228. *The Mechanism of the Bucherer Reaction. Part I. The Kinetics of the Conversion of Naphthylamines into Naphthols.*

By W. A. Cowdrey and C. N. Hinshelwood.

The kinetics of the Bucherer reaction for the conversion of naphthylamine derivatives into the corresponding naphthols have been elucidated. 4-Amino-, 5-amino-, and 5-dimethylamino-naphthalene-1-sulphonic acids all combine with sodium bisulphite during the rate-determining stage of the reaction by a bimolecular process which is of first order with respect to both naphthylamine derivative and bisulphite. The rates and energies of activation of the reactions have been determined. The manner in which the velocity varies with pH of the reaction medium indicates that the naphthylaminesulphonate ion, $C_{10}H_6(NR_2)\cdot SO_3^-$, and bisulphite ion are the reactant forms.

The mechanism of the reaction is discussed in the light of the observed kinetics, and it is suggested that addition of bisulphite to α-naphthylamines takes place directly at the C–C double bond.

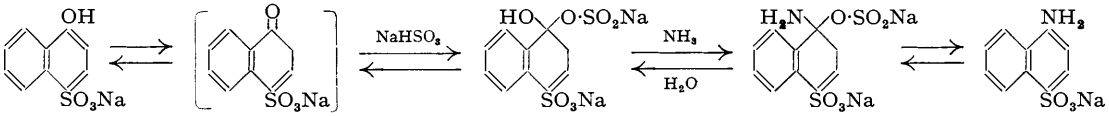
THE unusual catalytic effect of sulphites in the interconversion of naphthylamine and naphthol derivatives was first observed by Lepetit (Pli cacheté Nr. 888, May 16, 1896; *Bull. Soc. Mulhouse*, 1903, 326; see also

Ber., 1921, **54**, 620), who found that naphthionic acid could readily be converted into 1-naphthol-4-sulphonic acid by heating with aqueous sodium bisulphite. Bucherer (*J. pr. Chem.*, 1904, **69**, 49) subsequently demonstrated the more general nature of the reaction and showed that it was reversible, in the sense that naphthols heated with aqueous solutions of amines and amine sulphites yield naphthylamines. The reaction is of considerable technical importance in that it provides a means of converting α-naphthylamine compounds (available *via* α-nitronaphthalene) into α-naphthols, or β-naphthol derivatives (obtained from β-naphthalenesulphonic acid) into β-naphthylamines and *N*-substituted β-naphthylamines. Detailed summaries and bibliographies of the reaction are given in Thorpe's "Dictionary of Applied Chemistry," 1922, Vol. IV, p. 415, and in "Organic Reactions" (Adams), Vol. I, p. 105.

There has been considerable speculation regarding the mechanism of this reaction. Bucherer showed that a very soluble intermediate bisulphite compound is formed, stable to acid but readily hydrolysed by alkali to the corresponding naphthol. This he thought was the naphthyl hydrogen sulphite (I), and therefore formulated the mechanism :

$$\begin{array}{ccccc} \text{Naphthylamine} & \underset{\text{NH}_3}{\overset{\text{NaHSO}_3}{\rightleftarrows}} & \text{Naphthyl hydrogen sulphite} & \underset{\text{NaHSO}_3}{\overset{\text{Alkali}}{\rightleftarrows}} & \text{Naphthol} \\ \text{R·NH}_2 & & \text{R·O·SO·OH (I.)} & & \text{R·OH} \end{array}$$

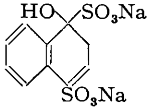
Woroshtzow (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1669) suggested that the compound was a derivative of the keto-form of the naphthol (II), and he assigned to it structure (III). Fuchs and Stix (*Ber.*, 1922, **55**, 662) postulated a further bisulphite compound (IV) derived from the naphthylamine, and they advanced for the conversion of a naphthol into a naphthylamine the following type of mechanism :

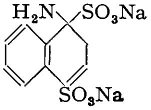


(II.) (III.) (IV.)

The structure of these bisulphite compounds is based on the assumption that the bisulphite compound of a ketone has the structure $R_2C(OH)·O·SO·ONa$. but more recently Raschig and Prahl (*Annalen*, 1926, **448**, 265) have shown that the correct structure is in fact $R_2C(OH)·SO_3Na$. Thus the above structures (III) and (IV) require to be corrected to (V) and (VI) respectively.

(V.)





(VI.)

The evidence for the Fuchs and Stix type of mechanism is based largely on the fact that bisulphite compounds can be isolated from naphthols, and by analogy with the properties of simple aldehyde-bisulphite compounds these would be expected readily to react with ammonia to yield bisulphite compounds analogous to (VI) (cf. Raschig, *Ber.*, 1926, **59**, 859). No serious attempt has been made to determine the kinetics of the reaction in either direction. Kogan and Nikolaeva (*J. Appl. Chem. U.S.S.R.*, **11**, 653) did follow the progress of the conversion of 5-aminonaphthalene-1-sulphonic acid into the corresponding naphthol by the rate at which ammonium ion was formed, but they attempted no mathematical analysis of their results. The present series of papers describes a systematic study of the kinetics of the Bucherer reaction in both directions designed to obtain more fundamental information about the mechanism.

The conversion of naphthylamines into naphthols was first investigated, the original reaction of Lepetit for the conversion of naphthionic into 1-naphthol-4-sulphonic acid being selected as the most suitable example. Naphthionic acid is precipitated almost quantitatively from solutions of its salts by addition of strong acid, and this provides a convenient and accurate method for following the reaction. It became apparent during the course of this work that the bisulphite compounds formed during the reaction did not react with iodine in acid solution, and this enabled the concentrations both of free and of combined bisulphite to be determined throughout the course of the reaction by iodine titration. The reaction was studied in the presence of a large excess of a buffer solution in order to avoid changes in pH which would seriously interfere with the interpretation of the results.

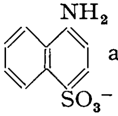
Under these conditions the initial rate of reaction was directly proportional to the product of the concentrations of naphthionate and bisulphite over quite a wide range of each (see Table I). Moreover, at temperatures between 60° and 100° in presence of a large excess of bisulphite (about 4 mols.) the falls in molar concentrations of naphthionate and bisulphite were parallel, so that the progress of the reaction over substantially the whole of its course could be expressed accurately by the usual formula for a bimolecular process, *viz.*,

$$k_2t = \frac{1}{(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

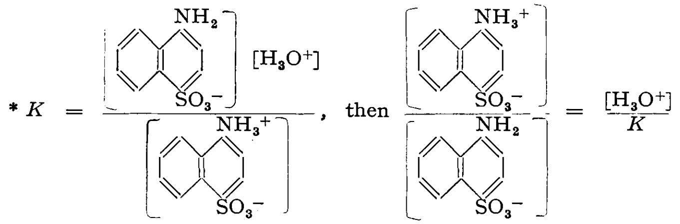
where a and b are the initial concentrations of bisulphite and naphthionate respectively, and x the fall in naphthionate or bisulphite or the rise in ammonium-ion concentration after a time t. On increasing the temperature to 120° the fall in bisulphite concentration became significantly less than that of naphthionate, owing to subsequent partial dissociation of the bisulphite compound into naphthol and bisulphite. Under these conditions the method of analysing the results required modification, because the concentration of bisulphite at a time t was not accurately given by $(a - x)$. This was allowed for by calculating the pseudo-unimolecular constant (k_1) for various reaction times, assuming the constancy of the bisulphite concentration, and then dividing these k_1 values by the mean bisulphite concentrations over the same time period to obtain the true bimolecular constant k_2. The mean bisulphite concentrations were estimated from the observed variation in bisulphite concentration with time by graphical integration.

The plot of log k_2 against $1/T$ for temperatures from 60° to 120° c., where T is the absolute temperature, was linear, with a slope corresponding to 11,800 cals. per g.-mol. for the energy of activation. The velocity of the reaction could thus be expressed by the equation

$$k_2 = 4{\cdot}3 \times 10^2 e^{-11{,}800/RT} \text{ g.-mol.}^{-1} \text{ l. sec.}^{-1}$$

This value of $4{\cdot}3 \times 10^2$ for the pre-exponential factor A is very low, but it is not inconsistent with the view that reaction occurs between ions of like charge, *e.g.*,  and HSO_3^- (cf. Bell., *J.*, 1943, 629).

The nature of the ionic species participating in the process was investigated by carrying out the reaction in a range of buffers, and observing the variation of the rate with pH. With sodium acetate–acetic acid buffers which have a pH not seriously dependent on temperature between 25° and 100°, the rate was observed to be only slightly decreased on passing from pH 3·5 to pH 4·4. Making the assumptions that the dissociation constant of naphthionic acid, given by Ebersbach (*Z. physikal. Chem.*, 1893, **11**, 624) as $2{\cdot}0 \times 10^{-3}$ at 25°, is not very different at 100°, and that it is given by :



The ratio of $R{\cdot}NH_3^+$ to $R{\cdot}NH_2$ should thus vary from 0·16 at pH 3·5 to 0·02 at pH 4·4, so that over this range the concentration of $R{\cdot}NH_3^+$ changes markedly whilst that of $R{\cdot}NH_2$ is not seriously affected. Since the rate is insensitive to pH in this range it follows that it is the free base $R{\cdot}NH_2$ and not its conjugate acid $R{\cdot}NH_3^+$ which reacts. The pH range was extended to 6·9 using sodium hydroxide–potassium dihydrogen phosphate buffers (for which, unfortunately, no information has been found for the change of pH between 25° and 100°), and the variation in rate of reaction at 100° with pH at 20° is shown in the Fig. The dotted line shows the calculated variation of rate with pH assuming that HSO_3^- is the reactant form of the sulphite, and further that the pH of the buffers and the second dissociation constant of sulphurous acid ($5{\cdot}0 \times 10^{-6}$ at 25°) do not change seriously between 25° and 100°. These assumptions are only rough approximations, and the measure of agreement between observed and calculated values affords reasonable support for the HSO_3^- mechanism.

Similar but less detailed investigations have also been carried out on the hydrolyses of 5-amino- and 5-dimethylamino-naphthalene-1-sulphonic acids to 1-naphthol-5-sulphonic acid. The kinetics of the reactions of both substances were formally the same as those of the naphthionic acid reaction. For 5-aminonaphthalene-1-sulphonic acid the rate at 100° was about 1/6th of that of naphthionic acid, the energy of activation 13,700 cals. per g.-mol., and the pre-exponential factor $9{\cdot}7 \times 10^2$ g.-mol.$^{-1}$ l. sec.$^{-1}$, whilst for the di-*N*-methylated derivative the corresponding values were 1/34th, 18,300 cals. per g.-mol. and $2{\cdot}9 \times 10^5$ g.-mol.$^{-1}$ l. sec.$^{-1}$. Further work on a series of nuclear-substituted naphthylaminesulphonic acids would be of interest in correlating

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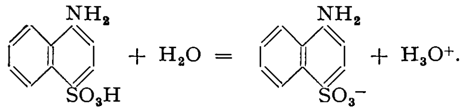
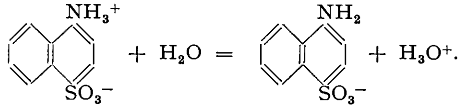
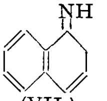
* Ebersbach gives this value for the dissociation constant assuming it refers to the equation



Obviously, however, the sulphonic acid grouping is completely ionised in aqueous solution, and the results actually refer to the reaction :

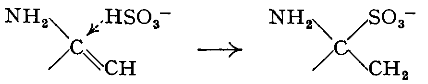


structure with rate of reaction and energy of activation, but so far it has not been possible to prepare the necessary naphthalene compounds.

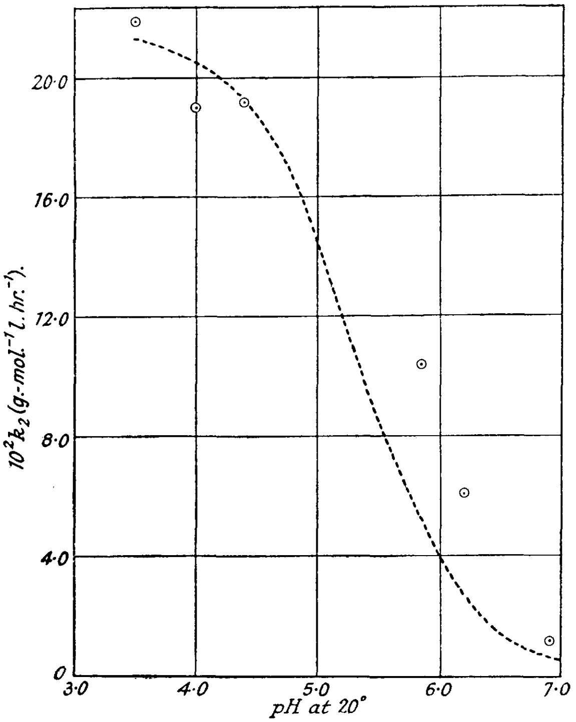


(VII.)

Meanwhile the fact that the di-*N*-methylated derivative undergoes the bisulphite hydrolysis by a process kinetically similar to that of the unmethylated compound is informative regarding the way in which the bisulphite ion combines with the naphthylamine. Clearly, the dimethylamino-compound cannot form an aminosulphinic acid $R{\cdot}NH{\cdot}SO_2H$ similar to the sulphurous ester of the naphthol put forward by Bucherer, nor can it react in an imino-form (VII) analogous to the keto-form suggested by Woroshtzow. More probably the bisulphite ion first attaches itself to the carbon atom attached to the amino-group, the resultant carbanion then picking up a proton and the sulphonic acid group ionising thus :



This would result in 1 : 2-addition of bisulphite, yielding the same compound as postulated in the Fuchs and Stix mechanism. The possibility of 1 : 4-addition, however, cannot be excluded. This type of direct addition of bisulphite to C═C linkages is known, *e.g.*, acraldehyde adds two molecules of bisulphite, one to the C═O and the other to the C═C linkage (Rosenthal, *Annalen*, 1886, **233**, 36). It has also been suggested by Fuchs and Stix to account for the mode of attachment of the second molecule of bisulphite to 1 : 5-dihydroxynaphthalene (*Ber.*, 1922, **55**, 658).



Variation of rate with pH.

EXPERIMENTAL.

Materials.—Sodium naphthionate was prepared from commercial naphthionic acid, and repeatedly recrystallised from water. 5-Aminonaphthalene-1-sulphonic acid (Laurent acid) was obtained commercially and purified by acetylation and recrystallisation of the *p*-toluidine salt of its acetyl derivative (cf. Forster, Harrison, and Watson, *J. Soc. Chem. Ind.*, 1928, **47**, 155). 5-Dimethylaminonaphthalene-1-sulphonic acid was prepared by Dr. R. H. Wilson from purified Laurent acid by methylation with methyl sulphate and sodium hydroxide in aqueous solution.

Kinetic Measurements with Naphthionic Acid.—For carrying out reactions at pH 4·2 solutions were prepared 0·5M in acetic acid and 0·2M in sodium acetate and containing the required concentration of sodium bisulphite. The ionic

TABLE I.

Initial Rates of Reaction at 100° *with Various Concentrations of Naphthionate and Bisulphite.* (*Buffer pH* 4·2 *at* 20°.)

Initial concentrations.		Initial velocity,	$\frac{\text{Initial velocity}}{\text{[Naphthionate][Bisulphite]}}$.
[Naphthionate].	[Bisulphite].	g.-mol./l./hr.	
0·154	0·150	0·0040	0·17
0·154	0·300	0·0080	0·17
0·075	0·150	0·0021	0·18
0·0375	0·150	0·0011	0·19
0·0363	0·300	0·0026	0·24
0·0348	0·450	0·0038	0·24

TABLE II.

Comparison of the Rates of Naphthionate Disappearance and Ammonium Ion Appearance at 100°.

(Initially 0·30M-bisulphite and 0·035M-naphthionate.)

Time (hours).	[Naphthionate].	[NH_4].	[NH_4] + [Naphthionate].
1·0	0·0352	0·0026	0·0378
3·0	0·0310	0·0068	0·0378
6·0	0·0252	0·0127	0·0379
10·0	0·0199	0·0179	0·0378
18·0	0·0121	0·0255	0·0376
24·0	0·0078	0·0296	0·0374
37·0	0·0028	0·0340	0·0368

These results show that no significant amount of naphthionic acid is converted into 4 : 4′-dinaphthylamine-1 : 1′-disulphonic acid.

strength of these solutions was kept constant by addition of sodium chloride. Sodium naphthionate (1·000 g.) was accurately weighed into soft-glass tubes, a measured quantity of the bisulphite–buffer solution was added, and the air was displaced to prevent oxidation of the bisulphite. The tubes were sealed and heated for known times in baths at the various temperatures. To stop the reaction the tubes were cooled rapidly in cold water; unchanged naphthionic acid was then precipitated by addition of concentrated hydrochloric acid (2 c.c.). After 30 minutes to complete the precipitation, the naphthionic acid was filtered off on a sintered-glass crucible, washed with water (10 c.c.), dried at 90°, and weighed. Ammonium ion was estimated in the filtrate by the usual Kjeldahl method. A separate series of tubes was used to follow the change in bisulphite concentration by titration with N/10-iodine in strongly acid solution. Concentrations are expressed as g.-mol./l.

More accurate determination of bimolecular constants.

(Two values are given for the bisulphite concentration, the one as determined by iodine titration, the other expressed as $a - x$ calculated as the difference between the initial bisulphite concentration, a, and the concentration of naphthionate reacted, x.)

(i) At 60·6°.

t (hours).	[Naphthionate] $(b - x)$.	[Bisulphite] (actual).	[Bisulphite] $(a - x)$.	10^2k_2 (g.-mol.$^{-1}$ l. hr.$^{-1}$).
0·0	0·0767	0·285	0·285	—
5·0	0·0736	—	0·282	2·94
10·0	0·0709	0·280	0·279	2·76
18·0	0·0661	—	0·274	2·92
41·5	0·0553	0·264	0·263	2·86
64·0	0·0469	—	0·255	2·86
91·5	0·0379	0·245	0·246	2·93
115·5	0·0317	—	0·240	2·96
143·0	0·0270	0·227	0·235	2·86
188·0	0·0192	0·227	0·227	2·96

Average $k_2 = 2·90 \times 10^{-2}$

(ii) At 120·2°.

(Here the integrated mean bisulphite concentrations are given instead of those calculated as $a - x$.)

t (hours).	[Naphthionate] $(b - x)$.	k_1, hrs.$^{-1}$.	[Bisulphite] (actual).	[Bisulphite] (integ. mean).	10^2k_2 (g.-mol.$^{-1}$ l. hr.$^{-1}$).
0·00	0·0740	0·115	0·291	0·291	—
0·50	0·0699	0·112	—	0·289	39·8
2·00	0·0591	0·121	0·276	0·283	39·6
2·50	0·0546	0·120	—	0·282	42·9
3·50	0·0486	0·120	0·268	0·280	42·6
4·50	0·0436	0·117	—	0·277	42·2
6·00	0·0377	0·113	0·259	0·273	41·4
7·50	0·0323	0·111	—	0·267	41·9
9·50	0·0241	0·118	0·253	0·265	44·1
11·50	0·0193	0·117	0·253	0·264	44·3

Average $k_2 = 42·1 \times 10^{-2}$

The average bimolecular rate constants (g.-mol.$^{-1}$ l. hr.$^{-1}$) at intermediate temperatures were $8·52 \times 10^{-2}$ at 80·5° and $19·1 \times 10^{-2}$ at 99·8°.

Variation in the velocity with pH. A series of buffer solutions was prepared, each approximately 0·15M in total sulphite, and having pH's varying from 3·5 to 6·9 at 20°. For buffers of pH 3·5—4·4 acetic acid–sodium acetate mixtures were used, sodium hydroxide–potassium dihydrogen phosphate combinations being employed for the remainder. Velocity determinations were carried out by adding the bisulphite–buffer solution (40 c.c.) to sodium naphthionate (1·000 g.) and heating the mixture in sealed tubes at 100°. In all cases the buffer solution was in large excess over that of the naphthionate, so that no serious pH change occurred from formation of ammonia during the course of the reaction.

The variation of the bimolecular velocity constant at 100° with the pH of the reaction mixture (measured with a glass electrode at 20°) was as follows:

pH	3·5	4·0	4·4	5·8	6·2	6·9
10^2k_2 (g.-mol.$^{-1}$ l./hr.$^{-1}$)	21·9	19·0	19·2	10·4	6·1	1·25

The figure shows these values along with the calculated plot (dotted line), the bisulphite ion being assumed to be the reactive species. The latter was obtained from the relationship

$$[HSO_3^-] = \frac{T}{1 + K_D/[H_3O^+]}$$

where T is the total sulphite concentration, $[HSO_3^-] + [SO_3^{=}]$, and K_D is the second dissociation constant of sulphurous acid at 25°.

Kinetic measurements with 5-*aminonaphthalene*-1-*sulphonic acid.* A set of rate determinations was carried out in buffer pH 4·2 at various temperatures as already described above for naphthionic acid. In this case, however, free 5-aminonaphthalene-1-sulphonic acid (0·800 g.) was used in place of sodium naphthionate, and to compensate for this the buffer was prepared 0·472M in acetic acid and 0·278M in sodium acetate.

At 80·0°.

t (hours).	[Laurent acid] ($b - x$).	[Bisulphite] (actual).	[Bisulphite] ($a - x$).	$10^2 k_2$ (g.-mol.$^{-1}$ l./hr.$^{-1}$).
0·0	0·0809	0·292	0·292	—
24·0	0·0751	—	0·286	1·06
65·5	0·0654	0·273	0·276	1·13
69·0	0·0647	—	0·276	1·15
97·0	0·0558	0·270	0·270	1·20
119·0	0·0540	—	0·263	1·22
168·0	0·0470	0·258	0·258	1·18
217·5	0·0410	—	0·252	1·16
263·5	0·0354	0·249	0·246	1·18
365·5	0·0264	—	0·237	1·18
452·5	0·0204	—	0·231	1·20

Average k_2 = 1·17 × 10^{-2}

The average bimolecular rate constants at higher temperatures were 3·44 × 10^{-2} at 99·9° and 8·68 × 10^{-2} at 120·2°.

Kinetic measurements with 5-*dimethylaminonaphthalene*-1-*sulphonic acid.* These measurements were carried out as described for Laurent acid above, using 0·900 g. of free dimethylaminonaphthalene-1-sulphonic acid per tube.

At 120·0°.

t (hours).	[Dimethyl-L-acid] ($b - x$).	[Bisulphite] (actual).	[Bisulphite] ($a - x$).	$10^2 k_2$ (g.-mol.$^{-1}$ l./hr.$^{-1}$).
0·0	0·0842	0·300	0·300	—
21·0	0·0744	—	0·290	1·98
39·2	0·0667	0·270	0·283	1·94
63·7	0·0564	—	0·272	2·20
79·0	0·0560	0·255	0·272	1·82
94·7	0·0445	—	0·261	2·45
117·0	0·0432	0·244	0·259	2·06
171·5	0·0313	—	0·252	2·20
221·2	0·0191	0·237	0·235	2·59

Average k_2 = 2·15 × 10^{-2}

The average bimolecular rate constants were 0·64 × 10^{-2} at 99·9° and 6·3 × 10^{-2} at 138·0°.

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