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Author(s): Uemura, Sakae; Tanaka, Fumio; Sasaki, Osamu; Okano, Masaya

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Thallium(III) Chloride Catalyzed Hydrolysis of Trichloromethyl Compounds

Sakae Uemura, Fumio Tanaka, Osamu Sasaki

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Trichloromethyl compounds such as carbon tetrachloride and benzotrichloride were hydrolyzed readily to phosgene and benzoic acid respectively in the presence of TlCl$_3$·4H$_2$O or anhydrous TlCl$_3$. Chloroform and 1,1,1-trichloroethane, however, did not suffer the hydrolysis with this catalyst. The observed catalytic activity of TlCl$_3$·4H$_2$O and TlCl$_3$ for hydrolysis of carbon tetrachloride was somewhat weaker than SbCl$_5$, FeCl$_3$ and GaCl$_3$ in contrast to the lack of activity of AlCl$_3$, ZnCl$_2$, SbCl$_3$ and FeCl$_3$·6H$_2$O.

INTRODUCTION

While studying the halogenation and carboxylation reactions of aromatics with thallium salts in carbon tetrachloride,$^{1,2}$ we found that carbon tetrachloride was hydrolyzed to phosgene in the presence of TlCl$_3$·4H$_2$O.$^3$ It had already been reported that trichloromethyl compounds could be readily hydrolyzed with metal chloride catalysts such as FeCl$_3$, GaCl$_3$ and SbCl$_5$.$^3$ This paper reports the results of the experiments on the TlCl$_3$·4H$_2$O and anhydrous TlCl$_3$ catalyzed hydrolysis of trichloromethyl compounds such as carbon tetrachloride, benzotrichloride, 1,1,1-trichloroethane and chloroform, and a rough comparison of catalytic activities of Tl chlorides with certain metal chlorides.

EXPERIMENTAL

Hydrolysis of carbon tetrachloride. A mixture of carbon tetrachloride (100 ml) and commercial TlCl$_3$·4H$_2$O (9.5 g, 25 mmol) was stirred at refluxing temperature (78°C) for 2 hr. After 10 minutes a vigorous evolution of phosgene and hydrogen chloride gases began. All mixed gases were swept by nitrogen into a 500 ml of ethereal solution of aniline (54 g) to give diphenylurea and aniline hydrochloride (see eq. 2). The mixed precipitates were collected and dried, 24.3 g, and then slurried with water to recover the diphenylurea; mp 240°C (lit.$^4$ 241–242°C). This plus a small amount obtained by concentration of the ether weighed 6.3 g (29.7 mmol); 29.7% yield based on 100 mmol of water added in the hydrated form. The weight of aniline hydrochloride was 18.3 g (141 mmol).

* 植村 栄, 田中啓雄, 鶴羽 守, 阿部正彦: Laboratory of Petroleum Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.
When one more equivalent (0.1 mole) of water was added dropwise over a period of 5 minutes to the reaction mixture after 2 hr and the heating was continued for additional 2 hr, the yields of diphenylurea and aniline hydrochloride rose to 71.8 mmol (35.9%) and 352 mmol respectively.

**Hydrolysis of benzotrichloride.**

(A) To a mixture of carbon tetrachloride (50 ml), commercial TiCl₅·4H₂O (0.95 g, 2.5 mmol) and water (0.9 g, 50 mmol), benzotrichloride (1.9 g, 10 mmol) was added at refluxing temperature and the reaction mixture was heated for 1 hr. After filtration of insoluble precipitates the filtrate was washed with aqueous HCl to remove the Ti⁺⁺ salt, and then extracted with 10% aqueous NaOH. The alkaline extract was acidified with aqueous HCl to give 0.44 g of benzoic acid; mp 119-122°C (lit. 122.4°C). By ether extraction of the acidic washings an additional 0.43 g of benzoic acid was obtained. Total yield; 0.87 g (7.1 mmol), 71%. Gaseous products were trapped as described above; a trace of diphenylurea and 5.3 mmol of aniline hydrochloride were obtained.

In certain cases benzoic acid was determined as its methyl ester by the addition of an ethereal diazomethane solution to the filtrated reaction mixture.

(B) To a mixture of chloroform containing 1% of ethanol as stabilizer (50 ml), commercial TiCl₅·4H₂O (2.5 mmol) and water (50 mmol), 10 mmol of benzotrichloride was added at refluxing temperature (61°C), and the reaction mixture was kept for 2 hr under stirring. After filtration of precipitates and washing with water the solvent was distilled off to give 7.33 mmol of ethyl benzoate; bp 20 98°C. Ether extraction of the washings gave 0.19 g (0.79 mmol) of benzoic acid. Total yield of the acid and its ethyl ester was 8.12 mmol (81.2%).

No significant amounts of unreacted benzotrichloride were found at the end of both reactions (A) and (B).

**RESULTS AND DISCUSSION**

In the presence of commercial TiCl₅·4H₂O, carbon tetrachloride and benzotrichloride were hydrolyzed readily to phosgene and benzoic acid respectively (eq. 1 and 3). Phosgene was determined as diphenylurea by introducing the evolved gases into an ethereal solution of aniline (eq. 2), while benzoic acid was determined as itself or its alkyl esters. Data are summarized in the Table 1 and 2 including the results by Fe and Sb chloride catalysts.

\[
\begin{align*}
\text{CCl₄} + \text{H₂O} \xrightarrow{\text{TiCl₅·4H₂O}} & \text{COCl₂} + 2\text{HCl} \\
\text{COCl₂} + 2\text{HCl} + 6\text{C₆H₅NH₂} \rightarrow & \text{C₆H₅NHCONHC₆H₅} + 4\text{C₆H₅NH₃Cl} \\
\text{C₆H₅CCl₃} + 2\text{H₂O} \xrightarrow{\text{TiCl₅·4H₂O}} & \text{C₆H₅CO₂H} + 3\text{HCl}
\end{align*}
\]

Although Hill\(^5\) reported ca. 90% yield of phosgene using anhydrous FeCl₃ or SbCl₅ catalysts, our experiments gave much lower yield, \textit{i.e.}, 36.2 and 42.5% (Table 1). Because of the competitive hydrolysis of metal chloride catalysts, the yield of phosgene...
TlCl₃·4H₂O Catalyzed Hydrolysis of Trichloromethyl Compounds

Table 1. Hydrolysis of Carbon Tetrachloride.

<table>
<thead>
<tr>
<th>CCl₄ (ml)</th>
<th>Catalyst</th>
<th>React. Temp. (°C)</th>
<th>React. Time (hr.)</th>
<th>Products (mmol) COCl₂</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>TlCl₃·4H₂O</td>
<td>78</td>
<td>1</td>
<td>7.3</td>
<td>34.8</td>
</tr>
<tr>
<td>100</td>
<td>TlCl₃·4H₂O</td>
<td>78</td>
<td>2</td>
<td>29.7</td>
<td>141</td>
</tr>
<tr>
<td>100</td>
<td>TlCl₃·4H₂O</td>
<td>78</td>
<td>20</td>
<td>23.2</td>
<td>115.5</td>
</tr>
<tr>
<td>100</td>
<td>TlCl₃</td>
<td>78</td>
<td>2.5</td>
<td>16.4</td>
<td>85.3</td>
</tr>
<tr>
<td>100</td>
<td>FeCl₃</td>
<td>78</td>
<td>2.5</td>
<td>42.5</td>
<td>210</td>
</tr>
<tr>
<td>100</td>
<td>FeCl₃·6H₂O</td>
<td>78</td>
<td>2.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>100</td>
<td>SbCl₃</td>
<td>78</td>
<td>2.5</td>
<td>36.2</td>
<td>180</td>
</tr>
<tr>
<td>100</td>
<td>SbCl₃</td>
<td>78</td>
<td>2.5</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a) Water (100 mmol) was added all at once.
b) Water (100 mmol) was added dropwise over 10 minutes.

seems to depend highly on the period over which water is added dropwise (10 minutes in our experiment and 4 hr in Hill’s one).

If the reaction proceeds via equation 1 and 2, it is expected that the ratio of aniline hydrochloride to diphenylurea is 4 in theory. However, in all experiments using TlCl₃·4H₂O catalyst this ratio is near 5 which means that HCl is formed or phosgene disappears by another route. Since the fact is known that phosgene can act as dehydrating agent of various hydrated metal chlorides including TlCl₃·4H₂O according to eq. 4, such a change in the ratio may be conceivable in spite of the short contact time of TlCl₃·4H₂O and phosgene.

\[
\text{COCl}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{HCl}
\]  

In the hydrolysis with TlCl₃·4H₂O (without direct addition of water), the hydrated salt which initially was dispersed in a molten state was observed to become crystalline and elongation of the reaction time did not lead to the increase of the yield of phosgene. It was found, however, that by an addition of proper amount of water to the above system in the course of reaction the catalyst could be reactivated and the yield of phosgene could be improved (see Experimental). In view of low-melting property of TlCl₃·4H₂O (mp 37°C), it may be suggested that its effectiveness is due partly to its efficient contact with the solvent.

Anhydrous TlCl₃ which was prepared by the dehydration of TlCl₃·4H₂O in thionyl chloride can be used as a catalyst, but the anhydrous salt-water system showed somewhat lower activity than the hydrated system.

FeCl₃·6H₂O, SbCl₃ and thallium salts other than chloride showed no catalytic activity in the hydrolysis of carbon tetrachloride.

With TlCl₃·4H₂O catalyst as in the case of anhydrous FeCl₃ catalyst benzotrichloride could be hydrolyzed more easily than carbon tetrachloride and the yield of the hydrolysis product was high. However, 1,1,1-trichloroethane and chloroform could not be hydrolyzed with TlCl₃·4H₂O catalyst and so chloroform was used as a solvent in the hydrolysis of benzotrichloride.

Considering the facts that 1,1,1-trichloroethane is readily hydrolyzed with FeCl₃,

(99)
<table>
<thead>
<tr>
<th>C₆H₅CCl₃ (mmol)</th>
<th>Solvent (ml)</th>
<th>TICl₄·4H₂O (mmol)</th>
<th>H₂O (mmol)</th>
<th>React. Temp. (°C)</th>
<th>React. Time (hr)</th>
<th>Products (mmol)</th>
<th>C₆H₅CO₂H</th>
<th>COCl₂</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>CCl₄ 100</td>
<td>—</td>
<td>50</td>
<td>78</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>25</td>
<td>CCl₄ 100</td>
<td>1</td>
<td>50</td>
<td>78</td>
<td>0.5</td>
<td>13 a) trace</td>
<td>trace</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>CCl₄ 50</td>
<td>2.5</td>
<td>50</td>
<td>78</td>
<td>1</td>
<td>7.1 b) trace</td>
<td>5.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>CCl₄ 100</td>
<td>25</td>
<td>—</td>
<td>78</td>
<td>2</td>
<td>10 a) 18.8</td>
<td>117</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>CHCl₃ 50</td>
<td>2.5</td>
<td>50</td>
<td>50</td>
<td>10</td>
<td>7.4 c)</td>
<td>—</td>
<td>3.5</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>CHCl₃ 50</td>
<td>2.5</td>
<td>50</td>
<td>61</td>
<td>2</td>
<td>8.1 c)</td>
<td>—</td>
<td>3.5</td>
<td>—</td>
</tr>
</tbody>
</table>

a) determined as methyl ester.

b) determined as acid itself.
c) determined as ethyl ester and acid.

catalyst and that the yield of phosgene is higher with anhydrous FeCl₃ or SbCl₅ catalyst than with anhydrous or hydrated TiCl₄ (Table 1), it is safe to say that TiCl₄ and TiCl₄·4H₂O are somewhat milder catalyst than FeCl₃, SbCl₅ and GaCl₃. It is reported that anhydrous AlCl₃ and ZnCl₂ are inactive for the hydrolysis of carbon tetrachloride, so the generally accepted order of Lewis acid strength would not be applicable.

A strong activation of chlorinated hydrocarbons by the weak Lewis acids seems a principal factor influencing the reaction. Baaz et al. summarized the ability of metal chlorides to accept the chloride ion by determining the equilibrium constant K between trityl chloride and metal chlorides in various solvents (eq. 5):

$$K = \frac{(C₆H₅)₃CCl + MCl₅}{(C₆H₅)₃C⁺ + MCl₅⁻}$$  \hspace{1cm} (5)

These values are large for Sb and Ga chlorides, small for Zn and Al chlorides and moderate for TiCl₄ (eg., K > 10⁵, InCl₃, SbCl₅, GaCl₃; 10³ > K > 10², TiCl₃; 10² > K > 10, ZnCl₂, AlCl₃, HgCl₂; 1 > K, PCl₃, CCl₄). It is also known that FeCl₃ has nearly the same activity as SbCl₅ in a similar reaction in acetic acid. Thus, the first step of this hydrolysis seems to be the interaction between chlorine atom of trichloromethyl compound and metal chloride (regardless of its molecularity), followed by the attack of water molecule on the positive carbon of this complex.

REFERENCES