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Ion-Molecule Reactions Initiated by the β-Decomposition of Tritium in Tritiated Compounds

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Ion-molecule reactions initiated by the β-decomposition of tritium in various compounds are examined and a systematic account is given. The theoretical and experimental foundations of the radiochemical method for the investigation of this important type of chemical interactions are described. The ion-molecule reactions investigated are combined in two groups: the reactions of the ions HeT^+ and the reactions of carbonium ions. Conclusions concerning the reactivity of the intermediate species, the mechanisms of their interaction with various substances, and the prospects for the utilisation of the radiochemical method of investigating ion-molecule reactions are reached on the basis of the experimental results presented.
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I. INTRODUCTION

As early as the end of the last century, the existence of molecular ions was discovered from the study of the electrical conductivities of flames and gases subjected to an electrical discharge. In 1905, Langevin[1] and subsequently also other investigators[2] attempted a theoretical development of models of the gas-phase interaction of charged species with neutral molecules. However, the first experimental study[3] specially devoted to ion–molecule reactions was not published until 1952. During the two decades elapsed since its publication, there has been a sharp growth of intensity of research in this field. In the USA alone, more than one hundred papers have been published annually during the last few years on ion–molecule reactions and the expenditure by the state on this research exceeds at the present time 2 500 000 dollars annually[4].

The interest in ion–molecule reactions is due to the fact that the knowledge of the mechanism, thermochemistry, and kinetics of these interactions is extremely important for the understanding of the processes developing under the influence of radiation and light, in the flame, in electrical discharges, in mass spectrometers, in the upper layers of Earth's atmosphere, in the atmospheres of other planets, and in heterolytic organic reactions. Thus, for example, as early as the beginning of this century, it was established that certain organic substances are capable of dissociating into molecular ions[5]. Numerous subsequent investigations by organic chemists showed that the majority (approximately 60%) of organic reactions proceed via a stage involving the formation of charged molecular species—carbonium ions. The processes accompanying the interaction of radiation or light with matter also take place with participation of ionised species. The hypothesis of the occurrence of ion–molecule reactions in radiation processes, put forward by Lind[6] as early as 1912, has now been widely adopted in radiation chemistry[7-11]. Bimolecular reactions between ions and molecules have been observed in mass spectrometry as secondary processes already in the first instruments. However, these reactions were regarded for a long time as fundamental obstacles to the development of analytical mass spectrometry[12-14]. For this reason, despite their early observation, the systematic study of these reactions did not begin until the 1960s.[3,15-17] Ion–molecule reactions also play an important role in astrochemistry. For example, Libby[18] suggested that the ion–molecule reactions developing in Jupiter's atmosphere may give rise to "petroleum rain"†.

Ion–molecule reactions are studied at present mainly by the following methods: (1) mass spectrometry; (2) ion–cyclotron resonance; (3) the method of the total elimination of charge; (4) the discharge technique; (5) the radiochemical method. With the exception of the last procedure, all these methods have been discussed in detail in numerous reviews of ion–molecule reactions[20-40] and also in a review[41] specially devoted to the experimental techniques for the investigation of these processes. The lack in the above publications of information about the radiochemical method for the investigation of ion–molecule reactions can apparently be accounted for by the fact that the first studies in this field were begun less than ten years ago[42-45]. Despite the comparatively recent introduction of the method, it has now been used successfully in more than 30 investigations.

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† This striking picture of the atmospheric phenomena on Jupiter was described by Libby at a lecture devoted to the 50th anniversary of the National Scientific Council of Canada in 1966. The arguments presented reduced to the following. The components of Jupiter's atmosphere are known to be hydrogen and methane, which ionise under the influence of intense cosmic radiation. The H_2^+ and CH_4^+ ions generated thereby react with methane, forming the highly reactive species CH_5^+, which is capable of giving rise to the synthesis of heavy hydrocarbons[19].

The method is based on a fundamentally new procedure for the initiation of ion–molecule reactions, consisting in the generation of molecular ions by the spontaneous nuclear-chemical transformation of tritiated compounds:

$$RT \xrightarrow{-\beta^-} [RHe^+] \rightarrow [R^+He] \rightarrow R^+ + He \quad .$$

The use of repeatedly tritiated starting compounds made it possible to obtain labelled charged molecular species, the chemical state of which may be followed from their radioactivity.

In the present review, an attempt is made to discuss the theoretical and experimental foundations of the method and also to examine systematically the experimental results published up to May, 1974.

II. THEORETICAL AND EXPERIMENTAL FOUNDATIONS OF THE APPLICATION OF β-DECOMPOSITION PROCESSES IN THE STUDY OF ION–MOLECULE REACTIONS

The possibility of employing β-decomposition processes in the study of ion–molecule reactions is based on a series of theoretical and experimental investigations of nuclear transformations of this type and their chemical consequences.

The first result of the β-transformation of a radioactive atom is known to be the formation of a singly charged atom of a neighbouring element in the Periodic Table (the daughter atom) in accordance with the following scheme:

$$^{A}_{z}M_{A-z} \rightarrow {}^{A}_{z+1}[D]^{+}_{A-z-1} + e^- + \tilde{\nu} \ ,$$

where P and D are the symbols for the parent and daughter elements, A and z are the mass number and nuclear charge of the atom of the parent element, and e^- and $\tilde{\nu}$ are the β-particle and antineutrino respectively. For the β-decomposition of the tritium atom, this scheme assumes the following form: $^{3}_{1}H_2 \rightarrow {}^{3}_{2}He^{+}_{1} + e^{-1} + \tilde{\nu}$.

The subsequent fate of the $[D]^+$ ion formed depends on a number of factors, which include in the first place the shaking effect. The shaking effect, i.e. the perturbation of the electron shells in consequence of the sudden change in nuclear charge, is one of the most important causes of excitation and additional ionisation of the singly charged ion of the daughter element. Calculations of the probabilities of the excitation and additional excitation of daughter atoms have shown[46,47] that a considerable proportion of these ions (up to 80%) are in the ground electronic states and that the overall yield of multiply charged ions does not exceed 20%, most of them consisting of ions having the +2 charge.

Similar calculations for the β-decomposition of isolated tritium atoms[48] showed that 70% of the decomposition steps lead to the formation of non-excited He^+ daughter ions, 25% give rise to daughter ions in the first excited level (40.5 eV), 2.5% yield daughter ions in levels with energies between 40.5 and 54.4 eV, and only 2.5% lead to the formation of doubly charged He^{2+} daughter ions. A characteristic feature of the β-decomposition of tritium atoms is the impossibility of the formation of ions of the daughter element with a charge greater than +2. The highly charged states arising in the β-decomposition of the atoms of other elements can be produced as the result of the ionisation of the inner electron shells in consequence of the shaking effect and the subsequent cascades of vacancies. In the β-decomposition of tritium, the development of vacancy cascades is impossible owing to the presence of only one electron shell.

We have discussed hitherto processes leading to the excitation and ionisation of the daughter atom formed on β-decomposition of isolated tritium atoms. We shall now consider how these effects are manifested when the atom undergoing decomposition forms part of a molecule. The electronic processes developing in the atom as a result of β-decomposition take place over a period much shorter than the period of atomic vibrations; one can therefore assume that these processes, occurring in atoms, predetermine the set of energy and charge states of the molecular ions. Since the yield of non-excited He^+ daughter ions formed in β-transformations of isolated tritium atoms is about 70%, one may expect approximately the same yield of non-excited primary molecular ions $[RHe]^+$ in the β-decomposition of tritium atoms forming part of the molecules RT.

The primary molecular ions subsequently undergo a number of transformations, which include in the first place electronic transitions, accompanied by the migration of charge, from the helium atom to other atoms in the primary molecular ions:

$$\left[\overset{\curvearrowleft}{RHe^+}\right] \rightarrow \left[R^+He\right] \quad .$$

Such a charge distribution can be accounted for by the fact that the ionisation potential of the helium atom (24.581 eV) is much higher than the ionisation potential of organic radicals (< 10 eV).

The next process undergone by the species generated is their decomposition with formation of the ion R^+ and a helium atom. Since the energy of the C–He bond is estimated as only 0.18 eV,[49] this decomposition should occur over a period close to the period of the atomic vibrations. Subsequent spatial separation of the species produced takes place owing to the momentum acquired by the helium atom as a result of radioactive recoil.

Radioactive recoil is due to the emission of a nuclear electron and an antineutrino. The maximum recoil energy is defined by the expression[50]

$$E_{max} = 536 \cdot 10^6 E^{\beta}_{max} \left(\frac{E^{\beta}_{max} + 1.02}{M_D} \right) ,$$

where E_{max} is the maximum recoil energy (MeV), E^{β}_{max} the maximum energy of the β-particle (MeV), and M_D the mass of the daughter atom (a.m.u.).

Since the emission energy of tritium is minimal ($E^{\beta}_{max} = 0.0186$ MeV) compared with the emission energies of other β-radioactive isotopes, the recoil energy in the decomposition of tritium is small. The maximum recoil energy calculated from the above formula is only 3.35 eV.

In the β-decomposition in atomic systems, the recoil energy is generated in the form of the kinetic energy of the daughter atoms. In the general case of β-decomposition of an atom in a molecular system, part of the recoil energy can be consumed in the dissociation of the bond between the daughter atom and the remainder of the molecule. This component is determined by the rotational-vibrational coefficient $(M - M_D)/M$, i.e. depends on the ratio of the mass of the residue $M - M_D$ and the mass of the molecule M.[51] In the decomposition of tritium forming part of various organic molecules, the rotational-vibrational coefficient is close to unity and one can therefore expect that a considerable proportion of the recoil energy will be consumed in the excitation of the molecular ion as a whole. However, owing to the virtually zero energy of the C–He bond, the helium atom in the intermediate

species [R^+He] can be regarded as free and the entire recoil energy is therefore generated as the kinetic energy of the helium atoms.

Thus theoretical studies of the β-decomposition processes and the accompanying transformations lead to the following conclusion important for the problem under consideration: the main chemical consequence of the β-decomposition of tritium atoms forming part of the molecule RT is the formation of non-excited singly charged molecular ions R^+.

Among the systems investigated at the present time, only one instance is known in which the above rule does not hold. This applies to the simplest tritium-containing compound—tritiated hydrogen (R = H or T). The primary molecular ions $^3HeH^+$ and $^3HeT^+$, formed in the β-decomposition of tritium forming part of the TH and T_2 molecules respectively, are extremely stable charged molecular species. The high stability of the protonated and tritonated helium species is not surprising, since their isoelectronic analogue, the $^4HeH^+$ ion, has been detected in mass spectrometers as early as the 1920s. The latter ion, which is the simplest two-electron heteronuclear particle, has been the subject of numerous theoretical calculations. Its dissociation energy, calculated by a number of workers [52-65] using different methods, is in the range between 1.46 and 2.04 eV. A value of the dissociation energy of the HHe^+ ion close to the calculated results has been obtained in the photoionisation studies of Chupka and Russell [66].

According to Cantwell's calculation [67], the major proportion of the primary molecular ions formed in the β-decomposition of tritium in the T_2 molecule are in the ground state, 11% are in the first excited level, and 4.5% are in the second excited level. Schwartz [68] estimated the fraction of primary molecular ions in the ground state as 93%. Taking these data into account as well as all that has been said previously about the excitation energy acquired by the primary molecular ions in consequence of the shaking effect and radioactive recoil, one may conclude that, in the vast majority of these ions, energy sufficient for the dissociation of the HeH bond cannot be located in the latter. For this reason, the main result of the β-decomposition of tritium in the TH and T_2 molecules is the formation of the non-excited molecular ions $^3HeH^3$ and $^3HeT^+$.

Table 1. The relative yields of ionic fragments in the β-decomposition of TH.

Ion	Yield, % according to Ref.69	Yield, % according to Ref.70	Ion	Yield, % according to Ref.69	Yield, % according to Ref.70
$^3HeH^+$	93±1.9	89.5±1.1	H^+	1.55±0.16	2.3±0.4
$^3He^+$	5.1±0.3	8.2±1.0	$^3He^{2+}$	0.14±0.01	—

The results of theoretical studies on the chemical consequences of the β-decomposition of tritiated compounds have been confirmed in numerous experimental investigations. Among these, one can isolate two groups of studies which differ fundamentally as regards the methods used to investigate the consequences of β-transformations. One of these groups comprises investigations where the charged fragments arising on β-decomposition of the tritium incorporated in various molecules were studied by the mass-spectrometric technique [69-78]. The other group comprises investigations devoted to the study of the same problem by radiochemical methods [42,79].

Without considering in detail the methodological problems of mass-spectrometric studies, we may note that in all cases instruments were used which made it possible to analyse the ions formed directly on β-decomposition of gaseous tritium-containing compounds. Table 1 presents the results of two independent mass-spectrometric determinations of the yields of ionic fragments arising on β-decomposition of the TH molecule [69,70].

Despite certain differences between the instruments used in these studies, the results are in good agreement. The principal characteristic feature of the latter is the high yield of the $^3HeH^+$ molecular ions.

Table 2. The relative yields of ionic fragments in the β-decomposition of T_2.

Ion	Yield, %
T^3He^+	94.5±0.6
$T^+ + {}^3He$	5.5±0.6

Wexler [70] established that the primary molecular ion $^3HeT^+$ formed on β-decomposition of the T_2 molecule is still more stable (Table 2).

The yields of fragment ions formed on β-decomposition of tritium in the CH_3T, [71] C_2H_5T, [72] n- and iso-C_3H_7T, [73] C_6H_5T, [74] $C_6H_5CH_2T$, and *o*-, *m*-, and *p*-$CH_3C_6H_4T$ [73] molecules have also been determined by the mass-spectrometric technique. As predicted by theoretical studies, the principal charged molecular species in the above instances proved to be the corresponding carbonium ions R^+. The yields of these species are compiled in Table 3.

The radiochemical method for the investigation of the chemical consequences of tritium decomposition processes in certain hydrocarbons has been used by Italian investigators [42,79]. It is important to note that these studies were carried out at the usual pressures, where the fragments arising as a result of the decomposition of the primary molecular ions were able to interact with the molecules of the initial substances and certain additives. A conclusion concerning the nature of the processes involving the primary molecular ions was reached on the basis of the nature and yields of the products of these reactions. For example, it was established [42] that the β-decomposition of one of the tritium atoms in the CT_4 molecule in a mixture containing 84% C_3H_8, 14% CT_4, and 2% O_2 is accompanied by a change in the isotope composition of methane. Together with the initial CT_4 molecules, those of CT_3H appeared, the radioactivity of the latter amounting to 74% of the total radioactivity of the primary CT_3He^+ molecular ions generated during the experiments. The formation of the triply labelled methane can be accounted for by the exothermic hydride ion transfer reaction between the labelled methyl cation and propane:

$$CT_3^+ + C_3H_8 \rightarrow CT_3H + C_3H_7^+ \quad . \qquad (1)$$

Since CT_3H is the main product of the reaction and its formation can be accounted for only in terms of reaction (1), the authors [42] concluded that the principal result of the

decomposition of tritium in methane is the formation of the methyl cations CT_3^+. It is noteworthy that in the case under consideration the initial mixture was at atmospheric pressure. The similarity of the results of the mass-spectrometric studies and the studies carried out by the Italian workers permits the conclusion that the yields of the charged fragments are independent of the pressure at which they are formed.

Table 3. The yields of carbonium ions in the β-decomposition of tritium forming part of hydrocarbons.

Initial cpd.	Carbonium ion	Yield, %	References	Initial cpd.	Carbonium ion	Yield, %	References
CH_3T	CH_3^+	83	71	$2\text{-}C_3H_7T$	$2\text{-}C_3H_7^+$	41	73
C_2H_5T	$C_2H_5^+$	80	72	C_6H_5T	$C_6H_5^+$	72	74
$1\text{-}C_3H_7T$	$1\text{-}C_3H_7^+$	56	73	C_7H_7T	$C_7H_7^+$	78	73

Thus it follows from the theoretical and experimental studies discussed above that the processes involving the β-decomposition of tritium in molecular systems lead to the formation of the corresponding molecular ions. These processes in fact constitute the basis of the radiochemical method for the investigation of ion-molecule reactions.

III. FOUNDATIONS OF THE EXPERIMENTAL TECHNIQUES IN THE RADIOCHEMICAL METHOD FOR THE INVESTIGATION OF ION-MOLECULE REACTIONS

In order to investigate the reactions of 1-propyl and 2-propyl cations, the ions must be generated from [1-T]propane in the former case:

$$CH_3CH_2CH_2T \xrightarrow{-\beta^-} CH_3CH_2CH_2^+ + He$$

and from [2-T]propane in the latter case:

$$CH_3CHTCH_3 \xrightarrow{-\beta^-} CH_3C^+HCH_3 + He \quad .$$

For ion-molecule reactions, such labelled compounds are then introduced into a medium containing the substances involved in the reaction of the propyl cations to be investigated and the resulting mixture is kept until the products of the ion-molecule interactions accumulate.

In order to identify the products formed on interaction of the small number of ions arising in the β-decomposition during a time interval suitable for the experiment and to determine their yields, it is necessary to employ polytritiated compounds[80], i.e. compounds containing at least two tritium atoms. In this case the β-decomposition of one of the radioactive atoms leads to the formation of a molecular ion and the presence of another tritium atom ("the label") in the ion makes it possible to investigate the products of the ion-molecule reactions. For example, in the case considered here one must employ [1-T_2]propane {or [1-T_3]propane} and [2-T_2]propane. The interaction of the labelled ion obtained as a result of the reactions

$$CH_3CH_2CT_3 \xrightarrow{-\beta^-} CH_3CH_2CT_2^+ + He \quad , \qquad (2)$$

$$CH_3CT_2CH_3 \xrightarrow{-\beta^-} CH_3C^+TCH_3 + He \qquad (3)$$

with the molecules of the surrounding medium leads to the formation of radioactive products. They are analysed by the usual methods employed for labelled compounds.

Thus the experimental method for the investigation of ion-molecule reactions initiated by the β-decomposition of tritiated compounds include three main stages:

1. the synthesis of a suitable polytritiated source of molecular ions;
2. the preparation of the reaction mixture and accumulation of the products of the ion-molecule reactions;
3. analysis of the reaction products.

1. Synthesis of the Initial Polytritiated Compound

The simplest and most readily available tritium-containing compound which may be used as the source of HeT^+ ions is molecular tritium, which is used by the isotope industry in large amounts and is very pure (up to 99%).

Other polytritiated compounds are not manufactured on an industrial scale and are synthesised under laboratory conditions. Such syntheses involve considerable experimental difficulties[81,82]. Several tens of syntheses of polylabelled compounds have now been described, most of the products being tritiated derivatives[83-89].

2. Preparation of the Reaction Mixture and Accumulation of the Products of the Ion-Molecule Reactions

By virtue of the characteristics of the nuclear-chemical processes mentioned above, the radiochemical method for the investigation of ion-molecule reactions permits the study of the interaction of molecular ions with both individual substances and with their mixtures in any state of aggregation. In the preparation of the reaction mixture, the choice of the optimum specific radioactivity is important. The use of a low specific activity of the mixture leads to an increase of the duration of the experiment. The accumulation of a sufficient amount of products for detection at a low specific activity requires a long exposure time. For example, the molecular ions CT_3^+ formed in one month as a result of the decomposition of tritium in CT_4 have an overall activity of only about 1% of the total activity of the source of these ions, i.e. CT_4.

On the other hand, the employment of a high specific activity involves the possibility of undesirable radiolytic processes, because, as a result of the β-decomposition, the reaction system is exposed not only to molecular ions but also to β-particles with an average energy of 5.6 keV. The latter can decompose a definite fraction of the initial tritiated compound, which leads to the formation of labelled products indistinguishable from the products of the ion-molecule reactions investigated. In order to prevent these secondary processes, it is necessary to prepare reaction mixtures with a fairly low level of specific activity. Calculations based on the G factors and estimates of the dose received by the system have shown, for example, that the rate of formation of tritiated radiolysis products in alkanes is negligibly small for a specific activity less than 0.5 mc $mmole^{-1}$.[42]

This conclusion was confirmed experimentally by the so called "blank" experiments involving the employment of singly labelled compounds with the same specific activity as the corresponding polylabelled compounds[42,79]. Since the decomposition of monotritiated molecules leads to the formation of ions without a radioactive label, the detection in such experiments of any tritiated products different from the initial compound indicates the occurrence of radiolytic processes. "Blank" experiments carried out for a number

of systems have shown that the radiation-induced decomposition of the specimens is not a significant source of tritiated products if the system has a specific activity less than 0.5 mc mmole^{-1}.

In order to suppress the radiolytic processes, suitable diluents are added to the specimens until the attainment of the required specific activity. Italian investigators[42,79] used for this purpose suitable carriers, while the experiments carried out at Leningrad University[140-146] involved the employment of noble gases (argon or xenon). In contrast to carriers, the inert gases suppress radiolytic processes but do not take part in the reactions with the molecular ions formed and do not therefore complicate the ion–molecule interactions investigated.

The mixture of the initial polytritiated compound and the substrate, diluted until the attainment of a specific activity of several tenths of mc mmole^{-1}, is sealed in tubes with a volume of several milli-metres and is maintained until the accumulation of the products of the ion–molecule reactions. The accumulation time, which depends on the specific activity of the mixture and the sensitivity of the analytical method, varies from several days to several months.

3. Analysis of the Products of the Ion–Molecule Reactions

The relatively low radioactivity of the molecular ions formed during the experiment and consequently the low radioactivity of the products of their interaction as well as the fact that the latter are always analysed in the presence of a large amount of the undecomposed polytritiated starting compound necessitates the employment of a sensitive and effective analytical technique. The most convenient methods for the qualitative and quantitative analysis of the labelled products of ion–molecule interactions are chromatographic procedures and particularly the gas radiochromatographic method‡.

Apart from the qualitative and quantitative analyses of the products, the determination of the intermolecular distribution of tritium in such products is extremely interesting. The available information about the intramolecular distribution of the label throws light on the mechanisms of the processes leading to the formation of such products. The study of the distribution of tritium within the molecule is usually based on the change of the specific activity of the compound when a hydrogen atom in a given position (or a whole group of atoms) is substituted by a suitable inactive group. Such analysis has been carried out, for example, in the study of the products of the interaction of HeT^+ ions with toluene[95,96].

It is noteworthy that, in order to investigate the processes involving the neutralisation of the molecular ions formed on β-decomposition of tritiated compounds, the method proposed by Lloyd and coworkers[97,98] is extremely promising. In this method, the products of the neutralisation of the molecular ions (radicals) are investigated by electron spin resonance.

‡ In order to become acquainted with the method of gas radiochromatography, the reader may be recommended to consult Refs. 90–94.

IV. ION–MOLECULE REACTIONS INITIATED BY THE β-DECOMPOSITION OF MOLECULAR TRITIUM

As already mentioned, the β-decomposition processes involving molecular tritium can be used to generate ionised molecules of tritiated helium (HeT^+) and to investigate a wide variety of reactions of these species.

The possibility of ion–molecule reactions with participation of HeT^+ ions was first reported by Wilzbach[99]. Subsequently this study constituted the basis of a new and extremely promising method for synthesising tritiated compounds, which has now been called the "Wilzbach method": a mixture of organic substances is prepared with an amount of gaseous tritium such that the radioactivity of the mixture is equal to several curies and the system is allowed to stand for several days. The nuclear-chemical processes developing in the system lead to the formation of a wide variety of labelled compounds.

The bulk of the studies employing this method involved its preparative aspect. However, there have been several investigations whose subject was the mechanisms of the formation of tritiated compounds. For example, Yang and Gant carried out a series of studies[100-103] designed to elucidate the role of various pathways to the formation of tritiated products from ethane, ethylene, cyclopropane, and propane containing gaseous tritium. The principal conclusion derived from these investigations is that labelled compounds are formed via two types of reaction: the reactions initiated by HeT^+ ions and the reactions initiated by β-particles.

In conformity with the point of view adopted at the present time[104], the formation of labelled compounds by the Wilzbach method involves mainly radiation processes. For this reason, studies on the introduction of a label into organic compounds by the Wilzbach method yield only limited information about the reaction of HeT^+ ions. On the other hand, the radiochemical method for the investigation of ion–molecule reactions examined here is free from this disadvantage.

1. The Reactions of HeT^+ Ions with Alkanes and Cycloalkanes

The reactions of the molecular ions HeT^+, formed on β-decomposition of molecular tritium, with methane, ethane, propane, butane, and isobutane as well as cycloalkanes ranging from C_3 to C_6 have been the subject of detailed studies by a group of workers at Rome University[105-107]. Tables 4 and 5 list the yields of the labelled products of the interaction of HeT^+ ions with alkanes and cycloalkanes respectively.

Table 4. The products of the interaction of HeT^+ ions with alkanes.

Alkane	Yields of products, %						Overall yield
	CH_3T	C_2H_5T	C_3H_7T	C_3H_7T	n-C_4H_9T	iso-C_4H_9T	
CH_4	40	2	13	—	—	—	55
C_2H_6	14	34	—	—	—	—	48
C_3H_8	12.8	5.1	—	12.3	—	—	30.2
n-C_4H_{10}	15.2	6.2	2.5	2.3	15.3	—	41.5
iso-C_4H_{10}	23.4	1.7	3.5	3.2	—	17.9	49.7

The following main conclusions can be drawn from the tabulated results: (a) the overall yield of the tritiated hydrocarbons is relatively low (from 25 to 55%); the

authors suggest that the remaining activity corresponds to HT §; (b) in all the systems investigated, the labelled initial hydrocarbon is formed in a high yield; (c) the reactions of HeT^+ ions with alkanes are not accompanied by isomerisation processes; (d) when HeT^+ ions react with cycloalkanes, high yields of the corresponding labelled cyclic hydrocarbons are formed, which indicates the retention of the cyclic structure of the intermediate species.

Table 5. The products of the interaction of HeT^+ ions with cycloalkanes.

Cycloalkane	Yields of products, %						
	HT	CH_3T	C_2H_5T	C_3H_7T	C_4H_9T	$C_5H_{11}T$	initial [T] cycloalkane
Cyclopropane	~35	23.0	3.7	12.1	2.2	6.7	19.2
Cyclobutane	~45	1.3	6.1	11.1	—	8.4	6.9
Cyclopentane	~65	—	2.6	4.1	4.6	3.4	11.1
Cyclohexane	75	—	1.2	1.6	2.7	3.0	9.7

In their discussion of the results of studies on the reactions of HeT^+ ions with alkanes, Cacace and coworkers[105,106] assumed that the first stage in these reactions is the protonation (or more precisely tritonation) of the initial hydrocarbons in accordance with the following general mechanism:

$$C_nH_{2n+2} + HeT^+ \rightarrow [C_nH_{2n+2}T]^+ + He \quad . \qquad (4)$$

Reaction (4) is analogous to the gas-phase protonation of the simplest hydrocarbons, for example methane by H_3^+, D_3^+, CHO^+, CH_5^+, and CH_4^+ ions[108-117], ethane by CH_5^+, H_3^+, D_3^+, and CHO^+ ions[108,111,115], and deuteriated propane by CH_5^+ ions[118], which is well known in mass spectrometry.

The $[CnH_{2n+2}T]^{+}$ carbonium ions formed as a result of reaction (4) are in an excited state and their excitation energy increases with increase of n. Some of these excited molecular ions are stabilised on collisions with the molecules of the surrounding medium:

$$[C_nH_{2n+2}T]^+_{exc} + S \rightarrow [C_nH_{2n+2}T]^+ + S_{exc} \qquad (5)$$

while some undergo monomolecular decomposition via various energetically allowed pathways, the most probable and general of which for all the systems investigated are the following fragmentation reactions:

$$[C_nH_{2n+2}T]^+_{exc} \nearrow [C_nH_{2n+1}]^+ + HT \qquad (6a)$$

$$\searrow [C_nH_{2n}T]^+ + H_2 \quad . \qquad (6b)$$

The stabilised tritonated hydrocarbons then undergo neutral thermal reactions with the inactive substrate molecules, involving proton transfer and reforming the initial labelled hydrocarbons¶:

$$[C_nH_{2n+2}T]^+ + C_nH_{2n+2} \rightarrow C_nH_{2n+1}T + [C_nH_{2n+3}]^+ \quad . \qquad (7)$$

Thus the consecutive processes (4), (5), and (7) explain the formation of the labelled initial compound—one of the principal products of the reactions of HeT^+ ions with alkanes, while the decrease of the stability of the $[CnH_{2n+2}T]^+$ carbonium ions with increase of the number of carbon atoms explains the decrease of the yield of the corresponding tritiated hydrocarbons on passing from methane to butane.

As already mentioned, one of the characteristics of the reactions of HeT^+ ions with alkanes is the comparatively low overall yield of tritiated hydrocarbons. Although Cacace and coworkers did not determine the yield of hydrogen tritide, one can be certain that the remaining fraction of radioactivity corresponds to this compound. This hypothesis is supported by the high yield of HT in the reactions of HeT^+ ions with cycloalkanes (Table 5).

According to the general mechanisms of the first stages of the ionic processes quoted above, the formation of labelled hydrogen can be accounted for by the fragmentation of a considerable proportion of the excited $[CnH_{2n+2}T]^+$ carbonium ions via reaction (6a). However, if it is supposed that all the hydrogen atoms in the excited tritiated hydrocarbon are equivalent, then, as a result of the statistical distribution of tritium atoms, the ratio of the activity of hydrogen (A_{HT}) and that of the corresponding carbonium cation ($A_{C_nH_{2n}T^+}$) is $2/(2n+1)$ and this in turn implies that the overall yield of the tritiated hydrocarbons, formed mainly in the successive interactions of the $[CnH_{2n}T]^+$ carbonium ions, should be much higher than the yield of HT. For example, in the interaction between HeT^+ and butane about 80% of the radioactivity should pass to the hydrocarbons. Similar considerations have served as a basis for the hypothesis that the HeT^+ molecular ions not only manifest powerful protonating properties but also the properties of Lewis acids, i.e. these species are capable of abstracting a hydride ion from hydrocarbons, forming HT as the single tritium-containing product:

$$C_nH_{2n+2} + HeT^+ \rightarrow C_nH^+_{2n+1} + HT + He \quad .$$

This hypothesis explains the low yield of labelled hydrocarbons.

The present authors believe that, while attributing to the HeT^+ ions the properties of Lewis acids in the reaction of these species with alkanes ranging from C_2 to C_4, Cacace and coworkers[105,106] unjustifiably failed to mention the possibility of reactions involving the abstraction of a hydride ion in the T_2–CH_4 system. Indeed, if HeT^+ reacted solely as a Brønsted acid via reactions (4)–(7), the yield of labelled hydrocarbons should be much higher than that obtained by the authors. According to Aquilanti and Volpi[111], about 50% of the methyl carbonium ions should be stabilised and should then give rise to tritiated methane via reaction (7). The remaining 50% of ions decompose via reaction (6), forming 20% HT and 30% CH_3T in accordance with the formula quoted above. Thus the overall radioactivity of the hydrocarbons should be 80%, which is much higher than the experimental value.

The formation of the remaining products of the interaction of HeT^+ ions with alkanes can be explained by the subsequent reactions of the $[CnH_{2n}T]^+$ carbonium ions formed via reaction (6b) with substrate molecules and also via other pathways involving the fragmentation of the excited $[CnH_{2n+2}T]^+$ carbonium ions. For example, it has been suggested[106] that CH_3T, found in high yields in all the systems investigated, is formed as a result of the following monomolecular decomposition of tritonated hydrocarbons:

$$[C_nH_{2n+2}T]^+_{exc} \rightarrow [C_{n-1}H_{2n-1}]^+ + CH_3T \quad . \qquad (8)$$

§ Unfortunately the authors of the studies quoted here did not carry out an analysis for hydrogen tritide in the reactions between HeT^+ ions and alkanes.

¶ Similar reactions are well known in mass spectrometry[111].

The results of studies on the reactions of HeT^+ ions with cycloalkanes can be explained similarly (Table 5). It is interesting to note that, with increase of the molecular weight of the initial cyclic hydrocarbons, the yield of HT rises from 35% for cyclopropane to 75% for cyclohexane. The authors explain this behaviour by the fact that, when there is competition between triton transfer

$$\text{cyclo-}C_nH_{2n} + HeT^+ \rightarrow [C_nH_{2n}T]^+_{exc} + He \qquad (9)$$

and the abstraction of a hydride ion

$$\text{cyclo-}C_nH_{2n} + HeT^+ \rightarrow [\text{cyclo-}C_nH_{2n-1}]^+ + HT + He \qquad (10)$$

reaction (10) becomes dominant on passing from cyclopropane to cyclohexane.

The detection of labelled cyclic hydrocarbons among the products of the ion–molecule interactions shows that the carbonium ions formed by reaction (9) also have a cyclic structure. These results constitute direct proof of the formation of gas-phase cycloalkyl carbonium ions, the existence of which has been postulated for a long time but has not been demonstrated experimentally†.

2. The Reactions of HeT^+ Ions with Aromatic Hydrocarbons

The gas-phase ion–molecule reaction initiated by the β-decomposition of T_2 in aromatic hydrocarbons (toluene, anisole, fluoro-, chloro-, and bromo-benzenes, and $\alpha\alpha\alpha$-trifluorotoluene) have been reported[121–124]. We shall begin the discussion of these results from three standpoints: the mechanisms of the formation of the products, the intramolecular distribution of tritium in the products, and the relative reactivities of the aromatic compounds.

Table 6. The products of the interaction of HeT^+ ions with aromatic compounds.

Aromatic cpd.	Yields of products, %		
	initial [T] cpd.	[T] benzene	other products
$C_6H_5CH_3$	60±8	3.8±0.5	[T] methane (about 8%)
$C_6D_5CD_3$	60±8	3.6±0.5	[T] methane (about 6%)
$C_6H_5C_4H_9$	65±10	25±4	[T] toluene (0.9 ± 0.1%), [T] ethylbenzene, and [T] xylenes (3.6 ± 0.4%)
$C_6H_5OCH_3$	49±10	2.0±0.2	—
C_6H_5F	67±10	<0.2	—
C_6H_5Cl	76±10	3.7±0.8	—
C_6H_5Br	69±10	8±1	—
$C_6H_5CF_3$	81±10	2.9±0.3	—

Table 6 presents the yields of the identified products of the reactions considered. Evidently the main products in all the systems investigated are the labelled initial compounds and benzene, the overall yield of the tritium-containing hydrocarbons being much higher than in reactions of HeT^+ ions with alkanes and cycloalkanes. These data led to the hypothesis that the higher stability of the protonated arenes, formed via the extremely exothermic (−100 kcal mole^{-1}) reaction

$$ArX + HeT^+ \rightarrow [ArXT]^+_{exc} + He \qquad (11)$$

enables a considerable proportion of these ions to become stabilised on collision with the molecules of the aromatic hydrocarbon ArX (X = CH_3, C_4H_9, OCH_3, F, Cl, Br, or CF_3). The stabilised tritiated ion then transfers a proton to the substrate molecule in accordance with the neutral thermal reaction

$$[ArXT]^+ + ArX \rightarrow \overline{ArX} + [ArXH]^+ \quad , \qquad (12)$$

where $\overline{ArX}$ denotes a labelled compound.

Thus reactions (11) and (12) lead to the formation of the main products of the reactions investigated—the tritiated initial aromatic hydrocarbons.

Some of the excited tritonated molecules which have not been stabilised undergo monomolecular fragmentation:

$$[ArXT]^+_{exc} \rightarrow ArT + X^+ \quad .$$

As already mentioned, the overall radioactivity of the products identified was lower than the radioactivity of the HeT^+ ions generated during the experiment. Cacace and coworkers do not explain this radioactivity deficit in most instances[121,122] and sometimes[123] assume that part of the radioactivity is lost on the walls of the reaction vessel or is contained in products, undetected under the given conditions of analysis, which are formed in the reaction between HeT^+ and nucleophilic impurities present in the reaction mixture in trace amounts. We believe that a more logical and more consistent hypothesis, in the light of previous investigations, would be that, as in the reactions with alkanes and cycloalkanes, in the reactions considered here HeT^+ ions possess not only protonating properties but also the properties of Lewis acids, i.e. they react with aromatic compounds as follows:

$$C_6H_5X + HeT^+ \rightarrow C_6H_4X^+ + HT + He$$

forming HT, whose yield was not unfortunately determined.

Furthermore, there is no doubt that in the reactions with aromatic compounds having substituents with lone electron pairs ($C_6H_5OCH_3$, C_6H_5Cl, C_6H_5Br, C_6H_5F), some of the HeT^+ ions interact with the electron pairs, forming the corresponding oxonium and halogenonium ions. The monomolecular fragmentation of subsequent bimolecular reactions of these ions lead to the formation of labelled alcohols or hydrogen halides. For example, the reactions

$$C_6H_5OCH_3 + HeT^+ \rightarrow [C_6H_5\overset{+}{\underset{T}{O}}CH_3]_{exc} + He \quad ,$$

$$\left[C_6H_5\overset{+}{\underset{T}{O}}CH_3\right]_{exc} \rightarrow \begin{cases} C_6H_5OT + CH_3^+ \\ CH_3OT + C_6H_5^+ \end{cases} ,$$

which compete with those determined previously, can account for the relatively low yield (51%) of labelled products found by Cacace et al.[123] It is regrettable that the authors did not attempt to detect among the reaction products labelled compounds formed as a result of the electrophilic attack by HeT^+ ions on the heteroatoms of the substituents.

Extremely important information about the ion–molecule processes developing in the system and about the nature of the intermediate protonated arenes may be obtained by studying the intramolecular distribution of tritium in the final reaction products. Here one can assume that the distribution of the label in the final products reflects the selectivity of the initial interactions of the HeT^+ ions with various positions of the reacting molecule.

†There have been numerous reports of the formation of such ions in solution[119,120].

The intramolecular distribution of tritium in the products of the reaction of HeT^+ ions with toluene, anisole, $\alpha\alpha\alpha$-trifluorotoluene, and halogenobenzenes has been investigated[121-124]. The results of these studies, illustrated in Fig. 1, lead to the following general conclusion. In their gas-phase interaction with the π electrons of the aromatic ring, HeT^+ ions exhibit an appreciable selectivity, although the latter is not high. The fact that the selectivity of the protonation reaction is low is satisfactorily consistent with the general rule familiar for electrophilic substitution in solutions, according to which an increase of the reactivity of the electrophilic species entails a decrease of the positional selectivity[125]. Among the known Brønsted acids, the gaseous non-solvated HeT^+ ion is one of the most reactive species. It is therefore not surprising that it exhibits a low selectivity in the reactions investigated.

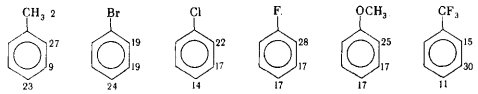


Figure 1. The intramolecular distribution of tritium in the products of the interaction of HeT^+ ions with aromatic hydrocarbons. The numerals denote the relative proportions of radioactivity (%) belonging to each position.

Table 7 presents data obtained in a study of the selectivity of aromatic compounds in reactions of HeT^+ ions (competing reactions). These data show that the reactivity of all the substances investigated, with the exception of $\alpha\alpha\alpha$-trifluorotoluene, in relation to HeT^+ ions is higher than the reactivity of benzene. One should note that the reactivity of aromatic compounds in reactions with HeT^+ ions is low. These results can also be explained by the high electrophilic reactivity of tritonated helium.

Table 7. The relative reactivities of aromatic compounds in the reaction with HeT^+ ions.

Aromatic cpd.	Reactivity in relation to benzene
$\alpha\alpha\alpha$-Trifluoro-toluene	0.8
Benzene	1.0
Fluorobenzene	1.2
Toluene	1.5
Chlorobenzene	1.6
Bromobenzene	2.0
Benzonitrile	2.2
Anisole	3.0

The results of studies on the reactions of the close analogue of tritonated helium, namely the D_2T^+ ion, with gaseous aromatic hydrocarbons (at a pressure of 750 mmHg and room temperature) are in good agreement with the results of the studies discussed above[126,127].

In conclusion of this section, we may note that the β-decomposition of molecular tritium in systems containing noble gases (Y) makes it possible to investigate the reactions of the tritiated ions YT^+ of the noble gases[128]. The radiochemical method for the generation of the tritiated ions of noble gases is based on the exothermic reaction

$$HeT^+ + Y \rightarrow He + YT^+ .$$

The only study on these lines was devoted to the investigation of the reactions of NeT^+ and XeT^+ ions with methane[128]. It was established that these reactions are analogous to those of HeT^+ ions with methane discussed previously.

The further employment of the radiochemical method for the study of the reactions of protonated noble gases will undoubtedly supplement the available information obtained in mass-spectrometric[129-134], radiation[135], and theoretical[65] studies on these interesting, reactive species.

V. ION-MOLECULE REACTIONS INITIATED BY THE β-DECOMPOSITION OF TRITIATED HYDROCARBONS

1. Reactions of Carbonium Ions with Alkanes and Cycloalkanes

Most of the studies on the reactions of carbonium ions generated in the β-decomposition of tritiated hydrocarbons are concerned with the bimolecular interaction of these species with non-radioactive sources of the corresponding ions. For example, studies have been made on the reactions of methyl cations with methane[42], of ethyl cations with methane[45,79], of propyl cations with propane[86], and of cyclopentyl cations with cyclopentane[87]. The results of these investigations are presented in Tables 8-11.

Table 8. The products of the interaction of methyl cations CT_3^+ with methane.

Product	Yield, %
CHT_3	<5.0
HT	28.7
Ethylene	10.9
Ethane	1.0
Propane	0.8
Propene	<0.02
n-Butane	0.3

Table 9. The products of the interaction of ethyl cations $C_2H_4T^+$ with ethane.

Product	Yield, %
Hydrogen	11.6±0.10
Methane	3.0±0.10
Ethylene	5.5±0.03
Propane	1.6±0.50
Butane	2.7±0.20
Propene	—

It is noteworthy that the experimental technique used in these investigations did not enable the authors to determine the yields of the products of the very important reaction involving the abstraction of an H^- ion from the reacting

molecules by carbonium ions (with the exception of the methyl cation). Such hydride ion transfer reactions result in the formation of the molecules of the initial hydrocarbons but with one tritium atom less. For example, processes of this kind developing in the $C_2H_4T_2$–C_2H_6 system,

$$C_2H_4T_2 \xrightarrow{-\beta^-} C_2H_4T^+ + He \quad , \qquad (13)$$

$$C_2H_4T^+ + C_2H_6 \rightarrow C_2H_5T + C_2H_5^+ \, , \qquad (14)$$

lead to the formation of monotritiated ethane, the yield of which cannot be determined against the background of the large amount of the initial doubly tritiated ethane‡. However, despite the fact that direct experimental proof of the occurrence of processes analogous to reactions (13) and (14) has not been obtained for the ethyl, propyl and cyclopentyl cations, the low yield of the identified products (ranging from 23 to 7%) suggests that such processes play a significant role.

Table 10. The products of the interaction of propyl cations $C_3H_6T^+$ with propane.

Product	Yield, %
Hydrogen	9.3
Methane	7.9
Ethane	1.9
Ethylene	4.9
Acetylene	0.7
Propane	6.0
Methylacetylene + allene	~4.9

Table 11. The products of the interaction of cyclopentyl cations $C_5H_8T^+$ with cyclopentane.

Products	Yield, %
Methane	1.6
Ethane	0.4
Propane	0.5
Butane	0.7
Pentene	3.5

Making this assumption and taking into account the decrease of the yield of the detected tritiated products with increase of the molecular weight of the ion, one may conclude that the transfer of a hydride ion from the hydrocarbon molecule to the carbonium ion is more characteristic of heavy ions. There have been numerous mass-spectrometric studies in which it has been shown that the hydride ion transfer reaction is characteristic of all the lower alkanes[113,115,116,138].

Another characteristic reaction of carbonium ions is known to be the condensation reaction[139]

$$[C_nH_{2n+1}]^+ + C_nH_{2n+2} \rightarrow [C_{2n}H_{4n+1}]^+ + H_2 \quad .$$

Such reactions lead to the formation of new carbonium ions. Their subsequent involvement in the hydride ion transfer reaction is responsible for the formation of heavier hydrocarbons. Thus condensation of the methyl cation and methane leads to the formation of a labelled ethyl cation. The latter does not react with methane, but, in the presence of even a small amount of propane, it is rapidly involved in the hydride ion abstraction reaction, forming labelled ethane (Table 8). It is also possible that similar processes take place in the $C_2H_4T_2$–C_2H_6 system. In this case the condensation reactions give rise to labelled butane.

Having examined the two main types of reactions of carbonium ions generated by the β-decomposition of tritiated hydrocarbons (with alkanes and cycloalkanes), we shall not discuss in detail the mechanism of the processes involving the formation of all the remaining products detected and we shall only note that the secondary ions produced by the fragmentation of the excited primary molecular ions are involved in such processes. A more detailed discussion of this problem can be found in the original papers quoted previously.

Table 12. The products of the interaction of methyl cations CT_3^+ with benzene and toluene.

Aromatic hydrocarbon	Yields of products, %				
	benzene	toluene	*p*-xylene	*m*-xylene	*o*-xylene
Benzene	52±3	48±3	—	—	—
Toluene	7±1	24±2	14±2	39±2	17±2

Table 13. The products of the interaction of methyl cations CT_3^+ with isomeric xylenes.

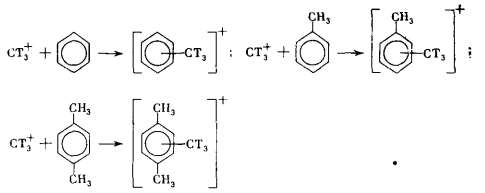
Substrate	Yields of products, %					
	p-xylene	*m*-xylene	*o*-xylene	mesitylene	pseudocumene	hemimellitene
p-Xylene	31±2	—	—	13±1	49±1	7±1
m-Xylene	—	42±2	—	20±1	26±2	12±2
o-Xylene	—	—	49±3	16±1	24±3	11±1

2. The Reactions of Carbonium Ions with Aromatic Compounds

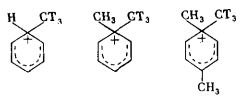
The radiochemical method for the investigation of ion–molecule reactions has been used to investigate the gas-phase interactions of free methyl cations with benzene, toluene, and *m*-, *o*-, and *p*-xylenes[140] and also of the liquid-phase reactions of phenyl cations with benzene[89]. Tables 12 and 13, which list the relative yields of the labelled products of the interaction of methyl cations with benzene, toluene, and the isomeric xylenes, show that tritiated aromatic hydrocarbons having the same structures as the initial compounds as well as the products of the methylation of the latter are mainly formed.

‡ A gas-chromatographic method of isotope analysis is available only for methane[136,137].

When methyl cations interact with aromatic hydrocarbons, the free p-orbital of the carbonium atom overlaps with the π orbitals of the aromatic ring, which results in the formation of the corresponding π complexes:

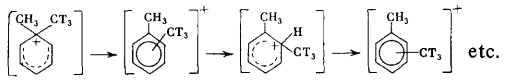


Such π complexes are known to be capable of isomerising to σ structures of the type



The further reactions of these σ complexes can proceed via two mechanisms. The first involves unimolecular decomposition with reformation of the molecules of the initial compounds§. The formation of labelled substrates by this mechanism is demonstrated by the discovery of labelled xylenes having the same structure as the initial compounds among the products of the interaction of methyl cations with xylenes.

The second mechanism of the reaction of the intermediate σ complexes involves their deprotonation. The deprotonation processes lead to the formation of labelled products of the methylation of the initial aromatic compounds. It is interesting to note that, as a result of such processes, labelled m-xylene is formed in the CT_4–toluene system in a yield exceeding those of o- and p-xylenes. These results are inconsistent with the familiar directing rule for electrophilic substitution reactions in solution. This discrepancy can probably be accounted for by a rearrangement in the corresponding phenonium ions¶:

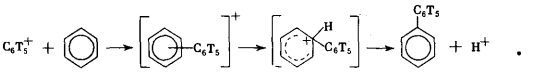


The monomolecular deprotonation reactions of the intermediate phenonium ions are endothermic ($\Delta Q \simeq 100$ kcal mole^{-1}) and therefore occur only on collisions between ions and molecules capable of combining with a proton (in the present case toluene molecules are species of this kind). The interval between the collisions of the species in the reaction system is about 10^{-9} s. The time of the rearrangements is probably close to the period of the atomic vibrations (10^{-13} s). Thus rearrangements associated with the migration of methyl groups can occur several times before the phenonium ion loses a proton in a bimolecular collision with the surrounding molecules. The rearrangements of phenonium ions are proved convincingly by the results of experiments designed to investigate the interaction of methyl cations with xylene isomers. Regardless of the isomers used as the starting material, all three possible trimethylbenzene isomers were formed.

§The high yield of tritiated benzene in the CT_4–C_6H_6 system is probably associated with the isotope exchange between the tritium and protium atoms in the intermediate phenonium ions.

¶Such processes occur, for example, in the isomerisation of xylenes in the presence of acid catalysts[141].

The study of the reactions of phenyl cations, generated in the β-decomposition of tritium in fully tritiated benzene, with non-radioactive benzene molecules showed that the only product of such reactions is labelled biphenyl[89]. Its formation can be accounted for by the same processes as in the formation of the methylation products in the reactions of methyl cations with aromatic compounds. These processes can be represented schematically as follows:



Together with labelled biphenyl, [T_5] benzene can also be formed. This product may be obtained via the reaction involving the abstraction of hydride ions, which is well known for carbonium ions:

$$C_6T_5^+ + C_6H_6 \rightarrow C_6T_5H + C_6H_5^+ \quad .$$

Unfortunately the method used in the above investigation[89] to analyse the products did not allow the isotope analysis of the tritiated benzene molecules.

3. The Reactions of Carbonium Ions with Compounds Containing Atoms having Lone Electron Pairs

In order to investigate this group of ion–molecule reactions, the starting materials used were inorganic and organic oxygen (water, alcohols, and ethers)[44,142-144], halogen (hydrogen and ethyl halides)[145], and nitrogen (amines)[146] compounds.

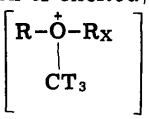
(a) Reactions of carbonium ions with oxygen compounds. Tables 14 and 15 present the results of the analysis of the products of the interaction of methyl cations with water, alcohols, and ethers. Evidently the main product of the interaction of methyl cations with water and alcohols is tritiated methanol and the products of the interaction of methyl cations with ethers are the corresponding labelled methyl-containing ethers.

Table 14. The products of the interaction of methyl cations CT_3^+ with water and alcohols.

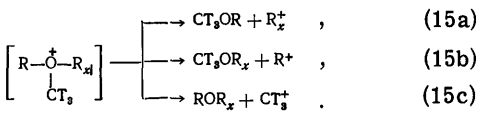
Starting material	Yields, %					
	H_2O	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH	$C_5H_{11}OH$
H_2O	11±1	89±1	—	—	—	—
CH_3OH	4±1	86±2	10±1	—	—	—
C_2H_5OH	2±1	80±2	—	18±1	—	—
n-C_3H_7OH	—	85±2	—	—	15±1	—
iso-C_3H_7OH	—	100	—	—	—	—
n-C_4H_9OH	—	94±1	—	—	—	6±1
s-C_4H_9OH	—	100	—	—	—	—
iso-C_4H_9OH	—	100	—	—	—	—

To facilitate the consideration of these results, the initial oxygen-containing substances will be designated by ROR_X (where R and R_X = H or organic group). By virtue of the electrophilic nature of carbonium ions, the most characteristic processes in the interaction of methyl cations with compounds of the type considered involve the addition of these species to atoms with lone electron pairs

(in the present instance oxygen atoms). Such addition results in the formation of excited† oxonium ions:



Such ionium ions are known to exist in both gas and liquid phases[111,113,147]. Since the collision frequency of the species at atmospheric pressure is lower by 2–3 orders of magnitude than the bond vibration frequency, sufficient time elapses before the collision of the oxonium ion formed with any other species for the redistribution of the excitation energy throughout the ion. If part of the energy localised at the O–organic group bond exceeds the activation energy for the decomposition of the oxonium ion at this bond, the latter is ruptured under these conditions. The possible modes of fragmentation of the oxonium ion are represented below:



$$\left[R-\overset{+}{O}(CT_3)-R_X\right] \longrightarrow CT_3OR + R_X^+ \quad (15a)$$

$$\left[R-\overset{+}{O}(CT_3)-R_X\right] \longrightarrow CT_3OR_X + R^+ \quad (15b)$$

$$\left[R-\overset{+}{O}(CT_3)-R_X\right] \longrightarrow ROR_X + CT_3^+ \quad (15c)$$

Table 15. The products of the interaction of methyl cations CT_3^+ with ethers.

Initial ether ROR_X	Products	Q*, %	$Q_{ROCT_3}/Q_{ROCT_3}+Q_{R_XOCT_3}$	I_{R_X}**, eV
CH_3OCH_3	CT_3OCH_3	100	0.50	9.86
$CH_3OC_2H_5$	CT_3OCH_3	74±4	0.74	8.8
	$CT_3OC_2H_5$	26±3	—	—
$CH_3OC_3H_7$	CT_3OCH_3	90±3	0.90	8.69
	$CT_3OC_3H_7$	10±3	—	—
$CH_3OC_3H_7$-iso	CT_3OCH_3	91±2	0.91	7.9
	$CT_3OC_3H_7$-iso	9±2	—	—
$CH_3OC_4H_9$	CT_3OCH_3	90±4	0.90	8.64
	$CT_3OC_4H_9$	10±4	—	—
$CH_3OC_4H_9$-t	CT_3OCH_3	91±5	0.91	7.42
	$CT_3OC_4H_9$-t	9±4	—	—
$CH_3O(CH_2)OH$	CT_3OCH_3	19±1	0.50	7.0
	$CT_3O(CH_2)OH$	1	—	—
	CT_3OH	79±1	—	—
$CH_3OC_6H_5$	CT_3OCH_3	44±2	0.55	9.4
	$CT_3OC_6H_5$	36±1	—	—
	$CT_3C_6H_5$	1	—	—
	$CT_3C_6H_4OCH_3$	20±4	—	—
$CH_3OCH_2C_6H_5$	CT_3OCH_3	51±4	0.88	7.73
	$CT_3OCH_2C_6H_5$	7±1	—	—
	$CT_3C_6H_5$	26±5	—	—
	$CT_3C_6H_4CH_2OCH_3$	15	—	—
$C_2H_5OCH_3$	$CT_3OC_2H_5$	26±3	0.26	9.86
	CT_3OCH_3	74±4	—	—
$C_2H_5OC_2H_5$	$CT_3OC_2H_5$	100	0.50	8.8
$C_2H_5OC_3H_7$	$CT_3OC_2H_5$	72±2	0.72	8.69
	$CT_3OC_3H_7$	28±2	—	—
$C_2H_5OCH_2C_6H_5$	$CT_3OC_2H_5$	61±3	0.95	7.73
	$CT_3OCH_2C_6H_5$	3±1	—	—
	$CT_3C_6H_5$	22±4	—	—
	$CT_3C_6H_4CH_2OC_2H_5$	14±4	—	—
$C_3H_7OC_3H_7$	$CT_3OC_3H_7$	100	0.5	9.4
$C_3H_7OC_4H_9$	$CT_3OC_3H_7$	54±3	0.54	8.64
	$CT_3OC_4H_9$	46±3	—	—

* Q is the yield of reaction products.
** I is the ionisation potential.

†The excitation energy of the transition complex is determined by the excitation energy of the carbonium ion and its affinity for the ether molecule. The latter exceeds 100 kcal mole^{-1} for the majority of the reactions investigated[148].

One of the most important factors on which the probability of the decomposition of the ion via a particular channel depends is the stability of the products formed and in the first place the stability of the charged fragments[149]. It follows from Eqn. (15) that such charged fragments are the carbonium ions CT_3^+, R^+, and R_X^+. The ionisation potentials of the corresponding radicals can serve as a measure of the stability of the carbonium ions[150]. The ions which may be regarded as products of the ionisation of the radical with the lowest ionisation potential are the most stable.

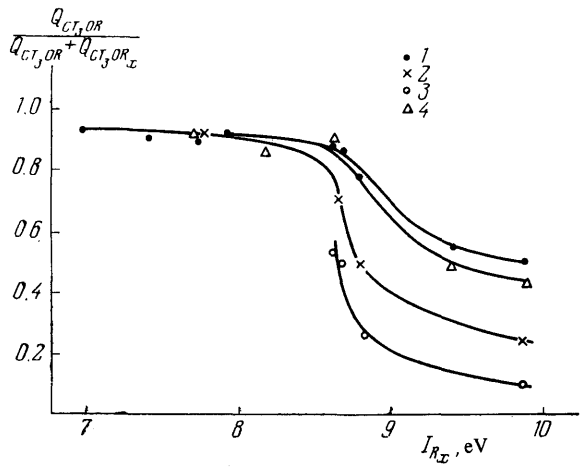


Figure 2. Dependence of the relative yields of the products of the interaction of methyl cations with the ethers ROR_X on the ionisation potentials of R_X: 1) CH_3OR_X; 2) $C_2H_5OR_X$; 3) $C_3H_7OR_X$; 4) $C_6H_5OR_X$.

Within the limits of each of the series of ethers ROR_X investigated, reactions (15b) and (15c) lead to the formation of the same charged fragments (CT_3^+ and R^+). Different R_X^+ ions are formed only in reaction (15a) for different initial ethers. It might have been expected that the stability of these ions will largely determine the mode of fragmentation of the intermediate oxonium ion. Indeed, it is seen from Table 15 that, when methyl cations interact with the ethers ROR_X, the relative yields of the ethers CT_3OR vary in parallel with the ionisation potentials of the groups R_X. Fig. 2 presents a graphical representation of the variation of these quantities for the reaction of methyl cations with ethers. Evidently the yields of the ethers $ROCT_3$ vary in accordance with a nearly exponential law up to a certain value of I_{R_X} (above 8.6 eV) and then remain virtually constant as the ionisation potentials are varied further. In order to account for the absence of a dependence of the yield of products on the ionisation potentials of the radicals when $I < 8.6$ eV, one can make the following assumption. The β-decomposition of tritium in CT_4 may lead to the formation of a certain amount of methyl cations. These cations react with the ethers and give rise to highly excited oxonium ions whose fragmentation proceeds via different pathways having equal probabilities.

The absence of labelled ethers among the products of the interaction of methyl cations with alcohols shows that the monomolecular abstraction of the thermodynamically relatively unstable H^+ ion from the intermediate hydrodialkyloxonium ion $CT_3-\overset{H}{\overset{|}{\overset{+}{O}}}-R_X$ is an unlikely process compared with the abstraction of the much more stable R_X^+ ion. In the reactions of methyl cations with aromatic ethers, account must be taken of the possibility of the alkylation of the aromatic ring. These processes will be discussed in greater detail below.

(b) The reactions of carbonium ions with halogen compounds. The results of a study [145] of the ion–molecule reactions of methyl cations with halogen halides (HCl, HBr, and HI) and ethyl halides (C_2H_5Cl, C_2H_5Br, and C_2H_5I) are presented in Table 16.

Table 16. The products of the interaction of methyl cations CT_3^+ with hydrogen halides and ethyl halides.

Initial cpd.	Yields, %			
	CH_3X	C_2H_5X	*изо*-C_3H_7X	*н*-C_3H_7X
HCl	100	—	—	—
HBr	100	—	—	—
HI	100	—	—	—
C_2H_5Cl	15±1	49±2	25±2	11±3
C_2H_5Br	37±1	43±2	20±3	—
C_2H_5I	100	—	—	—

It is seen from the data in Table 16 that the reactions of methyl cations with hydrogen halides lead to the formation of the corresponding labelled methyl halides, while the reactions of these species with ethyl halides give rise to methyl, ethyl, and propyl halides.

There is no doubt that the first stage in these reactions is the interaction of the free *p* orbital of the carbonium ion with the lone electron pairs of the halogen atoms. The interaction results in the formation of the corresponding halogenonium ions $[CT_3XR]^+$. The monomolecular decomposition of the complex $[CT_3XR]^+$ can proceed via two pathways. The first pathway involves the reaction which is the reverse of the process investigated. On the other hand, the transformation of the complex via the second pathway

$$[CT_3XR]^+ \overset{1}{\underset{2}{\rightleftarrows}} \begin{matrix} RX + CT_3^+ \\ CT_3X + R^+ \end{matrix}$$

leads to the formation of the corresponding labelled methyl halide. This mechanism of the formation of tritium-containing methyl halide may be adopted only for the reactions of methyl cations with ethyl halides. On the other hand, the heat of reaction of CT_3^+ with hydrogen halides,

$$CT_3^+ + HX \rightarrow CT_3X + H^+$$

is approximately 100 kcal $mole^{-1}$, which implies that the transformation of the 'onium ion proceeds monomolecularly. In order to account for the mechanism of the formation of labelled methyl halides, one could resort to processes involving bimolecular fragmentation of the intermediate ions:

$$CT_3\overset{+}{X}H + HX \rightarrow CT_3X + H\overset{+}{X}H \quad .$$

However, comparison of the proton affinities of hydrogen halides and the corresponding methyl halides showed that this reaction is also energetically unfavourable. Indeed, the proton affinities of HCl, HBr, and HI are 140, 141, and 145 kcal $mole^{-1}$, [151] while the affinities of CH_3Cl, CH_3Br, and CH_3I are 160, 163, and 170 kcal $mole^{-1}$ respectively [152]. The mechanism of the formation of methyl halides in the gas-phase interaction of methyl cations with hydrogen halides therefore still remains obscure.

(c) Reactions of carbonium ions with nitrogen compounds. Only one study has been published so far [146] in which gas-phase reactions of free carbonium ions with the given class of compounds were investigated. These are the reactions of methyl cations with diethylamine (Table 17).

Table 17. The products of the interaction of methyl cations CT_3^+ with diethylamine.

Product	Yield, %	Product	Yield, %
Diethylamine	26±1	Ethylpropylamine	10±1
Diethylmethylamine	55±1	Ethylisopropylamine	9±1

The main products of the reaction of methyl cations with diethylamine are labelled diethylamine, diethylmethylamine, ethylpropylamine, and isopropylamine. The formation of these products cannot be accounted for in terms of the mechanisms which we invoked in the discussion of the reactions of carbonium ions with other classes of compounds. This can probably be explained by the fact that, in contrast to the other substances investigated, the amines are characterised by the highest proton affinities (> 215 kcal $mole^{-1}$). [153] By virtue of this feature and also by virtue of the relatively low proton affinity of the methylene group (120 kcal $mole^{-1}$), [153] the most characteristic reaction in this case is apparently the exothermic proton transfer from the methyl cation to the amine molecule and not the formation of the intermediate ammonium ion:

$$CT_3^+ + (C_2H_5)_2NH \rightarrow CT_3 + [(C_2H_5)_2NTH]^+ \quad .$$

The subsequent reactions of the tritium-containing methylene group and the diethylammonium ion make it possible to explain the formation of all the products detected. Thus the isotope exchange reaction

$$(C_2H_5)_2NTH^+ + (C_2H_5)_2NH \text{—} (C_2H_5)_2NT + (C_2H_5)_2\overset{+}{N}H_2$$

leads to the formation of the labelled initial diethylamine, while the reactions involving the insertion of methylene groups in various bonds of the amine molecule‡ give rise to the other products detected.

4. Reactions of Carbonium Ions with Compounds whose Molecules Contain Several Nucleophilic Centres

In the study of ion–molecule reactions of this type, methyl cations were used as the molecular ions and the starting materials consisted of a number of organic compounds whose molecules contained an aromatic ring and

‡ Similar reactions are well known in the chemistry of carbenes [154,155].

atoms with lone electron pairs. Such substances include bromobenzene[156], nitrobenzene[157], and alkyl phenyl and alkyl benzyl ethers[144].

The results obtained in the above studies show that the interaction of methyl cations with compounds of the given group leads to the formation of two types of products. One type comprises products resulting from the alkylation of the aromatic ring and the other comprises compounds whose formation involves attack by methyl cations on the lone electron pair. Thus, in the ion–molecule reactions considered here, there is competition between the interactions of methyl cations with the π electrons of the aromatic ring and with the free electron pairs of the substituent atoms.

Table 18 lists the intramolecular competition factors $f$comp, which are defined as the ratios of the yields of the products of the interaction of methyl cations with the lone electron pairs (Q_p) to the yields of the products of the interaction with the π electrons of the aromatic ring (Q_π). It follows from Table 18 that, in the interactions of free methyl cations with the compounds investigated, the lone electron pairs of the substituent atoms are more reactive than the π electrons of the aromatic ring. The reactivities of the free electron pairs of bromine atoms, the nitro-group, and ether oxygen in alkyl benzyl ethers are similar, but much lower than the reactivities of the lone electron pairs of the oxygen atoms in alkyl phenyl ethers.

Table 18. The relative yields of the products of competing reactions and competition factors.

Starting material	Q_p, %	Q_π, %	f_{comp}
C_6H_5Br	65	35	1.86
$C_6H_5NO_2$	65	35	1.86
$CH_3OCH_2C_6H_5$	58	42	1.38
$C_2H_5OCH_2C_6H_5$	64	36	1.78
$CH_3OC_6H_5$	80	20	4.00
$C_4H_9OC_6H_5$	82	18	4.55
iso-$C_5H_{11}OC_6H_5$	88	12	7.34

Presumably the observed changes in the competition factor are associated with the changes in the ratio of the basicities of the nucleophilic centres in these compounds. However, one should note that studies on the relative basicities of the nucleophilic centres in a single molecule have not been made. We believe that extremely valuable information in this field of theoretical chemistry can be obtained with the aid of the radiochemical method considered here for the investigation of ion–molecule reactions.

5. Competitive Reactions of Carbonium Ions

The possibility of using the radiochemical method for the study of competitive intermolecular reactions may be demonstrated by the results of a recent study of the gas-phase reactions of methyl cations with ethylene–water mixtures for different molar ratios of the components, namely $[C_2H_4]:[H_2O] = 1:1$, 2:1, 3:1, 4:1, and 5:1.[158] It was established that the main products of these reactions are aliphatic alcohols.

The carbonium ions generated in unsaturated hydrocarbons are known[159] to initiate cationic polymerisation reactions. When methyl cations are generated in ethylene, these reactions can be represented by the equation

$$CT_3^+ + CH_2{=}CH_2 \rightarrow CT_3CH_2CH_2^+ \xrightarrow{C_2H_4} CT_3(CH_2)_3CH_2^+ \text{ etc.} \qquad (16)$$

For a reaction mixture containing water molecules, two competing processes will occur: the polymerisation reaction (16) and the reactions with water of all the varieties of the carbonium ions produced, leading to the formation of alcohols:

$$\begin{array}{ccccccc} CT_3^+ & \xrightarrow{C_2H_4} & C_3H_4T_3^+ & \xrightarrow{C_2H_4} & C_5H_8T_3^+ & \xrightarrow{C_2H_4} & \text{etc.} \\ \downarrow H_2O & & \downarrow H_2O & & \downarrow H_2O & & \\ CT_3OH & & C_3H_4T_3OH & & C_5H_8T_3OH & & \end{array} \qquad (17)$$

With increase of the concentration of ethylene, an increase of the contribution of reaction (16) may be expected and hence an increase of the yield of alcohols with a larger number of carbon atoms. Experimental data confirm this hypothesis.

It is noteworthy that straight-chain alcohols were not detected among the products of the reactions of the intermediate carbonium ions, although the formation of such alcohols might have been expected bearing in mind the position of the carbonium centre at the instant of formation of these ions. This experimental finding permits the conclusion that there is sufficient time for the cations formed in reaction (16) to isomerise to thermodynamically more stable structures. Similar isomerisation reactions of carbonium ions are well known in organic chemistry.

It is also interesting that, for all the $[C_2H_4]:[H_2O]$ ratios, the yield of labelled methanol exceeds the value which might have been expected for a statistical mechanism of reactions (17). For example, for an equimolar ethylene : water ratio, a 50% yield of methanol could have been expected. The experimental yield (82.5%) greatly exceeds this value. The data obtained make it possible to estimate the competition factor for the reaction of methyl cations with methylene and water: $f_{comp} \simeq 4$. The higher reactivity of methyl cations in relation to water molecules compared with their reactivity in relation to ethylene molecules is due to the higher affinity of the CH_3^+ ions for H_2O (82 kcal mole^{-1})[148] compared with their affinity for C_2H_4 (69.5 kcal mole^{-1}).[160]

Analogous studies on the competitive reactions involving a wider range of substances will make it possible, in our view, not only to determine the competition factors in such reactions but also to supplement the nucleophilicity scale for substances, the construction of which is based on the equation $\lg(k_P/k_{H_2O}) = Sn$, where k_P/k_{H_2O} is the competition factor for the reactions of the carbonium ion with a base P and water, n is the nucleophilicity constant, and S the constant characterising the substrate[161].

VI. PROSPECTS FOR THE USE OF THE RADIOCHEMICAL METHOD OF INVESTIGATING ION–MOLECULE REACTIONS

On the basis of the theoretical considerations discussed previously and the experimental results published at the present time, one may reach certain conclusions about the scope of the radiochemical method for the investigation of ion–molecule reactions and about the prospects for its application in studies on the chemistry of molecular ions.

One of the most important features of this method is the possibility of obtaining molecular ions having the desired composition, structure, and initial location of the charge.

The composition and structure of molecular ions are determined by the composition and structure of the initial tritiated compounds and the initial location of the charge depends on the position of the tritium atom in these compounds.

The employment of the covalent tritides of certain elements as the initial compounds makes it possible to obtain the isosteric molecular ions of these elements (with a sextet of outer electrons), which are analogues of carbonium ions. As an example, we shall quote certain mechanisms for the formation of nitrogen-, oxygen-, and silicon-containing analogues of carbonium ions:

$$NT_3 \xrightarrow{-\beta^-} \overline{N}T_2^+ + He \ ,$$
$$T_2O \xrightarrow{-\beta^-} TO^+ + He \ ,$$
$$SiT_4 \xrightarrow{-\beta^-} SiT_3^+ + He \ .$$

It should be noted that tritium-containing compounds, behaving as radiochemical sources of molecular ions, are characterised by a constant and prolonged action. They can be used for several years.

The radiochemical method leads to considerable possibilities not only for the generation of unique charged molecular species but also for the investigation of their chemical behaviour under a wide variety of conditions. This method makes it possible to investigate the reactions of molecular ions both with any individual substances and with their mixtures. A characteristic feature of the method is also the possibility of carrying out ion–molecule reactions in any state of aggregation.

The ion–molecule reactions initiated by the β-decomposition of tritiated compounds can be used to solve many important chemical problems. Such reactions can be applied in the experimental study of the relative basicities of substances (intermolecular competing reactions). Labelled electrophilic species constitute a kind of detector of electron densities in the molecule (intramolecular competing reactions).

Furthermore, ion–molecule reactions can be used to study processes where the involvement of molecular ions is postulated and also to study the individual stages of cationic polymerisation reactions.

The reactions of tritium-containing molecular ions have found application in the synthesis of a wide variety of tritiated compounds[162].

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