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THE CHEMICAL EFFECTS OF NUCLEAR REACTIONS. THE ISOTOPIC EFFECT IN SECONDARY REACTIONS OF RECOIL ATOMS, ACCOMPANYING (n,γ) REACTIONS

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CONTENTS

Introduction 383

1. Secondary reactions of recoil atoms in organic compounds. The "apparent isotopic effect" and its origin 383

2. The behaviour of recoil atoms in inorganic systems 385

3. The influence of the chemical state of the recoil atoms on subsequent reactions in which they take part 387

4. The isotopic effect regarded as the result of super--thermal ion–molecule reactions 389

INTRODUCTION

In view of their marked theoretical and practical importance, the chemical changes accompanying nuclear reactions have recently been extensively studied[1-5]. The study of the chemical effects of nuclear reactions is theoretically important in relation to the kinetics of chemical reactions involving atoms with excess kinetic energy or excitation energy. The practical importance of such studies lies in the possibility of preparing "labelled" compounds by direct irradiation in a reactor, cyclotron, etc. The synthesis of new compounds by irradiating substances with neutrons from a uranium reactor has been developed extensively. Here the simplest process is the (n,γ) reaction, which gives isotopes of the original element. As recent studies have shown, the radioactive isotopes of a given element, produced as the result of a nuclear reaction, in a number of cases do not always show identical behaviour. The difference is shown as a difference in the magnitude of the retention for each isotope, *i.e.* the proportion of labelled products formed in secondary chemical processes taking place after the nuclear reaction.

For example, when certain alkyl bromides, such as CCl_3Br, were irradiated with neutrons, it was found that the retention for the ^{82}Br isotope was 48%, while that for the ^{80m}Br isotope produced at the same time was 38%. This difference is small and therefore cannot play an important part in problems of the practical preparation of labelled compounds, but the existence of such differences, which have been called "isotopic effects", has further stimulated the development of the theory of the secondary reactions of recoil atoms.

1. SECONDARY REACTIONS OF RECOIL ATOMS IN ORGANIC COMPOUNDS. THE "APPARENT ISOTOPIC EFFECT" AND ITS ORIGIN

The difference in the behaviour of isotopes formed as a result of the same nuclear process (the isotopic effect) may be due to a difference in the kinetic energy of recoil resulting from the emission of γ-quanta after neutron capture, or to a difference in the energy state of the electron clouds of the recoil atoms. Many studies have been made on the influence of the initial kinetic energy of recoil on the yield of the products of the secondary chemical reactions. From Libby's work[6,7] it follows that the initial kinetic energy of recoil atoms activated by nuclear reactions may influence the yield of organic derivatives if the nuclear reactions are carried out in a solid organic medium. The radioactive isotopes of a given element, even if they are activated by one type of nuclear reaction, may give different yields of organic compounds. This conclusion is based on the assumption that elastic and inelastic collisions take place between the recoil atoms and the atoms and molecules of the medium. Let us consider the deceleration of a "hot" atom in more detail. The recoil atom, which as a result of the nuclear reaction has acquired a high kinetic energy, is "cooled" by collision with the atoms of the surrounding medium; some of the atoms, as a result of elastic collision, enter the organic compounds and replace those atoms in the surrounding molecules whose masses do not differ significantly from that of the recoil atom. When the kinetic energy of the recoil atom decreases to a value comparable to the energy of the bonds formed by the atoms in the molecules, inelastic collisions between the recoil atom and the molecules become possible. Dissociation of the molecules then takes place with the formation of compounds containing radioactive recoil atoms. On going from the liquid to the solid phase, the quantity of products formed by elastic collisions remains unchanged, since the collision process takes place as a single elementary act and the bonds between the atoms do not change with change in the state of aggregation. The yield of compounds, whose formation is regarded as the result of inelastic collisions between the recoil atoms and the molecules, increases sharply on going to the solid phase, since the recoil atom has to move in a medium where the intermolecular bonds have become much stronger. According to Libby's calculations[6], a recoil atom with an initial energy of 0.3 MeV forms a "liquid drop" in the solid phase as the result of the fusion of a small local volume. The reaction involving elastic collisions takes place at the start and in the central part of the path of the recoil atom, *i.e.* in the centre of the "liquid drop", while reactions involving inelastic collision take place at the end of the path, at the boundary with the solid phase, where the physical properties of the medium change considerably. It is possible that at the end of the path the recoil atom, as a result of the loss of a considerable proportion of its energy, is unable to break the bond between the molecules to an extent sufficient to form a "liquid drop", as suggested by Libby. It is possible that at the end of the path of the recoil atom the substance again exists as a crystalline solid phase with some degree of amorphous character. For substances whose molecules consist chiefly of atoms whose masses differ considerably from those of the recoil atoms (for example ^{82}Br), such as CH_3Br, C_2H_5Br, C_3H_7Br, etc., we should expect a considerable increase in the yield of organic products or retention on going to the solid phase, as a result of the considerable proportion of super-thermal processes of inelastic collision. According to Libby's views, the yield of organic products in the solid phase *increases with decrease in the initial energy* of recoil, since in this case the medium surrounding the recoil atom will show less resemblance to the liquid phase, in which the retention is generally smaller. In other words, with decrease in the initial energy there is an increase in the local concentration of molecular fragments, leading to an increase in the yield of organic compounds as a result of fragment recombination. For other substances, such as CBr_4, in which the deceleration of the "hot" ^{82}Br atom takes place chiefly at bromine atoms, the retention will not change significantly on going to the solid phase, since in this case the major contribution to the retention is made by reactions induced by elastic collisions. In the case of CBr_4 we should not expect a difference in the behaviour of the bromine isotopes ^{80m}Br and ^{82}Br, although the recoil energy of ^{80m}Br is greater than that of ^{82}Br.

According to Libby's theory, a difference in retention for isotopes of a given element may result on irradiation in the solid phase because of a difference in recoil energy. This difference should be revealed as a difference in the yield of products formed in reactions induced by inelastic

collisions in the super-thermal energy range. In the irradiation of n-propyl bromide[7] in the crystalline state by thermal neutrons, the values of the retention or yield of organic compounds for the three bromine isotopes obtained by the reactions $^{81}Br\ (n,\gamma)\ ^{82}Br$ and $^{79}Br\ (n,\gamma)\ ^{80m}Br$ were 86.7% and 78.2% respectively, whereas in the irradiation of solid CBr_4 the values of the retention for ^{82}Br and ^{80m}Br were 86.8% and 86.9% respectively, *i.e.* it therefore appears that an isotopic effect exists for compounds in which super--thermal processes play a significant part in the stabilisation of the recoil atom. Other data, however, indicate the absence of an isotopic effect. Schuler and McCauley[8] carried out experiments involving the irradiation of n-propyl bromide with fast neutrons, in order to examine the influence of the initial kinetic energy of recoil on the yield of organic products after an (n,γ) reaction. The maximum fraction of the kinetic energy which a neutron can transfer on collision with a nucleus can be calculated from the formula[5]

$$E_m = \frac{4M}{(M+1)^2} E,$$

where E is the energy of the neutron and M the mass of the recoil atom.

The authors obtained bromine recoil atoms with an initial kinetic energy of ~100 000 eV, which is about 10^3 times greater than the recoil energy of bromine atoms on irradiation with thermal neutrons; no isotopic effect was observed. Data on the retention of ^{82}Br and ^{80m}Br isotopes activated by neutrons with different energies, given by different authors, are shown in Table 1.

The behaviour of the ^{78}Br isotope (6.4 min), obtained by the reaction $^{79}Br\ (n,2n)\ ^{78}Br$, was found to be different, its retention being higher in both liquid and solid phases, with mean values of 93% and 43% respectively. These data do not agree with Libby's suggestions regarding the relationship between the initial recoil energy and the retention. It is evident that the "liquid drop" in a solid body is of little importance in determining the fate of the recoil atom.

The "chance fragmentation" model proposed by Willard[3] may partly explain the increase in retention for a high recoil energy, as has been found for ^{78}Br recoil atoms. The fragmentation of molecules is obviously greater for a high recoil energy, so that an isotopic effect may be produced during subsequent diffusion–recombination reactions.

During the deceleration of, for example, a ^{78}Br recoil atom at propyl bromide molecules radical fragments are formed in much larger quantities than during the deceleration of ^{80}Br, ^{80m}Br, or ^{82}Br recoil atoms. But the recoil energy for the ^{78}Br isotope is 10^3 times greater than the kinetic energy of recoil of the latter! Labelled organic molecules are formed by subsequent radical reactions between the fragments and the recoil atoms. There will naturally be more molecules labelled with the ^{78}Br isotope than with, for example, the ^{82}Br isotope. If this is the case, the isotopic effect should disappear when small quantities of elementary bromine are added as radical acceptor before irradiation. Schuler and McCauley found that the isotopic effect, *i.e.* the difference in the retention for ^{78}Br and ^{82}Br, was equal to 7.0% in the absence of bromine, 5.5% in the presence of 5 mole % bromine, and 1.5% in the presence of 25 mole % bromine, *i.e.* the effect does in fact disappear. Richardson and Voigt[9] carried out experiments on the preparation of ^{80m}Br, ^{77}Br, and ^{76}Br isotopes by means of the photonuclear reactions $^{81}Br\ (\gamma,n)\ ^{80m}Br$, $^{79}Br\ (\gamma,2n)\ ^{77}Br$, and $^{79}Br\ (\gamma,3n)\ ^{76}Br$ in n-propyl bromide and isopropyl bromide in the liquid and solid states. Their values of the retention for ^{80m}Br, ^{77}Br, and ^{76}Br in the absence of bromine were found to be 87%, 62%, and 67% respectively. It would appear, as the authors state, that an isotopic effect exists for ^{80m}Br on the one hand and ^{77}Br and ^{76}Br on the other. When 5 mole % of elementary bromine was added, however, the retention for the bromine isotopes obtained by the (n,γ) and (γ,n) reactions became almost identical (24.0% and 27.6% respectively). Thus an isotopic effect may appear at high recoil energies due to the large number of radicals formed by the moving atoms, and disappears on the addition of bromine, which effectively combines with the radicals. The data in Table 2 show that in fact the yield of organic products obtained during the irradiation of propyl bromine with neutrons and γ-quanta depends on the type of activation. The difference in the type of activation is reflected in the yields of the dibromo--derivatives produced as a result of fragmentation of the mother compound (methylene bromide). The addition of 5 mole % of elementary bromine before irradiation decreases considerably the yield of the mother compound in the case of both (n,γ) and (γ,n) reactions, and also decreases to a considerable extent the yield of 1,2-dibromopropane. In solid propyl bromide no difference in retention was observed for the ^{80m}Br and ^{82}Br isotopes at -196°, but there was an overall increase in the retention, chiefly in the form of the mother compound, and also as 1,3-dibromopropane and ethyl bromide.

These results do not agree with Libby's theory, which predicts the appearance of isotopic differences only in the solid phase. The yields of the products can be explained qualitatively on the basis of Willard's theory, which assumes the random formation of radicals in the track of the hot atom. With increase in the recoil energy there is an increase in the proportion of C–C bonds broken, and a result of this may be an increase in the yield of organic products, which are formed in subsequent diffusion–recombination reactions. Thus in the liquid phase a difference in the retentions for the ^{82}Br and ^{80m}Br isotopes (see Table 2) is produced. In the solid phase, where diffusion is much less marked, there should be no such differences, since the part played by diffusion–recombination reactions is much smaller. At first sight this shows good agreement with experiment. According to Richardson and Voigt's data, the difference in the retention for isotopes obtained by the same nuclear reactions can also be explained from Willard's viewpoint, *i.e.* it is attributed to the difference in the recoil energy, leading to the production of different quantities of radicals in the track of the hot atom.

There are, however, certain facts which cannot be explained by Willard's theory. The retention does indeed

TABLE 1. Retention for different bromine isotopes in propyl bromide (%).

Reaction	Type of neutron	Phase		References
		liquid	solid	
$^{79}Br(n,2n)^{78}Br$	fast	42.6	92.5	8
$^{79}Br(n,\gamma)^{80}Br$	thermal	37.8	79.1	8
		34.0	—	6
$^{79}Br(n,\gamma)^{80m}Br$	thermal	34.0	78.2	6,7
$^{81}Br(n,\gamma)^{82}Br$	fast	33.4	76.2	8
		36.5	79.4	8
$^{81}Br(n,\gamma)^{82}Br$	thermal	—	86.7	7
(with 5% Br_2)	thermal	24.0	—	9
$^{81}Br(\gamma,n)^{80m}Br$		54.0	88.7	9
$^{79}Br(\gamma,2n)^{77}Br$		62.0		9
$^{81}Br(\gamma,n)^{80m}Br$		67.0		9
(with 4.7% Br_2)		27.6		9

TABLE 2. Yields of products (%) containing the radioactive isotopes ^{80m}Br and ^{82}Br obtained by (γ, n) and (n, γ) reactions respectively in propyl bromide.

Reaction	Phase	Total retention	Yields of products								
			CH_3Br	C_2H_5Br	isopropyl bromide	n-propyl bromide	CH_2Br_2	1,2-dibromoethane	1,2-dibromopropane	1,3-dibromopropane	polymeric substances
$^{81}Br(\gamma, n)^{80m}Br$	liquid	54	1.4	1.2	1.9	19.7	4.0	5.8	13.0	4.7	2.2
	solid	88.7	2.0	2.9	3.8	32.3	2.3	5.0	15.6	10.0	15.0
$^{81}Br(n, \gamma)^{82}Br$	liquid	34.7	—	0.7	1.7	17.1	1.8	3.1	2.8	2.7	1.5
	solid	88.4	—	2.7	3.4	26.9	2.4	6.0	6.0	17.8	12.1

increase with increase in the recoil energy, as predicted by Willard's theory, but this increase is too small compared with the change in the recoil energy. For a change in the recoil energy by a factor of 10^3, the retention changes by a factor of only 1.5 (see Table 1). Thus some other factor, not the recoil energy, influences the retention. Moreover, according to Willard's views, there should be no differences in retention in the solid phase, but Rowland and Libby[7], and later Milman[10,11], observed that the yields of organic compounds in the secondary reactions of recoil atoms with the medium depend on whether the substance irradiated exists in the crystalline or vitreous state. In the vitreous state, the size of the "liquid drop" will be greater, and the retention less, than in the crystalline state. This is due to the fact that fusion of a substance in the vitreous state requires less energy than fusion of the same substance in the crystalline state. The volume of the resulting "liquid drop" will in this case be greater in the vitreous substance, so that the retention and isotopic effect will be less. The retention data for ^{80}Br in solid ethyl bromide[10,11], obtained for different times of freezing of an ethyl bromide–bromine mixture, indicate a considerable (up to 10%) decrease in the retention for the vitreous state of C_2H_5Br. This result to some extent confirms Libby's theory.

The problem of the difference in the behaviour of recoil atoms in the crystalline and vitreous states can, however, be approached from another viewpoint. As already noted[12], the radiation yield of elementary iodine in the irradiation of ethyl iodide with γ-rays depends on its structure. In the vitreous state the radiation yield of iodine is three times that [for bromine ? (Ed. of Translation)] in the irradiation of ethyl bromide in the crystalline state. Thus it is not the size of the "liquid drop" which is the chief determining factor in the irradiation of vitreous or crystalline substances, but the orientation of the molecules relative to one another, and the related difference in the secondary reactions. As a result, isotopic effects may be produced.

Let us summarise briefly. With increase in the recoil energy an increasing quantity of fragment radicals appears in the track of the hot atom. In the subsequent reactions this gives an increase in the yield of labelled organic substances. This increase is slight compared with the increase in the recoil energy. Thus the isotopic effect (as defined above) is not directly related to the recoil energy. Experimental data show that the isotopic effect is not observed in the presence of radical acceptors, so that this type of isotopic effect should be referred to as an "apparent isotopic effect". Impurities and the accompanying γ-radiation (which cannot be excluded on irradiation in a reactor) can also produce an isotopic effect (as a result of differences in the half-lives of the isotopes). Willard[2], contrary to Capron, claims that the latter factor is of decisive importance and relates it to the isotopic differences accompanying the irradiation of substances in the liquid phase; this is apparently correct. As far as experiments on the irradiation of vitreous and crystalline structures are concerned, it is necessary, before final conclusions are reached, to carry out more detailed experiments with the addition of radical acceptors, since in the solid phase diffusion reactions are not completely blocked.

2. THE BEHAVIOUR OF RECOIL ATOMS IN INORGANIC SYSTEMS

A difference in the behaviour of isotopes as a result of the formation by them of unequal quantities of fragments is predicted by Maddock's theory[13], which is used to describe the processes taking place in the thermal annealing of substances irradiated by γ-rays, neutrons, protons, and other particles. In the irradiation of crystalline potassium chromate with, for example, neutrons, the radioactive chromium atoms obtained by the (n, γ) reaction are stabilised in the form of CrO_3, CrO_2^{2+}, and CrO^{4+} (possibly Cr^{6+}) fragments as a result of the loss of oxygen atoms along the path of their movement. The yield of the mother compound (retention) containing radioactive chromium increases during the subsequent annealing as a result of recombination processes, whose rate depends on the temperature of the experiment. Maddock obtained an expression for the dependence of the rate of recombination of recoil atoms on the distance between them:

$$dR/dt = e^{-A/kT} e^{V/kTX},$$

where X is the least distance between the fragments at time t (between CrO_2^{2+} and O^{2-} for example), T the absolute temperature, k the Boltzmann constant, and V a constant taking account of the charge, dielectric constant, etc.

It follows that since different isotopes of a given element can form different quantities of fragments, the appearance of an isotopic effect is possible after thermal annealing. The thermal annealing of specimens of $NaBrO_3$ and $RbBrO_3$[14] irradiated by thermal neutrons gave for the two bromine isotopes ^{82}Br and ^{80m}Br, data (Table 3) which show that the initial retention is the same for the two isotopes, but that when the irradiated salt specimens are heated, the values of the retention become different. It was considered[14] that the magnitude of the recoil energy does not influence the retention, but since a difference is shown as a result of the processes of recombination between the fragments and recoil atoms during subsequent heating, it must be assumed that the quantities of these fragments are not the same. The quantity is possibly greater for ^{82}Br, and this gives an increase in the retention for this isotope relative to ^{80m}Br as a result of annealing, despite the fact that the initial energy of the ^{80m}Br recoil atom is slightly higher. The difference in the quantities of fragments obtained during deceleration of the ^{82}Br and ^{80m}Br recoil atoms may be due to a difference in their chemical states after the radiation capture of a neutron.

The results given in Table 3 cannot be interpreted in terms of the influence of the recoil energy on the retention. In fact, when the bromates are annealed, the retention for the ^{82}Br isotope increases more rapidly than that for the ^{80m}Br isotope, but the recoil energy of the ^{82}Br isotope is not greater than that of ^{80m}Br. The initial recoil energy

TABLE 3. The influence of thermal annealing on the retention of bromates irradiated with neutrons (t = 200°).

Duration of annealing, min	Retention, %			
	$NaBrO_3$		$RbBrO_3$	
	^{80m}Br	^{82}Br	^{80m}Br	^{82}Br
0	11	11	13	13
10	22	17	—	—
20	23	30	—	—
30	25	33	31	40
90	31	40	35	45
180	34	41	38	49
360	37	45	40	50

thus has no significant influence on the secondary reactions of the recoil atoms, as has been established not only for halogen recoil atoms but also for ^{14}C,[15] tritium,[16] ^{60}Co,[18] and a number of others. The recoil atoms evidently begin to react with the molecules of the medium to form intermediate or stable compounds after preliminary loss of energy. The isotopic effect which has been observed during the thermal annealing of bromates is apparently the result of a difference in the chemical states of the ^{82}Br and ^{80m}Br recoil atoms after the radiation capture of a neutron.

Differences in the behaviour of the isotopes of a given element have also been observed in the study of the (n,γ) reaction in certain metal compounds. Thus a considerable difference was observed in the values of the retention for ^{65}Zn and ^{69}Zn isotopes, obtained by the reactions $^{64}Zn(n,\gamma)^{65}Zn$ and $^{68}Zn(n,\gamma)^{69}Zn$, in the study of the complex formed by zinc with phthalocyanine[17]. The authors erroneously assume, however, that the reason for the production of the isotopic effect is the difference in the initial recoil energy†, which in their opinion leads to a difference in the probability of return to the original molecule. The probability of return to the original molecule for ^{65}Zn recoil atoms, with a recoil energy of 477 eV, is less than that for ^{69}Zn atoms with a kinetic energy of 238 eV. It is assumed[17] that this results in a difference in the values of the retention for the two zinc isotopes (29.4% for ^{65}Zn, 38.2% for ^{69}Zn). It has now been established, however, that the return of the recoil atoms to the original mother molecule is impossible. The recoil atoms form the mother compound in subsequent secondary reactions with other molecules, as a result of the excess energy which they possess, or during subsequent thermal annealing, as a result of recombination with fragments formed during deceleration. Other work[18] has shown that the retention in metal complexes is independent of the initial recoil energy and is determined only by the type of nuclear reaction and the nature of the complex compound. In the case of the two cobalt isotopes ^{58}Co and ^{60}Co obtained by the reactions $^{59}Co(\gamma,n)^{58}Co$ and $^{59}Co(n,\gamma)^{60}Co$ when bisindenylcobalt nitrate is irradiated with γ-quanta or neutrons, the values found for the activity in the form of the original compound were 16.2 ± 1.2% and 2.5 ± 0.2%. These results do not agree with data obtained in the study of the retention in complex compounds of zinc. The recoil energy after the (γ,n) reaction in the cobalt complexes is greater by several powers of ten than that after the (n,γ) reaction. If the above hypothesis were correct, the retention after the (γ,n) reaction should be less than that after the (n,γ) reaction, due to the lower probability of return to the original molecule. The results were contradictory, however. The magnitude of the recoil energy does not influence the retention in metal complexes, as has been proved for organic compounds. The recoil atoms evidently react with the medium to form stable or intermediate compounds in the last stages of the "cooling" process, when their energy decreases to values of the order of 10–100 eV.

Table 4 gives data on the retention for ^{122}Sb and ^{124}Sb isotopes after the (n,γ) reaction in crystalline triphenylantimony, obtained by Hall and Sutin[19]. They consider that the reason for the difference in the values of the retention for the antimony isotopes is to be found in the difference in the recoil energies after the (n,γ) reaction. Making use of the theories developed by Libby, they suggest that the ^{122}Sb recoil atom has apparently a smaller recoil energy, which leads to a greater retention for this isotope, as a result of the higher local concentration of fragments. There are, however, no data for the recoil energies of ^{122}Sb and ^{124}Sb, so that this explanation of the isotopic differences is not convincing. The isotopic effect may be the result of a difference in the degree of conversion of the electron clouds of the ^{122}Sb and ^{124}Sb isotopes formed after isomeric transition in 3.5 min from ^{122m}Sb and in 21 min and 1.3 min from the two isomers of ^{124m}Sb. As a result of isomeric transition, the antimony atoms acquire a positive charge and leave the mother molecule due to coulombic repulsion. The internal conversion coefficients are different for the isomeric transitions $^{122m}Sb \rightarrow {}^{122}Sb$ and $^{124m}Sb \rightarrow {}^{124}Sb$, and this may lead to a difference in the number of ^{122}Sb and ^{124}Sb atoms leaving the molecules in which they are stabilised directly after the (n,γ) reaction. The quantity of ^{122m}Sb and ^{124m}Sb excited states produced is only 1%, however,[19] so that this cannot significantly influence the distribution of ^{122}Sb and ^{124}Sb isotopes among the individual products.

According to Maddock's data[17,20], the difference in the values of the retention for the ^{122}Sb and ^{124}Sb isotopes, and also for the isotopes ^{186}Re and ^{188}Re, may be related to the difference in the degree of conversion of the soft γ-rays of the capture radiation of thermal neutrons. This is a probable explanation of the production of isotopic differences, since it has been confirmed experimentally that a relationship exists between the internal conversion coefficients and the retention[21]. In a study of the removal of the chemical species C_6H_5Pb(ThB, RaD)Cl, as a result of the β-decay of the lead isotopes ThB and RaD and their conversion to the bismuth isotopes ThC and RaE, it was found that the ratio

TABLE 4. Yields of products containing the radioactive isotopes ^{122}Sb and ^{124}Sb during the irradiation of crystalline triphenylantimony with neutrons.

Products	^{122}Sb, %	^{124}Sb, %	$^{122}Sb/^{124}Sb$
$(C_6H_5)_3Sb$	4.4	3.2	1.37±0.02
$(C_6H_5)_2SbO(OH)_2$	13.9	13.8	1.01±0.05
$(C_6H_5)SbO$ and $(C_6H_5)SbO(OH)_2$	32.7	30.7	1.06±0.04
Sb	29.7	33.8	0.88±0.01

† The reader is advised to consult Ref.17, p.499, however (Ed. of Translation).

of ThC and RaF in the original compound is equal to $1 - k_1/1 - k_2$, where k_1 and k_2 are the internal conversion coefficients for the β-decay of the ThB and RaD isotopes. In fact for the β-decay of heavy isotopes, the recoil energy is insufficient to rupture a chemical bond, and the probability of removal from the mother compound is determined by the degree of conversion of the electron cloud. The marked isotopic effect in the β-decay of ThB and RaD (retention 50 ± 2% and 19 ± 1% respectively) indicates that the state of the electron cloud of the recoil atoms is the decisive factor influencing the magnitude of the retention.

3. THE INFLUENCE OF THE CHEMICAL STATE OF THE RECOIL ATOMS ON SUBSEQUENT REACTIONS IN WHICH THEY TAKE PART

Considerable attention has recently been paid to the possibility of ion–molecule reactions during the stabilisation of recoil atoms activated by nuclear reactions. This possibility is based on the fact, first observed by Wexler and Davies[22,23], that the recoil atoms obtained by an (n, γ) reaction have a positive charge. It was found that approximately 25% of the ^{82}Br recoil atoms, 18% of ^{82m}Br atoms, 12% of ^{80}Br atoms, 45% of ^{128}I atoms, and 21% of ^{38}Cl atoms are obtained with positive charges and can be collected at a negative electrode in the gas phase. The average charge on the ^{80}Br atoms (18 min) is +10, and that on the ^{38}Cl atoms +4.[23] The quantity of charged ^{82}Br atoms is greater than the quantity of ^{80m}Br atoms, so that the fragmentation of the molecules is greater for the ^{82}Br recoil atoms. Some authors[14] have tried to explain the difference in the values of the retention for ^{82}Br and ^{80m}Br isotopes from this viewpoint. Others[24-28] suggest that the isotopic effect is a direct result of ion–molecule reactions between the recoil atoms and the molecules of the medium.

It is known[29] that chlorine atoms readily remove hydrogen from hydrocarbon molecules with the formation of HCl. The activation energy for this process is less, the longer the hydrocarbon chain. Aditya and Willard[30], found, however, that the retention for ^{38}Cl obtained by the reaction $^{37}Cl(n, \gamma)\,^{38}Cl$ in CCl_4 diluted with various hydrocarbons is constant and independent of the nature of the solvent or the chain length of the hydrocarbon molecule. This unexpected feature of the retention cannot be satisfactorily explained in terms of the existing theory of stabilisation of recoil atoms and cannot be attributed to reaction between the "cooled" chlorine recoil atoms and the hydrocarbon molecules. The value of 21% found experimentally for the retention[30] shows remarkable agreement with the proportion of positively charged ^{38}Cl atoms (21%) obtained after the (n, γ) reaction, as shown by Wexler and Davies. This suggests the possibility of ion–molecule reactions involving charged chlorine atoms. When C_3H_7Cl was diluted with methane in the gaseous phase, the retention for ^{38}Cl resulting from the (n, γ) reaction was found to be 17%;[31] for dilution with ethane the retention was 10%[16] and for dilution with butane 7%.[16] The fact that in these cases the retention was found to be less than the 21% found in Aditya and Willard's experiments indicates that the nature of the solvent has a certain influence, but this is not surprising from the viewpoint of the ion–molecule reaction theory, since the rates of loss of charge may be different in different media. The yields of C_2H_5Cl and $C_2H_4Cl_2$, obtained during the irradiation of methyl chloride with neutrons [(n, γ) reaction], show that the CH_3Cl molecule is able to react with another CH_3Cl molecule to form a C–C bond. The possibility of the formation of chains in the reactions of the recoil atoms with the medium exists in principle. Willard[32] suggested the following mechanism of chain formation resulting from the secondary reactions of tritium recoil atoms with methane in the gas phase:

$$T^+ + CH_4 \rightarrow CH_3T^+ + H_2, \quad (1)$$
$$CH_3T^+ + CH_4 \rightarrow C_2H_4T^+ + H_2. \quad (2)$$

There are strong objections to this mechanism of chain formation, however, as Willard himself pointed out[31]. These arise from the fact that the tritium atoms are assumed to be neutralised before their energy decreases to ~100 eV, *i.e.* to a value which is still sufficiently high for the formation of stable products by inelastic collisions.

Studies by Wolfgang and coworkers help to resolve this contradiction. They have shown[33-35] that the relative kinetic energy of the most probable reactions of tritium with methane molecules,

$$T + CH_4 \rightarrow T^+ + CH_4 + e^-$$
$$T + CH_4 \rightarrow T^- + CH_4^+$$
$$T^- + CH_4 \rightarrow T + CH_4 + e^-$$
$$T^+ + CH_4 \rightarrow T + CH_4^+$$

has the values (eV) 30 000, 25 000, 90, and 30 respectively. From this it can be seen that tritium atoms with an initial kinetic energy greater than 30 000 eV [$^6Li(n, \alpha)T$ reaction] are gradually slowed down and become able to ionise or be ionised, and at lower velocities of 100 eV and below they effectively neutralise one another. This, however, is the upper kinetic energy limit where reactions of inelastic collision between the tritium recoil atoms and the molecules become possible. It is therefore possible that ion–molecule reactions of charged tritium recoil atoms can take place, so that Willard's initial assumption is correct.

The reactions of the ions of radioelements dispersed in high-tension fields have recently been studied, in order to obtain a model for processes taking place after nuclear reactions. Wolfgang[33] has obtained data on the distribution of tritium between different compounds during reactions of tritium ions, dispersed at 100 eV, with organic substances. Analogous experiments by Lemmon[36,37] on the reaction of dispersed $^{14}C^+$ ions with benzene have shown that the ion–molecule reactions taking place when the charged $^{14}C^+$ ions collide with benzene molecules lead to the formation of the following compounds, labelled with carbon-14: carbon dioxide, benzene, cycloheptatriene, and hydrocarbons from propane to pentane. The ratio of the yields of these products changes with change in the energy of the moving $^{14}C^+$ ions. The preparation of labelled compounds by means of the reactions of artificially dispersed ions is of considerable theoretical importance in explaining the regular features of the secondary reactions of recoil atoms obtained as a result of nuclear reactions. Work in this direction is undoubtedly of practical importance for the synthesis of various compounds containing radioactive atoms.

Willard *et al.*[38-40] have shown that ~50% of the ^{128}I atoms obtained by the reaction $^{127}I(n, \gamma)\,^{128}I$ in a mixture of iodine and methane are stabilised (at pressures of 0.2 mm Hg and 400 mm Hg respectively) in the form of organic compounds, whereas during photochemical dissociation under the same conditions, less than 1% of the iodine enters the organic compounds. The authors discuss the possibility of the introduction of iodine into organic compounds by reactions of the type

$$I + CH_4 \rightarrow CH_3I + H \quad (3)$$

or

$$I^+ + CH_4 \rightarrow CH_3I + H^+. \quad (4)$$

Both reactions are endothermic, the first requiring the expenditure of ~50 kcal mole^{-1} and the second 100 kcal × × mole^{-1}. The ratio of the masses of methane and iodine is such that the proportion of the energy which can be transferred by the iodine atom in one collision with a methane molecule is 40%. On the average, 20% of the initial kinetic energy is used up in one collision. Assuming that when a neutron is captured by the atom, one γ-quantum is emitted with an energy of 8 MeV, we find that the initial energy of the ^{128}I recoil atom is 268 eV. Since reaction (3) requires an activation energy of 50 kcal mole^{-1} or ~2 eV, the number of collisions necessary to decrease the initial energy of the iodine recoil atom to this value is

$$n = \ln \frac{268}{2} \Big/ \eta = 2.3 \log (134)/0.4 \simeq 12,$$

where η is the logarithmic decrement of the loss in energy when an iodine atom collides with a methane molecule.

Despite the fact that the ^{128}I recoil atom undergoes ~12 collisions with methane molecules and at each collision has an energy greater than the activation energy of reaction (3), the formation of methyl iodide as a result of these collisions is impossible, for the following reasons. The maximum proportion of the kinetic energy which can be possessed by the activated complex and can hence be used for the rupture of the C–H bond is equivalent to the ratio of the mass of the methane molecule to the sum of the masses of the methane molecule and iodine atom

$$\frac{M_{CH_4}}{M_{CH_4} + M_I},$$

and has the value ~0.1.

Thus the iodine atom should have an energy of not less than 20 eV if it is to transfer, on collision with a methane molecule, an amount of energy sufficient to dissociate a C–H bond. In this case the activated complex will have an energy of 460 kcal mole^{-1} (20 × 23 = 460). It is unlikely that the C–I bond in such a molecule will be preserved on collision with other molecules. As a result, the formation of methyl iodide according to reaction (3) is impossible. The ionisation potential of the methane molecule is 14.4 eV, and that of iodine 10.6 eV, so that the iodine atom collides with methane molecules without losing its positive charge. In the presence of iodine the following reaction is possible:

$$^{128}I^+ + I_2 \rightarrow I_2^+ + {}^{128}I \quad (5)$$
$$^{128}I^+ + I_2 \rightarrow I^{128}I^+ + I, \quad (6)$$

since the ionisation potential of the I_2 molecule is lower than that of the iodine atom (10.1 eV and 10.6 eV respectively), so that subsequently, as suggested by Willard, a reaction may take place between the iodine molecules, which acquired an excitation energy in reactions (5) and (6), and methane molecules:

$$I^{128}I + CH_4 \rightarrow CH_3{}^{128}I + HI$$
$$I^{128}I + CH_4 \rightarrow CH_3I + H^{128}I.$$

Developing Willard's initial hypothesis of ion–molecule reactions in the iodine–methane system, let us assume that charge transfer takes place according to the following scheme:

$$II^+ + CH_4 \rightarrow CH_3I^+ + HI \quad (7)$$
$$II^+ + CH_4 \rightarrow CH_3I + HI^+. \quad (8)$$

The heat of the reaction can be calculated from the formula

$$Q = A - B + P_1 - P_2,$$

where Q is the heat, A the energy of formation of the new bonds, B the dissociation energy of the old bonds, and P_1 and P_2 the ionisation potentials of the newly formed ionised molecule and the original compound.

A reaction of type (4) is impossible for the same reasons as those which apply to reaction (3), and also because the ionisation potential of the hydrogen atom is 4.59 eV greater than the ionisation potential of the I atom, leading to an increase in the activation energy of reaction (4), calculated by Polyani's rule, by several kcal mole^{-1}. For reactions (5) and (6), we obtain Q = 0.5 eV, *i.e.* the heat of ion–molecule reactions of types (5) and (6) is equal to the difference in the ionisation potentials of the iodine atom and molecule. In the comparison of the heats of reactions (7) and (8) only the ionisation potentials are taken into account, since the nature of the products obtained by these reactions is the same:

$$Q(7) = (A - B) + 0.33,$$
$$Q(8) = (A - B) - 1.71,$$

where $(A–B)$ is the heat of the reaction without allowance for the ionisation potentials. Reaction (7) is more probable, since the heat is higher.

In the absence of added elementary iodine, it is possible that the determining reaction is the introduction of charged iodine atoms into the methane molecule according to the scheme

$$^{128}I^+ + CH_4 \rightarrow CH_3{}^{128}I^+ + H, \quad (9)$$

which is energetically more favourable than the corresponding reaction with uncharged atoms.

Experiments[39] carried out by Willard on the activation, by thermal neutrons, of a mixture of iodine and methane in the presence of substances with higher ionisation potentials than that of iodine (He 24.58 eV, Ar 15.76 eV, and Xe 12.13 eV) and substances with lower ionisation potentials (CH_3I 9.67 eV, C_2H_5I 9.47 eV, and C_3H_7I 9.41 eV) indicated the absence of any effect when the inert substances were added and a marked decrease in the retention when substances with lower ionisation potentials were added. These data provide very significant evidence in support of the hypothesis that ion–molecule reactions take place.

For the three radioactive bromine isotopes ^{80}Br, ^{80m}Br, and ^{82}Br, obtained by (n,γ) reactions from the natural mixture of isotopes, the ratio of the retentions for the isotopes should be 1.5 : 1 : 2, as postulated by Willard *et al.*[40], if it is assumed that positively charged bromine atoms take part in the reaction. They carried out experiments on the neutrons of bromobenzene, of a mixture of benzene and bromine, and of n-propyl bromide. The data are given in Table 5. They concluded that there is no difference in the behaviour of the three bromine isotopes. The ionisation potentials of the substances which they used are in all cases lower than the ionisation potential of bromine (C_6H_6 9.5 eV, C_6H_5Br 9.4 eV, Br 11.8 eV, Br_2 10.9 eV), so that if some of the reactions occurred through positively charged bromine atoms, this would be clearly shown for the ^{82}Br isotope. The negative result of these experiments indicates that ion–molecule reactions do not take place in the systems chosen. The benzene molecule has a lower ionisation potential than the bromine atom, so that the bromine recoil atom loses its charge in the earliest stages of the

TABLE 5. Retention for the bromine isotopes ^{80}Br, ^{80m}Br, and ^{82}Br during slow-neutron irradiation of compounds mixed with bromine.

Mixture irradiated	Retention, %		
	^{80}Br	^{80m}Br	^{82}Br
C_6H_5Br + 3 mole % Br_2	5.56	5.89	5.40
C_6H_5Br + 0.1 mole % Br_2	16.6	17.4	16.5
C_6H_6 + 5 mole % Br_2	1.77	1.77	2.32
C_6H_6 + 2 mole % Br_2	2.68	2.64	2.75
n-C_3H_7Br + 0.5 mole % Br_2	5.28	5.74	5.43

"cooling" process. At the moment when super-thermal reactions become possible, it no longer possesses a charge. Ion–molecule reactions can be expected only in a system where the ionisation potentials of the substances are greater than the ionisation potentials of the recoil atoms and the products obtained have a lower ionisation potential. Then, in the first place, the recoil atom has not lost its charge up to the moment when super-thermal inelastic interactions begin to take place, and secondly, reactions will take place with the formation of products whose ionisation potentials are lower than those of the original substances and the ion–molecule reactions may compete with ordinary radical reactions. From this viewpoint the latest experiments[40] cannot be considered successful.

4. THE ISOTOPIC EFFECT REGARDED AS THE RESULT OF SUPER-THERMAL ION–MOLECULE REACTIONS

In the study of the reactions of "hot" bromine atoms activated by (n,γ) reactions in mixed liquid chlorobromomethanes an isotopic effect was observed[24-27] for ^{82}Br and ^{80m}Br in the case of the following compounds: CCl_3Br, CCl_2Br_2, CH_2ClBr, $CHCl_2Br$, and $CHClBr_2$. The retention for ^{82}Br was greater than that for ^{80m}Br and was independent of both the duration of irradiation and the addition, before irradiation, of elementary bromine over a wide concentration range. An analogous result was obtained for fluorobromomethanes in the liquid phase[28]. To explain the isotopic effect, Nesmeyanov and Filatov put forward a theory of ion–molecule reactions in the super-thermal energy range according to the scheme

$$\overset{+}{Br}{}^{*} + RClBr \longrightarrow \begin{cases} \overset{+}{R}ClBr^{*} + Br^{\cdot} & (6) \\ R\overset{+}{B}rBr^{*} + Cl^{\cdot} & (7) \\ RCl^{\cdot} + Br\overset{+}{B}r. & (8) \end{cases}$$

These reactions are possible because the ionisation potentials of the compounds formed in the reactions are less than the ionisation potential of the bromine so that the activation energy of the reactions is less than usual. The introduction of a radioactive bromine atom into the organic compounds will be greater for the ^{82}Br isotope, since the number of positively charged ions is greater for $^{82}Br^{+}$ than for $^{80m}Br^{+}$, and inorganic radiobromine will appear in the form of Br–Br, and not Br–Cl, since the ionisation potential of the latter is greater. (The reactions occur in the direction of substances with the lower ionisation potentials.)

In iodobromomethane the isotopic effect is opposite to that observed for the chlorobromomethanes[26]. The effect of elementary iodine on the retention was studied, but over a wide concentration range the iodine had no influence on the isotopic effect. The influence of polar and non-polar solvents on the retention for ^{82}Br and ^{80m}Br was also studied. It was observed that when polar solvents are added, the retention for ^{82}Br decreases more rapidly than for ^{80m}Br; the isotopic effect decreases; for CH_2BrI the opposite effect is observed. Thus the polarity of the solvent influences the isotopic effect, but the polarity of the compound being irradiated has no significant influence on the magnitude of the retention, since, for example, the values of the retention for ^{82}Br and ^{80m}Br in 1,2-chlorobromoethane and bromopicrin were found to be identical.

An apparent isotopic effect has been observed[25] in the irradiation of bromoform with neutrons at an elementary bromine content of less than 10^{-3} mole. When specimens containing more than 10^{-3} mole of Br_2 were irradiated, the isotopic effect disappeared, and it was also absent when the irradiation was of short duration (at a bromine content of less than 10^{-4} mole), indicating that in this compound the isotopic effect results from diffusion–recombination reactions. In chlorobromomethanes the isotopic effect does not change with change in the duration of irradiation from 4 h to 120 h, indicating that the isotopic effect in these compounds is due to high-energy reactions.

An interesting fact is that the isotopic effect (ΔR) is related to the fraction of diffusion reactions (R_D) in the compounds studied (Table 6). It was found that for all the compounds, except $CHCl_2Br$, the isotopic effect was smaller, the greater the part played by diffusion–recombination reactions in the stabilisation of the recoil atoms. This indicates that the isotopic effect in the substances studied cannot be due to diffusion reactions of the recoil atoms, since otherwise the isotopic effect would increase with increase in the proportion of the diffusion reactions, as a result of the greater average lifetime of the ^{82}Br isotope compared with the ^{80m}Br isotope.

When substances with ionisation potentials lower than that of bromine (benzene, toluene) are added, the retention remains unchanged for both ^{82}Br and ^{80m}Br. This agrees with Willard's data on the neutron irradiation of $C_6H_6 + Br_2$ mixtures (Table 5).

In all the mixed halogenobromomethanes, in which an isotopic effect was observed on irradiation in the liquid phase, no difference in the behaviour of ^{82}Br, ^{80m}Br, and ^{80}Br was observed in the solid phase[28]. This can apparently be attributed to an increase in the rate of neutralisation of the charge of the bromine recoil atoms in the solid medium because of the higher forces of adhesion between the molecules in the molecular crystal. In a liquid medium the isotopic effect had the greatest value in non-polar substances (CCl_3Br, CCl_2Br_2, and CBr_3F). In polar substances it was generally absent ($CHBr_3$, CBr_3NO_2, and CH_2Br_2). This also confirms the assumption that neutralisation of the charge of the recoil atoms is possible during deceleration

TABLE 6. Retention, isotopic effect, and proportion of diffusion reactions in halogenobromomethanes in the liquid phase.

Substance	R_D	$R_{^{82}Br}$	$R_{^{80m}Br}$	$R_{^{80}Br}$	ΔR
CCl_3Br	14	48.0	38.0	—	10
CCl_2Br_2	18	54.0	450	—	9
$CHBr_2F$	20	54.0	48.0	49.0	9
$CHBr_2Cl$	24	63.3	57.5	—	9
$CHCl_2Br$	30	64	53.1	—	11
CH_2BrCl	30	58.9	57.7	—	3
CBr_3F	—	67.2	56.8	55.5	10

in the solid phase. It is not yet clear, however, why the isotopic effect was observed specifically in mixed halogenobromomethanes.

The isotopic effect observed in mixed halogenobromomethanes differs significantly from the "apparent isotopic effect" considered earlier (Section 1). The "apparent isotopic effect" is associated with the last stage of the "cooling" of the recoil atoms — with diffusion–recombination reactions. The small quantities of impurity, which cannot be controlled, or the accompanying γ-radiation, play a significant part at this stage. To eliminate the influence of these last factors, the experiments on halogenobromomethanes were carried out with the addition of bromine. The isotopic effect did not disappear, which means that the reactions producing the isotopic differences in this case take place in the high-energy stage. It is possible that these processes are ion–molecule reactions of the recoil atoms with the molecules of the medium.

The problem of the origin of the isotopic effects in the secondary reactions of recoil atoms is still unsolved. The available experimental data do not agree with the theories of Libby and Willard. According to Libby's theory, the difference in the kinetic energy of the recoil atoms should be revealed as a difference in the size of the "liquid drop" in the solid substance and should thus lead to a difference in the proportion of organic products for isotopes with different recoil energies, as a result of the difference in the local concentration of radicals. Evidence against this theory is provided, however, not only by the experimental data considered above, but also by certain fundamental considerations, which may be summarised as follows.

1. With smaller "liquid drop" in a solid body for recoil atoms with a lower kinetic energy of recoil, there is an increase in the local concentration not only of the organic fragments, but also of the inorganic fragments, so that a decrease in the size of the "liquid drop" should not lead unambiguously to an increase in the retention (in the form of organic compounds).
2. The temperature inside the "liquid drop" is too high (10 000°K). No reactions other than intense dissociation of the molecules can take place in it.
3. With increase in the initial recoil energy of the atom from 100 eV to 1 MeV the change in the size of the "liquid drop" should lead to a considerable change in the yield of organic products, but this is not observed.

The "chance fragmentation" (or "pocket of radicals") theory of Willard assumes that the isotopic differences, which depend on the energy of recoil (or charge), are produced as a result of subsequent diffusion–recombination reactions between the recoil atoms and the fragments in the track of the "hot" atom. In this case, however, a change in the recoil energy by several powers of ten should lead to a considerable change in the yield of organic products. Experiments show that there is no clear significant relationship between the recoil energy and the yield of organic products.

On the basis of Brinkman[41,42] and Seitz's[43] theory of radiation damage in solids, Harbottle[5,44] suggested a mechanism for the reaction of the recoil atoms with the medium, involving the formation, by the recoil atom, of a "hot zone" with non-uniform heating from the centre of the zone to the periphery. An advantage of this theory is its more definite character and the possibility of using the fundamental hypotheses and mathematical apparatus of solid state physics. Harbottle also points out that chemical super-thermal and thermal reactions may play an important part in the stabilisation of recoil atoms. The "hot zone" theory predicts the possibility of isotopic effects, the mechanism of their production being assumed to be the same as in Willard's "chance fragmentation" theory, *i.e.* diffusion–recombination reactions between the recoil atoms and the radicals and organic fragments created in the "hot zone". As already pointed out, however, there is no definite relationship between the recoil energy and the isotopic effects, so that the "hot zone" theory cannot explain the production of the isotopic differences. The isotopic differences may possibly be explained by the widely circulating theory of ion–molecule reactions, whose existence, in the gas phase at any rate, is accepted by most workers[45]. As already pointed out, considerable success in the treatment of the results obtained in experiments on the activation of halogens and tritium in different media has been achieved by the ion–molecule reaction theory. If this theory is adopted, deceleration and charge transfer by the recoil atom can be represented as follows. The recoil atoms leaving the mother molecules generally have a recoil energy which is insufficient to lead to ionisation of the atoms during movement. If the recoil atoms are to be able to ionise during movement, they must have the energy[5]

$$E = \frac{M}{m_e} P,$$

where M is the mass of the recoil atom, m_e the mass of the electron, and P the ionisation potential of the recoil atom.

Thus the ^{11}C recoil atom, whose ionisation potential is 11.26 eV, should have an initial kinetic energy of at least 228 keV if it is to ionise during movement. It is known[15] that the ^{11}C atoms obtained by the reaction $^{12}C\ (n, 2n)\ ^{11}C$ with fast neutrons have a recoil energy of about 1 MeV, *i.e.* they are able to ionise and subsequently react in the form of charged ions. For the ^{14}C atoms obtained by the reaction $^{14}N\ (n, p)\ ^{14}C$, the recoil energy is 45 000 eV and is thus insufficient for ionisation. For heavier recoil atoms such as ^{82}Br and ^{128}I, the values of E are 1740 eV and 2440 eV respectively, so that the ^{82}Br and ^{128}I recoil atoms obtained as a result of the capture of thermal neutrons have a recoil energy of ~100 eV and cannot ionise. As already pointed out, however, some of the recoil atoms such as ^{82}Br, ^{128}I, ^{38}Cl, etc. are obtained in ionised form after an (n, γ) reaction.

Let us assume that the ionisation potential of the surrounding molecules is lower than the ionisation potential of the recoil atoms. The recoil ions then rapidly lose their charge before they are able to take part in super-thermal ion–molecule reactions. In this case an isotopic effect may appear for isotopes with different quantities of charged recoil atoms as a result of diffusion–recombination reactions, since the ionised molecules dissociate at any of the bonds and give a much greater quantity of fragments in the track of the charged recoil atom. If the ionisation potential of the molecules surrounding the recoil atom is greater than the ionisation potential of the recoil atom, the latter, on collision, will not lose its charge and subsequently, when the energy decreases to super-thermal values, it may take part in ion–molecule reactions. Moreover, if the compounds obtained by these reactions have ionisation potentials lower than that of the recoil atom, the process by which the compound is obtained may compete successfully with ordinary radical reactions and produce an isotopic effect.

This hypothesis obviously requires confirmation. Ordinary chemical methods of study may be insufficient, and it is possible that solution of the problem of the mechanism of the secondary reactions of recoil atoms requires detailed study (for example by mass-spectrometry) of the chemical state and subsequent reactions of the recoil atoms with molecules. An important contribution may be made by the study of the reactions of accelerated ions.

The problem of the mechanism of the reactions of "hot" atoms is not distinct from the solution of other chemical problems (despite the specific features of their behaviour). This apparently is the main difficulty for workers in this field; the chemistry of "hot" atoms is evidently closely interwoven with such fields of chemistry as reaction kinetics and reactivity of atoms and radicals, radiochemistry, and high-temperature chemistry.

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