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CHEMICAL CHANGES DURING β-DECAY PROCESSES

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I. INTRODUCTION

The study of the chemical consequences of nuclear transformations is one of the most interesting and at the same time one of the most complex fields of radiochemistry; it has been called the chemistry of hot and excited atoms[1-11]. Studies in this field are of considerable theoretical and practical interest for both radiochemistry and chemistry in general, since they make it possible to obtain important information on the characteristic features of the behaviour of atoms of elements existing in particular energy and charged states and in completely new and unusual experimental conditions. From the practical view point, the study of the behaviour of atoms produced in different kinds of nuclear process is of considerable importance for the concentration of radioactive isotopes, the separation of nuclear isomers, and the preparation of various labelled compounds.

The study of the chemical changes during β-decay processes has revealed new possibilities in studies of this type. The processes of the electron- and positron-decay of atoms have provided a new method of exciting and ionising molecules and an original source of positive and negative molecular ions of any degree of complexity and with different initial localisation of the charge and excitation. Such ions may be generated both in highly rarified (gaseous) and in condensed (liquid and solid) phases. This makes it possible to examine how their behaviour is influenced by effects associated with the possibility of transfer of excitation energy to the surrounding medium, reaction with this medium, and other processes. Comparison of the consequences of excitation produced by the β-decay of atoms with other forms of molecular excitation (electron collision, photoionisation) makes it possible to observe the characteristic features of the redistribution of the energy of the nuclear transformation between the emitted β-particle and the molecular system and also to study the ways in which the excitation energy is redistributed in the molecular ion.

Methods making use of the chemical effects accompanying β-transformations and based on the processes of stabilisation and breakdown of molecular ions make it possible to prepare compounds of the daughter element with the highest possible specific activity, extremely difficult to prepare by ordinary methods. These new methods may be particularly important for the preparation of compounds of typical radioactive elements such as polonium, francium, and astatine. Moreover, in recent years extremely simple and elegant methods have been developed for the separation of radioactive isotopes by making use of the phenomenon of chemical-bond rupture during β-decay.

The importance of studies of chemical changes during β-decay processes extends beyond the limits of radiochemistry and the general chemistry of the elements, since such studies in a number of cases make it possible to reach conclusions regarding the nuclear transformations themselves. On the other hand, it is impossible to explain the chemical changes accompanying β-decay without making use of the results of special nuclear or related studies. It will therefore be appropriate to begin with a description of those factors in the field of nuclear physics which determine the state of the daughter atoms produced during β-decay processes.

II. FACTORS DETERMINING THE STATE OF DAUGHTER ATOMS

By the factors determining the state of daughter atoms we mean those factors which influence the energy and charged states of these atoms and thus determine their distribution between the stable and labile forms of the element possible under the given conditions. These factors include the kinetic energy of the daughter atom (recoil energy), acquired as the result of the emission of β-particles, conversion electrons, or γ-quanta; the internal conversion of the γ-radiation of the daughter atom in its electron shells; and changes in the electron shells of the atoms as a result of the sudden change in the charge of the nucleus [12,13].

The final chemical state of the elements formed in β-decay processes is influenced to a considerable extent by the chemical state of the mother elements and the conditions under which breakdown of the mother molecule takes place.

1. Recoil during β-Decay

The atoms produced in nuclear transformations very often acquire a high kinetic energy, many times greater than the average energy of thermal movement. These atoms are called hot atoms.

The maximum recoil energy for β-decay is calculated from the formula:

$$E_{M(\max)} = 548\frac{E_{\beta(\max)}}{M} + 536\frac{E^2_{\beta(\max)}}{M}, \qquad (1)$$

obtained with allowance for the relativistic dependence of the mass of the β-particles on velocity [1]. In this formula the maximum recoil energy $E_{M(\max)}$ is expressed in eV, the maximum energy of the β-particles in MeV, and M, the mass of the recoil atom, in atomic mass units.

For light nuclei exhibiting a high maximum β-radiation energy, the recoil energy may reach very high values. For ^{12}B, for example, the maximum recoil energy is 8.68×10^3 eV, and for ^{8}Li it is as high as 11.7×10^3 eV. For intermediate and heavy nuclei and the maximum β-radiation energies most frequently encountered (1-2 MeV), the recoil energy is close to the energy of the chemical bond formed by the atoms. In the case of heavy nuclei with low β-particle energy, the recoil energy may be much less than the chemical bond energy. This is the case, for example, for the transformations RaD(^{210}Pb)–RaE(^{210}Bi), ThB(^{212}Pb)–ThC(^{212}Bi), etc. For RaD–RaE the maximum recoil energy for the emission of a β-particle is only 0.04 eV.

Formula (1) can be used to calculate the maximum recoil energy, *i.e.* it is applicable only for those comparatively rare cases of β-decay where the energy removed by the neutrino is equal to zero. In the general case, the energy of the β-particles emitted during the decay of a given isotope varies from zero to a certain maximum value. The difference between the maximum energy and the actual energy of the β-particle is removed by the neutrino. Thus in the general case, in the calculation of the energy of recoil atoms, it is necessary to make allowance for the simultaneous emission of two particles (the β-particle and the neutrino). The observed recoil energy in this case will depend on the distribution of the total energy of decay between these particles and also on the angle between the directions of their escape. Since there are different combinations of energy distribution between the β-particle and the neutrino and the directions of their escape, the recoil atoms have different energies. We therefore have to deal with a recoil atom energy spectrum. The calculation of this energy spectrum involves a number of difficulties. The available data on the angular correlation of the β-particle and neutrino are indefinite, and this prevents rigorous quantitative calculation of the energy spectrum of recoil atoms.

The proportion of recoil atoms with energies above certain minimum depends to a marked extent on the nature of the angular correlation between the β-particle and the neutrino [2]. Fig. 1 gives the energy spectra of recoil atoms for an atom with mass 100 and $E_{\beta(\max)} = 2.0$ MeV, for different types of angular correlation: (a) escape of β-particle and neutrino in the same direction, (b) escape of β-particle and neutrino in opposite directions, and (c) isotropic radiation.

Thus the angular correlation between the β-particle and the neutrino should influence the efficiency of chemical-bond rupture resulting from recoil phenomena. This forms a basis for obtaining qualitative information on correlation phenomena during β-decay.

β-Decay is often accompanied by the emission of γ-rays and conversion electrons, which also bring about recoil effects. It is easy to make allowance for these effects and they are not usually important†.

Suess [14] showed that for diatomic molecules, the recoil energy used up directly for bond rupture depends on the ratio $R/(R + M)$, where R is the mass of the molecular residue and M the mass of the recoil atom. This means that only a fraction of the recoil energy, equal to $E = E_M\frac{R}{R+M}$, where E_M is the recoil energy, can be used up in bond rupture. The remaining fraction of the recoil energy is realised as the kinetic energy of the whole molecule.

When the part played by the phenomenon of recoil is assessed, we find that in different cases of β-decay, recoil may have a decisive influence or an insignificant influence

† The recoil energy for the emission of γ-quanta is calculated from the formula $E_M = 536E^2_\gamma/M$, where E_M is the recoil energy in eV, $E\gamma$ the energy of the γ-quanta in MeV, and M the mass of the atom in atomic units. In the case of emission of conversion electrons, the recoil energy is greater than that for the emission of the corresponding γ-quantum and is given approximately by the formula $E_M = 541E_e/M$, where E_M is the recoil energy in eV, E_e the energy of the conversion electron in MeV, and M the mass of the recoil atom in atomic units.

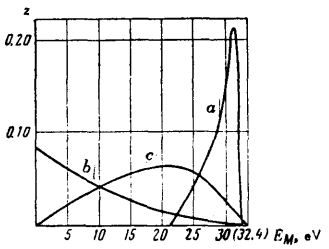


Fig. 1. Energy spectrum of recoil atoms for different cases of corelation between β and ν.

on chemical-bond rupture. The contribution of the phenomenon of recoil can be estimated in each individual case with satisfactory accuracy.

2. Excitation and Ionisation of an Atom during β-Decay

The excitation and ionisation of atoms during radioactive transformations may be produced by three factors which are approximately independent: (a) recoil of the nucleus (kinetic activation of the recoil atoms), (b) direct reaction of the radiation emitted by the nucleus with the atomic electrons, and (c) the sudden change in the charge of the nucleus.

These factors influence the degree of excitation or ionisation of the atoms to different extents during β-decay. The perturbations undergone by different electrons of the same atom also differ. For some electrons they may arise slowly (adiabatically) and for others suddenly (non-adiabatically).

By means of the criterion of sudden perturbation, formulated by Pauli[12,15], it can readily be shown that during β-decay (and also α-decay) the velocity acquired by the atom as a result of recoil is insufficient to bring about ionisation of even the outer electrons. (Ionisation as a result of recoil takes place, for example, during nuclear fission, where the divergence of the fission fragments is adiabatic only with respect to the internal electrons[16-19].)

Migdal[20], Feinberg[21], and others have shown theoretically that in the general case the direct reaction of β-particles with atomic electrons is negligible.

In β-decay, the chief part in the excitation and ionisation of recoil atoms is played by another mechanism. Migdal[20], Feinberg[21], Schwartz[22], Levinger[23], Winther[24] and others have shown that the chief part in the excitation and ionisation of recoil atoms in the emission (or absorption) of charged particles is played by the effect of the "shaking" undergone by the electrons as a result of the sudden change in the charge of the nucleus. The perturbation undergone an electron shell of the atom during β-decay is nonadiabatic, since the β-particle leaves the atom at a velocity immeasurably greater than the rate of movement of the orbital electrons. According to theoretical calculations, the probability of ionisation during the sudden change in the charge of the nucleus is proportional to $1/Z_{\text{eff}}^2$ (Z_{eff} is the effective charge of the nucleus).

Calculations carried out using the hydrogen-like wave function for atoms with a nonadiabatic approximation concern chiefly the K, L, and M shells. The results of the calculation, by different authors, of the probabilities of ionisation in these shells for atoms with high values of Z are compared in Table 1.

Screening decreases the effective charge of the nucleus Z_{eff} fairly rapidly, so that the electrons in the outer shell have the highest probability of excitation to the state of ionisation.

The most detailed quantum-mechanical calculations of the excitation and ionisation of daughter atoms have been made by Winther[24,25] for the $^6He \xrightarrow{\beta^-} {}^6Li$ transformation, since for this case the wave function describing the ground state of helium and several states of lithium is known. The distributions of the daughter atoms with respect to excitation energies, obtained by Migdal and Winther, show a sharp decrease in the probability of conversion into the excited state with increase in the excitation energy, and up to 70% of the daughter atoms are formed in the ground state. At the same time calculations show that 25% of the $(^3He)^+$ has 20.5 eV excitation relative to the ground state, and for 17% of the $(^6Li)^+$ the figure is about 60 eV.

Green[26] has carried out theoretical calculations of the probabilities of ionisation of daughter atoms for the case of $^{79}Kr \xrightarrow{\beta^-} {}^{79}Rb$ decay. These results were later tested experimentally and satisfactory agreement with theory was obtained.

Serber and Snyder[27] made a theoretical estimate of the average excitation energy for β-decay by averaging the probabilities of distribution for conversion from the ground state of the mother atom to different final states of the daughter atom. They obtained the following expression for the average excitation energy for the case of heavy nuclei:

$$\Delta E = 22.85\, Z^{2/5}(Z' - Z)^2,$$

where ΔE is the mean excitation energy of the daughter atom in eV, and Z and Z' are the atomic numbers of the elements. As already noted, however, this expression does not give a picture of the actual distribution of the daughter atoms with respect to excitation energies.

Theory predicts[20,23] that the effect of "shaking" during positron-decay is of approximately the same magnitude as that for β^--decay.

In general, published calculations of the probabilities of ionisation during β-decay are inaccurate because of the approximations made. In this connection it is important to estimate the applicability of the nonadiabatic approximation used in these calculations; this is fairly satisfactory for the inner shells of heavy atoms. For other cases the accuracy of the nonadiabatic approximation decreases with increase in the shell number and with increase in the charge of the nucleus. For the outer electrons of the cloud, the

TABLE 1. Calculated values of the ionisation probability for the β-decay of atoms.

Shell	Ionisation probability $\times Z_{\text{eff}}^2$, from:			
	Migdal[20]	Feinberg[21]	Schwartz[22]	Levinger[23]
K	0.6	0.64	0.66	0.65
L	6.8	—	2.26	2.1
M	14	—	4.28	—

"shaking" resulting from change in the charge on the nucleus will be "delayed" and not so powerful as that for the electrons of the inner shells. Nevertheless the probability of ionisation during decay increases with increase in the shell number, since the outer electrons are less firmly bound and the effective nuclear charge with respect to these electrons is low.

Experimental confirmation of the "shaking" theory was until recently based on absolute counting of the characteristic X-radiation accompanying β-decay. The calculated and experimental values of the probabilities of ionisation of the internal electron shells were compared. The results obtained confirm the theory over a wide range of atomic numbers. Examples include the data given by Renard[28] for ^{32}P and RaE, Robinson and Howland[29] for ^{35}S, Michalowicz[30] for $^{90}Sr-^{90}Y$ and RaE, Boehm and Wu[31] for ^{147}Pm and RaE, Langevin-Joliot[32,33] for ^{147}Pm, and by other authors[34,35].

Despite the importance of such studies, it must be remembered that they can be used for the experimental verification of Migdal's theory only for the inner electron shells. The first experimental studies of the effect of "shaking" on the outer electron shells were made by Wexler for the case of the β-decay of tritium, ^{14}C, and ^{41}Ar.[36] The results of these experiments (Table 2) show that in all cases (even for the atoms of elements such as carbon, for which the "shaking" effect should be strongest), the average charge of the daughter atoms is close to unity. This is apparently due to the fact that the presence of a relatively small quantity of ions with multiple charges (chiefly doubly charged) could not be recorded with sufficient accuracy by the methods used.

Basic information on the effect of "shaking" on the outer electron clouds of atoms has recently been given by the charge spectrometry of recoil atoms. Snell and Pleasonton[37-39] have made a systematic study of the charge spectra of recoil atoms during the β-decay of various isotopes of the inert gases. The use of the monatomic inert gas for the observations made it possible to avoid the influence of molecular effects. The results of the studies[39] of the charge spectra of recoil atoms during the β-decay of ^{6}He, ^{39}Ar, ^{85}Kr, and ^{133}Xe (Table 3) show that singly charged ions predominate in the charge spectra. In the case of β-decay the singly charged ion is produced directly by the emission of a nuclear β-particle and the resulting increase in the charge of the nucleus by one unit. Thus in 80–90% of all decays there is insufficient excitation energy for ionisation. The loss of one orbital electron leads to a charge of +2. Thus in the case of pure β-decay, the relative yield of the ion with charge +2 in the charge spectrum gives almost exactly the probability of ionisation of the outer shell as a result of the "shaking" effect. The experiments show that this

TABLE 2. Average charge of the daughter atoms for the β-decay of T, ^{14}C, and ^{41}Ar.

Isotope	Chemical formula	Maximum energy of β-particles in MeV	Average charge of daughter atoms
T	T_2	0.018	0.9±0.1
^{14}C	$^{14}CO_2$	0.155	1.0±0.2
^{41}Ar	Ar	1.245	1.0±0.1

TABLE 3. Charge distribution of recoil atoms for the β-decay of various isotopes (% of total number of decays).

charge	Isotope ^{6}He	^{39}Ar	^{85}Kr	^{133}Xe
1+	89.4±3	86 ±3	79.2 ±0.4	80
2+	10.6±1.0	10.5±2.0	10.9 ±0.2	8
3+	0.04±0.01	2.5±0.8	3.91 ±0.12	4
4+	—	0.9±0.4	3.12 ±0.13	3
5+		0.3±0.2	1.51 ±0.07	—
6+		<0.05	0.66 ±0.04	~5
7+			0.40 ±0.02	
8+			0.18 ±0.02	
9+			0.093±0.01	
10+			0.026±0.006	
11+			<0.003	

removal of one of the outer electrons takes place in approximately 10% of all decays. If the primary ionisation takes place in an inner shell, the atom may be even more extensively ionised as a result of subsequent Auger transitions. The relatively small quantity of ions with multiple charge in the charge spectrum indicates that the removal of the inner orbital electrons is much less frequent than removal of the outer electrons. These results confirm Winther's data[25] for the $^{6}He \xrightarrow{\beta^-} {}^{6}Li$ transformation. According to the theoretical calculations of the author, the loss of one electron takes place in 10.5 ± 5% of cases and the loss of two electrons in less than 0.1%. These calculations show good agreement with the experimental data (10.6 ± 1.0 and 0.04 ± ± 0.01% respectively).

On the whole, the data at present available show fairly good agreement with the model based on the "shaking" resulting from sudden changes in atomic number.

3. The Emission of γ-Quanta by the Excited Nuclei of Daughter Atoms and the Phenomenon of Internal Conversion during β-Decay

β-Decay leads fairly frequent to excited states of the nuclei of daughter atoms and the daughter nucleus may return to the ground state by two competing processes: radiation of the excess energy in the form of γ-quanta, or internal conversion[40,41]. The phenomenon of γ-quanta emission by excited nuclei may itself lead to additional, albeit weak, effects (recoil during the emission of the γ-quantum).

The probability of the discharge of the excited state of nuclei by internal conversion, *i. e.* by direct transfer of the excitation energy of the nucleus to the electron shells of the atom, depends to a considerable extent on the atomic number of the element and the energy, nature and multipolarity of the radiation. These processes are most marked in the case of heavy nuclei[40,41].

Internal conversion leading to the removal of electrons from deeply lying shells, for example the K or L shells, is often followed by Auger transitions without radiation. It is now well known that the cascade of vacancies developing in the process leads to the accumulation of a considerable positive charge (multiple ionisation of the atom). The development of analogous cascades of vacancies is due to capture of an orbital electron (K-capture) and also, to a slight extent, to processes of β-decay as a result of the ionisation of inner electron shells when the nuclear charge changes suddenly.

Experimental confirmation of these ideas is provided by the work of various authors on the determination of the average charge of the daughter atoms when conversion phenomena are involved in the case of K-capture and isomeric transition[42-49]. The examples which have been studied in most detail include K-capture in ^{37}Ar. In the first work on the determination of the charge state of ^{37}Ar atoms by collection of the ions in an electrical field[42-44], average charge values close to +3 were obtained.

Snell and Pleasonton[47,48] made a detailed study of the charge distribution of recoil atoms for K-capture in ^{37}Ar by the methods of mass-charge spectroscopy. The distribution with respect to the charges of the recoil atoms, expressed as percentages of the total number of disintegrations, is given in Fig. 2. This distribution of recoil atoms with respect to charges arises because the cascades of vacancies are the predominating processes. The "shaking" effect is shown to a much smaller extent than with β^--decay, since the change in the nuclear charge is smoothed out to some extent by the loss of the K-electron. This feature was first noted by Primakoff and Porter[49].

The high efficiency for ionisation of the atom, shown by the processes of internal conversion, can be seen from the charge spectrum (Fig. 3) of the recoil atoms formed during the decay of ^{131m}Xe (isomeric transition, converted to the extent of 98%). The average charge in this case is +7.9.[48] An even higher charge state (+10.5) was obtained by Wexler[36] for the decay of ^{80m}Br (in the form of C_2H_5Br).

In addition to these charge spectra for simple cases (pure β-decay, Table 3; K-capture, Fig. 2; highly converted isomeric transition, Fig. 3), Snell and Pleasonton[48] give data on the spectra of recoil atoms for the case of complex decay schemes. These complex spectra are as it were, composed of simple spectra and have several maxima due to different processes.

Conversion phenomena are of considerable importance with elements of high atomic number which are very soft β-irradiators; the nuclei of the daughter atoms from these elements are in intermediate excited levels immediately after decay. This is particularly true of the chains: RaD(^{210}Pb)–RaE(^{210}Bi), ThB(^{212}Pb)–ThC(^{212}Bi); RaB(^{214}Pb)–RaC(^{214}Bi), etc. As shown below, the study of the chemical state of RaE, ThC, and RaC, produced by the decay of RaD, ThB, and RaB in certain organolead compounds shows that the phenomenon of internal conversion is one of the

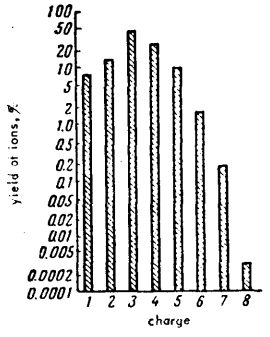


Fig. 2. Charge distribution of recoil atoms for K-capture in ^{37}Ar.

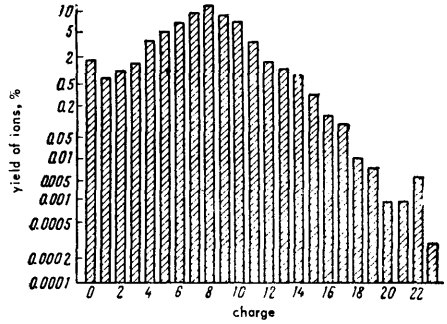


Fig. 3. Charge distribution of recoil atoms for ^{131m}Xe.

main causes of chemical-bond rupture during the β-decay of these isotopes. This is indicated, in particular, by the fact that the internal conversion coefficients coincide with the maximum yield of the inorganic forms of RaE, ThC, and RaC.

We shall conclude this description of the various mechanisms of excitation and ionisation of atoms during β-decay by considering the process noted by Wolfsberg and Perlman[51], who suggest that the emission of conversion electrons brings about electrostatic "shaking" analogous to that which is observed during the sudden change in nuclear charge, and that this may lead to excitation and ionisation of atoms. There are no experimental data in support of this mechanism and it may be assumed to accompany Auger transitions to some extent.

III. PROCESSES DEVELOPING IN MOLECULAR SYSTEMS DURING β-DECAY

Since after emission of a β-particle the daughter atom may possess a single positive charge even in the absence of further ionisation, it is obvious that if the decaying atom is part of a molecule, the first direct result of the β-decay process will be the production of a primary molecular ion with an electronic charge of +1. Data obtained in theoretical and experimental studies show that a considerable proportion of the primary molecular ions exists in various excited levels immediately after their formation. Here we may have not only electronic excitation but also the excitation of vibrational and rotational levels of the molecular ion. The main cause of the electronic excitation is the nonadiabatic character of the β-decay processes ("shaking" effect), whereas the initial excitation of the vibrational and rotational levels is due chiefly to the effect of radioactive recoil.

It should be remembered that a particularly important factor in the behaviour of the primary molecular ions is the change in the chemical nature and charge state of one of the atoms of the molecular system and the resulting thermodynamic stability or instability of these molecular ions. The Frank–Condon principle shows that for adiabatic transitions the cause of the excitation of the vibrational levels of the molecular ions is the change in the chemical nature and charge state of the decaying atom. The configuration of the nuclei in the molecular ion at the moment of its

formation is "inherited" from the initial molecular system and will not in general correspond to the minimum potential energy of this ion. This means that the so-called vertical transitions on the potential-energy diagram, associated with the change in the chemical character and electronic state of the atom, will lead to the production of molecular ions existing in different excited vibrational levels.

The behaviour of excited molecular ions depends on many factors: the nature of the initial molecular system, the composition and structure of the molecular ions, their stability in the ground level and excited levels, the distribution function of the daughter atoms with respect to energies, the extent and rate of the transfer of the excitation energy of these atoms to the molecular ion, and the surrounding medium, etc. Subsequent changes may involve either stabilisation processes or fragmentation processes, depending on the energy state of the initial molecular ion and the above factors. Either type of process leads finally to stable chemical forms of the daughter elements. Processes involving neutralisation of the primary molecular ions, existing in ground levels, by electrons and negatively charged ions may lead to the formation of stabilisation products of these ions. Processes involving the fragmentation of excited molecular ions lead to the production of various types of fragment, which may be stabilised in the form of different chemical products.

The use of β-decay processes for the preparation and further study of molecular ions is an extremely effective method compared with classical techniques using relatively inefficient methods of excitation. Another important advantage of these processes is the possibility of bringing about excitations and ionisations which initially are highly localised. An interesting feature is that whereas in β^--decay in molecular systems, positively charged ions are produced, positron-decay should lead to the appearance of negatively charged molecular ions. This is of particular interest for the production of negatively charged ions in condensed phases.

Despite the intensive theoretical and experimental studies of the consequences of β-decay for atomic systems, until recently very little theoretical work had been done on the nature of excitation processes and their consequences in molecular systems. Existing work includes the general theoretical studies of Schwartz[22], Cantwell[52], and Wolfsberg[53], on the excitation of molecular systems during β-decay processes. These studies were based on quantum-mechanical methods. The approximate calculations showed that, as in the case of atomic systems, a large proportion of the singly charged ions formed in β-decay exist in ground levels or levels with similar energies. For excitation resulting from the $^{14}C \xrightarrow{\beta^-} {}^{14}N$ transition, Wolfsberg[53] showed that as a first approximation the probability of transition to the ground level is the same for molecular and atomic systems. Cantwell[52] calculated the probabilities of transition from the ground electronic state of TH and T_2 to different vibrational levels of their daughter products.

The data obtained in these theoretical studies were verified experimentally for the decay of tritium in the TH and T_2 systems and for ^{14}C in the $^{14}CH_3-{}^{14}CH_3$ system[54-56]. The theoretical and experimental results are of the same order of magnitude, but the problem as a whole is too complex for detailed theoretical solution. The problem is even further complicated on going to the real polyatomic molecular systems studied, for which the number of different vibrational and rotational states is extremely high.

Recent studies by Wexler and others, which we shall examine in more detail later, show that the behaviour of the complex molecular ions formed during β-decay processes may in some cases be described quantitatively by means of the statistical theory of fragmentation, developed by Eyring, Rosenstock, and others for electron collision[57-59]. The application of this theory to β-decay processes by Wexler and others is based on the fact that an analogy should exist in the behaviour of identical molecular ions formed on β-decay and electron collision. For example, there is no essential difference between the $C_6H_5^+$ ion formed by the β-decay of monotritiated benzene and the analogous ion formed by benzene on electron collision, apart from the total energy and its distribution. We may thus also expect an analogy in the appearance of the different type of fragmentary ion formed during the decay of a corresponding mother ion. In this connection an extremely important factor in the kinetics of the monomolecular decay of the mother ion is the relationship between the potentials at which the different ionic fragments appear and their relative yields.

The basis of the theory put forward by Rosenstock and others[57-59] for this monomolecular decay process is that the excess electronic energy acquired is not localised in a definite bond but is distributed throughout the various degrees of freedom of the whole molecular ion by means of radiationless transitions. The subsequent decay of the vibrationally excited mother ions takes place by competing quasi-equilibrium monomolecular processes. The initial postulates of this theory are confirmed by a number of experimental facts established in the study of phenomena accompanying electron collision in polyatomic molecules (the lack of proportionality between the yield of molecular ions and the number of corresponding bonds, the detection of so-called metastable peaks, etc.)[60].

A fundamental feature of the work of Rosenstock and others is the statistical approximation, which is useful for polyatomic molecules. A disadvantage of this method is the somewhat indefinite nature of the choice of parameters. Moreover, this theory can hardly be applied to the description of phenomena accompanying β-decay in condensed phases, although it may serve for a qualitative description of the processes taking place. It should be noted that other theoretical approaches to the problem of electron collision also exist[61-65].

In the foregoing discussion we did not deal with the important question of the possibility of formation of multiply charged molecular ions. The production of multiply charged ions is an important consequence of β-decay. A similar effect is also apparently to be expected for molecular systems. It has been shown that a particularly marked accumulation of positive charge takes place in internal conversion processes. Since the phenomenon of internal conversion often accompanies β-decay processes, it will have a considerable effect on the behaviour of the original molecular system. Intensive molecular breakdown is obviously to be expected when internal conversion processes start cascades of vacancies. Recent work[66] showed that the most important result of this type of process for molecular systems is the rapid internal redistribution of charge in the molecular and the subsequent coulombic repulsion. The distribution of the fragments with respect to mass and charge in isomeric transition in $CH_3{}^{80m}Br$ and $CCl_3{}^{80m}Br$ has been studied. The distribution with respect to charge for ^{80}Br, ^{35}Cl, and ^{12}C atoms in isomeric transition in $CCl_3{}^{80m}Br$ is shown in Fig. 4.

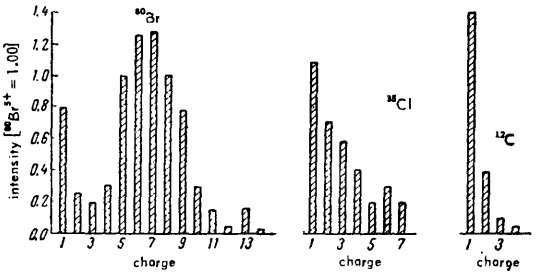


Fig. 4. Charge distribution of recoil atoms for isomeric transition in $CCl_3{}^{80m}Br$.

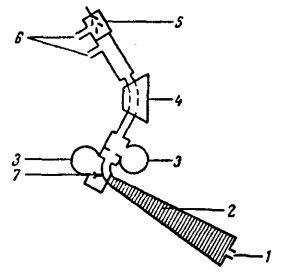


Fig. 5. Diagram of charge mass-spectrometer:
1) gas inlet, 2) system of rings, 3) 450 litre sec^{-1} pump, 4) 60° magnetic analyser, 5) photomultiplier, 6) to pump, 7) reflector.

It can be seen that in this case, in addition to ^{80}Br atoms with multiple charges of up to +14 (the maximum lies at +7), the spectrum shows ^{35}Cl and ^{37}C atoms with multiple charges of up to +7 and ^{12}C atoms with charges of up to +4. The charge spectra of the carbon and chlorine atoms show that although internal conversion and subsequent Auger transitions take place in the bromine atom, the charge is distributed throughout the whole molecule. This internal charge transfer is a fairly rapid and intensive process leading to extensive molecular breakdown as a result of the coulombic repulsion of the distributed charges.

IV. EXPERIMENTAL METHODS OF STUDYING CHEMICAL CHANGES DURING β-DECAY PROCESSES

The following experimental methods are used at present to study the chemical changes during β-decay processes: (1) the charge mass-spectrometry of the fragments formed as a result of radioactive decay, and (2) the radiochemical study of the final products of radioactive transformations (the use of compounds with more than one labelled atom is a special form of the second method).

A special mass-spectrometer can be used to measure the charge of the ions formed as a result of decay in a highly evacuated gas. Measurement of the distribution of the resulting fragments with respect to mass and charge in this way before the ions collide with other ions or molecules can give a detailed picture of the changes resulting from the radioactive decay of the atoms present in different molecules. The charge mass-spectrometer used by Wexler[67] is illustrated in Fig. 5. The radioactive gas passes through a capillary opening into a conical source with a volume of 80 litres, where it decays at a pressure of 10^{-6}–10^{-5} mm Hg. The conical source contains a system of rings to which is applied a potential of 150–500 V in such a way that the positively charged ions formed during radioactive decay are directed towards the apex of the cone. On leaving the cone, the ions are accelerated between two grids with a high accelerating potential (up to 600 V). After passing a reflector and condenser (to separate the ions from neutral molecules) the positively charged ion beam is directed into a magnetic analyser which measures the relative quantities of ions of different charge. After further acceleration to 3600 V the ions are detected by means of an electron multiplier. High differential evacuation is maintained throughout the whole system to prevent the passage of radioactive gas into the region of the detector. Apparatus of other design has also been described[66,68].

Charge mass-spectrometry is extremely effective for establishing the initial picture of the distribution of the fragments with respect to mass and charge. It makes it possible to study the consequences of radioactive decay in isolated atoms and molecules, and the daughter atoms may not be radioactive.

In the radiochemical method of studying chemical changes during nuclear processes in general and β-decay in particular, the initial distribution of the fragments with respect to mass and charge is estimated from the composition of the final products. Essential conditions for the application of this method are that the daughter atom should be radioactive and that there should be no isotopic exchange reactions which might lead to breakdown of the initial distribution of the daughter element between different chemical forms. The method of isotopic carriers is widely used for the identification and determination of the quantity of the different chemical forms of the daughter element. For the same purpose, use has recently also been made of a chromatographic method which in many cases makes it possible to do without carriers.

An extremely valuable method for studying the chemical consequences of β-decay is that using compounds labelled with more than one atom. The radioactivity of the radicals and groups combined with the decaying mother atom in this case makes it possible to follow the fate not only of the mother atom but also the other fragments of the molecule. The extensive introduction of this method is restricted by the low degree of development and complexity of the synthesis of compounds labelled with more than one atom[69].

When radiochemical methods of analysis are used to study the consequences of β-decay, it must be remembered that the observed chemical forms may appear as a result of the rearrangement of the mother molecule (survival), as a result of the recombination of fragments, or as a result of the interaction of certain forms with one another, with carriers, and with the surrounding medium. On this basis the chemical forms of the daughter element may be classified as primary, secondary, and tertiary. The primary forms are those produced as a result of the transformation of the molecular ions formed directly after β-decay. The secondary forms are those produced as a result of the recombination of fragments. Such processes would be expected to have a high probability under conditions of decay in

crystals, since the migration of the fragments formed during decay is almost impossible in this case. In addition to processes leading to the appearance of primary and secondary forms, we may also have subsequent redistribution of the daughter element as a result of the reaction of these forms with the surrounding medium and with carriers. The forms thus produced may be described as tertiary forms.

V. REVIEW OF EXPERIMENTAL WORK

1. Inorganic Systems

The study of the chemical changes during the β-decay of atoms in inorganic molecules, until recently, was carried out exclusively by radiochemical methods. In work of this kind, an essential condition is that the daughter element should be able to exist in several stable valence states or in different stable compounds incapable of undergoing isotopic exchange under the conditions of the separation. It is particularly difficult to satisfy these conditions for inorganic systems and this makes correct interpretation of the results difficult.

Charge mass-spectrometry is to a considerable extent free from these disadvantages, and this method has been used to study three very simple gaseous inorganic molecules: tritium hydride (TH), tritium (T_2), and carbon dioxide ($^{14}CO_2$).[48,54,55] The compounds were studied at a pressure of 10^{-5}–10^{-6} mm Hg, which excluded the possibility of intermolecular and interionic interaction. The ions formed as a result of β-decay were recorded by the spectrometer in a time interval of 10^{-4}–10^{-5} sec. This is much longer than the time required for radiative transitions (10^{-8} sec) and, more particularly, the period of atomic vibrations (10^{-14} sec), so that the energy of the excited molecular ion produced initially can be redistributed through all the degrees of freedom, and, in addition to the primary molecular ions, experiment reveals ions formed by the decay of the excited molecular ion. The results of a study of the distribution of the ions formed during the β-decay of tritium in the simplest inorganic molecules are given in Table 4.

The data on the decay of TH were obtained on two spectrometers with markedly different ionic optics and may give some idea of the reproducibility of the results obtained using different experimental techniques.

TABLE 4. Mass and charge distribution of ions formed during the β-decay of tritium in TH and TT.

Molecule	Ions formed	Concentration of ion, %	
		results of Snell et al.[56]	Wexler's results[55]
TH	$^3HeH^+$	93.2 ±1.9	89.5±1.1
	$^3He^+$	5.1 ±0.3	8.2±1.0
	H^+	1.55±0.16	2.3±0.4
	$^3He^{2+}$	0.14±0.01	
TT	$^3HeT^+$		94.5±0.6
	$T^+ + {}^3He^+$		5.5±0.6

The first noteworthy feature is that after decay a large proportion of the molecules remain combined in the form of the helium hydride ion $(^3HeH)^+$ or the helium tritide ion $(^3HeT)^+$. This is a stable combination, familiar in mass-spectrometry. The data also show how sharply the removal of an electron takes place by the "shaking" mechanism. This mechanism should lead unavoidably to the appearance of H^+ or He^{2+}, but the observed total intensity of these ions amounts to only 1.7% (2.3% according to Wexler). Moreover, this is an upper limit, since H^+ and He^{2+} may be formed in other ways. This value of 1.7–2.3% is comparable with the theoretical value of 2.5%[20] for the probability of removal of an electron in the conversion of atomic tritium into the ^3He ion. Comparison of the yields of $(H^3He)^+$ and $(T^3He)^+$ (89.5 and 94.5%) shows that the heavy isotopic molecules are more stable towards dissociation as a result of β-decay. This is due to the slight difference in the zero-point energies of the TH and TT molecules. An interesting feature is that similar effects associated with mass were observed for H_2, D_2 and T_2 molecules on electron collision[70,71].

The molecular changes accompanying the β-decay of atoms in diatomic molecules may be discussed from the viewpoint of Frank–Condon transitions, since the movement of the nuclei is very slow compared with that of the electrons and nuclear particles. The logical application of the Frank–Condon principle to explain the dissociation of TH and T_2 during β-decay has been carried out by Wexler[55].

Of considerable importance in the study of the chemical change accompaying β-decay is the ^{14}C isotope, which has been used in a large number of organic and biochemical studies. Here we shall examine some data on the consequences of β-decay in ^{14}C in the $^{14}CO_2$ molecule[48]. Mass-spectrometric studies have been made with radioactive carbon enriched to the extent of 38% in ^{14}C. Data on the decay of $^{14}CO_2$ (Table 5) show that the nitrogen atom formed as a result of the β-decay of ^{14}C remains for the most part bound in the form of $(NO_2)^+$. The formation of the $(NO_2)^{2+}$ ion is undoubtedly due to the "shaking" effect, leading to the removal of one orbital electron without further dissociation of the ion. In this case it would be extremely interesting to observe the negative oxygen ions, since this would make it possible to construct a more complete picture of the processes of molecular breakdown in this system.

There are a number of papers devoted to the study of the consequences of β-decay in inorganic systems by radiochemical methods. Davies[72] tried to explain the influence of certain primary processes accompanying β-decay on the valance state of the daughter element for the chain $^{143}La \xrightarrow{\beta^-} {}^{143}Ce$. One result of the primary changes may be an increase in the valence of the daughter atom by one unit on β^--decay.

TABLE 5. Distribution of ions for the β-decay of $^{14}CO_2$.

Ion	Yield, %	Ion	Yield, %
NO_2^+	81.4±1.6	O_2^+	0.2 ±0.4
NO^+	8.4±0.4	NO^{2+}	0.06±0.04
O^+	5.9±0.6	N^{2+}	0.02±0.01
N^+	3.6±0.4	O^{2+}	<0.01
NO_2^{2+}	0.4±0.06		

This process may be represented schematically as follows:

$$(^{143}La)^{3+} \xrightarrow{\beta^-} (^{143}Ce)^{4+}.$$

The $(^{143}Ce)^{3+}$ and $(^{143}Ce)^{4+}$ were separated by adsorbing the Ce^{4+} on zirconium iodate. It was found that in nitric acid solution, ~60% of the ^{143}Ce is in fact in the quadrivalent state. This result is not rigorous, since a considerable part of the $(^{143}Ce)^{3+}$ might be formed by exchange with stable Ce^{3+}, which is a common impurity in lanthanum. Exchange in the $Ce^{3+} + (^{143}Ce)^{4+} \rightleftharpoons (^{143}Ce)^{3+} + Ce^{4+}$ system is very rapid.

Davies[72] also studied the chemical changes taking place in the chains: $^{83}Se \xrightarrow{\beta^-} {}^{83}Br$, $^{84}Se \xrightarrow{\beta^-} {}^{84}Br$, and $^{132}Te \xrightarrow{\beta^-} {}^{132}I$. In the case of these systems it was possible to study the influence of the chemical state of the mother element on the form in which its decay products exist. In the decay of radioselenium, a study was made of the distribution of the resulting radiobromine between the bromate ion and its reduced forms. It was found that the quantity of radiobromine existing in the form of the bromate ion at pH 7–11 amounts to ~35% of the total quantity of radiobromine and does not depend to any significant extent on whether the mother element exists as selenate or selenite ions. When ethylene bromide, which is capable of reacting only with atomic bromine, was introduced into the system, ~23% of the radiobromine was transferred to the organic phase. This appears to indicate the formation of extremely reactive atomic bromine during the β-decay of radioselenium. The fact that the ratio of the quantities of radiobromine formed in the oxidised and reduced states is approximately constant may indicate that the decay of radioselenium is accompanied by complete breakdown of the original selenite and selenate ions. The nature of the subsequent reaction of the bromine atoms with the surrounding molecules (chiefly water molecules) is almost independent of the initial chemical state of the mother element.

The processes taking place during decay in the chain $^{132}Te \xrightarrow{\beta^-} {}^{132}I$ show a certain similarity to the processes taking place during the decay of radioselenium. The greatest proportion of the radioiodine is again present in the reduced form, although there also appears to be some dependence on the chemical state of the mother substance. The breakdown of the initial structure of the tellurite ion in this case is apparently due to internal conversion, accompanying the β-decay of ^{132}Te.

Burgus and Kennedy[73] studied the valence state of the radiochromium produced by the positron-decay of ^{51}Mn and investigated the part played by various factors determining the chemical state of the daughter atoms. They made a large number of studies of the valence states of radiochromium formed during the β^+-decay of ^{51}Mn in $Cs^{51}MnO_4$, $^{51}MnO_2$, and $^{51}MnCO_3$ and accumulating in solutions and crystals of these compounds. They studied the distribution of radiochromium only between Cr^{3+} and Cr^{6+} since other valence states of chromium are unstable or capable of exchange under the separation conditions. The main results of this work are summarised in Table 6.

Change in the temperature (from room temperature to -180°) at which the accumulation of ^{51}Cr took place had no significant influence on the distribution of chromium between the different valence states.

The observed chemical changes are evidently extremely complex and result from various simultaneous little-studied processes. One of the most interesting results is the detection of a considerable proportion of chromium (30%) in the highest valence state when ^{51}Cr accumulates in $^{51}MnCO_3$ crystals. The appearance of sexivalent chromium as a result of decay indicates considerable ionisation, since otherwise the transition $(^{51}Mn)^{2+} \xrightarrow{\beta^+} (^{51}Cr)^+$ should have taken place. The detection of Cr^{6+} in this case, however, may also result from the fact that the chromium is stabilised in $MnCO_3$ crystals in some intermediate form capable of undergoing rapid isotopic exchange with the chromate ion. The fact that during accumulation in solution almost all the radiochromium is found in the lower valency state was attributed to reduction reactions, activated by radioactive recoil, with water molecules. The possibility of such processes in the case of the hot atoms produced in $(n\gamma)$ reactions was pointed out earlier[74]. Experiments carried out with the aim of decreasing this effect (by decreasing the mole fraction of water by the addition of acetone of dioxan) also support this suggestion. The fact that the reduction of $(^{51}Cr)^{6+}$ is not complete during accumulation in permanganate solutions is probably due to the transfer of kinetic recoil energy to the entire group of atoms CrO_4^{2-} and not to the individual chromium atom. In this case the kinetic energy of the CrO_4^{2-} amounts to only 44% of the Cr^{6+} recoil energy.

TABLE 6. Valency states of ^{51}Cr produced by the decay of ^{51}Mn.

Compound	Accumulation conditions	Quantity of radiochromium in the form of Cr^{3+}, %
$^{51}MnCO_3$	*a*) in solution with carriers	98 ±2.0
	b) in solution with molar fraction of acetone or dioxan 0.6	88 ±2.0
	c) in crystals	70.5±2.0
$Cs^{51}MnO_4$	*a*) in solution at different pH and concentrations	49 ±2.0
	b) in crystals	0.4±1.3
$^{51}MnO_2$	suspension in solutions	43.8±0.6

On the whole, the study of the chemical changes accompanying the process of β-decay in inorganic systems by radiochemical methods, despite the considerable difficulty of interpreting the results, are of considerable interest for the chemistry of various elements. By changing the experimental conditions valuable information may be obtained on the types of chemical reaction undergone by the daughter element: radioactive decay may lead to the appearance of quite unusual chemical species, whose study is of importance for the development of general chemical theory.

2. Organic Systems

Until comparatively recently no papers had been published on the study of the chemical changes accompanying the β-decay of atoms in organic molecules. One reason for this was the absence of radioactive decay chains for isotopes of carbon, hydrogen, sulphur, and other elements found in organic compounds. At the same time the chemical changes accompanying the β-decay of ^{14}C are of considerable interest, since this isotope is widely used as a radioactive tracer in chemical and biological studies and moreover is found in considerable quantities in the biosphere[75,76]. The use of compounds labelled with more than one atom and, more particularly, the use of mass-charge spectrometry have brought the first significant results in this field.

The first work in this direction was carried out by Wolfgang *et al.*[56]. Using double labelling with ^{14}C, they studied

the rupture and stability of the C–N bond during the β-decay of ^{14}C in the molecule of doubly labelled ethane ($^{14}CH_3$–$^{14}CH_3$).

The use of double isotopic labelling makes it possible to observe some of the stable daughter atoms thanks to the radioactivity of the second atom. With decay of one of the carbon atoms in $^{14}CH_3$–$^{14}CH_3$ and preservation of the bond formed by the daughter atom, the ethane molecule should be converted into methylamine. This change should apparently take place according to the scheme

$$^{14}CH_3–^{14}CH_3 \xrightarrow{\beta^-} [^{14}CH_3–^{14}NH_3]^+ \longrightarrow {}^{14}CH_3–NH_2 + H^+.$$

The use of a gaseous compound as starting material eliminates to a considerable extent the complications associated with various types of secondary process. The work was carried out essentially as follows: $^{14}CH_3$–$^{14}CH_3$ (enriched with ^{14}C to the extent of 25%) was prepared and kept until sufficient decay products had accumulated. Stable methylamine was then added to the system as carrier, the components of the mixture were separated, purified thoroughly, and identified. The proportion of $^{14}CH_3$–$^{14}CH_3$ molecules whose decay was accompanied by the formation of $^{14}CH_3NH_2$ was found by determining the activity of the methylamine or its derivatives. Special careful control experiments showed that the $^{14}CH_3NH_2$ produced is in fact a primary product, *i.e.* it is formed as a result of the preservation of C–N bonds during the β-decay of ^{14}C and not as a result of secondary reactions such as exchange reaction with the carrier or reaction under the influence of radiation, etc. The results show that the $^{14}CH_3$–$^{14}CH_3$ molecule, after β-decay of one of the carbon atoms, gives methylamine ($^{14}CH_3NH_2$) in 47 ± 2% of all decays.

The processes taking place during the β-decay of ^{14}C in ethane were examined theoretically by Wolfsberg[53]. Approximate quantum-mechanical calculation gave for the "survival" of the C–N bond a value of 60 ± 20%.

Thus the available data on the β-decay of ^{14}C (decay in $^{14}CO_2$ was examined earlier) show that a considerable proportion of the atoms formed remain in the original molecule, which undergoes an internal rearrangement not accompanied by extensive decomposition. From this it may be assumed that the formation of complex nitrogen-containing organic molecules should take place readily and simply if the primary molecule contains a radioactive ^{14}C atom. It is not impossible that such processes might be one means of formation of various amino-derivatives in nature.

The mass spectrometric method has been used to study the consequences of the β-decay of tritium in the following organic compounds: CH_3T,[48] C_2H_5T,[67] i-C_3H_7T, n-C_3H_7T,[77] C_6H_5T,[68] α-$CH_2TC_6H_5$, *o*-$CH_3C_6H_4T$, *m*-$CH_3C_6H_4T$, *p*-$CH_3C_6H_4T$,[77] and of the β-decay of ^{82}Br in 1,2-C_2H_4. $^{82}BrBr$[66,67], and $^{82}BrCCl_3$.[66] Table 7 gives as an example the yield of ions obtained during the decay of tritium in C_2H_5T.[67]

A noteworthy feature of the results obtained for C_2H_5T is that the C–He bond is broken in almost every β-decay act, the charge remaining on the organic fragment. This initial $C_2H_5^+$ mother ion is preserved in 78% of decays, whereas in the other cases a greater velocity of ions is obtained, forming a spectrum similar to that for C_2H_6 on electron collision. The process may be represented schematically as follows:

$$C_2H_5T \xrightarrow{\beta^-} C_2H_5He^+ \rightarrow C_2H_5^+ + He$$
$$\swarrow \downarrow \searrow$$
$$\sim 13 \text{ fragments (22\%)}$$

TABLE 7. Yields of ions in the decay of tritium in C_2H_5T.

Ion	Yield, %	Ion	Yield, %
$C_2H_5{}^3He^+ + C_2H_5T$	<0.2	C_2H^+	4.1±0.4
Mass 31	1.0±0.5	C_2^+	1.7±0.2
$^{12}C^{13}CH_3^+$	1.5±0.5	CH^+	<1.0
$C_2H_5^+$	78 ±1	$^3H^3He^+$	<0.2
$C_2H_4^+$	<0.5	H_3^+	<0.2
$C_2H_3^+$	6.5±0.7	H^+	<0.2
$C_2H_2^+$	6.9±0.7		

An even greater variety of fragments is observed in the decay of tritium in compounds with a large number of carbon atoms. The yield of the initial mother ion always predominates, however. We shall not consider the complete composition of the spectra in detail, but shall give only the ratios of the number of initial mother ions to the total number of ions detected. These ratios, corresponding to cases of decay which do not lead to appreciable excitation of the primary molecular ion, are given in Table 8.

The results vary on the average between 70% and 80%, with the exception of those for propane. An interesting feature is that for propane, the splitting of H_2 from $C_3H_7^+$ requires very little energy and it is probable that some of the mother ions with low excitation energy are capable of overcoming the corresponding energy barrier. Thus for the propane the sum of $C_3H_7^+$ and $C_3H_5^+$ represents with a high probability transitions to low-lying levels of the propyl ion. This sum amounts to 70% for n-C_3H_7T and 63% for i-C_3H_7T.

Theoretical calculations[20] show that for the decay $T \xrightarrow{\beta^-} He^+$, 70% of the transitions take place to the ground state of He^+, 25% to the first excited level with energy 20.5 eV, 2.5% to a level with energy 54.1 eV, and 2.5% to He^{2+}. An analogous distribution also appears to be obtained in the case of molecular system containing tritium. The data in Table 8 show that in fact 70–80% of the molecular ions are formed without appreciable excitation energy.

Certain general features of the changes in organic molecules during the β-decay of tritium may be noted: (1) after the conversion of RT into $(R^3He)^+$ the C–He bond is always broken, since the strength of the bond between an element and an inert gas is in all cases close to zero — an exception being the case of the $(H^3He)^+$ ion; (2) on rupture of the C–He bond, the positive charge remains on the organic fragment, the ^3He splitting off in the form of the neutral atom, since the ionisation potential of helium is much higher than that of organic radicals; (3) after the helium has split off, the initial mother molecular ion is preserved in 70–80% of all decays, and in the remaining cases of β-transitions the initial molecular ion acquires an excitation energy

TABLE 8. Yield of primary ions in the β-decay of tritiated hydrocarbons.

Substance	Mother ion	Concentration of ion in the spectrum, %	Substance	Mother ion	Concentration of ion in the spectrum, %
CH_3T	CH_3^+	83	α-C_7H_7T	$C_7H_7^+$	79
C_2H_5T	$C_2H_5^+$	78	*o*-C_7H_7T	$C_7H_7^+$	78
i-C_3H_7T	$C_3H_7^+$	56	*m*-C_7H_7T	$C_7H_7^+$	79
n-C_3H_7T	$C_3H_7^+$	41	*p*-C_7H_7T	$C_7H_7^+$	76
C_6H_5T	$C_6H_5^+$	72			

sufficient for subsequent fragmentation; (4) there is some analogy with the process of electron collision in the formation of various types of fragment ion, but the relative yields of fragments are different for the processes of β-decay and electron collision.

It was previously shown that the ionisation produced by the β-decay of nuclei with high values of Z takes place chiefly in the outer electron shell. Thus if the decaying atom is part of a molecule it is probable that, initially, the excitation energy will affect chiefly the bonding and other valency electrons of the ion undergoing the change. This localised excitation may be accompanied by an isomeric effect. There exist, however, certain rapid processes which take place in the time interval between the excitation of the molecule and its fragmentation, and these smooth out the effects of localised excitation. These are, firstly, the non-radiative transitions postulated by the theory of quasi-equilibrium monomolecular dissociation, as a result of which the excitation energy is rapidly redistributed throughout the molecule, and, secondly, the migration of an H atom through the carbon chain, or other transformations which eliminate the structural differences in the initial molecular ions. Wexler *et al.*[77] tried to study these effects for the case of the isomers of propane and toluene, labelled with tritium in different positions.

Experimental data on the yields of different ions during the β-decay of tritium in α-, *o*-, *m*-, and *p*-tritiumtoluenes (Fig. 6) show that the yields of different fragments agree not only qualitatively, but also quantitatively, showing that the localised excitation in these systems is eliminated by the rapid redistribution of the excitation energy and by transformations preceding fragmentation. Analogous observations have been made in the study of the consequences of electron collision for monodeuterated toluenes[78]. According to Wexler *et al.*, this confirms that fragmentation is preceded by the transformation of the tolyl and benzyl structures to a seven-membered ring, the tropylium ion, in which the carbon atoms, like the hydrogen atoms, are indistinguishable. A possible scheme for the fragmentation of the isomers of tritiated toluenes, resulting from β-decay, is shown in Fig. 7.

The above characteristic features of the fragmentation of tritiated organic derivatives do not result from the

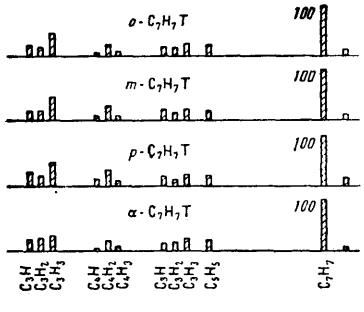


Fig. 6. Yields of ions for the β-decay of tritium in toluenes.

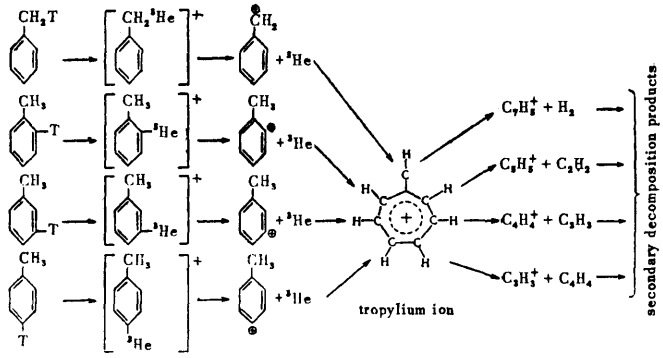


Fig. 7. Fragmentation of tritiated toluenes.

characteristic features of the nuclear transition $T \xrightarrow{\beta^-} {}^3He$. This assertion is based, in particular, on the fact that the spectrum of ions for the β-decay of ^{82}Br in $1,2\text{-}C_2H_4 \cdot {}^{82}BrBr$ [66,76] and $^{82}BrCCl_3$ [66] shows all the features characteristic of the spectrum of ions formed during the decay of tritium. As in the case of the β-decay of tritium, the initial mother ions $C_2H_4Br^+$ and CCl_3^+ predominate in the spectra of the organic derivatives (69.8 ± 2% and 64 ± 1.4% respectively). The C–^{82}Kr bond is always broken and the positive charge remains on the organic fragment. In 30–35% of the nuclear transitions, the initial ions acquire sufficient excitation energy for subsequent fragmentation. It should also be noted that the β-decay of ^{82}Br appears to be accompanied by very little removal of orbital electrons, as indicated by the absence of doubly charged ions in the spectra. This may, however, be due to the breakdown of molecular ions with a charge greater than unit, as a result of coulombic repulsion, so that they are not recorded in the mass-spectrometer.

3. Organoelemental Systems

The study of the consequences of β-decay organoelemental systems is now attracting increasing attention. These compounds have a number of advantages in studies of this type, including the extensive possibilities for preparing compounds with different physical and chemical properties for the elements studied; the absence or retardation, in many cases, of isotopic exchange reactions which distort the initial picture of chemical changes; etc.

The first investigation in this direction was made as early as 1934 by Martenson and Leighton[79], who studied the possibility of retention of the initial structure by molecules of organoelemental derivatives during β-decay in the chain $RaD(^{210}Pb) \xrightarrow{\beta^-} RaE(^{210}Bi) \xrightarrow{\beta^-} RaF(^{210}Po)$. They studied the readily volatile tetramethyllead $Pb(RaD)(CH_3)_4$. If decay had been accompanied by complete decomposition of the original molecule, the resulting radiobismuth and polonium would have been obtained in inorganic forms and would not have exhibited the volatility of the methyl derivatives of these elements. When $Pb(RaD)(CH_3)_4$ was kept for a period sufficient for the accumulation of RaE and RaF, the authors detected the β-activity of RaE and the α-activity of RaF in the volatile fraction. On this basis they suggested that these

processes involved the formation of the organometallic compounds of bismuth $^{210}Bi(CH_3)_3$ and polonium $^{210}Po(CH_3)_2$ according to the following possible scheme:

$$^{210}Pb(CH_3)_4 \xrightarrow{\beta^-} {}^{210}Bi(CH_3)_3^+ + CH_3;$$

$$^{210}Bi(CH_3)_3^+ + e \rightarrow {}^{210}Bi(CH_3)_3;$$

$$^{210}Bi(CH_3)_3 \xrightarrow{\beta^-} {}^{210}Po(CH_3)_2 + CH_3;$$

$$^{210}Po(CH_3)_2^+ + e \rightarrow {}^{210}Po(CH_3)_2.$$

In 1953 Edwards *et al.* [80] made a more detailed study of the same system and examined the distribution of the β-activity of ^{210}Bi between the volatile and non-volatile fractions for different conditions of accumulation in solutions and in the gaseous phase. For accumulation in solution in benzene, octane, and carbon tetrachloride, at sufficiently high molar fractions of $Pb(RaD)(CH_3)_4$, they found that the greater part of the RaE (60–80%) was present in the form of a non-volatile fraction. The appearance of this fraction was evidently due to processes of internal conversion and cascades of vacancies [81–84], leading to complete decomposition of the original tetramethyllead molecule. On the other hand, in the decay of $Pb(RaD)(CH_3)_4$ in solutions at low concentrations of this compound and in the gaseous phase, an anomalously low yield of radiobismuth (up to 10%) in the form of the non-volatile fraction was observed. It is possible, however, that the last result is due to an experimental error as a result of the formation of stable aerosols or of secondary effects [85], particularly since the forms in which the radiobismuth was obtained were not identified.

Essentially the same method was used in more recent work by Baulch *et al.* [86] in a study of the consequences of the decay of RaD in tetramethyllead. These authors examined the relationship between the quantity of radiobismuth deposited on the walls of the vessel during the decay of $Pb(RaD)(CH_3)_4$ in the gaseous state and the vapour pressure of the gas. They found that the percentage of radiobismuth deposited on the walls was low (5–30%) and decreased with increase in pressure. On this basis they concluded that the processes of excitation and internal conversion either are insufficiently effective for complete breakdown of the original tetramethyllead molecule or are suppressed by secondary processes before the molecule reaches the walls of the vessel. It was also concluded that the molecular ion $Bi(CH_3)_4^+$ formed – $^{210}Pb(CH_3)_4 \xrightarrow{\beta^-} {}^{210}Bi(CH_3)_4^+$ – is more stable than previously assumed, and that when it acquires sufficient excitation energy it decomposes according to the scheme: $Bi(CH_3)_4^+ \rightarrow {}^{210}Bi(CH_3)_3 + CH_3^+$. Thermochemical calculation showed that this process is more probable than that involving the removal of a neutral methyl radical.

It should be noted that in these cases the forms in which the daughter elements were obtained were not identified.

Here it would be desirable to use other improved methods such as mass-charge spectrometric study of the resulting fragments or gas chromatography.

Another series of studies was made of the consequences of β-decay in organometallic systems with aromatic derivatives. The aromatic derivatives have the advantage not only of stability and variety of chemical form, but also the possibility of exact identification and determination of the distribution of the daughter element between these forms.

The first study of the chemical state of the RaE produced by the decay of RaD in the phenyl derivatives $Pb(RaD)(C_6H_5)_4$ and $Pb(RaD)(C_6H_5)_3Cl$ was that of Nefedov and Andreev [87], who used the isotopic carrier method with subsequent chemical separation to study the distribution of radiobismuth between the forms $Bi(C_6H_5)_3$, $Bi(C_6H_5)_3Cl_2$, and inorganic bismuth, with accumulation in crystals and in solutions of these compounds. The most interesting result of the study was the detection of a considerable proportion of RaE atoms in the form of the complex organometallic compounds $Bi(C_6H_5)_3$ and $Bi(C_6H_5)_3Cl_2$. It was found that the yield of radiobismuth in the form of these compounds for accumulation in crystals is greater than that for accumulation in solutions. This may be due both to an increase in the probability of recombination of the fragments of the decomposing molecule in the crystals and also possibly to the nearby presence of analogous molecules, facilitating the rapid redistribution of the excitation energy between the identical entities.

Comparison of the data on the distribution of RaE between the different compounds in the decay of RaD in $Pb(RaD)Ph_4$ and $Pb(RaD)Ph_3Cl$ indicates that the nature of the mother molecule has a marked influence on the chemical form of the daughter RaE. For example, the decay of $Pb(RaD)Ph_4$ gives almost no RaE in the form of $BiPh_3Cl_2$, whereas in the decay of $Pb(RaD)Ph_3Cl$ it is one of the chief products. Moreover, it was found that the maximum yield of radiobismuth (~70%) for accumulation in solution is obtained in inorganic forms. An interesting feature is that this value lies in the range of values of the total conversion coefficients for RaD (60–80%) found by different authors [81–84]. The presence of RaE in inorganic form is undoubtedly related to the process of internal conversion, which generally leads to complete breakdown of the original molecule.

Analogous results were obtained in a study [88] of the chemical state of ThC formed by the decay of ThB in the phenyllead derivatives $Pb(ThB)(C_6H_5)_4$ and $Pb(ThB)(C_6H_5)_3Cl$. The most interesting result of the comparison of these with the previous data is the influence of the decay schemes of different lead isotopes (RaD and ThB) on the yield of different forms of radiobismuth, particularly its inorganic form. The yield of ThC in inorganic form with accumulation in the crystals was found to be 21%. For accumulation is solutions, the yield of inorganic forms of radiobismuth (ThC) (30%) almost coincides with the total internal conversion coefficient for the decay ThB $\xrightarrow{\beta^-}$ ThC. [89] These results indicate that the bismuth isotopes formed by the β-decay of different lead isotopes show different behaviour.

Detailed studies have been made of this problem [90,91]. Special experiments were carried out to study the influence of the decay schemes of the natural lead isotopes RaD, ThB, and RaB on the yields of radiobismuth in different forms. For this purpose, as well as identical conditions of synthesis, accumulation, etc., identical methods of analysis of the compounds containing the different radioactive lead isotopes were used. In addition, two different radioisotopes of lead were introduced simultaneously into the same compound with subsequent radiochemical and radiometric analysis.

The results of studies of the isotopic effects for RaD and ThB by the carrier method (Table 9) indicate firstly that the different bismuth isotopes (RaE and ThC) show different behaviour. In particular, in the case of $BiPh_3Cl_2$, displacement of the isotopic composition was revealed by the relative enrichment of this form with ThC. The data in Table 9 also show that the experimentally observed displacement of the isotopic composition did not depend significantly on whether the mother substance had been labelled separately or simultaneously. The difference in the chemical behaviour of the bismuth isotopes can be due only to

TABLE 9. Isotopic effects in the β-decay of RaD and ThB.

Mother substance	Daughter substance	Fraction of RaE in a given form, %	Fraction of ThC in a given form, %
$Pb(ThB)Ph_3Cl$	$BiPh_3Cl_2$	19±1	50±2
$Pb(RaD)Ph_3Cl$	Bi^{3+}	43±3	17±1
$Pb(ThB, RaD)Ph_3Cl$	$BiPh_3Cl_2$	17±1	49±2
	Bi^{3+}	42±3	17±3

differences in the radioactive decay schemes of the mother isotopes. Data obtained by chromatrographic analysis of compounds containing the other lead isotope (RaB) are given in Table 10.

These show clearly the characteristic types of isotopic effect for the β-decay of the natural lead isotopes (RaD, ThB, RaB) in complex organometallic compounds. The observed effects are due chiefly to differences in the values of the total internal conversion coefficients (60–80% for RaD,[81-84] 30% for ThB,[89] and 15% for RaB[92]); this is shown by the fact that the yield of inorganic forms is directly proportional to the internal conversion coefficients.

The previous papers showed the complex character of the changes taking place during the β-decay of the central atom in organolead derivatives, revealed primarily in the variety of chemical compounds formed by the daughter radiobismuth. The appearance of higher organometallic bismuth compounds ($BiPh_3$ and $BiPh_3Cl_2$) as a result of the rearrangement of the mother molecule is possible only when the latter contain a sufficient number of radicals. It may, however, be suggested that the formation of these compounds is due, albeit only partly, to such processes as interaction with the surrounding molecules (particularly molecules of the mother substance).

The part played by individual processes leading to the appearance of higher organometallic bismuth derivatives was examined in a study[93] of the chemical changes accompanying the β-decay of RaD in the radical-deficient lead derivative $Pb(RaD)(C_6H_5)_2Cl_2$. It was found that for this compound the yield of higher bismuth derivatives $BiPh_3$ and $BiPh_3Cl_2$ is very low. It was therefore concluded that the chemical changes accompanying the β-decay of the central lead atom in the organometallic derivatives in this case do not involve the surrounding molecules.

An analogous study[94] was made of the chemical state of the RaE obtained by the β-decay of RaD in $(PbPh_3)_2$, $PbPh_3NO_3$, and $PbPh_2(NO_3)_2$.

These studies were made using the isotopic carrier method and established a number of characteristic features of the β-decay of lead isotopes in complex organometallic compounds. The isotopic carrier method cannot, however, reproduce all the complex features of the changes taking place, since a number of latent changes and intermediate or unstable forms are not detected. Chromatography, particularly on paper, is a more precise method. An important advantage of this method is often the possibility of isolating daughter forms without carrier. Fig. 8 gives as an example the chromatogram for the decay products of $Pb(RaD)Ph_3Cl$, obtained by successive elution with benzene and petroleum ether without the use of carriers[95]. This method gave more fundamental information on the essential features of the processes accompanying the decay of the central atom in phenyllead derivatives and, in particular, revealed a new, previously unknown form of RaE and the processes of its evolution, and also the evolution of other forms of radiobismuth under different conditions.

Important information on processes taking part in organometallic compounds may be obtained by studying the β-decay of other radioisotopes. Thus, studies have been made of the chemical changes accompanying the β-decay of ^{125}Sb in the derivatives $Sb(^{125}Sb)R_3$ and $Sb(^{125}Sb)R_3Cl_2$ (where R represents the phenyl or *p*-tolyl radical)[96]. The various chemical forms of the resulting ^{125m}Te were separated by paper chromatography. The results confirm the marked influence of the chemical state of the ^{125}Sb on the yield of ^{125m}Te in different forms. With accumulation in the $Sb(^{125}Sb)R_3$ crystals, the ^{125m}Te was found chiefly in the form of the two compounds TeR_2 (60–63%) and TeR_3Cl (27–29%), and with accumulation in $Sb(^{125}Sb)R_3Cl_2$ the ^{125m}Te was found chiefly in the form of TeR_2Cl_2 (83–90%).

These results can be explained qualitatively on the basis of the theory of molecular-ion fragmentation. In the β-decay of ^{125}Sb in $^{125}SbR_3$, a direct result of decay in the absence of further excitation should be the appearance of the primary molecular ion $^{125m}TeR_3^+$, formed according to the scheme: $^{125}SbR_3 \xrightarrow{\beta^-} {}^{125m}TeR_3^+$. The TeR_3Cl found in 27–29% yield is probably the product of the stabilisation of this primary molecular ion. As shown previously, however, a considerable proportion of the molecular ions formed during β-decay are in an excited state. Electron-collision studies of organometallic and similar compounds[97] and other studies[86] show that the most probable form of realisation of the excitation energy in these cases is the removal of positively charged radicals. The removal of a positively charged radical from the excited molecular ion $^{125m}TeR_3^+$ according to the scheme $^{125m}TeR_3^+ \rightarrow {}^{125m}TeR_2 + R^+$ leads to the stabilisation of a considerable proportion of the ^{125m}Te (60–63%) in the form of TeR_2.

TABLE 10. Isotopic effects in the β-decay of RaD, ThB, and RaB.

Daughter substance	Mother substance Pb^*Ph_3Cl yield of daughter substance, %	Mother substance Pb^*Ph_4 yield of daughter substance, %
RaE^{3+}	47±1	45±1
ThC^{3+}	24±2	25±2
RaC^{3+}	11±1	10±1

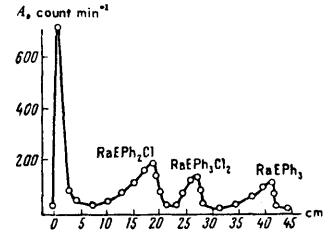


Fig. 8. Chromatogram for the decay products of $Pb(RaD)(C_6H_5)_3Cl$.

In the β-decay of ^{125}Sb in $Sb(^{125}Sb)R_3Cl_2$, the primary molecular ion is $^{125m}TeR_3Cl_2^+$. Such structures are not characteristic of organic compounds of tellurium, so that this ion is thermodynamically unstable. Assuming that the breakdown of this ion should also involve the removal of a positively charged radical, the greater part of the ^{125m}Te should be found in the form of TeR_2Cl_2, produced according to the scheme: $^{125m}TeR_3Cl_2^+ \rightarrow {}^{125m}TeR_2Cl_2 + R^+$. The experimental results in fact show that with accumulation in $Sb(^{125}Sb)R_3Cl_2$ crystals a high yield of ^{125}Te in the form of TeR_2Cl_2 (83–90%) is obtained.

A number of studies have been made of the decay $^{131}Te \xrightarrow{\beta^-} {}^{131}I$ in organoelemental compounds[98,99]. An attempt was made to find the stable form of the radioactive iodine during the decay of ^{131}Te in dibenzyltellurium[98]: the radioiodine appears in the form of different compounds (C_6H_5I, CH_3I, etc.). The separation method (fractional distillation) which they used, however, introduces considerable errors and makes it difficult to establish the nature of the primary chemical changes. Nevertheless the use of β-decay processes to prepare various organic derivatives of radioiodine is of considerable interest.

Keneshea and Kahn[99] also showed the possibility of preparing iodobenzene labelled with ^{131}I, by the β-decay of ^{131}Te when a mixture of tellurium tetrachloride and benzene is irradiated in a reactor.

The use of β-decay processes in organoelemental compounds for the synthesis of a variety of products on the one hand and for the separation of radioactive isotopes without the use of carriers on the other is of considerable theoretical and practical interest. These two possibilities result from the use of different aspects of the same process. When the original bonds are preserved and the changes in the original molecule are slight in β-decay processes, we may expect the production of various compounds of the daughter element. An important feature is that in a number of cases these compounds can be obtained without carriers, with the highest possible specific activity. If, however, the decay of the isotope is accompanied by marked excitation of the original molecule, leading to its complete breakdown, the daughter isotope is obtained in a chemical form differing sharply from that of the mother element and can be easily separated from the latter.

A good illustration of this is provided by work on the synthesis of new organic compounds of polonium[100,101] and work on the separation of various radioisotopes when chemical-bond rupture takes place as a result of β-decay[87,88,104,105].

The exceptional progress observed in recent years in the chemistry of organoelemental compounds as a whole has not extended to a number of elements such as francium, astatine, and polonium, althought the ability of these elements to form such compounds is indicated by their position in the Periodic System and from the general features first noted by Mendeleev and later formulated in modern terms by Nesmeyanov[106,107].

Murin *et al.*[100] were the first to show conclusively that organic compounds of polonium (RaF) are produced during the β-decay of RaE in various aromatic derivatives, as a result of the stabilisation and fragmentation of the molecular ions formed. The polonium accumulated in $Bi(RaE)(C_6H_5)_3$ and $Bi(RaE)(C_6H_5)_3Cl_2$ crystals. The chief task was to isolate and identify the daughter compounds of polonium (RaF). The chief method used was paper chromatography. The analogous tellurium derivatives $Te(C_6H_5)_3Cl$, $Te(C_6H_5)_2Cl_2$, and $Te(C_6H_5)_2$ labelled with ^{127m}Te were used as "markers" to establish the positions of the various organic compounds of polonium on the chromatogram. The chromatograms were analysed radiometrically from the α-activity of the polonium and the β-activity of the ^{127m}Te, and the α-active peaks of the various polonium compounds were identified by comparing their positions with those of the analogous β-active tellurium derivatives. Fig. 9 shows a chromatogram obtained for the case of accumulation in $Bi(RaE)Ph_3$ crystals, using ethyl acetate as mobile phase. As in the decay of different isotopes of lead and antimony, the chemical state of the RaF has a marked influence on the yield of the different forms of polonium. Fig. 10 gives for comparison a chromatogram for the products of the decay of $Bi(RaE)Ph_3Cl_2$, obtained under identical conditions. This influence makes it possible to use the chemical changes accompanying the β-decay of RaE to synthesise certain organic derivatives of polonium.

These studies were continued in work[101,102] on the chemical state of polonium produced by the β-decay of RaE in various p-tolyl and α-naphthyl derivatives. An analogous method was used to isolate and identify another series of new polonium compounds:

$$Po(p\text{-}CH_3C_6H_4)_2,\ Po(p\text{-}C_7H_7)_2Cl_2,\ Po(p\text{-}C_7H_7)_3Cl,$$
$$Po(\alpha\text{-}C_{10}H_7)_2,\ Po(\alpha\text{-}C_{10}H_7)_3Cl,\ Po(\alpha\text{-}C_{10}H_7)_2Cl_2,$$

and to study the distribution of polonium between these compounds under different conditions.

It is clear that methods of synthesis based on the chemical changes accompanying β-decay processes will make it possible in the near future to open up a new field of knowledge — the chemistry of organic derivatives of polonium.

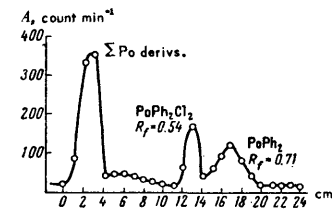


Fig. 9. Chromatogram for the decay products of $Bi(RaE)(C_6H_5)_3$.

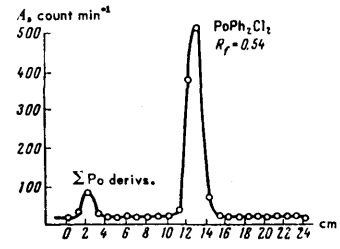


Fig. 10. Chromatogram for the decay products of $Bi(RaE)(C_6H_5)_3Cl_2$.

Analogous methods can be used successfully for other typical radioactive elements such as astatine and francium.

It was pointed out earlier that under certain conditions the radioactive recoil and secondary processes in electron shells of the daughter atoms may lead to conversion of the greater part of the daughter atoms into the simplest inorganic forms. This phenomenon has been used very successfully to isolate a number of radioactive isotopes without the use of carriers. The chief advantages of these methods are that the differences in the physicochemical properties of the original compound of the mother element and the simplest forms of the daughter element are incomparably greater than the differences in the physicochemical properties of any inorganic compounds of these elements.

Examination of the table of isotopes suggests the possibility of using analogous methods to isolate numerous valuable radioactive isotopes. Systems for study include the transformation chain formed by radioelements obtained by fission, spallation reactions, radiative neutron capture, ordinary cyclotron reactions, and decay in series. In particular, the method may be used to isolate the following radioactive isotopes without the use of carriers: ^{32}P, ^{68}Ga, ^{71}Ge, ^{72}As, ^{93}Nb, ^{99m}Tc, ^{113m}In, ^{119}Sb, ^{125}Sb, ^{132}I, ^{178}Ta, ^{188}Re, ^{191}Au, ^{193}Pt, ^{200}Tl, ^{210}Bi, ^{212}Bi, and others. Up to the present, methods have been developed for separating the following radioactive isotopes and nuclear isomers without the use of carriers, based on chemical-bond rupture during β-decay processes: ^{188}Re,[103] RaE,[87] ThC,[88] ^{99}Tc,[102] and ^{113}In.[104] The specimens of radioactive isotopes and nuclear isomers obtained have been used successfully in studies in nuclear physics and chemistry. An important feature is that in the great majority of cases, long-acting sources of short-lived isotopes of a number of elements can be produced. A characteristic feature of these methods is the simplicity of the isolation of the radioactive isotope without the use of carriers after the preparation of the source. For example, ^{99m}Tc and ^{188}Re have been isolated by extraction from chloroform solutions of the hexacarbonyls $Mo(^{99}Mo)(CO)_6$ and $W(^{188}W)(CO)_6$ with distilled water. The isotopes ^{210}Bi and ^{212}Bi were isolated by adsorbing inorganic bismuth from solutions of organic radiolead compounds.

In conclusion, the authors express the hope that the study of the chemical changes accompanying β-decay processes will attract the attention of a wider circle of research workers and will find a number of new and extremely important applications in various fields of study. The undoubted interest in this topic is indicated by the considerable number of papers by Soviet and other authors, published while the present paper was in the press[108-125].

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ADVANCES IN THE USE OF INFRARED SPECTROSCOPY FOR THE CHARACTERISATION OF OH BONDS

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