

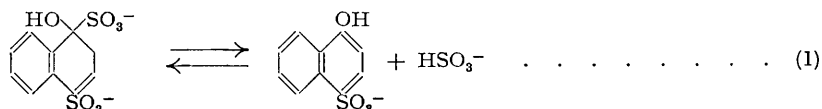
**230. *The Mechanism of the Bucherer Reaction. Part III. Kinetics of the Reaction between Naphtholsulphonic Acids and Sodium Hydrogen Sulphite.***

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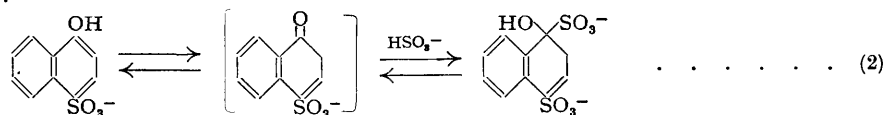
The reaction between sodium 1-naphthol-4- and -5-sulphonates and sodium bisulphite has been studied kinetically. The process is reversible, the naphthol-bisulphite compound being formed by a bimolecular combination of naphthol and bisulphite and destroyed by a unimolecular dissociation. The rates and energies of activation of both the formation and the dissociation processes have been measured, together with the equilibrium constants.

The mechanism of the reaction is discussed in relation to the earlier suggestion of Woroshtzow that naphthols ketonise before addition of bisulphite.

THE scheme outlined in Part II for the mechanism of the Bucherer reaction in the conversion of naphthylamines into naphthols involves six interconnected equilibria, only one of which can be studied in complete absence of the rest, namely, that between the naphthol-bisulphite compound and the free naphthol plus bisulphite :



This type of reaction has been widely discussed in connection with the Bucherer reaction, and Woroshtzow (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1669) suggested that the actual addition of bisulphite takes place to the keto-form of the naphthol :



(cf. Adams, "Organic Reactions," Vol. I, p. 106).

This reaction has now been studied kinetically (in the light of the earlier observations of Parts I and II that bisulphite compounds of this type do not react with acid iodine) by measuring the rate at which the equilibrium is attained and also its composition. As in Part I, the kinetics were carried out in a large excess of sodium acetate-acetic acid buffer of pH 4.2 to avoid changes in pH which complicate analysis of the results.

Ignoring for the moment the possibility of the intermediate formation of the keto-form of the naphthol, and considering only the type of equilibrium of equation (1) above, then if *a* and *b* are the initial concentrations of naphthol and bisulphite, respectively, and *x* the concentration of bisulphite compound formed after a time *t*, the rate of disappearance of naphthol or bisulphite should be given by the expression

$$\frac{dx}{dt} = k_2(a - x)(b - x) - k_1x \quad \dots \quad (3)$$

Here *k*<sub>2</sub> is the bimolecular velocity constant for the formation of the bisulphite compound and *k*<sub>1</sub> the unimolecular velocity constant for its dissociation. On integration this gives :

$$k_2 = \frac{1}{t(a + b + K - 2x_e)} \ln \frac{(a + b + K - x - x_e)x_e}{(a + b + K - x_e)(x_e - x)} \quad \dots \quad (4)$$

where the equilibrium constant *K* = *k*<sub>1</sub>/*k*<sub>2</sub> = [Free naphthol] [HSO<sub>3</sub><sup>-</sup>]/[Bisulphite compound] and *x*<sub>e</sub> is the equilibrium concentration of bisulphite compound (*t* = ∞).

Kinetic measurements have been made with both 1-naphthol-4- and -5-sulphonic acids, and the results obtained could be quite satisfactorily interpreted on the basis of equation (4). The value of *x*<sub>e</sub> was determined as the difference between the initial and the equilibrium bisulphite concentrations as measured by iodine titration, and from *x*<sub>e</sub> the equilibrium constant could be calculated as (a - *x*<sub>e</sub>)(b - *x*<sub>e</sub>)/*x*<sub>e</sub>. Then, by measuring

$x$ , the fall in iodine titre over a time  $t$ , for a series of values of  $t$ ,  $k_2$  could be determined and hence  $k_1$ . Further more, by carrying out the reaction at a series of temperatures the energies of activation of both formation and dissociation processes were determined, and also the pre-exponential factor for the formation. The energies of activation were 16,800 and 20,800 cal./g.-mol. for the formation, and 24,200 and 25,600 cal./g.-mol. for the dissociation of the bisulphite compounds of 1-naphthol-4- and -5-sulphonic acids respectively, whilst the corresponding pre-exponential factors were 4.3 and  $150 \times 10^6$  g.-mol.<sup>-1</sup> l. sec.<sup>-1</sup> (cf. Part I for the pre-exponential factors for the reaction of bisulphite with the corresponding amino-compounds).

The kinetic results are consistent with a simple equilibrium of the type represented by equation (1), it being assumed that the bisulphite adds directly to the  $C=C$  linkage in the manner suggested in Part I for the addition of bisulphite to naphthylamines. However, a mechanism involving the keto-form of the naphthol (equation 2) is also feasible provided that the equilibrium between keto- and enol forms of the naphthol is mobile (as it would be), the rate-determining step then being the addition of bisulphite ion to the keto-form. In this case the observed bimolecular constant  $k_2$  will be a function of the equilibrium constant  $K_1$  ( $= [Enol]/[Keto]$ ) of the keto-enol equilibrium and the true bimolecular constant  $k_2'$ , so that  $k_2 = k_2'/(1 + K_1)$ , whilst the observed energy of activation  $E$  is related to the true energy of activation of the reaction between the keto-form and bisulphite,  $E'$ , by an expression which reduces to  $E = E' + \Delta H$  if  $K_1 \gg 1$  and  $\Delta H$  is the heat absorbed in the conversion of enol to ketone.

It has not been possible to decide between these two possible types of mechanism by kinetic study.

#### EXPERIMENTAL.

*Materials.*—1-Naphthol-4- and -5-sulphonic acids were purified as their zinc salts by repeated recrystallisation from water (cf. Friedländer and Taussig, *Ber.*, 1897, **30**, 1459). The zinc salts were converted into sodium salts by addition of sodium carbonate, filtration from zinc carbonate, and salting out with sodium chloride from acid solution. They were dried at 90°, and analysis then showed them to be anhydrous.

*Kinetic Measurements with 1-Naphthol-4-sulphonic Acid.*—At 120.3°. Two solutions were prepared both 0.55M in acetic acid, 0.20M in sodium acetate, and 0.20M in sodium bisulphite, and containing sodium 1-naphthol-4-sulphonate (24.60 and 49.20 g. per 500 c.c.) corresponding to concentrations of 0.20M and 0.40M. These solutions were sealed up in 20-c.c. portions in glass tubes under nitrogen to prevent oxidation, and heated for known times at 120.3° before being cooled rapidly, diluted, and titrated by running into acidified iodine solution. The results were as follows, concentrations being expressed in g.-mol./l., and  $k_2$  in g.-mol.<sup>-1</sup> l. hr.<sup>-1</sup>:

| $t$ (hours).                       | [Bisulphite]. | $x$ .  | $10^2 k_2$ . | $t$ (hours). | [Bisulphite]. | $x$ .  | $10^2 k_2$ . |
|------------------------------------|---------------|--------|--------------|--------------|---------------|--------|--------------|
| (a) 0.20M-1-Naphthol-4-sulphonate. |               |        |              |              |               |        |              |
| 0.0                                | 0.2025        | —      | —            | 18.0         | 0.1721        | 0.0304 | 7.2          |
| 3.0                                | 0.1939        | 0.0086 | 7.9          | 40.5         | 0.1634        | 0.0391 | 6.1          |
| 7.5                                | 0.1872        | 0.0153 | 6.2          | 69.5         | 0.1587        | 0.0438 | —            |
| 11.0                               | 0.1810        | 0.0215 | 6.7          | 150.0        | 0.1585        | 0.0440 | —            |

Average  $k_2 = 7.4 \times 10^{-2}$

$$K = 0.56 \text{ g.-mol./l.}; k_1 = Kk_2 = 0.042 \text{ hr.}^{-1}.$$

0.40M-1-Naphthol-4-sulphonate.

|       |        |        |      |       |        |        |      |
|-------|--------|--------|------|-------|--------|--------|------|
| 0.0   | 0.2000 | —      | —    | 15.00 | 0.1492 | 0.0508 | 7.37 |
| 3.00  | 0.1818 | 0.0182 | 7.55 | 20.00 | 0.1425 | 0.0575 | 7.18 |
| 5.00  | 0.1765 | 0.0235 | 7.16 | 26.00 | 0.1360 | 0.0640 | 7.41 |
| 6.75  | 0.1690 | 0.0310 | 7.57 | 35.00 | 0.1312 | 0.0688 | 7.35 |
| 9.50  | 0.1618 | 0.0382 | 7.22 | 45.00 | 0.1294 | 0.0706 | —    |
| 12.00 | 0.1550 | 0.0450 | 7.41 | 77.50 | 0.1259 | 0.0741 | —    |

Average  $k_2 = 7.36 \times 10^{-2}$

$$K = 0.555 \text{ g.-mol./l.}; k_1 = 0.0408 \text{ hr.}^{-1}.$$

The determinations at other temperatures were carried out with a solution corresponding to (b) above; at 100.2°, the values were  $k_2 = 2.26 \times 10^{-2}$ ,  $k_1 = 0.00640$ ,  $K = 0.283$ , and at 80.0°,  $k_2 = 0.657 \times 10^{-2}$ ,  $k_1 = 0.00117$ ,  $K = 0.179$ .

The plots of both  $\log k_2$  and  $\log k_1$  against  $1/T$  are linear, and the slopes correspond to energies of activation of 16,800 and 24,200 cal./g.-mol., respectively.

*Kinetic Measurements with 1-Naphthol-5-sulphonic Acid.*—These measurements were carried out using the same concentrations and conditions as developed for 1-naphthol-4-sulphonic acid above, and  $k_2$  is in the same units.

At 120.4°

| $t$ (hours). | [Bisulphite]. | $x$ .  | $10^2 k_2$ . | $t$ (hours). | [Bisulphite]. | $x$ .  | $10^2 k_2$ . |
|--------------|---------------|--------|--------------|--------------|---------------|--------|--------------|
| 0.0          | 0.2017        | —      | —            | 84.5         | 0.1598        | 0.0419 | 1.32         |
| 18.2         | 0.1844        | 0.0173 | 1.39         | 97.0         | 0.1568        | 0.0449 | 1.44         |
| 31.3         | 0.1802        | 0.0215 | 1.12         | 119.0        | 0.1558        | 0.0459 | 1.30         |
| 42.7         | 0.1711        | 0.0306 | 1.33         | 138.0        | 0.1540        | 0.0477 | 1.30         |
| 53.7         | 0.1701        | 0.0316 | 1.12         | 240.0        | 0.1520        | 0.0497 | —            |
| 66.5         | 0.1617        | 0.0400 | 1.47         |              |               |        |              |

Average  $k_2 = 1.32 \times 10^{-2}$

At 137.2°, the corresponding values were  $k_2 = 4.47 \times 10^{-2}$ ,  $k_1 = 0.0531$ ,  $K = 1.19$ ; and at 100.3°,  $k_2 = 0.360 \times 10^{-2}$ ,  $k_1 = 0.00244$ ,  $K = 0.678$ .

Both  $\log k_2$  and  $\log k_1$  gave a linear plot against  $1/T$ , the slopes of which correspond to 20,800 and 25,600 cal./g.-mol. for the energies of activation.