Studies on the Reaction between Ammonia and Carbon Disulfide at High Pressures. (I) : Influences of the Charging Quantity of NH₃ and CS₂, and their Mol Ratio on the Formation of Ammonium Thiocyanate

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The rate of condensation increased exponentially with the increase in the
catalyst concentration and, naturally, with temperature.

Alcoholic solvents had no appreciable influence upon the reaction rate in com-
parison with that of the homogeneous, solvent less, reaction. A retarding action
of water was observed in the case of the methanol solvent but in butanol as sol-
vent the effect was hardly observable.

The condensation product was analyzed by the hydrogenation in the presence
of nickle catalyst at 120°C. under a hydrogen pressure of about 100 atm., followed
by fractional distillation. It was found that the content of the higher condensates
containing more than twelve carbon atoms in the molecule and the condensates
of the cyclic nature in the product increased with the catalyst concentration, the
mol ratio of the catalyst to the crotonaldehyde used, and the reaction tempera-
ture.

26. Studies on the Reaction between Ammonia and
Carbon Disulfide at High Pressures. (I)
Influences of the Charging Quantity of NH₃ and CS₂, and
their Mol Ratio on the Formation of Ammonium Thioeyanate

Shinjiro Kodama, Ken-ichi Fukui, Susumu Fukushima and Toshiaki Nagai
(Kodama Laboratory)

The reaction of ammonia with carbon disulfide giving NH₄SCN was studied
in an autoclave at 110°C. changing the reaction times. After the autoclave was
heated in an oil bath for a definite time, it was cooled quickly bringing into a bath
cooled with running water and allowed to stand over night continuing to cool with
water and then the pressure was released in cold state, the products were dissolved
in methanol, and NH₄SCN in the products was determined with N/10 AgNO₃
solution.

In a case where the mol ratio of NH₃ to CS₂ is 2:1, the yield of NH₄SCN
is decreased, as the charging density of NH₃ and CS₂ is increased. When the mol
ratio of NH₃ to CS₂ is 4:1, the yield of NH₄SCN is independent on the charg-
ing density, and amounted to 90%. As the mol ratio of NH₃ to CS₂ is increased,
the formation of NH₄SCN is increased. Released the pressure in the autoclave at a
hot state immediately after the reaction has ended, a remarkable decrease in the
yield of NH₄SCN is observed.

The results may be interpreted as follows. In the autoclave the following
reactions exist in a state of an equilibrium.

(79)
\[2\text{NH}_3 + \text{CS}_2 \rightleftharpoons \text{NH}_4\text{SCN} + \text{H}_2\text{S} \quad (1a),
\]
\[\text{NH}_3 + \text{H}_2\text{S} \rightleftharpoons \text{NH}_4\text{HS} \quad (1b),
\]
\[\text{NH}_3 + \text{NH}_4\text{HS} + \text{CS}_2 \rightleftharpoons (\text{NH}_4)_2\text{CS} \quad (1c).
\]

As the gas in the autoclave is released, the following dissociations take place gradually:

\[(\text{NH}_4)_2\text{CS} \rightarrow \text{NH}_4\text{SCN} + 2\text{H}_2\text{S} \quad (2),
\]
\[2\text{NH}_3 + \text{CS}_2 + \text{H}_2\text{S} \quad (3),
\]

so that when the pressure in the autoclave is released in a hot state, a decrease in the yield of \(\text{NH}_4\text{SCN}\) will be resulted, according to equation (3). Furthermore, the experimental result that by increasing charging density of \(\text{NH}_3\) and \(\text{CS}_2\) the formation of \(\text{NH}_4\text{SCN}\) is decreased can be explained quantitatively with a rate equation derived on above reaction schema from the standpoint of chemical kinetics.

\[\]

27. Preparation of Organo-mercurisulfides. (I)

Seishi Takagi, Hiroaki Tsukatani and Hisashi Tanaka

(S. Takagi Laboratory)

Merthiolate, \textit{i.e.}, sodium ethylmercurithiosalicylate, which was synthesized by Kharasch \textit{et al.} in 1926, has strong sterilizing power.

But, the material mercuri-compound of this substance is expensive.

The authors, also with the same purpose, prepared the following compounds, using easily obtainable aromatic mercuri-compounds.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>p-Ethylmercaptomercuribenzoic acid.</td>
<td>179.5°–181°</td>
</tr>
<tr>
<td>p-(β-Hydroxyethylmercaptomercuri)-benzoic acid.</td>
<td>168°–170°</td>
</tr>
<tr>
<td>p-Carboxylphenylmercurithiosalicylic acid.</td>
<td>215.5°–216.5°</td>
</tr>
<tr>
<td>o-(β-Hydroxyethylmercaptomercuri)-benzoic acid.</td>
<td>142°–144°</td>
</tr>
<tr>
<td>4-(β-Hydroxyethylmercaptomercuri)-2-chloro-benzoic acid.</td>
<td>147°–149°</td>
</tr>
<tr>
<td>3-Chloro-4-carboxylphenylmercuri-thiosoalicylic acid.</td>
<td>204.5°–205.5°</td>
</tr>
<tr>
<td>2-Chloro-tolyl-4-mercurithiosalicylic acid.</td>
<td>153.5°–154.5°</td>
</tr>
<tr>
<td>2-Chloro-tolyl-4-mercuripseudothiourea chlorohydrate.</td>
<td>140°–150°</td>
</tr>
</tbody>
</table>

(71)