

## KINETICS AND MECHANISM OF THE DUFF REACTION\*

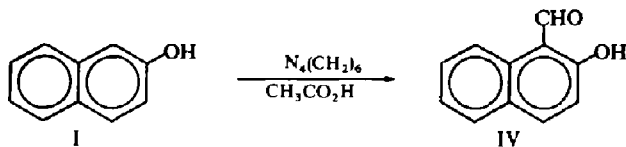
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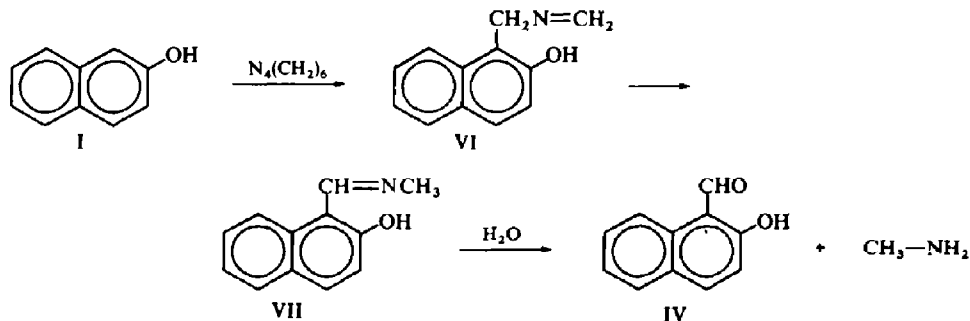
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**Abstract**—The Duff reaction of  $\beta$ -naphthol (I) with hexamine in glacial acetic acid at 100° gives 2,2'-dihydroxy-1-naphthylidene-1'-naphthylmethylamine (II), but at lower concentrations of starting materials 2-hydroxy-1-naphthaldehyde (IV) is the main product. The rate law for the latter reaction is expressed as:  $d[IV]/dt = k[I]^m[\text{hexamine}]^n$  ( $m \geq 1$ ,  $n \sim 0.4$ ). 2-Hydroxy-1-naphthylmethylamine (III) also reacts with hexamine to produce IV, the rate being higher than that of  $\beta$ -naphthol with hexamine. The rate law is a similar type:  $d[IV]/dt = k'[III]^{m'}[\text{hexamine}]^{n'}$  ( $m' \geq 1$ ,  $n' \sim 0.3$ ). The reaction of this amine III with formaldehyde alone also yields IV and this reaction has an induction period. The addition of *n*-butylamine or ammonia to the system of III-HC! and formaldehyde eliminated the induction period and increased the rate considerably. The addition of tri-*n*-butylamine to the same system shortened the induction period, but the rate constant was little increased, while addition of  $\beta$ -naphthol had no appreciable effect on the rate. A mechanism involving the fast aminomethylation of  $\beta$ -naphthol and then the rate-determining dehydrogenation of the amine to the imine, followed by the rapid hydrolysis of the imine is proposed and discussed.

THE introduction of a formyl group into the *ortho* position of phenols known as the Duff<sup>1</sup> reaction has been applied in a number of synthetic studies,<sup>1-5</sup> but the kinetics of the reaction has not been investigated. The mechanism proposed by Duff for the transformation of  $\beta$ -naphthol to 2-hydroxy-1-naphthaldehyde (IV) as a main product,

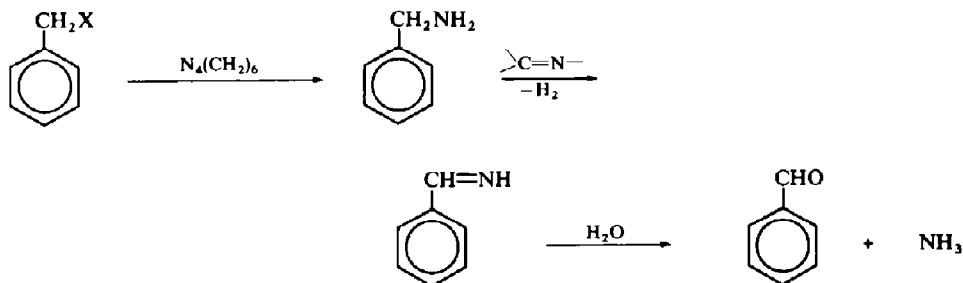


involves the following prototropy between methyleneamine VI and Schiff base VII.



\* Contribution No. 105.

The Sommelet reaction, in which benzyl halides react with hexamine to produce benzaldehydes is similar to the Duff reaction, and has been studied by Angyal *et al.*,<sup>6,7</sup> who proposed a generally accepted mechanism involving the dehydrogenation of amines to imines.<sup>6-8</sup>



In order to clarify the mechanism of the Duff reaction,  $\beta$ -naphthol (I) was chosen as the substrate and glacial acetic acid as the solvent and the rates were measured by following the formation of the product spectrophotometrically.

#### RESULTS

*Reaction of  $\beta$ -naphthol with hexamine.*  $\beta$ -Naphthol (I; 0.002–0.007 mole  $l^{-1}$ ) was treated with a 3–20 fold excess hexamine in glacial acetic acid at 100°. Under these conditions, 2-hydroxy-1-naphthaldehyde (IV) is the main product and the amounts of 2,2'-dihydroxy-naphthylidene-1'-naphthylmethylamine (II) in Eqn 4 are almost negligible. The apparent first- and second-order rate constants of the aldehyde formation with  $\beta$ -naphthol,  $k_1$  and  $k_2$ , were calculated by the usual integral equations. The results are shown in Table 1.

When the initial concentration of  $\beta$ -naphthol was kept constant, both the values of  $k_1$  and  $k_2$  increased only slightly with increasing concentration of hexamine. When the initial concentration of hexamine was kept constant, the value of  $k_1$  increased slightly with increasing concentration of  $\beta$ -naphthol, while the value of  $k_2$  decreased. The rate law is expressed as:

$$\frac{d[\text{aldehyde}]}{dt} = k [\beta\text{-naphthol}]^m [\text{hexamine}]^n, \quad m \gtrsim 1, \quad n = 0.4\text{--}0.5.$$

*Hydrolysis of Schiff base II.* Under similar conditions but in the absence of  $\beta$ -naphthol, the rate of hydrolysis of Schiff base II was measured spectrophotometrically. The hydrolysis was very fast in glacial acetic acid, Schiff base II disappearing after a few minutes. After hydrolysis was complete, the yield of 2-hydroxy-1-naphthaldehyde (IV) gradually increased to over 150%. This result indicates that 2-hydroxy-1-naphthylmethylamine (III), formed by the hydrolysis, reacted with hexamine to form aldehyde IV.

*Reaction of 2-hydroxy-1-naphthylmethylamine (III) with hexamine.* The reaction of amine III with hexamine to form 2-hydroxy-1-naphthaldehyde (IV) was faster than that of  $\beta$ -naphthol with hexamine (Fig. 1).

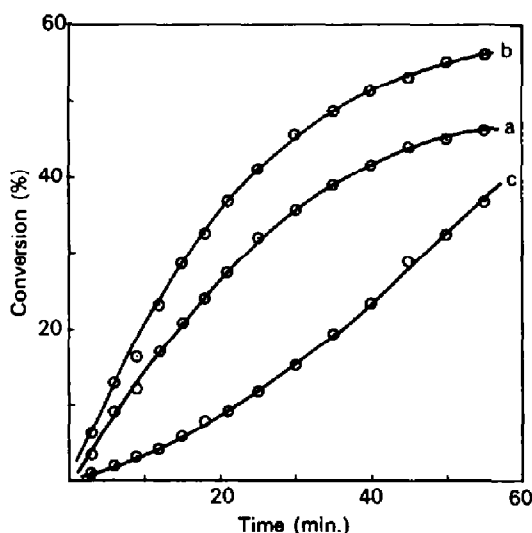
The rates of the reaction with a 5–20 fold excess hexamine in glacial acetic acid at 100° were measured spectrophotometrically, and the pseudo first- and second-order

TABLE I. PSEUDO FIRST- AND SECOND-ORDER RATE CONSTANTS ( $k_1, k_2$ ) FOR THE REACTION OF  $\beta$ -NAPHTHOL (I) WITH HEXAMINE AT 102°(A) Initial concentration of  $\beta$ -naphthol ( $2.94\text{--}3.00 \times 10^{-3}$  mole l.<sup>-1</sup>)

[Hexamine] $\times 10^2$ (mole l. <sup>-1</sup> )	$k_1 \times 10^2$ (min <sup>-1</sup> )	$k_2 \times 10$ (min <sup>-1</sup> l. mole <sup>-1</sup> )
0.99	0.71	0.74
2.00	0.80	0.77
3.50	0.91	0.92
4.11	0.92	0.97
4.50	1.09	1.04
5.00	1.20	1.09
6.00	1.49	1.23

(B) Initial concentration of hexamine ( $4.10\text{--}4.12 \times 10^{-2}$  mole l.<sup>-1</sup>)

[ $\beta$ -naphthol] $\times 10^3$ (mole l. <sup>-1</sup> )	$k_1 \times 10^2$ (min <sup>-1</sup> )	$k_2 \times 10$ (min <sup>-1</sup> l. mole <sup>-1</sup> )
2.38	1.18	1.33
2.98	1.23	1.38
4.00	1.49	1.30
4.99	1.48	1.06
5.97	1.34	0.90
6.99	1.65	0.90

FIG. 1 Comparison of reactivity of  $\beta$ -naphthol and 2-hydroxynaphthylmethylamine (III) in glacial acetic acid at 100°.

- a  $\beta$ -Naphthol ( $0.96 \times 10^{-3}$  mole l.<sup>-1</sup>) and hexamine ( $0.018$  mole l.<sup>-1</sup>).  
 b III-HCl ( $0.95 \times 10^{-3}$  mole l.<sup>-1</sup>) and hexamine ( $0.018$  mole l.<sup>-1</sup>).  
 c III-HCl ( $0.91 \times 10^{-3}$  mole l.<sup>-1</sup>) and formaldehyde ( $0.11$  mole l.<sup>-1</sup>).

rate constants,  $k_1$  and  $k_2$ , and shown in Table 2. A similar rate equation was obtained.

$$\frac{d[\text{aldehyde}]}{dt} = k'[\text{III}]^{m'}[\text{hexamine}]^{n'}, \quad m' \gtrsim 1, \quad n' = 0.3-0.4$$

*Reaction of 2-hydroxynaphthylmethylamine (III) with formaldehyde.* Amine III reacted with formaldehyde in glacial acetic acid at  $100^\circ$  in the absence of hexamine to form 2-hydroxy-1-naphthaldehyde (IV). The reaction has an induction period (ca. 13 min), and was slower than the reaction of III with hexamine. The effect of addition of *n*-butylamine, tri-*n*-butylamine, ammonium acetate and  $\beta$ -naphthol for the reaction of III ( $0.9 \times 10^{-3}$  mole  $l^{-1}$ ) with formaldehyde ( $0.11$  mole  $l^{-1}$ ) was studied in acetic acid at  $100^\circ$ , and the rates were compared with that of III with formaldehyde. These results are shown in Fig. 2. A small amount of water had no appreciable effect on the rate under these conditions.

The presence of *n*-butylamine or ammonium acetate increased the reaction rate and eliminated the induction period. The presence of tri-*n*-butylamine reduced the induction period, but increased the rate only slightly. No appreciable change of rate and induction period was observed on addition of either  $\beta$ -naphthol alone or a mixture of  $\beta$ -naphthol and *n*-butylamine.

*Reaction of N-methylenebenzylamine (VI, Ar = C<sub>6</sub>H<sub>5</sub>).* N-methylenebenzylamine (VI, Ar = C<sub>6</sub>H<sub>5</sub>) was heated in glacial acetic acid at  $100^\circ$  with and without the addition of hexamine. The results are shown in Fig. 3. In the absence of hexamine, formaldehyde was detected by the benzidine test even at room temperature.

*Effect of water.* As reported in the Duff reaction,<sup>2</sup> the addition of water decreased the rate of formation of IV from  $\beta$ -naphthol and hexamine or III-HCl and hexamine.

#### DISCUSSION

Four possible pathways are considered for the Duff reaction.

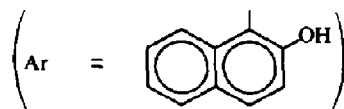
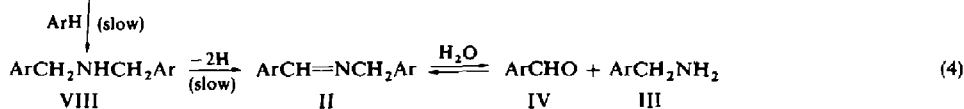
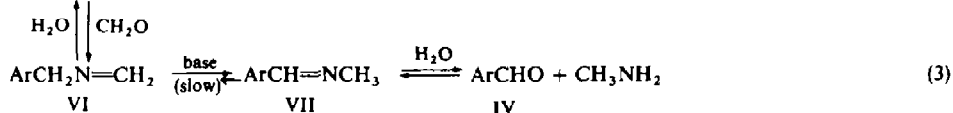
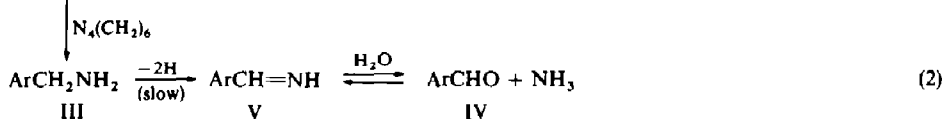


TABLE 2. PSEUDO FIRST- AND SECOND-ORDER RATE CONSTANT ( $k'_1$ ,  $k'_2$ ) FOR THE REACTION OF 2-HYDROXYNAPHTHYLMETHYLAMINE (III) WITH HEXAMINE AT 100°  
(A) Initial concentration of amine III ( $0.93\text{--}0.96 \times 10^{-3}$  mole l.<sup>-1</sup>)

[Hexamine] $\times 10^2$ (mole l. <sup>-1</sup> )	$k'_1 \times 10^3$ (min <sup>-1</sup> )	$k'_2 \times 10^2$ (min <sup>-1</sup> mole <sup>-1</sup> l.)
5.86	8.29	2.58
12.14	8.87	2.74
14.98	9.50	3.00
18.17	9.23	3.00
21.14	10.6	3.40

(B) Initial concentration of hexamine ( $6.00 \times 10^{-2}$  mole l.<sup>-1</sup>)

[Amine III] $\times 10^3$ (mole l. <sup>-1</sup> )	$k'_1 \times 10^3$ (min <sup>-1</sup> )	$k'_2 \times 10^2$ (min <sup>-1</sup> mole <sup>-1</sup> l.)
2.39	6.25	7.91
3.60	7.70	6.07
4.87	9.05	5.44
7.27	8.40	3.83
9.45	10.0	4.00

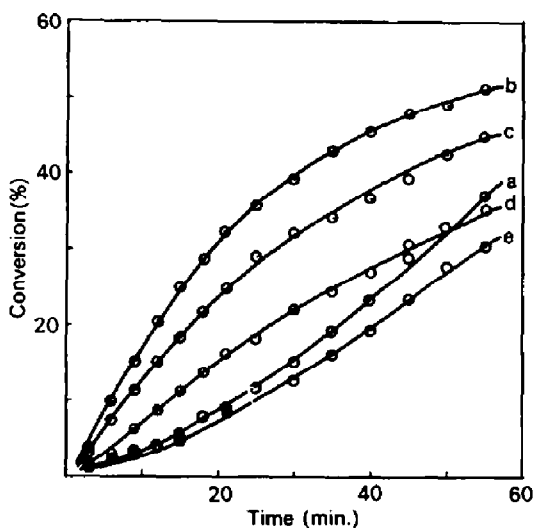


FIG. 2 The reaction of 2-hydroxy-1-naphthylmethylamine (III) hydrochloride ( $0.91 \times 10^{-3}$  mole l.<sup>-1</sup>) with formaldehyde in glacial acetic acid at 100°.

- a No additive.
- b Addition of ammonium acetate ( $0.073$  mole l.<sup>-1</sup>).
- c Addition of n-butylamine hydrochloride ( $0.073$  mole l.<sup>-1</sup>).
- d Addition of tri-n-butylamine ( $0.074$  mole l.<sup>-1</sup>).
- e Addition of  $\beta$ -naphthol ( $0.001$  mole l.<sup>-1</sup>).

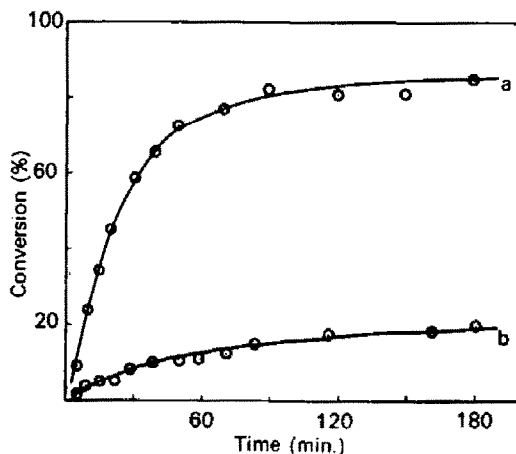


FIG. 3 Reaction of *N*-methylenebenzylamine (VI) ( $1.02 \times 10^{-3}$  mole  $l^{-1}$ ) in the presence (a) or absence (b) of hexamine ( $3.09 \times 10^{-3}$  mole  $l^{-1}$ ) in glacial acetic acid at  $100^\circ$ .

Hydroxymethyl compounds are assumed to be intermediates in pathway 1 by the fast hydroxymethylation of phenols. Pathways 2 and 4 involve the dehydrogenation of amines by methyleneimine or by  $RCH=NR'$  such as VI,<sup>4</sup> which has been suggested for the Sommelet reaction.<sup>6,7</sup> Pathway 3 involves formation of Schiff base VII by the prototropy of methyleneimine VI.<sup>5</sup> Any mechanism proposed must take into account the following observations:

(i) Little benzaldehyde is formed by the treatment of benzyl alcohol with hexamine under the conditions of the Duff reaction.

(ii) The rate law for the reaction of  $\beta$ -naphthol with hexamine is

$$\frac{d[\text{aldehyde}]}{dt} = k [\beta\text{-naphthol}]^m [\text{hexamine}]^n, \quad m \geq 1, \quad n = 0.4-0.5.$$

(iii) The rate law for the reaction of 2-hydroxy-1-naphthylmethylamine (III) with hexamine is of a similar type.

$$\frac{d[\text{aldehyde}]}{dt} = k' [\text{III}]^{m'} [\text{hexamine}]^{n'}, \quad m' \geq 1, \quad n' = 0.3-0.4$$

This reaction of III is faster than that of  $\beta$ -naphthol with hexamine.

(iv) Since the hydrolysis of Schiff bases II and VII is very rapid under the conditions of the Duff reaction, it cannot be a rate-determining step. Amine III formed by the hydrolysis of II is gradually converted to aldehyde IV under similar conditions.

(v) Aldehyde IV is formed by the reaction of amine III hydrochloride with formaldehyde alone and the yield is over 76%. But this reaction has an induction period.

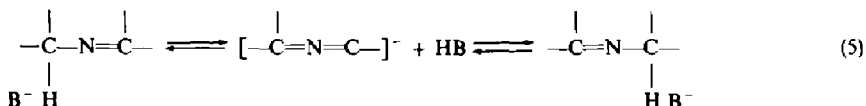
(vi) The addition of tri-*n*-butylamine to the system of III-HCl and formaldehyde shortened the induction period, but the rate was little increased, while the addition of *n*-butylamine or ammonia resulted in a disappearance of the induction period and in a marked rate enhancement.

(vii) The addition of  $\beta$ -naphthol irrespective of the presence of *n*-butylamine to the system of III-HCl and formaldehyde has no appreciable effect on the rate.

Pathway 1 is ruled out, because little benzaldehyde was produced by the reaction of benzyl alcohol with hexamine (observation i; Table 1). The rate law (observations ii and iii) indicates that one or more molecules of  $\beta$ -naphthol and a fragment from hexamine participates in the transition state. The rate law for the reaction of III with hexamine (observation iii) is similar to that of  $\beta$ -naphthol with hexamine; the former reaction is faster than the latter. These facts suggest that the amine III is an intermediate and that a rate-determining step is after the formation of III. This assumption is supported by the fact that the hydrolysis of Schiff base II in acetic acid in the presence of hexamine produced aldehyde IV in over 150% yield, i.e. one of the hydrolysis products, 2-hydroxy-1-naphthylmethylamine (III), may also be converted to the aldehyde IV.

Since  $\beta$ -naphthol cannot be detected in the reaction mixture of amine III and hexamine under the conditions analogous to the Duff reaction, the conversion of  $\beta$ -naphthol to amine III is virtually irreversible. The interconversion between amine III and methyleneimine VI may be rapid and reversible as in the case of the formation of Schiff bases under these conditions.

The prototropy of methyleneazomethine system is generally promoted by a base,<sup>9-11</sup> and proceeds via a carbanion intermediate<sup>12</sup> rather than by a concerted mechanism.<sup>13</sup>

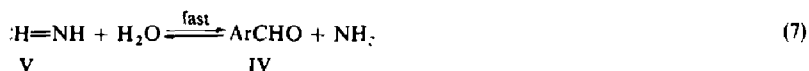
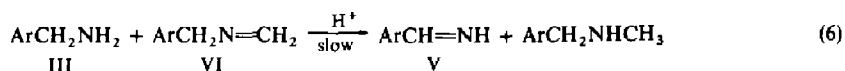


Accordingly, if the pathway 3 involving the prototropy is correct, the reaction should be promoted with increasing basicity of the catalyzing base. Fig. 2 shows, however, that the rate in the presence of tri-*n*-butylamine increases a little, whereas the presence of *n*-butylamine having similar basicity or ammonia having lower basicity increases the rate considerably (observation vi). These facts indicate that the pathway 3 is at least not important for the formation of the aldehyde. Furthermore, it seems impossible that the reaction in acetic acid proceeds through a carbanion intermediate. Duff has reported that VI ( $\text{Ar}=\text{C}_6\text{H}_5$ ) is converted to substituted benzaldehyde in the presence of tertiary amines instead of hexamine and no formaldehyde is detected in the vapor, and hence he supposed that this pathway probably involves the prototropy but no hydrolysis of VI to III.<sup>5</sup> However, since formaldehyde was detected in an acetic acid solution of VI even at room temperature and *N*-methylenebenzylamine (VI,  $\text{Ar}=\text{C}_6\text{H}_5$ ) was converted to benzaldehyde on heating in acetic acid in the absence of hexamine or other bases (Fig. 3), the present reaction involves no prototropy of VI to VII.

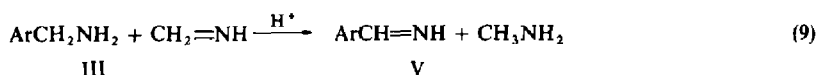
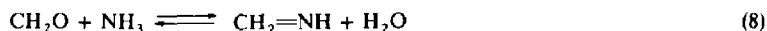
As the Duff and Sommelet reactions proceed under similar conditions, pathway 2 is possible after the formation of amine III and this agrees with the observed kinetics.

As obvious from Fig. 2, the reaction of III with formaldehyde proceeds much faster in the presence of an imine-forming base such as *n*-butylamine or ammonia, compared with the reaction in the presence of tri-*n*-butylamines (vi). These facts suggest that compounds having a  $\text{N}=\text{C}$  double bond as methylene-*n*-butylimine  $\text{CH}_2=\text{NBu}$  or methyleneimine  $\text{CH}_2=\text{NH}$  act as effective dehydrogenating agents.

The reaction of 2-hydroxynaphthylmethylamine (III) with formaldehyde has an induction period (observation v). In this system at an early stage of the reaction only VI (in an equilibrium with III) has a C=N double bond and it may act as dehydrogenating agent as suggested by Angyal *et al.* (steps 6 and 7).<sup>6,7</sup>



It is probable that the dehydrogenation of amine III by methyleneimine VI is much slower than that by methyleneimine  $\text{CH}_2=\text{NH}$ , hence the induction period appears. As the reaction proceeds, the concentration of ammonia formed by Eqn 7 increases, then methyleneimine, formed by Eqn 8, is added to the system as an effective dehydrogenating agent in acetic acid (steps 8 and 9). Consequently, the reaction is promoted as the reaction proceeds.



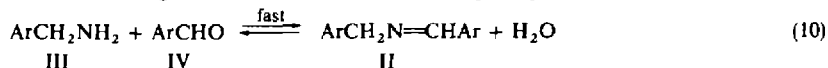
Reaction 9 is a main pathway, although the reaction 6 occurs at an early stage of reaction.

Methyleneimine,  $\text{CH}_2=\text{NH}$ , is formed rapidly in the presence of hexamine by the decomposition of hexamine and acts as an oxidizing agent for III. Thus, the induction period disappears as observed.

If the reaction proceeds by pathway 4 alone, the yield of IV cannot exceed 50%, but actually it is over 76% (observation v). Moreover, no appreciable increase in rate was observed by the addition of  $\beta$ -naphthol or a mixture of  $\beta$ -naphthol and *n*-butylamine to the system of III-HCl and formaldehyde (observation vii). These facts show that the pathway 2 is a main reaction rather than the pathway 4.

The observed rate laws (observations ii and iii) agree with the assumption that the rate-determining step is dehydrogenation of III to V mainly by methyleneimine (first-order in I) and partly by IV (second-order in I).

It was found that the ratio of II to IV in the products increases with increasing concentration of reactants. This is explicable by the condensation equilibrium (Eqn 10) of III with IV in glacial acetic acid containing only a trace of water.

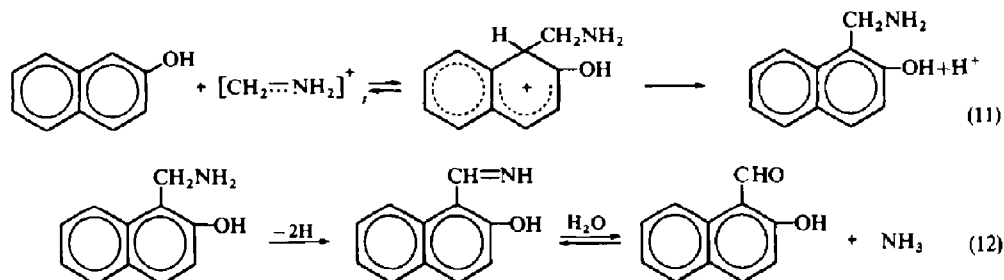


The mechanism by which the conjugate acid of Schiff base  $\text{>C}=\overset{+}{\text{N}}\text{H}_2 \leftrightarrow \text{>}\overset{+}{\text{C}}-\text{NH}_2$  abstracts  $\alpha$ -hydrogen from III as a hydride ion<sup>6-8</sup> is considered to be one of dehydrogenation.

The Duff reaction probably involves the fast aminomethylation of phenols by hexamine itself or its fragment molecule (Eqn 11), followed by the rate-determining dehydrogenation of the amines III to the imines V as in the case of Sommelet reaction



and then by the rapid hydrolysis of the imines (Eqn 12), where reaction 9 is much more important than reaction 6.



### EXPERIMENTAL

**Materials.** Glycerol, b.p. 181.2–182.0° (20 mm), 2-methoxyethanol, b.p. 122–123° (lit.<sup>14</sup> 124.4°), 2-butoxyethanol, b.p. 166.8° (lit.<sup>15</sup> 171°) and glacial AcOH, b.p. 118–119° (lit.<sup>16</sup> 118.5°) were purified by rectification. Commercial  $\beta$ -naphthol was recrystallized from 40 vol % aqueous EtOH, m.p. 120.7–121.0° (lit.<sup>17</sup> 122°). Benzaldehyde and benzyl alcohol were purified by vacuum distillation under  $N_2$ , b.p. 78° (26 mm) and 80.0–80.5° (5.6–5.8 mm), respectively. Commercial 40% aqueous formaldehyde of guaranteed reagent grade was used. *n*-Butylamine hydrochloride was prepared by evaporating an equimolar mixture of the amine and HCl, m.p. 186.0–187.5° (lit.<sup>18</sup> 192°). *N*-Methylenebenzylamine, m.p. 44–46° (lit.<sup>19</sup> 46°) was prepared from benzylamine and formaldehyde.

**Reaction products.** Compounds II, III, and IV were prepared from  $\beta$ -naphthol and hexamine,<sup>1</sup> II: 68%, m.p. 207–209° (dec),  $\lambda_{\max}^{\text{EtOH}}$  423  $\mu$  ( $\log \epsilon$  4.1); III hydrochloride: 70%, m.p. 210.5–213.0° (lit.<sup>20</sup> 224–225°); IV: 76%, m.p. 80.1–80.9° (lit.<sup>21</sup> 80.0–81.0°),  $\lambda_{\max}^{\text{EtOH}}$  360  $\mu$  ( $\log \epsilon$  3.8).

**Rate measurements.** IV and II have absorption maxima in EtOH at 360 and 423  $\mu$ , respectively, and their absorbances satisfy the Lambert–Beer's law. The concentration of above compounds can be estimated by the spectrophotometry. The molar extinction coefficients ( $\epsilon$ ) in EtOH are  $5.65 \times 10^3$  at 360  $\mu$  and zero at 423  $\mu$ . The  $\epsilon$  values of II are  $2.30 \times 10^3$  at 360  $\mu$  and  $11.8 \times 10^3$  at 423  $\mu$ . The concentrations of these compounds were calculated from absorbances of the soln at 360  $\mu$ .

A typical rate measurement is as follows. AcOH solns of I ( $4.00 \times 10^{-3}$  mole  $l^{-1}$ ) and of hexamine ( $8.02 \times 10^{-2}$  mole  $l^{-1}$ ) were mixed in a 3-necked flask fitted with a reflux condenser and a thermometer after reaching thermal equilibrium ( $100 \pm 0.5^\circ$ ). Aliquots (each 1 ml) were taken out at regular intervals, diluted with EtOH, and their absorbances measured at 360  $\mu$ . Under the kinetic conditions at a low concentration, the amount of II is almost negligible compared with that of IV.

**Attempted reaction of benzyl alcohol with hexamine.** Benzyl alcohol (2.0 ml) and hexamine (20 g) were dissolved in 70 ml glacial AcOH and heated on an oil bath for 6 hr at 95–102°. A mixture of conc HCl (100 ml) and water (160 ml) was added and the mixture refluxed for 10 min. After cooling, the mixture was

TABLE 3. THE REACTION OF BENZYL ALCOHOL WITH HEXAMINE

Benzyl alcohol (mole)	Hexamine (mole)	Solvent	Temp. (°C)	Time (hr)	Yield (%)
0.20	0.14	$CH_3CO_2H$	95–102	6	16
0.25	0.18	Glycerol + $B(OH)_3$	150–155	$\frac{1}{2}$	0
0.20	0.30	2-Butoxyethanol + conc HCl	85–95	6	0
0.20	0.07	2-Methoxyethanol + $B(OH)_3$	110–114	2	0

extracted with benzene. neutralized with 10% NaHCO<sub>3</sub> aq, washed with water and dried over MgSO<sub>4</sub>. Benzene was removed by distillation. The resulting soln was analyzed by GLC. A mixture of glycerol-boric acid,<sup>2</sup> 2-butoxyethanol-conc HCl,<sup>4</sup> or 2-methoxyethanol-boric acid was used as solvent. The results are shown in Table 3.

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- <sup>4</sup> J. C. Duff and V. I. Furness, *Ibid.* 1512 (1951).
- <sup>5</sup> J. C. Duff and V. I. Furness, *Ibid.* 1159 (1952).
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