The transformation of ammonium thiocyanate into thiourea under high pressures

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THE TRANSFORMATION OF AMMONIUM THIOCYANATE INTO THIOUREA UNDER HIGH PRESSURES

By TAKAO YANAGIMOTO

Introduction

The intramolecular rearrangement of ammonium thiocyanate into thiourea has been studied under atmospheric or autogenous pressure by several investigators. According to them, the following facts are found: 1) when either ammonium thiocyanate or thiourea alone or with additional solvents, such as water, anhydrous n-propyl alcohol, anhydrous butyl alcohol or ethylene glycol, is heated above about 130°C for a long time, the intramolecular rearrangement occurs reversibly, 2) the point of equilibrium reached by heating ammonium thiocyanate and by heating thiourea is the same at each temperature, where the ratio of ammonium thiocyanate to thiourea are 73.3 to 26.7 at 156°C and 77.0 to 23.0 at 182°C, 3) the rate of the transformation of ammonium thiocyanate into thiourea in the absence of the solvent increases greatly above 150°C, melting point of ammonium thiocyanate. And they have concluded that this reaction is unimolecular unlike the transformation of ammonium cyanate into urea.

In this experiment the effect of pressure on the transformation has been studied under the pressure of 1-3,000 kg/cm² at 140-220°C using ammonium thiocyanate or thiourea as the sample without additional solvent.

Experimental

Sample

Thiourea: commercial thiourea is recrystallized from the hot aqueous solution and washed with ethyl alcohol. Its purity is found 100% from the iodine-titration.

Ammonium thiocyanate: ammonium thiocyanate made by Merk is recrystallized from the aqueous solution. Its purity is 99.8% from the silver nitrate-titration and its melting point is 149.4°C.

Procedure

The experiments at ordinary pressure were carried out as follows: glass test tubes...
of about 5 cc in capacity, each containing 0.3 gr of the sample, were sealed and kept at the fixed temperature for a definite time in an oil bath.

Under high pressures the experimental apparatus and procedures were the same as the reports of this Journal. To retard the progress of this transformation during the manipulation of compressing and heating, about 0.3 gr of the sample in the pressure vessel made with 13Cr-steel were compressed to the desired pressure and then heated to the fixed temperature. But a few per cent of ammonium thiocyanate were transformed into thiourea during this operation and the values obtained were used as the initial concentration. To prevent the corrosion of the steel vessel in the progress of the reaction the sample was covered with lead-plate.

After the sample was heated at the desired temperature for the definite hours under high or ordinary pressure, it was dissolved in 50 cc of methyl alcohol and analysed.

Analytical method

Though several analytical methods for the mixtures of ammonium thiocyanate and thiourea are known, their results are undoubtedly somewhat in error because Ag ion makes the complex with thiourea in the case of silver nitrate titration for ammonium thiocyanate. As regards the analysis for urea, it is well known that the xanthodyl method gives good results, and it is reported that thiourea makes the additional compound with xanthodyl as well as urea. Therefore, ammonium thiocyanate was titrated after thiourea was removed by using xanthodyl.

Thiourea: 10 cc of the methanol solution mentioned above was diluted with 100 cc of water and added a definite quantity of dil. H₂SO₄, and then air was bubbled through such solution for about 2-3 hours at room temperature to displace hydrogen sulfide present in the solution. The amount of thiourea in the solution was determined with 0.1 N-iodine solution.

Ammonium thiocyanate: 10 cc of the methanol solution was added to 12-24 cc of a mixture of 2% xanthodyl-methanol solution and glacial acetic acid (in the ratio of 2 mole xanthodyl to 1 mole thiourea) and diluted with 80 cc of water and then was preserved for two days. The white precipitate formed was filtered off with a glass filter and a definite quantity of dil. HNO₃ added to the filtrate and then air was bubbled through this solution as in the case of thiourea. The amount of ammonium thiocyanate was determined with 0.1 N-silver nitrate solution.

* The outer part of the sample reacted at high temperatures and pressures becomes black on account of the corrosion of the lead plate by hydrogen sulfide formed in the decomposition of thiourea, but inner part becomes yellow as well as at ordinary pressure. The each part of the reacted sample was analysed separately, but the results were essentially identical. That is, the influence of the lead on the transformation was not observed.

10) R. Kiyama and T. Yanagimoto, This Journal, 21, 32 (1951)
11) R. Kiyama, ibid., 19, 1 (1949)
14) R. Fosse, A. Robyn and F. Francois, Compt. Rend., 159, 367 (1914)
15) R. Fosse, ibid., 145, 813 (1907)
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Results

1) In the case of heating ammonium thiocyanate at 140~220°C under the pressure of 1~3,000 kg/cm² for an hour, the yield of thiourea is shown in Table 1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (kg/cm²)</th>
<th>Yield of thiourea, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1,000</td>
</tr>
<tr>
<td>140</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>17.5</td>
<td>0.9</td>
</tr>
<tr>
<td>170</td>
<td>22.9</td>
<td>11.9</td>
</tr>
<tr>
<td>180</td>
<td>24.8*</td>
<td>26.2*</td>
</tr>
<tr>
<td>200</td>
<td>25.1*</td>
<td>26.0*</td>
</tr>
<tr>
<td>220</td>
<td>21.8*</td>
<td>24.0*</td>
</tr>
</tbody>
</table>

The yield of thiourea is shown in the per cent of thiourea per the total amount of ammonium thiocyanate and thiourea, neglecting a small amount of the decomposition product formed by heating the sample.

* In equilibrium.

On the above table it is observed that, when the reaction temperature is elevated under the definite pressure, the yields of thiourea increase suddenly at a temperature of 150°C under ordinary pressure, 170°C under 1,000 kg/cm², 180°C under 2,000 kg/cm² and 200°C under 3,000 kg/cm².

Under ordinary and high pressures the rate of the transformation of ammonium thiocyanate into thiourea is accelerated as the temperature increases, but at the definite temperature it is retarded by increasing pressure as shown in the above table and Fig. 1, showing the relations between the yields of thiourea and time at 200°C under various pressures.

2) The amount of thiourea in the equilibrium mixture starting from ammonium thiocyanate or thiourea is shown in Table 2.

The length of time required to reach equilibrium is short either in the case of higher temperature under the definite pressure or in that of lower pressure at the definite temperature. Under ordinary pressure it is within 180, 60, 15 and 10 minutes at 160, 180, 200 and 220°C respectively. In the case of high pressure, under 1,000 kg/cm² it is all within 60 minutes, under 2,000 kg/cm² within 60 minutes except 120 minutes at 180°C and under 3,000 kg/cm² within 60 minutes except 75 minutes at 200°C.

3) When the sample is heated above 190°C for a long time, the formation of guanidine thiocyanate and cyanamide is expected. Guanidine thiocyanate was analysed qualitatively from the test of picric acid and cyanamide.
T. Yanagimoto

Table 2

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Pressure kg/cm²</th>
<th>Amount of thiourea in the equilibrium composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1,000</td>
</tr>
<tr>
<td>160 Exp.</td>
<td>27.4</td>
<td>26.2</td>
</tr>
<tr>
<td>180 Exp.</td>
<td>24.8</td>
<td>26.9</td>
</tr>
<tr>
<td>200 Exp.</td>
<td>22.4</td>
<td>25.1</td>
</tr>
<tr>
<td>200 Calc.</td>
<td>22.4</td>
<td>24.3</td>
</tr>
<tr>
<td>220 Exp.</td>
<td>20.4</td>
<td>21.8</td>
</tr>
<tr>
<td>220 Calc.</td>
<td>20.4</td>
<td>22.1</td>
</tr>
<tr>
<td>200 Exp.</td>
<td>22.5</td>
<td>24.0</td>
</tr>
<tr>
<td>200 Calc.</td>
<td>22.5</td>
<td>24.3</td>
</tr>
</tbody>
</table>

by ammoniacal silver nitrate solution"16).

Guanidine thiocyanate is not detected even above 190°C under ordinary pressure so far as the heating time is short. On the other hand, when the sample is heated for about 1~1.5 hours above 200°C under high pressures, the formation of guanidine thiocyanate is detected, but the equilibrium values of thiourea formation from ammonium thiocyanate are not influenced. The formation of cyanamide is not detected in either case of ordinary or high pressures.

Considerations

1) It is observed that the yields of thiourea increase suddenly with the rise of the reaction temperature under the definite pressure, as shown in Table 1. It is well known that the melting point of material rises in general with increasing pressure, corresponding to the fact that the liquid usually has a larger volume than the solid, and the elevation in the melting point is shown as the following equation, \( t-t_0 = aP + bP^2 \), where \( a \) and \( b \) are the constants of the parabolic formula"17). On the other hand, it is reported by Waddell" that the reaction rate of the transformation of ammonium thiocyanate into thiourea is accelerated suddenly with the change to the liquid state reaction from the solid state one. Therefore, it seems most reasonable to assume that the sudden increases on the yields of thiourea under high pressures are due to the elevation of the melting point. Although the melting point of ammonium thiocyanate is 149.4°C under ordinary pressure, it is considered that the melting point is elevated between 160~170°C under the pressure of 1,000 kg/cm², 170~180°C under 2,000 kg/cm² and 180~200°C under 3,000 kg/cm². These values of the melting point under high pressures are almost applicable to the above-mentioned parabolic formula.

2) When the transformation is started from either ammonium thiocyanate or thiourea, it is found in the experiments at 200°C, as shown in Table 2, that each equilibrium value is much the same under high pressures as under ordinary pressure.

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3) The equilibrium constant of the transformation of ammonium thiocyanate into thiourea is represented by $K$ and the amount of the reactant $\text{NH}_4\text{SCN}$ and reaction product $(\text{NH}_3)_\text{CS}$ in the equilibrium state by $C_{\text{NH}_4\text{SCN}}$ and $C_{(\text{NH}_3)_\text{CS}}$. Then, $K$ is given by the following equation,

$$K = \frac{C_{(\text{NH}_3)_\text{CS}}}{C_{\text{NH}_4\text{SCN}}}$$  \hspace{1cm} (1)

At each temperature and pressure the values of $K$ are given in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Pressure kg/cm²</th>
<th>1</th>
<th>1,000</th>
<th>2,000</th>
<th>3,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>0.3774</td>
<td>0.3550</td>
<td>0.4045</td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>0.3250</td>
<td>0.3311</td>
<td>0.3514</td>
<td>0.3986</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.2887</td>
<td>0.3158</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>0.2563</td>
<td>0.3532</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the above data, it is found that the equilibrium shifts to thiourea by either increasing the pressure or decreasing the temperature. That is, this transformation is an exothermic reaction. At each pressure the relation between $\log K$ and reciprocal absolute temperature $1/T$ is given in Fig. 2. From the van't Hoff isochore,

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}.$$  \hspace{1cm} (2)

By using this equation the heat of reaction $\Delta H$ at each pressure and in each range of temperature can be obtained. These results are given in Table 4.

4) The effect of pressure on a chemical equilibrium is given as follows\textsuperscript{18},

$$\frac{d\ln K}{dP} = -\frac{\Delta V}{RT}.$$  \hspace{1cm} (3)

\textsuperscript{18} M. G. Evans and M. Polanyi, Trans. Farad. Soc., 31, 875 (1935); 32, 1333 (1936)
where, $K_p$ is the equilibrium constant under a constant pressure and $dV$ is the difference in the molecular volume between ammonium thiocyanate and thiourea. Though $dV$ is changed with the temperature and pressure, it is postulated that the change is negligible, and equation (3) is integrated, thus,

$$
\ln \frac{K_p}{K_p'} = -\frac{dV}{RT}(P - P').
$$

(4)

The molecular volumes of ammonium thiocyanate and thiourea obtained from the densities\(^{19}\) at 20°C under atmospheric pressure are 58.328 cc/mole and 54.177 cc/mole respectively. The difference is 4.151 cc/mole. By using the equilibrium constants under ordinary pressure the equilibrium values can be calculated at each temperature and high pressure from equation (4), and the values are shown in Table 2 as the calc. value. These calculated values were essentially identical with the experimental values.

5) The rate of this transformation is accelerated with elevating the temperature, but retarded by increasing the pressure in the initial period of the reaction as shown in Fig. 1. The effect of pressure on the reaction rate is given as follows\(^{18,20}\).

$$
\frac{d\ln k_p}{dP} = -\frac{dV^*}{RT},
$$

(5)

where, $k_p$ is the rate constant under a constant pressure and $dV^*$ is the difference in the molecular volume between the reactant and the activated complex.

Considering this transformation as first order since the logarithm of the concentration of the reactant, ammonium thiocyanate, has the linear relation with the time, and representing the rate constants under 2,000 and 3,000 kg/cm\(^2\) at 200°C as $k_{2,000}$ and $k_{3,000}$ respectively, $k_{2,000}/k_{3,000} = 1.7$ is obtained for the initial period of this reaction. Postulating that the change of $dV^*$ is little with pressure and temperature, the above equation (5) is integrated and the relation of $k_{2,000}/k_{3,000}$ is put in it. From this calculation, $dV^*$ is determined as about 20 cc/mole. If the transformation of ammonium thiocyanate of larger volume into thiourea of smaller volume, occurs as first stage, the positive value of $dV^*$ will be contrary to the expectation. Perrin and others\(^{21,22}\) studied the pressure effect on the various organic reaction in liquid state and pointed out that the unimolecular decomposition only has the positive value of $dV^*$. On the other hand, by heating

\(^{19}\) Int. Crit. Table, 1, p. 177
\(^{20}\) H. Erying, The Theory of Rate Process, p. 470 (1941)
ammonium thiocyanate the following decomposition occurred as Krall reported\textsuperscript{12},

\[
\text{NH}_4\text{SCN} \rightleftharpoons \text{NH}_3 + \text{HSCN}.
\]

On the basis of the above facts, it seems reasonable to expect the existence of the above decomposition step in the process from ammonium thiocyanate to thiourea to make clear the large positive value of \(\Delta V^*\) known from the present investigation.

The molecular volumes of \(\text{NH}_3\) and \(\text{HSCN}\) can be calculated approximately as follows: the molecular volume of liquid \(\text{NH}_3\) at 20°\(\text{C}\) is about 28 cc/mole from the International Critical Table\textsuperscript{21}) and that of \(\text{HSCN}\) is expected about 50 cc/mole from the additivity of molecular volume in liquid state by using Allen’s experimental result\textsuperscript{24}) of densities on the esters of thiocyanic acid.

Considering the molecular volume of about 20 cc in \(\Delta V^*\) and 58 cc in the reactant ammonium thiocyanate as mentioned above, the molecular volume of the activated complex is about 78 cc and its value is identical with the sum of the molecular volumes of \(\text{NH}_3\) and \(\text{HSCN}\). Therefore, the result of approximate calculations on the molecular volumes gives some supports to the above expectation of the decomposition. Then, it seems most reasonable to assume that the mechanism of this transformation is considered to be the following equation as well as the transformation of ammonium cyanate into urea\textsuperscript{20}.

\[
\text{NH}_4\text{SCN} \rightleftharpoons \text{NH}_3 + \text{HSCN} \hspace{1cm} (a)
\]

\[
\text{NH}_3 + \text{HSCN} \rightleftharpoons \text{HN} = \text{CS} \hspace{1cm} (b)
\]

It is expected that the equation (b) proceeds easily from left to right of the equation with the decrease of volume, being accelerated by pressure, like the urea formation from ammonia and cyanic acid. It follows that the retardation of the reaction rate by increasing pressure is due to the pressure effect on the equation (a).

6) The formation of guanidine thiocyanate has been considered\textsuperscript{12} to be the following equation,

\[
(\text{NH}_2)_2\text{CS} \rightleftharpoons \text{CN}_2\text{H}_2 + \text{H}_2\text{S}
\]

\[
\text{CN}_2\text{H}_2 + \text{NH}_4\text{SCN} \rightleftharpoons \text{NH}_3 + \text{C(\text{NH}_2)_2}\cdot \text{HSCN}.
\]

In the case of heating the sample at high temperatures and pressures for a long time, the formation of guanidine thiocyanate was observed, but it had scarcely any influence on the equilibrium value. It may be considered that this fact is due to the small formation of guanidine thiocyanate because the decomposition of thiourea is retarded.

\textsuperscript{22}) M. W. Perrin, \textit{Trans. Farad. Soc.}, 34, 144 (1938)
\textsuperscript{23}) \textit{Int. Crit. Table}, 3, p. 234
\textsuperscript{24}) P. Allen, \textit{J. Am. Chem. Soc.}, 57, 198 (1935)
\textsuperscript{25}) F. D. Chattaway, \textit{J. Chem. Soc.}, 101, 170 (1912)
by applying pressure.

At ordinary pressure, when the reaction was suspended in a short length of the time even if at high temperatures, the constant equilibrium values at each temperature could be determined satisfactorily.

In closing, the author has a great pleasure in expressing his hearty thanks to Professor R. Kiyama for his valuable guidance during the course of this investigation.

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Kyoto University.