Heat of Formation of Nitronium Perchlorate

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Calorimetric measurements of the heat of solution of nitronium perchlorate (NO₂CIO₄) and of a mixture of potassium nitrate and potassium perchlorate in aqueous potassium hydroxide have been made. These are combined to give:

\[
\text{NO}_2\text{CIO}_4(\text{c}) + 4\text{KOH(\text{in } 5300 \text{ H}_2\text{O})} \rightarrow \text{KClO}_4(\text{c}) + \text{KNO}_3(\text{c}) + 2\text{KOH(\text{in } 5300 \text{ H}_2\text{O})} + \text{H}_2\text{O(\text{liq})}
\]

\[ \Delta H = -285.80 \pm 0.38 \text{ kj/mole} \]
\[ = -68.31 \pm 0.09 \text{ kcal/mole} \]

from which the standard heat of formation of nitronium perchlorate is calculated as

\[ \Delta H^\circ_{f}(25^\circ \text{C}) \text{NO}_2\text{CIO}_4(\text{c}) = 37.19 \pm 1.0 \text{ kj/mole} \]
\[ = 8.89 \pm 0.25 \text{ kcal/mole} \]

in which the uncertainty represents twice the estimated overall standard deviation of the result.

1. Introduction

This investigation was carried out in the Thermochemistry Section of the National Bureau of Standards as part of a program, currently in progress, on the determination of the thermodynamic properties of the "light element" compounds. Nitronium perchlorate is a white crystalline material stable at temperatures up to 120 °C. It is extremely hygroscopic, reacting rapidly with water to form nitric and perchloric acids. The heat of formation of NO₂CIO₄ can be determined by measuring this heat of decomposition. In this investigation, aqueous solutions of potassium hydroxide were used, as the potassium salts of the acids provided more suitable reference substances.

2. Materials

The potassium nitrate and potassium perchlorate were reagent grade materials, dried at 120 °C and stored in a desiccator over anhydrous magnesium perchlorate. The potassium hydroxide was reagent grade material; the calorimetric solutions were prepared with CO₂-free distilled water, and standardized against potassium acid phthalate. The NO₂CIO₄ was obtained from the Callery Chemical Company as a white crystalline powder; an analysis furnished by them showed:

<table>
<thead>
<tr>
<th>Component</th>
<th>Actual</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>6.75-6.74</td>
<td>6.874 milliatoms/g</td>
</tr>
<tr>
<td>Chlorine</td>
<td>6.90-6.82</td>
<td>6.874 milliatoms/g</td>
</tr>
<tr>
<td>Total acid</td>
<td>13.61-13.71</td>
<td>13.75 milliequiv/g</td>
</tr>
<tr>
<td>NO⁺</td>
<td>0.06-0.1</td>
<td>0.00 milliequiv/g</td>
</tr>
</tbody>
</table>

Analyses for total acid by titrations with standard base, and for NO⁺ by oxidation with standard ceric sulfate solution and back titration with standard ferrous ammonium sulfate gave:

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total acid</td>
<td>13.74 ± 0.01 milliequiv/g</td>
<td></td>
</tr>
<tr>
<td>NO⁺</td>
<td>0.06 ± 0.01 milliequiv/g</td>
<td></td>
</tr>
</tbody>
</table>

The addition of silver nitrate to the acid solution gave a negative test for chloride ion.

From the ratio of total acid measured to total acid theoretical, the purity of the sample was estimated to be 99.93 mole percent or 99.65 weight percent. Since NO₂CIO₄ is extremely hygroscopic the major impurity is presumed to be water.

3. Units of Energy, Molecular Weights, and Conversion Factors

The joule was taken as the unit of energy. All instruments were calibrated in terms of standards maintained at the National Bureau of Standards. For conversion to the conventional thermochemical calorie, one calorie is taken as 4.1840 joules. All weights are corrected to vacuum.

All atomic weights were taken from the 1957 International Table of Atomic Weights [1]. The heat capacities were taken, where possible, from the literature [2]. For NO₂CIO₄, an estimated value of 36 cal/deg mol was used.

4. Apparatus and Procedure

The glass calorimeter, thermometric system, apparatus for measurement of electrical energy, and general calorimetric procedure have been described [3, 4, 5]. The calorimeter contained 454.6
The results of the experiments on the hydrolysis
and neutralization of NO₃ClO₄ in solution I are given
in table 3. Here, \( \Delta H \) is the change in the energy
from the reaction of NO₃ClO₄, due to deviations
in the mass of the glass bulb and sample from
that of the reference bulb and sample. The term
\( q(\text{dil}) \) represents the correction for the dilution of the
individual final solutions to a uniform concentration.
This was calculated from the data in [2],
assuming that only the KOH(aq) contributed any
heat effect. The total energy, \( q \), is shown by the
equation \( q = \Delta H + (E_e + \Delta e) + q(\text{dil}) \).

The results of the electrical calibration experiments
on the KNO₃/KClO₄ system, and heat of solution experiments with the equimolar mixture of
KNO₃ and KClO₄, are given in tables 2 and 3,
respectively. The term \( q(KNO₃) \) in table 4 is the product of
the difference between moles of KClO₄ and moles
of KNO₃ and the heat of solution of KNO₃. It is
applied to make the molar quantities of KNO₃ and KClO₄ exactly equal.

**TABLE 2. Electrical calibration on KNO₃/KClO₄ system**

<table>
<thead>
<tr>
<th>Exp</th>
<th>Ohm</th>
<th>( \Delta H )</th>
<th>Ex</th>
<th>Ex</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.049286</td>
<td>1.9388</td>
<td>21.138 6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.097357</td>
<td>2.0323</td>
<td>21.132 6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.097357</td>
<td>2.0438</td>
<td>21.138 6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.092029</td>
<td>2.0282</td>
<td>21.123 5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.092029</td>
<td>2.0334</td>
<td>21.123 6</td>
<td></td>
</tr>
</tbody>
</table>

Mean: 21.138 6
Standard deviation of the mean: ±0.5

**TABLE 3. Results of the experiments on the hydrolysis of NO₃ClO₄**

<table>
<thead>
<tr>
<th>Exp</th>
<th>( \Delta \gamma )</th>
<th>( \Delta H )</th>
<th>( q(\text{dil}) )</th>
<th>( q )</th>
<th>Weighed NO₃ClO₄</th>
<th>Titrated NO₃ClO₄</th>
<th>( -\Delta H ) (cal/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10 6</td>
<td>0.0329757</td>
<td>0.94</td>
<td>499.11</td>
<td>0.00248990</td>
<td>0.0022389</td>
<td>98.7</td>
</tr>
<tr>
<td>2</td>
<td>0.10 1</td>
<td>0.0329757</td>
<td>0.15</td>
<td>604.95</td>
<td>0.00248990</td>
<td>0.0022389</td>
<td>100.3</td>
</tr>
<tr>
<td>3</td>
<td>0.32 2</td>
<td>0.044091</td>
<td>0.00</td>
<td>577.73</td>
<td>0.00248990</td>
<td>0.0022389</td>
<td>96.4</td>
</tr>
<tr>
<td>4</td>
<td>0.70 7</td>
<td>0.044091</td>
<td>0.00</td>
<td>640.24</td>
<td>0.00248990</td>
<td>0.0022389</td>
<td>100.2</td>
</tr>
<tr>
<td>5</td>
<td>0.70 2</td>
<td>0.044091</td>
<td>0.00</td>
<td>652.76</td>
<td>0.00248990</td>
<td>0.0022389</td>
<td>96.6</td>
</tr>
<tr>
<td>6</td>
<td>0.70 2</td>
<td>0.044091</td>
<td>0.00</td>
<td>620.34</td>
<td>0.00248990</td>
<td>0.0022389</td>
<td>96.6</td>
</tr>
<tr>
<td>7</td>
<td>0.09 9</td>
<td>0.044091</td>
<td>0.00</td>
<td>600.73</td>
<td>0.00248990</td>
<td>0.0022389</td>
<td>96.6</td>
</tr>
</tbody>
</table>

Mean: 262.24
Standard deviation of the mean: ±17.1
TABLE 4. Results of the experiments on the solution of KNO₃ and KClO₄

<table>
<thead>
<tr>
<th>Exp.</th>
<th>dT</th>
<th>dRc</th>
<th>KNO₃</th>
<th>KClO₄</th>
<th>dH (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.47</td>
<td>0.00133</td>
<td>0.0048656</td>
<td>0.0048508</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>-1.43</td>
<td>0.00543</td>
<td>0.0043259</td>
<td>0.0045000</td>
<td>3.36</td>
</tr>
<tr>
<td>3</td>
<td>-1.32</td>
<td>0.00045</td>
<td>0.0046571</td>
<td>0.0049433</td>
<td>6.63</td>
</tr>
<tr>
<td>4</td>
<td>-1.35</td>
<td>0.00046</td>
<td>0.0046581</td>
<td>0.0046603</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Therefore eq (1) actually corresponds to

0.9682 NO₂ClO₄(c) + 0.0283 HNO₃(liq) + 0.0283 HClO₄(liq) + [4 KOH + 5300 H₂O](soln) ——

[0.9965 KNO₃ + 0.9965 KClO₄ + 2.0070 KOH + 5301 H₂O](soln)

\[\Delta H = -199.02 \pm 0.35 \text{ kJ} = -47.57 \pm 0.08 \text{ kcal.}\]

For 1 mole of NO₂ClO₄ this becomes

NO₂ClO₄(c) + 0.0292 HNO₃(liq) + 0.0292 HClO₄(liq) + 1.0328 [4 KOH + 5300 H₂O] ——

[1.0292 KNO₃ + 1.0292 KClO₄ + 2.0728 KOH + 5475 H₂O] + 1.0584 H₄O(liq)

\[\Delta H = -205.56 \pm 0.36 \text{ kJ/mole} = -49.13 \pm 0.09 \text{ kcal/mole.} \text{(1a)}\]

From data in the literature [2], eq (1b) may be evaluated:

\[\text{HClO}_4\text{(liq)} + \text{HNO}_3\text{(liq)} + [4 \text{ KOH} + 5300 \text{ H}_2\text{O}] ——\]

[\text{KClO}_4 + \text{KNO}_3 + 2 \text{ KOH} + 5300 \text{ H}_2\text{O}] + 2 \text{ H}_2\text{O}\text{(liq)}

\[\Delta H = -230.9 \text{ kJ/mole} = -55.2 \text{ kcal/mole.} \text{(1b)}\]

Appropriate combination of eqs (1a) and (1b) gives

\[\text{NO}_2\text{ClO}_4(c) + 1.0036 [4 \text{ KOH} + 5300 \text{ H}_2\text{O}] ——\]

[\text{KClO}_4 + \text{KNO}_3 + 2.0144 \text{ KOH} + 5320 \text{ H}_2\text{O}] + 2 \text{ H}_2\text{O}\text{(liq)}

\[\Delta H = -198.82 \text{ kJ/mole} = -47.52 \text{ kcal/mole.} \text{(2)}\]

From table 4 we have

\[\text{KNO}_3(c) + \text{KClO}_4(c) + [2 \text{ KOH} + 5300 \text{ H}_2\text{O}]\text{(soln)} ——\]

[\text{KNO}_3 + \text{KClO}_4 + 2 \text{ KOH} + 5300 \text{ H}_2\text{O}]\text{(soln)}

\[\Delta H = 86.98 \pm 0.07 \text{ kJ/mole} = 20.79 \pm 0.02 \text{ kcal/mole.} \text{(3)}\]

Combining eqs (2) and (3) and neglecting small dilution effects, we obtain:

\[
\text{NO}_2\text{ClO}_4(c) + 4 \text{ KOH (in 5300 H}_2\text{O)} ——
\text{KClO}_4(c) + \text{KNO}_3(c) + 2 \text{ KOH (in 5300 H}_2\text{O)} + \text{H}_2\text{O (liq)}
\]

\[
\Delta H = -285.80 \text{ kJ/mole} = -68.31 \text{ kcal/mole.} \text{(4)}
\]

If we take the following values for the heats of formation of the other substances in the reaction [7]

<table>
<thead>
<tr>
<th>Substance</th>
<th>(\Delta H_f^{\circ}\text{soln}(\text{kcal/mole}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>KClO₄(c)</td>
<td>-103.45</td>
</tr>
<tr>
<td>KNO₃(c)</td>
<td>-118.12</td>
</tr>
<tr>
<td>H₂O(liq)</td>
<td>-68.314</td>
</tr>
<tr>
<td>KOH(2650 H₂O)</td>
<td>-115.23</td>
</tr>
</tbody>
</table>

we compute for NO₂ClO₄(c)

\[
\Delta H_f^{\circ}\text{soln} = -37.19 \pm 1.0 \text{ kJ/mole} = 8.89 \pm 0.25 \text{ kcal/mole.}
\]

The uncertainty interval for the measured heats has been taken as twice the overall standard deviation of the mean based on the sum of the variances from the calibration and reaction experiments and reasonable variances assigned to the auxiliary data and the analysis for total acid.

6. Discussion

Cordes and Fetter [8] measured the heat of reaction of NO₂ClO₄ with water, they report a value for the heat of formation of NO₂ClO₄(c) of 8.0 \(\pm 0.4\) kcal/mole. Recalculating their data with the more recent auxiliary heats of formation used for this work, their value becomes 8.7 \(\pm 0.4\) kcal/mole, in excellent agreement with the results obtained here.

7. References