THE CLUSTERING OF O2 AND HE TO Li(+)
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THE CLUSTERING OF O₂ AND He TO Li⁺

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May 1976

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ABERDEEN PROVING GROUND, MARYLAND
The clustering of oxygen and helium to positive lithium ions has been studied using a drift tube-mass spectrometer at 319K. For oxygen clustering, the rate coefficients for cluster ion formation and collisional dissociation were measured as a function of E/N. For clustering to helium, only an equilibrium constant was determined. The relative importance of the clustering of several atmospheric gases to positive lithium ions in the ionosphere is discussed.
SUMMARY

The clustering of oxygen and helium to positive lithium ions has been studied using a drift tube-mass spectrometer at 319K. For oxygen clustering, the rate coefficients for cluster ion formation and collisional dissociation were measured as a function of E/N. For clustering to helium, only an equilibrium constant was determined. The relative importance of the clustering of several atmospheric gases to positive lithium ions in the ionosphere is discussed.

INTRODUCTION

The performance of communications systems, radars, and other defense systems are predicted using phenomenology codes which employ simplified chemistry. Extensive chemical codes of the lower ionosphere are being developed in our laboratory to check the reliability of the simplified chemistry. The development of those large chemical codes requires both in situ measurements of ionic- and neutral-constituent densities in the lower ionosphere and laboratory measurements of relevant reaction rate coefficients. This report contains recent results of the BRL laboratory measurements program which determines these reaction rate coefficients.
RESULTS AND DISCUSSION

The clustering of $O_2$ to $Li^+$ has been studied using a drift tube-mass spectrometer at 319K. The gas pressure was varied between 66.7 and 200.0 N/m$^2$ (0.5 and 1.5 Torr) and the $E/N$ (the ratio of the uniform electric field in the drift region to the neutral number density) between 1.2 and $2.4 \times 10^{-20}$ V m$^{-1}$. The only ions observed were $Li^+$ and $Li^+(O_2)$; therefore, we assume that the reactions:

$$k_1 \frac{Li^+ + O_2}{m} \rightarrow \frac{Li^+(O_2) + O_2}{m}$$

dominate the ion chemistry.

The apparatus and experimental technique have been described previously$^1,^2$ in papers describing the clusters of $Ar$ and $N_2$ to $Li^+$. Time-of-arrival spectra for $Li^+$ and $Li^+(O_2)$ were recorded for various pressure and $E/N$ combinations within the ranges given above. These spectra were compared with spectra computed using the method of Gatland$^3$ for two interconverting ions. At a given $E/N$ we sought the set of parameters which resulted in the best comparison of the experimental and theoretical spectra for both ions at three different pressures. Typical comparisons are shown in Figures 1 and 2.

The deduced rate coefficients are shown in Table I as a function of $E/N$. Note that the association-rate coefficients are essentially constant over the range of $E/N$ studied, whereas the collisional-dissociation-rate coefficients increase with increasing $E/N$. The amounts by which these rate coefficients may be in error are estimated to be $\pm 24\%$ for the association-rate coefficients and $\pm 22\%$ for the collisional-dissociation-rate coefficients.

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$^2$AD #773668.
$^4$AD #A21522.

Figure 1. Comparison of experimental data with model calculations for Li$. E/N = 1.8 \times 10^{-16}$ V cm$^2$, $p = 1.00$ Torr, $T = 319$ K. The dots are measurements, and the smooth curves are the model calculations.
Figure 2. Comparison of experimental data with model calculations for Li+(O₂) under the same conditions as in Figure 1. The dots are measurements and the smooth curves are model calculations.
<table>
<thead>
<tr>
<th>E/N</th>
<th>$k_1$</th>
<th>$k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($\times 10^{-20} \text{V m}^2$)</td>
<td>($\times 10^{-42} \text{m}^6 \text{sec}^{-1}$)</td>
</tr>
<tr>
<td>1.2</td>
<td>1.08</td>
<td>3.5</td>
</tr>
<tr>
<td>1.5</td>
<td>1.10</td>
<td>4.0</td>
</tr>
<tr>
<td>1.8</td>
<td>1.10</td>
<td>4.2</td>
</tr>
<tr>
<td>2.1</td>
<td>1.08</td>
<td>4.6</td>
</tr>
<tr>
<td>2.4</td>
<td>1.09</td>
<td>4.9</td>
</tr>
</tbody>
</table>
The mobilities of the two ions were also deduced. The Li\(^+\) arrival profiles have the expected skewed Gaussian shape plus a contribution at late times from ions which emerged from the tube but had spent some time as the slower cluster ions. We used the mean arrival time of the skewed Gaussian portion of these profiles to determine the mobility of Li\(^+\) in O\(_2\). The reduced mobility was found to be \(4.10 \times 10^{-4} \text{ m}^2/\text{V sec}\) at 319 K and was constant over the range of B/N studied. Considering data scatter, possible errors in the determination of temperature, pressure, drift field, drift distance and time, and the possible error introduced by the hot source, the error in this mobility (one standard deviation) was found to be 3.6%. The reduced mobility of the cluster ion Li\(^+\) (O\(_2\)) was determined from the spectra comparisons to be \(2.05 \times 10^{-4} \text{ m}^2/\text{V sec}\) and was also independent of B/N. The error in this value (one standard deviation) is estimated to be 6.2%.

The clustering of He to Li\(^+\) was also studied briefly at 1 Torr pressure. Only two ions were observed, Li\(^+\) and Li\(^+\)(He). We assume that the clustering process can be described by the reactions:

\[
\text{Li}^+ + 2\text{He} \xrightleftharpoons{k_2}{k_{-2}} \text{Li}^+\text{(He)} + \text{He}
\]

The small number of cluster ions which could be counted made it impossible to deduce \(k_2\) and \(k_{-2}\) separately, but the ratio of the counting rates for Li\(^+\)(He) and Li\(^+\) was used to deduce the equilibrium constant, \(K_e = k_2/k_{-2} = 1 \times 10^{-2} \text{d}^3\) at 309 K and B/N = 1.8 \(\times\) \(10^{-20}\text{V m}^2\). We assume that the masses of these ions are sufficiently close to minimize problems due to differences in detection sensitivities so that this determination should be correct to within a factor of two. We did not determine the mobility of Li\(^+\) in He. Although we know of no other direct observation of the Li\(^+\)(He) cluster ion, its presence...
has been inferred from low temperature mobility measurements and its binding energy has been calculated to be between 0.05 and 0.07 eV. Lithium has been observed in the atmosphere with a peak number density of a few million atoms per m$^3$ at about 80 km. Since a significant fraction of the lithium is expected to be positively charged, it is appropriate to examine three-body loss processes of Li$^+$ that are revealed by our studies. Table II gives room-temperature time constants for reactions of Li$^+$ with N$_2$, O$_2$, and Ar at number densities appropriate to 80 km. The switching reaction that could transform the initial cluster ions into Li$^+$(CO$_2$) is included in the table. Since the temperature dependence of the reactions involving N$_2$ and those involving O$_2$ should be very similar, N$_2$ should be more important than O$_2$ in the three-body loss of Li$^+$ at 80 km. Further, the time that a Li$^+$(N$_2$) cluster survives before being broken up in a collision with another molecule is long compared to the time required for it to be converted to Li$^+$(CO$_2$). Thus Li$^+$(N$_2$) has a much higher probability of being transformed into a more stable cluster ion than does Li$^+$(O$_2$) or Li$^+$(Ar). This result causes us to suggest that N$_2$ should be investigated as an important reactive species in studies of other B-region ionic constituents.

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<table>
<thead>
<tr>
<th>Reference</th>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Time Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Li$^+$ + N$_2$ + N$_2$ → Li$^+$ (N$_2$) + N$_2$</td>
<td>$2.0 \times 10^{-42}$ m$^6$/sec</td>
<td>4.1 sec</td>
</tr>
<tr>
<td>2</td>
<td>Li$^+$ (N$_2$) + N$_2$ → Li$^+$ + N$_2$ + N$_2$</td>
<td>$7.0 \times 10^{-21}$ m$^3$/sec</td>
<td>0.36 sec</td>
</tr>
<tr>
<td>this work</td>
<td>Li$^+$ + O$_2$ + O$_2$ → Li$^+$ (O$_2$) + O$_2$</td>
<td>$1.1 \times 10^{-42}$ m$^6$/sec</td>
<td>28 sec</td>
</tr>
<tr>
<td>this work</td>
<td>Li$^+$ (O$_2$) + O$_2$ → Li$^+$ + O$_2$ + O$_2$</td>
<td>$3.5 \times 10^{-19}$ m$^3$/sec</td>
<td>$7.2 \times 10^{-3}$sec</td>
</tr>
<tr>
<td>1</td>
<td>Li$^+$ + Ar + Ar → Li$^+$ (Ar) + Ar</td>
<td>$1.8 \times 10^{-43}$ m$^6$/sec</td>
<td>$3.8 \times 10^3$ sec</td>
</tr>
<tr>
<td>1</td>
<td>Li$^+$ (Ar) + Ar + Li$^+$ + Ar + Ar</td>
<td>$2.0 \times 10^{-19}$ m$^3$/sec</td>
<td>$12. \times 10^{-3}$sec</td>
</tr>
<tr>
<td>estimate</td>
<td>Li$^+$ (M) + CO$_2$ → Li$^+$ (CO$_2$) + M</td>
<td>$1.0 \times 10^{-15}$ m$^3$/sec</td>
<td>$8.4 \times 10^{-3}$sec</td>
</tr>
</tbody>
</table>

**TABLE II.** ROOM-TEMPERATURE RATE COEFFICIENTS AND TIME CONSTANTS FOR THE CLUSTERING OF ATMOSPHERIC GASES TO Li$^+$ AT Pressures Appropriate To 80 KM. THE SYMBOL M REFERS TO N$_2$, O$_2$, OR Ar.
REFERENCES


