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MECHANISM OF SULPHOMETHYLATION OF β-NAPHTHOL

KINETICS OF THE FORMATION OF SODIUM 2-HYDROXY-1-NAPHTHYLMETHANESULPHONATE FROM BIS-(2-HYDROXY-1-NAPHTHLYL)METHANE*

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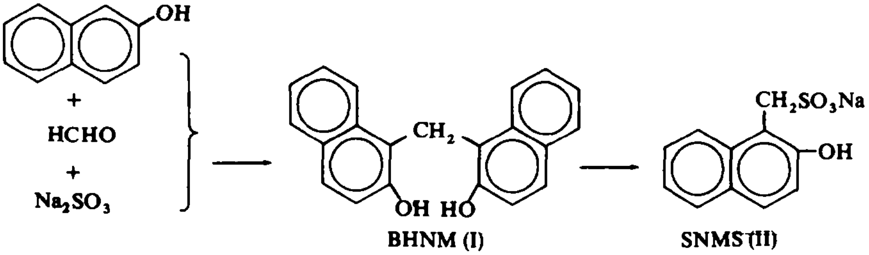
Abstract — Sulphomethylation of β-naphthol, i.e. the reaction of bis-(2-hydroxy-1-naphthyl)methane (BHNM; I) with sodium sulphite to form 2-hydroxy-1-naphthylmethanesulphonate (SNMS; II), has been studied kinetically by iodometry of sodium sulphite. The rate law, $v = k\,[\text{BHNM}]$, together with the relation k vs. $[\text{OH}^-]$ suggests a S_N1 mechanism via the dianion of BHNM (V) and quinone-methide (VIII). This shows that quinonemethide (VIII) and not BHNM is an intermediate in the sulphomethylation of β-naphthol. The behaviour of BHNM in aqueous alkali is discussed in terms of the alkalimetric titration and UV spectra.

"Sulphomethylation" is the substitution of sulphomethyl group ($-CH_2SO_3-$) generally using a mixture of formaldehyde and sulphite (or bisulphite) ion. This reaction is applied to phenols,[1] amines,[2] and ketones.[1c] Few reports on the kinetics and mechanism of this reaction have appeared. In the sulphomethylation of ammonia,[3] the proposed mechanism, based on a kinetic study, involves hydroxymethylamine ($H_2N—CH_2—OH$) as an intermediate. On the other hand, it has been reported that salicyl alcohol reacts with sulphite (or bisulphite) below pH 10 to form the corresponding sulphonic acid through a S_N2 mechanism.[4] Therefore, it is probable that the formation of a methylol compound is the first step in sulphomethylation.

However, in the sulphomethylation of β-naphthol, no 1-hydroxymethyl-β-naphthol has been isolated; instead, bis-(2-hydroxy-1-naphthyl) methane (BHNM, I) has been reported as an intermediate.[1b,c]



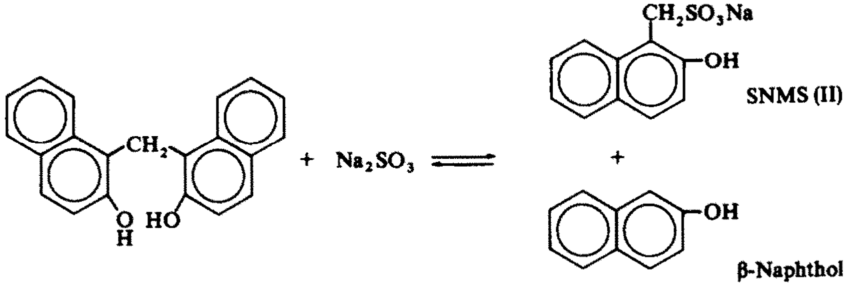
The present paper presents evidence that BHNM is not the true intermediate in the sulphomethylation of β-naphthol. The behaviour of BHNM in a basic solution and the kinetics of reaction of BHNM with sulphite, leading to the mechanism of sulphomethylation of β-naphthol and BHNM, are discussed.

RESULTS AND DISCUSSION

The reaction of β-naphthol with a mixture of formaldehyde and sodium sulphite in an aqueous solution at 100° gave colorless needles within 5 min from the start of the reaction, and the crystals dissolved slowly, giving sodium 2-hydroxy-1-naphthylmethanesulphonate (SNMS, II). Clutterbuck and Cohen reported these crystals to be 1-hydroxymethyl-β-naphthol,[1a] but later they were shown to be BHNM (I) by other workers.[1b,c] We confirmed the BHNM structure by comparison with an authentic sample,[5] UV spectra and m.p. (Experimental).

The reaction of BHNM (I)

BHNM has been isolated as a by-product in the reaction of β-naphthol with formaldehyde or its derivatives.[6] It has been reported that BHNM decomposes under mild conditions;[1b,7] for example, the following reversible reaction (Eq. 1) occurs.[1b]



SNMS (II)

(1)

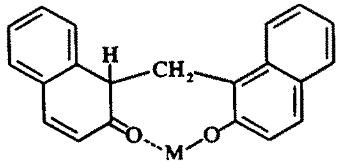
β-Naphthol

BHNM (I)

Careful examination, however, indicated that BHNM does not react with sulphite in the absence of a strong base. Furthermore, treatment of BHNM with aqueous sodium hydroxide for 6 hr at 100° gives β-naphthol and a red amorphous substance having a carbonyl group. On the other hand, the dimethyl ether as well as the monomethyl ether of BHNM does not react with sodium sulphite in the presence of alkali at 100°. These facts indicate that the fission of BHNM requires the dissociation of the OH group.

Dissociation of the hydroxyl group of BHNM (I)

It has been reported that treatment of BHNM with aqueous alkali yields the mono-alkali salt but not the di-alkali and that the former has a more stable 8-membered



(III)

ring structure (III).[8] As stabilization by formation of an 8-membered ring is not enough to cancel the destabilization effect by loss of aromaticity, the behaviour of BHNM in aqueous alkali was studied.

The titration curve of the BHNM with aqueous sodium hydroxide is shown in Fig. 1. This curve shows that only one of the two OH groups of BHNM dissociates at pH below 12.

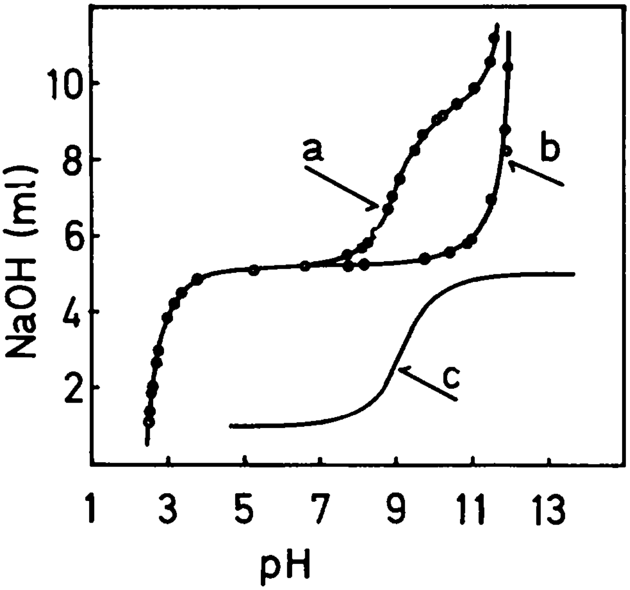


FIG. 1. Titration curve of 3·77 × 10^{-3} M BHNM with 0·0905N aquous NaOH in EtOH–H_2O (3 :2 in vol) at 30°.
(a) BHNM and excess aquous HCl; (b) aquous HCl; (c) the difference between curve a and b (corresponding to the curve for BHNM alone).

In order to clarify the second dissociation of BHNM, UV absorption spectra of BHNM (1·00 × 10^{-5}M) were measured in aqueous ethanol (EtOH–H_2O; 3:2 in vol) at various alkali concentrations (0–5N) (Fig. 2).

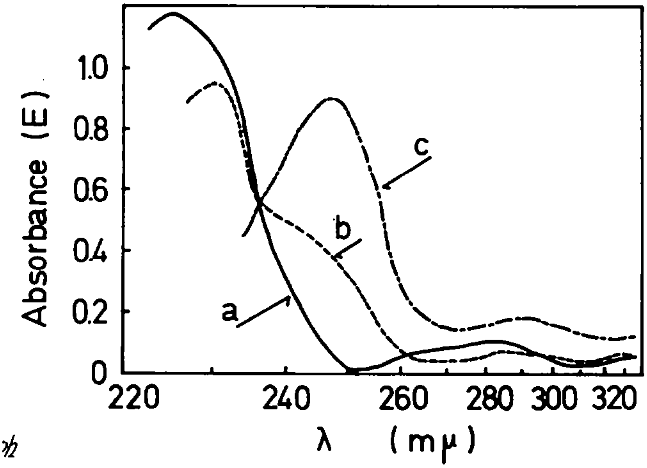


FIG. 2. Ultraviolet absorption spectra of BHNM at various concentrations of NaOH in EtOH–H_2O; 3 :2 in vol.
(a) 0–10^{-4}M NaOH; (b) 10^{-3}–10^{-1}M NaOH; (c) above 1M NaOH.

There is no change in the UV absorption in a region of alkali concentration below 10^{-4}M (curve a in Fig. 2), but if this concentration is increased to 10^{-4}–10^{-3}M, the peak shifts from 226 to 230 mμ, its absorbance diminishes, and a shoulder appears at 247·5 mμ (curve b in Fig. 2). No change in absorption spectra is observed at 10^{-3}–10^{-1}M, but in alkali concentration above 10^{-1}M, the absorbance at 230 mμ diminishes, and a shoulder at 247·5 mμ becomes apparent as a peak. This change continues to ca. 1M alkali but no further change occurs above 1M (curve c in Fig. 2).

These spectra (curves b and c) revert to the original (curve a) on acidification of the alkaline solutions with aqueous HCl. Fig. 3 gives the relationship between the absorbance at 247·5 mμ and the logarithm of alkali concentration. Comparing Fig. 3 with the titration curve, the first lift in Fig. 3 corresponds to the first dissociation of I. Two explanations may be given for this second lift in Fig. 3, i.e. tautomerism to structure III and the simple dissociation of the second OH group. If the first explanation is true, the absorption would not have the isobestic point (237·5 mμ), and would not show a systematic change in these absorption spectra (curves a, b, and c); i.e. the structure III should give the absorption band of Ph—C═C—C═O. On the other hand, IR spectra of the mono-sodium salt of BHNM do not show the absorption of C═O. Therefore, the second lift in Fig. 3 corresponds to the second dissociation of BHNM and the behaviour of BHNM in a basic solution is explained by Eq. 2.

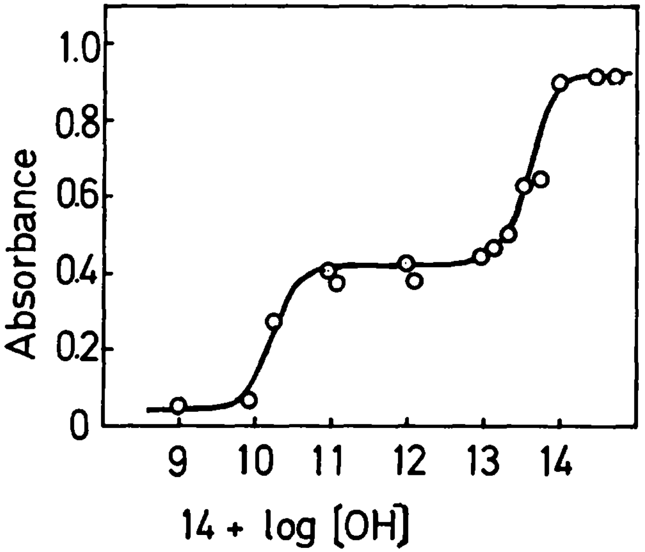
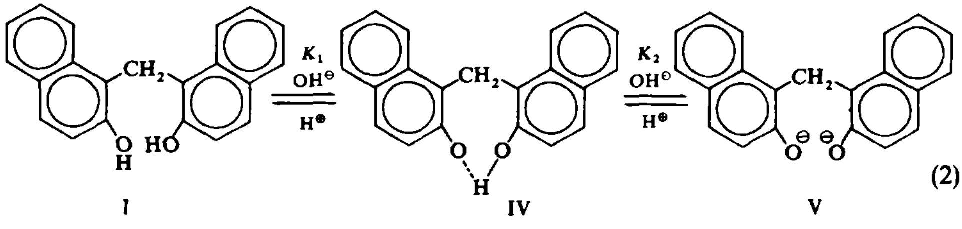


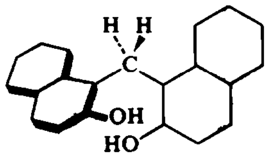
FIG. 3. The relationship between absorbance of BHNM at 247·5 mμ vs. log [OH⁻] at room temperature.



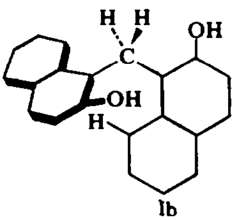
(2)

It is concluded that structure III cannot be stable. The very weak acidity of the second OH group of BHNM is ascribed to the stabilization of IV by the formation of intramolecular H-bonding and the instability of V by the electrostatic repulsion between two anionic O atoms forced by the steric interaction of H atoms in the 8-position of naphthalene.

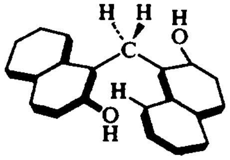
It is known that the di-alkali salt of BHNM as well as diphenol-methane having alkyl groups at both 6 and 6′-positions can not be isolated.[9] The Stewart model indicates that the configuration Ia is the most stable of the possible configurations in view of the steric requirement and the H-bonding between two O atoms in IV. The steric and/or electrostatic repulsion in the other three configurations, i.e. the interactions between naphthyl and naphthyl for Ib, naphthyl and hydroxyl for Ic, naphthyl and naphthyl, and hydroxyl and hydroxyl, for Id, occur. Structure Ia implies that the second dissociation of BHNM (IV to V) is difficult.



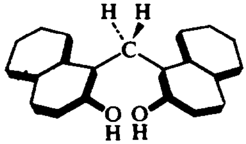
Ia



Ib



Ic



Id

The first dissociation constant, pK_{a1}, was determined by the acidimetry to be 9·05 in EtOH–H_2O (3:2 in vol) at 30°, and the half equivalence point for the second dissociation was determined by the UV spectra to be $3·16 \times 10^{-1}$N sodium hydroxide ($14 + \log[OH^-] = 13·5$ corresponding to pK_{a2}) in EtOH–H_2O (3:2 in vol) at room temperature. The UV spectral data: λ^{max} (log ε) are 226 mμ (5·06), 282 mμ (3·89), 294 mμ (3·88), and 338 mμ (3·71) for I in EtOH–H_2O (3:2 in vol); 230 mμ (4·98) and 286 mμ (3·87) for IV in EtOH–H_2O (3:2 in vol); 247·5 mμ (4·94) and 291·5 mμ (not determined) for V in H_2O.

Kinetics of the formation of SNMS (II) *from BHNM* (I) *and sodium sulphite*

As stated above, BHNM reacts with sodium sulphite to form SNMS (II) in the presence of aqueous alkali. The reaction was followed by the consumption of sulphite by means of iodometry. The reaction reached an equilibrium at 46% conversion of BHNM. The kinetic data are shown in Table 1.

TABLE 1. RATE CONSTANTS FOR THE REACTION OF BHNM WITH SODIUM SULPHITE IN WATER AT 90°

BHNM(M)	Na_2SO_3(M)	NaOH(M)	$k^* \times 10^5$ (sec^{-1})	$10^5 k^{\dagger}_{calc}$ (sec^{-1})
0·050	0·034	0·093	4·69	4·73
0·038	0·034	0·093	4.65	4·73
0·025	0·034	0·093	4·91	4·73
0·013	0·034	0·093	4·61	4·73
0·050	0·127	0·138	4·61	5·25
0·050	0·110	0·138	4·35	5·12
0·050	0·088	0·138	4·50	4·91
0·050	0·065	0·138	4·16	4·58
0·050	0·042	0·138	4·67	4·01
0·050	0·045	0·996	0·269	0·469
0·050	0·032	0·760	0·640	0·528
0·050	0·032	0·500	1·02	1·12
0·050	0·045	0·498	1·28	1·21
0·050	0·032	0·320	2·74	1·66
0·050	0·032	0·200	3·47	2·68
0·050	0·045	0·199	2·81	3·07
0·050	0·032	0·100	4·48	4·35
0·050	0·045	0·100	4·61	4·93
0·050	0·045	0·080	4·86	5·46

* First-order rate constants for BHNM.

† First-order rate constant calculated from Eq. 13.

Since the observed first-order rate coefficients with BHNM are independent of the initial concentration of BHNM and sodium sulphite under the conditions of 0·1M sodium hydroxide at 90°, the rate is first-order in BHNM and zero-order in sulphite, i.e.

$$v = k_{obs}(a - x) \tag{3}$$

Here, a is the initial concentration of BHNM and x is the consumed concentration of sulphite.

The observed rate constants at the various concentrations of sodium hydroxide are listed in Table 1, and the relationship between log [NaOH] and log k_{obs} is plotted in Fig. 4 (solid line a).

The reaction needs a base and mono- and dimethyl ethers of BHNM do not react, hence the undissociated BHNM (I) cannot be a main reactant. The reaction is first-order in BHNM and zero-order in sulphite, but the dianion of β-naphthol (VI) cannot be formed under these conditions; therefore, the β-naphthoxide anion (VII) and the quinonemethide (VIII) should intervene in this reaction. VIII is known to be so reactive that it cannot be isolated because of the resonance (VIII ↔ VIII′, see later).[6a, 10]

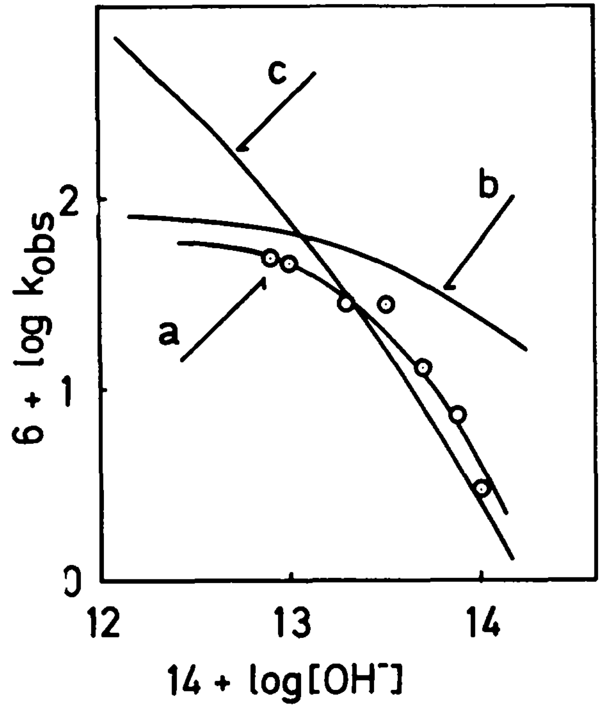
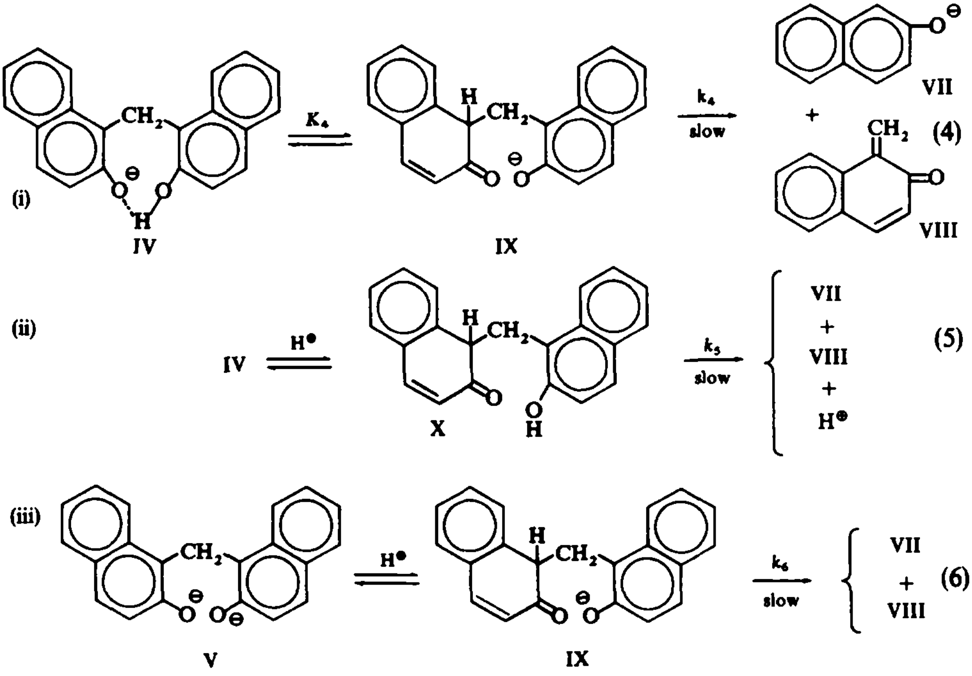


FIG. 4. The effect of concentration of hydroxide ion on the reaction of BHNM with sodium sulphite in water at 90°.
(a) Plot of observed first-order rate constant vs. log [OH]: [BHNM] = 0·050M, $[SO_3]$ = 0·045M (or 0·032M). (b) Plot of Eq. 9 (or Eq. 11); (c) Plot of Eq. 10.



In pathway (i), IX existing in equilibrium with IV and V decomposes to give VII and VIII. The equilibrium concentration of I is negligible under these basic conditions. The rate equation is expressed as follows. (See Eqs. 2 and 7).

$$v = k_4[\mathrm{IX}] = \frac{k_4K_4[\mathrm{H}^+]}{(1 + K_4)[\mathrm{H}^+] + K_2}[\mathrm{BHNM}] \tag{7}$$

Comparison of Eq. 7 with Eq. 3 gives the expression 8 of observed rate constant.

$$k_{\mathrm{obs}} = \frac{k_4K_4[\mathrm{H}^+]}{(1 + K_4)[\mathrm{H}^+] + K_2} \tag{8}$$

Since $K_4 \ll 1$, eq 8 is simplified to:

$$k_{\mathrm{obs}} = \frac{k_4K_4[\mathrm{H}^+]}{[\mathrm{H}^+] + K_2} \tag{9}$$

Assuming $pK_2 = 13{\cdot}5$, the relation of Eq. 9 is drawn as curve b in Fig. 4.

On the other hand, in pathway (ii), the observed rate constant is expressed as:

$$k_{\mathrm{obs}} = \frac{k_5[\mathrm{H}^+]^2}{[\mathrm{H}^+] + K_2} \tag{10}$$

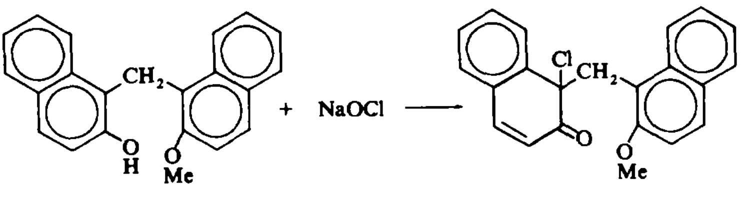
This relationship is shown as curve c in Fig. 4.

In the pathway (iii), the observed rate constant is expressed as:

$$k_{\mathrm{obs}} = \frac{k_6K_2[\mathrm{H}^+]}{[\mathrm{H}^+] + K_2} \tag{11}$$

Hence, Eq. 11 is essentially identical with Eq. 9. Therefore, Eq. 11 is drawn as curve b in Fig. 4.

The intermediary formation of IX or X is probable, since compound XI has been isolated as a derivative of monomethyl ether of BHNM (Eq. 12).[11]



(12)

However, the theoretical curves b and c do not agree with the observed curve a. It is reported that the nucleophilicity of hydroxide ion is ca. 1/8 of sulphite ion.[12] Therefore, an attack of hydroxide ion on the quinonemethide (VIII) may be negligible at low hydroxide ion concentration, but it cannot be neglected at high $[\mathrm{OH}^-]$, i.e. hydroxide ion may compete with sulphite ion for VIII. The rate equation of the formation of SNMS (II) is not Eq. 3 but Eq. 13.

$$v = \frac{k_S[\mathrm{SO}_3^{2-}]}{k_S[\mathrm{SO}_3^{2-}] + k_{\mathrm{OH}}[\mathrm{OH}^-]}k(a - y) \tag{13}$$

Here, a and y are initial and consumed concentrations of BHNM, respectively, and k_S and k_{OH} are the rate constants of sulphite and hydroxide ions, respectively. Hence, the observed rate constant can be expressed as:

$$k_{obs} = \frac{kk_S[SO_3^{2-}]}{k_S[SO_3^{2-}] + k_{OH}[OH^-]} \tag{14}$$

Eq. 14 can be rewritten as Eq. 15, which needs a linear relationship between $1/k_{obs}$ and $[OH^-]/[SO_3^{2-}]$.

$$1/k_{obs} = \frac{1}{k}\left(1 + \frac{k_{OH}[OH^-]}{k_S[SO_3^{2-}]}\right) \tag{15}$$

Since the measured value is not $(a - y)$ but $(a - x)$ (y: consumed BHNM, x: consumed sulphite), Eq. 15 is an approximation, but $(a - x) \approx (a - y)$ at low conversion. The data are listed in Table 2, and a linear plot in Fig. 5 agrees with the relationship of Eq. 15. Fig. 5 gives for k_{OH}/k_S a value of 1/4·5 from curve a, or 1/7·7 from curve b. These values agree with the reported value (1/8) within the experimental error.

TABLE 2. THE EFFECT OF THE CONCENTRATION OF SODIUM SULPHITE ON THE RATE CONSTANT AT THE CONSTANT $[OH^-]$ OF 0·500M OR 1·00M AND [BHNM] OF 0·050 AT 90°

NaOH(M)	Na_2SO_3(M)	$k^* \times 10^5$ (sec^{-1})	$10^5k^\dagger_{calc.}$ (sec^{-1}
0·500	0·400	3·84	2·84
0·500	0·324	2·56	2·72
0·500	0·169	3·20	2·30
0·500	0·090	1·92	1·83
0·500	0·077	2·56	1·65
0·500	0·045	1·28	1·23
0·500	0·032	1·02	0·953
1·000	0·579	2·16	1·65
1·000	0·220	1·62	1·21
1·000	0·055	0·864	0·539
1·000	0·027	0·540	0·295

* First-order rate constant for BHNM.

† First-order rate constant calculated from Eq. 13.

Considering the attack of hydroxide ion as well as sulphite ion, curve a in Fig. 4 should become closer to curve b. In fact, the observed first-order rate constants show fairly good agreement with the calculated ones (the last column in Table 1) from Eq. 14 by assuming that $K_2 = 3{\cdot}17 \times 10^{-14}$, $k_{OH}/k_S = 1/6$ and $k_0 = k_6K_2 = k_4K_4 = 8{\cdot}9 \times 10^{-5}$. Therefore, the pathway (ii) is excluded. On the other hand, it is difficult to distinguish between the pathway (i) and (iii). Since monomethyl ether of BHNM, which cannot give V, does not react under the same conditions, the pathway (iii) should be preferred to (i).

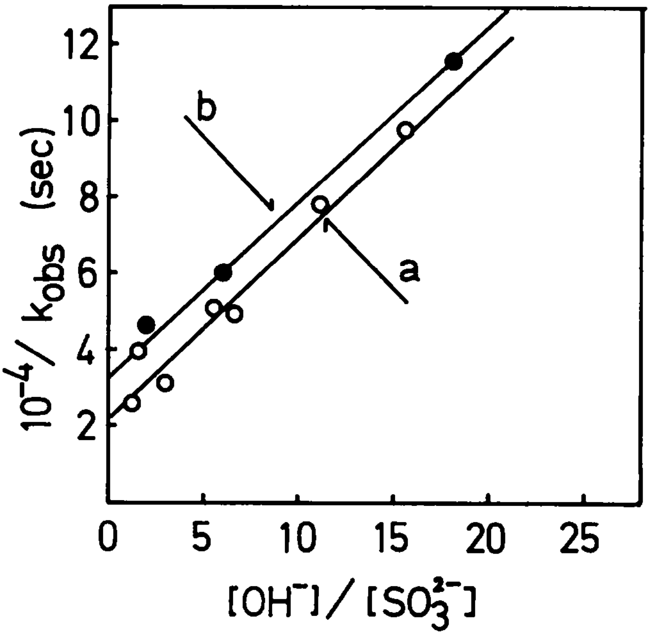


FIG. 5. Plot of $1/k_{obs}$ vs. $[OH^-]/[SO_3^{2-}]$.
(a) Initial concn.: [BHNM] = 0·050M, [NaOH] = 0·500M. (b) Initial concn.: [BHNM] = 0·050M, [NaOH] = 1·000M.

The energy of activation was calculated to be 30 kcal/mole, and the entropy of activation was 1·4 e.u. The observed entropy of activation is with those for unimolecular reaction.

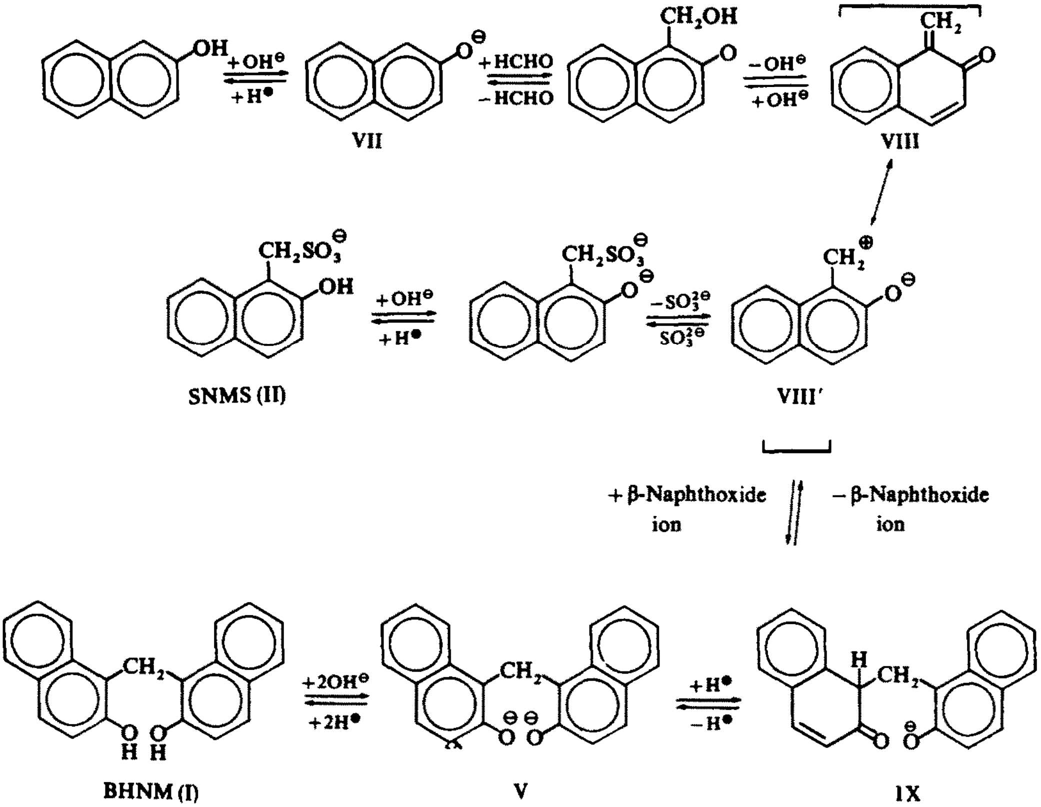
TABLE 3. THE EFFECT OF TEMPERATURE ON THE REACTION OF BHNM WITH SULPHITE IN WATER AT [BHNM] OF 0·025M, $[Na_2SO_3]$ OF 0·045M and [NaOH] OF 0·080M

Temp.	$k^* \times 10^5$ (sec^{-1})	E^a (kcal $mole^{-1}$)	$\Delta S^‡$ (eu)
95°	13·6	30·0	1·4
90°	4·36		
80°	1·46		
70°	0·411		

* First-order rate constant for BHNM.

Mechanism of the sulphomethylation

From the results and the discussion above, a probable mechanism is as follows



An important intermediate may be quinonemethide (VIII). The attacks of sulphite, β-naphthoxide, and hydroxide ions on it give SNMS (II), BHNM (I), and 1-hydroxymethyl-β-naphthol, respectively. The hydroxymethylation of phenols is well established.[13] The diarylmethanes are generally formed under acidic conditions, but those from β-naphthol can be formed under both acidic[7] and basic conditions. The difference may be ascribed to the facile formation of quinonemethide (VIII) of β-naphthol by the dissociation of hydroxyl group in an alkaline medium.

(i) No isolation of the methylol derivative of β-naphthol under these conditions suggests a rapid reaction of the methylol compound probably via the quinonemethide (VIII).

(ii) BHNM (I) reacts with aqueous alkali and sulphite to give β-naphthol and SNMS (II), which suggests the intervention of VIII, since the reaction is first-order in I.

(iii) The treatment of SNMS (II) with aqueous sodium hydroxide at 100°, and also the reduction[5] of 2-hydroxy-1-naphthaldehyde or 2-hydroxy-1-naphthoic acid with lithium aluminum hydride give BHNM (I), suggesting VIII as an intermediate.

The formation of BHNM at an early stage of the reaction of sulphomethylation of β-naphthol indicates that the rate of the attack of β-naphthoxide ion on VIII is comparable or higher than that of sulphite ion.

The dissociation of BHNM to form dianion (V) was proved by the UV spectrophotometry. The resulting dianion (V), which is unstable because of the electrostatic interaction between two anionic oxygen atoms, may convert a less restricted intermediate (IX).

Since the reaction of BHNM (I) with sulphite ion is first-order in BHNM and independent of sulphite, the rate-determining step may be the decomposition of IX to quinonemethide (VIII) and β-naphthoxide, followed by the rapid attack of sulphite or hydroxide ion to give SNMS (II) or 1-hydroxymethyl-β-naphthol. In a strongly alkaline medium, the attack of hydroxide ion is comparable to that of sulphite ion, hence it may reduce the rate of the consumption of sulphite.

The kinetic results indicate the S_N1 mechanism for the reaction of BHNM (I), i.e. BHNM (I) is not a true intermediate as reported[1b, c] but one of the by-products which can give SNMS (II).

EXPERIMENTAL

Materials

Authentic BHNM (I) was prepared from β-naphthol (1·0 g, 0·05 moles), 37% HCHO (0·8 g, 0·01 moles), and NaOH (1·0 g, 0·05 moles) in water (75 ml) at 100° with stirring for 1 hr.[5] Acidification of the mixture gave crude BHNM, 2·8 g, 93·3%; m.p. 180–181° (dec). Recrystallisation from 60% aqueous ethanol gave pure BHNM, m.p. 202–202·5° (dec), lit. 196–197°,[14] 200°,[15] 205–207°[6a] (dec). UV: $\lambda_{max}(\log \varepsilon)$; 226 mμ (5·06), 282 mμ (3·89), 294 mμ (3·88), 338 mμ (3·71) in EtOH–H_2O (3:2 in vol) lit.[16] 230 mμ (4·9), 280 mμ (4·0), 292 mμ (3·9), 338 mμ (3·7) in EtOH.

Mono- and dimethyl ethers of BHNM were prepared as follows: an aqueous solution (100 ml) of NaOH (4 g, 0·10 moles) and BHNM (15 g, 0·05 moles) was cooled at 0–2° with stirring. A half amount of dimethyl sulphate (12·6 g, 0·10 moles) was added with stirring to the solution over 30 min. The remaining dimethyl sulphate was then added to the reaction mixture and heated at 60–80°. The reaction was continued at 60–80° for 1 hr, the mixture being allowed to cool and filtered. The precipitate was washed with ether and recrystallised from EtOH–H_2O. After the first crop [monoethyl ether (5·2 g, 33%), m.p. 137–142° (lit.[11] 142°)] had been filtered, the second crop [dimethyl ether 4·4 g (27%)] was precipitated, m.p. 144–145° (lit.[17] 144–147°).

Sodium sulphite, sodium hydroxide, iodine, and sodium thiosulphate were of guaranteed reagent grade.

The preparation of SNMS (II)

37% HCHO (10·3 g, 0·125 moles), $Na_2SO_3 \cdot 5H_2O$ (31·5 g, 0·25 moles), and β-naphthol (18 g, 0·125 moles) were dissolved in water (125 ml). The reaction mixture was heated at 90° with stirring for 4 hr. After ca. 5 min, the mixture became thick sludge of needles (A), and then it dissolved within 30 min. After the reaction had been completed, the mixture was allowed to cool and acidified with cold dil H_2SO_4. Precipitate was filtered off and washed with water and then with ether. Recrystallisation from 50% EtOH gave pure II, 17·5 g (54·3%).

Identification of needles (A)

(A) was taken out of the reaction mixture and purified by recrystallisation; m.p. [200–201° (dec)] and UV spectra [226, 282, 294 and 338 mμ in EtOH–H_2O (3:1 in vol)] agreed with these of authentic BHNM.

Reaction of BHNM

BHNM (6 g, 0·02 moles) and $Na_2SO_35H_2O$ (10 g, 0·04 moles) were added to water (75 ml), and heated at 90° with stirring for 10 hr, but the starting material was completely recovered.

On the other hand, BHNM (15 g, 0·05 moles) and $Na_2SO_35H_2O$ (12·6 g, 0·05 moles) were dissolved in aqueous solution (100 ml) of NaOH (4 g, 0·10 moles) and heated at 90° for 4 hr. The mixture was allowed to cool, acidified with dil H_2SO_4 and filtered. SNMS (II) 4·3 g. In the absence of $Na_2SO_35H_2O$, BHNM (6 g, 0·02 moles) and NaOH (2·0 g, 0·05 moles) in water (75 ml) was heated at 100° with stirring for 6 hr.

Pale yellow resinous material was obtained by filtering the hot reaction mixture. This material did not dissolve in hot aqueous alkali. After acidification of the filtrate, the precipitate was obtained. A small amount of red amorphous material and β-naphthol was extracted with hot water. IR spectra confirmed the presence of C=O (1720 cm^{-1}) in this red product.

Attempted reaction of mono- and dimethyl ethers of BHNM with sodium sulphite

Monomethyl ether (2 g, 0·0064 moles) and $Na_2SO_35H_2O$ (10 g, 0·04 moles) were added to aqueous NaOH (2·0 g, 0·05 moles, 50 ml), and heated at 95° with stirring for 8 hr, but monomethyl ether was quantitatively recovered.

Dimethyl ether (3·3 g, 0·01 moles) and anhydrous K_2SO_3 (1·6 g, 0·01 moles) were added to aqueous dimethylformamide (5:8 in vol, 100 ml), and the mixture was heated at 100° for 5 hr, but the reactant was quantitatively recovered; BHNM reacted with K_2SO_3 as Na_2SO_3 under these conditions.

Preparation of sodium-salt of BHNM and titration of BHNM[18]

BHNM (6 g, 0·02 moles) was dissolved in boiling water (20 ml) containing NaOH (4 g, 0·1 moles). The mixture was cooled in an ice bath for 1 day. Platelet crystals of sodium salt of BHNM were obtained.

A $3{\cdot}77 \times 10^{-3}$ BHNM solution in $EtOH–H_2O$ (3:2 in vol) and a 0·0905N aqueous NaOH solution were prepared. Excess aqueous HCl was poured into the BHNM solution (50 ml). The solution was immersed in a thermostat at 30°. After the thermal equilibrium had been reached, the solution was titrated with NaOH. For the measurement of pH, a Hitachi–Horiba pH meter model M4 was used. The difference between the curve of sample and that of blank showed that the consumed alkali by BHNM ($3{\cdot}62 \times 10^{-3}$N) was equivalent to the existing BHNM.

$1{\cdot}00 \times 10^{-5}$M BHNM solutions ($EtOH–H_2O$, 3:2 in vol) containing various concentrations of NaOH were prepared, and their UV spectra were measured by a Shimadzu UV spectrophotometer type SV50A.

Rate measurements

A solution (5 ml) of Na_2SO_3 $5H_2O$ was pipetted into an aqueous solution of BHNM (20 ml) containing various concentrations of NaOH under nitrogen atmosphere in ampoules which had reached a thermal equilibrium in a thermostat. Sampling was preformed by removing ampoules from the thermostat. In order to stop the reaction, the sample (10 ml) was diluted with water (30 ml) and was acidified with cold acetic acid (1 ml). The sulphite concentration was determined by iodometry.

The reaction of SNMS (II)

An aqueous solution (20 ml) of SNMS (3 g, 0·01 moles) and NaOH (2 g, 0·05 moles) was refluxed. The mixture was allowed to cool and acidified with cold dil H_2SO_4, and then filtered off. The recrystallisation from $EtOH–H_2O$ gave BHNM (0·2 g, 13·3% based on SNMS added). SNMS was recovered from the filtrate (1·8 g, 60%).

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