# The Interaction of *N*-Bromo-*N*-sodiobenzenesulphonamide (Bromamine B) with *p*-Nitrophenoxide Ion

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By using the interaction with *p*-nitrophenol as a mechanistic probe it has been established that solutions of *N*-bromo-*N*-sodiobenzenesulphonamide (bromamine B) in dilute alkali contain two reactive brominating species, the conjugate acid ($PhSO_2NHBr$) and hypobromous acid; formation of the latter can be suppressed by the addition of the parent sulphonamide. These solutions are fully described by a system of four equilibria: three are proton transfer reactions, for which $pK_a$ values have been obtained, and the fourth is the alkaline hydrolysis of the conjugate acid, for which an equilibrium constant has been estimated from model experiments with sodium 3-(*N*-bromophenylsulphonamido)propanesulphonate. These data have been used to establish a species distribution diagram and the predictive value of this has been tested.

THE chemistry of *N*-chloro-*N*-sodiosulphonamides in aqueous solution is reasonably well understood. Recent kinetic studies have established that the reactivity of weakly alkaline solutions of *N*-chloro-*N*-sodiotoluene-*p*-sulphonamide (chloramine T) towards *p*-cresol,[1] succinimide,[2] and sulphides [3,4] is due to the presence of the conjugate acid, $p$-$MeC_6H_4SO_2NHCl$, and/or the disproportionation product, $p$-$MeC_6H_4SO_2NCl_2$; hypochlorite was not implicated. Both the dissociation [5] and disproportionation [6,7] constants for *N*-chlorotoluene-*p*-sulphonamide have been measured. Surprisingly, almost no information is available on the composition and properties of corresponding solutions of the *N*-bromo-*N*-sodiosulphonamides.

We are interested in the potential of *N*-halogenosulphonamide ion as a nucleophile in aqueous solution and have recently described the reactions of the *N*-chloro-species with ethylene oxide and propanesultone.[8] As essential groundwork for an extension of our nucleophilicity studies to *N*-bromosulphonamide ion it was decided to investigate the composition of aqueous alkaline solutions of an *N*-bromo-*N*-sodiosulphonamide using some convenient organic substrate as a kinetic probe. This work is described in the present paper.

## EXPERIMENTAL

*Reagents.*—Reagents used were of the highest grade commonly available. *p*-Nitrophenol and toluene-*p*-sulphonamide were crystallised from toluene and aqueous ethanol (50%), respectively, before use. Bromamine B (1) was prepared from the sulphonamide, bromine, and aqueous sodium hydroxide by a published procedure.[9] Repeated recrystallisation from dilute aqueous sodium hydroxide ($10^{-3}$N) and drying *in vacuo* ($P_2O_5$) gave the sesquihydrate (Found: C, 25·55; H, 2·8; av. Br, 55·55; N, 5·05. Calc. for $C_6H_5BrNNaO_2S,1{\cdot}5H_2O$: C, 25·25; H, 2·85; av. Br, 56·15; N, 4·9%). The three *p*-substituted *N*-bromosulphonamides examined in this study were prepared and purified in similar fashion.

*Kinetic Measurements.*—The reaction vessel and pH-stat equipment have been described previously.[10] Experiments were performed at both 25 and 35° (±0·05°) and the ionic strength was adjusted to 0·1 with sodium chloride (blank experiments confirmed the absence of specific chloride ion effects). *N*-Bromo-*N*-sodiobenzenesulphonamides, substituted benzenesulphonamides, and *p*-nitrophenol concentrations were in the ranges $6 \times 10^{-3}$—$1{\cdot}2 \times 10^{-2}$, $2 \times 10^{-4}$—$2 \times 10^{-2}$, and $3 \times 10^{-2}$—$1{\cdot}5 \times 10^{-1}$M, respectively. pH Values (9·50—11·00) were maintained by automatic addition of sulphuric acid (0·2N). Reactions were followed for 3—4 half-lives and the extent of reaction was estimated by monitoring available bromine concentration iodometrically.

*Product Analysis.*—Authentic samples of 2-bromo-4-nitrophenol and 2,6-dibromo-4-nitrophenol were prepared by reaction of *p*-nitrophenol with dioxan dibromide [11] and bromine in acetic acid,[12] respectively: the corresponding methyl ethers were obtained by treatment with diazomethane in ether.

The product from the reaction of the parent *N*-bromosulphonamide ($6 \times 10^{-3}$M) with *p*-nitrophenol ($6 \times 10^{-2}$M) at pH 11 was extracted with ether and methylated with diazomethane. The methyl ethers were analysed by g.l.c. (10% Apiezon L; 210°; thermal conductivity detector) and preparative t.l.c. [Kieselgel G; benzene–light petroleum (1 : 1)]. Recovery from thin-layer chromatograms was virtually quantitative and the recovered compounds were identified by comparison (mixed m.p.; i.r.) with the authentic methyl ethers.

*Epoxidation of 1,3-Diphenylpropenone.*[13]—(i) To a solution of 1,3-diphenylpropenone (0·1 g, $5 \times 10^{-4}$ mol) in pyridine (2 ml) was added dropwise with stirring a solution of freshly prepared sodium hypochlorite [14] (1·53 ml, $2{\cdot}4 \times 10^{-3}$ mol). After 1 h, the solution was extracted with ether, dried ($Na_2SO_4$), and evaporated to dryness. Crystallisation of the residue from ethanol afforded the required epoxide, 1,3-diphenyl-2,3-epoxypropan-1-one (3), m.p. 88—90° (90%).

(ii) The foregoing was repeated using aqueous sodium

[1] T. Higuchi and A. Hussain, *J. Chem. Soc.* (*B*), 1967, 549.
[2] T. Higuchi, K. Ikeda, and A. Hussain, *J. Chem. Soc.* (*B*), 1968, 1031.
[3] K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Japan*, 1969, **42**, 2631.
[4] F. Ruff and A. Kucsman, *Acta Chim. Acad. Sci. Hung.*, 1969, **62**, 438.
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[7] F. G. Soper, *J. Chem. Soc.*, 1924, 1899.
[8] F. E. Hardy, *J. Chem. Soc.* (*B*), 1971, 1899.
[9] E. Roberts, *J. Chem. Soc.*, 1923, 2707.
[10] F. E. Hardy and P. Robson, *J. Chem. Soc.*, 1967, 1151.
[11] L. A. Yanovskaya, A. P. Terentev, and L. I. Belenkii, *J. Gen. Chem.* (*U.S.S.R.*), 1952, **22**, 1594.
[12] W. W. Hartman and J. B. Dickey, *Org. Synth.*, 1948, **2**, 173.
[13] S. Marmor, *J. Org. Chem.*, 1963, **28**, 250.
[14] F. E. Hardy, *J. Chem. Soc.* (*C*), 1970, 2087.

hypobromite in place of sodium hypochlorite. The epoxide (3) (identity established by mixed m.p., i.r., and t.l.c.) was isolated in 50% yield by preparative t.l.c.

(iii) The foregoing was repeated using an aqueous solution of bromamine B at pH 10 in place of sodium hypochlorite. No epoxide was formed even after 24 h as judged by t.l.c. analysis. A material, which was more mobile on t.l.c. than either the starting enone or the anticipated epoxide product, was formed but was not characterised.

p$K_a$ *Determination.*—(i) *Disproportionation studies.* The approach used was similar to that of Higuchi *et al.*[6] The very rapid disproportionation reaction of bromamine B was followed by means of a Durrum–Gibson stopped-flow u.v. spectrophotometer. In a typical experiment, the pH of a solution of bromamine B ($4 \times 10^{-4}$M) at pH 7 (25° ± 0·1°) was (within 2 ms) reduced to 2·2 with perchloric or sulphuric acid and the change in absorbance at 250 nm was followed. Equilibrium was re-established within *ca.* 10 s. The experiment was repeated on further samples of this solution containing differing amounts of benzenesulphonamide. The use of hydrochloric acid resulted in complications, with two processes being observed on 20 ms and 2 s time scales.

(ii) *Titration studies.* Solutions of bromamine B ($1·25 \times 10^{-3}$M) in conductivity water were titrated potentiometrically with 0·1N-acid, the pH after each addition being measured by means of the pH meter of a Radiometer TTT1 titrator equipped with glass and saturated potassium chloride electrodes. In some experiments addition and pH measurement proceeded and were recorded automatically.

*Sodium 3-(N-Bromophenylsulphonamido)propanesulphonate* (4).—(i) *Synthesis.* The corresponding *N*-chlorosulphonamide (60 g) (prepared by reaction of *N*-chloro-*N*-sodiobenzenesulphonamide with propanesultone [8]), was dissolved in water (500 ml) at 35° and sodium bromide (20 g) was added. The solution was stirred at 35° for 15 min and then concentrated *in vacuo*. On cooling, the required N-*bromosulphonamide* (4) (51 g) crystallised; this material was recrystallised from water (Found: C, 27·45; H, 3·35; N, 3·55. $C_9H_{11}BrNNaO_5S_2,H_2O$ requires C, 27·15; H, 3·25; N, 3·5%). It was shown to be free from *N*-chloro-compounds by the method of Farkas and Lewin.[15]

(ii) *Hydrolysis.* As a preliminary, the extinction coefficient of hypobromite ion was accurately determined and found to be 311·6 at 332 nm [both hypobromite ion and the *N*-bromosulphonamide (4) obeyed Beer's law in the required concentration range [16]]. The absorbance at 332 nm of solutions of the *N*-bromosulphonamide (4) ($7·5 \times 10^{-3}$M), was measured at various pH values between 7 and 11·2. The pH was accurately determined before and after the absorbance measurements.

*Spectroscopic Measurements on Bromamine B at High Alkalinity.*—The absorbance of freshly prepared solutions of bromamine B ($7·55 \times 10^{-3}$M) in aqueous sodium hydroxide (3·45 and 5·18M) was measured at 332 nm. Hypobromite ion concentrations ($x$) were calculated from expression (1) where $A_2$ is the absorbance of the solution,

$$\Delta A = A_2 - A_1 = (\varepsilon_{OBr^-} - \varepsilon_{PhSO_2NBr^-})x \qquad (1)$$

$A_1$ the absorbance of a similar solution in dilute alkali (constant), $\varepsilon_{OBr^-} = 311·6$, and $\varepsilon_{PhSO_2NBr^-} = 40·5$. The sodium hydroxide concentrations were converted to activities (and hence pH values) and the resultant data were plotted in Figure 2.

## RESULTS AND DISCUSSION

For this mechanistic study, aromatic *N*-bromo-*N*-sodiosulphonamides were chosen in preference to their aliphatic counterparts on the basis of their higher stability and crystallinity which facilitated purification.[14] Preliminary experiments revealed that *p*-nitrophenol would make a suitable kinetic probe for the processes occurring in alkaline solutions of bromamine B (1). Thus, a 1 : 1 stoicheiometry was established for the interaction by both g.l.c. and t.l.c., with 2-bromo-4-nitrophenol being the major phenolic product (>95% of total) when a nine-fold excess of *p*-nitrophenol was

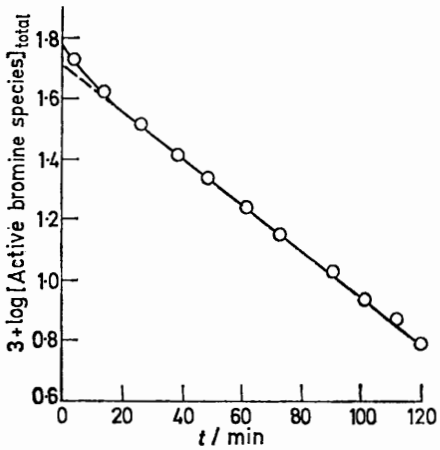



FIGURE 1 First-order plot of the kinetic data for the reaction of bromamine B with *p*-nitrophenol at pH 10·95 and 25°

employed. Furthermore, the rate of reaction fell comfortably within the range of the measuring devices available. A similar approach has been used previously [17] in a study of the alkaline hydrolysis of *N*-chloro-*N*-methylbenzamides.

$PhSO_2NBrNa$
(1)

Kinetic investigations were carried out mainly at 25°, under pH-stat conditions (pH range 10—11), with a large excess of *p*-nitrophenol. First-order plots of the kinetic data for the disappearance of active bromine species showed an initial curvature before linearity was achieved (Figure 1). The extent of the curvilinear section was reduced when benzenesulphonamide was added to the reaction mixture until, with sulphonamide concentrations approaching that of the *N*-bromosulphonamide, it disappeared altogether leaving a good linear plot to 3—4 half-lives.

Further kinetic studies revealed linear relationships between the pseudo-first-order rate constant

[15] L. Farkas and M. Lewin, *Analyt. Chem.*, 1947, **19**, 662.
[16] M. W. Lister and P. E. McLeod, *Canad. J. Chem.*, 1971, **49**, 1987.
[17] M. L. Burstall, M. S. Gibson, J. S. Grieg, B. McGhee, and D. G. Stewart, *J. Chem. Soc.*, 1960, 3717.

($k_{obs}$) and *p*-nitrophenol concentration and between $1/k_{obs}$ and hydroxide ion concentration (Table 1), thus establishing the rate expression (2) where [NBr]

$$-d[NBr]/dt = k_1([NBr][PNP])/[OH^-] \quad (2)$$

is the total concentration of active bromine-containing species and [PNP] represents the concentration of

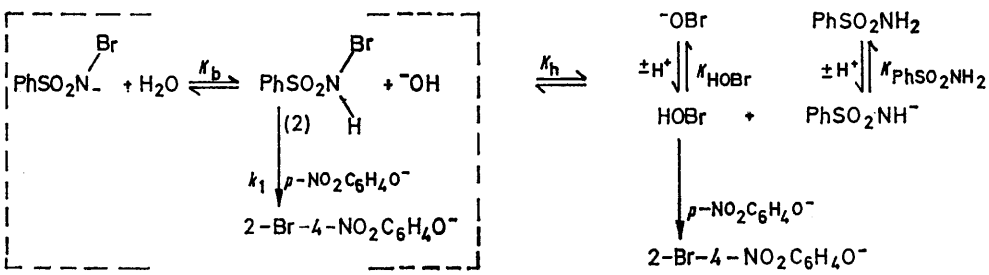
TABLE 1

Effect of alkalinity on the rate of interaction of bromamine B with *p*-nitrophenol at 25°

| pH | $10^4 k_{obs}/s^{-1}$ [a] | $10^5[OH^-]/M$ | $10^{-2}k_{obs}^{-1}/s$ [b] |
|---|---|---|---|
| 9·50 | 63·7 ± 5 [c] | 4·17 | 1·57 |
| 9·97 | 22·4 ± 0·6 | 12·3 | 4·46 |
| 10·30 | 10·6 ± 0·1 | 26·3 | 9·43 |
| 10·50 | 6·90 ± 0·05 | 41·7 | 14·5 |
| 10·70 | 4·65 ± 0·07 | 66·1 | 21·5 |
| 10·80 | 3·57 ± 0·03 | 83·2 | 28·0 |
| 10·90 | 2·77 ± 0·02 | 105 | 36·1 |
| 10·95 | 2·80 ± 0·03 | 118 | 35·7 |
| 11·00 | 2·42 ± 0·02 | 132 | 41·3 |

[a] Experiments were performed with $6 \times 10^{-2}$M-*p*-nitrophenol in the presence of benzenesulphonamide ($10^{-2}$M). [b] A plot of $1/k_{obs}$ *vs.* [OH⁻] is linear, slope 3·36 ± 0·10 × $10^6$ l mol$^{-1}$ s$^{-1}$. [c] Standard deviations.

*p*-nitrophenol. The foregoing data can be rationalised in terms of Scheme 1. The mechanistic features which

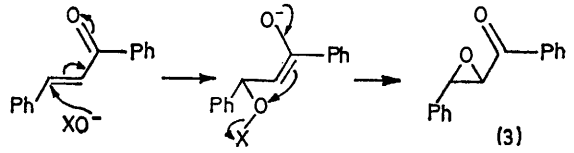



SCHEME 1

dominate the kinetics appear in brackets, *viz.*, a rapid protonation of the *N*-bromosulphonamide ion followed by a rate-determining bromination of *p*-nitrophenoxide ion. The initial deviations from linearity of the first-order plots of disappearance of active bromine species are explicable in terms of hydrolysis of the conjugate acid (2) to hypobromous acid which also serves to brominate *p*-nitrophenoxide. It is to be expected that this second contribution to the bromination will decrease in importance as the reaction proceeds and the concentration of sulphonamide increases, becoming insignificant when the reaction is performed in the presence of excess of sulphonamide.

Efforts were made to find unambiguous evidence for the presence of hypobromite in alkaline solutions of bromamine B; both trapping and spectroscopic techniques were applied. The former approach stemmed from the knowledge that sodium hypochlorite reacts with αβ-unsaturated ketones to produce epoxides [13] (Scheme 2). Here, model experiments showed that sodium hypobromite behaved in the same way. Thus, by use of this reaction, hypobromite should, in principle, be easily differentiated from any other active bromine-containing species in the system. However, attempts to isolate epoxide (3) from the interaction of bromamine B with 1,3-diphenylpropenone under a variety of weakly basic conditions met with failure. This result was in accord with the kinetic data which suggested that the overall contribution of hypobromite to the reactivity of bromamine B in dilute alkaline solution (pH 10—11) was extremely small. U.v. spectroscopy also failed to detect the presence of hypobromite ($\lambda_{max.}$ 332·5 nm) in such solutions but a positive response was obtained at high alkalinity: quantitative aspects of this work are discussed later.

The influence of *para*-substituents on the reactivity of bromamine B was also examined. Remarkably small substituent effects were observed which showed no Hammett correlation (see Table 2). This insensitivity of the rate of bromination to aryl substitution can easily be rationalised in terms of the suggested mechanism. Thus, it is apparent that any change in the reactivity of the N–Br bond of the conjugate acid will be parallelled by a similar change in the reactivity of the N–H bond. The result is that in the case of an electro-negative substituent, for example, the greater reactivity of the substituted conjugate acid when compared to the parent is offset by its lower concentration.[18]




SCHEME 2

Once the basic mechanism had been established further work was aimed at evaluating the equilibrium constants

TABLE 2

Effect of aryl substituents on the rate of interaction of bromamine B with *p*-nitrophenol [a]

| Substituent | Mean $10^4 k_{obs}/s^{-1}$ | Hammett σ value |
|---|---|---|
| *p*-Me | 4·98 ± 0·03 [b] | −0·17 |
| *p*-H | 4·35 ± 0·03 | 0 |
| *p*-Br | 5·02 ± 0·05 | 0·23 |
| *p*-$NO_2$ | 4·95 ± 0·05 | 0·78 |

[a] Experiments were performed at 35° and pH 10·95 with $6 \times 10^{-2}$M-*p*-nitrophenol in the presence of sodium chloride (0·1M) and the appropriate sulphonamide ($10^{-2}$M). [b] Standard deviations.

[18] W. P. Jencks, 'Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969, p. 480.

$K_b$ and $K_h$ and the second-order rate constant $k_1$; values for $K_{PhSO_2NH_2}$ and $K_{HOBr}$ were already available in the literature.[19,20] $K_b$ Is, of course, related to the dissociation constant ($K_a$) of the conjugate acid (2) by $K_b = K_w/K_a$. In parallel with *N*-chloro-*N*-sodiotoluene-*p*-sulphonamide (chloramine T) it was anticipated that measurement of the dissociation constant would be complicated by the occurrence in acid solution of a disproportionation reaction [reactions (3) and (4)].

$$PhSO_2NHBr\ (2) \overset{K_a}{\rightleftharpoons} PhSO_2NBr^- + H^+ \quad (3)$$

$$2PhSO_2NHBr \overset{K_d}{\rightleftharpoons} PhSO_2NH_2 + PhSO_2NBr_2 \quad (4)$$

This disproportion was followed spectrophotometrically by acidifying a neutral solution of bromamine B (1) to pH 2·2 and determining the total change in absorbancy at 250 nm.[6] Because of the high reactivity of the *N*-bromo-species it was necessary to employ a stopped-flow technique. (In preliminary experiments using chloramine T it had been shown that the stopped-flow method gave $K_d$ values in good agreement with published data,[6] *viz.*, 0·058 at 25°.) Absorbancy changes in experiments with sulphuric and perchloric acids were similar and on analysis led to a value of 0·113 for $K_d$. However, the behaviour in hydrochloric acid was much more complex, with two distinct processes being observed. The absorbance changes associated with the faster process were in accord with it being the disproportionation and the increased rate of equilibration (*ca.* 100×) suggested a chloride catalysis [reactions (5) and (6)]. The nature of the slower process is unclear

$$PhSO_2NHBr + Cl^- \rightleftharpoons PhSO_2NH^- + ClBr \quad (5)$$

$$ClBr + PhSO_2NBr^- \rightleftharpoons PhSO_2NBr_2 + Cl^- \quad (6)$$

but possibly involves *N*-chlorosulphonamide species.

Once $K_d$ was known, the dissociation constant was derived from potentiometric titration data using equation (7).[5]

$$K_a = (1 + 2\sqrt{K_d})\left[\frac{[H^+](B - A + [H^+])}{A - [H^+]}\right] \quad (7)$$

where $B$ is the initial concentration of bromamine B, $[H^+]$ represents the measured hydrogen ion concentration, and $A$ is the concentration of acid added. By this method an acceptable value of 4·95 was obtained for the p$K_a$ of the conjugate acid (2) (*cf.* p$K_a$ 4·55 for chloramine T [5]) and hence $K_a$ is $8{\cdot}18 \times 10^{-10}$.

Since the alkaline hydrolysis of the conjugate acid (2) could not be studied in isolation from dissociation and disproportionation it was decided to examine the hydrolysis of an *N*-alkyl-*N*-bromobenzenesulphonamide as a model for this process. Although the electronic and steric influence of such an alkyl group will clearly differ from those of a hydrogen atom, it was reasoned that these differences would affect formation and hydrolysis reactions to a similar degree and thus the equilibrium constant ($K_h'$) should provide a good approximate value for $K_h$.

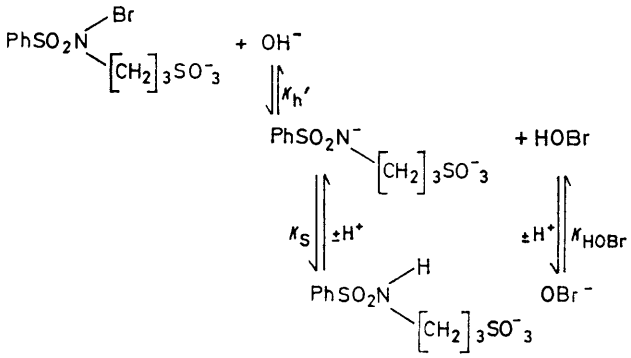
The particular compound chosen for study was the 3-sulphopropyl derivative (4) which is stable, crystalline, and freely water-soluble. Potentiometric titration [21]

$$PhSO_2NX{\cdot}[CH_2]_3{\cdot}SO_3Na \quad (4)\ X = Br \quad (5)\ X = H$$

of the *N*-alkylsulphonamide (5) provided a value of $5{\cdot}0 \times 10^{-12}$ for the acid dissociation constant $K_S$. Hypobromite ion concentrations were measured spectrophotometrically over a range of pH [in some experiments known concentrations of the *N*-alkanesulphonamide (5) were added to the system] and $K_h'$ values were calculated using the equation (8) where $a$ is the

$$K_h' = \frac{\left[\frac{K_S(b + x)}{K_S + [H^+]}\right]\left[\frac{x[H^+]}{[H^+] + K_{HOBr}}\right]}{(a - x)[OH^-]} \quad (8)$$

initial concentration of the *N*-bromo-species, $b$ is the concentration of added sulphonamide, and $x$ represents




SCHEME 3

TABLE 3

The alkaline hydrolysis of sodium 3-(*N*-bromophenylsulphonamido)propanesulphonate [a]

| pH | $\Delta A$ | $10^3$[OBr$^-$]/ M | Concentration of added sulphonamide/ M | $10^3K_h'$ |
|---|---|---|---|---|
| 10·19 | 0·32 | 1·31 | | 4·04 |
| 10·70 | 0·565 | 2·30 | | 4·10 |
| 11·16 | 0·985 | 4·02 | | 4·65 |
| 10·98 | 0·495 | 2·02 | $3{\cdot}75 \times 10^{-3}$ | 3·82 |
| 10·98 | 0·245 | 1·00 | $1{\cdot}5 \times 10^{-2}$ | 4·42 |
| | | | Mean | 4·21 ± 0·40 [c] |

[a] The *N*-bromo-species concentration was $7{\cdot}5 \times 10^{-3}$M. [b] $\Delta A$ Is the increase in absorbance at 332 nm on basifying an aqueous solution of the *N*-bromosulphonamide and is related to [OBr$^-$] by the equation [OBr$^-$] = $\alpha\Delta A$ where $\alpha$ is the reciprocal of the difference between the extinction coefficients of hypobromite ion and the *N*-bromo-species. [c] 95% Confidence limits.

the combined concentrations of hypobromous acid and hypobromite ion. A mean value for $K_h'$ of $4{\cdot}21 \times 10^{-3}$ was obtained (see Scheme 3 and Table 3).

[19] C. M. Kelly and H. V. Tarter, *J. Amer. Chem. Soc.*, 1956, **78**, 5752.

[20] A. V. Willi, *Helv. Chem. Acta*, 1956, **39**, 46.

[21] 'Physical Methods of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 1960, vol. 4, p. 2953.

With values for $K_b$, $K_h'$, $K_{PhSO_2NH_2}$, and $K_{HOBr}$, it was possible to predict the equilibrium concentrations of conjugate acid (2), hypobromous acid, and hypobromite ion in alkaline solutions of bromamine B.

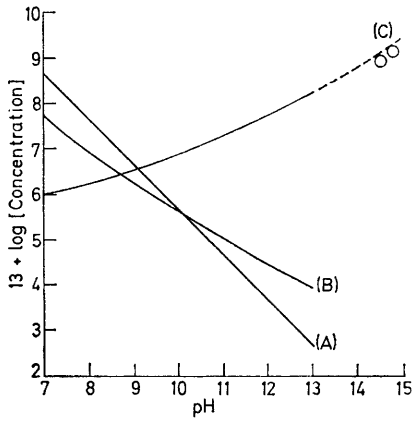



FIGURE 2 Calculated pH dependence of concentrations of conjugate acid ($PhSO_2NHBr$) (A), hypobromous acid (B), and hypobromite ion (C) in aqueous bromamine B ($6 \times 10^{-3}$M). Two determinations of hypobromite ion concentration are included

The necessary calculations were performed for a $6 \times 10^{-3}$M solution in the pH range 7—13 and the results are presented in Figure 2. The concentrations of both the conjugate acid and hypobromous acid are seen to decrease with increasing pH whilst the concentration of hypobromite ion increases. As mentioned earlier, it was observed during u.v. spectroscopic examination of bromamine B that, in more concentrated alkali (>1M) absorption at 332 nm due to hypobromite ion reached measurable proportions. Two determinations were performed and the resultant hypobromite concentrations are included in Figure 2 (pH was calculated using published values for the activity of hydroxide ion). It may be seen that these points lie close to an extrapolation of the curve describing the hypobromite concentration *vs.* pH relation.

The second-order rate constant ($k_1$) for the interaction of the conjugate acid (2) with *p*-nitrophenoxide was obtained from a plot of the $1/k_{obs}$ *vs.* $[OH^-]$ data given in Table 1. By applying the stationary state approximation to the conjugate acid it can be shown that equation (9) obtains where $k_b$ is the rate constant for interaction

$$1/k_{obs} = [OH^-]/k_1K_b[PNP] + 1/k_1[PNP] + 1/k_b \quad (9)$$

of bromamine B with water and thus the slope of the above plot will be $1/k_1K_b[PNP]$. In this way, a slope of $3{\cdot}36 \times 10^6$ leads to a value of $9{\cdot}88 \times 10^3$ l mol$^{-1}$ s$^{-1}$ for the rate constant for bromination ($k_1$).

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