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Thermally latent reaction of hemiacetal ester with epoxide controlled by Schiff-base–zinc chloride complexes with tunable catalytic activity

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Abstract

Schiff-base–zinc chloride complexes ($ZnCl_2/\mathbf{1}_R$) thermal-latently catalyze the reaction of glycidyl phenyl ether (**2**) and 1-propoxyethyl-2-ethylhexanate (**3**) that proceeds at appropriate temperatures for latent curing. This reaction proceeds via the nucleophilic addition of carboxylic acid generated from the thermal dissociation of **3** to **2**, which takes place faster than the reaction without $ZnCl_2/\mathbf{1}_R$. Catalytic activities of $ZnCl_2/\mathbf{1}_R$, depending on the basicities of the α-diimine ligands controllable by the substituents on the aromatic rings, were evaluated by kinetic parameters; namely the reaction rate constants (k), the activation energies (E_a), and the frequency factors (A). $ZnCl_2/\mathbf{1}_{Cl}$ bearing the electron-withdrawing chlorine group initiates the reaction above 80 °C, whereas $ZnCl_2/\mathbf{1}_{OMe}$ bearing the electron-donating methoxy group initiates the reaction above 100 °C. The E_a values in the reactions with $ZnCl_2/\mathbf{1}_{Cl}$ and $ZnCl_2/\mathbf{1}_{OMe}$ were estimated to be 52.2 and 177 kJ mol^{-1}, respectively, which agree with the latencies at ambient temperatures. The A values also differ with the catalysts (6.46×10^2 and 2.04×10^{19} L mol^{-1} s^{-1} for $ZnCl_2/\mathbf{1}_{Cl}$ and $ZnCl_2/\mathbf{1}_{OMe}$, respectively). The very high A values for the catalysts with electron-donating groups manifest the very good latencies under ambient conditions, in spite of the high activities at elevated temperatures. The coordination behavior of $ZnCl_2/\mathbf{1}_R$ was evaluated by ^{1}H NMR, ^{13}C NMR, ^{15}N NMR, and IR spectroscopies to understand the substituent effects.

1. Introduction

Typical catalysts are demanded to decrease activation energies of specific reactions for acceleration and increase in selectivity. However, some reactions, for example, latent reactions, do not require simple acceleration. Latent reactions, which are inactive under ambient conditions but active only with specific external stimulation such as heating and photoirradiation, have been widely applied to adhesives, coatings, paintings, and photo-resists [1,2]. Such reactions allow simple processing, because mixtures of precursors ready to use may be treated with simple procedures.

Desirable thermally latent reactions should have sharp temperature dependence, and it means that the rates of the reactions should increase vigorously with temperatures. Temperature dependence is evaluated with the well-known Arrhenius equation, by which the activation energies (E_a) and the frequency factors (A) are calculated. Although a large E_a value typically decreases a reaction rate constant (k) as shown in the Arrhenius equation, a large A value can compensate to achieve a practical reaction rate at high temperatures [1,3b]. As an example, Pappas and Hill et al. reported that sulfonium salts are promising catalysts for latent curing [1], in which polymerization of epoxides shows large E_a and A value (e.g., 208 kJ mol^{-1} and 1.8×10^9 s^{-1}, respectively). Endo et al. have reported phosphonium ylides as thermally latent catalysts for the reaction of epoxides with phenol-resins [3]. The large E_a values of phosphonium ylides bearing bulky substituents are ascribed to the thermal stability of the linkages between the carbon and phosphorous atoms that directly affects the catalytic activity [3b].

As substrates for latent reactions, we have been focusing on hemiacetal ester derivatives of useful thermally latent car-

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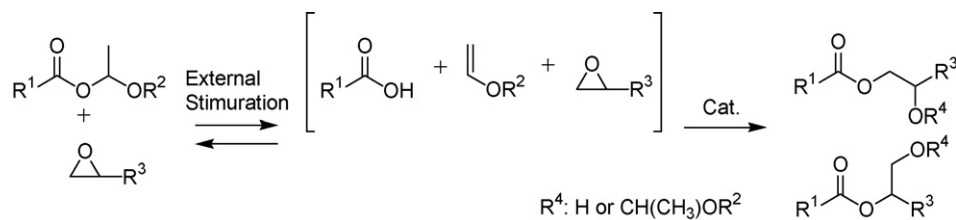
Scheme 1.

boxylic acids, which thermally dissociate into carboxylic acids and vinyl ethers (Scheme 1) [4]. Catalysts are required for the reactions of hemiacetal esters so that carboxylic acids thermal-latently generated from hemiacetal esters can nucleophilically react with epoxides under appropriate temperature for curing (e.g., 120–160 °C) [4c,5,6], because spontaneous dissociation of hemiacetal esters typically takes place only at very high temperature (>160 °C) [5,6].

We have recently reported that Schiff-base–zinc halide complexes ($ZnX_2/1_H$) thermal-latently catalyze addition of a hemiacetal ester with an epoxide [6]. Unexpectedly, the catalytic activity of the Schiff-base–zinc halide complexes ($ZnI_2/1_H > ZnBr_2/1_H \geq ZnCl_2/1_H$) does not correlate with the electronegativities of the halides. This result supposes that the Schiff-base ligand does not coordinate with ZnI_2 sufficiently owing to the steric hindrance of iodide. In order to design Lewis acid complexes with more tunabilities, we have focused on the basicities of the Schiff-base ligands that may be tuned by *para*-substituents on the aromatic rings. The introduction of *para*-substituents on the aromatic rings is expected to control both the activity and the latency. For example, we presume that the introduction of electron-donating groups increases the latency by decreasing the Lewis acidity of the complex. Therefore, we have investigated thermally latent reaction of a hemiacetal ester and an epoxide using zinc chloride complexes with various Schiff-base ligands ($ZnCl_2/1_R$). The catalytic activity of the Schiff-base–zinc chloride complexes ($ZnCl_2/1_R$) was also evaluated from kinetic analysis.

2. Experimental

2.1. Materials

Ethylene diamine, *p*-chlorobenzaldehyde, benzaldehyde, *p*-methylbenzaldehyde, *p*-tert-butylbenzaldehyde, *p*-methoxy-benzaldehyde, *p*-ethoxybenzaldehyde, and *p*-*N,N*-dimethyl-aminobenzaldehyde (Kanto Kagaku, Tokyo, Japan) were used as received. Zinc chloride in diethyl ether solution [(1 M), Sigma Aldrich, Missouri, MO] was used as received. Glycidyl phenyl ether (**2**) (Kanto Kagaku, Tokyo, Japan) was dried over CaH_2, and distilled under reduced pressure. 1-Propoxyethyl-2-ethyl hexanoate (**3**) was prepared as reported [7]. 2-Ethylhexanoic acid (**4**) (Kanto Kagaku, Tokyo, Japan) was used as received. Other chemicals were commercial products with extra-pure grade, and used as received.

2.2. Measurements

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded with a Varian INOVA 500 spectrometer using tetramethylsilane as an internal standard in $CDCl_3$ at an ambient temperature (500 and 125 MHz for ^1H and ^{13}C NMR, respectively). ^{15}N NMR spectra (40.5 MHz) were recorded with a JEOL ECX 400 spectrometer using nitromethane as an internal standard in $CDCl_3$ at an ambient temperature. The δ values are given in ppm. Fourier-transform infrared (FT-IR) spectra were recorded with a JASCO FT/IR-470 plus spectrometer. Gas chromatography mass spectra (GC–MS) were measured with a Shimadzu GCGS-QP5050A instrument. Elemental analysis was carried out with a Perkin-Elmer PE2400-2 CHNS/O instrument. Melting points (T_m) were determined by differential scanning calorimetry (DSC) measurements on a SEIKO Instruments DSC 6200 and EXSTAR 6000 system at a scanning rate of 10 °C/min under a nitrogen atmosphere.

2.3. Syntheses of N,N'-bis(p-substituted benzylidene)-1,2-diiminoethane (1_R)

N,N'-Bis(benzylidene)-1,2-diiminoethane (1_H) was prepared as previously reported [6]. The other ligands were also prepared in similar manners, and their structures were confirmed by ^1H NMR, ^{13}C NMR, ^{15}N NMR, IR, and GC–mass spectroscopic and elemental analyses. The ligands were obtained as white needle crystals.

2.3.1. N,N'-Bis(p-chlorobenzylidene)-1,2-diiminoethane (1_{Cl}); yield: 91%

^1H NMR: 8.22 (s, 2H, −CH=N−), 7.63 (d, J = 11.0 Hz, 4H, −C_6H_4−), 7.36 (d, J = 11.0 Hz, 4H, −C_6H_4−), 3.95 (s, 4H, −CH_2−). ^{13}C NMR: 161.2 (−CH=N−), 136.5, 134.4, 129.1, 128.7 (−C_6H_4−), 61.3 (−CH_2−). ^{15}N NMR: 331.02 (−CH=N−). IR (KBr): 3030, 2915 (C=C, −CH_2−), 1644 (−CH=N−), 1592, 1486 (−C_6H_4−). GC–MS (m/z): 303. mp: 148.0–148.5 °C. Elem. Anal. for $C_{16}H_{14}Cl_2N_2$—Calcd.: C, 62.97; H, 4.62; N, 9.18. Found: C, 62.93; H, 4.52; N, 9.10.

2.3.2. N,N'-Bis(benzylidene)-1,2-diiminoethane (1_H); yield: 92%

^1H NMR: 8.30 (s, 2H, −CH=N−), 7.70 (m, 4H, −C_6H_5), 7.40 (m, 6H, −C_6H_5), 3.98 (s, 4H, −CH_2−). ^{13}C NMR: 162.8 (−CH=N−), 136.1, 130.5, 128.5, 128.0, (−C_6H_5), 61.5 (−CH_2−). ^{15}N NMR: 328.36 (−CH=N−). IR (KBr): 3060, 3032, 2934 (C=C, −CH_2−), 1642 (−CH=N−) 1597, 1489

(−C_6H_5). GC–MS (*m/z*): 236. mp: 55.1–56.4 °C. Elem. Anal. for $C_{16}H_{16}N_2$—Calcd.: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.24; H, 6.79; N, 11.82.

2.3.3. N,N'-Bis(p-methylbenzylidene)-1,2-diiminoethane (*1_{Me}*); yield: 90%

^{1}H NMR: 8.24 (s, 2H, −C*H*=N−), 7.59 (d, *J* = 8.0 Hz, 4H, −C_6H_4−), 7.19 (d, *J* = 8.0 Hz, 4H, −C_6H_4−), 3.94 (s, 4H, −CH_2−), 2.36 (s, 6H, −CH_3). ^{13}C NMR: 162.4 (−CH=N−), 140.7, 133.5, 129.1, 127.9 (−C_6H_4−), 61.6 (−CH_2−), 21.4 (−CH_3). ^{15}N NMR: 324.67 (−CH=*N*−). IR (KBr): 3046, 2923, 2911 (C=C, −CH_2−), 1637 (−CH=N−), 1605, 1508 (−C_6H_4−). GC–MS (*m/z*): 264. mp: 161.7–162.6 °C. Elem. Anal. for $C_{18}H_{20}N_2$—Calcd.: C, 81.78; H, 7.63; N, 10.60. Found: C, 81.54; H, 7.57; N, 10.53.

2.3.4. N,N'-Bis(p-tert-butylbenzylidene)-1,2-diiminoethane (*1_{tBu}*); yield: 92%

^{1}H NMR: 8.27 (s, 2H, −C*H*=N−), 7.64 (d, *J* = 9.5 Hz, 4H, −C_6H_4−), 7.41 (d, *J* = 9.5 Hz, 4H, −C_6H_4−), 3.95 (s, 4H, −CH_2−), 1.32 [s, 18H, −C(CH_3)$_3$]. ^{13}C NMR: 162.3 (−CH=N−), 153.8, 133.4, 127.8, 125.4 (−C_6H_4−), 61.7 (−CH_2−), 34.7 [−C(CH_3)_3$], 31.1 [−C($C$H_3)_3$]. ^{15}N NMR: 324.76 (−CH=*N*−). IR (KBr): 3020, 2901 (C=C, −CH_2−), 1644 (−CH=N−), 1605, 1503 (−C_6H_4−). GC–MS (*m/z*): 348. mp: 115.6–116.8 °C. Elem. Anal. for $C_{24}H_{32}N_2$—Calcd.: C, 82.71; H, 9.25; N, 8.04. Found: C, 82.93; H, 9.46; N, 8.04.

2.3.5. N,N'-Bis(p-methoxybenzylidene)-1,2-diiminoethane (*1_{OMe}*); yield: 90%

^{1}H NMR: 8.21 (s, 2H, −C*H*=N−), 7.64 (d, *J* = 7.5 Hz, 4H, −C_6H_4−), 6.90 (d, *J* = 7.5 Hz, 4H, −C_6H_4−), 3.91 (s, 6H, −OCH_3), 3.83 (s, 4H, −CH_2−). ^{13}C NMR: 162.0 (−CH=N−), 161.7, 129.7, 129.3, 114.0 (−C_6H_4−), 61.9 (−CH_2−), 55.5 (−OCH_3$). ^{15}N NMR: 320.46 (−CH=*N*−). IR (KBr): 3046, 2971, 2920 (C=C, −CH_2−), 1639 (−CH=N−). GC–MS (*m/z*): 296. mp: 112.7–113.4 °C. Elem. Anal. for $C_{18}H_{20}N_2O_2$—Calcd.: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.76; H, 6.76; N, 9.40.

2.3.6. N,N'-Bis(p-ethoxybenzylidene)-1,2-diiminoethane (*1_{OEt}*); yield: 90%

^{1}H NMR: 8.20 (s, 2H, −C*H*=N−), 7.62 (d, *J* = 7.5 Hz, 4H, −C_6H_4−), 6.89 (d, *J* = 7.5 Hz, 4H, −C_6H_4−), 4.05 (q, *J* = 7.0 Hz, 4H, −OCH_2−), 3.91 (s, 4H, −CH_2−), 1.42 (t, *J* = 7.0 Hz, 6H, −CH_3). ^{13}C NMR: 161.8 (−CH=N−), 160.8, 129.5, 128.9, 114.2 (−C_6H_4−), 63.4 (−OCH_2$−), 61.6 (−$CH_2$−), 55.5 (−$C$H_3). ^{15}N NMR: 320.21 (−CH=*N*−). IR (KBr): 2984, 2929 (C=C, −CH_2−), 1641 (−CH=N−), 1603, 1509 (−C_6H_4−). GC–MS (*m/z*): 324. mp; 115.7–116.1 °C. Elem. Anal. for $C_{20}H_{24}N_2O_2$—Calcd.: C, 74.04; H, 7.46; N, 8.64. Found: C, 74.13; H, 7.41; N, 8.65.

2.3.7. N,N'-Bis(p-dimethylaminobenzylidene)-1,2-diiminoethane (*1_{NMe_2}*); yield: 84%

^{1}H NMR: 8.16 (s, 2H, −C*H*=N−), 7.59 (d, *J* = 8.0 Hz, 4H, −C_6H_4−), 6.69 (d, *J* = 8.0 Hz, 4H, −C_6H_4−), 3.87 (s, 4H, −CH_2−), 2.99 [s, 6H, −N(CH_3)$_2$]. ^{13}C NMR: 162.4 (−CH=N−), 152.0, 129.4, 124.5, 111.5 (−C_6H_4−), 61.9 (−CH_2−), 40.0 [−N(CH_3)_3$]. ^{15}N NMR: 328.88 (−CH=*N*−), 47.36 [−*N*(CH_3)_2$]. IR (KBr): 2829 (C=C, −CH_2−), 1638 (−CH=N−), 1604 (−C_6H_4−). GC–MS (*m/z*): 322. mp: 179.0–179.8 °C. Elem. Anal. for $C_{20}H_{26}N_4$—Calcd.: C, 74.50; H, 8.13; N, 17.38. Found: C, 74.56; H, 8.15; N, 17.34.

2.4. Preparation of N,N'-bis(p-substituted benzylidene)-1,2-diiminoethane/zinc chloride complex (*ZnCl_2/1_R*)

$ZnCl_2/$**1**$_R$ [*N,N'*-bis(benzylidene)-1,2-diiminoethane/zinc chloride complex] was prepared as previously reported [6]. The other complexes ($ZnCl_2/$**1**$_H$) were also prepared in similar manners, and their structures were confirmed by ^{1}H NMR, ^{13}C NMR, and ^{15}N NMR and IR spectroscopic and elemental analyses. All the complexes were obtained as a white powder.

2.4.1. N,N'-Bis(benzylidene)-1,2-diiminoethane/zinc chloride complex (*ZnCl_2/1_H*); yield: 92%

^{1}H NMR: 8.60 (s, 2H, −C*H*=N−), 8.11 (d, *J* = 9.0 Hz, 4H, −C_6H_5), 7.59 (d, *J* = 9.0 Hz, 6H, −C_6H_5), 4.10 (s, 4H, −CH_2−). ^{13}C NMR: 170.5 (−CH=N−), 146.5, 134.2, 130.7, 129.2, (−C_6H_5), 59.7 (−CH_2−). IR (KBr): 3060, 3032, 2934 (C=C, −CH_2−), 1644 (−CH=N−), 1597 (−C_6H_4−). Elem. Anal. for $C_{16}H_{16}N_2Cl_2Zn$—Calcd.: C, 51.57; H, 4.33; N, 7.52. Found: C, 51.33; H, 4.44; N, 7.42.

2.4.2. N,N'-Bis(p-methylbenzylidene)-1,2-diiminoethane/zinc chloride complex (*ZnCl_2/1_Me*); yield: 90%

^{1}H NMR: 8.34 (s, 2H, −C*H*=N−), 8.00 (d, *J* = 8.0 Hz, 4H, −C_6H_4−), 7.35 (d, *J* = 8.0 Hz, 4H, −C_6H_4−), 4.03 (s, 4H, −CH_2−), 2.42 (s, 6H, −CH_3). ^{13}C NMR: 169.8 (−CH=N−), 145.1, 130.8, 129.8, 128.5, (−C_6H_4−), 59.7 (−CH_2−), 21.8 (−CH_3). ^{15}N NMR: 257.84 (−CH=*N*−). IR (KBr): 3046, 2937 (C=C, −CH_2−), 1637 (−CH=N−), 1607, 1512 (−C_6H_4−). Elem. Anal. for $C_{18}H_{20}Cl_2N_2Zn$—Calcd.: C, 53.96; H, 5.03; N, 6.99. Found: C, 53.36; H, 4.89; N, 6.88.

2.4.3. N,N'-Bis(p-tert-butylbenzylidene)-1,2-diiminoethane/zinc chloride complex (*ZnCl_2/1_{tBu}*); yield: 92%

^{1}H NMR: 8.50 (s, 2H, −C*H*=N−), 8.07 (d, *J* = 9.5 Hz, 4H, −C_6H_4−), 7.58 (d, *J* = 9.5 Hz, 4H, −C_6H_4−), 4.03 (s, 4H, −CH_2−), 1.34 [s, 18H, −C(CH_3)$_3$]. ^{13}C NMR (CDCl_3, 125 MHz): 169.7 (−CH=N−), 158.0, 130.8, 128.3, 126.2 (−C_6H_4−), 59.7 (−CH_2−), 35.2 [−C(CH_3)_3$], 30.9 [−C($C$H_3)_3$]. ^{15}N NMR: 257.36 (−CH=*N*−). IR (KBr): 3056, 2963 (C=C, −CH_2−), 1641 (−CH=N−), 1606, 1510 (−C_6H_4−). Elem. Anal. for $C_{24}H_{32}Cl_2N_2Zn$—Calcd.: C, 59.46; H, 6.65; N, 5.78. Found: C, 59.32; H, 6.57; N, 5.77.

2.4.4.
N,N'-Bis(p-methoxybenzylidene)-1,2-diiminoethane/zinc chloride complex (ZnCl₂/1_OMe); yield: 90%

^{1}H NMR: 8.44 (s, 2H, $-CH$=N−), 8.09 (d, J = 9.0 Hz, 4H, $-C_6H_4-$), 7.05 (d, J = 9.0 Hz, 4H, $-C_6H_4-$), 4.00 (s, 6H, $-OCH_3$). ^{13}C NMR: 168.9 ($-CH$=N−), 164.1, 133.0, 123.9, 114.6 ($-C_6H_4-$), 59.6 ($-CH_2-$), 55.5 ($-OCH_3$). ^{15}N NMR: 252.02 ($-CH$=N−). IR (KBr): 2935 (C=C, $-CH_2-$), 1632 ($-CH$=N−), 1600, 1514 ($-C_6H_4-$). Elem. Anal. for $C_{18}H_{20}Cl_2N_2O_2Zn$—Calcd.: C, 49.97; H, 4.66; N, 6.47. Found: C, 50.00; H, 4.54; N, 6.46.

2.4.5.
N,N'-Bis(p-ethoxybenzylidene)-1,2-diiminoethane/zinc chloride complex (ZnCl₂/1_OEt); yield: 90%

^{1}H NMR: 8.43 (s, 2H, $-CH$=N−), 8.06 (d, J = 9.0 Hz, 4H, $-C_6H_4-$), 7.00 (d, J = 9.0 Hz, 4H, $-C_6H_4-$), 4.13 (q, J = 7.0 Hz, 4H, $-OCH_2-$), 3.99 (s, 4H, $-CH_2-$), 1.43 (t, J = 8.0 Hz, 6H, $-CH_3$). ^{13}C NMR: 168.9 ($-CH$=N−), 163.6, 133.0, 123.6, 114.9 ($-C_6H_4-$), 63.8 ($-OCH_2-$), 59.6 ($-CH_2-$), 14.5 ($-CH_3$). ^{15}N NMR: 251.60 ($-CH$=N−). IR (KBr): 3051, 2925 (C=C, $-CH_2-$), 1635 ($-CH$=N−), 1601, 1512 ($-C_6H_4-$). Elem. Anal. for $C_{20}H_{24}Cl_2N_2O_2Zn$—Calcd.: C, 52.14; H, 5.25; N, 6.08. Found: C, 52.07; H, 5.14; N, 6.09.

2.4.6. N,N'-Bis(p-dimethylaminobenzylidene)-1,2-diiminoethane/zinc chloride complex (ZnCl₂/1_NMe₂); yield: 88%

^{1}H NMR: 8.30 (s, 2H, $-CH$=N−), 7.99 (d, J = 9.0 Hz, 4H, $-C_6H_4-$), 6.77 (d, J = 9.0 Hz, 4H, $-C_6H_4-$), 3.92 (s, 4H, $-CH_2-$), 3.07 [s, 6H, $-N(CH_3)_2$]. ^{13}C NMR: 168.5 ($-CH$=N−), 154.1, 133.2, 118.8, 111.5 ($-C_6H_4-$), 59.7 ($-CH_2-$), 39.6 [$-N(CH_3)_3$]. IR (KBr): 2909 (C=C, $-CH_2-$), 1628 ($-CH$=N−), 1593 ($-C_6H_4-$). Elem. Anal. for $C_{20}H_{26}Cl_2N_4Zn$—Calcd.: C, 52.36; H, 5.71; N, 12.21. Found: C, 52.00; H, 5.64; N, 12.03.

### 2.5. The reaction of 2 and 3 with ZnCl₂/1_H as a thermal latent catalyst (typical procedure)

A mixture of **2** (0.150 g, 1.00 mmol), **3** (0.230 g, 1.00 mmol), and ZnCl₂/**1**_H (22.3 mg, 60.0 μmol, 3.00 mol% to **2** and **3**) was heated to 30–140 °C for 3 h under a nitrogen atmosphere. The thermal dissociation of hemiacetal ester **3**, the consumption of **2**, and the reaction of **2** with the carboxylic acid from **3** were quantified by ^{1}H NMR spectroscopy.

3. Results and discussion

3.1. Preparation of Schiff-base–zinc chloride complexes

Schiff-base–zinc chloride complexes (ZnCl₂/**1**_R) bearing substituents on the *para*-position of the aromatic rings were prepared via the coordination of Schiff-base ligands (**1**_R) to zinc chloride. The complexes except ZnCl₂/**1**_NMe₂ were obtained as white solids, while ZnCl₂/**1**_NMe₂ was yielded as a pale yellow solid. The structures of the obtained products were confirmed
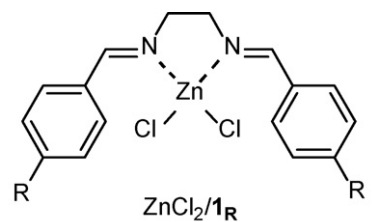
R: Cl, H, Me, tBu, OEt, OMe, NMe₂

Scheme 2.

by ^{1}H NMR, ^{13}C NMR, ^{15}N NMR, and IR spectroscopic and elemental analysis (Scheme 2).

The ^{1}H NMR, ^{13}C NMR, and ^{15}N NMR chemical shifts and the IR absorption bands of the ZnCl₂/**1**_R correlate with the basicities of the original Schiff-bases depending on the electronic characters of the substituents. Table 1 summarizes the ^{1}H NMR, ^{13}C NMR, and ^{15}N NMR chemical shifts and IR absorption band of the Schiff-base–zinc chloride complexes. Complexes with electron-donating substituents show the NMR signals of imine (CH=N) at higher magnetic field, demonstrating the electron densities of the imine groups depending on the electron character of the substituents. We estimated the degree of the donation by the ligand in ZnCl₂/**1**_R from the spectroscopic data. Specifically, the degree of donation of π-electrons in imine groups was evaluated from the differences between the ^{15}N NMR chemical shifts and IR absorption band of the imine groups in the complexes and the free ligands based on the fact that donation of π-electrons in the imine groups to acceptors shifts ^{15}N NMR chemical shifts and the IR absorption bands toward higher magnetic field and lower wavenumber, respectively [8,9]. The Δppm values from the ^{15}N NMR spectroscopic data increased as the increase in the electron-donating ability (i.e., the Hammett's σ_p values) of the substituents [10], although we could not evaluate ZnCl₂/**1**_H and ZnCl₂/**1**_NMe₂, because of their low solubility. The shifts toward higher magnetic field agree with the cases of the coordination of the nitrogen ligand to metals [11,12] and the protonation of amines [8] and imines [13], by which the electron densities of the nitrogen atoms decrease [8]. The larger shifts toward higher magnetic field are attributable to the stronger donation of the π-electron on the nitrogen atoms included in the conjugated π systems consisting of the aromatic rings and the conjugated diimines to zinc atom (Scheme 3). The electronic characters of the substituents also affect the IR absorption bands of the ligands and the complexes. The IR absorption bands for the imines in the Schiff-base ligands (CH=N stretching vibration) were observed at approximately 1640 cm^{-1}, and the wavenumbers decrease as the electron-donating ability of the substituents increases. The wavenumbers were shifted by the coordination, and the Δcm^{-1} values (i.e., the shifts in the wavenumbers of the imine group from those in the free ligands to those in the complexes) also increased with the increase in the electron-donating ability of the *para*-substituents on the aromatic rings. Lower wavenumber shifts are attributable to the decreases in the sp^2 characters of the imine group by stronger donation of the π-electron. These observations support that the strength of the coordination increases

Table 1

NMR chemical shift and IR absorption band of CH=N in Schiff-base–zinc chloride complexes (ZnCl$_2$/1$_R$) and their differential values to those of Schiff-base ligands (1$_R$) at 25 °C

| R (σ_p)[a]	^{15}N NMR chemical shift[b] of CH=N (Δppm)	IR absorption band[c] of CH=N (Δcm^{-1})	^{13}C NMR chemical shift[b] of CH=N (Δppm)	^{1}H NMR chemical shift[b] of CH=N (Δppm)
Cl (0.23)	_[d]	_[d]	_[d]	_[d]
H (0.00)	_[e]	1644.1 (+1.9)	170.52 (+7.76)	8.602 (+0.306)
Me (−0.17)	257.84 (−66.8)	1636.3 (−3.9)	169.89 (+7.41)	8.510 (+0.268)
Bu^t (−0.20)	257.36 (−67.4)	1641.1 (−3.9)	169.52 (+7.24)	8.502 (+0.246)
OEt (−0.25)	251.60 (−68.6)	1635.3 (−5.8)	168.85 (+7.01)	8.444 (+0.236)
OMe (−0.27)	252.02 (−70.4)	1632.4 (−6.8)	168.86 (+6.83)	8.427 (+0.226)
NMe$_2$ (−0.83)	_[e]	1628.4 (−9.8)	168.47 (+6.04)	8.269 (+0.168)

[a] σ_p values of the substituents on 1$_R$ in Ref. [14].

[b] Measured in CDCl$_3$. The difference in the NMR chemical shift (Δppm) of imine groups in the complexes and free ligand. Positive and negative values indicate shift toward lower and higher magnetic field, respectively.

[c] Measured as KBr disks. The difference in the IR absorption bands (cm^{-1}) of imine groups in the complexes and free ligand. Positive and negative values indicate shifts toward higher and lower wavenumber regions, respectively.

[d] Not isolable from the mixture of ZnCl$_2$/1$_{Cl}$ and unreacted 1$_{Cl}$.

[e] Resolved ^{15}N NMR spectrum could not be obtained due to the poor solubility of the metal complex in CDCl$_3$.
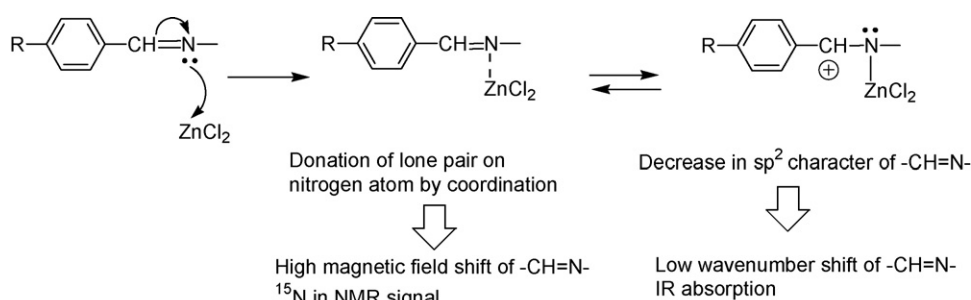
Scheme 3.

with increasing basicity of the ligand, and hence, ZnCl$_2$/1$_R$ with weakly basic ligands is assumed to consist of weak coordination. This assumption agrees with the fact that 1$_{Cl}$ did not make significant coordination with ZnCl$_2$, which results in affording the mixture containing a partial amount of ZnCl$_2$ and 1$_{Cl}$.

3.2. The reaction of hemiacetal ester (3) and epoxide (2) with Schiff-base–zinc chloride complex (ZnCl$_2$/1$_R$)

In order to evaluate the electronic effect of the *para*-substituents on the Schiff-base ligands (1$_R$) on the catalytic activity, 2 and 3 were allowed to react in the presence of

ZnCl$_2$/1$_R$ [Cl, H, Me, *t*Bu, OMe, OEt, NMe$_2$] (3.0 mol%) at various temperatures for 3 h (Scheme 4). Fig. 1 shows the relationship between temperatures versus conversion of 2. No addition reaction of 2 and 3 proceeded with ZnCl$_2$/1$_R$ within 24 h under ambient conditions (<70 °C), and this indicates that ZnCl$_2$/1$_R$ complexes show activity only at elevated temperatures. It is advantageous over bare ZnCl$_2$ that shows activity even at room temperature (e.g., approximately 10% amounts of 2 was converted at 25 °C) [6]. Among these catalysts, ZnCl$_2$/1$_{Cl}$ initiated the addition at the lowest temperature (80 °C). The complexes with electron-donating groups, ZnCl$_2$/1$_{OMe}$ and ZnCl$_2$/1$_{NMe_2}$ initiated the reaction at 100 °C and 110 °C,
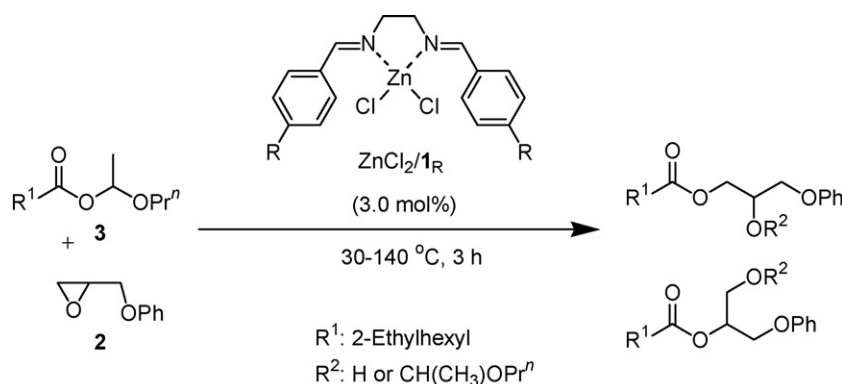
Scheme 4.
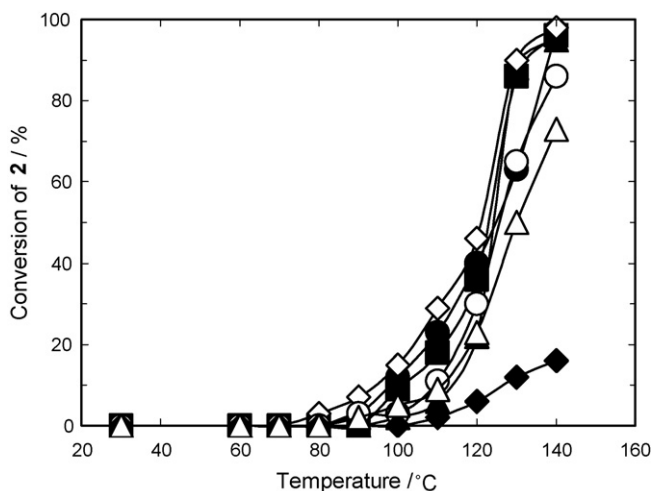
Fig. 1. Time vs. conversion of **2** relationship in the addition of **2** and **3** with 3.0 mol% amounts of ZnCl$_2$/1_R (1_{Cl}, ◇; 1_H; ●; 1_{Me}, ■; 1_{tBu}, ○; 1_{OEt}, △; 1_{OMe}, ▲; 1_{NMe_2}, ◆) at various temperatures.

respectively, and the other complexes did at 90 °C. The conversions became quantitative at 140 °C with ZnCl$_2$/1_{Cl}, ZnCl$_2$/1_H, ZnCl$_2$/1_{Me}, and ZnCl$_2$/1_{OMe}, but stayed approximately 80% and 70% at 140 °C with ZnCl$_2$/1_{tBu} and ZnCl$_2$/1_{OEt}, respectively. The low conversions in the reactions using ZnCl$_2$/1_{tBu} and ZnCl$_2$/1_{OEt} may be ascribed to their lower catalytic activities due to the electron-donating abilities of the substituents, although the reason for the high conversion with ZnCl$_2$/1_{OMe} is unclear. Very low conversion was observed for the reaction with ZnCl$_2$/1_{NMe_2}. This is assumed to originate from the suppressed dissociation of the hemiacetal ester due to the basicity of the dimethylamino group on the Schiff-base ligand (1_{NMe_2}) [15] in addition to the very low Lewis acidities due to the high electron-donating ability of the dimethylamino group. Fig. 2 shows the ^{1}H NMR spectra of the reaction mixtures before (A) and after (B) the reaction of **2** and **3** with ZnCl$_2$/**1** (3.0 mol%) at 140 °C. The products composed of three compounds, i.e., an ester with a hydroxyl group (**5**) and esters with acetal groups (**6** and **7**) [6].

Fig. 3(A) shows the relationship between the time and the conversion of **2** in the reaction of **2** and **3** with 3.0 mol% amounts of ZnCl$_2$/1_R at 120 °C. As the electron-donating ability of the

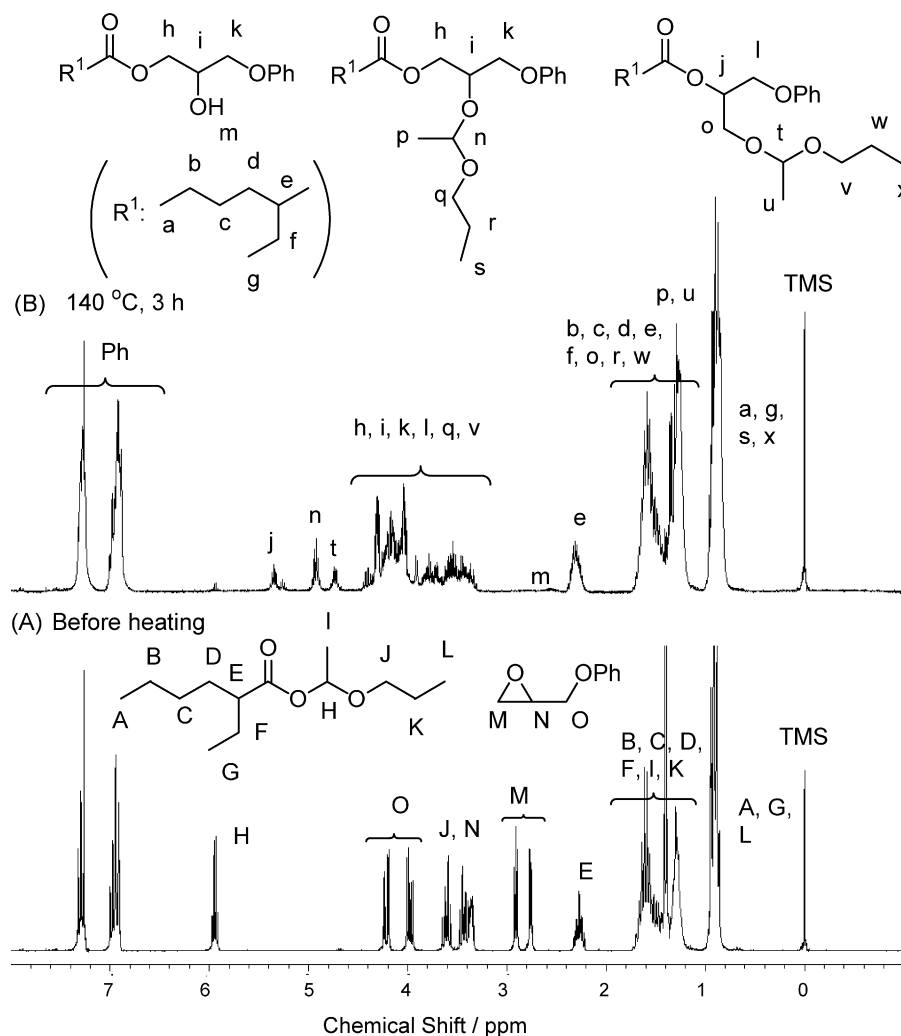Fig. 2. ^{1}H NMR spectra of the reaction mixtures before (A) and after (B) the reaction of **2** and **3** with ZnCl$_2$/**1** (3.0 mol%) at 140 °C for 3 h, recorded in CDCl$_3$.
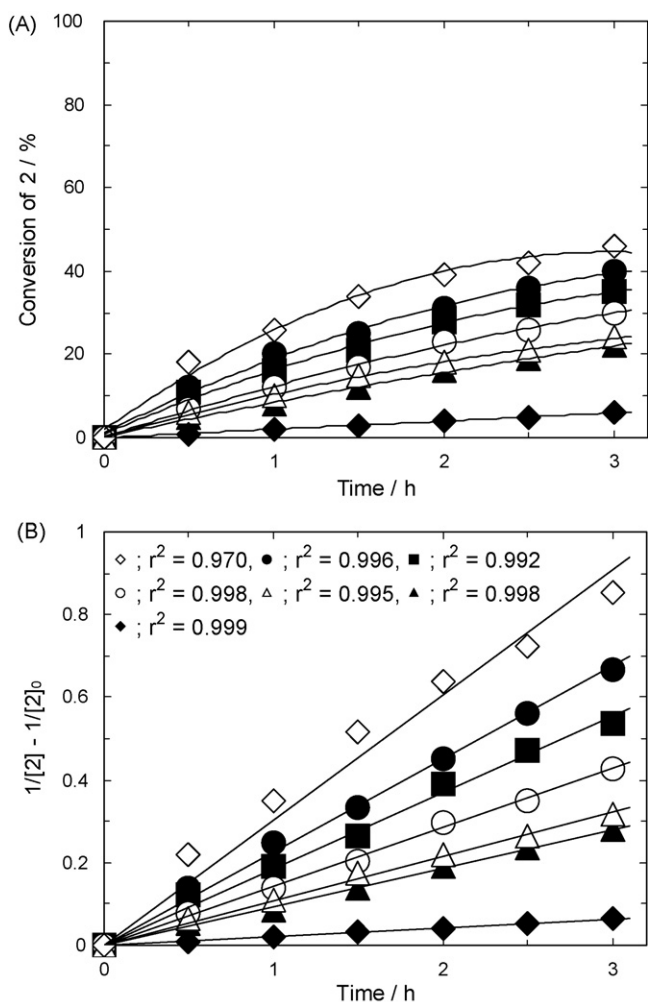
Fig. 3. (A) Relationship between the time vs. conversion of **2**, and (B) relationship between the time vs. $1/[2]-1/[2]_0$ values in the reaction of **2** and **3** with 3.0 mol% amounts of $ZnCl_2/1_R$, (1_{Cl}, $\Diamond$; 1_H, $\bullet$; 1_{Me}, $\blacksquare$; 1_{tBu}, $\bigcirc$; 1_{OEt}, $\triangle$; 1_{OMe}, $\blacktriangle$; 1_{NMe_2}, $\blacklozenge$) at 120 °C.

para-substituent increased, the conversions of **2** decreased. We attribute this behavior to the harder coordination abilities of the imines by the electron-donating groups that decrease the catalytic activity of $ZnCl_2/1_R$ by lowering the Lewis acidities.

We expressed the reaction of **2** and **3** in the presence of $ZnCl_2/1_R$ by the apparent second-order kinetics in a similar manner with the reaction with $ZnCl_2/1_H$, whose rate depends on both of the concentrations of **2** and **3** owing to the slower recombination of the carboxylic acid and the vinyl ether [6]. Based on the assumption that the concentration of unreacted **2** and **3** are equal in the reaction mixtures, the reactant rate constant (k) can be expressed by the equation below.

$$-\frac{d[C]}{dt} = k[C]^2 \quad \text{([C] : concentration of \textbf{2})} \tag{1}$$

Integrating Eq. (1) gives Eq. (2):

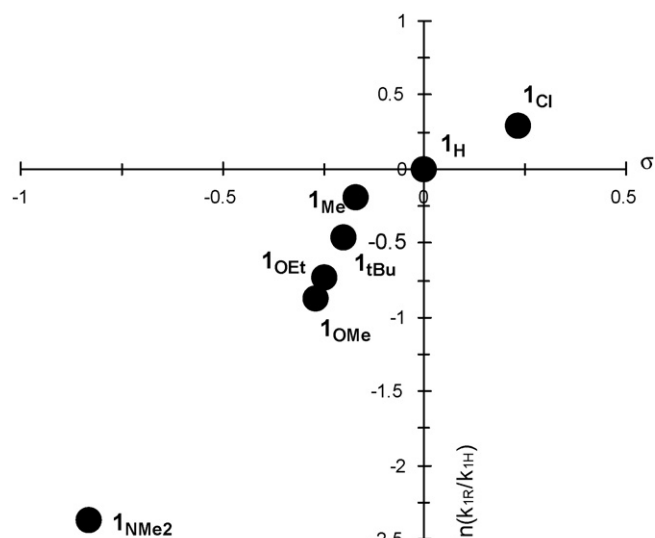$$\frac{1}{[C]} - \frac{1}{[C]_0} = kt \quad \text{([C]_0 : initial concentration of \textbf{2})} \tag{2}$$

Fig. 4. Hammett plot for the $\ln(k_{1R}/k_{1H})$ values in the reaction of **2** and **3** with $ZnCl_2/1_R$ at 120 °C.

Fig. 3(B) shows the time versus $1/[2]-1/[2]_0$ relationships in the reaction of **2** and **3** with 3.0 mol% amounts of $ZnCl_2/1_R$ at 120 °C. The second-order kinetic plots show linear relationships between the reaction time and the $1/[2]-1/[2]_0$ values, which indicate that the reactions with these complexes also obey the apparent second-order kinetics. The slopes of the lines reveal the apparent reaction rate constants (k_{app}): $k_{1_{Cl}} = 8.387 \times 10^{-5}\,\mathrm{L\,mol^{-1}\,s^{-1}}$, $k_{1_H} = 6.256 \times 10^{-5}\,\mathrm{L\,mol^{-1}\,s^{-1}}$, $k_{1_{Me}} = 5.153 \times 10^{-5}\,\mathrm{L\,mol^{-1}\,s^{-1}}$, $k_{1_{tBu}} = 3.958 \times 10^{-5}\,\mathrm{L\,mol^{-1}\,s^{-1}}$, $k_{1_{OEt}} = 3.003 \times 10^{-5}\,\mathrm{L\,mol^{-1}\,s^{-1}}$, $k_{1_{OMe}} = 2.603 \times 10^{-5}\,\mathrm{L\,mol^{-1}\,s^{-1}}$, and $k_{1_{NMe_2}} = 5.833 \times 10^{-6}\,\mathrm{L\,mol^{-1}\,s^{-1}}$.

As the electron-donating ability of the *para*-substituents on the aromatic rings increased, the rate constants in the reaction with $ZnCl_2/1_R$ decreased. In order to demonstrate the substituent effect clearly, we plotted the $\ln(k_{1R}/k_{1H})$ values against the Hammett's σ_p values (Fig. 4). The $\ln(k_{1R}/k_{1H})$ values correlated very well with σ_p values. This correlation clearly demonstrates that the electronic character of the *para*-substitutents on the Schiff-base ligands controls the kinetics of this latent reaction.

The kinetic constants were determined for the reactions at other temperatures (110, 130, and 140 °C), whose kinetics also obey the apparent second-order kinetics. The rate constants at the varied temperatures allowed us to calculate the activation energies (E_a) and the frequency factors (A) expressed by the Arrhenius's equation [Eq. (3)]:

$$k = Ae^{-E_a/RT} \tag{3}$$

Eq. (3) can be logarithmically transformed to Eq. (4):

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{4}$$

E_a and A values can be calculated from slopes of lines and extrapolated intercepts, if logarithms of rate constants ($\ln k$) cor-
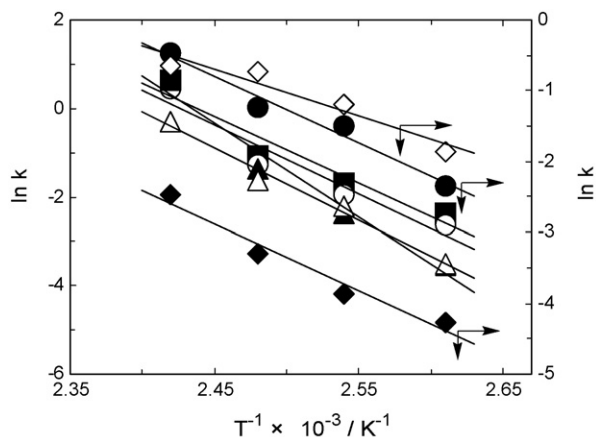
Fig. 5. Arrhenius plots in the reaction of **2** and **3** with 3.0 mol% amounts of $ZnCl_2/\mathbf{1}_R$ ($\mathbf{1}_{Cl}$, ◊; $\mathbf{1}_H$, ●; $\mathbf{1}_{Me}$, ■; $\mathbf{1}_{tBu}$, ○; $\mathbf{1}_{OEt}$, △; $\mathbf{1}_{OMe}$, ▲; $\mathbf{1}_{NMe_2}$, ◆) at 110–140 °C.

Table 2
Activation energy (E_a) and frequency factor (A) in the addition of **2** and **3** in the presence of $ZnCl_2/\mathbf{1}_R$ (3.0 mol%) at 110–140 °C

Additive	σ_p[a]	E_a[b] (kJ mol^{-1})	A[b] (s^{-1})
$ZnCl_2/\mathbf{1}_{Cl}$	0.23	52.2	6.46×10^2
$ZnCl_2/\mathbf{1}_H$	0	74.7	4.41×10^5
$ZnCl_2/\mathbf{1}_{Me}$	−0.17	126	3.20×10^{12}
$ZnCl_2/\mathbf{1}_{tBu}$	−0.20	129	3.31×10^{12}
$ZnCl_2/\mathbf{1}_{OEt}$	−0.25	130	8.82×10^{12}
$ZnCl_2/\mathbf{1}_{OMe}$	−0.27	177	2.04×10^{19}
$ZnCl_2/\mathbf{1}_{NMe_2}$	−0.83	78.3	1.38×10^5

[a] σ_p values of the substituents on $\mathbf{1}_R$ in Ref. [14].
[b] Calculated by the Arrhenius equation based on the reaction rate constants determined by the first-order plots at 110–140 °C.

relate linearly with reciprocals of temperatures (T^{-1}) as shown in Fig. 5. The plots show linear relationships between the ln k values and the reciprocals of temperatures, and allow us to determine the activation energies (E_a) and the frequency factors (A). Table 2 summarizes the E_a and A values in the reaction of **2** and **3** with 3.0 mol% amounts of $ZnCl_2/\mathbf{1}_R$ (R: Cl, H, Me, tBu, OEt, OMe, NMe$_2$). E_a values are 50–100 kJ mol^{-1} in smooth reactions, which proceed even at room temperature (e.g., a typical E_a value in an alcoholysis reaction of an isocyanate giving an urethane in the absence of catalysts is ca. 75 kJ mol^{-1} [16]). On the other hand, chemical reactions with E_a values larger than 100 kJ mol^{-1} typically require additional energies such as heating. Thermally latent reaction must have a large E_a value at ambient conditions to attain good latency, and should have a large A value to attain high reactivity at higher temperature. For example, polymerization of epoxides using sulfonium salts[1] shows large E_a and A values (e.g., 208–316 kJ mol^{-1}, 1.8×10^9 to 3.2×10^{18} s^{-1}, respectively), which result in good latency at ambient conditions and high activity at elevated temperatures. The reaction

with bare $ZnCl_2$ proceeded even at room temperature, and was accompanied by observable side reactions due to the polymerization of **2** above 110 °C. The E_a and A value of this reaction with bare $ZnCl_2$ involving side reactions was estimated to be approximately 45 kJ mol^{-1} and 4.20×10^4 s^{-1}, which are not high enough for a latent reaction. The reactions with $ZnCl_2/\mathbf{1}_R$ exhibit larger E_a and A values ranging from 52.2 to 170 kJ mol^{-1}, 6.46×10^2 to 2.04×10^{19} s^{-1}, respectively, except the reaction with $ZnCl_2/\mathbf{1}_{NMe_2}$. In particular, the complexes bearing electron-donating groups tend to exhibit the large E_a values and A factors. The A factors are comparable to those in thermally latent reaction of 2,6-dimethylphenol and glycidyl phenyl ether with phosphonium ylides (i.e.; 2.04×10^{-3} to 1.61×10 s^{-1}) [3b]. The complex bearing methoxy group ($ZnCl_2/\mathbf{1}_{OMe}$) exhibits the largest E_a and A values among the examined complexes. The large A value leads to an excellent latency, which was demonstrated by the fact that $ZnCl_2/\mathbf{1}_{OMe}$ accomplishes the addition quantitatively within 3 h at 140 °C in spite of the inertness below 90 °C. These results almost correlate with the aforementioned changes in the ^{15}N NMR chemical shifts (Δppm) and the IR absorption bands (Δcm^{-1}) by ligation, and suggest that the electronic characters of the Schiff-base ligands control both the latency and the activity in the reaction of hemiacetal esters with epoxides.
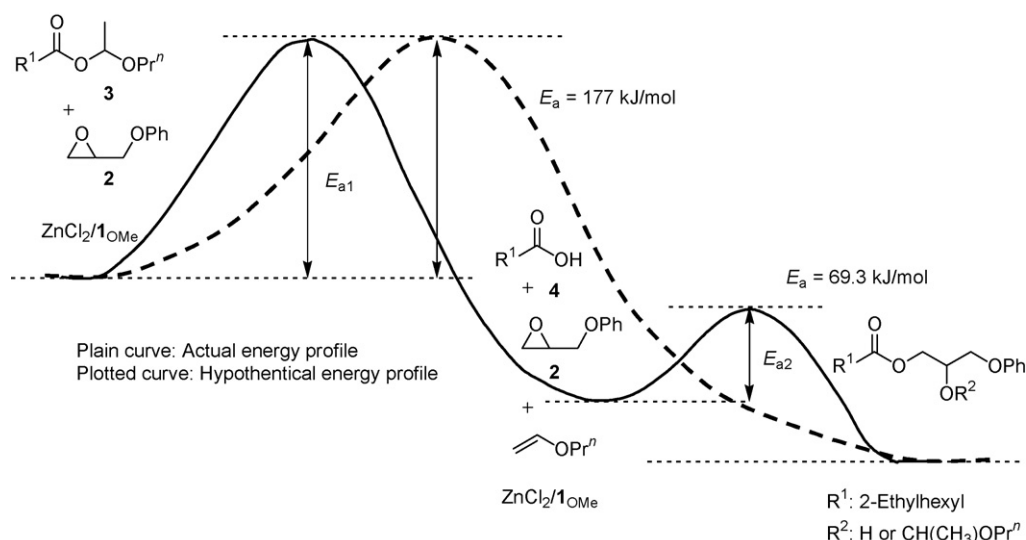

Fig. 6. Energy profile in the reaction of hemiacetal ester (**3**) and epoxide (**2**) with Schiff-base–zinc chloride complex ($ZnCl_2/\mathbf{1}_{OMe}$) at 140 °C.

The reaction of **2** and **3** proceeds via two-step reactions, which is assumed to involve an activation energy for each primary reaction (indicated as E_{a1} and E_{a2} for the first and second reactions, respectively, below and in Fig. 6), although the calculated E_a values are the apparent activation energies of the whole reactions. The E_{a1} value expresses the activation energy of the thermal dissociation of **3**, and the E_{a2} value expresses the activation energy of the reaction of **2** and 2-ethylhexanoic acid (**4**). Accordingly, we determined the E_{a2} value in the reaction of **2** and **4** with $ZnCl_2/\mathbf{1}_{OMe}$ in a similar manner to the addition of **2** and **3**. The E_{a2} value, 69.3 kJ mol^{-1} [17], is significantly lower than the E_a value (177 kJ mol^{-1}). This observation suggests that the E_a value is almost identical to the E_{a1} value and that the primary dissociation is the rate-determining step. Thus, we concluded that the control over the primary dissociation with $ZnCl_2/\mathbf{1}_{OMe}$ is a necessary condition for the high latency.

4. Summary

Schiff-base–zinc chloride complexes ($ZnCl_2/\mathbf{1}_R$) proved the effective Lewis acids meeting requirements for both latency and activity in the thermally latent reaction of a hemiacetal ester and an epoxide. Kinetic studies revealed that the activation energies and the frequency factors depend on the Lewis acidity of the catalysts controlled by the electronic characters of the substituents. For instance, $ZnCl_2/\mathbf{1}_{Cl}$ bearing an electron-withdrawing chlorine group promotes the reaction approximately three times as fast as $ZnCl_2/\mathbf{1}_{OMe}$ bearing an electron-donating methoxy group at 120 °C (i.e., 8.39×10^{-5} L mol^{-1} s^{-1} and 2.60×10^{-5} L mol^{-1} s^{-1}, respectively), although the rate for $ZnCl_2/\mathbf{1}_{OMe}$ is satisfactory for curing. The differing rates originate from the E_a values. The E_a value for $ZnCl_2/\mathbf{1}_{Cl}$ is one-third of that of $ZnCl_2/\mathbf{1}_{OMe}$ (i.e., 52.2 kJ mol^{-1} and 177 kJ mol^{-1}, respectively). As well as the activity, the latency also depends on the electronic characters of the substituents. The complexes with basic ligands tend to have higher A values, and the highest A value was observed for $ZnCl_2/\mathbf{1}_{OMe}$ (2.04×10^{19} s^{-1}) that attains very good latency.

The electronic characters of the substituents control the Lewis acidities of the Schiff-base–zinc chloride complexes that regulate both the activity and latency. The controllable activity and latency are effective in conducting curing under desired conditions. The fine-tuning of the Lewis acidities suggests the wide applicability of the Schiff-base–zinc chloride complexes not only for the curing system based on the reaction of hemiacetal esters and epoxides but also for catalysis of reactions involving activation of acid-sensitive substrates like epoxides.

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[17] The E_a and A values in the addition of **2** and **4** with $ZnCl_2/\mathbf{1}_{OMe}$ were determined in similar manners with those in the addition of **3** and **2**. The E_a (69.3 kJ moL^{-1}) and A (4.11×10^{-4} s^{-1}) were calculated from the slope and the extrapolated intercept of the linear plots on the relationship between the logarithm of the rate constants and the reciprocals of the temperatures (110–140 °C). The rate constants are follows; 110 °C, $k_{obs} = 1.44 \times 10^{-5}$ L mol^{-1} s^{-1}, 120 °C, $k_{obs} = 2.64 \times 10^{-5}$ L mol^{-1} s^{-1}; 130 °C, $k_{obs} = 4.47 \times 10^{-5}$ L mol^{-1} s^{-1}; and 140 °C, $k_{obs} = 8.17 \times 10^{-5}$ L mol^{-1} s^{-1}.