one Reihe von früheren Arbeiten 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 Chlorotierung erniedrigt; neuerdings fanden wir auch, daß sie durch eine Ti-Dotierung erhöht wird;
4. es gelang, einen quantitativen Zusammenhang zwischen der Leitfähigkeit und der Kornoberfläche pro Volumeneinheit herzuleiten.


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

\[
\text{Kr}^+ + \text{H}_2\text{O} \rightarrow (\text{Kr})^+ + (\text{H}_2\text{O})^- \rightarrow \text{OH}^+ + \text{H}
\]

\[
\text{NO}^+ + \text{NO} \rightarrow (\text{NO})^+ + (\text{NO})^- \rightarrow \text{N}^+ + \text{O}
\]

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 insight 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, the method of Cermak and Herman 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-
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 (\(<2.5 \text{ ev}\)) or perpendicular to this direction and the direction of analysis (\(<0.34 \text{ ev}\)). 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 $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_3\text{O}^+$ 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 $eE_T$ where $E_T$ is the voltage between the chamber and the trap. The lower energy limit of the primary ion beam is equal to $e(Ap - E_o)$ where $Ap$ is the appearance potential of the primary ion and $E_o$ the voltage between the filament and the ionization chamber. If $E_o$ 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 $E_o$ 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 $E_o$ equal to 10 and $E_T$ equal to 5 volts. Other combinations of $E_T$ and $E_o$, 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 $E_o$ 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

- current of secondary ion at $E_o = 8$ and $E_T = 40$ volts
- current of primary ion at $E_o = 40$ and $E_T = 40$ 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. $E_o = 8$, $E_T = 40$ volts) is proportional to the current in the more conventional operation of the source ($E_o = 40$ 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 $E_o = 8$ and $E_T = 40$ volts and $i_{A1}^+$ at $E_o = 40$ and $E_T = 40$ volts were measured. After the addition of compound B up to a total pressure of 550 $\mu$ the currents $i_{A2}^+$ ($E_o = 8$, $E_T = 40$), $i_{A2}^+$ ($E_o = 40$, $E_T = 40$), and $i_{B2}^+$ ($E_o = 40$, $E_T = 40$) were determined. The ratio of the cross sections $\sigma_{BA}$ and $\sigma_{AA}$ of the unsymmetrical and symmetrical electron transfer processes was calculated from these data by using the relations $i_{A1}^+ = k \sigma_{AA} i_{A1}^+$ and $i_{A2}^+ = k \sigma_{AA} i_{A2}^+ + k \sigma_{BA} i_{B2}^+ i_{A2}^+$ from which

\[
\frac{\sigma_{BA}}{\sigma_{AA}} = \frac{(i_{A2}^+ i_{A1}^+ - i_{A2}^+ i_{A1}^+) \cdot i_{A1}^+}{i_{B2}^+}.
\]

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 \( \sigma_{BA} / \sigma_{AA} \) 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 \( (H^+ + H_2O) \) 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 shows that \( (H^+ + H_2O) \) 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 3 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.

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

<table>
<thead>
<tr>
<th>No.</th>
<th>B</th>
<th>A</th>
<th>( IP(B)/IP(A) ) *</th>
<th>( \sigma_{BA}/\sigma_{AA} )</th>
<th>Reaction Partners</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Ar</td>
<td>Kr</td>
<td>1.7</td>
<td>0.02</td>
<td>atom-atom</td>
</tr>
<tr>
<td>b</td>
<td>Kr</td>
<td>Xe</td>
<td>1.8</td>
<td>0.005</td>
<td>atom-molecule</td>
</tr>
<tr>
<td>c</td>
<td>N(_2)</td>
<td></td>
<td>1.6</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>N(_2)</td>
<td></td>
<td>3.4</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>H(_2)</td>
<td></td>
<td>1.4</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>H(_2)</td>
<td></td>
<td>3.2</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>Ar</td>
<td>H(_2O)</td>
<td></td>
<td>3.1</td>
<td>1.3</td>
</tr>
<tr>
<td>h</td>
<td>Kr</td>
<td>H(_2O)</td>
<td></td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>i</td>
<td>H(_2O)</td>
<td>Xe</td>
<td>0.5</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>j</td>
<td>N(_2)</td>
<td></td>
<td>3.0</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>H(_2)</td>
<td></td>
<td>2.8</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>l</td>
<td>C(_2H_2)</td>
<td></td>
<td>2.5</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>H(_2O)</td>
<td></td>
<td>1.2</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>C(_2H_2)</td>
<td></td>
<td>1.2</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>o</td>
<td>C(_2H_2)</td>
<td></td>
<td>0.9</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>C(_6D_6)</td>
<td></td>
<td>0.4</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>q</td>
<td>H(_2O)</td>
<td></td>
<td>3.4</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>r</td>
<td>C(_6D_6)</td>
<td></td>
<td>0.9</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

* Values of the ionization potentials taken from reference 4.

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

can still occur. However, at higher voltages the process $\text{H}_2\text{O}^+ + \text{C}_2\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_2^+$ contributes to the formation of $\text{C}_2\text{H}_2^+$. This causes the secondary ionization efficiency curve of $\text{C}_2\text{H}_2^+$ to run between the curves of $\text{C}_2\text{H}_2^+$ and $\text{H}_2\text{O}^+$ formed in the pure compounds.

In all cases where the calculated cross section $\sigma_{\text{BA}}$ amounts to only a few per cent of $\sigma_{\text{AA}}$ 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 $\text{CS}_2^+$ ion ($AP = 13.3$) have recently been observed $^4$. Similarly, the $^3\text{P}_{3/2}$ level of the doublet ground state of $\text{Xe}^+$ (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 $\text{H}_2\text{O}^+ + \text{H}_4\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O}^+$. It seems surprising that the largest ratio of $\sigma_{\text{BA}}/\sigma_{\text{AA}}$ 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 $\text{CH}_4^+ + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{H}_2\text{O}^+$ occurs with a cross section about 10 times smaller than the reverse reaction.

**Dissociative Charge Transfer from Doubly Charged Ions**

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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 $E_T + E_o = 38$ volts, i.e., at the appearance potential of Kr$^{++}$. The following process is, therefore, postulated:

$$\text{Kr}^{++} + \text{H}_2\text{O} \rightarrow \text{Kr}^+ + \text{OH}^- + \text{H}. \quad (2)$$

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

$$\text{Kr}^{++} + \text{Kr} \rightarrow \text{Kr} + \text{Kr}^{++} \quad (3)$$

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:

$$\text{N}_2^{++} + \text{H}_2\text{O} \rightarrow \text{N}_2^+ + \text{OH}^- + \text{H}. \quad (4)$$

If the primary step of reaction (2) consists of

$$\text{Kr}^{++} + \text{H}_2\text{O} \rightarrow \text{Kr}^+ + (\text{H}_2\text{O})^+ \quad (5)$$

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

$$\text{NO}^{++} + \text{NO} \rightarrow \text{NO} + \text{NO}^{++} \quad (6)$$

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

$$\text{NO}^{++} + \text{NO} \rightarrow \text{NO}^+ + \text{N}^+ + \text{O} \quad (7)$$
$$\rightarrow \text{NO}^+ + \text{N} + \text{O} \quad (8)$$

must also be postulated since the secondary ions N$^+$ and O$^+$ have been found to appear at the second ionization potential of nitrous oxide ($\sim 42$ 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

$$\text{NO}^{++} + \text{NO} \rightarrow \text{NO}^+ + \text{NO}^{++} \quad (9)$$

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 $AP (\text{NO}^{++}) - AP (\text{NO}^+)$ where $AP (\text{N}^+$ 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 $AP (\text{NO}^{++}) - AP (\text{NO}^+)$ 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 $E_T + E_o$ 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

$$\text{CO}_2^{++} + \text{CO}_2 \rightarrow \text{CO}_2^{++} + \text{CO}_2^{++}. $$

Only traces of the CO$^+$ ion from the double charge transfer CO$^{++}_2 + \text{CO}_2$ could be observed. The C$^+$ ion was the only secondary ion found in carbon monoxide. Its formation is described by CO$^{++} + \text{CO} \rightarrow$ CO$^+$ + C$^+$ + O.
Proton and Hydride Ion Transfer

Protonated molecules formed by the process $\text{RH}^+ + \text{RH} \rightarrow \text{R} + \text{RH}_2^+$ have been observed in several hydrocarbons \(^1\). In the aliphatic series, $\text{CH}_5^+$ is formed with a large cross section in methane, while $\text{C}_6\text{H}_7^+$ 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 $\text{C}_3\text{H}_7^+$ ion is one of the most abundant ions in the mass spectra of nearly all aliphatic hydrocarbons \(^7\). Its structure may be described by

$$\text{CH}_2 \begin{array}{c} \\ H^+ \end{array} \text{CH}_2$$

where the proton is embedded in a molecular orbital formed by the overlap of the three $\text{sp}^2$ orbitals protruding from the three carbon atoms \(^8\). Fig. 3 shows the secondary ionization efficiency curves of $\text{C}_3\text{H}_6^+$ and $\text{C}_3\text{H}_7^+$ in cyclopropane as well as the current ratio $i_{\text{C}_3\text{H}_7^+}/i_{\text{C}_3\text{H}_6^+}$ as function of $E_T$.

at $E_T + E_r$ equal to $IP(\text{C}_3\text{H}_6^+)$ 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 $\text{C}_3\text{H}_7^+$ is not only formed by primary $\text{C}_3\text{H}_6^+$ but also by proton transfer from some other primary ion the appearance potential of which is higher than that of $\text{C}_3\text{H}_6^+$. Because of their high mass spectral abundances, the ions $\text{C}_3\text{H}_5^+$ and $\text{C}_3\text{H}_3^+$ may also be precursors of $\text{C}_3\text{H}_7^+$.

Proton transfer processes of rather large cross sections have been observed in water-acetylene and water-methane mixtures. The reaction $\text{H}_2\text{O}^+ + \text{C}_2\text{H}_2 \rightarrow \text{HO} + \text{C}_2\text{H}_3^+$ is faster than the proton transfer between two acetylene molecules. $\text{C}_2\text{H}_3^+$, therefore, appears at $IP(\text{H}_2\text{O}^+)$ 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:

$$\text{H}_2\text{O}^+ + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_5^+, \quad (10)$$
$$\text{CH}_4^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3 + \text{H}_3\text{O}^+. \quad (11)$$

CH$_3^+$ 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

\(^{7}\) P. N. Rylander and S. Meyerson, J. Amer. Chem. Soc. 78, 5799 [1956].

shape of its curve resembles that of the $\text{H}_3\text{O}^+$ ion in pure water. On the other hand, if methane is the major component of the mixture the curve of $\text{H}_3\text{O}^+$ is very similar to that of $\text{CH}_4^+$ 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. Reaction (11), however, has been observed by Lampe et al. although it was not possible to identify the precursor ion.

Other proton transfer reactions have been observed in the present work in acetylene (transfer in ethylene has previously been reported) and in carbon disulfide-water mixtures. Attempts to detect $\text{C}_6\text{H}_7^+$ 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 $\text{CH}_4^+$ ion in methane has been attributed to the process

$$\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_4 + \text{CH}_3^+ \quad (12)$$

since this takes into account that the secondary appearance potential of $\text{CH}_3^+$ is equal to $AP(\text{CH}_3^+)$. The ionization efficiency curve of $\text{CH}_3^+$ in Fig. 4 shows a rather sharp break at $E_T + E_c = 18.5$ volts. Since this agrees with $AP(\text{OH}^+)$ from water it is postulated that primary $\text{OH}^+$ ions contribute to the $\text{CH}_3^+$ formation at higher values of $E_T$:

$$\text{OH}^+ + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3^+ \quad (13)$$

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 $\text{CH}_5^+/\text{CH}_4^+$ and $\text{CD}_5^+/\text{CD}_4^+$ in pure methane and methane-d, respectively, are plotted as a function of the voltage $E_T$ in Fig. 5 ($E_c$ constant at 8 volts). These ratios have also been determined at the various combinations of $E_c$ 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 $\text{CH}_5^+/\text{CH}_4^+$ with increasing $E_T$ has been attributed 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 $\text{CH}_5^+$ 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.

If $E_o$ 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 $\text{CH}_5^+$ 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 $\text{CH}_5^+/\text{CH}_4^+$ 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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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

\[ \text{CD}_4^+ + \text{CD}_4 \rightarrow \text{CD}_3 + \text{CD}_5^+ \]  \hspace{1cm} (14)

either has a lower cross section than

\[ \text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_5^+ \]  \hspace{1cm} (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 Cermaak–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

\[ \text{CH}_4^+ + \text{CD}_4 \rightarrow \text{CH}_3 + \text{CD}_4\text{H}^+ \]  \hspace{1cm} (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$_3\text{O}^+$/H$_2\text{O}^+$ in water is shown by Fig. 6 to be higher than the ratio D$_3\text{O}^+$/D$_2\text{O}^+$ 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.\textsuperscript{10} report that D$_3\text{O}^+$ formation is slightly faster than that of H$_3\text{O}^+$. In the case of methane-d$_2$, proton and deuteron transfer reactions could simultaneously be observed. As can be seen from Fig. 7, the intensity of the deuteronated molecule again is smaller than that of the protonated one. The intensities of CD$_2\text{H}_3^+$ and CD$_3\text{H}_2^+$ were 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.

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 Cermaak–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 of 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 \((\sim 10^{-13} \text{ sec})\). The secondary ion carries the kinetic energy

\[
E_s = E_p \frac{M_1(M_2 + m)}{(M_1 + M_2)^2}
\]  

(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 \( \frac{1}{2} \) \( E_p \) in both transfer processes. Thus the substitution of \( \text{H} \) by \( \text{D} \) 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

\[
E_s = E_p \frac{m^2}{M_1(m + M_2)}
\]  

(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

\[ R \cdot \cdot \cdot \text{H}' \cdot \cdot \cdot M_2 \]

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.