium is in the form of a volatile compound. These observations led to the hypothesis that this element forms carbonyls [112,113], which was soon confirmed by direct synthesis of technetium carbonyl [114,115]. The dibenzyltechnetium cation [116] and the pentadienyl derivatives of this element [117] were obtained similarly with the aid of the β-decay process.

Table 2. Organic compounds of polonium obtained by the method of stabilisation and partial fragmentation of molecular ions.

Organic Group	Parent compound	Yield of polonium compounds, %			References
		R_2Po	R_2PoX_2	R_3PoX	
C_6H_5 (phenyl)	R_3Bi	24	15	61	86
	R_5Bi	5	—	95	108
	R_3BiCl_2	—	92	8	86
p-$CH_3C_6H_4$ (p-tolyl)	R_3Bi	32	—	68	19
	R_3BiF_2	—	95	5	109
	R_3BiCl_2	—	69	31	22
	R_3BiBr_2	—	7	93	109
o-$CH_3C_6H_4$ (o-tolyl)	R_3Bi	33	—	67	19
	R_3BiF_2	—	95	5	22
	R_3BiCl_2	—	67	33	22
	R_3BiBr_2	—	27	73	22
m-$CH_3C_6H_4$ (m-tolyl)	R_3Bi	61	—	39	19
	R_3BiF_2	—	94	6	22
	R_3BiCl_2	—	71	29	22
	R_3BiBr_2	—	13	87	22
p-$(CH_3)_2C_6H_3$ (p-xylyl)	R_3Bi	33	—	67	110
	R_3BiF_2	—	95	5	22
	R_3BiCl_2	—	56	44	22, 109
	R_3BiBr_2	—	7	93	22
α-$C_{10}H_7$ (α-naphthyl)		27	60	7	
	R_3BiCl_2	—	93	5	90
p-$CH_3OC_6H_4$ (p-anisyl)	R_3Bi	15	—	75	24
	R_3BiCl_2	—	75	15	24
p-$C_2H_5OC_6H_4$ (p-phenetyl)	R_3Bi	28	—	72	26
$(CH_3)_3C_6H_2$ (mesityl)	R_3Bi	17	33	35	23, 96
	R_3BiCl_2	—	89	11	
p-$NH_2SO_2C_6H_4$ (p-sulphonamidophenyl)	R_3Bi	52	—	48	111

4. The Use of β-Decay Processes for the Preparation of Inorganic and Organic Compounds of the Inert Gases

At the present time the β-decay processes of the constituent atoms in molecular systems attract attention in connection with their possible employment for the investigation of many problems in the chemistry of the inert gases. In particular it was suggested in 1963 that synthetic methods based on β-transformations can be extended to prepare inorganic and organic derivatives of the heavy inert gases [118,119]. The first experimental confirmation of the validity of these ideas came from a study [104] based on the following chain transformation:

$$^{129}I \xrightarrow[1.7\cdot10^7\ \text{years}]{\beta^-} {}^{129m}Xe \xrightarrow[7.15\cdot10^{-9}\ s]{} {}^{129}Xe$$

where iodine-129 was introduced into iodates, periodates, and $KICl_4$ and the Mössbauer emission spectra were investigated. Although the method employed by the authors made it possible to follow chemical changes occurring only in the lifetime of the excited level (about 10^{-9} s), the importance of this investigation is evident.

Several months later a more extensive series of studies on the chemical consequences of the β-decay of the isotopes of iodine in its various compounds was published. The studies were carried out by radioactive methods which permitted not only the identification but also the isolation of the corresponding compounds of radioactive xenon [99-102,119-129].

The use of the β-decay method for the preparation of organic compounds of the inert gases is of special interest [99-102].

Despite the exceptionally rapid progress in the chemistry of the inert gases, the problem of the organic compounds of these elements remained uninvestigated for a long time [130-136]. Nevertheless, long before Bartlett's investigations [137], Nesmeyanov put forward ideas concerning the possible existence of these compounds, their nature, and methods of synthesis [4]. On the basis of the general laws governing the formation of 'onium compounds, Nesmeyanov concluded that organic derivatives of the inert gases should in fact belong to this class of compounds.

Inorganic and organic 'onium derivatives are ionic compounds in which the cations are the molecular groups $H_{9-N}M^+$ and $R_{9-N}M^+$, where R is the organic substituent, N the Group number, and M the atom of a transition element in Groups V–VIII (0). Examples of such molecular groups ('onium cations) for the Second and Fifth Periods are R_4N^+, R_3O^+, R_2F^+, RHe^+, R_4Sb^+, R_3Te^+, R_2I^+, and RXe^+. These groups are isoelectronic analogues of fully hydrogenated and fully organic derivatives of the elements of Groups V–VII and VIII (0).

A fundamentally new method for the preparation of 'onium cations is one based on the β-decay of the central atom in the compound. The formation of 'onium cations in β-decay processes can be represented as follows. If the central atom of an element in Groups IV–VII is present in fully organic derivatives with electronic structures similar to those of the inert gases, the primary molecular ion formed directly in the β-transformation is the 'onium cation of the next element to the right (Table 3).

Table 3. The formation of 'onium cations in the β-decay of fully organic derivatives of elements in Groups IV–VII.

IV	V	VI	VII	VIII
$R_4Pb \rightarrow R_4Bi^+$				
	$R_3Bi \rightarrow R_3Po^+$			
		$R_2Po \rightarrow R_2I^+$		
			$RI \rightarrow RXe^+$	

The subsequent stabilisation by suitable anions of the 'onium cations thus produced leads to the formation of the corresponding 'onium derivatives.

The results of numerous studies have shown that 'onium compounds can form in β-decay processes also by a different pathway. If the central atom forms part of 'onium derivatives of elements in Groups V–VII, then the β-transformation of the central atom, accompanied by partial fragmentation of the primary molecular ion, leads directly to the formation of such derivatives (Table 4).

It follows from the above that 'onium cations of the inert gases can be obtained both from fully organic halogen compounds and their 'onium derivatives containing radioactive halogen atoms.

The first data concerning the existence of 'onium cations in the gas phase were obtained from mass-spectrometric studies on ion–molecule reactions [138-145] and also from studies on the products of the β-decay of iodine and bromine isotopes in certain halogen derivatives [77,80,81,138]. Thus, it has been established that the interaction of the atomic radical-ions of the inert gases and hydrocarbon molecules

results in the formation of molecular ions of the type HE^+ and RE^+ (E = Ne, Ar, Kr, or Xe). Similar ions were detected in the study of processes accompanying the β-decay of radioactive bromine and iodine isotopes in halogen derivatives. These molecular species (HXe^+, HKr^+, RXe^+, etc.) are none other than the 'onium cations of the inert gases and have all the characteristics of this group of molecular ions. These include the donor–acceptor type of bond between the ligand and the central atom, the corresponding inert gas electronic structure of the central atom, the fact that these species are isoelectronic with the fully hydrogenated and organic derivatives of elements located to their left in the Periodic System, and finally the presence of a single positive charge.

Table 4. The formation of 'onium derivatives as a result of the partial fragmentation of primary molecular ions.

V	VI	VII	VIII
$R_4BiX \rightarrow R_4PoX^+ \rightarrow R_3PoX + R^+$			
	$R_3TeX \rightarrow R_2IX \rightarrow R_2IX + R^+$		
		$R_2IX \rightarrow R_2XeX^+ \rightarrow RXeX + R^+$	

These considerations, which follow from the fact that the ions are isoelectronic with the corresponding neutral species, theoretical calculations, and results of experimental studies, suggest that isolated 'onium cations of the inert gases are quite stable. The bond energy in these ions (we are considering the breakdown of 'onium cations requiring the minimum energy expenditure, in which the charge is localised in the fragment with the smallest ionisation potential) is 2–4 eV according to the data of different workers[139,145]. Similar or even somewhat higher values (due, in particular, to the additional $d_\pi - p_\pi$ bonds in the case of aromatic derivatives) characterise the bond in organic 'onium cations of the inert gases. Thus in those cases where derivatives of the 'onium cations of the inert gases have not been obtained, the reason is other than the instability of the cations themselves.

'Onium cations are a constituent of 'onium derivatives. The other constituent is the anion. In crystals and solutions of these substances the 'onium cations must coexist with the corresponding anions. This implies that in such systems the vacant electronic level of the 'onium cations must lie above the occupied electronic levels in the anions and in the molecules of the medium containing the ions. Therefore, to ensure the stability of the 'onium derivatives, it is necessary to select anions with the lowest possible occupied electronic level (maximum electron affinity) and 'onium cations with the highest vacant level (minimum ionisation potential of the group of atoms comprising the given 'onium cation)[146]. Of the anions satisfying this requirement, one may mention ClO_4^-, BF_4^-, etc. For the 'onium cations, the relation between the position of the vacant electronic level and certain other characteristics is given by

$$J = I + D_0 - D\,,$$

where J is the energy of the vacant electronic level of the isolated 'onium cation, determined in this case by the ionisation potentials of the corresponding neutral groups (HXe, RXe, HAr, etc.), I the ionisation potential of the atoms or groups of atoms in which the positive charge is localised during the fragmentation process of the 'onium cation, requiring the minimum energy expenditure, D_0 the bond energy in the neutral species (HXe, RXe, HAr, etc.), and D the bond energy in the 'onium cations HXe^+, etc.

It follows from this relation that, for all these 'onium cations of the inert gases, except HXe^+ and HRn^+, the position of the vacant level is determined by the difference between the ionisation potential of hydrogen and the bond energy D in the corresponding cation, i.e. amounts to 10–11 eV. For the 'onium cations HXe^+ and HRn^+, the position of the vacant level, determined by the difference between the ionisation potentials of xenon and radon atoms and the bond energy, is higher by 1.5–3 eV.[139] These values exceed by a factor of more than two the ionisation potentials of the alkali metal atoms (the radii of whose ions are close to the radii of the corresponding 'onium cations of the inert gases, for example Cs^+ and HXe^+). This in fact probably explains the impossibility of obtaining unsubstituted 'onium derivatives of the inert gases.

The situation is different for certain organic (for example phenyl-substituted) 'onium derivatives of the inert gases such as xenon and radon. For the corresponding 'onium cations, the position of the vacant level is determined by the difference between the ionisation potential of the organic ligand and the bond energy. If one remembers that the ionisation potential of the phenyl group is 9.5 eV and the bond energy of the middle and heavy inert gases in substituted organic 'onium cations of these elements appreciably exceeds the bond energy in the unsubstituted 'onium cations, the position of the vacant electronic level in the substituted cation is found to be 6–7 eV, i.e. approaches the position of the corresponding levels in ammonium and alkali metal ions. Therefore one may hope that ions of the phenylxenonium type will coexist with the above anions. These anions (ClO_4^-, BF_4^-, etc.), characterised by high electron affinity, low bonding energy with organic radicals, low polarising capacity, and a large radius, are of interest also from the standpoint of the stability of the 'onium derivatives of the inert gases themselves.

The stability of compounds, including the 'onium derivatives of the inert gases in which we are interested, may be characterised by the difference between the standard free energies of the compounds and their decomposition products. Since in normal reactions the free energy changes due to entropy changes are small, the stability may be characterised by the difference between the enthalpies of formation of the products and the starting materials. Remembering that substituted organic derivatives of the 'onium cations decompose by the general mechanism

$$R_{9-N}MX \rightarrow R_{8-N}M + RX\S$$

and using Hess's law, it is possible to establish a relation between the heats of decomposition and the energetics of individual stages of the thermochemical cycle

$$\Delta H^0 = U + D^+ + E - D - I\,,$$

where ΔH^0 is the enthalpy of decomposition of the 'onium derivative, U the breakdown energy of its crystal lattice, D^+ the energy of the dissociation of R^+ from RXe^+ in the substituted 'onium cation, E the affinity of the electron for the atom or group of atoms substituting the anion X^-, D

§ The decomposition of organic 'onium derivatives of xenon should take place by the mechanism $RXeX \rightarrow Xe + RX$.

the energy of the homolytic dissociation of the C–X bond in RX, and I the ionisation potential of the organic group.

Since all the terms on the right-hand side of the above relation are greater than zero, the enthalpy of decomposition of the given substituted organic xenon derivative increases with the electron affinity of X and decreases with the energy for homolytic dissociation of the C–X bond in RX. Since for the above groups of atoms (ClO_4^-, BF_4^-, etc.) the electron affinity is a maximum and the energy of the homolytic dissociation of the C–X bond a minimum, the 'onium derivatives containing the above anions must have an enhanced stability.

On the other hand, the relation makes it possible to estimate the relative stabilities of the 'onium derivatives of particular cations containing different anions. Thus it can be shown that the enthalpies of decomposition of phenylxenonium perchlorate and chloride differ by not less than 100 kcal mole^{-1}. The difference between the heats of decomposition should be even greater for phenylxenonium perchlorate and hydroxide.

Summarising the above findings, one may say that, in choosing a system for stability of the 'onium cation, preference must be given to substituted aromatic 'onium cations of the heaviest inert gases (xenon, radon). For the stability of 'onium derivatives as individual species, it is desirable to choose compounds which contain both stable 'onium cations and anions with a high stabilising capacity.

Since the studies on the synthesis of organic 'onium derivatives of xenon are in the development stage, we shall consider them in greater detail.

From the standpoint of nuclear-physical characteristics, the most suitable isotope for the preparation of organic 'onium derivatives of xenon is iodine-133 obtained by the fission of uranium-235. Iodobenzene and diphenyliodonium salts are promising as the initial molecular systems [147].

Iodobenzene containing the above iodine isotope was obtained according to the following scheme:

$$(C_6H_5)_2ICl + K^{133}I \rightarrow (C_6H_5)_2I^{133}I \xrightarrow{180^\circ} C_6H_5{}^{133}I .$$

Various diphenyl diphenyliodonium derivatives containing iodine-133 were synthesised using the following reactions:

$$C_6H_5{}^{133}I + Cl_2 \rightarrow C_6H_5{}^{133}ICl_2 \xrightarrow{(C_6H_5)_2Hg} (C_6H_5)_2{}^{133}ICl ,$$

$$\xrightarrow{AgOH} (C_6H_5)_2{}^{133}IOH \xrightarrow{HX} (C_6H_5)_2{}^{133}IX ,$$

where X = NO_3^-, HSO_4^-, BF_4^-, or ClO_4^-. The purity of the diphenyliodonium salts was checked by thin-layer chromatography.

The products of the radioactive breakdown of iodine-133 in the test compounds were accumulated in iodobenzene and its solutions, in iodobenze deposited on crystals of potassium perchlorate, potassium tetrafluoroborate, etc., and also in crystals and solutions of various diphenyliodonium salts [99-102,147]. For this purpose, the systems were put in bubblers which were sealed and kept in the dark at 0°C for 2–3 days.

The formation of xenon compounds was demonstrated by comparing the radioactivities of the chemically free xenon formed in the β-decay of iodine-133 in the test systems with the radioactivity of the xenon isolated from solutions of $K^{133}I$¶. A $K^{133}I$ solution is used as a standard because here the entire xenon is present in a free state. In both cases the radioactive xenon was transferred to a radioactivity detector by a carrier gas (argon). The lower activity of the xenon accumulated in iodobenzene and diphenyliodonium salts is evidence that part of the xenon is chemically bound. The fraction of chemically bound xenon was determined by measuring the radioactivity of the free xenon after the decomposition of its compounds by substances containing anions capable of coexisting with the 'onium cations of the heavy inert gases (HCl, HI, KOH).

It has been shown that the breakdown of iodine-133 in iodobenzene leads to the formation of xenon compounds only when the substance is deposited on crystals of the corresponding salts. This is evident from the data in Table 5.

Table 5. The formation of xenon compounds in the β-decay of iodine-133 in iodobenzene*.

System in which products accumulate	Activity ^{133m}Xe			Yield of xenon compound
	free	bound	overall activity	
$C_6H_5{}^{133}I$	11500±300	not detected	11020±300	0
0.1% soln. of $C_6H_5{}^{133}I$ in benzene	10830±300	ditto	11020±300	0
0.1% soln. of $C_6H_5{}^{133}I$ in chloroform	9420±200	»	9600±200	0
$C_6H_5{}^{133}I - KClO_4$	2820±50	580±10	1670±30	30±3
$C_6H_5{}^{133}I - KB(C_6H_5)_4$	3360±50	740±10	4250±100	18±1
$C_6H_5{}^{133}I - KBF_4$	1645±30	145±10	1670±30	8±1
$C_6H_5{}^{133}I - K_2SO_4$	26910±300	1420±30	27100±300	5±1
$C_6H_5{}^{133}I - KNO_3$	4310±60	180±15	4250±100	4±1
$C_6H_5I^{133} - KCl$	26310±300	not detected	27100±300	0

*The figures in the second, third, and fourth columns are average values from 5–7 determinations of the yields of the xenon compounds.

The results of experiments on the accumulation of xenon in crystals and solutions of various diphenyliodonium salts are presented in Table 6, which shows that the xenon compounds are not observed when the products are accumulated in crystals and aqueous and hydrochloric acid solutions of diphenyliodonium chloride. In all other cases a considerable proportion of the xenon was present in a chemically bound state.

Further studies were undertaken to elucidate the nature of the xenon compounds (the identity of the chemical state of the xenon formed in the β-decay of iodine isotopes in iodobenzene and in diphenyliodonium salts, proof that xenon forms part of the cation, demonstration of the similarity between the behaviour of the xenon compound obtained and that of the 'onium derivatives of other elements).

To demonstrate that the xenon compounds investigated are of the 'onium type, i.e. that they contain a cationic group incorporating xenon, ion-exchange chromatography and ionophoresis were employed. The chromatographic behaviour of the xenon compounds was investigated in a 2 × 105 mm column filled with Dowex-50X-12 resin (in the H^+-form, 200–400 mesh). The eluent consisted of perchloric acid solutions of different concentrations (Table 7). The elution curves for the xenon compounds formed in the β-decay of iodine isotopes in iodobenzene and diphenyliodonium perchlorate are presented in Figs. 1 and 2.

The ionophoretic behaviour of the xenon compounds was studied in a multicell apparatus of type OE-100, the electrophoretic chamber of which consisted of five cells separated by semipermeable "kutizin" membranes. The outer pairs of cells were filled with 0.001 N perchloric acid and

¶ If the products were accumulated in crystals of the parent substances or in liquid substances deposited on salt crystals, the solid phase was dissolved immediately before the measurement of the radioactivity of free xenon.

the central cells with the solution of the test compound in perchloric acid of the same concentration. The phenylxenonium cations decompose at the cathode with liberation of free xenon. The carrier gas flowing through the cathodic cell passes through a collector and then to a counting chamber. The electrophoretic behaviour of diphenyliodonium cations was investigated at the same time. The results of these experiments are presented in Fig. 3.

Table 6. The formation of xenon compounds in the β-decay of iodine-133 in diphenyliodonium salts.

Accumulation conditions	Yield of Xe compound, %
0.05% soln. of $(C_6H_5)_2ICIO_4$ in 0.1 *N* $HClO_4$	35 ± 3
0.05% soln. of $(C_6H_5)_2IBF_4$ in 0.1 *N* HBF_4	22 ± 2
0.05% soln. of $(C_6H_5)_2IHSO_4$ in 0.1 *N* H_2SO_4	10 ± 2
0.5% soln. of $(C_6H_5)_2INO_3$ in 0.1 *N* HNO_3	6 ± 1
0.05% soln. of $(C_6H_5)_2ICl$ in 0.1 *N* HCl	0
Crystals of $(C_6H_5)_2ICIO_4$	22 ± 2
Crystals of $(C_6H_5)_2ICl$	0

The sum total of the data obtained in the study of the chromatographic and ionophoretic behaviour of the test xenon compounds permits the following conclusions:

(1) The sorption of the test xenon compounds on a cation exchanger and its migration towards the cathode are evidence that xenon forms part of a cationic group;

Table 7. Chromatographic behaviour of organic 'onium cations of xenon and iodine (percentage elution of the cations).

Eluent	Onium cation	Volume of eluent (in free volumes), %																	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
H_2O	$C_6H_5Xe^+$					is not desorbed														
	$(C_6H_5)_2I^+$					ditto														
0.1*N* $HClO_4$	$C_6H_5Xe^+$					»														
	$(C_6H_5)_2I^+$					»														
1*N* $HClO_4$	$C_6H_5Xe^+$	0	39	48	9	3	1	0												
	$(C_6H_5)_2I^+$					is not desorbed														
3*N* $HClO_4$	$C_6H_5Xe^+$	0	41	44	12	2	2	0												
	$(C_6H_5)_2I^+$															5	12	11	11	
5*N* $HClO_4$	$C_6H_5Xe^+$	0	40	43	11	4	2	0												
	$(C_6H_5)_2I^+$										7	14	14	11	11	11	8	7	7	
7*N* $HClO_4$	$C_6H_5Xe^+$	0	45	48	6	1	0													
	$(C_6H_5)_2I^+$	0	0	8	10	15	14	14	12	9	7	5	4	2	0					

(2) the identity of the chromatographic behaviour of the xenon compounds produced in the β-decay of iodine in iodobenzene and diphenyliodonium salts indicates that in both cases the same xenon compound is formed.

On the basis of the general relations governing the chemical changes following β-transformations of atoms in fully organic and 'onium organic derivatives and also mass-spectrometric data, one may conclude that in this case the cation is $(C_6H_5Xe)^+$.

The possibility of the formation of a xenon cation as such is excluded by the position of its vacant electronic levels. This is consistent with the failure of experiments designed to obtain the corresponding xenon compounds by the radioactive breakdown of iodine in the compound $C_6H_5^{133}I(ClO_4)_2$.

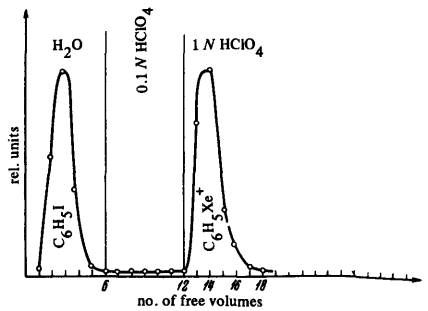


Figure 1. Elution curves of the xenon compound formed in the β-decay of iodine-133 in iodobenzene.

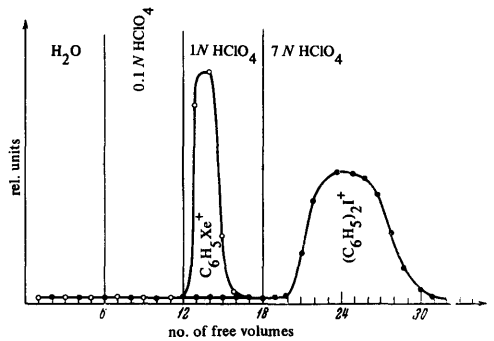


Figure 2. Elution curve of the xenon compound formed in the β-decay of iodine-133 in diphenyliodonium perchlorate.

It is important to note that the processes involving molecular ions formed in β-decay in molecular systems may be determined to a large extent. Thus, by selecting the isotopes of the parent elements with a definite mode of radioactive decay, the type of the initial compounds, and the nature of the substituents, and also by varying the conditions in which the breakdown takes place, it is possible to obtain definite compounds of the daughter elements. In particular mention should be made of the possibility of influencing the processes involving primary molecular ions by introducing substituents of various types into aromatic groups[23,24,26]. This is because electron-donor substituents increase the stability of the primary molecular ions (the yield of the stabilisation product increases at the same

time), while electron-acceptor substituents decrease the stability (the yield of the stabilisation products falls). Since the Hammett equation is applicable to processes involving primary molecular ions formed in the β-decay, it is possible to predict, without resorting to experiments, the fraction of the primary molecular ions which persist and hence also the yield of the products of their stabilisation and partial fragmentation.

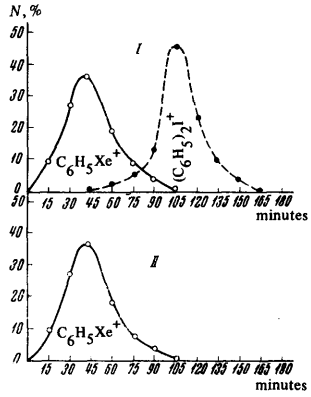


Figure 3. Electrophoretic curves for the xenon compounds formed in the β-decay of iodine-133 in diphenyliodonium perchlorate (I) and iodobenzene (II); N – the fraction of ions which have migrated to the cathodic compartment.

In conclusion we may note that further studies on organic compounds of the inert gases should be designed both to extend the range of investigations in the field of the chemical changes occurring in β-decay processes of halogen isotopes and also to obtain organic derivatives of the inert gases by the usual methods of chemical synthesis.

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