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Thermodynamic investigation of the AlINC and AlICN isomers by Knudsen cell mass spectrometry

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Equilibria involving the isomers AlINC and AlICN above a mixture of aluminum nitride, graphite, and gold contained in a graphite Knudsen cell were investigated with a mass spectrometer. The enthalpies of formation, $\Delta_f H_m^\circ$, and of atomization, $\Delta_a H_m^\circ$, in kJ mol$^{-1}$, for AlINC and AlICN, were derived as 281.3 ± 14 and 303.8 ± 14, and as 1228.1 ± 15 and 1205.6 ± 15, respectively. © 1999 American Institute of Physics. [S0021-9606(99)01627-X]

INTRODUCTION

In recent years the molecule AlINC/AlICN has received considerable attention by theorists$^{1-5}$ and spectroscopists,$^{4,8}$ because it is suspected to be the carrier of some of the unidentified spectral lines in the circumstellar envelope of the carbon star IRC+10216.$^{1,2}$ Related molecules such as NaCN,$^9$ MgNC,$^{10}$ and MgCN,$^{11}$ as well as AlCl and AlP,$^{12,13}$ have already been observed in this star. The latter two are of interest in view of the pseudohalogen character of the CN radical. Theoretical calculations$^{1,5,14}$ have predicted a linear geometry and a $^1\Sigma^+$ ground state for both isomers, AlINC and AlICN, AlINC being the more stable isomer by several kcal mol$^{-1}$.

The first observation of AlINC/AlICN and the presence of comparable concentrations of the two isomers in the vapor above AlIN(s) + graphite has been reported by Gingerich$^{15}$ from Knudsen effusion mass spectrometric measurements, and an estimate of its atomization energy, $\Delta_a H_m^{298}$ of 1255 kJ mol$^{-1}$, obtained from a second-law treatment. K.A.G. wishes to correct the percentage of fragmentation of AlINC (AlCNO) to AlIN$^+$ and AlC$^+$ in Ref. 15. It should read 0.5% instead of 5% using 30 V electrons. Additional mass spectrometric measurements yielded a preliminary third-law $\Delta_a H_m^{298}$ value of (1243 ± 21) kJ mol$^{-1}$ for this molecule.$^{16}$

In the present investigation we report the thermodynamic evaluation of the AlINC and AlICN isomers from mass spectrometric equilibrium measurements coupled with a fragmentation analysis and utilization of theoretical transi-
tion energies. Thermal functions have been calculated from experimental and theoretical molecular parameters of both isomers.

EXPERIMENT

The measurements were performed with a Nuclide Corporation 12-90 HT mass spectrometer. Additional design features of the instrument and the general experimental procedure have been described previously.$^{17}$ The graphite Knudsen cell was charged with finely powdered AlIN and graphite; gold was added for calibration purposes. The gold was present during the measurements of AlINC/AlICN and served also as a liquid metal vaporization catalyst,$^{18,19}$ since AlIN(s) has a low vaporization coefficient of $2.0 \times 10^{-3}$. $^{19,21}$ The energy of the ionizing electrons was 30 eV, the emission current 1 mA, the acceleration energy was 3 kV, and the voltage at the entrance shield of the multiplier was 1.5 kV. Temperatures were measured with a calibrated optical pyrometer. Identification of the vapor species was accomplished by their mass-to-charge ratio, shutter effect, ionization efficiency curves, and isotopic intensity distribution. Appearance potentials, in eV, were measured by the extrapolated voltage differences method$^{22}$ as 8.1 ± 0.5 for AlINC$^+$ or AlCNO$^+$, 16.3 ± 0.6 for AlIN$^+$, and 15.8 ± 0.6 for AlC$^+$. The electron energy scale was calibrated with Au (9.22 eV)$^{23}$ and N$_2$ (15.58 eV).$^{23}$ Previous experimental values$^{15}$ for AlINC$^+/AlCN^+ (7.4 ± 0.3 eV)$, AlICN$^+$, and AlIN$^+$ (approximately 15 eV) are lower, but still within the error limits.

<table>
<thead>
<tr>
<th>Ion intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>1668</td>
</tr>
<tr>
<td>1669</td>
</tr>
<tr>
<td>1697</td>
</tr>
<tr>
<td>1646</td>
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<tr>
<td>1612</td>
</tr>
<tr>
<td>1558</td>
</tr>
<tr>
<td>1558</td>
</tr>
<tr>
<td>1520</td>
</tr>
</tbody>
</table>

*Calculated using $\Delta E$ of 1880 cm$^{-1}$ (see text).
TABLE II. The Gibbs energy functions (GEF₀), (G¹ᵦ−H₀)/T, in J K⁻¹ mol⁻¹ and the heat content functions (HCF₀), H¹ᵦ−H₀⁾, in kJ mol⁻¹ for the isomers AlINC and AlICN.

<table>
<thead>
<tr>
<th>Species</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298.15</td>
</tr>
<tr>
<td>AlINC</td>
<td>GEF₀</td>
</tr>
<tr>
<td></td>
<td>HCF₀</td>
</tr>
<tr>
<td>AlICN</td>
<td>GEF₀</td>
</tr>
<tr>
<td></td>
<td>HCF₀</td>
</tr>
</tbody>
</table>

given, whereas theoretical values for AlINC⁺, 9.64³ and 9.2 eV,⁴ and for AlICN⁺, 9.59³ and 9.2 eV,¹⁴ are higher.

The pressure constants were determined from the known AlAu(g) = Al(g) + Au(g) equilibrium, using the measured corresponding ion currents and the known dissociation energy, D₀²¹(AlAu,g) = (322.2 ± 6.3) kJ mol⁻¹.²⁴ The multiplier gains, γᵢ, for the major species were measured with a 50% transmission grid as 10³ times 4.10, 1.93, 1.74, 6.24, and 4.36 for Al, Au, AlAu, N₂, and AlINC/AlICN, respectively. The relative ionization cross sections used, σᵢ, in 10⁻¹⁶ cm², were taken from experimental values reported in the literature; Al, 9.71,²⁵ Au, 5.70, by a logarithmic extrapolation;²⁶ AlAu, 11.6, as 0.75 × (σAl + σAu), AlINC/AlICN, 9.28, as 0.75 × (σAl + σC + σN), where σC and σN are taken from Ref. 27; N₂, 0.998.²⁸ The resulting pressure constants, kₓ, in bar A⁻¹ K⁻¹, are 0.841, 3.05, 1.67, 5.42, and 0.840 for Al, Au, AlAu, N₂, and AlINC/AlICN, respectively. The uncertainty of the kₓ values is estimated to be about 20%.

Table I lists the measured ion currents for the most abundant isotopes of the species pertinent to the present investigation.

RESULTS AND DISCUSSION

The Gibbs energy functions (GEF₀), (G¹ᵦ−H₀)/T, and the heat content functions (HCF₀), H¹ᵦ−H₀⁾, for AlINC and AlICN were calculated using the rigid-rotor harmonic-oscillator approximation.²⁹

In our evaluation of the thermal functions we used the experimental values for the vibrational frequencies, in cm⁻¹:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Second-law</th>
<th>Third-law</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔH¹ᵦoothing</td>
<td>ΔH₀⁾</td>
</tr>
<tr>
<td>2AlINC(g) + Au(g) = Al(g) + N₂(g) + 2AlAu(g) + 2C(graph.)</td>
<td>-229.1 ± 17.8⁸</td>
<td>-218.2 ± 17.8</td>
</tr>
<tr>
<td>2AlINC(g) = 2Al(g) + N₂(g) + 2C(graph.)</td>
<td>113.1 ± 19.3</td>
<td>114.3 ± 19.3</td>
</tr>
<tr>
<td>AlINC(g) + C(graph) = AlINC(g)</td>
<td>568.2 ± 12.7</td>
<td>572.5 ± 12.7</td>
</tr>
<tr>
<td>2AlINC(g) + Au(g) = Al(g) + N₂(g) + 2AlAu(g) + 2C(graph.)</td>
<td>-274.1 ± 17.8</td>
<td>-262.9 ± 17.8</td>
</tr>
<tr>
<td>2AlINC(g) + 2Al(g) + N₂(g) + 2C(graph.)</td>
<td>68.0 ± 19.3</td>
<td>69.4 ± 19.3</td>
</tr>
<tr>
<td>AlINC(g) + C(graph) = AlINC(g)</td>
<td>590.8 ± 12.7</td>
<td>594.9 ± 12.7</td>
</tr>
<tr>
<td>2AlINC(g) + Au(g) = Al(g) + N₂(g) + 2AlAu(g) + 2C(graph.)</td>
<td>-234.4 ± 17.8</td>
<td>-223.7 ± 17.8</td>
</tr>
</tbody>
</table>

The error terms are standard deviations.
The reaction enthalpies were calculated for AINC(g) and AICN(g) separately after proportioning the total measured ion current for m/e of 53 on the basis of the theoretically predicted energy difference of 1880 cm$^{-1}$ between the two isomers. The value of 1880 cm$^{-1}$ is the average between that calculated by Ma et al.$^3$ (1924 cm$^{-1}$), and that by Fukushima$^a$ (1831 cm$^{-1}$) at the CCD/6-311 G(d) level. Using the Gibbs energy functions of the isomers (see Table II) and the equation for the third-law enthalpy of the isomerization reaction, AINC(g) = AICN(g), $\Delta H_0^\circ = -RT \ln K_p - T \Delta [ ( G_T^0 - H_0^0) / T ]$, the equilibrium constant of the isomerization reaction was calculated,$^{32,33}$ and from that the ratio of AlCN to AINC. The corresponding ion currents of AlCN$^+$ and AINC$^+$ obtained from this ratio for each data set have been included in Table I.

The enthalpy changes, $\Delta H_0^\circ$, for the reactions (1)–(3) were calculated from the equilibrium data by the second-law method, based on a least-squares analysis of $\ln K_p$ vs $1/T$ plots, and by the third-law method. Table III lists the results of the second-law and third-law evaluations. To obtain a selected $\Delta H_0^\circ$ value for each reaction, the third-law value was given twice the weight of the second-law value.

The literature values for the enthalpies of formation, $\Delta H_0^\circ$, in kJ mol$^{-1}$, used to obtain the final values for the enthalpy of formation and atomization of AINC/AICN were: 327.3 ± 4.2,$^{30}$ 322.2 ± 6.3 ($D_0^0$ (AlAu, g))$^{24}$ – 313.0 ± 2.5,$^{30}$ 711.2 ± 0.5,$^{30}$ 470.8 ± 0.1,$^{30}$ for Al(g), AlAu(g), AlIN(s), C(g), and N(g), respectively. From the selected $\Delta H_0^\circ$ values (see Table III) and these auxiliary literature data, the respective $\Delta H_0^\circ$ and $\Delta H_0^\circ$ values were derived for each reaction. By giving the same weight to the reactions (1)–(3), we propose for the $\Delta H_0^\circ$ (AINC, g), $\Delta H_0^\circ$ (AICN, g), $\Delta H_0^\circ$ (AINC, g), $\Delta H_0^\circ$ (AICN, g), $\Delta H_0^\circ$ (AINC, g), $\Delta H_0^\circ$ (AICN, g), $\Delta H_0^\circ$ (AINC, g), $\Delta H_0^\circ$ (AICN, g), in kJ mol$^{-1}$, the values 281.3 ± 14, 303.8 ± 14, 278.2 ± 14, 300.9 ± 14, 1228.1 ± 15, 1205.6 ± 15, 1234.8 ± 15, and 1212.5 ± 15, respectively. Here the uncertainties are the overall error obtained as discussed in Schmude et al.$^{35}$

Table IV lists our results together with the theoretical values of Petrie$^3$ predicted by the GAUSSIAN-2 level of theory.

The theoretical values for the atomization energies of AINC and AICN are slightly higher than our experimental ones but agree within the error limits given.

Our value for the atomization energy of AINC/AICN, based on the total ion current of m/e = 53, $\Delta _a H_{298}^\circ$ (1228.3 ± 15) kJ mol$^{-1}$, can also be compared to the previous result of $\Delta _a H_{298}^\circ$ (1243 ± 21) kJ mol$^{-1}$, as reported, obtained by a third-law evaluation. Correcting the literature value of the atomization energy for the thermal functions of AINC(g) and the $k_X$ values used in the present investigation, gives $\Delta _a H_{298}^\circ$ (1212 ± 21) kJ mol$^{-1}$.

The upper value for the atomization energy, $\Delta _a H_{298}^\circ$ of (1278 ± 27) kJ mol$^{-1}$ reported by L’vov and Pelieva$^{36}$, has been determined by electrothermal atomic absorption spectrometry under the assumption that the observed decrease of absorption of elemental Al in the presence of nitrogen, N$_2$, inside a graphite furnace at high temperatures (e.g., 2700 K) in comparison with that in an argon atmosphere, to be solely due to the formation of gaseous aluminum monocyanide. The difference of 50 kJ mol$^{-1}$ with our value suggests that molecular carbides such as AlC$_2$, AlC$_2$ are formed by interaction of aluminum with graphite at 2700 K in addition to AINC/AICN.

Our proportioning of the m/e = 53 primary ion current to I(AIN)+ and I(AICN)+ has been based on the energy difference of 1880 cm$^{-1}$ between the two isomers AINC and AICN predicted by the most advanced theoretical calculations.$^{1,5}$ If we assume the same percentage of fragmentation for AINC yielding AIN$^+$ and AICN yielding AlC$^+$, our observation of approximately equal concentrations suggests that this energy difference would be smaller than the theoretical one and may even be reversed (AINC possibly being the more stable isomer).

**ACKNOWLEDGMENT**

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15 K. A. Gingerich, Naturwissenschaften 24, 646 (1967).