Effects of Boric Acid on the Rate and Equilibrium of Schiff Base Formation from Salicylaldehyde

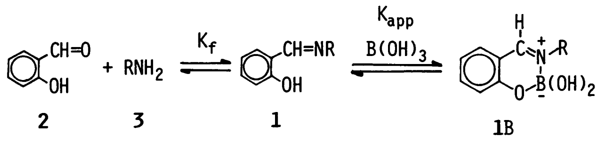
Hiroaki Nagamatsu, Tadashi Okuyama,* and Takayuki Fueno
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received April 25, 1984)

Effects of boric acid on the formation of the Schiff base from salicylaldehyde and 2-methoxyethylamine (or glycinate) were examined in aqueous solution. From the formation constants in the absence and presence of boric acid, the equilibrium constants for the borate-Schiff base complexation were determined. The structure of the complex was deduced from the UV spectral analysis. Formation of the Schiff base was found to be accelerated by boric acid (pH 7—10). A mechanism for the reaction involving the complex is presented.

Hydrolysis of Schiff bases derived from an α-hydroxy ketone[1] and salicylaldehyde[2,3] is greatly influenced by added boric acid. Intermediacy of a borate-Schiff base complex was substantiated from kinetic investigations of the hydrolysis.[1,3] Since the Schiff base formation is reversible in aqueous solution and Schiff bases are stable in the presence of an excess amount of amine, the complexation could be examined in more detail under equilibrium conditions.

In the present investigation, the formation of the Schiff base (**1**) from salicylaldehyde (**2**) has been examined under such conditions both in the absence and presence of boric acid (Scheme 1). The Schiff base formation was accelerated by added boric acid. Complexation between boric acid and **1** was analyzed and the structure of the complex was deduced on the basis of the UV spectra. A mechanism for the reaction involving the borate-Schiff base complex is presented.



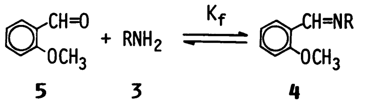
a, R = $(CH_2)_2OCH_3$
b, R = $CH_2CO_2^-$

Scheme 1.

Results

Schiff Base Formation in the Absence of Boric Acid. All the reactions and UV-measurements were carried out at 30 °C in aqueous solution of an ionic strength of 0.10 maintained with KCl. UV spectral data of salicylaldehyde (**2**) and its derivatives are summarized in Table 1. Spectra of Schiff bases (**1**) at higher pH were recorded under equilibrium conditions in the presence of **2** and an excess amount of amines (**3**). Appropriate corrections were made for concomitant **2** by using the formation constant K_f obtained below. The spectra in HCl solutions were obtained as an initial spectrum immediately after mixing.

When a small amount of **2** is added into an aqueous solution containing a primary amine **3**, the absortion of Schiff base **1** develops at the expense of the absorption of **2**. On the contrary, addition of **1** into the amine solution causes the Schiff base bands to diminish with simultaneous appearance of the aldehyde bands. Both changes accompany two isosbestic points at about 260 and 345 nm at lower pH(<8) and at 260 and 375 nm at higher pH(>8.5). These spectral changes are no doubt results of the equilibrium between Schiff base **1** and aldehyde **2**. *o*-Methoxybenzaldehyde (**5**) and its Schiff bases (**4**) showed similar spectral changes. The UV measurements were made in the same way.



(1)

a, R = $(CH_2)_2OCH_3$
b, R = $CH_2CO_2^-$

The equilibrium constant K_f can be determined from these spectral changes as described in Experimental

Table 1. Maximum wavelengths of UV absorption of salicylidene derivatives[a)]

No.[b)]	X	Y	Condition	λ_{max}/nm ($10^4\,\varepsilon$)	
1a (**1a**H+)	$N^+H(CH_2)_2OMe$	OH	1 M-HCl	275 (2.1)	348 (0.53)
1a (**1a**±)	$N^+H(CH_2)_2OMe$	O^-	pH 8.9	275 (1.3)	393 (0.63)
1b (**1b**±)	$N^+HCH_2CO_2^-$	O^-	pH 8.9	277 (1.4)	395 (0.67)
2 (**2**⁰)	O	OH	1 M-HCl	255 (1.2)	324 (0.34)
2 (**2**−)	O	O^-	1 M-NaOH	264 (0.74)	377 (0.67)
4a (**4a**H+)	$N^+H(CH_2)_2OMe$	OMe	1 M-HCl	276 (2.7)	347 (0.80)
4a (**4a**⁰)	$N(CH_2)_2OMe$	OMe	pH 8.9	249 (1.8)	305 (0.70)
4b (**4b**⁰)	$NCH_2CO_2^-$	OMe	pH 9.8	252 (1.8)	307 (0.74)
5	O	OMe	pH 8.9	255 (1.5)	322 (0.59)
1aB			pH 8.9	271 (1.5)	345 (0.41)
1bB			pH 8.9	273 (1.6)	345 (0.46)

a) o-YC_6H_4CH=X. b) A main form of the ionization states present is shown in parentheses.

Section. Results are summarized in Table 2.

Time-dependent changes of the absorbance gave pseudo-first-order rate constants k_{obsd}, which were not affected whether the reaction was started with **1** or **2**. The rate constant k_{obsd} linearly increased with the total amine concentration $[\mathbf{3}]_t$ (Fig. 1), but was independent of the buffer used to maintain pH constant. The observed rate constant k_{obsd} must be the sum of those for the forward and the reverse reactions (Eq. 2).

$$k_{obsd} = k_h + k_f[\mathbf{3}]_t \qquad (2)$$

The intercept and the slope of the plot of k_{obsd} against $[\mathbf{3}]_t$ correspond to the rate constants for the hydrolysis (k_h) and formation (k_f) of Schiff base **1**, respectively. These rate constants obtained over pH 7—11 are summarized in Table 2. Both k_f and k_h obtained from the reaction of **2** (in the presence of **3a**) agree with those obtained from the reaction of **1a** within experimental errors. The values of k_h for the hydrolysis of **1a** are identical to those obtained previously in the absence of the amine.[3] The equilibrium constants $K_f(=k_f/k_h)$ calculated from the rate constants agree well with those

Table 2. Equilibrium and rate constants for the formation of schiff bases, **1a** and **1b**[a]

pH[b]	K_f/M^{-1} [c]	$10\,k_f/M^{-1}\,s^{-1}$ [d]	$10^3\,k_h/s^{-1}$ [d]	K_f/M^{-1} [e]
		1a		
7.00[f]	15.4±1.4(20)	0.312±0.011	1.57±0.01	
8.00[f]	113±2(100)	1.63±0.01(1.63±0.03)	1.58±0.01(1.55±0.03)	2
8.94[g]	202±2(200)	4.07±0.06(4.22±0.06)	2.02±0.08(1.93±0.07)	26
9.58[h]	142±3(130)	4.50±0.03(4.56±0.03)	3.50±0.05(3.50±0.03)	54
10.02[h]	82.6±1.3(87)	5.07±0.03(4.95±0.09)	5.80±0.03(5.86±0.10)	68
10.83[i]	22.7±0.6(27)	6.18±0.06	23.0±0.1	
11.40[i]				98
		1b		
7.50[f]	20.8±1.7(22)	0.451±0.006	2.08±0.01	
8.00[f]	39.3±0.9(38)	0.673±0.011	1.75±0.02	
8.94[g]	82.3±0.3(73)	1.51±0.03	2.06±0.05	
9.38[h]	75.8±2.1(74)	1.68±0.04	2.28±0.06	10
9.78[h]	57.0±1.2(56)	1.81±0.02	3.25±0.04	
10.02[h]				20
10.21[j]	35.0±0.8(37)	2.05±0.07	5.50±0.12	
10.83[i]	(13)	2.58±0.07	19.5±0.1	28
11.19[i]				30

a) In aqueous solutions of the ionic strength of 0.10 at 30 °C. Standard deviations are given. b) pH(±0.03) were maintained with buffers(f—j) of 0.05 M. c) Obtained spectrophotometrically. Values in parentheses are calculated from k_f and k_h. d) Obtained from the reaction of **2**. Values in parentheses were obtained from the reaction of **1**. e) K_f for **4** obtained spectrophotometrically. f) *N*-Methylmorpholine. g) 1,4-Diazabicyclo[2.2.2]-octane. h) 2-(Dimethylamino)ethanol. i) Triethylamine. j) Trimethylamine.

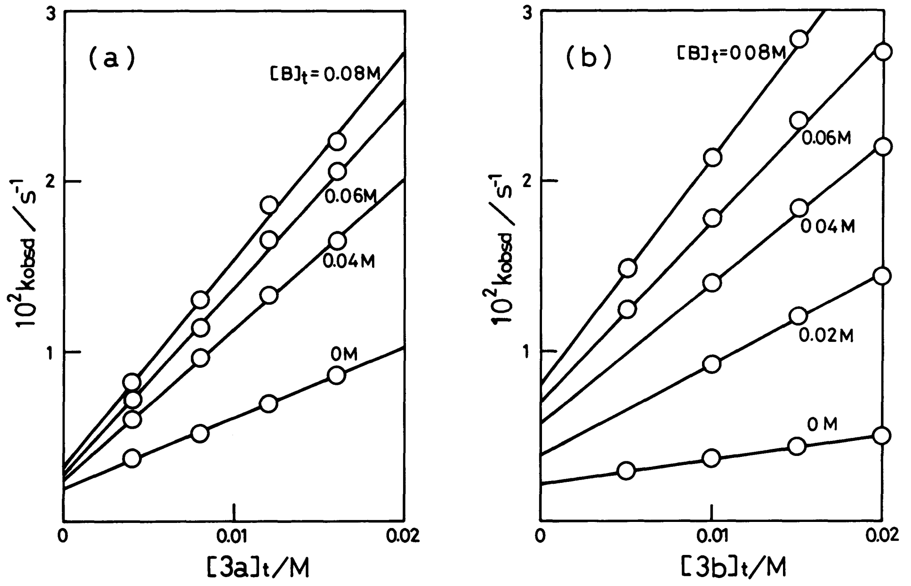


Fig. 1. Dependences of k_{obsd} on the amine concentrations for the formation of **1a** (a) and **1b** (b) from **2** at pH 8.94 and the boric acid concentrations indicated.

obtained spectrophotometrically, as summarized in Table 2.

Reactions in the Presence of Boric Acid. The UV spectra of **1** in the presence of boric acid were compared with those observed in its absence. On addition of boric acid, the absorbane at 393—395 nm of **1** diminished and a new absorption band appeared around 350 nm owing to the formation of a borate-Schiff base complex. The spectrum of aldehyde **2** was, however, not affected by the addition of boric acid; complexation between boric acid and **2** is negligible. The reactions involved are illustrated in Scheme 1. The apparent equilibrium constant K_f' for the Schiff base formation in the presence of boric acid can be spectrophotometrically determined in the same way as in the absence of boric acid. K_f' is defined by Eq. 3, where [**1B**] stands for the concentration of the complex **1B**. Since equilibrium constant K_{app} for the complexation is defined by Eq. 4,[3] the relation of Eq. 5 can bederived from Eqs. 3 and 4, where $[B]_t$ is total boric acid concentration.

$$K_f' = ([\mathbf{1}]+[\mathbf{1B}])/[\mathbf{2}][\mathbf{3}]_t, \tag{3}$$

$$K_{app} = [\mathbf{1B}]/[\mathbf{1}][B]_t, \tag{4}$$

$$K_f' = K_f + K_f K_{app}[B]_t. \tag{5}$$

The values of K_{app} were calculated as the ratio of the slope/intercept of the regression line of K_f' *vs.* $[B]_t$ (Fig. 2). Results are summarized in Table 3. The values of K_{app} for **1a** agree well with those obtained from the kinetic analysis of hydrolysis of **1a**.[3]

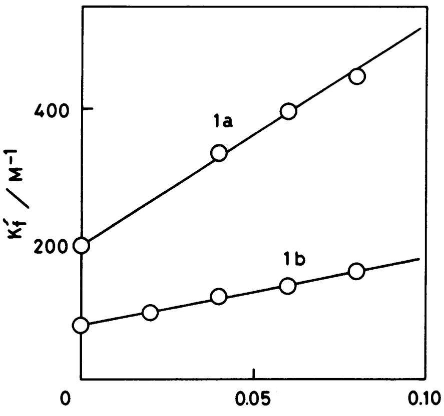


Fig. 2. Plots of K_f' against boric acid concentration at pH 8.94.

TABLE 3. EQUILIBRIUM AND RATE CONSTANTS FOR THE SCHIFF BASE FORMATION IN THE PRESENCE OF BORIC ACID[a)]

pH[b)]	K_{app}/M^{-1}	k_f^B/M^{-1} s^{-1}	$K_C/(K_T+1)$/M^{-1}
		1a	
7.02	27.4 ±0.7	1.36±0.03	27.6
8.02	24.7 ±0.8	9.09±0.12	26.3
8.94	16.3 ±0.4	11.7 ±0.2	25.3
9.58	5.68±0.19	4.16±0.09	19.3
		1b	
8.94	12.3 ±0.3	16.3 ±0.2	19.1
9.40	6.42 ±0.14	9.05±0.10	16.6

a) In aqueous solutions of the ionic strength of 0.10 at 30 °C. Standard deviations are given. b) ±0.03.

At a given ooncentration of boric acid $[B]_t$, the time-dependent absorbance changes followed the pseudo-first-order kinetics, and k_{obsd} increased linearly with the amine concentration $[\mathbf{3}]_t$ as observed in the absence of boric acid (Fig. 1).

$$k_{obsd} = k_h' + k_f'[\mathbf{3}]_t \tag{6}$$

The rate constant k_h' for the hydrolysis of **1a** agrees with that obtained in the absence of amine **3a**.[3] The rate

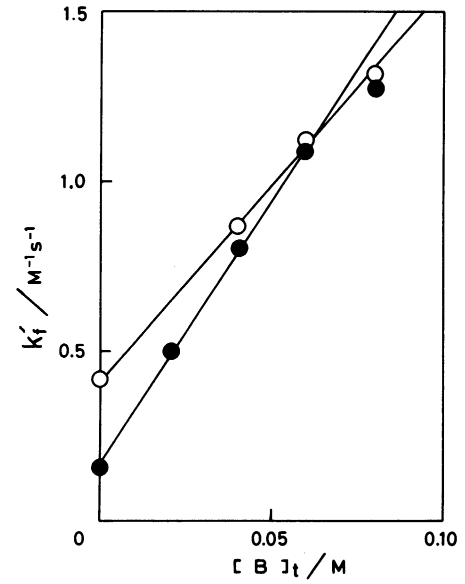


Fig. 3. Dependences of k_f' on boric acid concentration at pH 8.94 for the formation of **1a** (○) and **1b** (●).

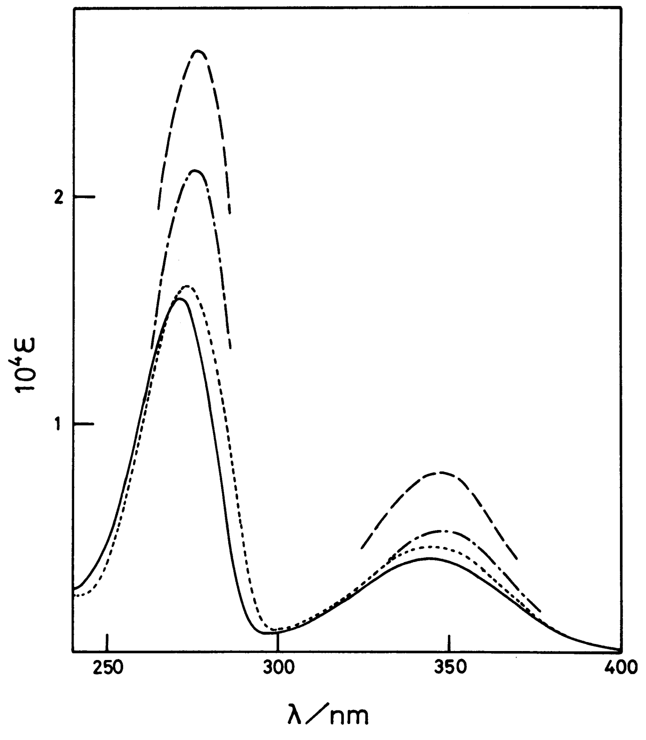


Fig. 4. UV spectra of borate complexes **1aB** (——) and **1bB** (······) at pH 8.94. Spectra of **1aH**$^+$ (— — —) and **4aH**$^+$ (— —) are also shown.

constant k_f' for the formation of **1** increased linearly with $[B]_t$ (Fig. 3).

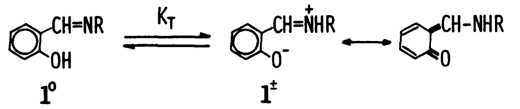
$$k_f' = k_f + k_f^B[B]_t \tag{7}$$

The intercepts of the plots of k_f' *vs.* $[B]_t$ are equal to the rate constants k_f obtained in the absence of boric acid ($[B]_t$=O). The third-order rate constants k_f^B are listed in Table 3.

Analysis of UV Spectra. The spectrum of Schiff base **1** in aqueous solution changes greatly by the addition of boric acid as mentioned above. In this aqueous solution, the complex **1B** must be present in an equilibrium concentration together with **1** and **2** as light-absorbing species (Scheme 1). Since we now know the equilibrium constants K_f and K_{app}, we can calculate the equilibrium fractions of **1**, **2**, and **1B**. The equilibrium fractions of **1aB**, **1a**, and **2** are, *e.g.*, 60, 37, and 3%, respectively, at pH 8.9, $[B]_t$=0.10 M,[4] and [**3a**]=0.625 M. The absorbances of **1aB** were thus calculated from the observed spectrum at every 5 nm over 240—400 nm using the extinction coefficients of **1** and **2** at each wavelength. The spectrum calculated in this way is shown in Fig. 4. The spectrum of **1bB** was also calculated in the same way. These spectra have two absorption maxima at 271(273) and 345 nm, which resemble closely those of the protonated Schiff bases **1aH**$^+$ and **4aH**$^+$ as may be seen in Fig. 4 (see also Table 1).

Discussion

UV Spectra. All the spectra of salicylaldehyde derivatives (o-$YC_6H_4CH{=}X$) listed in Table 1 have two absorption bands in the 250—275 and 305—395 nm regions. The iminium derivatives ($X{=}N^+HR$), as observed in HCl solutions, have a band at about 275 nm, while aldehyde (X=O) and the neutral imine (**4** in alkaline solution, X=NR) have a band around 255 nm. Although the spectra of **1** and **4** closely resemble each other in acid solutions, those observed in alkaline solutions are quite different. The spectra of **1** at pH 8.9 have a band typical of the iminium group (~276 nm) and largely red-shifted one (~394 nm). This feature of the spectrum of **1** conforms to the structure of the zwitterion **1**$^\pm$. The red-shift of the long-wavelength band (**1**$^\pm$ *vs.* **2**$^-$) by the iminium function is generally observed; *e.g.*, **1H**$^+$ *vs.* **2**^{0} and **4H**$^+$ *vs.* **5**^{0}. The conclusion that the main species of *N*-salicylidene amine is the zwitterion **1**$^\pm$ in the neutral aqueous solution was previously reached from the comparisons of the spectra in aqueous and organic media.[5] This is also compatible with the kinetic results of the hydrolysis of **1a**.[3]



1^0 **1**$^\pm$ (8)

The tautomeric equilibrium (8) is largely shifted to the right-hand side owing to the stabilization by the quinonoid resonance.

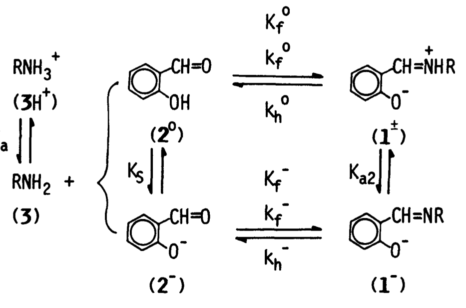
The absorption spectrum of the borate complex **1B**, as shown in Fig. 4, has two bands in the vicinity of the wavelengths characteristic of the iminium and the neutral phenolic groups. This strongly suggests the structure of **1B** involving a positive nitrogen and a neutral (phenolic) oxygen as a result of boron coordination. A reasonable structure is given in Scheme 1. Similar complexes involving a tetracoordinated boron have in fact been isolated as diacetates from the reaction of *N*-salicylidene amines with boric acid in acetic anhydride.[6] Diphenylborinate adducts have recently been found to have a similar structure.[7] It is also well-known that *N*-salicylidene amines form stable chelate complexes with various metal ions.[8,9] The UV spectra of Zn(II) and Ni(II) complexes have the absorption bands in the vicinity of 270 nm and 350 nm.[10]

Schiff Base Formation. Formation of Schiff bases occurs through a nucleophilic attack of free amine base on the carbonyl group as illustrated in Scheme 2.[11,12]

The pH-equilibrium constant profile is bell-shaped (Fig. 5) and is represented by Eq. 9 where K_a and K_S are the acid dissociation constants of ammonium ion **3H**$^+$ and salicylaldehyde **2**^{0}, respectively (pK_S 8.3).

$$K_f = \frac{K_a(K_f^0[H^+]+K_f^-K_S)}{(K_a+[H^+])(K_S+[H^+])} \tag{9}$$

Constants K_f^0 and K_f^- refer to the equilibria involving the neutral (**2**^{0}) and anionic (**2**$^-$) aldehyde, respectively.



Scheme 2.

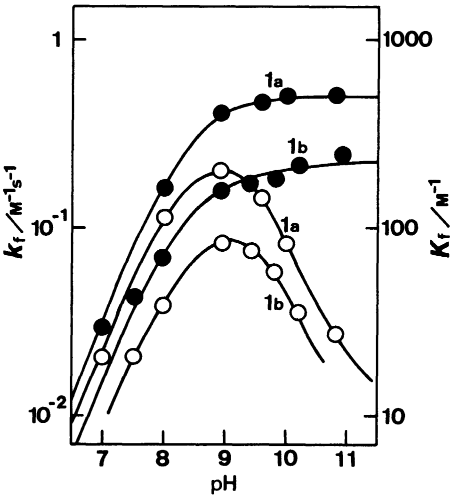


Fig. 5. pH profiles of rate constants k_f(●, left ordinate) and equilibrium constants K_f(○, right ordinate) for the formation of Schiff bases **1a** and **1b**.

The pH-rate profile also fits a similar equation (Eq. 10), although it appears to be different from the pH-K_f profile (Fig. 5).

$$k_f = \frac{K_a(k_f^\circ[H^+]+k_f^-K_S)}{(K_a+[H^+])(K_S+[H^+])} \tag{10}$$

The rate constant k_f^0 and k_f^- refer to the reactions of amine with **2**^{0} and **2**$^-$, respectively. Theoretical curves calculated by Eqs. 9 and 10 with parameters given in Table 4 are shown in Fig. 5. The values of K_f^0 and K_f^- for **1a** satisfy the relationship $K_f^-/K_f^0=K_{a2}/K_S$, which results from the equilibrium cycle in Scheme 2. Here, K_{a2} ($7.0\times10^{-12}M^{-1}$) obtained during the hydrolysis kinetics[3)] is used. The rate constants for the hydrolysis of **1a** can be calculated from previous results[3)]: $k_h^0(k_2)=1.5\times10^{-3}\,s^{-1}$ and k_h^- $(k_2'K_W/K_{a2})=7.8\times10^{-2}\,s^{-1}$. The individual formation constants, $K_f^0(k_f^0/k_h^0)=6.1\times10^3$ M^{-1} and $K_f^-(k_f^-/k_h^-)=7.6\,M^{-1}$, evaluated from these values agree well with those obtained spectrophotometrically. The formation constants for **1b** also agree with those reported.[9)]

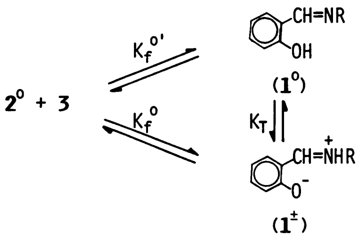
The equilibrium constants for the formation of Schiff base **4** corrected for the amine protonation are: **4a**, $K_f^0=100\,M^{-1}$ and **4b**, $K_f^0=31\,M^{-1}$. These values are smaller than those (K_f^0) for *N*-salicylideneamines **1** by a factor of 10^2. The large values for **1** cannot simply be ascribed to a possible stabilization of **1** by an intramolecular hydrogen bonding. Stabilization of the Schiff base in a tautomeric form, **1**$\pm$, must be responsible for the facile formation of *N*-salicylidene amines. The zwitterionic form **1**$\pm$ is in fact a main species in neutral and weakly alkaline aqueous solutions as has been confirmed by UV spectroscopy.

The tautomeric oonstant K_T in aqueous solution is hard to estimate. If we assume that the formation constant $K_f^{0\prime}$ for the neutral Schiff base **1**^{0} (Scheme 3) is the same as that for the methoxy derivatives **4**, $K_T(=K_f^0/K_f^{0\prime})$ can be calculated as 60 and 116 for **1a** and **1b**, respectively.

TABLE 4. SUMMARY OF EQUILIBRIUM AND RATE CONSTANTS[a)]

	1a	**1b**
pK_a[b)]	9.58	9.78
K_f°/M^{-1}	6.0×10^3	3.6×10^3
K_f^-/M^{-1}	7.8	3.8
$k_f^\circ/M^{-1}\,s^{-1}$	9.2	5.8
$k_f^-/M^{-1}\,s^{-1}$	0.61	0.24
$K_C/(K_T+1)/M^{-1}$	25	18
$k_f^{Bo}/M^{-2}\,s^{-1}$	560	1100

a) In aqueous solutions of the ionic strength of 0.10 at 30 °C. b) pK_a of **3**H^+ obtained as the pH of the solution of $[\mathbf{3}H^+]=[\mathbf{3}]$.



Scheme 3.

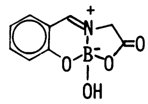
Similar evaluation for *N*-salicylideneaniline gave $K_T=6.3$.[13)] For the derivatives from less basic amines, the zwitterionic form tends to be less important. These estimations for K_T would be an upper limit in their magnitudes, as the neutral form of salicylidene derivatives **1** be stabilized by an intramolecular hydrogen bonding.

The complexation was considered to involve the neutral Schiff base and boric acid (acid form) from the bell-shaped change of K_{app} with pH.[3)] With the equilibrium constant K_C for the reaction (Eq. 11), K_{app} can be expressed as Eq. 12.

$$\begin{tikzcd} \mathbf{1}^\circ \arrow[d, shift left, "K_T"'] & + & B(OH)_3 \arrow[d, shift left, "K_{BH}"'] \arrow[r, shift left, "K_C"] & \mathbf{1B} \arrow[l, shift left] \\ \mathbf{1}^\pm \arrow[u, shift left] & & B(OH)_4^- \arrow[u, shift left] & \end{tikzcd} \tag{11}$$

$$K_{app} = K_C[H^+]/(K_{BH}+[H^+])(K_T+1) \tag{12}$$

Values of $K_C/(K_T+1)$ were calculated with $K_{BH}=6.3\times10^{-10}\,M^{-1}$ and are given in Table 3. Average values are: $K_C/(K_T+1)=25$ and $18\,M^{-1}$ for **1a** and **1b**, respectively. The value for **1a** agrees reasonably well with that obtained from the hydrolysis kinetics.[3)] By using the above estimated values for K_T, the K_C values are 1500 and $2100\,M^{-1}$ for **1a** and **1b**, respectively. The carboxylato group of **1b** does not appreciably participate in the complexation. The boron–carboxylato interaction, as considered for metal-ion complex,[9)] is not important. The bicyclic structure must be strained owing to the short B–O (B–N) distances.



Boric acid accelerates the Schiff base formation and the catalytic constants k_f^B change with pH taking a maximum value at pH 9. Because of the nature of the reaction, the reactive species involved must be a free amine base and boric acid (acid form). The catalytic constants k_f^B were corrected for such protonation states according to Eq. 13.

$$k_f^{B\prime} = k_f^B(K_a+[H^+])(K_{BH}+[H^+])/K_a[H^+] \tag{13}$$

The corrected constants $k_f^{B\prime}$ are plotted against the fraction of the neutral salicylaldehyde **2**^{0} in Fig. 6. For either of the amines, the plots seem to fit a straight line through the origin. Thus, only the neutral aldehyde **2**^{0} is involved in this reaction but the ionized aldehyde **2**$^-$ is not. To be strict, the transition state for the borate-catalyzed formation of the Schiff base **1** is neutral and consists of aldehyde, amine, and boric acid. The catalytic constants k_f^{B0} corrected for the neutral aldehyde are 560 and $1100\,M^{-2}\,s^{-1}$ for **3a** and **3b**, respectively, from the slopes of the plots in Fig. 6. These values correspond to accelerations of about 60- and 190-fold at $[B]_t=1\,M$.

A probable reaction sequence of the boric acid-

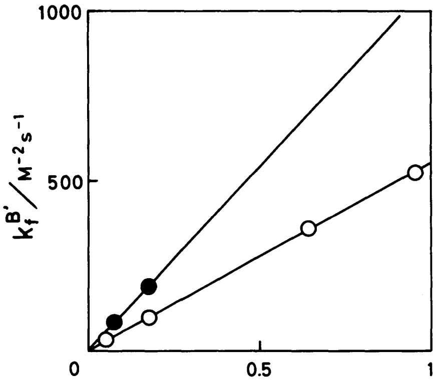
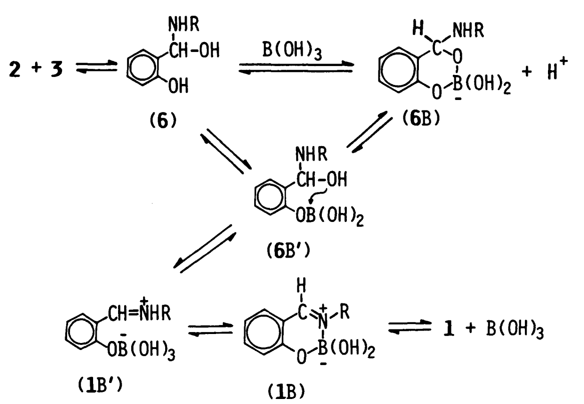
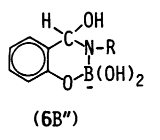


Fig. 6. Plots of $k_f^{B'}$ against the fraction of the neutral aldehyde 2^0 for the boric acid-catalyzed formation of **1a** (○) and **1b** (●).



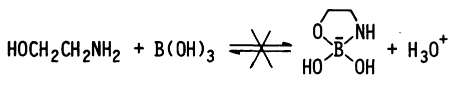
Scheme 4.

catalyzed Schiff base formation is given in Scheme 4. In alkaline pH region, formation of an α-amino alcohol intermediate (**6**) is rapid. **6** is a diol capable of forming a chelate complex (**6B**) with boric acid. However, the chelate complex cannot facilitate dehydration to lead to the Schiff base. The adduct (**6B′**) may exist in equilibrium at low concentration. Within this adduct, the hydroxyl group of the α-amino alcohol can readily transfer to the boron acceptor. The resulting zwitterion (**1B′**) rearranges to the stable borate-Schiff base complex (**1B**). This is precisely the microscopic reverse of the boric acid-assisted hydrolysis of the Schiff base.[3)] Formation of a chelate complex (**6B″**) involving the amino-coordination to the boron is unlikely.



(6B″)

Such complexes are not known in aqueous solution. The pH did not change when the two buffer solutions, each made from borate and 2-aminoethanol (or glycine) and adjusted at the same pH (≈9.2), were mixed (Eq. 14).



(14)

In conclusion, the formation of *N*-salicylidene amines catalyzed by boric acid takes place through a mechanism given in Scheme 4.

Experimental

The UV measurements were carried out in a stoppered 10-mm quartz cuvette at a slitwidth of 1 nm on a Shimadzu UV 200 spectrophotometer. Some kinetic runs were also performed on a Shimadzu UV 140 spectrometer. The pH values of the buffer and reaction solutions were measured on a Hitachi-Horiba F7 pH meter.

Materials. Glycine **3b** and *o*-methoxybenzaldehyde **5** were commercially obtained. *N*-(*o*-Methoxybenzylidene)-2-methoxyethylamine **4a** was prepared in the same way as described previously for **1a**[3)]: bp. 131 °C (4 mmHg).[14)] All the other chemicals were obtained as before.[3)]

Kinetic Measurement. All the aqueous solutions containing appropriate amounts of amine, boric acid, and buffers were prepared at room temperature and adjusted to the ionic strength of 0.10 with KCl. Reactions were started by adding 30 μl of a substrate soluion in acetonitrile from a microsyringe into 3 ml of a buffer solution equilibrated at 30±0.1 °C in a cuvette inserted in a water-jacketed cell holder. Pseudo-first-order rate constants were calculated usually by a modified Guggenheim method[15)] from the time-dependent absorbance changes at 275 nm for **1**, and 335 nm at higher pH(>7) or 282 nm at lower pH(<7) for **4**. The infinite absorbances were compared occasionally between those observed and calculated.

Determination of the Formation Constant. The equilibrium constants were calculated from UV absorbance. Since amine **3** has no absorption above 220 nm, the relative concentration at equilibrium is expressed by the absorbance change: $[\mathbf{1}(\mathbf{4})]/[\mathbf{2}(\mathbf{5})]=(A_e-A_0)/(\varepsilon_1[\mathbf{2}(\mathbf{5})]_0-A_e)$ starting with **2**(**5**), where A_0 and A_e are the absorbances at time zero and at equilibrium, and ε_1 and $[2]_0$ stand for the extinction coefficient for **1** and

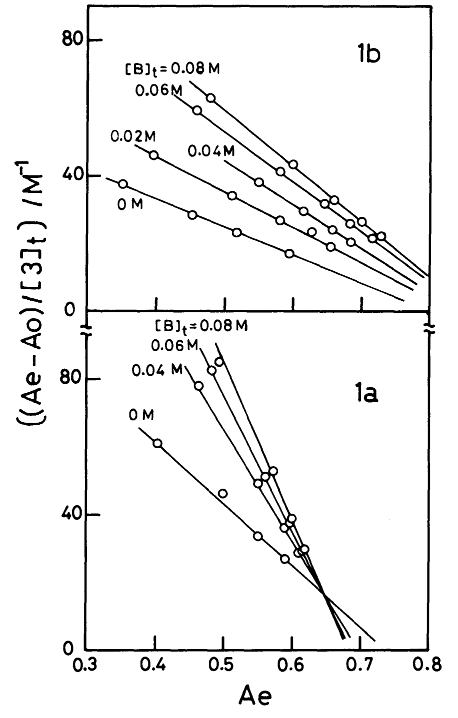


Fig. 7. Plots of $(A_e-A_0)/[3]_t$ against A_e at pH 8.94 and the boric acid concentrations indicated.

the initial concentration of **2**, respectively, or alternatively $[\mathbf{1}]/[\mathbf{2}]=(A_e-A_0)/(\varepsilon_2[\mathbf{1}]_0-A_e)$ starting with **1** whose concentration is $[\mathbf{1}]_0$. Here ε_2 stands for the extinction coefficient for **2**. The values of $\varepsilon_1[\mathbf{2}]_0$ and $\varepsilon_2[\mathbf{1}]_0$ correspond to the limiting absorbances A_∞ at the infinite concentration of **3**. Thus the values of $K_f(=[\mathbf{1}]/[\mathbf{2}][\mathbf{3}])$ were determined from the slope of the plots of $(A_e-A_0)/[\mathbf{3}]_t$ against A_e according to Eq. 15 (Fig. 7).

$$(A_e-A_0)/[\mathbf{3}]_t = K_f(A_\infty-A_e) \qquad (15)$$

References

1) H. Matsuda, H. Nagamatsu, T. Okuyama, and T. Fueno, *Bull. Chem. Soc. Jpn.*, **57**,500 (1984).

2) J. Hoffmann and V. Štěrba, *Collect. Czech. Chem. Commun.*, **37**, 2043 (1972).

3) H. Nagamatsu, T.Okuyama, and T. Fueno, *Bull. Chem. Soc. Jpn.*, **57**, 2502 (1984).

4) 1 M=1 mol dm^{-3}.

5) W. Bruyneel, J. J. Charette, and E.de Hoffmann, *J. Am. Chem. Soc.*, **88**, 3808 (1966).

6) S. M. Tripathi and J. P. Tandon, *J. Inorg. Nucl. Chem.*, **40**, 983 (1978).

7) E. Hohaus, *Monatsh. Chem.*, **111**, 863 (1980).

8) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Prog. Inorg. Chem.*, **7**, 83 (1966); L. Sacconi, *Coord. Chem. Rev.*, **1**, 126, 192 (1966).

9) D. L. Leussing, "Metal Ions in Biological Systems," H. Sigel ed., Marcel Dekker, New York (1976), vol. 5, chap. 1.

10) D. L. Leussing and K. S. Bai, *Anal. Chem.*, **4**, 575 (1968).

11) E. H. Cordes and W. P. Jencks, *J. Am. Chem.Soc.*, **84**, 826 (1962).

12) A. Williams and M. L. Bender, *J. Am. Chem. Soc.*, **88**, 2508 (1966).

13) J.J. Charette and E. de Hoffmann, *J. Org. Chem.*, **44**, 2256 (1979).

14) 1 mmHg≈133.322 Pa.

15) E. S. Swinbourne, *J. Chem. Soc.*, **1960**, 2371.