Mass Spectrometric Studies of Chemionization by Reaction of Electronically Excited Species

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During the last few years an increasing number of studies has been carried out on a class of reactions involving the formation of ions in gases by reactions of two neutral atoms or molecules. The reaction \( \text{Ar}^* + \text{N}_2 \rightarrow \text{ArN}_2^* + e \) is typical. Recently progress has been made toward determining the rate constants of these reactions, which turn out to be in the order of \( 10^{-9} \text{ cc./molecule/sec} \). In some instances several excited states are known to take part in the reaction.

The occurrence of diatomic ions of the rare gases has been noted by several experimenters \((29, 30, 43)\), but for a number of years the exact nature of the processes leading to their formation was not understood. In 1951, Hornbeck and Molnar \((18)\) measured the appearance potentials of the homonuclear diatomic ions for all of the rare gases. Their mass spectrometer was not ideally suited to studies of mass spectra of gases at elevated pressures. The instrument had relatively poor resolving power with the result that their appearance potentials were not precise. Nevertheless, they demonstrated that the appearance potentials of the diatomic ions were in all cases 0.7 to 1.5 e. v. below the ionization potentials of the corresponding rare gas atoms. The pressure dependence in each case was found to be second order. Both of these results show that the reaction did not involve atomic ions, and Hornbeck and Molnar concluded that the reaction involved attack of an excited atom upon an atom in the ground state—i.e.

\[ \text{X}^* + \text{X} \rightarrow \text{X}_2^* + e \]  

where the asterisk signifies electronic excitation. Reactions of this kind, in which an ion is formed by the reaction of two or more neutral entities,
Table I. Appearance Potentials of

<table>
<thead>
<tr>
<th>Excited Atom, X*</th>
<th>Lowest Excitation Energy</th>
<th>Ionization Potential</th>
<th>Appearance Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>19.8</td>
<td>24.6</td>
<td>23.2 (18)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23.3 (35)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23.4 (22)</td>
</tr>
<tr>
<td>Ne</td>
<td>16.8</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>11.5</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>9.9</td>
<td>14.7</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>8.3</td>
<td>13.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.1</td>
<td></td>
</tr>
</tbody>
</table>

* $^{2}P_{3/2}$ state.

is called chemionization. Following the studies of Hornbeck and Molnar (18), various workers have studied mixtures of certain of the rare gases in an effort to ascertain whether heteronuclear diatomic ions could be formed. Thus, Pahl and Weimer (36, 37) observed HeNe$^+$ in a glow discharge but failed to find HeAr$^+$ or NeAr$^+$ in mixtures of those gases. Fuchs and Kaul (13) studied NeAr$^+$ and ArKr$^+$, and the latter was examined in greater detail by Kaul, Lauterbach, and Fuchs (21). Kaul and Taubert (22) reported ArXe$^+$ and KrXe$^+$. Munson, Franklin, and Field made a rather complete study of the diatomic ions of the rare gases taken alone and in combination (35). They found that all of the possible rare gas diatomic gas ions are formed, and they measured appearance potentials of all except HeXe$^+$, which was formed in such small amounts that an appearance potential could not be determined satisfactorily. Table I gives all of the results of these studies as well as of the appearance potentials measured for the rare gas diatomic ions from the literature. It is surprising that, considering the relatively small intensities of these ions, there has been such good agreement among the measured appearance potentials.

Before discussing these measurements it would be of interest to note the shape of a typical ionization efficiency curve for a rare gas diatomic ion (Figure 1). This curve is reminiscent of the excitation curve for optically forbidden transitions by electron impact and is quite different...
the Rare Gas Diatomic Ions in e.v.

**Potential of XY⁺ where Y is**

<table>
<thead>
<tr>
<th></th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>23.4 (35)</td>
<td>17.9 (35)</td>
<td>19.9 (35)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.6 (22)</td>
<td>19.9 (35)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>20.9 (18, 35)</td>
<td>16.8 (35)</td>
<td>16.6 (35)</td>
<td>16.0 (35)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.5 (13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.7 (35)</td>
<td>14.0 (35)</td>
<td>13.5 (22, 35)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.1 (18, 20)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.0 (35)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.2 (18, 22)</td>
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<td>12.2 (22)</td>
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<td></td>
<td></td>
<td></td>
<td>12.3 (35)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>11.2 (35)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.6 (22)</td>
</tr>
</tbody>
</table>

*²P₁/₂ state.

from the typical ionization efficiency curve for the formation of monatomic ions by electrons, also shown in Figure 1 for comparison. As will be discussed in more detail later, the diatomic ions in all cases were second order in pressure. Further, the molecular-ion formation was independent of field strength, and thus the possibility of their formation by ion-molecule reactions is eliminated. Thus, we conclude that Hornbeck and Molnar’s (18) interpretation of their observations applies broadly and that the heteronuclear diatomic ions are formed by the following generalized reaction:

\[ \text{X}^* + \text{Y} \rightarrow \text{XY}^+ + e \]  

(2)

It will be of interest to note the appearance potentials of the heteronuclear ions in Table I. In each case the appearance potential is greater than the ionization potential of the constituent atom of lowest ionization potential so that the reaction must always involve an excited state of the atom of highest ionization potential. Possible exceptions to this would be ArKr⁺, ArXe⁺, and KrXe⁺. In the case of KrXe⁺ and ArKr⁺ the appearance potential is close to the lower \( (²P₁/₂) \) state of xenon and krypton, respectively. For ArXe⁺ the appearance potential is quite close to the higher \( (²P₁/₂) \) state of xenon. If indeed, a state of the atom of lower ionization potential is involved, it must be an ionic state if the appearance potentials are correct. Since the reaction of an ion with a neutral atom would be third order in pressure and these reactions are second order, it
seems certain that the reactions leading to the formation of ArKr\(^+\) and ArXe\(^+\) are reactions of the excited argon, and that for the formation of KrXe\(^+\) involves excited krypton.

In all of the heteronuclear molecular rare gas ions the energy at which the ion appears is greater than one of its possible decomposition asymptotes. There is thus a problem of understanding why such a molecular ion should be stable. There seems no doubt that they are, and we think that Figure 2 will illustrate the reason. Consider the case of HeNe\(^+\). Presumably, the interaction of Ne\(^+\) with helium is repulsive, whereas that of He\(^+\) with Ne is attractive. However, the noncrossing rule, as illustrated in Figure 2, results in a minimum in the potential energy curve which enables the ion to exist in spite of its energy.

In Table I the HeAr\(^+\) ion has two appearance potentials. The upper one at 19.9 e. v. corresponds closely to the energy of the helium metastable atom. The ionization efficiency curve shows a sharp change in slope at this point. There is, however, a rather long tail to the curve which has a lower appearance potential at around 17.9 e. v. This occurs in an energy range for which there are no known states for either argon or helium, and it is difficult to understand how an ion with this appearance potential...
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Studies of Chemionization

is formed. This was, however, a reproducible value and presumably represented a real phenomenon. There has been some evidence by mass spectrometrists employing electron beams of narrow energy spread which suggest that there are indeed states of argon in the ionization continuum, and one of these has been identified in the neighborhood of 18 e. v. (8). Perhaps it is this state that is responsible for the lower appearance potential of HeAr⁺. A similar result is found with NeXe⁺, whose appearance potential at 16.0 volts is well above the ionization potential of xenon and definitely below the lowest state of neon. Presumably, similar considerations would apply, but there have been no excited states of xenon reported to our knowledge.

The following reactions thus appear to account for the various rare gas diatomic ions:

\[
\begin{align*}
\text{He}^* + \text{He} &\rightarrow \text{He}_2^+ + e \\
\text{He}^* + \text{Ne} &\rightarrow \text{HeNe}^* + e \\
\text{He} (2s^8) + \text{Ar} &\rightarrow \text{HeAr}^* + e \\
\text{Ar}^* + \text{He} &\rightarrow \text{HeAr}^* + e \\
\text{He}(2s^8) + \text{Kr} &\rightarrow \text{HeKr}^* + e \\
\text{Ne}^* + \text{Ne} &\rightarrow \text{Ne}_2^* + e \\
\text{Ne}(3s^9P) + \text{Ar} &\rightarrow \text{NeAr}^* + e \\
\text{Ne}(3s^9P) + \text{Kr} &\rightarrow \text{NeKr}^* + e \\
\text{Xe}^* + \text{Ne} &\rightarrow \text{NeXe}^* + e \\
\text{Ar}^* + \text{Ar} &\rightarrow \text{Ar}_2^* + e \\
\text{Ar}^* + \text{Kr} &\rightarrow \text{ArKr}^* + e \\
\text{Ar}^* + \text{Xe} &\rightarrow \text{ArXe}^* + e \\
\text{Kr}^* + \text{Kr} &\rightarrow \text{Kr}_2^* + e \\
\text{Kr}^* + \text{Xe} &\rightarrow \text{KrXe}^* + e \\
\text{Xe}^* + \text{Xe} &\rightarrow \text{Xe}_2^* + e
\end{align*}
\]

The strength of the bond in \(\text{He}_2^+\) has been estimated in various ways with results varying from 0.05 e. v. to 2.2 e. v. Recently, Regan, Browne, and Matsen (38) made a careful and apparently definitive calculation which shows \(D(\text{He}_2^+)\) to be at least 2.2 e. v. This bond strength, if correct, would suggest that the appearance potential of \(\text{He}_2^+\) should be about 22.4 e. v. In fact, as is seen in Table I, the appearance potential is about 23.2 e. v., and the question arises as to why the potential is not
lower and nearer to 22.4 e. v. The following relevant states of helium atom and their energies (in e. v.) are known (33):

\[ 2^1P, 21.22; 3^3S, 22.72; 3^1S, 22.92; 3^3P, 23.01; 3^1P, 23.09. \]

At least four of these have sufficient energy to contribute to the formation of the diatomic ion. Recently, St. John et al. (39) have studied the cross-section for excitation of various electronic states of helium by electron impact. They find that all of the relevant states except \(^1P\) states dropped to vanishingly small values at about the ionization potential of helium. The \(^1P\) states show appreciable cross sections at voltages considerably below the ionization potential; hence, one concludes that in all probability it is the large cross section for excitation of the \(^1P\) states that determine the appearance potential of the diatomic ion. Thus, the \(^3P\), the \(^3S\) and \(^3S\), while being energetically capable of reaction, are present at low energies in such small amounts as to be undetectable. The \(2^1P\) state is of too low an energy to form the diatomic ion and thus, the appearance potential is limited to the \(3^1P\) state whose energy of 23.09 e. v. above the ground state corresponds closely to the average appearance potential determined by various mass spectrometrists for the diatomic ion. States of higher energy may contribute but would not be detected at onset.

Until now the discussion has been limited to rare gases. Although they have indeed played a large part in the development of this field, several other reactions have been reported involving the rare gases with other materials and indeed, involving atoms and molecules, exclusive of the rare gases. Cermak and Herman (6) and Cermak (4) have reported several reactions of the rare gases with mercury and of excited mercury atoms with ammonia, methane, acetylene, and methanol, as well as a reaction with nitrogen in which it could not be determined which reactant was the excited entity. Typical reactions involving mercury are listed below.

\[
\begin{align*}
\text{Xe}^* + \text{Hg} & \rightarrow \text{XeHg}^+ + e \\
\text{Kr}^* + \text{Hg} & \rightarrow \text{KrHg}^+ + e \\
\text{Ar}^* + \text{Hg} & \rightarrow \text{ArHg}^+ + e \\
\text{Hg}^* + \text{H}_2\text{O} & \rightarrow \text{HgH}_2\text{O}^+ + e \\
\text{Hg}^* + \text{NH}_3 & \rightarrow \text{HgNH}_3^+ + e \\
\text{Hg}^* + \text{CH}_4 & \rightarrow \text{HgCH}_4^+ + e \\
\text{Hg}^* + \text{C}_2\text{H}_2 & \rightarrow \text{HgC}_2\text{H}_2 + e \\
\text{Hg}^* + \text{CH}_3\text{OH} & \rightarrow \text{HgCH}_4\text{O}^+ + e
\end{align*}
\]
More recently Herman and Cermak (17) have found that the reaction of argon and mercury (Reaction 20) involves the metastable state of argon.

Munson, Field, and Franklin (34) have studied reactions of certain rare gases with nitrogen and carbon monoxide, and Field and Franklin (11) have studied reactions of the rare gases with methane, acetylene, and other simple gases. The latter observed the formation, by chemionization reactions, of compounds of xenon with methane, acetylene, oxygen, and water. The former reported reactions of argon, krypton, and xenon with nitrogen and carbon monoxide. In each case it appeared to be the excited rare gas atom that attacked, although this conclusion is somewhat speculative.

Figure 2. Schematic representation for non-crossing rule for states of \( R_1R_2^+ \)

Perhaps the earliest studies of chemionization were those of Mohler et al. (31, 32) of \( \text{Cs}_2^+ \) and \( \text{Rb}_2^+ \). In these studies monochromatic radiation from line spectra were passed into the vapor of Cs or Rb, and ionization was detected at energies definitely below the ionization potential of the alkali atom in question. Similar studies employing radiation have recently been made by Lee and Mahan (27), who confirmed the results of Mohler et al. and also observed the formation of \( \text{K}_2^+ \) by chemionization.

In further studies Munson, Field, and Franklin (34) observed \( \text{N}_4^+ \) and \( \text{C}_2\text{O}_2^+ \) respectively in nitrogen and carbon monoxide. Both exhibited ionization efficiency curves having the characteristic sharp maximum a few volts above the onset for forming the product ion. From the shape of the curve it was suspected that an excitation process was involved and
thus that the ions resulted from a chemionization reaction. These ions exhibited second-order dependence on pressure, and their intensities were independent of field strength; hence, they are clearly formed by a chemionization reaction. The $N_4^+$ and $C_2O_2^+$ ions were present in rather small intensities even at 300 microns pressure. When the pressure was reduced to 70–80 microns, they could no longer be detected. If, at this pressure of nitrogen, argon was then added in approximately equal amounts, $N_4^+$ reappeared and along with it $ArN_2^+$ was observed. A pressure study showed that $ArN_2^+$ depended on the first power of the pressure of each reactant and that $N_4^+$ depended on both the first power of the argon pressure and second power of nitrogen pressure. Further, $N_4^+$ formation depended upon field strength, suggesting that an ion-molecule reaction was involved. Clearly then, the $N_4^+$ appears to have been formed from the $ArN_2^+$ ion. The appearance potentials all correspond to that of $Ar_2^+$, and indeed the $Ar_2^+$ ion is reduced as the nitrogen pressure increases. Thus, it is evident that the same states which lead to $Ar_2^+$ lead also to $ArN_2^+$. The sequence of reactions would then appear to be as follows:

$$Ar^* + Ar \rightarrow Ar_2^+ + e \quad (26)$$
$$Ar^* + N_2 \rightarrow ArN_2^+ + e \quad (27)$$
$$ArN_2^+ + N_2 \rightarrow Ar + N_4^+ \quad (28)$$

Similar considerations apply to reactions of krypton and CO.

Along similar lines Cermak (5) has reported the formation of $N_3O^+$ ion by a chemionization process involving reaction of excited $N_2$ with NO according to Reaction 29.

$$N_2^* + NO \rightarrow N_3O^+ + e \quad (29)$$

The ionization efficiency curve showed the same general shape as that for $N_4^+$, reported by Munson, Field and Franklin (34). Herman and Cermak (17) have also reported the reaction of excited CO with sodium and potassium vapors to give the ions $CONa^+$ or $COK^+$ by chemionization. Recently Keenan and Clarke (23) have reported Reaction 30.

$$H_2^* + H_2 \rightarrow H_3^+ + H + e \quad (30)$$

This was a quite surprising result since the formation of $H_3^+$ had previously been considered to arise only from the reaction:

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

Similarly, Koyano et al. (25), using photoexcitation have observed the formation in acetylene of $C_2H_3^+$ and $C_2H_2^+$ by chemionization at energies well below the ionization potential of acetylene. These ions had previously been observed only in ion-molecule reactions between $C_2H_2^+$ and $C_2H_2$. 

Margrave; Mass Spectrometry in Inorganic Chemistry
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.
Rates of Chemionization Reactions

In studies of ion-molecule reactions it is relatively simple to obtain explicit determinations of reaction rate because the mass spectrometer clearly identifies and provides quantitative analysis for both reactant and product ions. Unfortunately, in chemionization processes the reactant is not charged and, hence, cannot be observed directly. The reactant must be inferred from other observations, and its quantitative measurement must be obtained indirectly. The most obvious approach is to relate the intensity of the diatomic ion to that of the monatomic ion which cannot undergo reaction at moderate pressures. Dahler et al. (10) employed this device in studying the rates of chemionization reactions of helium, neon, and argon to form the diatomic ions. They considered the reaction mechanism to be as follows.

\[ \text{Ar} + e \rightarrow \text{Ar}^* + e \]  \hspace{1cm} (31)

\[ \text{Ar} + e \rightarrow \text{Ar}^+ + 2e \]  \hspace{1cm} (32)

\[ k_u = \frac{1}{\tau_u} \]  \hspace{1cm} (33)

\[ \text{Ar}^* \rightarrow \text{Ar} + h\nu \]  \hspace{1cm} (34)

\[ k_r \]  \hspace{1cm} (35)

\[ \text{Ar}^* + \text{Ar} \rightarrow \text{Ar}_2^+ + e \]  \hspace{1cm} (34)

Assuming the steady state to apply to \( \text{Ar}^* \) we find

\[ (\text{Ar}^*) = \frac{k_e i_e(\text{Ar})}{k_u + k_r(\text{Ar})} \]  \hspace{1cm} (35)

Where \( i_e \) refers to electron current

\[ \frac{d(\text{Ar}_2^+)}{dt} = k_r(\text{Ar})(\text{Ar}^*) = \frac{k_e i_e(\text{Ar})^2}{k_u + k_r(\text{Ar})} \]  \hspace{1cm} (36)

\[ \frac{d(\text{Ar}^*)}{dt} = k_i (\text{Ar}) \]  \hspace{1cm} (37)

Dividing (36) by (35) and recalling that \( \frac{k_i}{k_e} = \frac{\sigma_i}{\sigma_e} \) where \( \sigma \) is cross-section, we find

\[ \frac{d(\text{Ar}^*)}{d(\text{Ar}_2^+)} = \frac{\sigma_i}{\sigma_e} \left[ 1 + \frac{k_u}{k_r(\text{Ar})} \right] \]  \hspace{1cm} (38)

Since \( (\text{Ar}^*) \) and \( (\text{Ar}_2^+) \) are independent of each other, we can write

\[ \frac{(\text{Ar}^*)}{(\text{Ar}_2^+)} = \frac{\sigma_i}{\sigma_e} \left[ 1 + \frac{1}{k_r(\text{Ar})} \right] = \frac{\sigma_i}{\sigma_e} \left[ \frac{i_{\text{Ar}^*}}{i_{\text{Ar}_2^+}} \right] \]  \hspace{1cm} (39)
where we assume the observed ion intensities are proportional to concentration and with the same constant of proportionality.

From Equation 39 it will be observed that a plot of \( \frac{^{7}Ar^+}{Ar_2^+} \) against the reciprocal of pressure should give a straight line whose intercept is \( \frac{\sigma_1}{\sigma_e} \) and whose slope is \( \frac{\sigma_1}{\sigma_0 T_{\tau u} k_r} \). Plots of experimental data did indeed give straight lines, and in Table II the results of Dahler et al. (10) for both the ratio of cross sections and the product of \( k_r \tau_u \) are reported. From these results, however, there is no way to determine \( \tau_u \) and \( k_r \) separately. Reasonable values of \( \tau_u \) would be in the range of \( 10^{-6} \) to \( 10^{-8} \) seconds so that \( k_r \) would necessarily be in the range of \( 10^{-10} \) to \( 10^{-8} \) cc./molecule sec.

Table II. Steady State Values for Rates of Diatomic Ion Formation

<table>
<thead>
<tr>
<th>Rare Gas</th>
<th>( \sigma_e/\sigma_1 )</th>
<th>( k_r \tau_u \times 10^{14} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.06</td>
<td>0.58</td>
</tr>
<tr>
<td>Ne</td>
<td>0.01</td>
<td>11.</td>
</tr>
<tr>
<td>Ar</td>
<td>0.055</td>
<td>3.6</td>
</tr>
</tbody>
</table>

In the studies of Dahler et al. (10) there was no way to vary the time of reaction, and this necessarily limited the information that could be obtained concerning rates. Lampe and Hess (26) and later Becker and Lampe (1, 2) extended the study of argon by using a time-of-flight mass spectrometer capable of pulsing the electron beam and ion draw-out potential. In this study they could, at various pressures, delay the draw-out pulse and hence vary reaction time in the ionization chamber. As a result they could obtain explicit measurements of reaction rates. The following equations developed this relationship, based upon the mechanism of Dahler et al. (10) (Equations 31-34). Since the electron pulse is of short duration, it can reasonably be assumed that excited atoms are formed without reaction and then decay by Reactions 33 and 34. We can then write

\[
-\frac{d(Ar^*)}{dt} = [k_u + k_r(Ar)](Ar^*)
\]

which integrates to

\[
(Ar^*) = (Ar^*)_0 \exp \left[-[k_u + k_r(Ar)]t\right]
\]

\[
d(Ar_2^*) = k_r(Ar^*)
\]
substituting Equation 41 into Equation 42 and integrating

\[
(Ar_2^+) = \frac{k_r(Ar^o)(Ar)}{k_u + k_r(Ar)} [1 - \exp [k_u + k_r(Ar)]t]
\] (43)

\[
(Ar^o) = \frac{ke}{k_t}(Ar^o) = \frac{\sigma e}{\sigma_i}(Ar^+)
\] (44)

Ar being incapable of reaction at the low pressures employed. Finally, then

\[
\frac{(Ar_2^+)}{(Ar^+)} = \frac{\sigma r k_r(Ar)}{\sigma_i[k_u + k_r(Ar)]} [1 - \exp [k_u + k_r(Ar)]t]
\] (45)

Obviously, studies of \(\frac{(Ar_2^+)}{(Ar^+)}\) against time at various pressures will permit separation of \(k_u\left(=\frac{1}{\tau_u}\right)\) and \(k_r\). Lampe and Hess (26) employed the value of \(\sigma_r/\sigma_i\) Dahler et al. (10) obtained by the steady-state method, together with their own results to obtain values of \(k_r = 4.3 \times 10^{10}\) cc. molecule\(^{-1}\) cm.\(^{-1}\) and \(\tau_u = 4.76 \pm 0.45 \times 10^{-7}\) sec. The product is in reasonable agreement with that of Dahler et al. (10). Cermak and Herman (7), using a beam of excited rare gas atoms found appreciable numbers of long lived (\(\gtrsim 10^{-5}\) sec.) excited atoms with states approaching in energy to the ionization potential. Qualitatively this supports the observations of Lampe (1, 2, 26).

Table III. Rate Constants for Various States Leading to Ar\(_2^+\)

<table>
<thead>
<tr>
<th>Electron Energy, e.v.</th>
<th>(k_r \times 10^9) cc/molecule/sec.</th>
<th>(\tau_u), micro sec.</th>
<th>(\sigma r/\sigma_i \times 10^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>1.7 ± 0.2</td>
<td>0.77 ± 0.07</td>
<td>3.0 ± 0.6</td>
</tr>
<tr>
<td>28</td>
<td>2.0 ± 0.1</td>
<td>0.55 ± 0.03</td>
<td>0.55 ± 0.15</td>
</tr>
<tr>
<td>65</td>
<td>1.3 ± 0.2</td>
<td>0.33 ± 0.05</td>
<td>0.34 ± 0.4</td>
</tr>
</tbody>
</table>

Several investigators have recently reported evidence for the participation of several excited states in forming diatomic ions of the rare gases. Kaul (19) observed three states of argon leading to Ar\(_2^+\), Comes (8) reported two peaks in the ionization efficiency curve for Ar\(_2^+\), and Melton and Hamill (28), employing an RPD method, found three states of argon and of krypton leading to their respective diatomic ions. Becker and Lampe (1, 2) obtained ionization efficiency curves for Ar\(_2^+\) at several delay times. They found three maxima in each curve—a sharp one at 18 e. v., a somewhat broader one at about 28 e. v., and a very broad one at about 65 e. v. These maxima suggest that three states (or sets of states) are contributing to the formation of Ar\(_2^+\). Further, with increasing delay (reaction) time the peaks varied in relative intensity, the 18 e. v.
one becoming increasingly prominent and the 65 e. v. one becoming progressively smaller. The contributions of the various states were not completely separable, but applying a rate treatment similar to that of Lampe and Hess (Equations 40-45) gave reasonable results for the lifetimes and reaction rate constants of the three states involved. Their results are given in Table III.

**Ions in Flames**

Flames formed by combustion of hydrocarbons with air or oxygen contain an abundance of ions, whereas hydrogen-oxygen flames have few ions, if any. In neither case is the temperature sufficiently high to bring about ionization thermally, and so one must conclude that ionization results from chemical reaction—i.e., from chemionization. The exact nature of the reaction has not been established, but in many cases free radicals formed from hydrocarbons seem to be involved. This suspicion is strengthened by the fact that adding a small amount of hydrocarbon to a hydrogen-oxygen flame brings about a great increase in ionization.

In all flames involving hydrogen or hydrocarbons the most abundant ion is $\text{H}_3\text{O}^+$ followed by $\text{NO}^+$ when nitrogen or nitrogen-containing fuels are present. In addition, many hydrocarbon ions are usually present, one of the most interesting being $\text{C}_9\text{H}_3^+$, which is suspected of having a cyclic structure. The subject of ions in flames has been extensively studied (24, 40, 42) and will not be reviewed here. However, most scientists concerned with the problem now think that chemionization produces the initial ions and that these then react with various neutral molecules and free radicals present to produce various ionic species.

Although the exact nature of the initial reaction has not been established, there is some evidence and a considerable body of opinion that the initial reaction is (3, 12, 41)

$$\text{CH} + \text{O} \rightarrow \text{CHO}^+ + e$$  \hspace{1cm} \text{(46)}

The $\text{CHO}^+$ ion can react with water as follows

$$\text{CHO}^+ + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_3\text{O}^+$$  \hspace{1cm} \text{(47)}

and with other hydrocarbons and oxygen containing compounds in a variety of ways.

Ionization has also been observed in other types of flames or high temperature environments. Thus, Gatz et al. (15, 16) have found that ions are formed when NO is added to the nitrogen afterglow and have
attributed their formation to chemionization, probably to one of the following reactions:

\[ \text{N}_2^* + \text{N} + \text{O} \rightarrow \text{N}_2 + \text{NO}^* + e \]  
\[ 2\text{N} + \text{NO}^* \rightarrow \text{N}_2 + \text{NO}^* + e \]  
\[ \text{N}_2^* + \text{NO}^* \rightarrow \text{N}_2 + \text{NO}^* + e \]

Gatz et al. (14) have also observed cesium ions when cesium was present in the nitrogen afterglow and attribute it to Reaction 51.

\[ 2\text{N} + \text{Cs} \rightarrow \text{N}_2 + \text{Cs}^* + e \]

In this laboratory we have found that ionization occurs when benzene is added to the nitrogen afterglow, but neither the ions nor the process of their formation has been identified. Ions also occur in shock waves and probably are formed by chemionization. However, the scope of this paper does not permit a discussion of these processes.

**Literature Cited**

(30) Ibid., 70, 671 (1946).
(43) Tüxen, O., Z. Physik 103, 463 (1936).

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