

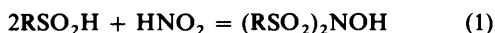
Kinetics and Mechanism of the Reaction of Benzenesulphonic Acid with Nitrous Acid

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Rate measurements on the reaction between benzenesulphonic acid (BSA) and nitrous acid over a range of acidity, show that reaction occurs rapidly *via* both the neutral acid molecule of BSA and its anion. The latter process is the faster, as expected: reaction takes place with the positive nitrosating species (H_2NO_2^+ or NO^+) at the diffusion rate. The first-order dependence on $[\text{BSA}]$ shows that the first stage, in which the intermediate nitrosobenzenesulphinic acid is formed, is rate-limiting; the intermediate then reacts with another BSA molecule (or its anion) to yield the hydroxylamine derivative as the final product. Catalysis by Cl^- , Br^- , SCN^- , and $\text{SC}(\text{NH}_2)_2$ was found, and the bimolecular rate constants for attack by NOCl etc. on both BSA and its anion form, were extracted by a kinetic analysis of the variation of the rate constant with acidity in the presence of Cl^- , Br^- , or SCN^- . Again the sulphinate anion is the more reactive, and the sequence $\text{NOCl} > \text{NOBr} > \text{NOSCN}$ was established; the rate of reaction of NOCl is close to that calculated for the diffusion limit.

Sulphonic acids particularly in their anionic forms are well known examples of *S*-nucleophiles,¹ reacting with alkyl halides, carbonyl compounds, alkenes, aromatic systems, etc. Their reactions with nitrous acid to give *N,N*-bis(alkyl or arylsulphonyl)hydroxylamines [equation (1)] have been known for



preparative purposes for a long time,² and have been used for characterisation of a long-chain aliphatic sulphonic acid.³ More recently⁴ a number of such derivatives have been prepared and their reactions studied, in particular in an attempt to generate neutral analogues of Fremy's radical ion by oxidation.

On the face of it the reaction with nitrous acid appears to be an example of a *S*-nitrosation in which the first-formed *S*-nitroso species reacts further to give the disubstituted hydroxylamine derivative. *S*-Nitrosation reactions are relatively uncommon in comparison with *N*-, *C*-, and *O*-nitrosations, but a number of examples have been reported and in some cases the kinetics have been measured and mechanisms established. The very rapid reaction between thiourea (and its methyl derivatives) and nitrous acid, particularly at higher acidities, is now well established;⁵ the first-formed product is a rather unstable *S*-nitrososulphonium ion. Thiols rapidly form thionitrites, and a number of substrates have been examined mechanistically.^{6,7} Most thionitrites are quite unstable, but a few have been well characterised.⁸ In general it appears that *S*-nitrosation takes place very readily, and is essentially irreversible (in contrast to *O*-nitrosation⁹) and not significantly affected by *S*-protonation. There is a developing interest in this area, e.g. in the involvement of *S*-nitroso species as catalysts in nitrosation and diazotisation,¹⁰ and also in the biological field where it is believed¹¹ that thionitrites formed by *in vivo* nitrosation of thiols are involved as active intermediates in the vasodilatory effects of organic nitrites (and nitrates), sodium nitrite, the nitroprusside anion, and nitric oxide.

It seemed to us of value to establish the mechanism of the nitrosation of sulphonic acids, particularly with regard to the nature and reactivity of any intermediate, and also with reference to the possible usefulness of sulphonic acids generally as traps for nitrous acid. In this connection it seems that water-soluble sulphonic acids might be particularly suitable if reaction is rapid and irreversible.

Results and Discussion

We have measured the rate constants for the nitrosation of benzenesulphonic acid (BSA) in water at 25 °C over the following concentration ranges, $[\text{HNO}_2]$ $(1-2) \times 10^{-3}\text{M}$, $[\text{BSA}]$ $(2-5) \times 10^{-2}\text{M}$, $[\text{HClO}_4]$ 0.05–2.0M. Under these conditions good first-order behaviour was found in each individual kinetic run, and the first-order rate constant was unchanged upon doubling the initial nitrous acid concentration. Reaction was also strictly first-order in $[\text{BSA}]$, i.e. the total stoichiometric concentration of substrate for the kinetic runs measured both at 360 nm (disappearance of nitrous acid) and at 260 nm (appearance of product). The collected results are given in Table 1. Values of $[\text{H}^+]$ represent free $[\text{H}^+]$ after allowance is made for the protonation of NO_2^- (complete) and PhSO_2^- (partial) since both were added as sodium salts. There is no evidence of reversibility in the reaction and the hydrogen ion catalysis, although marked, is not strictly first-order. A plot of the first-order rate constant k_0 vs. $[\text{H}^+]$ (Figure 1) shows linear behaviour above ca. 0.06M (but with a positive intercept), but is distinctly curved at lower acidities. This behaviour can readily be accounted for if it is assumed that reaction occurs *via* both the neutral acid form PhSO_2H (HA) and the sulphinate anion PhSO_2^- (A^-). The acid dissociation constant K_a of the former is taken¹² as 0.0145, although other values have been quoted in the earlier literature. The first-order dependence upon $[\text{HNO}_2]$ eliminates any reaction pathway involving N_2O_3 as the active nitrosating species, and given the hydrogen-ion catalysis, is consistent with reaction *via* H_2NO_2^+ or NO^+ . It has not been established¹³ which is the effective species in these acid concentrations; we will assume the former in the remainder of this discussion, although the choice is not important in the context of this paper. The overall rate of reaction (defined by $-\text{d}[\text{HNO}_2]/\text{d}t = k_0[\text{HNO}_2]$) is given by equation (2). Application of the protonation equilibrium for HA

$$\text{rate} = k_1[\text{H}^+][\text{HA}][\text{HNO}_2] + k_2[\text{H}^+][\text{A}^-][\text{HNO}_2] \quad (2)$$

leads to equation (3) as the expression for k_0 when $[\text{HA}] \gg$

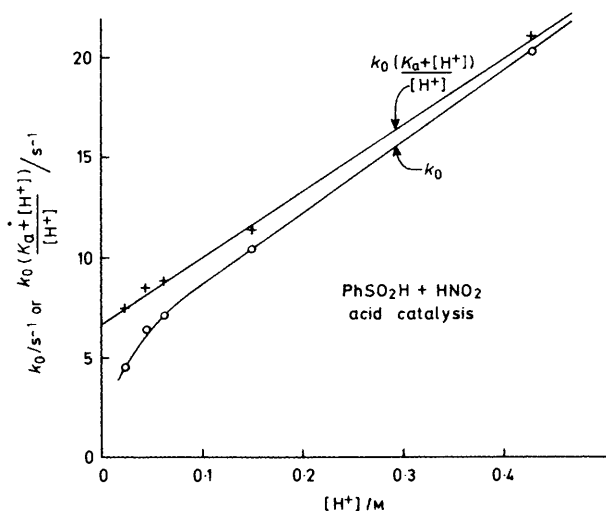
$$k_0 = (k_1[\text{H}^+]^2 + k_2K_a[\text{H}^+])[\text{HA}]_0 / (K_a + [\text{H}^+]) \quad (3)$$

$[\text{HNO}_2]$, and where K_a is the dissociation constant of BSA and $[\text{HA}]_0$ the total substrate concentration. It is easy to see that

Table 1. Values of k_0 for the nitrosation of BSA in water at 25 °C^a

[BSA] ₀ /M	[H ⁺]/M	k_0^{260}/s^{-1} ^b	k_0^{360}/s^{-1} ^b
0.040	0.060		7.08 ± 0.06
0.040*	0.060		7.04 ± 0.06
0.020	0.931 ^c	16.0 ± 0.3	16.0 ± 0.3
0.025	0.931 ^c	22.8 ± 0.8	21.7 ± 0.8
0.0375	0.931 ^c	34.6 ± 0.7	32.9 ± 1.1
0.050	0.931 ^c	46.1 ± 0.9	43.3 ± 0.4
0.040	0.022		4.5 ± 0.05
0.040	0.044		6.4 ± 0.2
0.040	0.060		7.1 ± 0.1
0.040	0.150		10.5 ± 0.1
0.040	0.428		20.4 ± 0.6
0.025	0.219		6.5 ± 0.1
0.025	0.480		11.5 ± 0.3
0.025	0.674	14.1 ± 1.2	14.4 ± 0.4
0.025	0.999	21.0 ± 2.3	20.3 ± 0.6
0.025	1.279	28.5 ± 0.8	28.8 ± 0.4
0.025	1.465	31.9 ± 1.5	30.8 ± 0.5
0.025	2.024	44.7 ± 0.8	44.3 ± 1.0

^a In all experiments [HNO₂] = 1 × 10⁻³ M except * where [HNO₂] = 2 × 10⁻³ M. ^b k_0^{260} measured at 260 nm; k_0^{360} at 360 nm. ^c This acid concentration is the total [HClO₄] added; the free [H⁺] will vary a little as [BSA]₀ is increased.

**Figure 1.** Plots of k_0 vs. $[H^+]$ and $k_0(K_a + [H^+])/[H^+]$ vs. $[H^+]$ for the nitrosation of benzenesulphonic acid

when $[H^+] \gg K_a$, the plot of k_0 vs. $[H^+]$ should be linear with a positive intercept, as is observed. A quantitative test of equation (3) requires that a plot of $k_0(K_a + [H^+])/[H^+]$ vs. $[H^+]$ should be linear throughout the acid concentration range, again with a positive intercept. This is observed experimentally (Figure 1). This plot allows the calculation of k_1 as 820 ± 10 l² mol⁻² s⁻¹ and k_2 as $11\,800 \pm 500$ l² mol⁻² s⁻¹. From these values and an acidity of 0.93 M, the calculated slope of k_0 vs. $[HA]$, (from data in Table 1) is 930 l mol⁻¹ s⁻¹, to be compared with the observed values of 920 l mol⁻¹ s⁻¹ for rate measurements at 260 nm and 870 l mol⁻¹ s⁻¹ for measurements at 360 nm. This provides a good internal check of the reliability of the values of k_1 and k_2 .

The value obtained for k_2 is of course crucially dependent on the value used for K_a , the dissociation constant of BSA. A range of values exists in the literature,^{12,14} and our choice¹² of pK_a 1.84 is somewhat arbitrary. However the close correspondence between k_2 and the value for the nitrosation of thiocyanate ion

Table 2. Values of k in rate = $k[H^+][HNO_2][\text{substrate}]$ for acid-catalysed nitrosation in water at 25 °C

Substrate	$k/l^2 \text{ mol}^{-2} \text{ s}^{-1}$	Ref.
CO(NH ₂) ₂	0.89	a
2,4-Dinitroaniline	2.5	a
HN ₃	160	a
NH ₂ NH ₃ ⁺	620, 611	a, b
MeOH	700	9
PhSO ₂ H	820	This work
HS[CH ₂] ₂ CO ₂ H	4 800	7
(NH ₂) ₂ CS	6 960	5
Sulphanilic acid	7 300	a
SCN ⁻	11 700	a
PhSO ₂ ⁻	11 800	This work

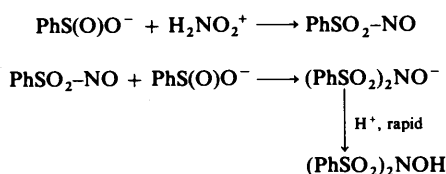
^a J. Fitzpatrick, T. A. Meyer, M. E. O'Neill, and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1984, 927. ^b J. R. Perrott, G. Stedman, and N. Uysal, *J. Chem. Soc., Dalton Trans.*, 1976, 2058.

(see later), where it is not unreasonable to expect reaction at or close to the diffusion-controlled limit, suggests that the choice of pK_a is not too misplaced. It seems in appropriate however, given the uncertainty over pK_a , to apply any ionic strength corrections, which are likely to be much smaller. The internal consistency of our treatment and the excellent linear plot in Figure 1 for the function $k_0(K_a + [H^+])/[H^+]$ also suggest that changes in ionic strength over the acid range considered are not significant factors in the calculation of the rate constants k_1 and k_2 .

For comparison purposes we list in Table 2 the corresponding third-order rate constants for the nitrosation of a range of other substrates. It is clear that both benzenesulphonic acid and the benzenesulphinic ion are amongst the most reactive substances towards acid-catalysed nitrosation. For neutral substrates it has been argued¹⁵ that the upper limiting value of k should be ca. $7\,000$ l² mol⁻² s⁻¹ for reactions involving NO⁺ or H₂NO₂⁺ in water at 25 °C. On this assumption we find that benzenesulphonic acid itself is very similar in reactivity to methanol, and both reactivities are about one power of ten below this limit. The limit is likely to be greater for reaction between a positively charged nitrosating species and a negatively charged substrate because of electrostatic effects; it is interesting that the benzenesulphinic ion and the thiocyanate ion have very similar values for k around $11\,800$ l² mol⁻² s⁻¹, which probably represents the limiting value.

This high reactivity of BSA towards nitrous acid coupled with the irreversibility of the reaction, compares very favourably with that of other conventional nitrous acid scavengers, e.g. azide, hydrazine, urea, etc.; thus BSA and probably sulphonic acids generally have all the necessary properties for very efficient trapping of nitrous acid.

All the rate constants measured at 360 nm refer to the disappearance of nitrous acid and as expected are first-order in both nitrous acid and total substrate concentration. We have also measured the rate constants for some of the experiments at 260 nm (absorbance due to the product hydroxylamine). In all cases k_0 is independent of the wavelength of measurement, within experimental error, and a first-order dependence on the total substrate concentration also applies to the rate of product formation. This means that if, as seems very likely from the stoichiometry and product structure, the reaction is at least a two-stage process, then the first stage is rate limiting, otherwise a second-order dependence upon [BSA]₀ would be expected. The outline mechanism is given in the Scheme, with the formation of the nitrososulphinic intermediate rate limiting. Such intermediates have been proposed previously for this



Scheme.

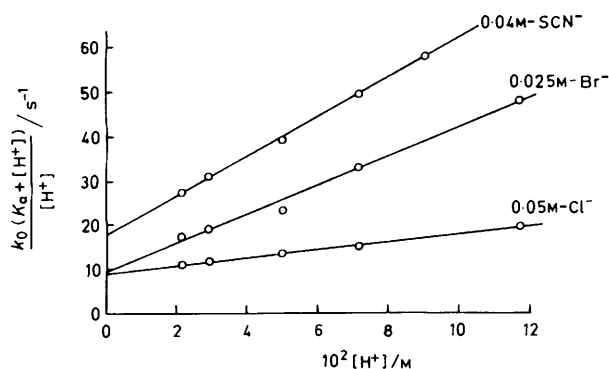


Figure 2. Plots of $k_0(K_a + [\text{H}^+])/[\text{H}^+]$ vs. $[\text{H}^+]$ for the nitrosation of benzenesulphonic acid in the presence of Cl^- , Br^- , and SCN^-

reaction,³ and also for the reaction of alkyl nitrites with sulphinic acids,¹⁶ and for the reaction of nitrosyl chloride with sulphinic acids in ether.¹⁷ They have recently been isolated,¹⁸ as rather unstable brown crystals, from the reactions of sulphinic acids with N_2O_4 in ether at -20°C . They appear to be the most powerful nitrosating agents known, readily reacting with amines,¹⁹ alcohols,⁸ and thiols,⁸ and often yielding some of the *N,N*-bis(arylsulphenyl)hydroxylamine product as well. A number of other *S*-nitroso compounds have been shown to act as transfer-nitrosating agents; for example the *S*-nitroso ion derived from thiourea can be used to nitrosate amines directly,¹⁰ whereas thionitrites can also effect nitrosation²⁰ although it is not yet established whether this occurs directly or indirectly.

As is the case for many amines,²¹ alcohols,⁹ and thiols,⁷ the nitrosation of BSA is also subject to catalysis by added Cl^- , Br^- , SCN^- , and $\text{SC}(\text{NH}_2)_2$, presumably *via* the intermediacy of the corresponding NOX derivatives. The data are presented in Table 3. It is likely that both the neutral sulphinic acid and the anion are reactive towards NOX. In order to extract the rate constants for both species we have measured the rate constants for nitrosation in the presence of KCl (0.05M), KBr (0.025M), KSCN (0.04M), and $\text{SC}(\text{NH}_2)_2$ ($6 \times 10^{-3}\text{M}$), in each case over a range of acid concentration. For each nucleophile (except thiourea) plots of $k_0(K_a + [\text{H}^+])/[\text{H}^+]$ were linear against $[\text{H}^+]$ with a positive slope and intercept. The expected rate expression for such a reaction is given in equation (4) where k_1 ,

$$k_0 = \{k_1[\text{H}^+]^2 + k_2K_a[\text{H}^+] + k_3[\text{H}^+]^2[\text{X}^-]K_{\text{NOX}} + k_4[\text{H}^+][\text{X}^-]K_{\text{NOX}}K_a\}[\text{HA}]_t/(K_a + [\text{H}^+]) \quad (4)$$

k_2 , K_a , and $[\text{HA}]_t$ have the same meaning as in equation (3), k_3 and k_4 are the second-order rate constants for attack of NOX on HA and A^- respectively, X^- is Cl^- , Br^- , or SCN^- , and K_{NOX} is the equilibrium constant for the formation of NOX from HNO_2 , X^- , and H^+ . Again, as for the uncatalysed reaction, plots of $k_0(K_a + [\text{H}^+])/[\text{H}^+]$ vs. $[\text{H}^+]$ should be linear, as observed, with slopes $(k_1 + k_3[\text{X}^-]K_{\text{NOX}})[\text{HA}]_t$ and intercepts $(k_2K_a + k_4[\text{X}^-]K_{\text{NOX}}K_a)[\text{HA}]_t$; by assuming the earlier values

Table 3. Catalysis by added Cl^- , Br^- , SCN^- , and $\text{SC}(\text{NH}_2)_2$ in the nitrosation of BSA^a

$10^3[\text{KCl}]/\text{M}$	k_0/s^{-1}	$10^3[\text{KBr}]/\text{M}$	k_0/s^{-1}
3.0	3.44 ± 0.03	0.7	3.65 ± 0.1
5.0	3.65 ± 0.02	3.4	4.82 ± 0.05
7.4	3.87 ± 0.01	5.0	5.44 ± 0.3
20.0	5.04 ± 0.07	7.4	6.46 ± 0.1
34.7	6.53 ± 0.1	10.1	7.43 ± 0.03
49.5	7.85 ± 0.05	20.0	11.1 ± 0.1
		35.0	15.8 ± 0.1
		50.0	21.5 ± 0.1

$10^3[\text{KSCN}]/\text{M}$	k_0/s^{-1}	$10^3[\text{SC}(\text{NH}_2)_2]/\text{M}$	k_0/s^{-1}
1.0	3.96 ± 0.1	1.0	3.5 ± 0.03
5.0	5.73 ± 0.1	3.4	4.0 ± 0.1
7.4	6.79 ± 0.1	5.0	4.4 ± 0.1
10.1	7.96 ± 0.1	6.0	4.6 ± 0.1
20.0	12.4 ± 0.2	7.4	4.8 ± 0.1
30.0	17.4 ± 0.5	10.0	5.2 ± 0.1
40.0	21.4 ± 1.1		

^a In all these experiments $[\text{HNO}_2] = 1 \times 10^{-3}\text{M}$, $[\text{BSA}] = 2.5 \times 10^{-2}\text{M}$, $[\text{HClO}_4] = 0.030\text{M}$.

Table 4. Slopes and intercepts of plots of $k_0(K_a + [\text{H}^+])/[\text{H}^+]$ vs. $[\text{H}^+]$ and values of k_3 and k_4 for reactions of NOCl, NOBr, and NOSCN with HA and A^- .

Nucleophile	Slope ($\text{l mol}^{-1} \text{s}^{-1}$)	Intercept (s^{-1})	$k_3/\text{l mol}^{-1} \text{s}^{-1}$	$k_4/\text{l mol}^{-1} \text{s}^{-1}$
Cl^-	86	9.2	4.6×10^7	2.4×10^8
Br^-	323	9.8	9.5×10^6	1.2×10^7
SCN^-	432	18	1.3×10^4	3.0×10^4

of k_1 and k_2 and the literature values of K_{NOX} it is easy to deduce values of k_3 and k_4 , from the slopes and intercepts. The plots for the three nucleophiles Cl^- , Br^- , and SCN^- are given in Figure 2 and show the expected form [from equation (4)] which is the same as for the non-nucleophile-catalysed reactions. Values of k_3 and k_4 for the three nucleophiles, together with the slopes and intercepts of the plots are given in Table 4. The plot for thiourea was not a good line, with rather large errors, so no meaningful values of k_3 and k_4 have been calculated.

As for the uncatalysed reaction, the anion form of BSA is the more reactive, but the difference is now not so large. This may be due to the fact that for the catalysed reaction we are dealing with a neutral reagent NOX, whereas for the uncatalysed process the reagent was positively charged (H_2NO_2^+ or NO^+) so that electrostatic effects are important.

As a further test of the reliability of the k_1 , k_2 , k_3 , and k_4 values, and of our kinetic analysis, we have compared the measured slopes and intercepts of the k_0 vs. $[\text{X}^-]$ plots (data from Table 3) with those calculated using the determined k_1 , k_2 , k_3 , and k_4 values. The results (Table 5) show excellent agreement.

The reactivity sequence $\text{NOCl} > \text{NOBr} > \text{NOSCN}$ is clear for both HA and A^- and is now a well established trend,²² applying very generally to reactions of amines, alcohols, thiols, and other nucleophilic species. As for the magnitude of k_3 and k_4 values for the BSA reaction, they are large and approach the calculated diffusion limit for NOCl in its reaction with the sulphinate ion. A rough comparison with other substrates shows that both benzenesulphonic acid and its anion are more reactive towards NOX than are some thiols such as cysteine and mercaptopropanoic acid,⁷ but somewhat less reactive than aniline.²³

Table 5. Observed and calculated values of the slopes and intercepts of k_0 vs. $[\text{Cl}^-]$, $[\text{Br}^-]$, and $[\text{SCN}^-]$

Nucleophile	Slope ($\text{l mol}^{-1} \text{s}^{-1}$)	Intercept (s^{-1})	
Cl^-	95	3.2	Observed
	93	3.3	Calculated
Br^-	356	3.7	Observed
	377	3.3	Calculated
SCN^-	442	3.4	Observed
	428	3.3	Calculated

Experimental

All materials used were of a high purity grade and were used as such. Benzenesulphonic acid was stored at 0°C . Reproducible kinetic results were obtained from samples stored for different times. Fresh sodium nitrite solutions were prepared daily. All kinetic experiments were carried out at 25°C in water, under first-order conditions with $[\text{BSA}] \gg [\text{HNO}_2]$. All reactions were followed kinetically by stopped-flow spectrophotometry, mostly at 360 nm (disappearance of nitrous acid) but sometimes at 260 nm (appearance of product). Good agreement between the two sets of data was found. Typical reaction conditions were: [sodium benzenesulphonate] 0.025M, [nitrous acid] $1 \times 10^{-3}\text{M}$, [perchloric acid] 0.047M. The quoted rate constants represent the mean of at least five separate determinations; the quoted error represents the standard deviation. The product *N,N*-bis(phenylsulphonyl)hydroxylamine was isolated from reaction solutions at concentrations somewhat higher than those of the kinetic experiments, as described by Birchall and Glidewell;⁴ its u.v. and i.r. spectra were measured. The i.r. spectrum was characterised by strong absorptions at 3300 cm^{-1} (O-H stretching) and at ca. 1080 cm^{-1} (N-OH stretching), again as noted in ref. 4 (Found: C, 47.1; H, 3.6; N, 4.6. Calc. for $\text{C}_{12}\text{H}_{11}\text{NO}_5\text{S}_2$: C, 46.0; H, 3.5; N, 4.5%).

Acknowledgements

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