einer Reihe von früheren Arbeiten [5, 9, 10] haben wir folgendes zeigen können:

1. Die Leitfähigkeit der inneren Kornoberfläche ist sicherlich nicht schlechter als die des kompakten Materials;
2. die Austrittsarbeit zeigt ein ähnliches Verhalten wie die Leitfähigkeit beim Tempervorgang;
3. die Austrittsarbeit wird durch eine Chlordotierung erniedrigt; neuerdings fanden wir auch, daß sie durch eine Tl-Dotierung erhöht wird;
4. es gelang, einen quantitativen Zusammenhang zwischen der Leitfähigkeit und der Kornoberfläche pro Volumeneinheit herzuleiten.

Die nunmehr hier mitgeteilten Ergebnisse ordnen sich recht gut in den Rahmen dieser Anschauungen ein. Demnach muß der Ladungsträgertransport vorwiegend in der Kornoberfläche erfolgen. Durch eine Halogendotierung werden die Energiebänder an den Kornoberflächen aufgebogen, so daß dadurch eine Anreicherungsrandschicht für Defektelektronen entsteht. Metalle mit einer starken chemischen Affinität zu den Halogenen biegen dagegen die Bänder an den Kornoberflächen ab. Für diese Bandverbiegungen sind bereits sehr geringe Verunreinigungskonzentrationen ausreichend.

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[9] H. Gobrecht, H.-J. Reiter u. A. Tausend, Z. angew. Phys. **14**, 53 [1962].

[10] H. Gobrecht, A. Tausend u. M. Plümecke, Z. angew. Phys., im Druck.

Mass Spectrometric Observation of Electron and Proton Transfer Reactions between Positive Ions and Neutral Molecules. Part II*

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The method of Cermak and Herman has been applied to studies of unsymmetrical charge and proton transfer reactions. If the charge is transferred between atoms low cross sections are observed since part of the kinetic energy of the reacting system has to be converted into internal energy of the reactants. Large cross sections, however, have been found for the charge transfer between polyatomic species where apparently no resonance restriction exists. In several instances the unsymmetrical transfer $B^+ + A \rightarrow B + A^+$ has a higher rate than either of the processes $B^+ + B$ or $A^+ + A$. If the ionization potential of B is lower than that of A the cross sections are in general low. In certain cases exceptionally large cross sections are observed and can be explained by the excess energy of a long lived excited state of the donor B^+. Dissociations following the transfer of one charge from a doubly charged ion to a neutral molecule such as

$$Kr^{++} + H_2O \rightarrow (Kr^+)^* + (H_2O^+)^* \rightarrow OH^+ + H\,,$$
$$NO^{++} + NO \rightarrow (NO^+)^* + (NO^+)^* \rightarrow N^+ + O$$

have also been observed. The results indicate that the doubly charged ion generally captures the electron into a high lying orbital.

Protonated cyclopropane is shown to be readily formed in ionized cyclopropane. In mixtures of water and methane, proton transfer has been observed in both directions. A large isotope effect on the secondary ion currents resulting from the transfer of a deuteron or a proton has been found in several simple systems. This isotope effect appears only if the secondary ions are observed in the Cermak–Herman method and is not found in the conventional operating of the ion source where reactions of slow ions predominate. This information provides some insite into the mechanistic details of the proton transfer since little isotope effect is expected if the reaction occurs via an inelastic collision complex while an isotope effect of the order of magnitude observed here is predicted by a stripping model.

In the first part of this work [1], the method of Cermak and Herman [2] was applied to studies of symmetrical electron and proton transfer processes in simple molecules. It was shown that essentially complete discrimination of primary ions formed between the chamber and electron trap of a conventio-

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[1] A. Henglein and G. A. Muccini, Z. Naturforschg. **17 a**, 452 [1962].

[2] V. Cermak and Z. Herman, Nucleonics **19**, No. 9, 106 [1961].

nal ion source can be achieved if the electron accelerating voltage between the filament and the chamber is kept at least two volts below the ionization potential of the gas. Secondary ions produced in the chamber were shown to be extractable into the analyzing section of the instrument as long as they do not possess significant kinetic energy in either the direction of the primary ion beam (<2.5 ev) or perpendicular to this direction and the direction of analysis (<0.34 ev). These conditions are fulfilled in ion-molecule reactions in which either the transfer of mass is small or which do not occur via long-lived complexes. Proton transfer reactions such as the process $H_2O^+ + H_2O \rightarrow OH + H_3O^+$ were postulated to occur via a "stripping" mechanism at least at kinetic energies above about 5 ev. These studies have been extended to investigations of electron and proton transfer processes between molecules of different structure and to dissociative charge transfer reactions induced by doubly charged ions.

Experimental

As has been described in the earlier report[1] the primary ions possess a spread of kinetic energies when they enter the ionization chamber. Most have energies near to the maximum value of $e\,E_T$ where E_T is the voltage between the chamber and the trap. The lower energy limit of the primary ion beam is equal to $e(AP - E_e)$ where AP is the appearance potential of the primary ion and E_e the voltage between the filament and the ionization chamber. If E_e is kept constant the average kinetic energy of the primary ions increases with increasing E_T and so does the energy spread and the intensity of the beam. Since E_T and E_e determine the upper and lower limit of the primary ion energy, suitable combinations of these two voltages can be used to produce primary ion beams of a desired energy spread. For example, if the ionization potential of the gas amounts to about 13 ev (such as in water or methane) a beam of primary parent ions having kinetic energies between 3 and 5 ev can be produced by setting E_e equal to 10 and E_T equal to 5 volts. Other combinations of E_T and E_e, as indicated in Fig. 5 and 6, have been used to produce beams of faster ions with a defined spread in energy. A drawback of this method is the unknown changes in the intensity of the primary ion beam when the different combinations are used. However, the method may well be applied to study the intensity ratios of two secondary ions resulting from competing reactions of the same precursor such as in the comparison of charge and proton transfer reactions. The results obtained by different sets of E_T and E_e are presented by the horizontal lines in Fig. 5 and 6 the length of which corresponds to the energy spread of the primary ion beam. The secondary ionization curves in all the figures have been normalized at an E_T of 40 volts in the case of singly charged primary ions and 150 volts for doubly charged ions.

In order to obtain relative cross sections of symmetrical charge transfer processes the ratio

$$\frac{\text{current of secondary ion at } E_e=8 \text{ and } E_T=40 \text{ volts}}{\text{current of primary ion at } E_e=40 \text{ and } E_T=40 \text{ volts}}$$

has been measured relative to the similar ratio for methane[1]. This procedure assumes that the primary ion current in the Cermak–Herman operation of the ion source (i. e. $E_e=8$, $E_T=40$ volts) is proportional to the current in the more conventional operation of the source ($E_e=40$ volts). Since the primary current contained ions of kinetic energies between about 5 and 40 volts the value of the cross section obtained is an average over this range. A similar method was used to determine the cross section of unsymmetrical charge transfer reactions $B^+ + A \rightarrow B + A^+$ relative to that of the symmetrical process $A^+ + A \rightarrow A + A^+$. The compound A was at first introduced into the gas reservoir at a pressure of $40-100\,\mu$ and the currents i'^{+}_{A1} at $E_e=8$ and $E_T=40$ volts and i^{+}_{A1} at $E_e=40$ and $E_T=40$ volts were measured. After the addition of compound B up to a total pressure of $550\,\mu$ the currents i'^{+}_{A2} ($E_e=8$, $E_T=40$), i^{+}_{A2} ($E_e=40$, $E_T=40$), and i^{+}_{B2} ($E_e=40$, $E_T=40$) were determined. The ratio of the cross sections σ_{BA} and σ_{AA} of the unsymmetrical and symmetrical electron transfer processes was calculated from these data by using the relations $i'^{+}_{A1} = k\,\sigma_{AA}\,i^{2+}_{A1}$ and $i'^{+}_{A2} = k\,\sigma_{AA}\,i^{2+}_{A2} + k\,\sigma_{BA}\,i^{+}_{B2}\,i^{+}_{A2}$ from which

$$\frac{\sigma_{BA}}{\sigma_{AA}} = \left(\frac{i'^{+}_{A2}}{i'^{+}_{A1}}\,\frac{i^{+}_{A1}}{i^{+}_{A2}} - \frac{i^{+}_{A2}}{i^{+}_{A1}}\right)\cdot\frac{i^{+}_{A1}}{i^{+}_{B2}}. \qquad (1)$$

Relative cross sections of proton transfer reactions were calculated in a similar way.

Charge Transfer Processes

The relative cross sections of a few resonance transfer reactions are listed in Table 1 in order to complete the results obtained in the first part of this study. The largest cross sections found to date have been observed in methyl and ethyl iodide. Table 2 shows the relative cross sections of a number of unsymmetrical charge transfer reactions of the type $B^+ + A \rightarrow B + A^+$ where the ionization potential of the charge donor B is higher than that of the acceptor A. In the case of the transfer between atoms (reactions a and b) the cross sections are low, i. e., only about one per cent of that of the resonance process $A^+ + A \rightarrow A + A^+$. Here part of the internal energy of the reacting system has to be converted into kinetic energy of the reactants. If the charge is transferred between polyatomic molecules (reactions j – s) the ratio of the cross section σ_{BA}/σ_{AA} often is larger than unity, i. e., there is no resonance restriction for the unsymmetrical process at all. This is explained by the large number of rotational and vibrational levels in each electronic state of a polyatomic molecule so that there always exists a possibility for the two transitions $B^+ \rightarrow B$ and $A \rightarrow A^+$ to occur with equal energy differences. The charge transfer from B^+ to A may either occur as $B^+ + A \rightarrow B^* + A^+$ or $B^+ + A \rightarrow B + A^{+*}$, i. e., either the molecule B or ion A^+ (or both) will be in a higher vibrational level after the interaction. In a few cases in Table 2, the unsymmetrical charge transfer $B^+ + A$ occurs faster than both resonance processes $B^+ + B$ and $A^+ + A$. Typical examples are the reactions $(H_2^+ + H_2O)$ and $(H_2O^+ + C_6H_6)$. A comparison of the relative cross sections in Table 2 with those of the resonance processes listed in Table 1 and Table 1 of the first part[1] shows that $(H_2^+ + H_2O)$ is 4 times faster than $(H_2O^+ + H_2O)$ and 10 times faster than $(H_2^+ + H_2)$, while $(H_2O^+ + C_6H_6)$ is 1.6 or 5 times faster than the resonance transfers in benzene and water, respectively. No correlation between the cross section and difference in the ionization potentials of the reacting molecules seems to exist in the data of Table 2. Several reactions between atoms of the noble gases and molecules are also shown in this table (reactions c – i). The cross section often is markedly lower than that of the resonance process as is illustrated by the reactions between nitrogen and krypton or xenon, respectively. In other cases, such as the charge transfer from argon or krypton to water the cross sections become comparable with those of the resonance processes. It appears, therefore, that resonance restrictions can occasionally be severe when the charge is transferred between an atom and a molecule.

Ion	Relative Cross Section
CH_4^+	(1)
CD_4^+	1.0
$CD_2H_2^+$	1.0
H_2^+	1.7
CO_2^+	4.3
N_2^+	5.5
n-$C_3H_8^+$	3.9
n-$C_3H_6^+$	7.4
CH_3I^+	47
$C_2H_5I^+$	68

Table 1. Relative Cross Sections of Some Resonance Charge Transfer Reactions of the Type $A^+ + A \rightarrow A + A^+$.

No.	B	A	IP(B)-IP(A)*	σ_{BA}/σ_{AA}	Reaction Partners
a	Ar	Kr	1.7	0.02	atom-atom
b	Kr	Xe	1.8	0.005	
c	N_2	Kr	1.6	0.06	atom-molecule
d	N_2	Xe	3.4	0.12	
e	H_2	Kr	1.4	0.47	
f	H_2	Xe	3.2	0.50	
g	Ar	H_2O	3.1	1.3	
h	Kr	H_2O	1.4	1.3	
i	H_2O	Xe	0.5	0.7	
j	N_2	H_2O	3.0	1.8	molecule-molecule
k	H_2	H_2O	2.8	4.0	
l	C_2H_2	CS_2	1.3	0.32	
m	H_2O	CS_2	2.5	0.48	
n	H_2O	C_2H_2	1.2	1.0	
o	CH_4	C_2H_6	1.2	1.2	
p	C_2H_2	C_2H_4	0.9	1.4	
q	C_6D_6	C_6H_5Cl	0.4	1.5	
r	H_2O	C_6H_6	3.4	1.6	
s	CS_2	C_6D_6	0.9	1.7	

* Values of the ionization potentials taken from reference [3].

Table 2. Charge Transfer Reactions of the Type $B^+ + A \rightarrow B + A^+$ where $IP(B) > IP(A)$.

Fig. 1 shows how the shape of the secondary ionization efficiency curve of the $C_2H_2^+$ ion from acetylene is affected by the unsymmetrical charge transfer $H_2O^+ + C_2H_2 \rightarrow H_2O + C_2H_2^+$ when water is present. $C_2H_2^+$ appears at $E_e + E_T = 11.5$ volts in pure acetylene, i. e., at the ionization potential of acetylene. The $C_2H_2^+$ ion observed in pure acetylene is, therefore, formed by the reaction $C_2H_2^+ + C_2H_2 \rightarrow C_2H_2 + C_2H_2^+$. H_2O^+ appears in pure water at $E_e + E_T = 13.0$ and has to be attributed to the reaction $H_2O^+ + H_2O \rightarrow H_2O + H_2O^+$. $C_2H_2^+$ appears at 11.5 volts in a mixture since the resonance process

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[3] F. H. Field and J. L. Franklin, Electron Impact Phenomena, Academie Press, Inc. Publ., New York 1957.

can still occur. However, at higher voltages the process $H_2O^+ + C_2H_2 \rightarrow H_2O + C_2H_2^+$ contributes to the formation of $C_2H_2^+$. This causes the secondary ionization efficiency curve of $C_2H_2^+$ to run between the curves of $C_2H_2^+$ and H_2O^+ formed in the pure compounds.

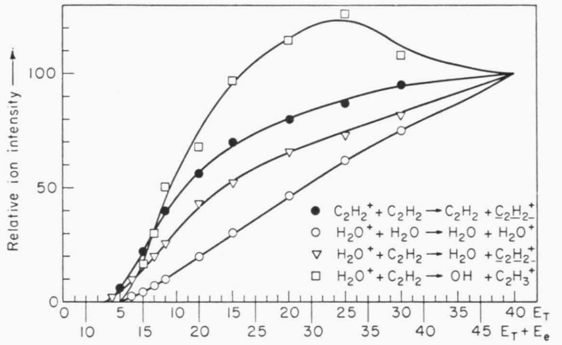

Fig. 1. Secondary ionization efficiency curves of $C_2H_2^+$ and H_2O^+ in pure acetylene and water (●, ○) and of $C_2H_2^+$ and $C_2H_3^+$ (▽, □) in a mixture of acetylene and water (1 : 4).

A number of unsymmetrical charge transfer reactions in which $IP(B)$ is lower than $IP(A)$ are listed in Table 3. In general, the cross sections are very much lower than those of the resonance processes since in order to satisfy the energetics, part of the kinetic energy of the ion has to be converted into internal energy of the electronic system of A.

No.	B	A	$IP(B) - IP(A)$	σ_{BA}/σ_{AA}	Reaction Partners
a	Kr	Ar	− 1.7	0.03	atom-atom
b	Xe	Kr	− 1.8	0.08	
c	Kr	N_2	− 1.6	0.02	atom-molecule
d	Xe	N_2	− 3.4	0.04	
e	Xe	H_2O	− 0.4	0.3	
f	H_2O	Kr	− 1.4	0.1	
g	H_2O	Ar	− 3.1	< 0.001	
h	C_2H_2	Xe	− 0.7	0.1	
i	H_2O	N_2	− 3.0	< 0.001	molecule-molecule
j	C_6H_6	H_2O	− 3.4	0.09	
k	C_6D_6	CS_2	− 0.9	0.16	
l	CS_2	C_2H_2	− 1.3	0.35	
m	CS_2	H_2O	− 2.5	0.18	
n	C_2H_2	H_2O	− 1.2	0.08	
o	H_2O	CH_4	− 0.4	5.0	

Table 3. Charge Transfer Reactions of the Type $B^+ + A \rightarrow B + A^+$ where $IP(B) < IP(A)$.

In all cases where the calculated cross section σ_{BA} amounts to only a few per cent of σ_{AA} ions observed might be mainly due to simple scattering of primary ions. Relatively high cross sections, however, have been observed in the transfer from carbon disulfide to acetylene and to water as well as from xenon to water. These large cross sections are explained by the excess energy of the primary ion which makes these processes exothermic. Several reactions of an excited long-lived state of the CS_2^+ ion ($AP = 13.3$) have recently been observed[4, 5]. Similarly, the $^2P_{3/2}$ level of the doublet ground state of Xe^+ (1.3 ev of excess energy) may be responsible for the fast charge transfer to water.

Reaction o in Table 3, which describes the charge transfer from water to methane, occurs as a remarkable exception to the generalizations given above. The cross section is 5 times higher than that of the resonance transfer in methane, although this large factor should not be over-emphasized since the transfer in methane is relatively low (Table 1). The cross section of reaction o, however, is still about as large as that of the process $H_2O^+ + H_2O \rightarrow H_2O + H_2O^+$. It seems surprising that the largest ratio of σ_{BA}/σ_{AA} has been observed for a reaction that is endothermic if the ground level of the primary ion is involved. Various values of the ionization potential of water (12.6 − 13.1 volts) and methane (12.8 − 13.8) have appeared in the literature[3]. The most probable values[3] of the two potentials lead to the conclusion that reaction o must be endothermic. If we do not want to question this conclusion the only alternative explanation of the large cross section consists in a water ion entering reaction o with excess energy. It may be of interest that the charge transfer $CH_4^+ + H_2O \rightarrow CH_4 + H_2O^+$ occurs with a cross section about 10 times smaller than the reverse reaction.

Dissociative Charge Transfer from Doubly Charged Ions

Dissociations following the transfer of the charge from a singly charged ion to a molecule have been reported by Cermak and Herman[2] as well as by Lindholm[6]. We observed several reactions in which

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[4] V. Cermak and Z. Herman, J. Chim. Phys. **57**, 717 [1960].

[5] A. Henglein, Z. Naturforschg. **17 a**, 37 [1962].

[6] E. Lindholm, Proc. Roy. Soc., Lond. A **66**, 1068 [1953]; Ark. Fys. **18**, 219 [1960]. — H. v. Koch u. E. Lindholm, Ark. Fys. **19**, 123 [1961].

one positive charge from a doubly charged atom or molecule was transferred to a neutral molecule and in which the secondary ion subsequently dissociated. The first example of this reaction type has been found in a mixture of krypton and water. It was mentioned in the earlier paper that OH^+ is not present in the secondary mass spectrum of water[1]. However, in a mixture of krypton and water OH^+ appears at $E_T + E_e = 38$ volts, i. e., at the appearance potential of Kr^{++}. The following process is, therefore, postulated:

$$Kr^{++} + H_2O \rightarrow Kr^+ + OH^+ + H . \qquad (2)$$

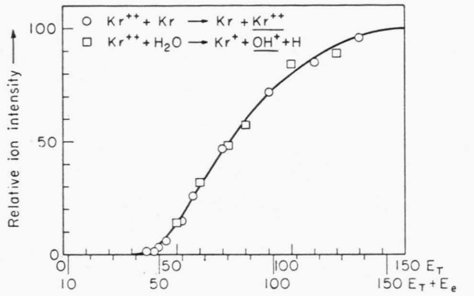


Fig. 2. Secondary ionization efficiency curves of Kr^{++} and OH^+ in a 1 : 1 mixture of krypton and water vapor.

As can be seen from Fig. 2, the secondary ionization efficiency curves of OH^+ and Kr^{++} have the same shape. Kr^{++} ions which are observed under Cermak–Herman conditions in the ion source result from the resonance process

$$Kr^{++} + Kr \rightarrow Kr + Kr^{++} \qquad (3)$$

which competes with reaction (2). The current ratio OH^+/Kr^{++} was found to be equal to 1 : 4,3, i. e., the resonance process has a much larger cross section than the charge transfer from Kr^{++} to water. OH^+ has also been found as a secondary ion in a mixture of nitrogen and water. In this case, N_2^{++} is the precursor:

$$N_2^{++} + H_2O \rightarrow N_2^+ + OH^+ + H . \qquad (4)$$

If the primary step of reaction (2) consists of

$$Kr^{++} + H_2O \rightarrow Kr^+ + (H_2O^+)^* \qquad (5)$$

the water ion formed should have a total energy of 24.6 ev, i. e., the difference in the second and first ionization potentials of krypton. Since the appearance potentials of OH^+ and O^+ from water amount to only $18-19$ volts the excited water ion formed by reaction (5) is expected to dissociate readily.

As already reported[1] the resonance process

$$NO^{++} + NO \rightarrow NO + NO^{++} \qquad (6)$$

occurs with a low cross section. Reactions (7) and (8)

$$NO^{++} + NO \rightarrow NO^+ + N^+ + O \qquad (7)$$

$$\rightarrow NO^+ + N + O^+ \qquad (8)$$

must also be postulated since the secondary ions N^+ and O^+ have been found to appear at the second ionization potential of nitrous oxide (~ 42 volts). The intensity ratio $NO^{++} : O^+ : N^+$ was found to be equal to 1 : 5 : 9 which shows that the resonance process (6) occurs less frequently than the dissociative charge transfer reactions (7) and (8). If the primary step of (7) and (8) is

$$NO^{++} + NO \rightarrow NO^+ + NO^{+*} \qquad (9)$$

the secondary ions resulting from the dissociation of the highly excited NO^+ ion could not be observed since their kinetic energy would be equal to about 12 ev (about 6 ev each), i. e., to the difference $AP(NO^{++}) - AP(NO^+) - AP(N^+ \text{ or } O^+)$ where $AP(N^+ \text{ or } O^+)$ is the appearance potential of N^+ or O^+ from NO. In order to explain why these ions can be observed it must be postulated that the NO^{++} ion captures the electron into a high lying electronic orbital and thus itself absorbs a large fraction of the excitational energy. The excess kinetic energy $AP(NO^{++}) - AP(NO^+)$ is therefore shared by either singly charged NO^+ ions formed in reaction (9). The higher frequency of the charge transfer (9) followed by (7) or (8) than that of the resonance double charge transfer (6) is explained by the large number of rotational and vibrational levels available in each of the NO ions and which makes reaction (9) resonance possible with respect to the energies involved in the transitions $NO^{++} \rightarrow NO^{+*}$ and $NO \rightarrow NO^{+*}$.

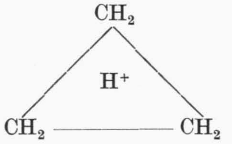
Similar results have been obtained in carbon dioxide where the secondary ions C^+, O^+, and CO^+ first appear at $E_T + E_e$ equal to about 40 volts. Their intensity ratio at $E_T = 150$ volts amounts to 1 : 4 : 8. They apparently result from dissociations as a consequence of the reaction

$$CO_2^{++} + CO_2 \rightarrow CO_2^{+*} + CO_2^{+*}.$$

Only traces of the CO_2^{++} ion from the double charge transfer $CO_2^{++} + CO_2$ could be observed. The C^+ ion was the only secondary ion found in carbon monoxide. Its formation is described by $CO^{++} + CO \rightarrow CO^{+*} + C^+ + O$.

Proton and Hydride Ion Transfer

Protonated molecules formed by the process $RH^+ + RH \rightarrow R + RH_2^+$ have been observed in several hydrocarbons [1]. In the aliphatic series, CH_5^+ is formed with a large cross section in methane, while $C_2H_7^+$ could hardly be detected in ethane [1]. No protonated molecule has been found in n-propane and cyclohexane. The substitution of H atoms in methane by larger groups R apparently makes the formation of the protonated molecule more difficult. This does not necessarily mean that the proton transfer becomes endothermic but more likely that the reaction has a low steric factor due to the increased complexity of the higher hydrocarbons. A proton transfer with a rather large cross section has been observed in cyclopropane. This was not unexpected since the cyclopropane ring is known to be easily cationated and the $C_3H_7^+$ ion is one of the most abundant ions in the mass spectra of nearly all aliphatic hydrocarbons [7]. Its structure may be described by



where the proton is embedded in a molecular orbital formed by the overlap of the three sp^2 orbitals protruding from the three carbon atoms [8]. Fig. 3 shows the secondary ionization efficiency curves of $C_3H_6^+$ and $C_3H_7^+$ in cyclopropane as well as the current ratio $i_{C_3H_7^+}/i_{C_3H_6^+}$. Since both ions appear at $E_T + E_e$ equal to $IP(C_3H_6^+)$ the parent ion of cyclopropane must be a precursor of both secondary ions. The current ratio increases with decreasing E_T as has been found in many other comparisons of proton and charge transfer reactions [1]. However, at low values of E_T the ratio decreases again. This can be understood if $C_3H_7^+$ is not only formed by primary $C_3H_6^+$ but also by proton transfer from some other primary ion the appearance potential of which is higher than that of $C_3H_6^+$. Because of their high mass spectral abundances, the ions $C_3H_5^+$ and $C_3H_3^+$ may also be precursors of $C_3H_7^+$.

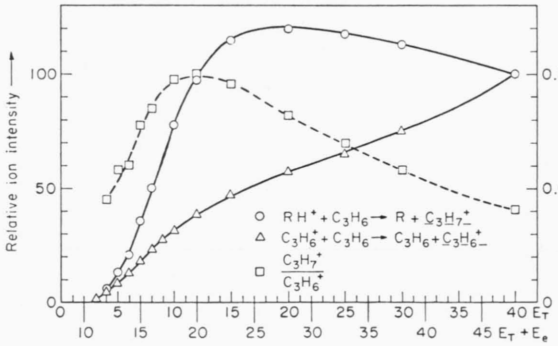


Fig. 3. Secondary ionization efficiency curves of $C_3H_6^+$ and $C_3H_7^+$ in cyclopropane as well as the current ratio $i_{C_3H_7^+}/i_{C_3H_6^+}$ as function of E_T.

Proton transfer processes of rather large cross sections have been observed in water-acetylene and water-methane mixtures. The reaction $H_2O^+ + C_2H_2 \rightarrow HO + C_2H_3^+$ is faster than the proton transfer between two acetylene molecules. $C_2H_3^+$, therefore, appears at $IP(H_2O^+)$ in a mixture in which acetylene is present at low concentration as can be seen from Fig. 1. Fig. 4 illustrates that proton transfer in mixtures of water and methane can occur in both directions:

$$H_2O^+ + CH_4 \rightarrow OH + CH_5^+, \qquad (10)$$

$$CH_4^+ + H_2O \rightarrow CH_3 + H_3O^+. \qquad (11)$$

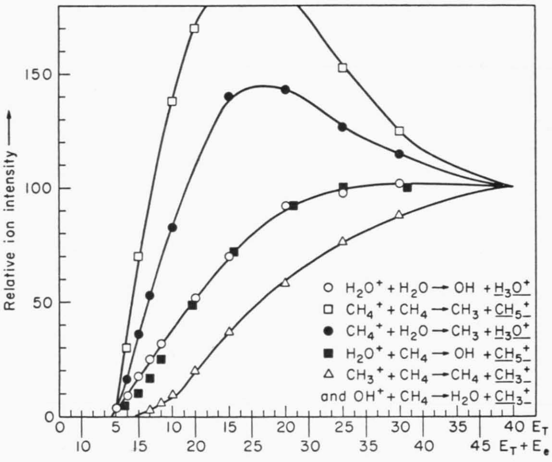


Fig. 4. Secondary ionization efficiency curves in pure methane (□) and pure water (○) and in mixtures of methane and water (1 : 5—■, △) (5 : 1—●).

CH_5^+ is mainly formed by reaction (10) if methane is present at low concentration. In that case, its secondary ionization efficiency curve is completely different from that obtained in pure methane. The

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[7] P. N. RYLANDER and S. MEYERSON, J. Amer. Chem. Soc. **78**, 5799 [1956].

[8] J. D. ROBERTS, C. C. LEE, and W. H. SAUNDERS, J. Amer. Chem. Soc. **76**, 4501 [1954].

shape of its curve resembles that of the H_3O^+ ion in pure water. On the other hand, if methane is the major component of the mixture the curve of H_3O^+ is very similar to that of CH_5^+ in pure methane. The cross section of reaction (11) has been calculated to be about twice as large as that of reaction (10) at a value of $E_T = 40$ volts. Reaction (11) is as fast as the proton transfer in pure water under this condition. It has not been possible to detect reaction (10) if the more conventional techniques are applied in studies on ion-molecule reactions [9]. Reaction (11), however, has been observed by LAMPE et al. although it was not possible to identify the precursor ion [10].

Other proton transfer reactions have been observed in the present work in acetylene (transfer in ethylene has previously been reported [1]) and in carbon disulfide-water mixtures. Attempts to detect $C_6H_7^+$ in benzene and in benzene-water mixtures have not been fruitful.

Two examples of hydride ion transfer reactions are also illustrated by Fig. 4. The secondary CH_3^+ ion in methane has been attributed to the process

$$CH_3^+ + CH_4 \rightarrow CH_4 + CH_3^+ \qquad (12)$$

since this takes into account that the secondary appearance potential of CH_3^+ is equal to $AP(CH_3^+)$ from methane and that relatively little kinetic energy is transferred to the secondary ion [1]. This process can still be seen in a methane-water mixture since CH_3^+ appears at $E_T + E_e = 14.7$ volts, i. e., at $AP(CH_3^+)$. The ionization efficiency curve of CH_3^+ in Fig. 4 shows a rather sharp break at $E_T + E_e = 18.5$ volts. Since this agrees with $AP(OH^+)$ from water it is postulated that primary OH^+ ions contribute to the CH_3^+ formation at higher values of E_T:

$$OH^+ + CH_4 \rightarrow H_2O + CH_3^+. \qquad (13)$$

This hydride transfer process occurs with a cross section 7 times larger than that of reaction (12) at $E_T = 40$ volts.

Isotope Effects

The ion intensity ratios CH_5^+/CH_4^+ and CD_5^+/CD_4^+ in pure methane and methane-d 4, respectively, are plotted as a function of the voltage E_T in Fig. 5 (E_e constant at 8 volts). These ratios have also been determined at the various combinations of E_e and E_T listed in the figure. The results of these measurements are presented by the horizontal lines the lengths of which indicate the spread in the kinetic energy of the primary ion beams. The decrease in the ratio CH_5^+/CH_4^+ with increasing E_T has been attributed [1] to the stronger discrimination of the protonated molecule over the product of the charge transfer reaction. Since protonated molecules can still be observed at values of E_T larger than 20 volts it has been concluded that the transfer of a proton does not occur via a completely inelastic collision complex. If a complex is formed the CH_5^+ ion would possess a large amount of kinetic energy in the direction of the primary ion. A stripping model has therefore been postulated to describe the reaction at least at higher kinetic energies [1].

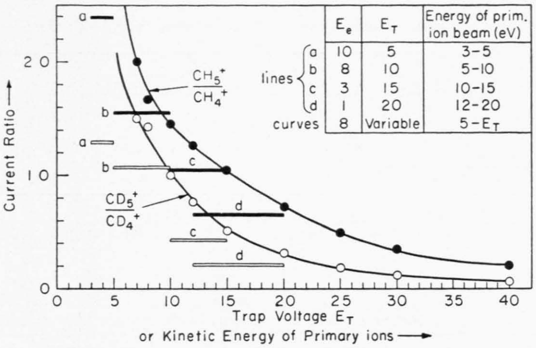

Fig. 5. Secondary ion current ratios in light and heavy methane as a function of E_T.

If E_e is kept constant at 8 volts the primary ion beam will always contain a tail of low energy ions at higher values of E_T. It could therefore be argued that the secondary ions observed at higher values of E_T exclusively result from reactions of that low energy component of the primary beam. In this respect, the experiment carried out with the voltage combination No. d in Fig. 5 may be emphasized since only primary ions of rather high kinetic energy (between 12 and 20 ev) have been used here. The fact that the CH_5^+ ion could still be observed clearly shows that mass transfer in an ion-molecule reaction is still possible even if the relative kinetic energy exceeds the strength of the chemical bonds in the reactants. The CH_5^+/CH_4^+ curve runs through the right hand sides of the horizontal lines in Fig. 5. This result is not unexpected, for most of the prima-

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[9] F. W. LAMPE and F. H. FIELD, J. Amer. Chem. Soc. **79**, 4244 [1957].

[10] F. W. LAMPE, F. H. FIELD and J. L. FRANKLIN, J. Amer. Chem. Soc. **79**, 6132 [1957].

ry ions will have kinetic energies near to the upper limit of the energy spread. Apparently, the contribution of the low energy tail in the primary ion beam to the observed ratio CH_5^+/CH_4^+ is not significant.

Fig. 5 shows that the current ratio CH_5^+/CH_4^+ is larger than the ratio CD_5^+/CD_4^+. This isotope effect is more pronounced at higher values of E_T, i. e., at higher kinetic energies of the primary ions. Since the cross section of the symmetrical charge transfer in methane is not affected by the substitution of H-atoms by deuterium (Table 1) there must be an isotope effect in the formation of the protonated and deuteronated molecules, respectively. Apparently, the process

$$CD_4^+ + CD_4 \rightarrow CD_3 + CD_5^+ \qquad (14)$$

either has a lower cross section than

$$CH_4^+ + CH_4 \rightarrow CH_3 + CH_5^+ \qquad (15)$$

or the Cermak–Herman method more effectively discriminates against CD_5^+ than CH_5^+ ions. Experiments have also been carried out to study this isotope effect under the more conventional operation of the ion source, i. e., at E_e equal to 70 volts. The cross section of the proton transfer in methane was found to be 1.1 – 1.2 times larger than that of the deuteron transfer in methane-d 4. This isotope effect is small and not comparable to the large effect obtained in the Cermak–Herman operation where a factor of 4 is involved (at $E_T = 40$ volts).

Similar isotope effects have been observed when a proton or deuteron is transferred in other compounds. The reaction

$$CH_4^+ + CD_4 \rightarrow CH_3 + CD_4H^+ \qquad (16)$$

in a mixture of methane and methane-d 4 was found to occur with the same cross section as the proton transfer in pure methane. The current ratio H_3O^+/H_2O^+ in water is shown by Fig. 6 to be higher than the ratio D_3O^+/D_2O^+ in heavy water. In the present work no isotope effect at all could be observed in water when these ratios were measured under the conventional conditions in the ion source. Lampe et al.[10] report that D_3O^+ formation is slightly faster than that of H_3O^+. In the case of methane-d2, proton and deuteron transfer reactions could simultaneously be observed. As can be seen from Fig. 7, the intensity of the deuterated molecule again is smaller than that of the protonated one. The intensities of $CD_2H_3^+$ and $CD_3H_2^+$ wer found to be equal under the conventional conditions in the ion source. As in methane itself the isotope effects in water and methane-d_2 became more pronounced as the kinetic energy of the primary ion was increased.

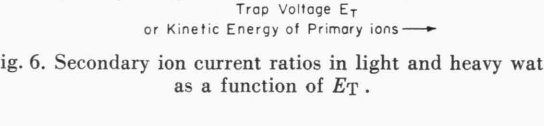

Fig. 6. Secondary ion current ratios in light and heavy water as a function of E_T.

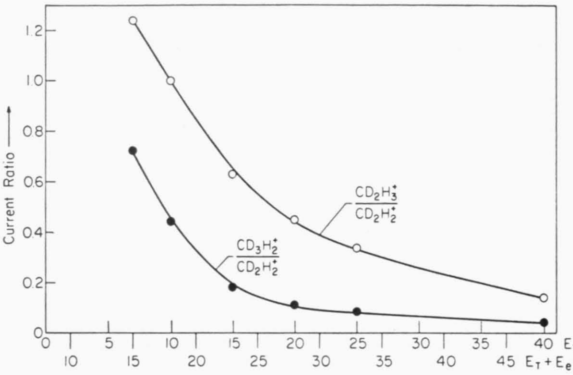

Fig. 7. Secondary ion current ratios in methane-d_2 as a function of E_T.

An isotope effect has also been found in the hydride transfer reaction (12) in methane which leads to secondary CH_3^+ ions. The methyl ion is much more abundant in the secondary mass spectrum of methane than of methane-d 4 while only a slight difference in the intensities of these ions exists in the regular spectra of these compounds.

Theory

Although the experimental results obtained by the simple Cermak–Herman method are not sufficiently sophisticated to justify any detailed theoretical explanation of the isotope effects, a few brief remarks on what might be expected from our present knowledge of the mechanism of ion-molecule reactions shall be made here. If a completely inelastic collision takes place the intermediate complex will move with the kinetic energy $E_p(M_1/M_1+M_2)$ in the direction o the primary ion and will have internal rotational plus vibrational energy with amount equal to $E_p(M_2/M_1+M_2)$. E_p is the kinetic energy of the primary ion, the neutral molecule is regarded to be at rest before the collision, and M_1 and M_2 are the masses of the ion and molecule. The complex will dissociate after a lifetime much longer than the time of an atomic vibration ($\sim 10^{-13}$ sec). The secondary ion carries the kinetic energy

$$E_s = E_p \frac{M_1(M_2+m)}{(M_1+M_2)^2} \tag{17}$$

in the direction of the primary ion, if m is the mass of the transferred proton or deuteron, respectively. Where M_1 and M_2 are similar and m very much smaller, E_s will amount to about $\frac{1}{4}$ E_p in both transfer processes. Thus the substitution of H by D in the reacting species is not expected to have any significant influence on either the formation of the intermediate complex or on the kinetic energy of the secondary ion if the reaction goes through a completely inelastic collision complex. As mentioned in part I, a secondary ion from such a collision can hardly be observed since its kinetic energy generally is much too high.

Isotope effects with respect to both the kinetic energy and the cross section for formation of the secondary ion have to be expected if the reaction takes place as a stripping process. In an ideal stripping reaction the neutral molecule is hit by only the proton or deuteron in the primary ion. Since the kinetic energy of the captured hydrogen ion is equal to $E_p(m/M_1)$ the kinetic energy of the secondary ion will amount to

$$E_s = E_p \frac{m^2}{M_1(m+M_2)} \tag{18}$$

i. e., it will depend on the transferred mass m. An ion resulting from the transfer of a deuteron will therefore have more kinetic energy perpendicular to the direction of analysis. However, the absolute values of E_s calculated from eq. (18) are so small that no significant discrimination of protonated as well as deuteronated molecules is expected at primary ion energies below 40 eV.

It is tentatively postulated that the transfer of a proton occurs through a lose collision complex

$$\mathrm{R} \cdots\cdots \mathrm{H}^+ \cdots\cdots M_2$$

in which the proton carries out a number of oscillations until it is finally handed over to the molecule. At low kinetic energies, the collision time is much longer than the time required for one atomic vibration. Kinetic energy can therefore readily be transferred from the heavy mass of the incoming ion to the heavy mass of the molecule, i. e. the complex acquires the properties of a completely inelastic collision complex. At higher energies, the number of oscillations becomes smaller which means an approach to the ideal stripping model. As long as a rather longlived complex is formed, no significant isotope effect is expected. This explains why rather small effects have been found at low kinetic energies. The failure to detect any isotope effects in the conventional operation of the ion source is probably due to the fact that most of the secondary ions are formed here by primaries of rather low energies. However, if the time of the collision becomes comparable with the time of an atomic vibration, the difference in the vibrational periods of a proton and deuteron will become important. The deuteron is expected to be transferred with a lower rate than a proton, the factor involved being of the order of $\sqrt{2}$. An additional isotope effect is expected in the case of a stripping mechanism, since most of the collisions of the transferred proton or deuteron will eccentrically occur. It is known from some diatomic systems that the potential curve possesses a maximum at a large distance, if rotational energy is present in the system. This maximum may act as a barrier for the capture of a particle in an eccentric collision. If the transfers of a proton and a deuteron are compared under comparable conditions, i. e. at the same kinetic energy of the primary ion and at the same collision parameter, the deuteron will enter the reaction with twice as much rotational energy as the transferred proton. The barrier is therefore expected to be higher for the transfer of the deuteron, i. e. an isotope effect larger than by a factor of $\sqrt{2}$ is predicted from the ideal stripping model.