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Remarkable catalytic effect of H^+ in Michael-type additions of anilines to 3-butyn-2-one

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Abstract—Second-order rate constants (k_N) for the Michael-type reaction of 3-butyn-2-one (**1**) with a series of anilines in H_2O have been determined spectrophotometrically. The k_N values are dependent on the free aniline fraction (F_N). The plot of log k_N vs pK_a of the conjugate acid of the anilines is linear for the reactions run at F_N=1.00. However, the Brønsted-type plot for the reactions performed at F_N=0.50 is nonlinear, suggesting a change in the reaction mechanism as the basicity of anilines changes. The analysis of the kinetic results has revealed that the reaction of anilines proceeds through the protonated form of the substrate **1** as well as the unprotonated. The protonated form of **1** is of the order of 10^9 times more reactive than the unprotonated form toward anilines. The contribution of the reaction with the protonated species to the k_N is suggested to be responsible for the nonlinear Brønsted-type plot obtained for the reactions run at F_N=0.50. © 2001 Elsevier Science Ltd. All rights reserved.

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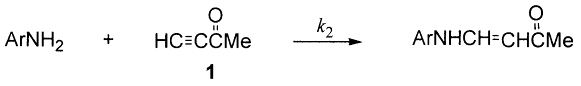
1. Introduction

Nucleophilic additions of amines to carbon–carbon double bonds conjugated with a strong electron withdrawing group (EWG) have been intensively investigated, and their reaction mechanisms are fairly well understood.[1–4] The corresponding reactions of carbon–carbon triple bonds with amine nucleophiles have also attracted a great deal of attention.[5–8] However, most studies have been focused on the stereochemistry of the reaction products (e.g. the *E*- and *Z*-isomers of enamines) due to synthetic interests.[5–8] Kinetic studies of addition reactions of amines to electron deficient acetylenes have been little investigated, and therefore, the reaction mechanism is not clearly understood.[9]

We recently performed Michael-type addition reactions of a series of aliphatic primary amines including α-effect nucleophiles such as methoxylamine and hydrazine to an electron deficient acetylene, 3-butyn-2-one (**1**).[9] We expected a large α-effect for the reaction of methoxylamine and hydrazine with the sp hybridized electrophile (**1**), since the magnitude of the α-effect has been reported to increase with increasing s character of the electrophile.[10–12] However, we found that the α-effect is unexpectedly small, and gave some explanations for the small α-effect.[9] It appeared to us as highly informative to investigate the reaction mechanism for additions of amines to electron deficient acetylenes. Therefore, we have expanded our study to reactions of **1** with a series of aromatic amines as shown in Eq. (1). We found the addition reaction is remarkably catalyzed by H^+ and report herein the detailed reaction mechanism.



$$\mathrm{ArNH_2} + \underset{\mathbf{1}}{\mathrm{HC{\equiv}C\overset{\overset{O}{\|}}{C}Me}} \xrightarrow{k_2} \mathrm{ArNHCH{=}CH\overset{\overset{O}{\|}}{C}Me} \qquad (1)$$

$ArNH_2$=Z-$C_6H_4NH_2$; Z=4-CN, 3-Cl, 4-Cl, 3-Me, 4-MeO, 4-OH.

2. Results and discussion

All the reactions obeyed pseudo-first-order kinetics, and pseudo-first-order rate constants (k_{obs}) were obtained from the well-known equation: $\ln(A_\infty - A_t) = -k_{obs}t + c$. The correlation coefficients of the linear regressions were always higher than 0.9995. Plots of k_{obs} vs total aniline concentration were linear and passed through the origin for all the anilines studied. Therefore, the rate law for the present reactions can be given as Eq. (2), in which S is the substrate **1**, k_N is the second-order rate constant, F_N is the free aniline fraction, and $[N]_{tot}$ is the concentration of total aniline (free aniline and its conjugate acid). The k_N values were obtained by dividing the slope of linear plots of k_{obs} vs $[N]_{tot}$ by F_N. The k_N values determined in this way are summarized in Table 1. It is estimated from replicate runs that the uncertainty in any particular measured rate constant is less than ±3%.

$$\mathrm{d[P]/d}t = k_{obs}[\mathrm{S}], \quad \text{where } k_{obs} = k_N F_N [\mathrm{N}]_{tot} \qquad (2)$$

One can see that the k_N values are dependent on F_N, i.e. the

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Keywords: Michael-type reaction; reaction mechanism; Brønsted-type plot; acid catalysis; acetylene; α-effect.

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Table 1. Summary of second-order rate constants, k_N (M^{-1} s^{-1}) for Michael-type addition reactions of substituted anilines (Z-$C_6H_4NH_2$) to **1** in H_2O at 25.0±0.1°C

Z	pK_a (Z-$C_6H_4NH_3^+$)	k_N (M^{-1} s^{-1})			
		F_N=1.00	F_N=0.75	F_N=0.50	F_N=0.25
4-CN	1.74	0.0151	0.0562	0.161	0.475
3-Cl	3.32	0.162	0.181	0.219	0.348
4-Cl	3.81	0.258	0.254	0.296	0.421
H	4.58	0.376	0.410	0.415	0.593
3-Me	4.67	0.536	0.536	0.560	0.654
4-OMe	5.29	1.36	1.35	1.40	1.56
4-OH	5.50	1.49	1.50	1.51	1.68

k_N value increases as the F_N value decreases for a given aniline. However, the dependence of k_N values on F_N is greater for the less basic anilines. For example, the k_N values for the least basic 4-cyanoaniline increases from 0.0151 M^{-1} s^{-1} to 0.0562, 0.161 and 0.475 M^{-1} s^{-1} as F_N decreases from 1.00 to 0.75, 0.50 and 0.25, respectively, while the k_N value for the most basic 4-hydroxyaniline increases from 1.49 to 1.68 M^{-1} s^{-1} as F_N decreases from 1.00 to 0.25.

The effect of basicity on the k_N values is demonstrated in Fig. 1. The Brønsted-type plot is linear for the reaction run at F_N=1.00. However, interestingly, the corresponding plot for the reactions performed at F_N=0.50 is nonlinear, i.e. anilines with an electron withdrawing substituent exhibit positive deviations from the linearity. (The plots for the reactions run at F_N=0.75 and 0.25 are also nonlinear, but figures are not shown.)

Aminolysis of esters with a good leaving group have often shown a break or a curvature in Brønsted-type plots from a large slope to a small one as the basicity of nucleophilic amines increases.[13–16] Such a break or curvature in a Brønsted-type plot has been interpreted as due to a change in the rate-determining step (RDS) as the basicity of amines increases.[13–16] Interestingly, as shown in Fig. 1, the slope of the Brønsted-type plot for the reactions run at F_N=0.50 is smaller for the less basic anilines than for the more basic ones, which is opposite to the nonlinear Brønsted-type plot obtained for most aminolysis reactions. Such a nonlinear Brønsted-type plot as in the present system has been rarely reported.[17,18] Cevasco et al. obtained a nonlinear Brønsted-type plot for the base catalyzed hydrolysis of aryl 4-hydroxybenzoates.[18] The rate of hydrolysis was found to be faster for esters with good leaving groups (low basic aryloxides) than was predicted from the Brønsted-type plot of esters with poor leaving groups (highly basic aryloxides). The nonlinear Brønsted-type plot was suggested to be due to a change in the reaction mechanism from a simple nucleophilic substitution reaction for esters of strongly basic aryloxides to an E1cb reaction mechanism for esters of weakly basic aryloxides.[18] Therefore, one might consider that the nonlinear Brønsted-type plot obtained in the present system is indicative of a change in the reaction mechanism as the basicity of $ArNH_2$ changes.

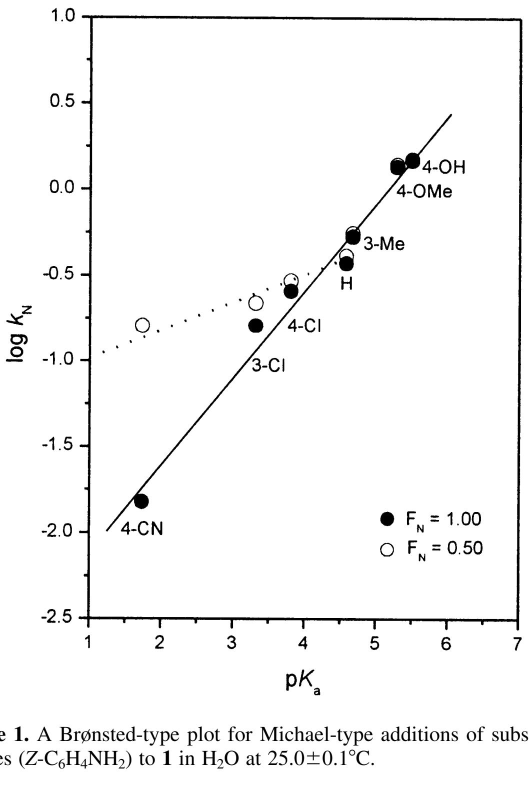
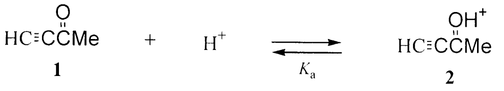
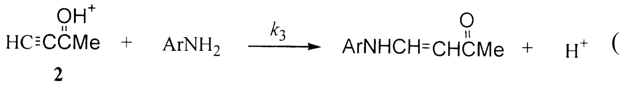


Figure 1. A Brønsted-type plot for Michael-type additions of substituted anilines (Z-$C_6H_4NH_2$) to **1** in H_2O at 25.0±0.1°C.

Since the positive deviation from the linear Brønsted-type plot in Fig. 1 is greater for the less basic $ArNH_2$ and for the reaction run at lower F_N (lower pH) for a given $ArNH_2$, the present reaction is considered to be specific acid catalyzed. Thus, one can propose that $ArNH_2$ reacts with the unprotonated substrate **1** and with the protonated species **2** as shown in Eqs. (1) and (4), respectively.



$$\underset{\mathbf{1}}{HC\equiv C\overset{O}{\overset{\|}{C}}Me} + H^+ \underset{K_a}{\rightleftharpoons} \underset{\mathbf{2}}{HC\equiv C\overset{OH^+}{\overset{\|}{C}}Me} \qquad (3)$$



$$\underset{\mathbf{2}}{HC\equiv C\overset{OH^+}{\overset{\|}{C}}Me} + ArNH_2 \xrightarrow{k_3} ArNHCH{=}CH\overset{O}{\overset{\|}{C}}Me + H^+ \qquad (4)$$

Let [S] and [SH^+] be the concentrations of the substrate **1** and its protonated form, respectively. Then, the total concentration of the substrate $[S]_{tot}$ is the sum of [S] and [SH^+]. One can derive Eqs. (5)–(7) from Eq. (3) and the relationship $[S]_{tot}=[S]+[SH^+]$.

$$K_a = [S][H^+]/[SH^+] \qquad (5)$$

$$[S] = [S]_{tot}/(1 + [H^+]/K_a) \qquad (6)$$

$$[SH^+] = [S]_{tot}/(1 + K_a/[H^+]) \qquad (7)$$

Then, the rate law can be expressed as Eqs. (8) and (9).

$$\text{Rate} = k_2[N][S] + k_3[N][SH^+] \qquad (8)$$

$$\text{Rate} = (k_2K_a + k_3[H^+])[N][S]_{tot}/(K_a + [H^+]) \qquad (9)$$

The K_a value of the conjugate acid of acetone has been reported to be 10^7 in H_2O.[19] The resonance effect due to the alkynyl–carbonyl conjugation may increase the base strength of **1**. However, one can expect an sp carbon is more electronegative than an sp^3 carbon and the Hammett σ_p constant is much larger for the ethynyl group

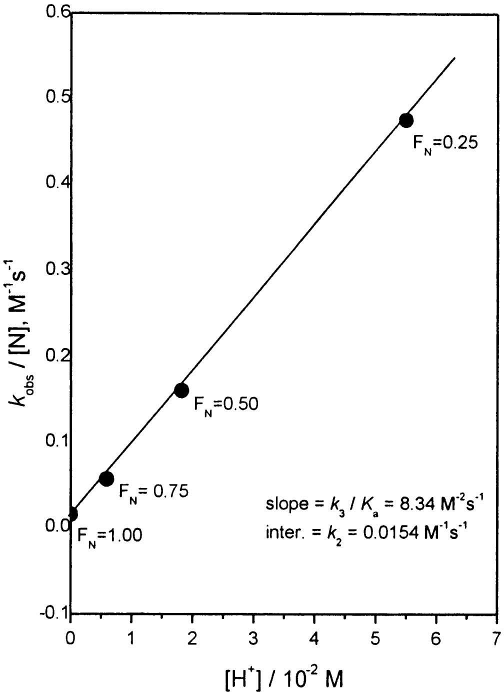


Figure 2. A plot of k_{obs}/[N] vs $[H^+]$ for the Michael-type addition of 4-cyanoaniline to **1** in H_2O at 25.0±0.1°C.

($\sigma_p=+0.23$) than for the methyl group ($\sigma_p=-0.17$). Since the resonance effect in **1** is opposite to the inductive effect in **1**, the K_a value for the conjugate acid of **1** would be of the order of 10^7.

Since the present reactions were performed under pseudo-first-order conditions (i.e. $[N]\gg[S]_{tot}$), Eq. (10) can be derived from Eq. (9). The pH of the reaction medium in the present system was above 1.0 even for the reaction with the least basic 4-cyanoaniline (i.e. $[H^+]<10^{-1}$), while K_a would be much larger than $[H^+]$ in the present system. Thus, Eq. (10) can be simplified to Eq. (11):

$$k_{obs} = (k_2K_a + k_3[H^+])[N]/(K_a + [H^+]) \qquad (10)$$

$$k_{obs}/[N] = k_N = k_2 + k_3[H^+]/K_a \qquad (11)$$

If the present reaction proceeds as described above, the plot of k_{obs}/[N] vs $[H^+]$ should be linear. In fact, as exemplified in Fig. 2, the plot of k_{obs}/[N] vs $[H^+]$ is linear with a positive intercept for all the anilines studied. Accordingly, the k_2 and k_3/K_a values were determined from the intercepts and slopes of the linear plots, respectively. The k_2 and k_3/K_a values obtained in this way are summarized in Table 2 and demonstrated graphically in Fig. 3. As shown in Table 2, the k_3/K_a value is much larger than the k_2 value for a given aniline, e.g. the k_3/K_a values are about 5.4×10^2 and 1.4×10^4 times larger than the k_2 values for 4-cyanoaniline and 4-hydroxyaniline, respectively. Since the K_a value of the protonated species **2** is considered to be of the order of 10^7, as mentioned above, the protonated species **2** will be of the order of 10^9–10^{11} times more reactive than the unprotonated species **1**, indicating that the catalytic effect of H^+ on the addition of $ArNH_2$ to the substrate **1** is remarkable.

Table 2. Summary of k_2 and k_3/K_a values for Michael-type addition reactions of substituted anilines (Z-$C_6H_4NH_2$) to **1** in H_2O at 25.0±0.1°C

Z	pK_a (Z-$C_6H_4NH_3^+$)	k_2 (M^{-1} s^{-1})	k_3/K_a (M^{-2} s^{-1})
4-CN	1.74	0.0154	8.34
3-Cl	3.32	0.163	127
4-Cl	3.81	0.246	368
H	4.58	0.375	2630
3-Me	4.67	0.530	1980
4-Ome	5.29	1.34	13800
4-OH	5.50	1.47	20600

There has been no previous report on the acid catalyzed addition of amines to activated acetylenes as in the present study. However, additions of amines to the carbonyl group have been suggested to proceed through acid catalyzed as well as uncatalyzed processes.[20] For acetoxime formation at 25°C in water, Jencks reported that the rate constant for the acid catalyzed process is 1.7×10^5 M^{-2} s^{-1}, while the one for the uncatalyzed process is 2.3×10^3 M^{-1} s^{-1}.[20] Since the K_a value for the conjugate acid of acetone has been reported to be 10^7 in H_2O,[19] the acid catalyzed process is of the order of 10^8–10^9 times faster than the uncatalyzed process. Therefore, the catalytic effect of H^+ in the present system is more remarkable than the one in the acetoxime formation reaction.

In Fig. 3 are shown linear Brønsted-type plots for both the k_2 and k_3 processes. Since log k_3/K_a=log k_3−log K_a and K_a is constant, the slope of the plot of log k_3/K_a vs pK_a ($ArNH_3^+$) is the same as that of log k_3 vs pK_a ($ArNH_3^+$). The β_{nuc} values in the present system have been calculated to be 0.51 and 0.93 for the k_2 and k_3 process, respectively. We recently reported that the β_{nuc} value is 0.32 for the corresponding reactions of **1** with a series of aliphatic primary amines in H_2O[9] and 0.28 for the reactions of an activated acetylene, methyl propiolate ($HC\equiv CCO_2Me$) with a series of alicyclic secondary amines in H_2O.[21] Therefore, the β_{nuc} value of 0.93 for the k_3 process in the present system is unusually large. The magnitude of β_{nuc} values has been suggested to represent the degree of relative bond formation between the nucleophile and the substrate at the rate-determining transition state (TS).[22] Therefore, one can suggest that the degree of bond formation for the acid catalyzed process is significantly more advanced than the uncatalyzed process and analogous reactions.

As shown in Fig. 3, the Brønsted-type plot for the present reactions is linear for both the k_2 and k_3 processes. Such a linear Brønsted-type plot clearly suggests that the reaction mechanism does not change upon changing the basicity of $ArNH_2$ in the present system. The nonlinear Brønsted-type plot shown in Fig. 1 for the reactions run at F_N=0.50 is definitely not due to a change in the reaction mechanism but due to the contribution of the $k_3[H^+]/K_a$ term to the k_N value. As shown in Eq. (11), the k_N value consists of two terms, k_2 and $k_3[H^+]/K_a$. The contribution of the latter term to the k_N value is negligible for the reactions run at F_N=1.00, since the pH of the reaction medium was higher than 7 when F_N=1.00 (i.e. $[H^+]<10^{-7}$). This argument can be supported by the fact that the k_2 value in Table 2 and the k_N value for the reactions run at F_N=1.00 in Table 1 are the same within experimental error. However, the contribution of the $k_3[H^+]/K_a$ term to the k_N value becomes significant as

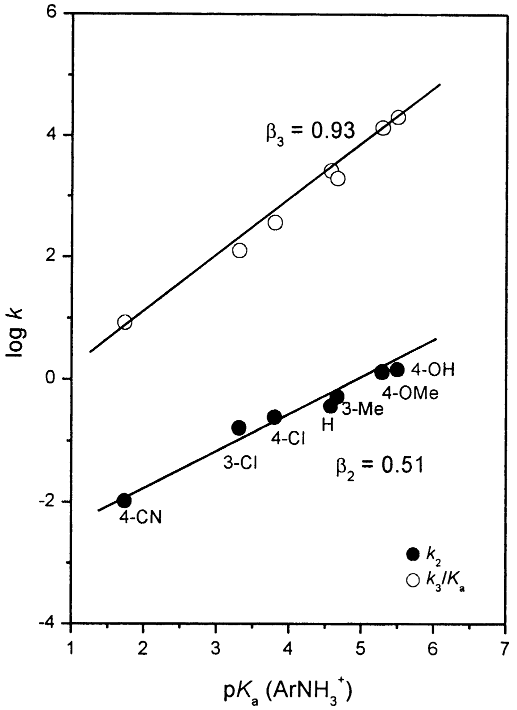


Figure 3. Plots of logarithmic k_2 and k_3/K_a vs pK_a of the conjugate acid of anilines for Michael-type additions of substituted anilines (Z-$C_6H_4NH_2$) to **1** in H_2O at 25.0±0.1°C.

the pH of the reaction medium decreases especially for weakly basic anilines. This is consistent with the fact that the k_N value for a given aniline increases with decreasing the F_N value (i.e. increasing $[H^+]$), and that the positive deviation from the linear Brønsted-type plot in Fig. 1 is more significant for the less basic $ArNH_2$.

We recently reported a similar result for the nucleophilic substitution reaction of 4-nitrophenyl X-substituted benzoates with a series of alicyclic secondary amines.[16a] The Hammett plots of log k_N vs the σ constant of the benzoyl substituent X were nonlinear for all the amines studied due to negative deviations by the π-electron donor substituents such as 4-MeO, suggesting a change in the RDS. However, the corresponding Yukawa–Tsuno plots resulted in good linear correlation with $\sigma+r(\sigma^+-\sigma)$, indicating that the nonlinear Hammett plots were not due to a change in the RDS but due to changes in the resonance supply of the π-electron donor substituent.[16a] Therefore, one can suggest that deductions of a reaction mechanism based just on a linear or a nonlinear Brønsted or Hammett plot can be misleading.

3. Experimental

3.1. Materials

3-Butyn-2-one **1** was prepared by oxidizing 3-butyn-2-ol with chromic acid as described in the literature.[23] Other chemicals including all the anilines used in the present study were of the highest quality available from Aldrich or Tokyo Kasei, and generally recrystallized or distilled before use. Doubly glass distilled water was further boiled and cooled under nitrogen just before use.

3.2. Kinetics

The kinetic study was performed with a Sinco S-1130 UV–Vis spectrophotometer equipped with a constant temperature circulating bath to keep the reaction mixture at 25.0±0.1°C. The reactions were followed by monitoring the appearance of the addition product at a fixed wavelength corresponding to the maximum absorption of the enamine. All the reactions were carried out under pseudo-first-order conditions in which the concentration of free $ArNH_2$ was at least 20 times greater than that of the substrate **1**. The kinetic study was performed under 4 different free aniline fractions (e.g. F_N=1.00, 0.75, 0.50 and 0.25). The F_N values were controlled by adjusting the ratio of $[ArNH_2]/\{[ArNH_2]+[ArNH_3^+Cl^-]\}$. At least five different $ArNH_2$ concentrations were used to obtain the second-order rate constant (k_N) for each $ArNH_2$ at a given F_N. Other detailed kinetic methods were reported previously.[16a]

3.3. Product analysis

Product analysis was performed by ^1H NMR spectroscopy. The ^1H NMR spectrum of the reaction mixture for the reaction of **1** with aniline revealed that no 1,2-addition product but only the Michael-type addition product, (*E*)-4-anilino-3-buten-2-one, was formed.

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