NOTES

Efficient Cobalt Complex on the Reaction between Isophorone Diisocyanate and Diethylene Glycol

Shin-ichi INOUE[†] and Yasuharu NAGAI

Department of Applied Chemistry, Aichi Institute of Technology,
1247 Yachigusa, Yakusa-cho, Toyota 470-0392, Japan

Polyurethane is widely used for new industrial materials. However, there is the problem of polyurethane prepared from aromatic isocyanates being colored by air and light. In order to solve this problem, aliphatic isocyanates, which are resistant to coloring by air and light, are used. However, it is already clear that aliphatic isocyanates are less reactive than aromatic isocyanates and they are not able to use conventional catalysts such as tertiary amines[1–5] in the reaction between aliphatic isocyanates and alcohols. Although dibutyltin dilaurate (DBTDL) is generally used as a catalyst,[6–8] this compound contains a little tributyltin which is notable for environmental contamination. Accordingly, it is unfavorable to use it as catalyst. Thus, the development of a new catalyst having a high catalytic activity is necessary.[9] Recently, a new group (or type) of catalysts, late transition metal complexes, are being researched with great interest as catalysts.[10,11] In particular, metal–β-diketone complexes $(Mt(acac)_n)$ are gaining much attention. For example, $Fe(acac)_3$ and $Cu(acac)_2$ complexes are used in the reaction between hexamethylene diisocyanate (HDI) and alcohols.[12,13] We have also already reported that $Mt(acac)_n$ and tertiary amine–$Mt(acac)_n$ complexes had adjective catalytic activity on the reaction between HDI and diethylene glycol (DEG).[14]

In the present paper, the catalytic activities and kinetics of $Mt(acac)_n$ and $Co(f_6acac)_2$–$Co(acac)_2$ complexes, on the reaction between isophorone diisocyanate (IPDI) and DEG are described. The resulting data clearly shows that the catalytic activity of $Co(f_6acac)_2$–$Co(acac)_2$ complex is the very highest on the reaction between IPDI and DEG.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, Nacalai Tesque Inc.) and diethylene glycol (DEG, Nacalai Tesque Inc.) were distilled immediately under reduced pressure (1 mmHg) before use. Manganese(II) $(Mn(acac)_2)$ and iron(III) acetylacetonates $(Fe(acac)_3)$ were obtained from Nacalai Tesque Inc. Cobalt(II) $(Co(acac)_2)$, nickel(II) $(Ni(acac)_2)$, and copper(II) acetylacetonates $(Cu(acac)_2)$, cobalt(II) hexafluoroacethylacetonate $(Co(f_6acac)_2)$ and dibutyltin dilaurate (DBTDL) were obtained from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Toluene (Nacalai Tesque Inc.) and *N,N*-dimethylformamide (DMF, Nacalai Tesque Inc.) were dehydrated over a molecular sieve (4 Å). Other reagents are commercially available and were used as received.

Reaction Catalyzed by $Co(f_6acac)_2$–$Co(acac)_2$ Complex between Isophorone Diisocyanate and Diethylene Glycol

A DMF solution containing a catalyst and a isocyanate was prepared from $Co(acac)_2$ (0.0798 g, 0.31 mmol), $Co(f_6acac)_2$ (0.0376 g, 0.08 mmol), IPDI (1.38 g, 6.20 mmol) and DMF (15 mL), and this DMF solution was degassed under an argon atmosphere. DEG (0.66 g, 6.20 mmol) and DMF (70 mL) solutions were placed in a 200 mL three-necked round bottom flask fitted with a mixer and an argon inlet tube, and then the resulting solution was stirred vigorously at the desired reaction temperature (for example 30 °C) for 30 min under an argon atmosphere. The reaction was started by addition of the DMF solution containing the catalyst and the isocyanate to DEG–DMF solution. Aliquots (8 mL) were produced

from the reaction mixture at regular time intervals (5 or 10 min), and it was added to a predetermined excess of 1 M di-n-dibulylamine solution (10 mL). The unreacted amine was back-titrated to a bromocresol green end-point by using standard hydrochloric acid solution (0.5 M). The rate constant (k) was calculated on the basis of simple second-order kinetics.

Characterization

IR spectra (in KBr pellets) were recorded on a JASCO FT/IR-5300 spectrometer.

RESULTS AND DISCUSSION

Table I summarizes the reactions catalyzed by various complexes such as Mt(acac)$_n$ between IPDI and DEG. From the theory of Farkas[3] and Hostettler,[4] the catalytic constant (K_c) was calculated from the following equation:

$$k = k_0 + K_c[\text{catalyst}]^n. \tag{1}$$

and the rate constants (k_0: uncatalyzed reaction and k: catalyzed reaction) were calculated on the basis of simple second-order kinetics. The reaction between IPDI and DEG did not proceed without a catalyst. However, when Mt(acac)$_n$ was used as a catalyst on this reaction, the reaction proceeded speedily. The Mn(acac)$_2$ catalyst reached a high conversion (>80%) after 120 min, whereas DBTDL showed <70% conversion after 120 min. In addition, the catalytic activity of Mn(acac)$_2$ was very high and it was more active than that of DBTDL. When the Mt(acac)$_n$ was used as catalysts, the resulting product, polyurethane, was colored by the catalytic color. For example, Mn(acac)$_2$ was yellow ocher and Fe(acac)$_3$ was red. If the colorless polyurethane elastomer need, it is unfavorable to use Mt(acac)$_2$ and Mt(acac)$_3$ complexes. Therefore, Mt(f$_6$acac)$_n$–Mt(acac)$_n$ complex was examined. The effect of f$_6$acac ligand to the reaction was reported already by Nahlovsky.[15] Thus, Co(f$_6$acac)$_2$–Co(acac)$_2$ complex was particularly selected in here.

Table I. The polyaddition reactions catalyzed by Mt(acac)$_n$ complexes between IPDI and DEG[a]

Catalyst	k/L mol^{-1} h^{-1}	$K_c \times 10^3$/L^2 eq^{-1} mol^{-1} h^{-1}
none	1.8	—
DBTL	31.7	8.3
Mn(acac)$_2$	35.5	9.4
Fe(acac)$_3$	11.7	2.8
Co(acac)$_2$	14.3	3.5
Ni(acac)$_2$	2.1	—
Cu(acac)$_2$	1.5	—

[a][Catalyst] = 0.0036 mol L^{-1}, [HDI] = [DEG] = 0.073 mol L^{-1}, Temp. = 30 °C, solvent = DMF.

Table II. The polyaddition reactions catalyzed by Co(f$_6$acac)$_2$/Co(acac)$_2$ complexes between IPDI and DEG[a]

Catalyst	k/L mol^{-1} h^{-1}	$K_c \times 10^3$/L^2 eq^{-1} mol^{-1} h^{-1}
none	1.8	—
DBTL	31.7	8.3
Co(acac)$_2$	14.3	3.4
Co(f$_6$acac)$_2$	—	—
Co(f$_6$acac)$_2$/Co(acac)$_2$*	36.9	9.8

[a][Catalyst] = 0.0036 mol L^{-1}, [HDI] = [DEG] = 0.073 mol L^{-1}, Temp. = 30 °C, solvent = DM. *Co(f$_6$acac)$_2$/Co-(acac)$_2$ = 0.25.

Table II summarizes the reactions catalyzed by Co(f$_6$acac)$_2$–Co(acac)$_2$ complex (a molar ratio: Co(f$_6$acac)$_2$/Co(acac)$_2$ = 0.25) between IPDI and DEG. The reaction catalyzed by only Co(f$_6$acac)$_2$ complex did not proceeded, and the Co(f$_6$acac)$_2$ complex was inactive on this reaction. However, when Co(f$_6$acac)$_2$ and Co(acac)$_2$ complexes were used together, the resulting complex, Co(f$_6$acac)$_2$–Co(acac)$_2$, showed a high catalytic activity on the reaction between IPDI and DEG, and it was higher than that of DBTDL and Mn(acac)$_2$. Co(f$_6$acac)$_2$ was used as a co-catalyst. It is clear that the existence of a co-catalyst such as Co(f$_6$acac)$_2$ was important to this reaction and the product obtained on the reaction catalyzed by Co(f$_6$acac)$_2$–Co(acac)$_2$ complex was colorless and transparent. In addition, the molar ratio of Co(f$_6$acac)$_2$ and Co(acac)$_2$ complexes was examined, and the results are shown in Figure 1. The activity of catalyst in the reaction was dependent on the molar ratio of Co(f$_6$acac)$_2$ and Co(acac)$_2$ complexes. When Co(f$_6$acac)$_2$/Co(acac)$_2$ was 0.25, the activity of this catalyst was the highest. It was higher than that of DBTDL and Mn(acac)$_2$ complex. The time-reciprocal
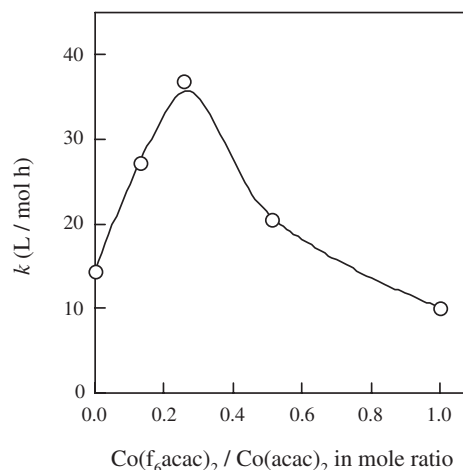

Figure 1. Effect of the Co(f$_6$acac)$_2$/Co(acac)$_2$ molar ratio on the reation between IPDI and DEG: [IPDI] = [DEG] = 0.073 mol/L; [Co(acac)$_2$] = 0.0036 mol/L.
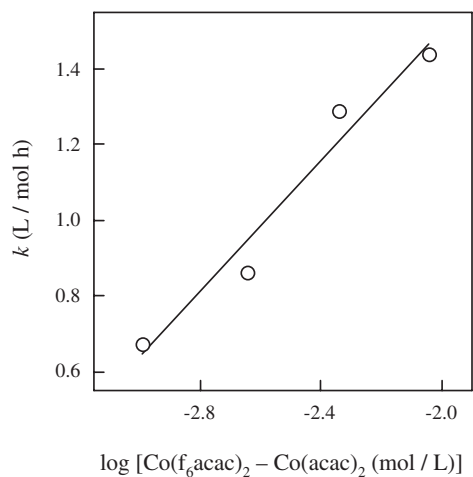
Figure 2. Dependence of the k on the $Co(f_6acac)_2$–$Co(acac)_2$ catalyst concentration ($[IPDI] = [DEG] = 0.073\,mol/L$, $Co(f_6acac)_2/Co(acac)_2 = 0.25$ in mole ratio, Temp. $= 30\,°C$, Solvent $=$ DMF).

of isocyanate concentration plots observed in the temperature range 30–50 °C. At the next kinetically investigation, the reciprocal of isocyanate concentration linearly increased with the reaction time. From an Arrhenious plot of the k on this reaction, the overall activation energy (E_a) of the reaction between IPDI and DEG was calculated to be 67.6 kJ/mol. In the case of DBTDL, the E_a was calculated to be 73.8 kJ/mol. The E_a of $Co(f_6acac)_2$–$Co(acac)_2$ complex was somewhat lower than that of DBTDL.

Figure 2 presents the relationship between the k and the catalyst concentration ($[Co(f_6acac)_2$–$Co(acac)_2]$). The plot of $\log(k/k_0 - 1)$ *vs.* $\log[Co(f_6acac)_2$–$Co(acac)_2]$ indicated a linear relation between the k and $[Co(f_6acac)_2$–$Co(acac)_2]$. The k was proportional to the 0.86 power of the $Co(f_6acac)_2$–$Co(acac)_2$ concentration. From these results, the k is expressed as follows:

$$k = k_0 + K_c[Co(f_6acac)_2/Co(acac)_2]^{0.86} \qquad (2)$$

We also examined about $Co(acac)_2$ complex, the k was proportional to the 0.84 power of the $Co(acac)_2$ concentration. The 0.86 power observed here is nearly equal to the 0.84 observed for the reaction catalyzed by $Co(acac)_2$. The FT/IR spectra (in KBr pellets) of 1:1 mixture of IPDI and $Co(acac)_2$ (a), 1:1 mixture of IPDI and $Co(f_6acac)_2$–$Co(acac)_2$ (a molar ratio: $Co(f_6acac)_2/Co(acac)_2 = 0.25$) (b), and 1:1 mixture of IPDI and $Co(f_6acac)_2$ (c) were found with appearance of the NCO peak at $2265\,cm^{-1}$, $2267\,cm^{-1}$ and $2269\,cm^{-1}$ (Figure 3). The additional effect of $Co(f_6acac)_2$ complex to $Co(acac)_2$ complex was involved with an upward shift $2\,cm^{-1}$ in NCO peak. Although the relation between the NCO peak shift value and an affinity for complex was not clear, this behavior
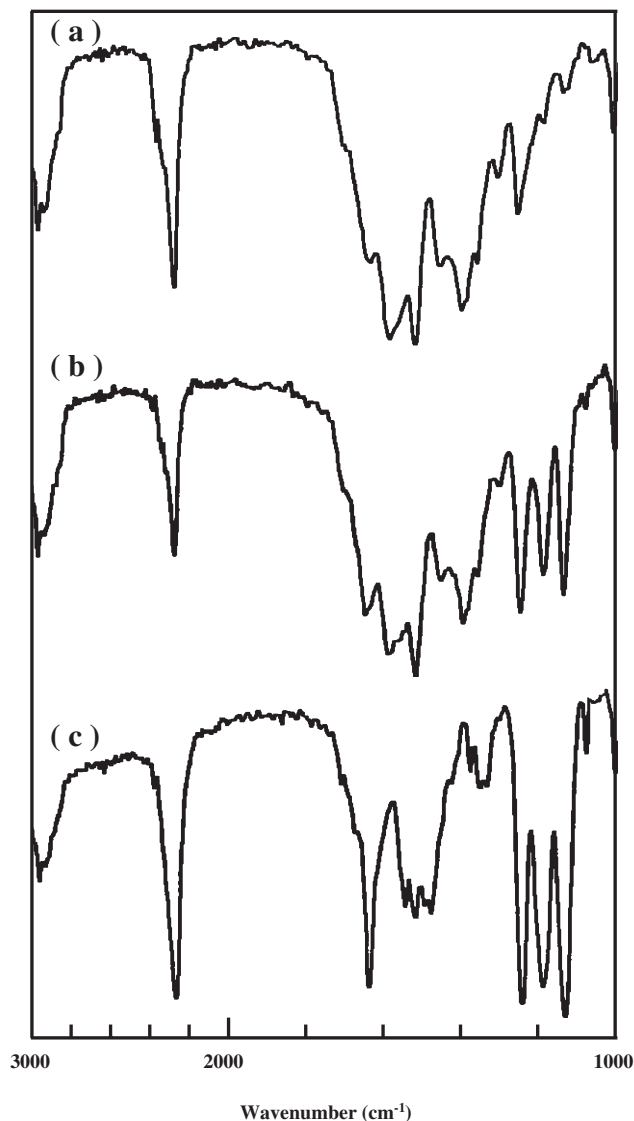

Figure 3. IR spectra of IPDI-Co complexes: (a) IPDI–$Co(acac)_2$ complex, (b) IPDI–$Co(f_6acac)_2$–$Co(acac)_2$ complex ($Co(f_6acac)_2/Co(acac)_2 = 0.25$), (c) IPDI–$Co(f_6acac)$ complex.

was due to the different active species. In the future, the behavior is clarified from further investigation.

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