klärt sich auch das Abnehmen der Ionenintensität im Massenspektrum mit steigender Temperatur für Bruchstückionen mit kleiner Aktivierungsenergie: Mit wachsendem T nimmt die Funktion $P(E, T)$ für kleine E ab und damit auch das Integral der Gl. (9). Ebenso lassen sich die häufig auftretenden Maxima in der Temperaturabhängigkeit verstehen.

Abb. 11 und Tab. 5 zeigen das Verhalten der Ionen aus dem Massenspektrum von 1-Hexen, die möglicherweise nur durch Spaltung einer C – C-Bindung entstanden sind. Die Temperaturabhängigkeit dieser Prozesse ist ebenso aus den unterschiedlichen Aktivierungsenergien zu erklären, wie es mit der C_4-Gruppe von 1-Buten geschehen ist.

Mass Spectrometric Studies of Ion-Molecule Reactions in Mixtures of Methane, Methanol, Water, Argon and Krypton with Iodine: Participation of Excited Ions and Atoms and some Radiation Chemical Considerations

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(Z. Naturforschg. **15 a**, 584—593 [1960]; eingegangen am 15. März 1960)

The mass spectrum of an iodine-methane mixture contains secondary ions of the type CH_nI^+ ($n=0-4$) which are attributed to the ion-molecule reactions $CH_n^+ + I_2 \rightarrow CH_nI^+ + I$ and $CH_{n+1} + I_2 \rightarrow CH_nI^+ + HI$. CH_4I^+ appears at 10.7 volts, i. e. 1.3 volts above the ionization potential of iodine and 1.6 volts below that of methane. The form of the ionization efficiency curve of CH_4I^+ resembles that of the excitation curves of atoms. The precursor of CH_4I^+ is therefore assumed to be an excited iodine ion: $I_2^{+*} + CH_4 \rightarrow CH_4I^+ + I$. It is shown that this reaction probably is endothermic when induced by an iodine ion without excess energy. The excited iodine ion is also the precursor of CH_4OI^+ and H_2OI^+ in iodine mixtures of methanol and water respectively. I_3^+ has been observed in iodine vapor. It is formed by $I_2^+ + I_2 \rightarrow I_3^+ + I$ where the iodine ion is not excited. AI^+ appears at the excitation potential of the metastable argon atom (11.5 volts). The reaction $A(^3P_2) + I_2 \rightarrow AI^+ + I + e$ is therefore postulated. However, the reaction $A^+ + I_2 \rightarrow AI^+ + I$ also occurs at higher electron voltages as could be concluded from repeller field studies. KrI^+ does not appear at the excitation potential of the metastable state since the reaction $Kr(^3P_2) + I_2 \rightarrow KrI^+ + I + e$ seems to be slightly endothermic. The KrI^+ ion appears 0.6 volts below the ionization potential of krypton which indicates the participation of a highly excited state in its formation.

Iodine appears as an efficient positive ion scavenger since it is able to react with many molecular and fragment ions with cross sections of the order of 50 Å^2. Simple calculations show that this action of iodine should be taken into consideration in radical scavenging experiments in radiation chemical studies.

Ion-molecule reactions in iodine-containing compounds have recently been reported by Hamill and coworkers [1, 2]. In the present work, reactions in gaseous mixtures of iodine with various substances have been investigated. Such systems are of interest since iodine has often been used as a radical scavenger in radiation chemical studies [3–5]. It will be shown that iodine is a good scavenger for many positive ions too. In addition, these iodine mixtures revealed some new types of ion-molecule reactions. Since iodine was present in all these mixtures at a concentration of 50 mole percent reactions of the I_2^+ ion could be studied. Some of the reactions of this ion occur only if it is formed with excess energy. Furthermore, some evidence has been obtained in rare gas-iodine mixtures of the occurence of reactions between excited krypton and argon atoms and iodine.

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[1] R. F. Pottie and W. H. Hamill, J. Phys. Chem. **63**, 877 [1959].

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[5] L. H. Gevantman and R. R. Williams, J. Phys. Chem. **56**, 569 [1952].

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Experimental

A Consolidated Electrodynamics Corporation Model 21-103 C mass spectrometer was used in these investigations after appropriate changes had been made for appearance potential measurements and for an increase in the sensitivity of the amplifier by a factor of 30. Ion molecule-reactions were recognized by the usual procedures, i. e. comparison of the appearance potentials and ionization efficiency curves of the parent and daughter ions and measurements of the repeller voltage and pressure dependence of the current ratio i_s/i_p of the secondary and primary ions [6]. In all studies the gaseous mixtures were made by introducing iodine and then adding the other gas into the reservoir of the inlet system. Cross sections of reactions in these two component mixtures were calculated by comparing the current ratio i_s/i_p with that of the known reaction

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

under identical conditions of operation, i. e. at constant total gas pressure and repeller field strength:

$$\sigma = \frac{2 \cdot i_s/i_p}{i_{H_3O^+}/i_{H_2O^+}} \sigma_w . \qquad (1)$$

σ_w is the cross section of the standard reaction which has been studied by LAMPE et al. [7].

Results

Methane-iodine

The mass spectrum of this mixture is recorded in Table 1. It contains the ions usually present in the spectra of the single components and in addition a number of organic iodide ions at low intensities.

Primary Ions			Secondary Ions		
Mass Number	Ion	Rel. Intensity	Mass Number	Ion	Rel. Intensity
12	C^+	0.15	139	CI^+	0.0027
13	CH^+	0,73	140	CHI^+	0.0017
14	CH_2^+	1.85	141	CH_2I^+	0.0058
15	CH_3^+	14.0	142	CH_3I^+	0.0240
16	CH_4^+	21.0	143	CH_4I^+	0.0081
127	I^+	22.0			
254	I_2^+	100.0			

Electron energy: 35 volts; Repeller field strength: 8 volts/cm; Pressure in the reservoir: 500 μ .

Table 1. Mass spectrum of a methane-iodine mixture.

In Fig. 1 and 2 the ratio i_s/i_p of these iodide ions is plotted versus the gas pressure in the reservoir of the inlet system and the repeller voltage respectively. The CH_4^+ ion was used in these figures as primary ion. Both figures show that these ions have the features of secondary ions from ion molecule reactions since $i_s/i_{CH_4^+}$ decreases with decreasing pressure and with increasing repeller field strength. However, it can be recognized that ion-molecule reactions are not the only source of many of these iodide ions. The only straight line in Fig. 1 which passes through the origin of the coordinate system is that of the CH_4I^+ ion which apparently is formed by an ion-molecule reaction exclusively. All other lines intercept the ordinate at finite values of $i_s/i_{CH_4^+}$. This indicates an additional process of the formation of iodide ions, the rate of which depends on the gas

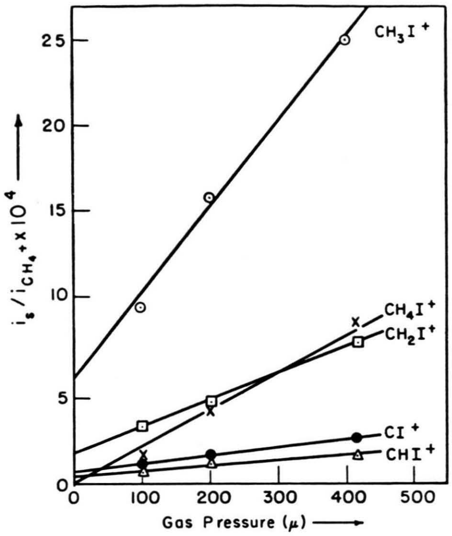

Fig. 1. Dependence of the ratio $i_s/i_{CH_4^+}$ on the pressure in the reservoir of the inlet system. (Repeller field: 8 volts/cm).

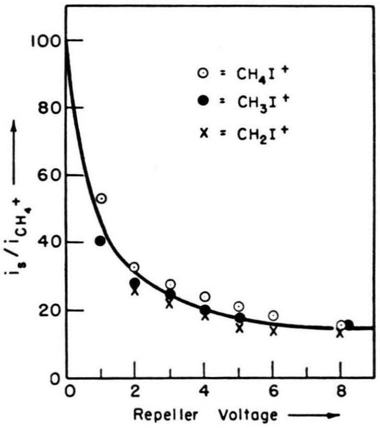

Fig. 2. Dependence of $i_s/i_{CH_4^+}$ on the repeller voltage (pressure in the reservoir: 500 μ. The current ratio at zero volts was made equal to 100).

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[6] see, for example, D. P. STEVENSON and D. O. SCHISSLER, J. Chem. Phys. **29**, 282 [1958].

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pressure the same way as $i_{CH_4^+}$. It seems plausible to identify this process with the thermal reaction of methane and iodine at the hot filament and the subsequent ionization of methyl iodide formed. The relative contribution of this process to the intensity of the iodide ions will decrease with increasing pressure. At 500 μ in the reservoir about 20 percent of the ions $CI^+ - CH_3I^+$ are formed via the thermal reaction.

The ionization efficiency curves of the primary and secondary ions are shown in Fig. 3 a and b. These curves have been normalized to the ion intensity for 35 ev electrons. The ionization efficiency curves of some ions produced in methyl iodide are presented in Fig. 4 for further comparisons. The following conclusions may be drawn from these figures:

(a) Formation of the ions $CI^+ - CH_3I^+$:

The appearance potentials of the secondary ions $CI^+ - CH_3I^+$ in Fig. 3 b are much lower than those of the corresponding primary ions $C^+ - CH_3^+$. They agree, however, with the appearance potentials of the corresponding ions $CI^+ - CH_3I^+$ from methyl iodide. This gives additional confirmation of the thermal formation of methyl iodide in the ion source. The contribution of this process is significant only at electron energies just above the appearance potentials. At higher voltages ion molecule reactions of the primary $C^+ - CH_3^+$ ions contribute more and more to the formation of $CI^+ - CH_3I^+$. This may be recognized from the differences in the forms of the curves in Fig. 4 and 3 b at higher electron energies.

It is assumed that the ions $CI^+ - CH_3I^+$ are formed by reactions of the type:

$$CH_n^+ + I_2 \rightarrow CH_nI^+ + I \,. \tag{2}$$

The relative cross sections of these reactions have been calculated according to Eq. (1). They generally are at little lower than that of the standard reaction as can be seen from Table 2. The absolute cross sections are of the order of 50 Å. The reason for this high reactivity of iodine toward aliphatic hydrocarbon ions may be the large difference in the ionization potentials of the species CH_n and CH_nI in Eq. (2) so that all these reactions are exothermic. In many cases even reactions of the type

$$CH_{n+1}^+ + I_2 \rightarrow CH_nI^+ + HI \tag{3}$$

will be possible. Such a process perhaps contributes to the formation of CI^+ since the calculated cross section of the process $C^+ + I_2 \rightarrow CI^+ + I$ appears unreasonably high (Table 2). The high reactivity of iodine towards aliphatic hydrocarbon ions is of interest to radiation chemical experiments in which

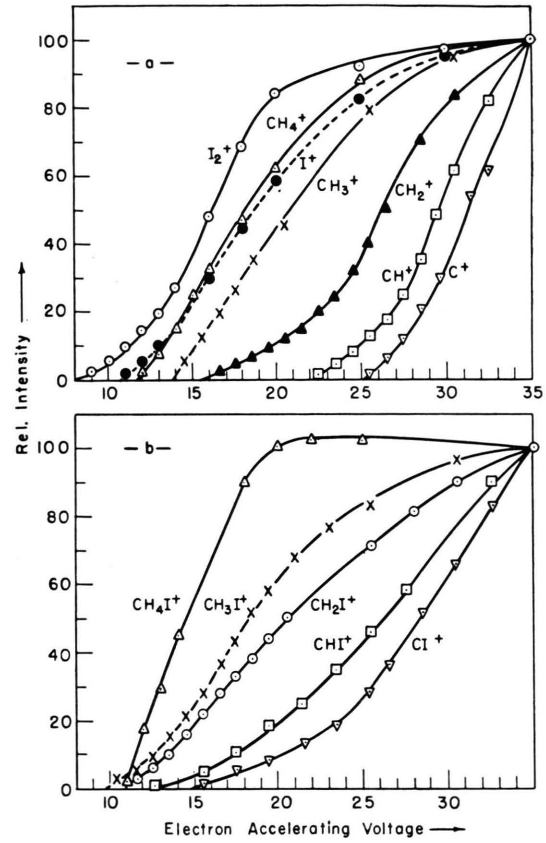

Fig. 3. a) ionization efficiency curves of primary ions in a methane-iodine mixture. b) ionization efficiency curves of secondary ions.

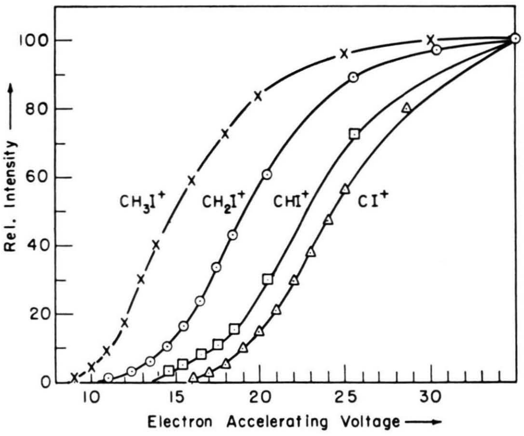

Fig. 4. Ionization efficiency curves of ions in methyl iodide.

iodine is used as a radical scavenger. These aspects will be discussed later.

(b) Formation of the CH_4I^+ ion:

The CH_4I^+ ion may be formed by either of reactions (4) or (5) or by both:

$$CH_4^+ + I_2 \rightarrow CH_4I^+ + I\,, \qquad (4)$$

$$I_2^+ + CH_4 \rightarrow CH_4I^+ + I\,. \qquad (5)$$

A decision can be made by comparing the appearance potentials and ionization efficiency curves of the three ions involved in (4) and (5). Reaction (4) must be ruled out since the appearance potential of CH_4^+ (12.3 volts) is higher than that of CH_4I^+ (10.7 volts). On the other hand, the ionization efficiency curves of I_2^+ and CH_4I^+ also are quite different. The ionization potential of I_2 is equal to 9.41 volts. The I_2^+ intensity gradually increases with increasing electron accelerating voltage in the range studied up to 35 volts while that of CH_4I^+ reaches a slight maximum at 22 volts. The only primary ion which can appear at 10.7 volts in the system methane-iodine is an excited iodine ion carrying 1.3 ev of excess energy. This could be an electronically excited I_2^+ or a highly vibrationally excited ion in its electronic ground state since $D(I_2^+)$ is larger than 1.3 ev. However, the concept of an electronically excited ion is favored since the ionization efficiency curve with its slight maximum about 10 volts above the appearance potential resembles very much the theoretical and observed curves of the excitation of atoms by electrons [8].

n	${}^iCH_nI^+/{}^iCH_n^+$	Relative cross section
0	$1.4 \cdot 10^{-2}$	4.5
1	$1.9 \cdot 10^{-3}$	0.61
2	$2.5 \cdot 10^{-3}$	0.80
3	$1.4 \cdot 10^{-3}$	0.45
${}^iH_3O^+/{}^iH_2O^+$	$6.2 \cdot 10^{-3}$	1[(b)]

(a) Calculated from the mass spectrum in Table 1 under the assumption that 20 percent of the secondary ions originate from the ionization of methyl-iodide formed in the ion source.
(b) The absolute cross section is equal to 130 Å^2 (calculated from reference 7).

Table 2. Current ratio of the ions CH_n^+ and CH_nI^+ ($n=0-3$) and relative cross sections of the corresponding reactions $CH_n^+ + I_2 \rightarrow CH_nI^+ + I$[(a)].

It must therefore be assumed that reaction (5) is endothermic if the I_2^+ ion enters the reaction without excess energy. Similar reactions of excited ions have already been postulated by MEISELS [9]. POTTIE and HAMILL [1] found a reaction in ethyl iodide in which the unexcited as well as excited molecular ions contributed. A rough estimation of the endothermicity of reaction (5) may be carried out as follows. Reaction (5) will occur fast enough (i. e. without any activation energy) only if the heat content of the system $I_2^{+*} + CH_4$ is higher than that of $CH_4I^+ + I$. Furthermore, the enthalpy of the latter system must be lower than that of $CH_4 + I^+ + I$ since otherwise CH_4I^+ would spontaneously decompose. It follows from these considerations that the following relation holds for the dissociation energy of CH_4I^+:

$$D(CH_4 - I^+) \geqq I(I) + D(I_2) - E(I_2^+) - I(I_2)\,. \qquad (6)$$

The spectroscopic values of the ionization energies $I(I)$ and $I(I_2)$ are 10.44 and 9.41 ev respectively [10]. The dissociation energy of iodine has been found to be 1.54 ev [11, 12]. Assuming at first zero excitation energy E of the iodine ion, a minimum value of 2.57 ev of $D(CH_4 - I^+)$ is obtained. This value appears much too high since $D(CH_3 - I)$ in methyl iodide amounts to only 2.29 ev [13]. If the assumption is made that $D(CH_3 - I) \geqq D(CH_4 - I^+)$, which seems reasonable, it must be concluded that reaction (5) is endothermic by at least 0.28 ev. However, if $E(I_2^+)$ is sufficiently high the minimum value of $D(CH_4 - I^+)$ which has to be postulated in order to make reaction (5) exothermic will become reasonably low. We are well aware that these considerations cannot be regarded as a proof but only as a possible explanation for reaction (5) being endothermic and therefore having a certain activation energy. The current ratio $i_{CH_4I^+}/i_{I_2^+}$ as calculated from the data in Table 1 amounts to only 8.1×10^{-5}. Probably only a small part of the iodine ions formed

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[8] H. S. W. MASSEY and C. B. O. MOHR, Proc. Roy. Soc., Lond. A **132**, 605 [1931].

[9] G. G. MEISELS, J. Chem. Phys. **31**, 284 [1959].

[10] see, for example, F. H. FIELD and J. L. FRANKLIN, Electron Impact Phenomena, Academic Press Inc., publishers, New York 1957.

[11] M. L. PERLMAN and G. K. ROLLEFSON, J. Chem. Phys. **9**, 362 [1941].

[12] G. HERZBERG, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, 2nd Edition, New York 1950.

[13] T. L. COTRELL, The Strength of the Chemical Bond, Butterworth Scientific Publications, London 1958, 2nd Edition.

at 35 volts will be excited. The ratio $i_{CH_4I^+}/i_{I_2^{+*}}$ therefore will be larger than 8.1×10^{-5}.

Finally, some other processes may be considered here which could be responsible for the formation of CH_4I^+. Reaction (4) has already been ruled out above because of the difference in the appearance potentials of CH_4I^+ and CH_4^+. The ionization efficiency curves of these two ions also show no similarity at higher ionizing voltages. Although reaction (4) is exothermic it does not contribute to the formation of CH_4I^+ at voltages above the appearance potential of CH_4^+. This may be explained by a higher frequency of the competing processes (7), (8) and (9):

$$CH_4^+ + I_2 \rightarrow CH_4 + I^+ + I\,, \qquad (7)$$

$$\rightarrow CH_4 + I_2^+, \qquad (8)$$

$$\rightarrow CH_3I^+ + HI\,. \qquad (9)$$

An alternative explanation of the low appearance potential of CH_4I^+ is reaction (10) which is induced by a highly excited methane molecule:

$$CH_4^* + I_2 \rightarrow CH_4I^+ + I + e\,. \qquad (10)$$

This reaction, however, must be ruled out because of the results obtained in water and methanol-iodine mixtures described below. It will be shown there that the ions H_2OI^+ and CH_4OI^+ have practically the same appearance potential as CH_4I^+. This means that the parent ion is the same in all these reactions.

Methanol-iodine

The mass spectrum of a methanol-iodine mixture (Table 3) also shows numerous ions which are not present in the spectra of the individual compounds. The formation of CH_4OI^+ and CH_3I^+ which are the most abundant secondary ions has been studied in detail. In the experiments shown by Fig. 5 and 6

Primary Ions			Secondary Ions		
Mass Number	Ion	Rel. Intensity	Mass Number	Ion	Rel. Intensity
12	C^+	0.014	139	CI^+	0.0027
13	CH^+	0.120	140	CHI^+	0.0021
14	CH_2^+	0.50	141	CH_2I^+	0.0070
15	CH_3^+	3.1	142	CH_3I^+	0.025
16	O^+ and CH_4^+	0.036			
17	OH^+	0.11			
28	CO^+	0.35			
29	CHO^+	6.7			
30	CH_2O^+	1.0	157	CH_2OI^+	0.0020
31	CH_3O^+	16.7	158	CH_3OI^+	0.0070
32	CH_4O^+	13.5	159	CH_4OI^+	0.068
127	I^+	22.0			
254	I_2^+	100.0			

Table 3. Mass spectrum of a methanol-iodine mixture.

X	$iXI^+/iI_2^{+(a)}$	Cross section(c)
CH_4	$8.1 \cdot 10^{-5}$	0.026(b)
CH_3OH	$8.5 \cdot 10^{-4}$	0.27(b)
H_2O	$5.3 \cdot 10^{-4}$	0.17(b)
I_2	$2.0 \cdot 10^{-3}$	0.32

(a) Total gas pressure in the reservoir: 500 μ; Electron accelerating voltage: 35 volts.
(b) These are minimum cross sections since only part of the I_2^+ will be excited to induce the reactions.
(c) Relative to the cross section of $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$.

Table 4. Current ratio i_s/i_p and cross section of some reactions of the type $I_2^+ + X \rightarrow XI^+ + I$.

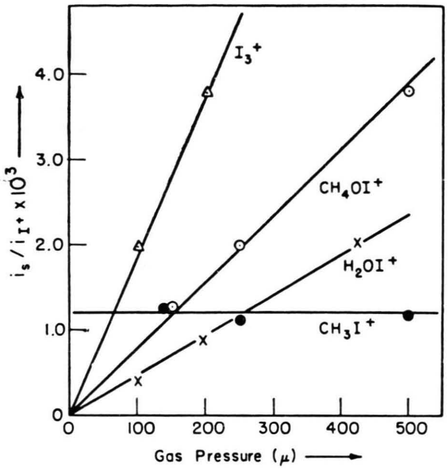

Fig. 5. Pressure dependence of i_s/i_{I^+} of different secondary ions.

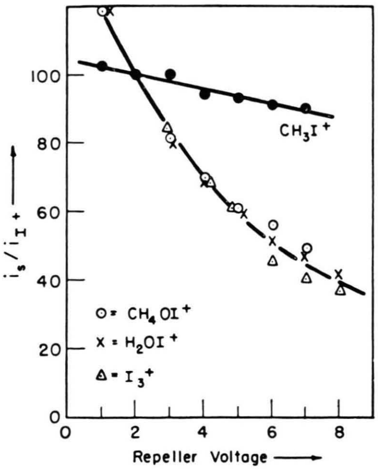

Fig. 6. Repeller voltage dependence of i_s/i_{I^+} of different secondary ions. (The current ratio at 2 volts was made equal to 100.)

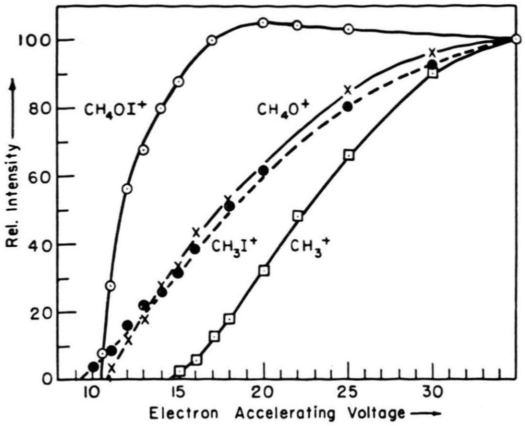

Fig. 7. Ionization efficiency curves of ions in methanol-iodide.

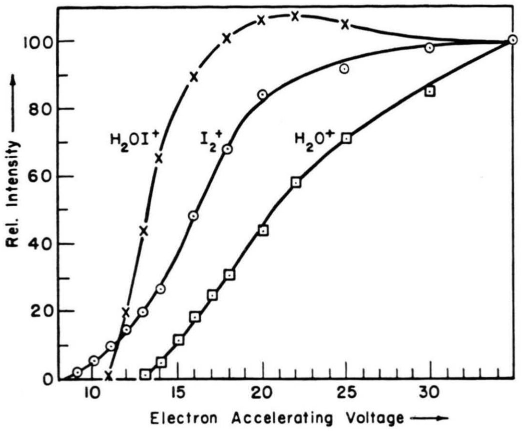

Fig. 8. Ionization efficiency curves of ions in water-iodine.

the I^+ ion has been chosen as primary ion. The current ratio $i_{CH_4OI^+}/i_{I^+}$ increases linearly with pressure while $i_{CH_3I^+}/i_{I^+}$ is practically independent on pressure (Fig. 5). CH_4OI^+ apparently is formed by an ion-molecule reaction exclusively while CH_3I^+ results from the ionization of some products of the thermal reaction between methanol and iodine in the ion source. This is confirmed by the results of the repeller field studies shown in Fig. 6. $i_{CH_4OI^+}/i_{I^+}$ strongly drops with increasing repeller voltage while $i_{CH_3I^+}/i_{I^+}$ is nearly independent of this.

The ionization efficiency curve of CH_4OI^+ in Fig. 7 has the same shape as that of CH_4I^+ in Fig. 3 b. It differs markedly from the curve of CH_4O^+ which therefore cannot be the precursor of CH_4OI^+. It is again postulated that I_2^{+*} is the primary ion:

$$I_2^{+*} + CH_3OH \rightarrow CH_4OI^+ + I\,. \qquad (11)$$

The cross section of this reaction is considerably higher than that of the corresponding process in a methane-iodine mixture as can be seen from Table 4.

Water-iodine

The ion H_2OI^+ has been observed in mixtures of water and iodine. The results of the pressure and repeller field studies are included in Fig. 5 and 6 respectively. They clearly show that this ion is formed by an ion-molecule reaction. The ionization efficiency curves in Fig. 8 show that I_2^{+*} must be the primary ion. The reaction may therefore be written as follows.

$$I_2^{+*} + H_2O \rightarrow H_2OI^+ + I\,. \qquad (12)$$

Iodine

The I_3^+ ion has been found in iodine vapor. The pressure and repeller field studies in Fig. 5 and 6 show that it is formed by an ion-molecule reaction. The ionization efficiency curve of I_3^+ has been found to be identical with that of I_2^+. It is therefore concluded that iodine is able to react with its own molecular ion:

$$I_2^+ + I_2 \rightarrow I_3^+ + I\,. \qquad (13)$$

Unlike reactions (5), (11) and (12), reaction (13) is possible with unexcited iodine ions. This may be the reason why (13) occurs with the highest cross section among all these processes (Table 4). Reaction (13) has already been observed in the case of negative ions [14]:

$$I_2^- + I_2 \rightarrow I_3^- + I\,. \qquad (14)$$

(13) and (14) seems to be the only pair of reactions between negative and positive ions with a neutral molecule where the same molecular and atomic species are involved. This may become of interest for a thorough comparison of positive and negative ion-molecule reactions. A number of negative ion-molecule reactions is already known which basically show the same behaviour as positive ion-molecule reactions [15]. However, differences may be expected in the dependence of the cross section on ion energy since the electric fields of positive and negative ions of the same species will be different because of the difference in their radii.

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[14] T. R. Hogness and R. W. Harkness, Phys. Rev. **32**, 784 [1928].

[15] A. Henglein and G. A. Muccini, J. Chem. Phys. **31**, 1426 [1959].

Rare gases-iodine

AI^+ and KrI^+ have been found in mixtures of iodine with the corresponding rare gases. XeI^+ has also been observed, however, the intensity of this ion was very low and no quantitative measurements have been carried out. We did not succeed in finding HeI^+ and NeI^+ in mixtures of iodine and the light rare gases. The pressure dependence studies in Fig. 9 show that AI^+ and KrI^+ are secondary ions from reactions following ionization or excitation of the rare gas or iodine.

The appearance potential of AI^+ amounts to 10.7 or 11.5 volts depending on the nature of the extrapolation of the ionization efficiency curve in Fig. 10. The value of 10.7 would be consistent with the appearance potential of I_2^{+*} mentioned above. However, the form of the ionization efficiency curve of AI^+ strongly deviates from that of the reaction products of I_2^{+*} in Fig. 3 b, 7 and 8. It must therefore be concluded that reaction

$$I_2^{+*} + A \rightarrow AI^+ + I \qquad (15)$$

is of minor importance if it occurs at all. The curve of I_2^+ in Fig. 10 has to be extrapolated at 2 volts above the first appearance of I_2^+ in order to obtain the spectroscopic ionization potential of 9.41 volts. A similar extrapolation of the AI^+ curve leads to an appearance potential of 11.5 volts. The precursor of AI^+ below the ionizing potential of argon (15.76 volts) must be an excited state of argon. It is emphasized that under the experimental conditions used only such reactions can be observed as have ionized or excited precursors of lifetime greater than about 10^{-6} seconds. If follows that only the metastable state of argon can be the precursor of AI^+ at low electron voltages. The energy of this state is equal to 11.55 ev [16] which agrees very well with the higher value of the appearance potential of AI^+ mentioned above. The formation of AI^+ may therefore be written as follows:

$$A(^3P_2) + I_2 \rightarrow AI^+ + I + e\,. \qquad (16)$$

A similar process has already been described by Hornbeck and Molnar [17].

$$A^* + A \rightarrow A_2^+ + e\,. \qquad (17)$$

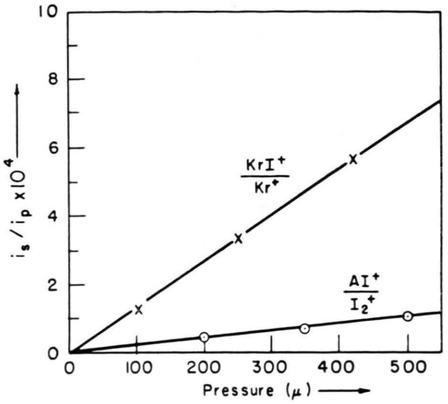

Fig. 9. Pressure dependence of i_s/i_p for AI^+ and KrI^+.

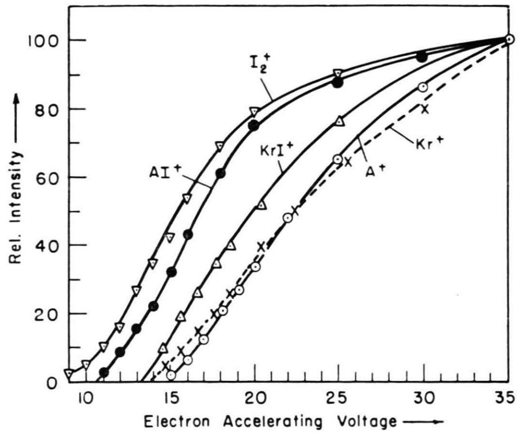

Fig. 10. Ionization efficiency curves of ions in iodine mixtures of argon and krypton.

The exothermicity of reaction (16) can be roughly estimated in the following manner*: The heat content of the system $A(^3P_2) + I_2$ must be higher than that of the system $AI^+ + I + e$. Furthermore, the enthalpy of the latter must be lower than that of the system $A + I^+ + I + e$. The minimum value of the bond strength of AI^+ which is required to make reaction (16) exothermic can be derived from these considerations:

$$D(A - I^+) \geqq I(I) + D(I_2) - E(^3P_2)\,. \qquad (18)$$

Taking $I(I) = 10.44$ ev, $D(I_2) = 1.54$ ev and $E(^3P_2) = 11.55$ ev, a minimum value of $D(A - I^+) = 0.43$ ev is obtained. On the other hand, $D(A - I^+)$

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* We assume in all theoretical calculations that only such ion-molecule reactions can be observed in a mass spetrometer as occur at every collision, i. e. without any activation energy. Since endothermic reactions always have some activation energy, the exothermicity of a reaction must be postulated as a preliminary condition of a possible observation of the reaction in a mass spectrometer.

may well be expected to be of the order of 2.15 ev, which is the dissociation energy of the isoelectronic ClI molecule[13]. It may therefore be estimated that reaction (16) is exothermic by about the 1.72 ev difference calculated from the above.

It seems noteworthy to mention that reaction

$$A(^3P_2) + I_2 \rightarrow A + I^+ + I + e \qquad (19)$$

is endothermic by 0.43 ev. Therefore it cannot compete with reaction (16). Reaction (20) however, is possible from an energetic point of view:

$$A(^3P_2) + I_2 \rightarrow A + I_2^+ + e\,. \qquad (20)$$

At electron accelerating voltages above the ionization potential of argon, there may be some formation of AI$^+$ by reaction (21) too. The charge transfer (22) and dissociative charge transfer (23) are also energetically possible:

$$\begin{aligned} &\nearrow AI^+ + I\,, && (21)\\ A^+ + I_2 &\rightarrow A + I_2^+\,, && (22)\\ &\searrow A + I^+ + I\,. && (23)\end{aligned}$$

The participation of excited atoms as well as of ions in the argon-iodine reaction may be recognized from the repeller field studies shown in Fig. 11. Here the AI$^+$ current is plotted versus the repeller voltage at 15 and 35 volts of electron accelerating voltage respectively. The corresponding curve of I$^+$ is added for comparison. The form of the curve of a primary ion such as I$^+$ does not depend on the electron energy. The curve of AI$^+$ at 15 volts resembles that of the I$^+$ ion although AI$^+$ is not a primary ion. This may be expected since the uncharged precursor of the AI$^+$ ion is not influenced by the repeller field and neither is the cross section of reaction (16). However, at 35 volts a large part of the AI$^+$ ions will have the charged precursor A$^+$ which will be accelerated by the repeller field. The cross section of reaction (21) will therefore decrease with increasing repeller voltage and the AI$^+$ current will be less dependent on the repeller voltage. As it is shown in Fig. 11 the AI$^+$ current has been found to be nearly independent on the repeller voltage in the voltage range studied.

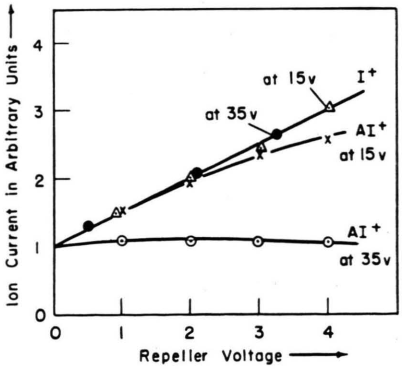

Fig. 11. Ion current as function of repeller voltage at 15 and 35 volts of electron accelerating voltage.

The ionization energy and energy of the metastable state of krypton are 14.0 and 9.91 ev respectively[16]. If the bond strength of KrI$^+$ is taken equal to that of the isoelectronic BrI molecule (1.82 ev[13]), the heat of reaction (24)

$$Kr(^3P_2) + I_2 \rightarrow KrI^+ + I + e \qquad (24)$$

will be equal to

$$E(^3P_2) + D(KrI^+) - I(I) - D(I_2) = -0.25 \text{ ev} \qquad (25)$$

i. e. the reaction is slightly endothermic and will therefore not be observed in a mass spectrometer. As can be seen from Fig. 10, no KrI$^+$ has been observed at electron voltages just above the excitation potential of the metastable state of krypton. KrI$^+$ appears at about 0.6 volts below the ionization potential of krypton and there are additional differences in the efficiency curves of KrI$^+$ and Kr$^+$ at higher electron energies (Fig. 10). It is therefore assumed that the krypton-iodine reaction is induced at electron energies below I(Kr) by a highly excited krypton atom:

$$Kr^* + I_2 \rightarrow KrI^+ + I + e\,. \qquad (26)$$

Hornbeck and Molnar[17] found that Kr$_2^+$ has an appearance potential 0.7 volts below the ionization potential of krypton which agrees well with the appearance potential of KrI$^+$ mentioned above. It seems therefore that a highly excited state which has a rather long lifetime is formed in krypton under electron impact.

The first excitation and the ionization potentials in helium and neon are to 21.0 and 24.46 (He) and 16.63 and 21.56 (Ne) respectively. All possible reactions with iodine are strongly exothermic. It may be that this favors dissociative autoionization corresponding to eq. (19) and dissociative charge transfer corresponding to eq. (23) over the formation of iodide ions corresponding to eq. (16). This would explain our failure to detect HeI$^+$ and NeI$^+$.

Discussion with respect to radiation chemistry

Since reactions of the type

$$X^+ + I_2 \rightarrow XI^+ + I \qquad (27)$$

apparently occur with many ionized molecules and radicals X and have very high cross sections, it is obvious that iodine may act as an efficient positive ion scavenger in radiation chemical experiments. This concept may, of course, influence some of the current theories of the action of iodine as a radical scavenger. The competing process of positive ion-iodine reactions is the neutralization of the ions. It does not matter in these considerations whether iodine reacts with primary ions or with secondary ions resulting from some chemical reactions of primary ions. The cross section of reaction (27) is assumed to be equal to 50 Å^2 in the following calculations. This corresponds to a bimolecular rate constant k of about 1×10^{-9} molecules^{-1} cc sec^{-1}.

Systems to which steady state kinetics is applicable may be described by the following formulas:

$$\mathrm{d}n/\mathrm{d}t = k_1 I, \qquad -(\mathrm{d}n/\mathrm{d}t)_r = \alpha n^2, \qquad (28, 29)$$

$$n = \sqrt{k_1 I/\alpha}, \qquad \tau = 1/\alpha n \qquad (30, 31)$$

(I: dose rate; α: coefficient of recombination; n: stationary concentration of ion pairs; τ: lifetime of the ions). When iodine is present in the system the rate of neutralization will not change since the charge does not disappear in reaction (27). The rate of ion scavenging will be:

$$-(\mathrm{d}n/\mathrm{d}t)_s = k\, c\, n \qquad (32)$$

(c: concentraton of I_2). The iodine concentration C at which scavenging and neutralization will occur with comparable rates will be approximately:

$$C = \frac{\alpha}{k} n \qquad (33)$$

Steady state conditions will be fulfilled in many gaseous systems under irradiation. α is of the order of 10^{-7} ions^{-1} cc sec^{-1} at atmospheric pressure [18]. The ratio α/k is therefore of the order of 100. $k_1 I$ amounts to about 3×10^{10} ions cc^{-1} sec^{-1} in a gas of density 10^{-3} grams/cc at a dose rate of 1,000 r/min. The stationary concentration and lifetime of the ions will be equal to about 5×10^8 ions/cc and 2×10^{-2} sec respectively. An iodine concentration C of 5×10^{10} molecules/cc is calculated from these data. This corresponds to an iodine pressure of about 2×10^{-6} mm Hg only. It must therefore be concluded that iodine cannot be used under the usual conditions of radical scavenging in gases [19] without scavenging many of the positive ions formed.

The role of iodine in liquids is more difficult to evaluate since the ions are probably not homogeneously distributed and α and k are less known. In dilute solutions only those ions will possibly react with iodine which escape primary neutralization [20]. We carry out at first a treatment which has recently been applied in the theory of ionic polymerizations by MAGAT [21]. He calculated the lifetime of ions according to eqs. (28) – (31) assuming that the ions escape primary neutralization and neutralization in the expanding tracks or spurs before they are homogeneously distributed in the solution. A neutralization coefficient of 5×10^{10} moles^{-1} liter sec^{-1} (8×10^{-11} ions^{-1} cc sec^{-1}) has been used, i. e. the measured rate constant for reactions of H^+ and OH^- with other ions in aqueous solutions [22]. The rate constant k of iodine-ion reactions in a liquid will mainly be determined by the diffusion. It is assumed that k is smaller by a factor of 10^3 than in the gas phase as is α, i. e. the ratio α/k is assumed to be roughly equal to 100 again. If 10 percent of the ions escape primary neutralization and reach a homogeneous distribution, a stationary concentration of 2×10^{11} ions/cc and a lifetime of 5×10^{-2} sec are calculated at a dose rate of 1,000 r/min (density of the liquid 1 g/cc). The corresponding iodine concentration C amounts to about 2×10^{13} molecules/cc or 3×10^{-8} moles/liter. It must therefore be concluded that iodine will react with positive ions that escape primary neutralization and neutralization in the expanding tracks or spurs.

The number of these ions, however, is probably very small. According to the theory of ionization in columns by JAFFE [23] half of the ions will be neutral-

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ized in the expanding track of an electron within 10^{-7} sec. This lifetime is 10^5 times shorter than that calculated above. The "effective" ion concentration in the expanding track and therefore also C will become about 10^5 times higher than above. Reactions between iodine and ions will now occur only at concentrations above 3×10^{-3} moles/liter. In fact, SCHULER et al. found abnormal iodine uptake and a decrease in H_2 yield in hydrocarbons at iodine concentrations above some 10^{-3} moles/liter [24–26]. Similar results have been obtained by BURTON et al. [27]. The formation of HI at iodine concentrations of about 10^{-2} moles/liter [24, 25, 28] may perhaps also be explained by ion-iodine reactions [eq. (3)].

Finally, iodine-ion reactions may compete with primary neutralization in more concentrated solutions. Such a competition may become possible by the simultaneous action of iodine as an electron trap. The cross section of thermal electron capture by iodine [29] has been found to be so high that this capture may compete with the recapture of the electron by its parent ion at iodine concentrations above 10^{-2} moles/liter [30]. The neutralization between I^- formed and the positive ion will require a much longer time than the $10^{-13} - 10^{-14}$ sec required for the electron-ion recombination. During that longer time period the positive ion may well undergo a reaction with another iodine molecule.

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Die Halbwertszeiten einiger Positronenstrahler mit übererlaubten Übergängen

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The half-lives of 15 superallowed β^+-emitters have been measured with high precision. There are deviations from the known values, especially for Sc^{41}.

A plot of log $T_{1/2}$ versus log $(Z/A^{1/3})$ for the mirror transitions and the $0^+ \rightarrow 0^+$ transitions of the nuclei with $A = 4\,n + 2$ contains breaks and irregularities, and therefore shows the effect of shell structure.

Übererlaubte β-Übergänge sind aus mehreren Gründen interessant. Die Matrixelemente für die Übergänge können näherungsweise nach rein theoretischen oder halbempirischen Methoden berechnet werden. Sie lassen sich dann mit den aus den experimentellen $F(E_{\beta\,\mathrm{max}}, Z) \cdot T_{1/2}$-Werten berechneten Matrixelementen vergleichen. Die Bestimmung der Matrixelemente steht im engen Zusammenhang mit der Ermittlung der universellen β-Wechselwirkungskonstanten [1, 2].

Weiter kann man die COULOMB-Energiedifferenzen [3–5] zwischen den analogen Niveaus von Isobarenmultipletts, die sich aus den experimentell bestimmten maximalen β-Energien ergeben, mit den theoretischen Ansätzen [4–8] für die COULOMB-Energien vergleichen.

Ziel dieser Arbeit ist es, die Halbwertszeiten einer Reihe von Positronenstrahlern mit übererlaubten Übergängen zu messen. Die Meßgenauigkeit gegenüber den bekannten Messungen sollte nach Möglichkeit verbessert werden, insbesondere bei den noch relativ ungenau gemessenen Lebensdauern von Sc^{41}, Ti^{43} und Sc^{42} oberhalb der doppelt magischen Schale bei $A = 40$.

1. Experimentelle Anordnung

Die zu untersuchenden Aktivitäten wurden in einer Hohlsonde des Heidelberger Zyklotrons durch Beschuß mit Deuteronen von 7 MeV oder α-Teilchen von 20,5 MeV erzeugt. Als Target dienten: Graphit, MnO_2, Mg^{24} und Mg^{25} auf Au-Unterlage, Si, SiO_2, FeS, Ca, NaF,

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