231. *The Mechanism of the Bucherer Reaction. Part IV. The Kinetics of the Conversion of Naphthols into Naphthylamines.*

By W. A. Cowdrey.

The rate at which naphthols (1-naphthol-4- and -5-sulphonates) are converted into the corresponding naphthylamines by heating with ammonia and ammonium sulphite depends directly upon naphthol, ammonium- and sulphite-ion concentrations, and is independent of the excess concentration of free ammonia. The reaction is reversible, however, and the position of the equilibrium is dependent on free ammonia concentration and does not appear to be influenced by the presence of ammonium or sulphite ion.

These kinetic results have been interpreted as supporting the mechanism already put forward for the Bucherer reaction by Fuchs and Stix, with definite provisos regarding the relative velocities of the component reactions.

Various mechanisms have been proposed for the process discovered by Bucherer (*J. pr. Chem.*, 1904, **69**, 49) for preparing naphthylamines and *N*-substituted naphthylamines from the corresponding naphthols by heating with an aqueous solution of an amine and an amine sulphite; the one now most generally accepted is that put forward by Fuchs and Stix (see Part I). Although this probably outlines correctly most of the types of intermediate compound formed during the process, yet it gives little information about the factors which control either the positions of the various equilibria or the rates at which they are established. For example, four consecutive equilibria are postulated, involving four forward and four back reactions; nothing is known, however, of the relative speeds of the various reactions, nor is there any information as to which constitute the rate-determining steps in either direction. Such factors are of considerable interest and it was hoped that more precise knowledge of them would follow from a kinetic study of the process. The conversion of 1-naphthol-5-sulphonic acid (oxy-L acid) into 5-aminonaphthalene-1-sulphonic acid (Laurent acid) has therefore been studied kinetically at about 140°, the progress of the reaction being followed by the technique developed in Part I, *i.e.*, by determining the sparingly soluble aminonaphthalenesulphonic acid.

Experiments keeping the initial concentrations of the naphthol (0·10M) and ammonium sulphite (0·20M) fixed and varying only the initial concentration of free ammonia (from 0·20 to 0·40M) led to the surprising observation that the rate of formation of the naphthylamine was almost independent of the free ammonia concentration. Conversion into the amine was not complete, however, and it was evident that an equilibrium state was reached containing both naphthylamine and naphthol in amounts dependent on the ammonia concentration. Thus the higher the free ammonia concentration of the solution the higher was the concentration of naphthylamine formed at equilibrium, *i.e.*, the more efficient was the amination of the naphthol.

In a further set of measurements the concentrations of both sulphite and ammonium ions were separately varied at constant initial ammonia concentration. Here the results were very different; the rate of amination was now dependent on the concentration both of ammonium and of sulphite ions, the reaction being approximately of the first order with respect to each of these components. Thus by doubling the concentration of sulphite ions and keeping that of the ammonium ion constant (using a mixture of sodium and ammonium sulphites) or by doubling the ammonium-ion concentration without changing that of the sulphite (using a mixture of ammonium sulphite and sulphate) the rate of conversion of naphthol into naphthylamine was approximately doubled. The doubling of the concentration of ammonium sulphite, of course, resulted in a four-fold increase in the reaction velocity. The compositions at final equilibrium were, however, almost independent of the concentrations of either ammonium or sulphite ions.

Finally, variation of the initial concentration of the naphthol with ammonia, ammonium and sulphite ion constant showed that the reaction was approximately of the first order with respect to the naphthol. Thus the initial rate of conversion of naphthol (R·OH) into naphthylamine ($R{\cdot}NH_2$) is given by the expression

$$d[R{\cdot}NH_2]/dt = -d[R{\cdot}OH]/dt = k_C[R{\cdot}OH][NH_4^+][SO_3^=] \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

Iodine titration showed that no significant change occurred in the free sulphite concentration throughout the reaction, indicating that no appreciable concentration of bisulphite compound is established at any stage. Thus in the conversion of naphthol into naphthylamine the net reaction can be represented by the equation

$$R{\cdot}OH + NH_3 \rightleftarrows R{\cdot}NH_2 + H_2O \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

which involves no change in the ammonium-ion concentration, and thus the rate expression (1) can be simplified to

$$d[R{\cdot}NH_2]/dt = k_C'[R{\cdot}OH] \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

where $k_C' = k_C[NH_4^+][SO_3^=]$.

This expression takes no account of the back reaction, *i.e.*, the conversion of naphthylamine into naphthol. If the rate of the forward reaction is governed by the expression (3), and the complete equilibrium is represented by equation (2), the expression for the back reaction must be of the type:

$$\frac{d[R{\cdot}OH]}{dt} = \frac{-d[R{\cdot}NH_2]}{dt} = k_D'\frac{[R{\cdot}NH_2]}{[NH_3]} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

Combining (3) and (4) for the expression for the rate of attainment of equilibrium, we have

$$\frac{d[R{\cdot}NH_2]}{dt} = k_C'[R{\cdot}OH] - k_D'\frac{[R{\cdot}NH_2]}{[NH_3]}$$

where both k_C' and k_D' depend directly on $[NH_4^+]$ and $[SO_3^=]$. Then if the initial concentrations of naphthol and ammonia are a and b respectively, and the concentration of naphthylamine increases from zero to x in a time t,

$$dx/dt = k_C'(a - x) - k_D'x/(b - x) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The integration of this expression as it stands is too cumbersome to be of simple application. By making the rough approximation, however, that the relative fall in ammonia concentration is small over the reaction, *i.e.*, that $(b - x)$ is not greatly different from b for all values of x, then the expression simplifies to

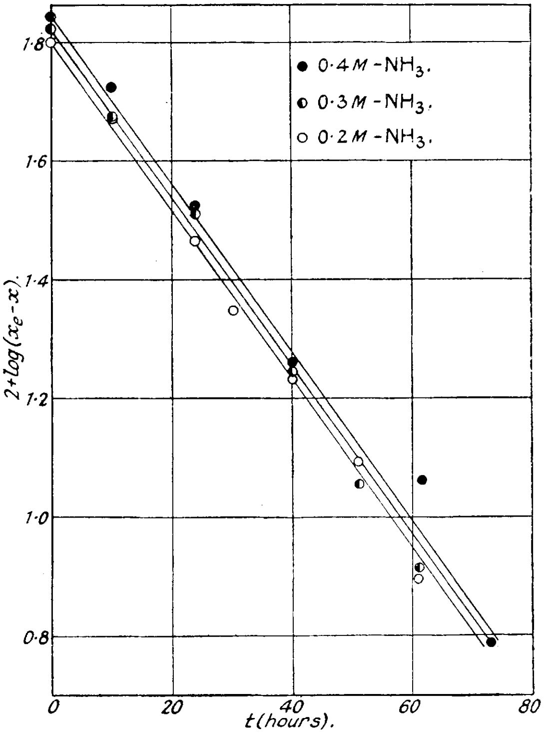
$$dx/dt = k_C'(a - x) - k_D'x/b \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which on integration gives for the first-order velocity constant of the forward reaction :

$$k_C' = k_C[NH_4^+][SO_3^=] = \frac{x_e}{at}\ln\frac{x_e}{(x_e - x)} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

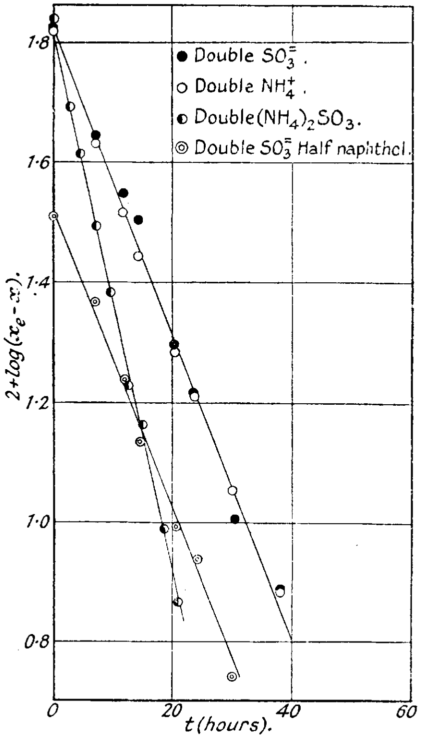
where x_e is the equilibrium naphthylamine concentration.

FIG. 1.



Variation of free ammonia concentration.

FIG. 2.



Variation in initial concentrations of naphthol, sulphite, and ammonium ion.

If equation (7) is applicable, a test plot of log $(x_e - x)$ against t should give a straight line of slope $\frac{-k_C[NH_4^+][SO_3^=]a}{2{\cdot}303\,x_e}$ and an intercept of log x_e. Fig. 1 illustrates such a test plot for the series of experiments in which only the initial free ammonia concentration was varied, whilst Fig. 2 shows the effect of separate variations in $[NH_4^+]$, $[SO_3^=]$, and [R·OH] at a constant initial ammonia concentration. Both sets of results satisfactorily confirm the applicability of the rate equation (7).

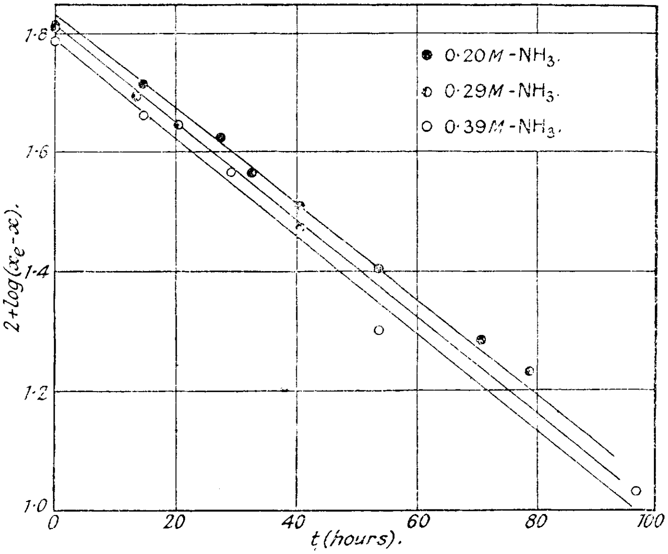
The equilibrium constant of the reaction given in equation (2) can be calculated from the equilibrium concentration x_e as

$$K = \frac{[R{\cdot}NH_2]}{[R{\cdot}OH][NH_3]} = \frac{x_e}{(a - x_e)(b - x_e)} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Calculations of K for various initial concentrations of naphthol, ammonia, ammonium and sulphite ion are given in Table I; in view of the fact that the measurements are not of high accuracy because they all refer to equilibria established well over towards naphthylamine formation, the agreement is quite reasonable.

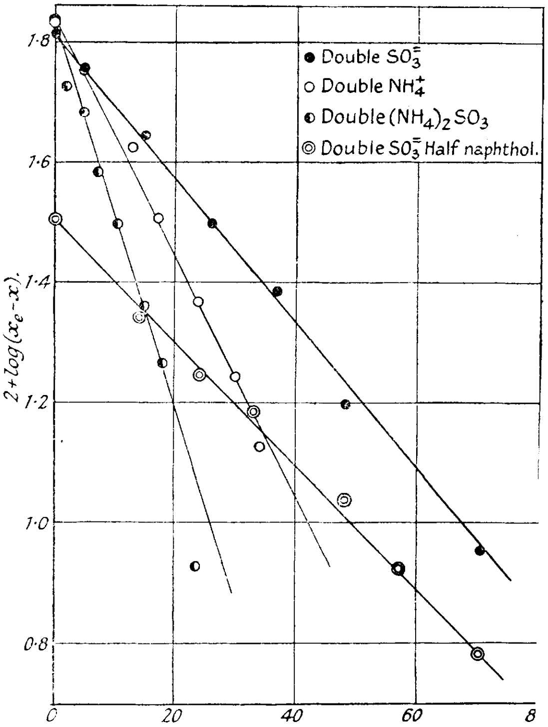
In a similar investigation of the conversion of 1-naphthol-4-sulphonic acid into naphthionic acid the kinetics were of the same general form, but the reaction was of significantly less than the first order with respect to both sulphite ion and naphthol (see Figs. 3 and 4). The rate of conversion of the 1 : 4- was slower than that of the 1 : 5-acid, in contrast with the reverse type of reaction discussed in Part I where the 1 : 4-compound reacted more rapidly.

FIG. 3.



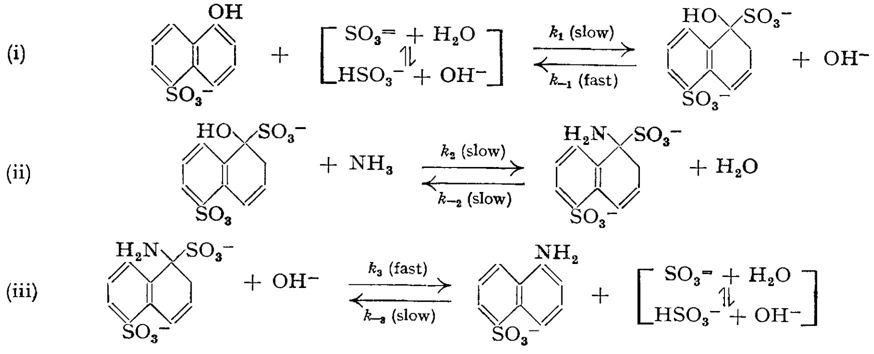
Variation of free ammonia concentration.

FIG. 4.



Variation in initial concentrations of naphthol, sulphite, and ammonium ion.

The systematic kinetics which have been observed are consistent with the Fuchs and Stix type of mechanism provided that the relative velocities of the various reactions are approximately as outlined in the following scheme :



Analysis of this reaction system by the method of Christiansen's formulation (*Z. physikal. Chem.*, **1936**, **33**, *B*, 145; 1937, **37**, *B*, 374) gives for the reciprocal velocities in either direction,

$$\frac{dt}{d[R\cdot NH_2]} = \frac{1}{k_1[R\cdot OH][SO_3^{=}]}\left\{1 + \frac{k_{-1}[OH^-]}{k_2[NH_3]} + \frac{k_{-1}k_{-2}}{k_2k_3[NH_3]}\right\} \qquad (9)$$

and

$$\frac{dt}{d[R\cdot OH]} = \frac{1}{k_3[R\cdot NH_2][SO_3^{=}]}\left\{1 + \frac{k_3[OH^-]}{k_{-2}} + \frac{k_2k_3[NH_3]}{k_{-2}k_{-1}}\right\} \qquad (10)$$

These two expressions correspond to the observed kinetics provided that $k_{-1} \gg k_2$ and $k_3 \gg k_{-2}$, when

$$\frac{d[R\cdot NH_2]}{dt} = \frac{k_2k_1}{k_{-1}K_B}[R\cdot OH][SO_3^{=}][NH_4^+] - \frac{k_{-2}k_{-3}}{k_3K_B}[R\cdot NH_2][SO_3^{=}][NH_4^+] \qquad (11)$$

where K_B is the basic dissociation constant of ammonia. This is of the same form as equation (4). The values of k_1 and k_{-3} must be considerably less than k_{-1} and k_3 to satisfy the condition that appreciable concentrations of bisulphite compounds are not set up at any stage.

No account has been taken in this analysis of the idea that the naphthol reacts in its keto-form as suggested by Woroshtzow. As in Part III, however, there is no need to postulate ketonisation before formation of bisulphite compound to account for the observed kinetics, but if it does occur then the keto-enol equilibrium must be mobile.

The simultaneous formation of the dinaphthylamine derivative has also been ignored, although it is very probable that it occurs to some extent. Any treatment taking account of this side reaction would be considerably more complicated, and in any case the absence of a satisfactory method of estimating the dinaphthylamine compound necessitates this omission.

EXPERIMENTAL.

Solutions were prepared having known concentrations of ammonium ion, sulphite ion, and free ammonia (estimated by iodine titration and Kjeldahl analysis) and containing the requisite concentration of the sodium naphtholsulphonate (by direct weighing). The total ionic strength was kept constant by adding sodium sulphate. Portions of the solutions (40 c.c.) were sealed under nitrogen in soft-glass tubes, preheated for 5 minutes in a bath at 100°, and then heated for known times in oil cups surrounded by a xylene-vapour bath at 139°. Reaction was arrested by dropping the tubes into a large bath of cold oil, and the contents of the tubes were acidified with concentrated hydrochloric acid (4 c.c.). The naphthylaminesulphonic acid thus precipitated was slightly contaminated with silica as a result of attack on the glass tube by the alkali. After the acid had been collected by filtration in a sintered-glass crucible and dried, the crucible was washed out with dilute ammonia to give the true weight of naphthylaminesulphonic acid x (g. per 40 c.c.) formed in a time t (hours) by difference. The equilibrium concentration x_e corresponds to the usual " infinity " measurement.

Amination of Sodium 1-*Naphthol*-5-*sulphonate*.—(1) Variations in initial ammonia concentration with fixed initial concentrations of $SO_3^{=}$ (0·200M), NH_4^+ (0·400M), sodium 1-naphthol-5-sulphonate (0·100M), and sodium sulphate (0·200M).

0·20M-NH_3.

t	10·0	24·0	30·0	40·0	51·0	61·0	∞
x	0·1537	0·3400	0·4075	0·4592	0·5058	0·5507	0·6300

0·30M-NH_3.

t	10·0	24·0	40·0	51·0	61·0	∞
x	0·1918	0·3446	0·4960	0·5560	0·5876	0·6700

0·40M-NH_3.

t	10·0	24·0	40·0	61·5	73·0	∞
x	0·1742	0·3710	0·5267	0·5895	0·6434	0·7050

(2) Variations in initial concentrations of ammonium ion, sulphite ion, and sodium 1-naphthol-5-sulphonate with fixed initial concentrations of free ammonia (0·30M).

0·200M-$(NH_4)_2SO_3$; 0·200M-Na_2SO_3; 0·100M-Na 1-naphthol-5-sulphonate.

t	7·50	12·0	14·5	20·5	24·0	30·0	38·0	∞
x	0·2340	0·3347	0·3857	0·4710	0·5010	0·5505	0·5870	0·6630

0·200M-$(NH_4)_2SO_3$; 0·200M-$(NH_4)_2SO_4$; 0·100M-Na 1-naphthol-5-sulphonate.

t	7·50	12·0	14·5	20·5	24·0	30·0	38·0	∞
x	0·2320	0·3197	0·3533	0·4749	0·5096	0·5720	0·5958	0·6730

0·200M-$(NH_4)_2SO_3$; 0·200M-Na_2SO_3; 0·050M-Na 1-naphthol-5-sulphonate.

t	7·50	12·0	14·8	20·5	24·0	30·0	38·0	∞
x	0·0900	0·1510	0·1860	0·2250	0·2370	0·2683	0·2892	0·3232

0·400M-$(NH_4)_2SO_3$; 0·100M-Na 1-naphthol-5-sulphonate.

t	3·50	5·00	7·50	10·0	13·0	15·0	18·5	21·0	24·0	∞
x	0·1880	0·2715	0·3760	0·4440	0·5170	0·5390	0·5875	0·6110	0·6285	0·6850

(3) Calculations of the equilibrium constant K (concentrations expressed as g.-mol. per l.).

TABLE I.

Initial $[NH_3]$.	Initial [Naphthol].	$[NH_4^+]$.	$[SO_3^{=}]$.	Equilibrium [Naphthylamine].	K.
0·20	0·10	0·40	0·20	0·071	19
0·30	0·10	0·40	0·20	0·075	13
0·40	0·10	0·40	0·20	0·079	12
0·30	0·10	0·40	0·40	0·074	13
0·30	0·10	0·80	0·20	0·075	13
0·30	0·05	0·40	0·40	0·036	10
0·30	0·10	0·80	0·40	0·077	15

Amination of Sodium 1-*Naphthol*-4-*sulphonate*.—(1) Variations in initial ammonia concentration with fixed initial concentrations of $SO_3^{=}$ (0·195M), NH_4^+ (0·390M), sodium naphthionate (0·100M), and sodium sulphate (0·200M).

0·20M-NH_3.

t	15·0	29·5	54·0	96·5	∞
x	0·1543	0·2445	0·4148	0·5075	0·6140

0·29M-NH_3.

t	14·0	21·0	33·0	41·0	79·0	∞
x	0·1461	0·2100	0·2830	0·3530	0·4800	0·6500

0·39M-NH_3.

t	15·0	28·0	41·0	54·0	71·0	∞
x	0·1388	0·2378	0·3367	0·4080	0·4685	0·6603

(2) Variations in initial concentrations of ammonium ion, sulphite ion, and sodium naphthionate with fixed initial concentrations of free ammonia (0·29M).

0·195M-$(NH_4)_2SO_3$; 0·202M-Na_2SO_3; 0·100M-sodium naphthionate.

t	5·0	15·0	26·0	36·7	48·0	70·0	∞
x	0·0852	0·2113	0·3385	0·4100	0·4950	0·5610	0·6500

0·195M-$(NH_4)_2SO_3$; 0·195M-$(NH_4)_2SO_4$; 0·100M-sodium naphthionate.

t	5·0	13·0	17·2	24·0	30·0	34·2	48·0	71·0	∞
x	0·1260	0·2695	0·3672	0·4550	0·5120	0·5530	0·5970	0·6395	0·6850

0·195M-$(NH_4)_2SO_3$; 0·200M-Na_2SO_3; 0·050M-sodium naphthionate.

t	14·0	24·0	33·0	48·0	57·0	70·0	∞
x	0·0998	0·1435	0·1672	0·2110	0·2365	0·2600	0·3205

0·392M-$(NH_4)_2SO_3$; 0·100M-sodium naphthionate.

t	2·0	5·0	7·25	10·5	15·0	18·0	23·5	41·2	∞
x	0·0840	0·2127	0·3118	0·3800	0·4624	0·5078	0·6060	0·6690	0·6900

(3) Calculations of the equilibrium constant.

TABLE II.

Initial $[NH_3]$.	Initial [Naphthol.	$[NH_4^+]$.	$[SO_3^{=}]$.	Equilibrium [Naphthylamine].	K.
0·20	0·10	0·39	0·20	0·069	17
0·30	0·10	0·39	0·20	0·073	21
0·40	0·10	0·39	0·20	0·075	24
0·30	0·10	0·39	0·40	0·073	21
0·30	0·10	0·78	0·20	0·077	27
0·30	0·05	0·39	0·40	0·036	10
0·30	0·10	0·78	0·39	0·077	27

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