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Kinetic studies for amination of ketenimines: change of rate-determining step by electron-withdrawing *N*-substituents through electronic effects

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Abstract—Kinetic studies for the amination of ketenimines **1a**–**d** and **2a**–**e** with *n*-BuNH$_2$ were carried out by means of UV spectrometry. Hammett equation was applied to the second-order rate constant (k_1) for the amination of **2a**–**e** and the Hammett plot demonstrated a linear free-energy relationship with a reaction constant (ρ_1) of 2.87, indicating that the second-order rate constant (k_1) corresponds to the first step of rate-determining C═N addition. In contrast, Hammett equation was applied to Kk_2 for the amination of **1a**–**d** and the Hammett plot was a convex curve with $\rho_D=\rho_1=7.08$ and $\rho_A=\rho_K+\rho_2=0.98$, indicating change of the rate-determining step. The electron-withdrawing *para*-substituents on the *N*-phenyl group of ketenimines significantly stabilize the first transition state of C═N addition, resulting in change of the rate-determining step to the second step of tautomerization. The *N*-substituent electronic effect has much more significant influence on the amination of ketenimines than the substituent electronic effect at C$_\beta$.

1. Introduction

Ketenimines and ketenes are important reactive intermediates, which occur as transients in many thermal and photochemical reactions.[1,2] There has been intense interest in their addition reactions, such as cycloadditions,[3] nucleophilic additions,[2b,2c,2g,4] electrophilic additions,[5] and radical additions.[6]

Recently, we have found that amination of ketenimines involved two steps including an initial addition to C═N, followed by tautomerization, and the metastable vinylidenediamine intermediate was caught and identified by proton NMR spectrometry.[7a] By means of proton NMR spectrometry and ab initio calculations, we also found that the rate-determining step for the amination of ketenimines was changed from the second step of tautomerization to the first step of C═N addition when *N*-substituent of the ketenimines is changed from phenyl group to *i*-propyl group[7b] (Fig. 1). We report herein kinetic studies for the amination of ketenimines by UV spectrometry to explore the substituent effect on the amination reactions.

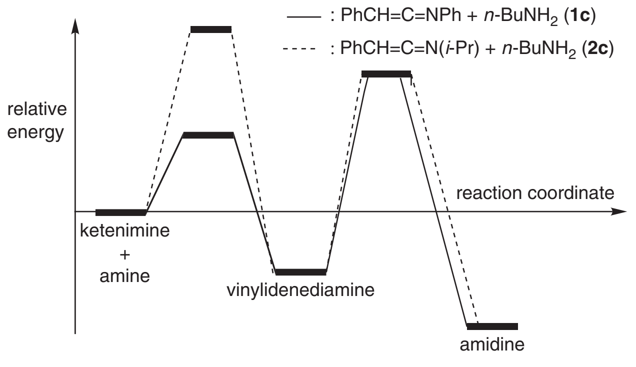

Figure 1. Cartoon picture of reaction profiles for the amination of **1c** and **2c**.

2. Results and discussion

Wavelength scan for the amination of *N*-phenylphenylketenimines **1c** with *n*-BuNH$_2$ in acetonitrile at both −10 and 20 °C by UV spectrophotometer showed a decaying absorption at $\lambda_{max}=260$ nm without any isosbestic point as shown in Figure 2, indicating the presence of appreciable amount of the corresponding reaction intermediate. This is consistent with our previous NMR and theoretical results that the rate-determining step is the second step of tautomerization and the reaction intermediate has been caught by low-temperature NMR spectrometry.[7] Therefore, accumulation of the reaction intermediate results in no isosbestic point in the wavelength scan of the amination reaction. On the other hand, wavelength scan for the amination of *N*-*i*-propyl-phenylketenimines **2c** with *n*-BuNH$_2$ in acetonitrile at 20 °C showed a decaying absorption at $\lambda_{max}=270$ nm with two isosbestic points as shown in Figure 3, indicating the absence of

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Keywords: Amination; Ketenimine; Kinetic study; Hammett plot.

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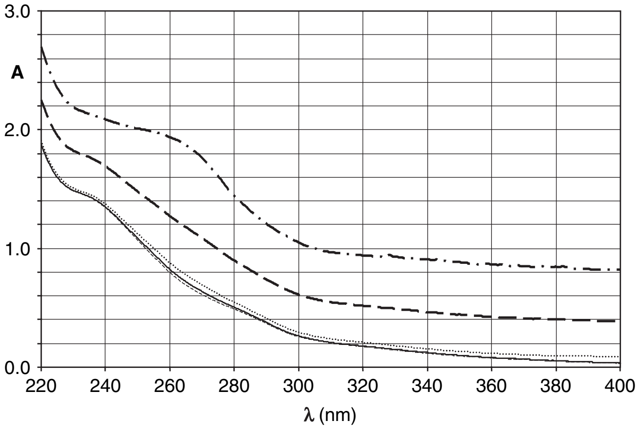


Figure 2. Wavelength scan for amination of **1c** with 0.37 mM n-BuNH$_2$ in CH$_3$CN at −10 °C at 0, 1, 3, 8, and 60 min with a decaying absorption at λ_{max}=260 nm.

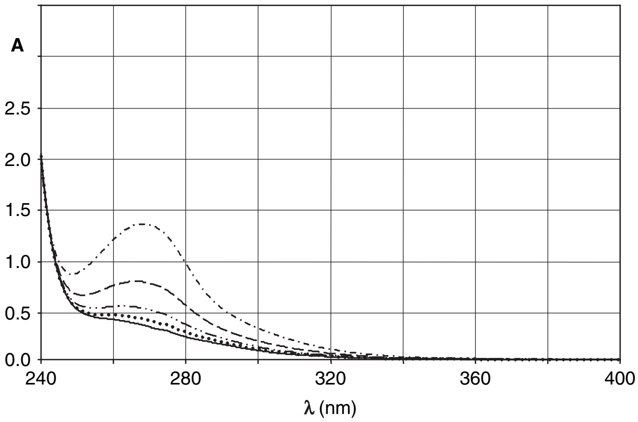


Figure 3. Wavelength scan for amination of **2c** with 0.4 M n-BuNH$_2$ in CH$_3$CN at 20 °C at 0, 1.5, 3, 4.5, and 17.5 h with a decaying absorption at λ_{max}=270 nm.

appreciable amount of the corresponding reaction intermediate. This is quite consistent with our previous NMR and theoretical results that the rate-determining step is the first step of C═N addition.[7b] The second step of tautomerization is much faster than the first step so that the corresponding reaction intermediate does not accumulate, resulting in appearance of isosbestic points in the wavelength scan of the amination reaction.

Time scans by UV spectrophotometer at λ=260 or 270 nm for the amination of **1a–d** or **2a–e** with excess of n-BuNH$_2$ in acetonitrile at 20 °C showed a first-order exponential decay for each of the reaction, and the observed rate constants (k_{obs}) are shown in Tables 1 and 2 (Schemes 1 and 2). The reactivity of **1a–d** to n-BuNH$_2$ is quite high, so kinetic studies of these reactions have been done in 0.2–0.6 mM of n-BuNH$_2$ in CH$_3$CN at 20 °C. On the other hand, the reactivity of **2a–e** to n-BuNH$_2$ is much lower, so kinetic studies of these reactions have been done at higher concentration (0.9, 0.8, 0.7, or 0.6 M for **2a–d**, and 0.05, 0.04, 0.03, or 0.02 M for **2e**) of n-BuNH$_2$ in CH$_3$CN at 20 °C.

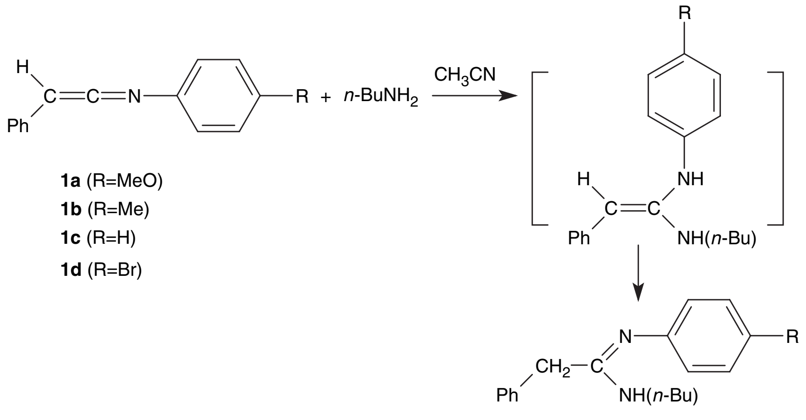
Based on our previous NMR and theoretical results,[7] a proposed mechanism for the amination of ketenimine is shown in Eq. 1. According to the steady-state approximation,[8] the rate law of the amination reactions was drawn in Eq. 2.

Table 1. Observed rate constants for the amination of **1a–d** in CH$_3$CN at 20 °C

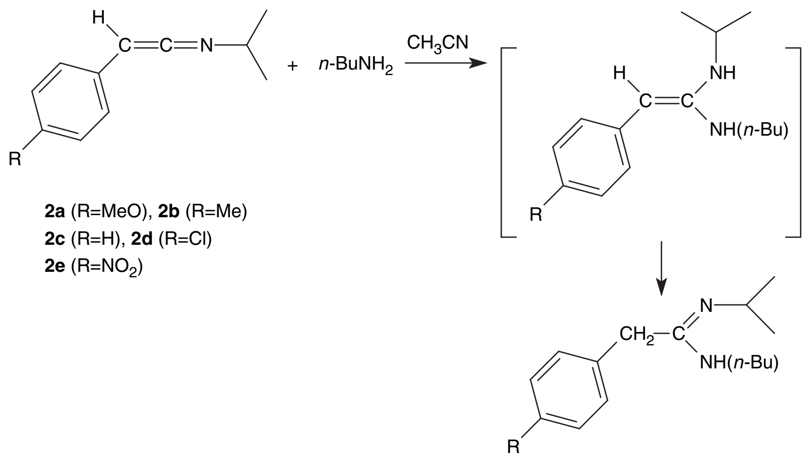
[n-BuNH$_2$] (mM)	R	k_{obs} (s^{-1})	[n-BuNH$_2$] (mM)	R	k_{obs} (s^{-1})
0.6	MeO	9.64×10^{-3}	0.6	H	5.20×10^{-2}
0.5	MeO	7.67×10^{-3}	0.5	H	4.34×10^{-2}
0.4	MeO	5.92×10^{-3}	0.4	H	3.11×10^{-2}
0.3	MeO	4.22×10^{-3}	0.3	H	2.13×10^{-2}
0.2	MeO	2.60×10^{-3}	0.2	H	1.11×10^{-2}
0.6	Me	5.28×10^{-2}	0.6	Br	9.74×10^{-2}
0.5	Me	4.45×10^{-2}	0.5	Br	8.04×10^{-2}
0.4	Me	3.52×10^{-2}	0.4	Br	6.18×10^{-2}
0.3	Me	2.63×10^{-2}	0.3	Br	4.18×10^{-2}
0.2	Me	1.72×10^{-2}	0.2	Br	2.27×10^{-2}

Table 2. Observed rate constants for the amination of **2a–e** in CH$_3$CN at 20 °C

[n-BuNH$_2$] (M)	R	k_{obs} (s^{-1})	[n-BuNH$_2$] (M)	R	k_{obs} (s^{-1})
0.9	MeO	2.51×10^{-4}	0.9	Me	3.60×10^{-4}
0.8	MeO	2.07×10^{-4}	0.8	Me	2.98×10^{-4}
0.7	MeO	1.57×10^{-4}	0.7	Me	2.28×10^{-4}
0.6	MeO	1.10×10^{-4}	0.6	Me	1.56×10^{-4}
0.9	H	7.25×10^{-4}	0.9	Cl	4.24×10^{-3}
0.8	H	5.95×10^{-4}	0.8	Cl	3.68×10^{-3}
0.7	H	4.77×10^{-4}	0.7	Cl	2.96×10^{-3}
0.6	H	3.85×10^{-4}	0.6	Cl	2.38×10^{-3}
0.05	NO$_2$	2.03×10^{-2}	0.04	NO$_2$	1.63×10^{-2}
0.03	NO$_2$	1.22×10^{-2}	0.02	NO$_2$	7.94×10^{-3}



Scheme 1.



2a (R=MeO), **2b** (R=Me)
2c (R=H), **2d** (R=Cl)
2e (R=NO$_2$)

Scheme 2.

Table 3. Second-order rate constants (k_1) for the amination of **2a–e** with n-BuNH$_2$ in CH$_3$CN at 20 °C[a]

R	k_1 (M^{-1} s^{-1})	σ_p
MeO	4.73×10^{-4}	−0.27
Me	6.83×10^{-4}	−0.17
H	1.14×10^{-3}	0
Cl	6.30×10^{-3}	0.23
NO$_2$	4.13×10^{-1}	0.78

[a] ρ_1=2.87 (r^2=0.981).

When $k_2 \gg k_{-1}$, the first step of C═N addition becomes the rate-determining step and the rate law can be simplified into Eq. 3. According to the previous NMR and theoretical results,[7] the amination of **2a–e** is likely to follow this mechanism with the C═N addition as the rate-determining step. Then, a plot of k_{obs} for the amination of **2a–e** versus [n-BuNH$_2$] was drawn and it was a straight line for each of these amination reactions, indicating that the monitored process involves one molecule of n-BuNH$_2$. The slopes of these straight lines represent the corresponding second-order rate constants (k_1) of the first step of C═N addition, which are shown in Table 3. Hammett equation was applied to the second-order rate constants (k_1) of the first step of rate-determining C═N addition for the amination of **2a–e**, and is shown in Eq. 4. Based on this equation, a plot of log k_1(X) versus Hammett's substituent constant σ_p[9] was drawn, and it was a straight line with ρ_1=2.87 and a correlation coefficient r^2=0.981 (Table 3).

$$\text{Ketenimine(K)} + \text{Amine(A)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Vinylidenediamine(V)} \xrightarrow{k_2} \text{Amidine} \qquad (1)$$

According to the steady-state approximation,

$$\frac{d[V]}{dt} = k_1[A][K] - k_{-1}[V] - k_2[V] = 0;\ \ [V] = \frac{k_1}{k_{-1}+k_2}[A][K]$$

$$\text{rate} = \frac{-d[A]}{dt} = k_2[V] = \frac{k_1k_2}{k_{-1}+k_2}[A][K] \qquad (2)$$

When $k_2 \gg k_{-1}$ and excess amine,

$$\text{rate} = \frac{-d[A]}{dt} = k_1[A][K] = k_{obs}[K] \qquad (3)$$

$$\log\left(\frac{k_1(X)}{k_1(H)}\right) = \log k_1(X) - \log k_1(H) = \rho_1\sigma \qquad (4)$$

When $k_2 \ll k_{-1}$ and excess amine, $K = k_1/k_{-1}$

$$\text{rate} = \frac{-d[A]}{dt} = \frac{k_1k_2}{k_{-1}}[A][K] = Kk_2[A][K] = k_{obs}[K] \qquad (5)$$

$$\begin{aligned}\log Kk_2(X) - \log Kk_2(H) &= \log\left(\frac{Kk_2(X)}{Kk_2(H)}\right)\\ &= \log\left(\frac{K(X)}{K(H)}\right) + \log\left(\frac{k_2(X)}{k_2(H)}\right)\\ &= \rho_K\sigma + \rho_2\sigma = (\rho_K + \rho_2)\sigma\end{aligned} \qquad (6)$$

The magnitude and sign of ρ of Hammett plot reflect the geometry of the transition state and indicate the electronic effects of the *para*-substituents to the remote reaction center.[8] Hammett plot for the amination of **2a–e** has a large and positive reaction constant ρ_1 (2.87), which indicates that the second-order rate constant (k_1) corresponds to the first step of rate-determining C═N addition for the amination of **2a–e**, the *para*-substituents on the phenyl group at C$_\beta$ have direct resonance interaction with the reaction center at C$_\alpha$, and the electron-withdrawing *para*-substituents on the phenyl group at C$_\beta$ accelerate the reaction rate.

When $k_2 \ll k_{-1}$ in Eq. 2, the second step of tautomerization becomes the rate-determining step and the rate law can be simplified into Eq. 5. According to the previous NMR and theoretical results,[7] the amination of **1a–d** is assumed to follow this mechanism with the tautomerization as the rate-determining step. Then, a plot of k_{obs} for the amination of **1a–d** versus [n-BuNH$_2$] was drawn and it was a straight line

Table 4. Kk_2 or k_1 for the amination of **1a–d** with *n*-$BuNH_2$ in CH_3CN at 20 °C

R	Kk_2 (M^{-1} s^{-1})	σ_p
MeO	17.5[a]	−0.27
Me	89.4	−0.17
H	104	0
Br	470	0.23

[a] k_1 (s^{-1}) value.

for each of these amination reactions. The slopes of these straight lines represent the corresponding products (Kk_2) of the equilibrium constants of the first step by the second-order rate constants of the second step, which are shown in Table 4.

When Hammett equation was applied to the Kk_2 for the amination of **1a–d**, which corresponds to the reaction that includes one step prior to the rate-determining step, the ρ value should be a composite of the ρ_K and ρ_2 values,[10] which is shown in Eq. 6. Based on this equation, a plot of log Kk_2(X) versus Hammett's substituent constant σ_p[9] was drawn, and a convex curve was found as shown in Figure 4, indicating change of the rate-determining step. This is very similar to the substituent effect on the semicarbazone formation.[11]

As far as the amination of **1a–d** is concerned, for electron-withdrawing *para*-substituents on *N*-phenyl group, the first transition state of C═N addition is highly stabilized, resulting in the second step of tautomerization being the rate-determining step ($k_2 \ll k_{-1}$) and $\rho_A = \rho_K + \rho_2 = 0.98$ (Fig. 3). The ρ_K value is small because the *N*-substituent electronic effect on the relative stability between ketenimines and their corresponding vinylidenediamines is quite small based on the previous theoretical results.[7b] The ρ_2 value is also small since the *para*-substituents are far away from and not directly conjugated with the reaction center in the second step of tautomerization. Therefore, the small composite ρ_A value (0.98) is expected.

On the other hand, for electron-donating *para*-substituents on *N*-phenyl group in the amination of **1a–d**, the first transition state of C═N addition is much less stabilized, leading to the first C═N addition step being the rate-determining step ($k_2 \gg k_{-1}$) and $\rho_D = \rho_1 = 7.08$. Actually the rate law of Eq. 3 and the Hammett equation of Eq. 4 should be applied to this case, and the Kk_2 is supposed to be replaced by the k_1. The large and positive reaction constant ρ_1 (7.08) indicates that the first step of C═N addition is the rate-determining step, the *para*-substituents on *N*-phenyl group have a direct resonance interaction with the reaction center at C_α, and the electron-donating *para*-substituents decelerate the reaction rate. The reaction intermediate for the amination of **1a** with *N*-*p*-methoxyphenyl group couldn't be caught by low-temperature NMR spectrometry at −10 °C, and that confirms this mechanism. This ρ_1 value (7.08) is much higher than the ρ_1 value (2.87) for the amination of **2a–e**, clearly indicating that the first step of these amination reactions, which is the rate-determining step, involves C═N addition, instead of C═C addition.

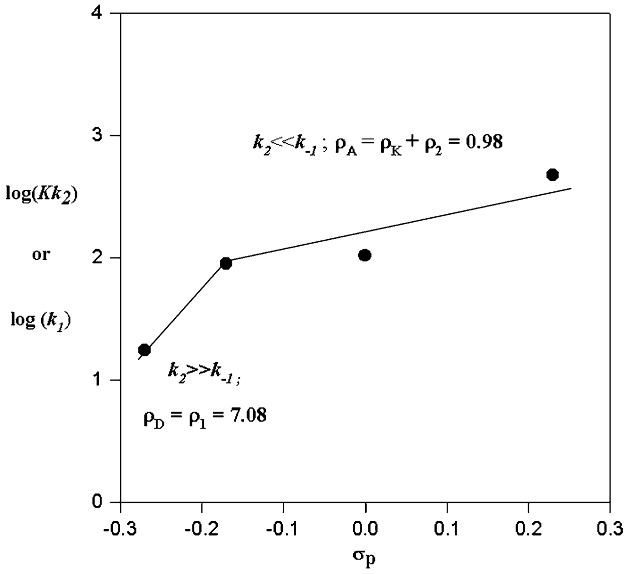


Figure 4. Hammett plot for the amination of **1a–d**.

In the amination of **2a–e**, electron-withdrawing *para*-substituents on the phenyl group at C_β stabilize the first transition state of C═N addition so that they accelerate the reaction rates. However, the extent to which they stabilize the first transition state is not significant enough to change the rate-determining step. On the other hand, in the amination of **1a–d**, electron-withdrawing *para*-substituents on *N*-phenyl group significantly stabilize the first transition state of C═N addition, and that does change the rate-determining step. It is known that steric effect of phenyl group is very close to that of *i*-propyl group,[12] so it is clear that the *N*-substituent electronic effect has much more significant influence on the amination of ketenimines than the substituent electronic effect at C_β.

In conclusion, the rate-determining step of the amination of **2a–e** is the first step of C═N addition, whose transition state is stabilized by electron-withdrawing substituents at C_β. On the other hand, electron-withdrawing *para*-substituents on *N*-phenyl group of ketenimines significantly stabilize the first transition state of C═N addition, resulting in change of the rate-determining step to the second step of tautomerization. Therefore, Hammett plot for the amination of **1a–d** is a convex curve, indicating change of the rate-determining step.

3. Experimental

3.1. General

Ketenimines **1a–c** and **2a–e** were known.[7] Ketenimine **1d** was prepared by the procedures given in the literature,[4h,4i,7] and its product analysis for the amination reaction is shown as follows. Product analyses for the kinetic studies of the amination of **1a–c** and **2a–e** have been done by NMR spectrometry and described in the previous publication.[7]

3.1.1. *N*-*p*-Tolylphenylketenimine (1d). Yield: 65%; ^1H NMR ($CDCl_3$) δ 2.39 (3H, s, CH_3), 5.26 (1H, s, CH), 7.18–7.40 (9H, m, PhH); ^{13}C NMR ($CDCl_3$) δ 21.1, 60.7, 123.6, 123.9, 124.6, 125.1, 125.4, 127.6, 128.2, 128.8, 129.3, 129.6, 132.7, 137.8, 190.5; IR (hexane) 2008 (C═C═N) cm^{-1}; HRMS (EI) *m/z* calcd for $C_{15}H_{13}N$ 207.1048, found 207.1050.

3.1.2. *N*-Butyl-*N*′-*p*-tolyl-2-phenylacetamidine. ^{1}H NMR (CDCl$_3$) δ 0.93 (3H, t, J=7.2 Hz, CH$_3$), 1.27–1.43 (4H, m, CH$_2$), 2.32 (3H, s, CH$_3$), 3.15 (2H, t, J=7.0 Hz, CH$_2$), 3.43 (2H, s, CH$_2$), 7.01–7.30 (9H, m, PhH); ^{13}C NMR (CDCl$_3$) δ 13.31, 20.07, 21.1, 31.17, 36.19, 41.02, 123.21, 124.52, 125.14, 128.28, 129.43, 129.82, 132.88, 136.01, 137.53; IR (thin film) 1653 (N–C=N) cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{19}H_{24}N_2$ 280.1939, found 296.1935.

3.1.3. Kinetic studies of amination of ketenimines 1a–d and 2a–e. Kinetics for the amination of **1a**–**d** and **2a**–**e** were carried out by injecting 2 μL of approximately 1 mM ketenimine solution in CH$_3$CN into 1 mL of *n*-BuNH$_2$ solution in CH$_3$CN, whose concentration was 0.6, 0.5, 0.4, 0.3, or 0.2 mM for **1a**–**d**, 0.9, 0.8, 0.7, or 0.6 M for **2a**–**d**, and 0.05, 0.04, 0.03, or 0.02 M for **2e**, in the thermostatic UV cell at 20 or −10 °C, monitoring the decrease in absorption at 260 or 270 nm with Perkin–Elmer Lambda 12 spectrometer. The SigmaPlot software was used to fit the exponential decays to get the rate constants. All rate constants were measured at least in duplicate with maximum deviations of ±5%.

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