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FORMIC ACID REDUCTION–XVII

KINETIC STUDIES ON THE FORMIC ACID REDUCTION OF N-BENZYLIDENEANILINE*[1]

M. Sekiya, K. Mori, K. Ito and K. Suzuki
Shizuoka College of Pharmacy, 2-2-1 Oshika, Shizuoka, Japan

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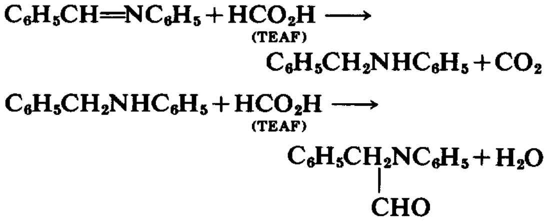
Abstract—The formic acid reduction of azomethine which has been reported[2] to proceed nearly quantitatively by the use of the formate reagent, $5HCO_2H \cdot 2NEt_3$, was kinetically investigated by the carbon dioxide trapping and UV spectroscopic methods, using N-benzylideneaniline as a representative. Rate data gave the rate equation, $v = (k + k'[NEt_3])[\text{N-benzylideneaniline}][HCO_2H]$, indicating two-path mechanism. By the technique of using deuterated formic acids, it was found that the hydrogen bound to the carbon of formic acid is transferred as hydride to the carbon of the C═N double bond in the rate determining step. The reaction is facilitated by the electron-releasing substituents of the two benzene rings of N-benzylideneaniline. On the bases of these results a possible mechanism is proposed.

Extensive investigation on the mechanism of the formic acid reduction has to be made, although in a few papers the formic acid reduction of triphenylcarbinol,[3] enamines[4] and bisamines[5] has been dealt in some mechanistic aspects.

The present paper deals with kinetic studies of the formic acid reduction of the azomethine double bond. In the previous paper,[2] has been introduced the quantitative reduction of Schiff's base with the constant boiling liquid of the formate, TMAF,[6] b.p. 92° (18 mmHg), corresponding to $5HCO_2H \cdot 2NMe_3$. For the kinetic studies on this formic acid reduction, we used the liquid formate, TEAF,[7] b.p. 98 (18 mmHg), corresponding to $5HCO_2H \cdot 2NEt_3$, in place of TMAF, because volatile trimethylamine in TMAF escaped during the course of the reaction as formic acid was consumed. Preliminary experiments confirmed that the reduction of some selected azomethines with TEAF proceeded nearly quantitatively in the same way as that with TMAF.

RESULTS

Rate of the reduction. Using N-benzylideneaniline as a representative azomethine, rate was measured under the selected conditions using diethyl carbitol as a solvent at a temperature of 85 ± 0·1°. The TEAF reduction of N-benzylideneaniline to N-benzyl-N-phenylformamide was considered to proceed through N-phenylbenzylamine.



$$C_6H_5CH{=}NC_6H_5 + HCO_2H \xrightarrow[\text{(TEAF)}]{} C_6H_5CH_2NHC_6H_5 + CO_2$$

$$C_6H_5CH_2NHC_6H_5 + HCO_2H \xrightarrow[\text{(TEAF)}]{} C_6H_5CH_2\underset{\substack{|\\ CHO}}{N}C_6H_5 + H_2O$$

This was confirmed by isolation of the N-phenylbenzylamine intermediate by carrying out the reaction with less TEAF.

In order to obtain reliability, kinetic runs were carried out by the two methods, which were based on measurement of amount of CO_2 evolved and of the decrease in the UV absorption of N-benzylideneaniline.

By the CO_2 trapping method, effect of concentrations of N-benzylideneaniline and of TEAF on the rate of the reduction were determined. Results are shown in Table 1. The kinetic equation of the first order with respect to N-benzylideneaniline was demonstrated from runs 2 and 3. From the results in Table 1, a straight line having an intercept was obtained by plotting $v/[B][TEAF]$ against [TEAF] as in Fig 1, where B is N-benzylideneaniline. Consequently, the following equation was obtained.

$$v = (k_T^{CO_2} + k_T'^{CO_2}[TEAF])[B][TEAF] \quad (1)$$

Values of $k_T^{CO_2}$ and $k_T'^{CO_2}$ were calculated to be $(3{\cdot}05 \pm 0{\cdot}337) \times 10^{-5}$ l/mole·sec and $(9{\cdot}78 \pm 0{\cdot}730) \times 10^{-5}$ l^2/mole^2·sec, respectively. Concentration of TEAF can be replaced by concentration of formic acid or triethylamine. It was then needed to deter-

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Table 1. The effect of the concentration of N-benzylideneaniline and TEAF

Run No	[B] (mole/l)	[TEAF] (mole/l)	$v \times 10^6$ (mole/l·sec)
1	0·250	0·150	1·490
2	0·250	0·250	3·840
3	1·250	0·250	15·07
4	0·250	0·400	6·873
5	0·250	0·500	10·07
6	0·250	0·750	19·21

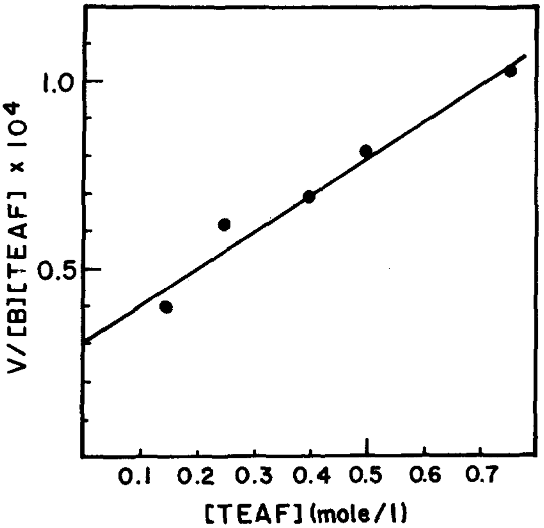


Fig 1. The plot of v/[B][TEAF] against [TEAF] (carbon dioxide trapping method).

mine independent effects of concentrations of formic acid and triethylamine on the rate. In order to carry out the reaction with fairly small change of basicity or acidity of the reaction medium, TEAA (triethylammonium acetate) was used in place of triethylamine to see effects of the concentration of formic acid and of triethylamine. A liquid, TEAA, b.p. 74° (16 mmHg), was prepared for the present work, which analyzed as $7CH_3CO_2H \cdot 2NEt_3$ by potentiometric titration. Results of the experiments carried out by the CO_2 trapping method are shown in Tables 2 and 3.

Straight lines obtained by plotting the rates against $[HCO_2H]$ and $[NEt_3]$ are shown in Figs 2 and 3. As can be seen linear relationship of the rate to $[HCO_2H]$ intersecting at the origin and that to $[NEt_3]$ having an intercept were demonstrated. Since the rate is proportional to [B] as described above, the following rate equation is established.

$$v = (k + k'[NEt_3])[B][HCO_2H] \qquad (2)$$

Since the kinetic runs shown in Tables 2 and 3 were carried out in the medium containing both

Table 2. The effect of the concentration of formic acid

[TEAF] (mole/l)	[TEAA] (mole/l)	$[HCO_2H]$ (mole/l)	$v \times 10^6$ (mole/l·sec)
0·100	0·900	0·500	1·475
0·200	0·800	1·00	3·418
0·300	0·700	1·50	5·643
0·400	0·600	2·00	7·827

[B] = 0·250 mole/l; $[NEt_3]$ = 2·00 mole/l

Table 3. The effect of the concentration of triethylamine

[TEAA] (mole/l)	$[NEt_3]$ (mole/l)	$v \times 10^6$ (mole/l·sec)
0	0·800	6·873
0·200	1·200	7·168
0·400	1·600	7·515
0·600	2·000	7·827

[B] = 0·250 mole/l; [TEAF] = 0·400 mole/l

TEAF and TEAA, proper values of k and k' in Eq. 2 must be obtained from the data shown in Table 1. By inserting $[HCO_2H] = 5[TEAF]$ and $[NEt_3] = 2[TEAF]$ into Eq. 2, the following equation is derived.

$$v = (5k + 10k'[TEAF])[B][TEAF]$$

Consequently, $k = k_T^{CO_2}/5 = (6{\cdot}10 \pm 0{\cdot}672) \times 10^{-6}$ l/mole·sec and $k' = k_T'^{CO}/10 = (9{\cdot}78 \pm 0{\cdot}730) \times 10^{-6}$ l^2/mole²·sec are obtained.

By carrying out the reaction under the same conditions, rate measurements by the UV method were also made to see effect of concentrations of N-benzylideneaniline and TEAF. Results are summarized in Table 4. Runs 1 and 3 demonstrate the first order equation with respect to N-benzylideneaniline, giving $v = k_{obs}[B]$. As for the relationship between k_{obs} and [TEAF], a straight line having an intercept in plotting k_{obs}/[TEAF] against [TEAF] was obtained (Fig 4) from the results in runs 2, 3, 4 and 5 of Table 4. Consequently, the following Eq. 3 identical with Eq. 1 is obtained.

$$k_{obs} = (k_T^{UV} + k_T'^{UV}[TEAF])[TEAF]$$

since $v = k_{obs}[B]$

$$v = (k_T^{UV} + k_T'^{UV}[TEAF])[B][TEAF] \qquad (3)$$

From the data, $k_T^{UV} = (3{\cdot}78 \pm 0{\cdot}577) \times 10^{-5}$ l/mole·sec and $k_T'^{UV} = (1{\cdot}15 \pm 0{\cdot}122) \times 10^{-4}$ l^2/mole²·sec were calculated. The similarity between the values of $k_T^{CO_2}$ and $k_T'^{CO_2}$ and the values of k_T^{UV} and $k_T'^{UV}$ appears to indicate high accuracy of the obtained results.

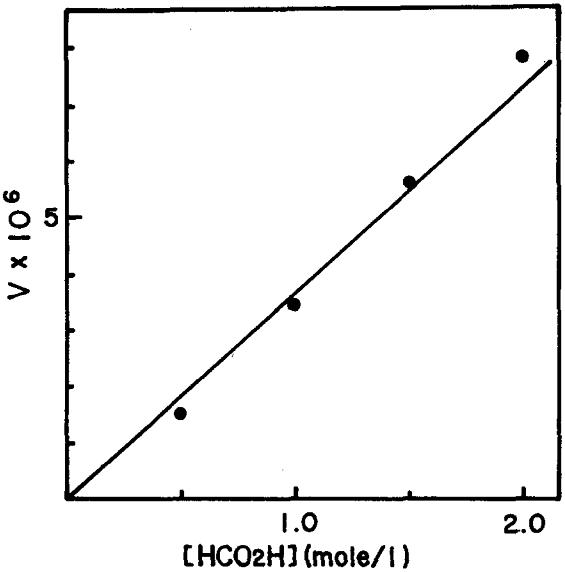


Fig 2. The plot of v against $[HCO_2H]$ (carbon dioxide trapping method).

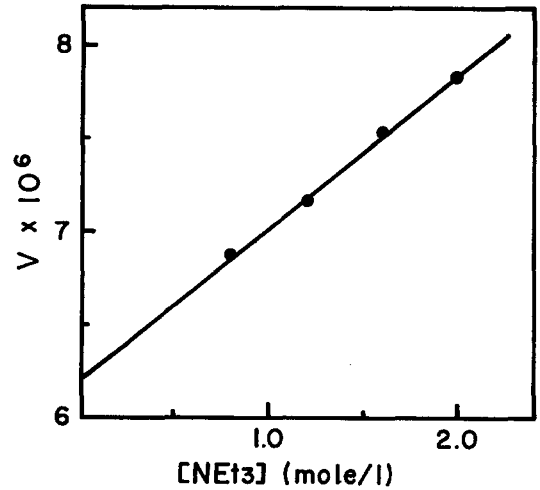


Fig 3. The plot of v against $[NEt_3]$ (carbon dioxide trapping method).

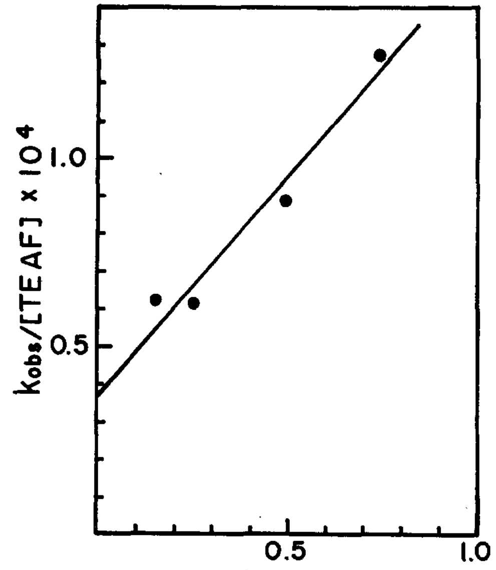


Fig 4. The plot of k_{obs}/[TEAF] against [TEAF] (UV method).

Table 4. The rate measurement by UV spectroscopic method

Run No	[B] (mole/l)	[TEAF] (mole/l)	$k_{obs} \times 10^5$ (sec^{-1})
1	0·050	0·250	1·938
2	0·250	0·150	0·932
3	0·250	0·250	1·530
4	0·250	0·500	4·433
5	0·250	0·750	9·633

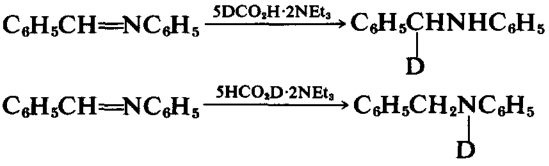
Reduction mode and isotope effect. On the reduction of N-benzylideneaniline to the secondary amine, in order to determine addition mode of the two different hydrogens of formic acid and to examine isotope effect, the TEAF reagents composed of formic acid-*d* (HCO_2D) and formic-*d* acid (DCO_2H) were used. Reactions of N-benzylideneaniline with less amount of the two deuterated formates were carried out so as not to form the N-formylated product. Since in the NMR spectrum of N-phenylbenzylamine in $CDCl_3$ the methylene and the NH protons appeared as singlets at τ 5·78 and 6·26, respectively, deuterated position and deuterium contents in the products were determined from the contents of the protons at these two positions. As shown in Table 5, the peak of the methylene protons of the product obtained by the use of $5DCO_2H{\cdot}2NEt_3$ indicates isotopic purity of 55%. On the other hand, no substitution of deuterium at the methylene position was observed in the product obtained by the use of $5HCO_2D{\cdot}2NEt_3$. The above facts indicate that the formyl hydrogen of formic acid attacks on the double bond carbon of N-benzylideneaniline in the reaction. Proton analyses at the nitrogens of the produts were inaccurate, because of the rather broad peak and exchangeability of the proton in the presence of protic materials. Although, in such 1 : 1 molar reaction, the reaction with $5HCO_2D{\cdot}2NEt_3$ is expected to give N-phenylbenzylamine-N-*d* in contrast to that with $5DCO_2H{\cdot}2NEt_3$, the insufficient amount of the NH proton of the product obtained by the use of $5HCO_2D{\cdot}2NEt_3$ may be due to the influence of moisture during the isolation procedures. From the above deuterium substi-

Table 5. Deuterated N-phenylbenzylamine

Formate used for the reaction[a]	Content of Proton of N-Phenylbenzylamine obtained —CH$_2$—	—NH—
5DCO$_2$H·2NEt$_3$	45%	90%
5HCO$_2$D·2NEt$_3$	100%	43%

[a] Substrate of the reaction: N-Benzylideneaniline

tution results, mode of the reaction can be expressed as follows.



$$C_6H_5CH{=}NC_6H_5 \xrightarrow{5DCO_2H\cdot 2NEt_3} C_6H_5\underset{D}{C}HNHC_6H_5$$

$$C_6H_5CH{=}NC_6H_5 \xrightarrow{5HCO_2D\cdot 2NEt_3} C_6H_5CH_2\underset{D}{N}C_6H_5$$

Isotope effect in the reaction with 5DCO$_2$H·2NEt$_3$ was then examined. Rate constants, k_D and k'_D were obtained by the CO$_2$ trapping method and compared to the constants, k and k', obtained in the foregoing. As shown in Table 6, considerable isotope effects, 2·49 for k/k_D and 2·16 for k'/k'_D, were obtained. This indicates that the C—H bond of formic acid is broken at the rate determining step. Next, whether the formyl hydrogen of formic acid is tranferred as hydride or proton to the carbon of N-benzylideneaniline must be determined. There has been reported[8] that the isotope effect value for simple hydride transfer from C to C is 1·8–2·6 in contrast to the value of wide range of 0·84–11·7, for proton transfer, Swain[9] has reported in his theoretical treatment that isotope effect increases markedly on introduction of an electron-attracting substituent for proton transfer but is less sensitive for hydride transfer. In order to see influence of substituent, isotope effects on the reductions of N-*p*-methoxybenzylideneaniline and N-*p*-chlorobenzylideneaniline were examined. Results are shown in Table 6. The small changes in the isotope effect values obtained with these compounds are in agreement with that of the hydride transfer from C to C.

Substituent effects. In order to obtain further information for the reaction mechanism, kinetic substituent effects on the TEAF reduction of N-benzylideneanilines were examined by the CO$_2$ trapping method.

The rate measurements with N-benzylideneanilines possessing substituents at the two benzene rings (Table 7) in varying concentration of TEAF were carried out by the initial rate method. The rate constants k_{sub} and k'_{sub}, listed in Table 7, were obtained in accordance with eq 2. Figs 5 and 6 show plots of log (k_{sub}/k) and log (k'_{sub}/k') vs Hammett's σ values for the substituents on the two benzene rings of the benzylidene and aniline residues. Adherence of the four plots to the Hammett equation were not so excellent, but showed tendencies to have negative ρ values. By the least square method the following ρ values

Table 6. Deuterium isotope effects for the reduction of N-benzylideneanilines

Substrate	$k\times 10^6$ (l/mole·sec)	$k'\times 10^6$ (l^2/mole^2·sec)	$k_D\times 10^6$ (l/mole·sec)	$k'_D\times 10^6$ (l^2/mole^2·sec)	k/k_D	k'/k'_D
$C_6H_5CH{=}NC_6H_5$	6·10	9·78	2·45	4·52	2·49	2·16
p-$CH_3OC_6H_4CH{=}NC_6H_5$	12·7	11·0	6·33	4·73	2·01	2·32
p-$ClC_6H_4CH{=}NC_6H_5$	3·30	4·93	1·34	2·87	2·46	1·72

Table 7. The substituent effects for the TEAF reduction of N-benzylideneanilines by carbon dioxide trapping method

Substituent[a] X	Y	$k_{sub}\times 10^6$ (l/mole·sec)	$k'_{sub}\times 10^6$ (l^2/mole^2·sec)	log (k_{sub}/k)	log (k'_{sub}/k')
p-CH$_3$O	H	12·7	11·0	0·320	0·048
p-CH$_3$	H	7·77	11·4	0·106	0·066
m-CH$_3$O	H	8·40	8·38	0·139	−0·067
p-Cl	H	3·30	4·93	−0·267	−0·297
p-NO$_2$	H	2·63	2·30	−0·365	−0·626
H	H	6·10	9·78	0	0
H	p-CH$_3$O	7·87	9·62	0·111	−0·008
H	p-CH$_3$	8·25	10·6	0·131	0·033
H	m-Cl	1·51	4·17	−0·607	−0·371
H	p-NO$_2$	1·64	2·48	−0·570	−0·596

[a] X shows p- and m-substituent on benzylidene residue and Y shows that on aniline residue of N-benzylideneaniline.

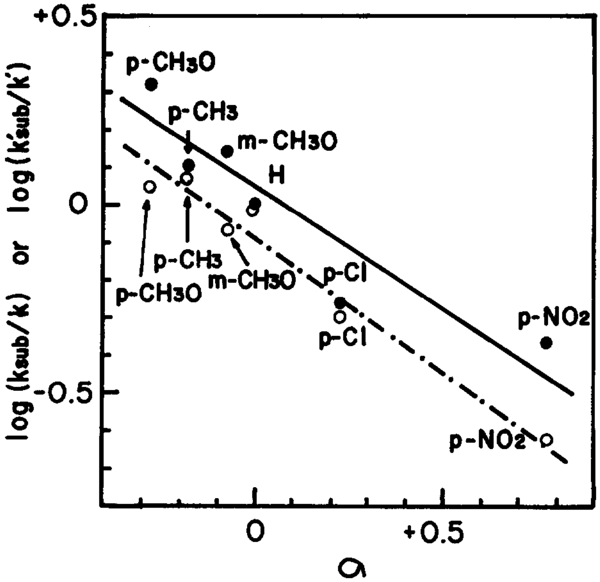


Fig 5. The Hammett plot for the rates of the TEAF reduction of N-benzylideneaniline possessing substituents at the benzylidene residue. ●—●—● the plot of log (k_{sub}/k) against σ value. ○–·–○–·–○ the plot of log (k'_{sub}/k') against σ value.

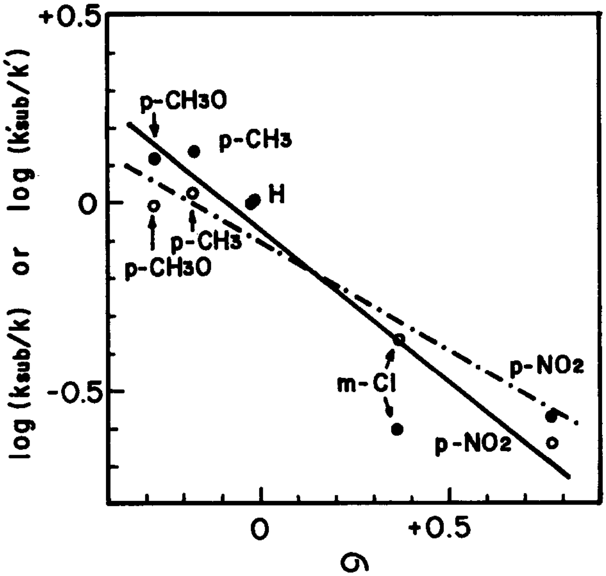


Fig 6. The Hammett plot for the rates of the TEAF reduction of N-benzylideneaniline possessing substituents at aniline residue. ●—●—● the plot of log (k_{sub}/k) against σ value. ○–·–○–·–○ the plot of log (k'_{sub}/k') against σ value.

were obtained: for X—$C_6H_4CH{=}NC_6H_5$, $\rho = -0{\cdot}643$ for k, $\rho = -0{\cdot}701$ for k'; for $C_6H_5CH{=}NC_6H_4$—Y, $\rho = -0{\cdot}792$ for k, $\rho = -0{\cdot}561$ for k'. In summary, the reaction is facilitated by introduction of the electron-releasing substituent into each of the two benzene rings.

DISCUSSION

The results described in the foregoing sections are summarized as follows.

1. The rate equation is $v = (k + k'[NEt_3])[B][HCO_2H]$, indicating a mechanism involving two parallel paths.

2. The formyl hydrogen of formic acid attacks on the double bond carbon of N-benzylideneaniline and the proton of formic acid attacks on the nitrogen of the same.

3. The formyl hydrogen of formic acid is transferred as hydride at the rate determining step.

4. Both paths involving in the reaction are facilitated by the introduction of electron-releasing substituents into each of the two benzene rings.

A possible reaction path which is comprehensible for the above results is proposed as shown in Chart 1.

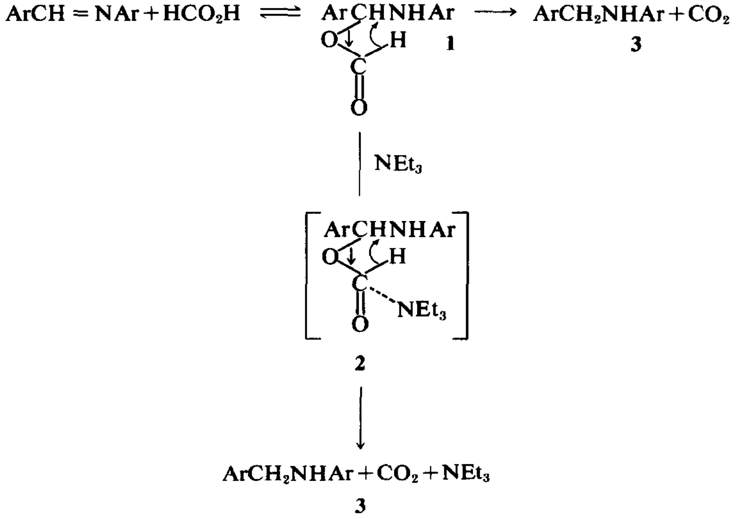


Chart 1. Pathway of the TEAF reduction of N-benzylideneaniline

The initial stage of the reaction appears to involve the formation of the short-living unstable ester-like intermediate (**1**). Decarboxylation of **1** to the secondary amine (**3**) may proceed alone and in the presence of triethylamine. The two decarboxylation steps which involve hydride transfer to the methine carbon are inferred to be the rate determining steps and consist the two reaction paths expressed by the k term independent of $[NEt_3]$ and the k' term involving $[NEt_3]$ in the rate equation. The acceleration of the decarboxylation of malonic acid and β-keto acid by influence of tertiary amine such as quinoline and pyridine has been known[10,11] suggesting release of the bond adjacent to carboxyl by its attack on the carbonyl carbon. The catalytic action of triethylamine on the decarboxylation of **1** may proceed similarly as shown in Chart 1. Electron-releasing substituent on each of the benzene rings of N-benzylideneaniline may also accelerate the reduction by way of releasing the ester bond of **1**.

EXPERIMENTAL

Material—The following N-benzylideneanilines were prepared from the corresponding benzaldehydes and anilines according to the previously reported paper:[2] N-benzylideneaniline, m.p. 48–49°; N-*p*-methoxybenzylideneaniline, m.p. 63–64°; N-*m*-methoxybenzylideneaniline, b.p. 124–127° (0·2 mmHg); N-*p*-methylbenzylideneaniline, m.p. 42–43°; N-*p*-chlorobenzylideneaniline, m.p. 63–64°; N-*p*-nitrobenzylideneaniline, m.p. 89–90°; N-benzylidene-*p*-anisidine, m.p. 71·5–72·5°; N-benzylidene-*p*-toluidine, m.p. 34–36°; N-benzylidene-*m*-chloroaniline, m.p. 32–34°; N-benzylidene-*p*-nitroaniline, m.p. 116–117°.

The formate reagent, TEAF, $5HCO_2H \cdot 2NEt_3$, was prepared by the previously reported method[7] and purified by drying over $MgSO_4$ for several days followed by distillation so as to give a liquid of b.p. 98° (18 mmHg). This material dissolved in chloroform-acetic acid was titrated potentiometrically with a 0·01 N standard soln of perchloric acid in dioxane. Content of NEt_3, Found: 46·84%. Calcd. for $5HCO_2H \cdot 2NEt_3$: 46·79%.

Both formates composed of formic-*d* acid ($5DCO_2H \cdot 2NEt_3$) and of formic acid-*d* ($5HCO_2D \cdot 2NEt_3$) were prepared according to the previously reported method.[12] By NMR spectroscopic measurements, these materials were shown to be almost pure.

The acetate, TEAA, was obtained as a constant-boiling fraction by distillation of a mixture of AcOH and NEt_3 in *ca* 5:3 molar proportion. The pure material, b.p. 74° (16 mmHg), was obtained by drying over $MgSO_4$ followed by redistillation. Content of NEt_3 of this material was determined by potentiometric titration in the same way as described in TEAF. Content of NEt_3, Found: 33·53%. Calcd. for $7CH_3CO_2H \cdot 2NEt_3$: 32·50%. Elemental analyses and proportion of peak areas of the inherent hydrogens in its NMR spectrum were also in agreement with the composition, $7CH_3CO_2H \cdot 2NEt_3$. (Found: C, 50·23; H, 9·56; N, 4·63. Calc. for $C_{26}H_{58}N_2O_{14}$: C, 50·95; H, 9·54; N, 4·57%); NMR (20% soln in $CDCl_3$) τ: 8·70 (18H, tr, J = 7·4 c/s, $-CH_3$), 6·80 (12H, qu, J = 7·4 c/s, $-CH_2-$), 7·90 (21 H, s, $-COCH_3$), 0·73 (7H, s, $-OH$). There has been reported[13] the relationship of liquid and gas phases between NEt_3 and AcOH under ordinary pressure, where the azeotropic mixture is described to have the composition which approximates the above one.

Diethyl carbitol was purified by refluxing over metallic Na followed by distillation so as to give a liquid of b.p. 184°. Chloroform was dried over $CaCl_2$ and rectified repeatedly so as to show b.p. 61·5°.

Kinetic measurement

Carbon dioxide trapping method. Rates of the formate reduction of N-benzylideneaniline were determined by measurement of the evolved CO_2 at $85 \pm 0{\cdot}1°$. A stream of CO_2 free, dried and prewarmed N_2 was bubbled through the reaction vessel (30 ml), where the flow of N_2 was controlled in a constant rate of 50 ml/min. The N_2 containing CO_2 from the reaction vessel was passed through a tube packed with H_2SO_4-silica gel, granular P_2O_5 and anhyd magnesium perchlorate to remove a trace of NEt_3 and water, and then CO_2 was absorbed in soda asbestos and analyzed by weighing. Accuracy of the analysis was tested by the use of $KHCO_3$ sample and set at $99{\cdot}75 \pm 0{\cdot}437\%$. The amount of the evolved CO_2 was analyzed at appropriate intervals of time and the rate was measured within initial 10% of the reaction.

For kinetic runs, standard solns, 1 mole/l diethyl carbitol soln of N-benzylideneaniline, 10 mole/l (based on HCO_2H) diethyl carbitol soln of TEAF and 3 mole/l (based on NEt_3) diethyl carbitol soln of TEAA were prepared. To start a run, 6·25 ml of the N-benzylideneaniline soln, appropriate volume of the TEAF soln and that of the TEAA soln, if necessary, were pipetted into the reaction vessel and diluted with diethyl carbitol to 25 ml.

Rate measurements with the substituted N-benzylideneanilines for the work on kinetic substituent effect were made by the same way as described above, except the runs with less soluble substrates, N-*p*-nitrobenzylideneaniline and N-benzylidene-*p*-nitroaniline, where 25 ml of the reaction solution of the same concentration of substrate was prepared by controlling the dilution with diethyl carbitol.

UV spectroscopic method. Rates of the formate reduction of N-benzylideneaniline were determined by measurement of the decrease of the absorbance at 320 nm with a Hitachi EPS-3T spectrophotometer. The absorption at this wavelength does not overlap with the absorption of the reduction products, N-phenylbenzylamine and N-benzyl-N-phenylformamide (Fig 7). Adherence to Beer's law at this wavelength was excellent.

To start a run, 1 mole/l diethyl carbitol soln of N-benzylideneaniline (usually 5 ml) and 10 mole/l (based on HCO_2H) diethyl carbitol soln of TEAF were pipetted into a reaction vessel and diluted to 20 ml. Samples of the mixture were pipetted at appropriate intervals, diluted with chloroform and then subjected to the measurement of the UV absorbance.

Deuterated reaction products

N-*Phenylbenzylamine-α-d.* A mixture of 4·5 g (0·025 mole) of N-benzylideneaniline and 6·5 g (0·075 mole based on DCO_2H) of TEAF composed of formic-*d* acid, $5DCO_2H{\cdot}2NEt_3$, was heated at 100°. Dry air free from CO_2 was passed through the reaction vessel in order to check the transfer of evolved CO_2 by a $Ba(OH)_2$ aq. After 12 hr, the soln was concentrated under reduced pressure to remove the formate. Distillation of the residual liquid under reduced pressure gave 3·4 g (74%) of a solid distillate, b.p. 118–125° (1 mmHg). Recrystallization from light petroleum gave colorless needles of N-phenylbenzylamine-*α-d*, m.p. 36·5–37·5°. In the NMR spectrum in $CDCl_3$, the NH and the methylene protons appeared as singlets at τ 6·23 and 5·95, respectively, and peak area of the latter showed 45% content of proton owing to the deuterium substitution.

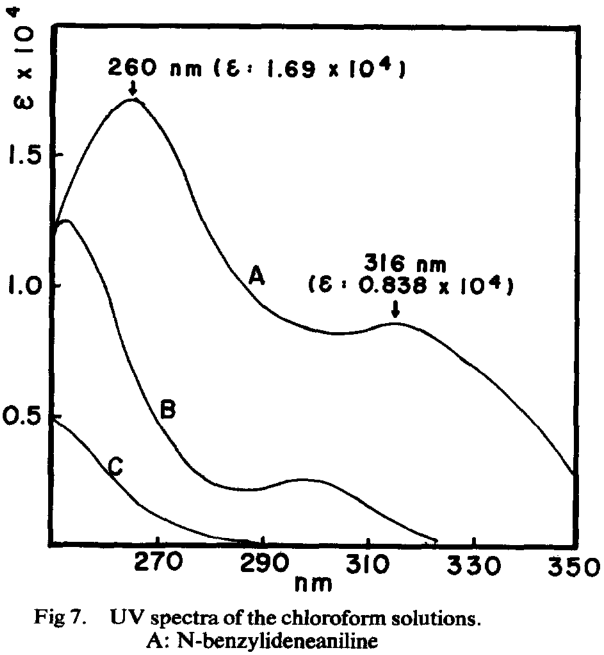


Fig 7. UV spectra of the chloroform solutions.
A: N-benzylideneaniline
B: N-phenylbenzylamine
C: N-benzyl-N-phenylformamide

N-*Phenylbenzylamine-N-d*. A mixture of 4·5 g (0·025 mole) of N-benzylideneaniline and 6·5 g (0·075 mole based on HCO_2D) of TEAF composed of formic acid-*d*, $5HCO_2D \cdot 2NEt_3$, was heated at 100° by the same manner described in the above. After 6 hr, distillation of the mixture under reduced pressure gave 3·2 g (70%) of a solid distillate, b.p. 125–130° (3 mmHg). Recrystallization from light petroleum gave colorless needles of N-phenylbenzylamine-N-*d*, m.p. 35–36°. In the NMR spectrum the NH and the methylene protons appeared as singlets at τ 6·28 and 5·90, respectively, and the peak area of the former showed 43% content of proton owing to the deuterium substitution.

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