Catalytic Activity of Bismuth(III) Chloride for Dehydrochlorination of Poly(vinyl chloride)

Yoshio UEMICHI,* Kazuhiko TAKUMA,† Masatoshi SUGIOKA, and Takaji KANAZUKA
Department of Applied Chemistry, Muroran Institute of Technology, Mizumoto, Muroran 050
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Synopsis. Bismuth(III) chloride was found to be highly active as a catalyst for the dehydrochlorination of poly(vinyl chloride). The degree of dehydrochlorination was 97% at the highest. The catalyst showed high activity even in water vapor.

It is well-known that many metal chlorides with surface acidity catalyze various reactions such as alkylation, acylation, isomerization, polymerization, halogenation, etc.[1,2] In particular, chlorides of Fe, Al, Sb, Sn, and Ti are effective catalysts. However, there have been few reports to date on the catalytic activity of bismuth(III) chloride. In this paper, we report that $BiCl_3$ is an active catalyst for the dehydrochlorination of poly(vinyl chloride) (PVC). The reaction has recently attracted considerable attention in connection with the disposal of PVC waste[3] or the transformation of PVC into a polyene material which is one of the electrically conductive polymers.[4]

Experimental

Guaranteed-grade $BiCl_3$ purchased from Kishida Chemical Co. was used as catalyst after grinding it into a fine powder of 160 mesh or under. The chloride was so hygroscopic that it was handled in a dry nitrogen atmosphere. A commercial PVC (Aldrich Chemical Co.) was used without further purification. Its particle size and average molecular weight were 100—160 mesh and 48,000, respectively.

The dehydrochlorination of PVC was carried out at 100—175 °C in a stream of He (30 $ml \cdot min^{-1}$). A powdered mixture of PVC (5.6 mmol in monomer units) and $BiCl_3$ (0.3—2.2 mmol) was loaded into a U-shaped glass tube reactor. The reaction was started by immersing the reactor in an oil bath with a prescribed temperature. The evolved HCl gas was absorbed by water and the aqueous solution was periodically titrated with a sodium hydroxide solution. The total HCl consisted of HCl evolved from PVC and that from $BiCl_3$. The amount of HCl from the reaction of $BiCl_3$ with trace amounts of H_2O adsorbed on the chloride was evaluated from the decrease in the Cl content of catalyst. The content was determined by the Mohr's method; $BiCl_3$ was dissolved in water and the free Cl^- ions were titrated with silver nitrate after filtration of the precipitated BiClO. In some cases, the Cl content in dehydrochlorinated PVC was measured by combustion of the sample, followed by titration with silver nitrate. The total fraction of the eliminated plus residual Cl was 95% or more.

Results and Discussion

The experimental data showing the HCl evolution from PVC and $BiCl_3$ are given in Table 1. The dehydrochlorination of PVC in the absence of catalyst scarcely occurred at 175 °C, while in the presence of $BiCl_3$ it readily proceeded even at lower temperatures. However, HCl was also formed from the catalyst according to the reaction:

$$BiCl_3 + H_2O \longrightarrow BiClO + 2HCl \qquad (1)$$

since the $BiCl_3$ originally contained trace amounts of water. The occurrence of Eq. 1 has been verified experimentally; i.e., the amount of HCl evolved from $BiCl_3$ agreed with the decrease in the Cl content of catalyst on heating $BiCl_3$ alone. Therefore, the net HCl from PVC was calculated by subtracting this decrease from the total HCl evolved.

Table 1 indicates that a considerable amount of HCl was evolved when only $BiCl_3$ was heated, but with the mixture of PVC and $BiCl_3$ the HCl evolution from the catalyst decreased remarkably. This result could be

Table 1. HCl Evolution from PVC and $BiCl_3$ at 125 °C

Sample	Bi/PVC	Reaction time	Total HCl	Cl decrease in $BiCl_3$/mmol	HCl from PVC[a]
	mol/mol	h	mmol		mmol
PVC[b]	—	3	0.03	—	0.03 (0.5)
$BiCl_3$[c]	—	6	0.65	0.66	—
$BiCl_3$[c,d]	—	6	0.64	0.63	—
PVC+$BiCl_3$	0.1	6	2.33	0.14	2.19 (39.1)
PVC+$BiCl_3$	0.2	6	3.35	0.03	3.32 (59.3)
PVC+$BiCl_3$	0.3	6	3.38	trace	3.38 (60.4)
PVC+$FeCl_3$	0.2[e]	20	4.50	3.53[f]	0.97 (17.3)

a) Values in parentheses denote the degree of dehydrochlorination (%). b) At 175 °C. c) 1.1 mmol was used: the same applies to the case of Bi/PVC=0.2 for PVC+$BiCl_3$ samples. d) Outgassed under vacuum at room temperature for 4 h prior to use. e) Fe/PVC molar ratio. f) Cl decrease in $FeCl_3$.

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† Present address: Hokkaido Technological Research Laboratory, Sumitomo Coal Mining Co., Ltd., Akabira 079-11.

rationalized as follows. Eq. 1 is a reversible reaction, so that the equilibrium between $BiCl_3$ and BiClO favors the former in the presence of HCl eliminated from PVC. This explanation was supported by the result shown in Fig. 1, in which the evolution of HCl from $BiCl_3$ at 150 °C started after about 3 h where the dehydrochlorination of PVC, and hence the HCl evolution from PVC, became very slow. This also suggests that a significant amount of water remained on the catalyst surface even after 3 h. Therefore, water is probably not desorbed from the surface as separate molecules. Hydrolysis of $BiCl_3$ resulted in the formation of BiClO and HCl. The catalytic activity of bismuth chloride oxide will be commented on later.

The degree of dehydrochlorination of PVC was heavily dependent on the reaction conditions. Table 1 shows that the degree of dehydrochlorination increases by raising the molar ratio of $BiCl_3$ to the vinyl chloride unit of PVC (Bi/PVC), but the increase is almost saturated at the molar ratio of 0.2. Figure 1 illustrates the time course of PVC dehydrochlorination at various temperatures. A significant dehydrochlorination activity of the $BiCl_3$ catalyst was observed at temperatures higher than 125 °C, while a sublimation of catalyst took place at 175 °C. The degree of dehydrochlorination increased almost linearly up to about 60% with the reaction time. This result suggests that no essential deactivation of the catalyst occurred. Nevertheless, complete dehydrochlorination was not attained under the conditions employed in this study. The degree of dehydrochlorination was 97% at the highest at 150 °C and Bi/PVC=0.4. The existence of the limit of the dehydrochlorination level may be attributed to the formation of Cl atoms isolated from reactive neighbors, such as -CH=CH-CH(Cl)-CH=CH-, by random elimination of HCl.[5] In the course of the reaction, the PVC sample rapidly turned from white to black. This color development seems to be a result of the formation of polyene sequences. In thermal dehydrochlorination of PVC without any additive, PVC particles strongly adhered each other and to the reactor wall. The adhesion made it difficult to handle the dehydrochlorinated residue. In the presence of $BiCl_3$, in contrast, the PVC residue remained fine powdery throughout.

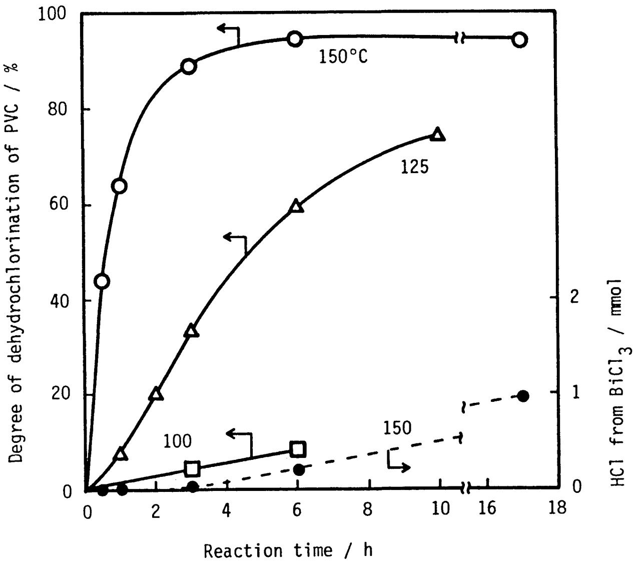

Fig. 1. Time course of PVC dehydrochlorination at various reaction temperatures. Bi/PVC=0.2.

Thus, $BiCl_3$ is active as a catalyst for dehydrochlorination of PVC. There have been many studies on the stabilization of PVC. In this regard, oxides or chlorides of Al, Cd, Fe, Mo, and Zn[6–10] were found to catalyze dehydrochlorination of PVC although their catalytic activities were not always assayed quantitatively. Silica-supported $FeCl_3$ was claimed to be an active catalyst for dehydrochlorination of PVC; the degree of dehydrochlorination was about 90% at 200 °C in 3 h under air, while it was 50% in a N_2 stream.[8] In this study, the catalytic activity of $BiCl_3$ was compared with that of $FeCl_3$ (Merck Co.). The latter was slightly more active than the former in the initial stage of the reaction. However, a rapid reduction in the reaction rate with time was observed and consequently the final dehydrochlorination level was much lower with $FeCl_3$ as catalyst (Table 1). Hence the overall catalytic activity is higher for $BiCl_3$ than for $FeCl_3$.

To obtain further information about the catalysis by $BiCl_3$, the effects of adsorbed pyridine and water on its activity were examined. The results are summarized in Table 2. $BiCl_3$ was treated with 4 Torr (1 Torr=133.322 Pa) of pyridine at room temperature for 10 min in a vacuum system, followed by outgassing at the same temperature for 30 min. After pyridine adsorption the activity of catalyst was reduced by roughly an order-of-magnitude. This strongly suggests that the acidic property of $BiCl_3$ is responsible for the dehydrochlorination activity. In general, the catalytic activity of solid acids is remarkably influenced by addition of water. Since $BiCl_3$ used in this study contained water, removal of water was attempted by outgassing the catalyst at room temperature for 4 h. However, this pretreatment exerted little effect on the catalytic activity, due probably to strong adsorption of the water molecules. The strong adsorption is also substantiated by the observation that no decrease in the amount of HCl evolved from

Table 2. Dehydrochlorination Activity of $BiCl_3$ after Various Treatments

Treatment	Activity/%[a)]
None	59.3
After pyridine adsorption at room temperature	6.5
After outgassing at room temperature	58.5
After treatment with water vapor (3 mol% in He) at 125 °C	0.5
In the presence of water vapor (3 mol% in He)	55.5

a) At 125 °C for 6 h.

$BiCl_3$ took place by the outgassing (Table 1). On the other hand, when $BiCl_3$ was treated with water vapor (3 mol% in He) at 125 °C for 10 h prior to use, the catalytic activity disappeared almost completely. During the pretreatment $BiCl_3$ was transformed mostly into BiClO according to Eq. 1, and the resulting chloride oxide showed no catalytic activity for dehydrochlorination of PVC. This was the reason for the complete loss of the catalytic activity. Then, water vapor was introduced into the reaction system simultaneously with the start of PVC dehydrochlorination and was continuously supplied throughout the reaction. Here the formation of BiClO occurred only to a small extent, most probably because the HCl eliminated from PVC interfered with the formation of the chloride oxide. Owing to this behavior, which is advantageous on a practical viewpoint, the $BiCl_3$ catalyst remains sufficiently active even in the presence of water.

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