The Wallach Rearrangement. Part XIV.[1] Rearrangements of Azoxynaphthalenes in Sulphuric Acid. Kinetics and Mechanisms

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The rates of rearrangement of the 1-naphthyl-, 2-naphthyl-, and phenyl-substituted azoxy-compounds (1)—(6) in moderately concentrated sulphuric acid solutions have been investigated. A mechanism involving quinonoid type intermediates is used to explain the acidity dependence of the observed rate constants for compounds (1), (2), and (4)—(6) at H_2SO_4 concentrations below *ca.* 83% w/w. Equilibrium protonation of the substrates (K_{SH^+}) is followed by nucleophilic attack (HSO_4^-) on aromatic carbon yielding the uncharged quinonoid intermediates (S'). Another equilibrium protonation of S' ($K_{S'H^+}$) on the N–OH function is followed by rate-determining abstraction of an aryl-bound hydrogen with simultaneous loss of H_2O. In contrast, compound (3) exhibits a linear log (rate) correlation with log $a_{H_2SO_4}$ at all acidities, indicative of general acid catalysed formation of a dicationic intermediate; the other compounds also appear to react by this mechanism above 83% H_2SO_4. Thus in the low acid region the isomeric reactants (2) and (3) follow different reaction pathways while yielding a common product.

RECENTLY we found that the Wallach rearrangement of hexamethylazoxybenzene in sulphuric acid occurs by two different mechanisms.[1] At high acidity a dicationic intermediate [2] mechanism is involved, similar to that applicable to azoxybenzene itself at all acidities.[3] At low acidities a mechanism was proposed involving intermediates with only one positive charge.[1]

In a further investigation of this reaction,[4] we have studied the rearrangements of naphthalene-1-*NNO*-azoxybenzene (1), naphthalene-2-*NNO*-azoxybenzene (2), naphthalene-2-*ONN*-azoxybenzene (3), 1,1'-azoxynaphthalene (4), 1,2'-*ONN*-azoxynaphthalene (5), and 2,2'-azoxynaphthalene (6). We have already reported on the product orientation in this series (Scheme 1),[5a,b] and on a preliminary kinetic study for the reactions of (2) and (3).[5c] In the present paper we report the results of a detailed kinetic study of these reactions and their interpretation.

RESULTS AND DISCUSSION

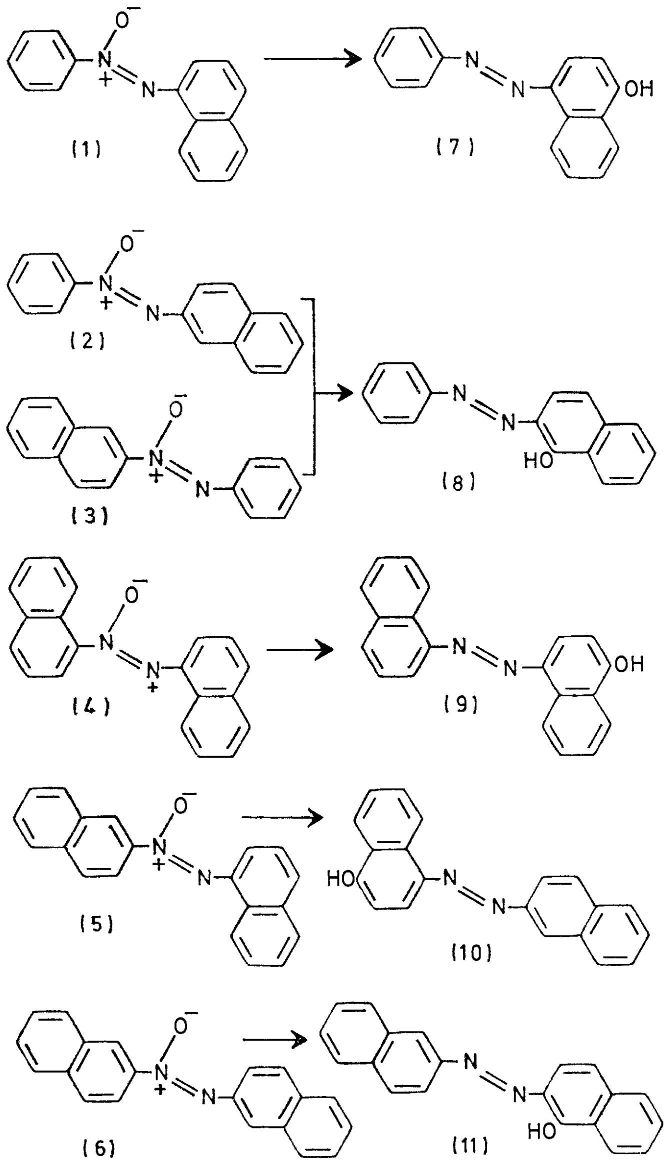
The kinetic data obtained are given in Tables 1—6, Values of log k_ψ for the different reactions are plotted as a function of $-H_0$ in Figure 1. Also shown in Figure 1 are the previously measured pK_{SH^+} values [6] of these compounds. In Figure 2, the rate data, corrected to full monoprotonation by subtracting log ($C_{SH^+}/C_S + C_{SH^+}$) from the log k_ψ values,[7] are plotted as a function of log $a_{H_2SO_4}$; plots of this type have previously been found to be linear for azoxybenzene and hexamethylazoxybenzene.[1,3a]

The rate data represented in Figures 1 and 2 provide several interesting features. It is apparent from Figure 1 that the reactions at 44·4° can be divided into two categories. Into the first fit compounds (1), (4), and (5), all of which undergo 4-naphthyl substitution, have pK_{SH^+} values *ca.* −6, and the initial slopes of their log (rate) $-H_0$ profiles are *ca.* 2. Into

[1] Part XIII, R. A. Cox and E. Buncel, *J. Amer. Chem. Soc.*, in the press.
[2] (*a*) P. H. Gore, *Chem. and Ind.*, 1959, 191; (*b*) E. Buncel and B. T. Lawton, *ibid.*, 1963, 1835.
[3] (*a*) R. A. Cox, *J. Amer. Chem. Soc.*, 1974, **96**, 1059; (*b*) E. Buncel and W. M. J. Strachan, *Canad. J. Chem.*, 1970, **48**, 377; (*c*) E. Buncel and B. T. Lawton, *ibid.*, 1965, **43**, 862.
[4] (*a*) H. J. Shine, 'Aromatic Rearrangements,' Elsevier, Amsterdam, 1967, p. 272; (*b*) D. L. H. Williams, in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, vol. 13, 1972; (*c*) E. Buncel, in 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Wiley, New York, vol. 1, 1968; (*d*) R. A. Cox and E. Buncel, in 'The Chemistry of Hydrazo, Azo, and Azoxy Groups,' ed. S. Patai, Interscience, New York, 1975.
[5] (*a*) E. Buncel and A. Dolenko, *Tetrahedron Letters*, 1971, 113; (*b*) A. Dolenko and E. Buncel, *Canad. J. Chem.*, 1974, **52**, 623; (*c*) E. Buncel, R. A. Cox, and A. Dolenko, *Tetrahedron Letters*, 1975, 215.
[6] A. Dolenko, K. Mahendran, and E. Buncel, *Canad. J. Chem.*, 1970, **48**, 1736.
[7] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1917.

the second fit compounds (2), (3), and (6), which undergo 1-naphthyl substitution, have pK_{SH^+} values *ca.* −5, and their initial slopes are *ca.* 1. All the log (rate) $-H_0$ profiles are curved; the curvature is least for (3), and for (1) at 25°. Compounds (1), (4), and (5) all appear to reach a limiting rate of *ca.* 10^{-3} s^{-1}. Compounds (2) and (6) seem to level off at *ca.* $10^{-3.5}$ s^{-1}, *except* for one point due to (2), which falls on the extrapolated curve due to (3).

Upon subtracting the term log $(C_{SH^+}/C_S + C_{SH^+})$ from the log k_ψ values, which corrects these for the fraction of unprotonated substrate present at H_0 values near pK_{SH^+}, all six compounds have initial slopes *ca.* 1. This similarity of initial slopes can also be seen from Figure 2, as $-H_0$ and log $a_{H_2SO_4}$ are almost (but not quite) linear functions of one another below log $a_{H_2SO_4}$ = −1. In other words the reaction is still acidity dependent beyond the full monoprotonation stage, in accord with previous observations for azoxybenzene and hexamethylazoxybenzene. Figure 2 also shows the approach to a limiting rate, especially for (1), (4), and (5),



SCHEME 1

TABLE 1

Pseudo-first-order rate constants, degree of substrate protonation, and solution acidity parameters, for reaction of (1) in H_2SO_4 media at 25 and 44·4°

H_2SO_4 (%) [a]	$-H_0$ [b]	C_{SH^+} [c] / ($C_S + C_{SH^+}$)	k_ψ (s^{-1}) 44·4°
66·66	5·29	0·287	$1·32 \times 10^{-5}$
69·65	5·74	0·516	$9·33 \times 10^{-5}$
72·64	6·22	0·751	$3·87 \times 10^{-4}$
74·63	6·52	0·852	$8·14 \times 10^{-4}$
76·62	6·83	0·919	$1·18 \times 10^{-3}$
78·61	7·13	0·956	$1·36 \times 10^{-3}$
H_2SO_4 (%)	$-H_0$ [e]	−log $a_{H_2SO_4}$ [f]	k_ψ (s^{-1}) 25·0°
83·28 [d]	8·01	1·404	$1·82 \times 10^{-4}$
85·93 [d]	8·41	1·039	$3·03 \times 10^{-4}$
86·12 [d]	8·44	1·013	$3·19 \times 10^{-4}$
89·06 [d]	8·87	0·689	$5·56 \times 10^{-4}$
90·13 [d]	9·03	0·587	$8·40 \times 10^{-4}$
92·47 [d]	9·42	0·401	$1·14 \times 10^{-3}$

[a] w/w After mixing with 0·5% ethanol. [b] Data from ref. 18*b,c*. [c] Calculated using pK_{SH^+} = −5·71 (ref. 6). [d] No co-solvent present. [e] Data from ref. 18*b,c* (substrate is >99% protonated at these acidities). [f] Data from C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 24.

TABLE 2

Rate and acidity data for reaction of (2) in H_2SO_4 solution at 44·4°

H_2SO_4 (%) [a]	$-H_0$ [b]	C_{SH^+} [c] / ($C_S + C_{SH^+}$)	k_ψ (s^{-1})
69·65	5·74	0·821	$6·35 \times 10^{-6}$
72·64	6·22	0·928	$2·41 \times 10^{-5}$
76·62	6·83	0·979	$1·17 \times 10^{-4}$
78·61	7·13	0·989	$2·09 \times 10^{-4}$
80·60	7·43	0·994	$2·78 \times 10^{-4}$
84·58	8·11	0·999	$5·74 \times 10^{-4}$

[a] w/w After mixing with 0·5% ethanol. [b] Data from ref. 18*b,c*. [c] Calculated using pK_{SH^+} = −5·03 (ref. 6).

TABLE 3

Rate and acidity data for reaction of (3) in H_2SO_4 solution at 44·4°

H_2SO_4 (%) [a]	−log $a_{H_2SO_4}$ [b]	C_{SH^+} [c] / ($C_S + C_{SH^+}$)	k_ψ (s^{-1})
69·65	3·321	0·828	$1·96 \times 10^{-6}$
72·64	2·860	0·927	$7·37 \times 10^{-6}$
74·63	2·557	0·960	$1·83 \times 10^{-5}$
76·62	2·250	0·980	$4·25 \times 10^{-5}$
78·61	1·952	0·989	$8·82 \times 10^{-5}$
80·59	1·671	0·994	$1·75 \times 10^{-4}$

[a] w/w After mixing with 0·5% ethanol. [b] Data from C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 24. [c] Calculated using pK_{SH^+} = −5·00 (ref. 6).

even more clearly. In Figure 2, the only linear correlations apparent are for compound (3) at 44·4°, upon which the topmost point due to (2) also falls, and for compound (1) at 25·0°. Discussion of these aspects will be deferred until later.

TABLE 4

Rate and acidity data for reaction of (4) in H_2SO_4 solution at 44·4°

H_2SO_4 (%) [a]	$-H_0$ [b]	$\frac{C_{SH^+}}{C_S + C_{SH^+}}$ [c]	k_ψ (s^{-1})
59·89	4·66	0·094	$1·10 \times 10^{-5}$
60·89	4·79	0·120	$2·53 \times 10^{-5}$
61·92	4·92	0·153	$3·45 \times 10^{-5}$
62·88	5·05	0·192	$7·70 \times 10^{-5}$
63·83	5·16	0·232	$1·26 \times 10^{-4}$
64·77	5·26	0·272	$2·21 \times 10^{-4}$
65·74	5·37	0·321	$3·03 \times 10^{-4}$
66·79	5·51	0·390	$5·45 \times 10^{-4}$
67·75	5·65	0·463	$5·94 \times 10^{-4}$
68·20	5·71	0·495	$6·23 \times 10^{-4}$
69·20	5·87	0·579	$8·25 \times 10^{-4}$
70·72	6·09	0·688	$9·71 \times 10^{-4}$

[a] w/w After mixing with 5·0% dioxan. [b] Data from ref. 18*a*. [c] Calculated using $pK_{SH^+} = -5·72$ (ref. 6).

TABLE 5

Rate and acidity data for reaction of (5) in H_2SO_4 solution at 44·4°

H_2SO_4 (%) [a]	$-H_0$ [b]	$\frac{C_{SH^+}}{C_S + C_{SH^+}}$ [c]	k_ψ (s^{-1})
65·25	5·27	0·224	$1·38 \times 10^{-5}$
66·73	5·49	0·322	$4·11 \times 10^{-5}$
68·20	5·71	0·438	$1·08 \times 10^{-4}$
69·97	5·97	0·584	$2·57 \times 10^{-4}$
72·63	6·36	0·772	$6·56 \times 10^{-4}$
74·60	6·67	0·872	$1·03 \times 10^{-3}$

[a] w/w After mixing with 5·0% dioxan. [b] Data from ref. 18*a*. [c] Calculated using $pK_{SH^+} = -5·82$ (ref. 6).

TABLE 6

Rate and acidity data for reaction of (6) in H_2SO_4 solution at 44·4°

H_2SO_4 (%) [a]	$-H_0$ [b]	$\frac{C_{SH^+}}{C_S + C_{SH^+}}$ [c]	k_ψ (s^{-1})
69·97	5·97	0·836	$2·98 \times 10^{-5}$
72·63	6·36	0·915	$8·15 \times 10^{-5}$
74·60	6·67	0·952	$1·63 \times 10^{-4}$
76·06	6·92	0·970	$2·53 \times 10^{-4}$
77·06	7·10	0·978	$2·63 \times 10^{-4}$

[a] w/w After mixing with 5·0% dioxan. [b] Data from ref. 18*a*. [c] Calculated using $pK_{SH^+} = -5·13$ (ref. 6).

Previously we found that, at low acidity, hexamethylazoxybenzene undergoes reaction *via* a succession of equilibrium proton transfers, followed by rate-determining nucleophilic attack.[1] A similar mechanism can be considered for compounds (1), (2), and (4)—(6) at 44·4°. (In the case of hexamethylazoxybenzene, nucleophilic attack occurs on a hydrogen of the *p*-methyl group,[8] whereas in the azoxynaphthalene series the nucleophile attacks an aromatic carbon atom, though in both cases quinonoid intermediates result.) The reaction scheme for compound (1) is presented in Scheme 2. The substrate S is first protonated on oxygen in an equilibrium defined by K_{SH^+}, giving SH^+, which then undergoes reversible nucleophilic attack by Nu^- (probably HSO_4^-)[1,9] giving a 'new' neutral substrate S′, a quinonoid type intermediate.[10] This

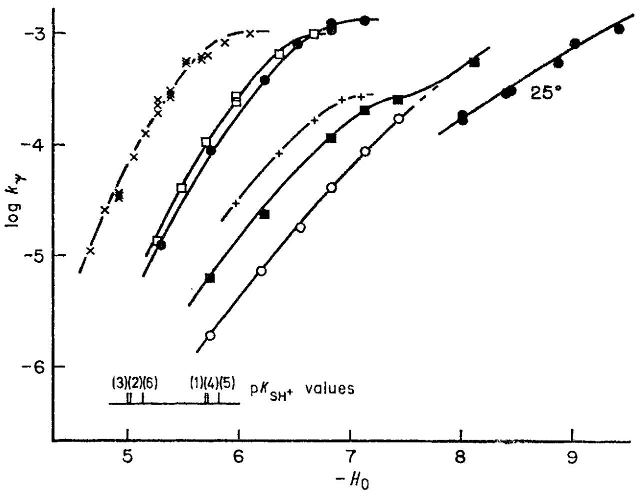


FIGURE 1 Graphs of log k_ψ against $-H_0$, for the Wallach rearrangements of (1) (●); (2) (■); (3) (○); (4) (×), (5) (□); and (6) (+), all at 44·4°; and of (1) (●) at 25·0°, in sulphuric acid

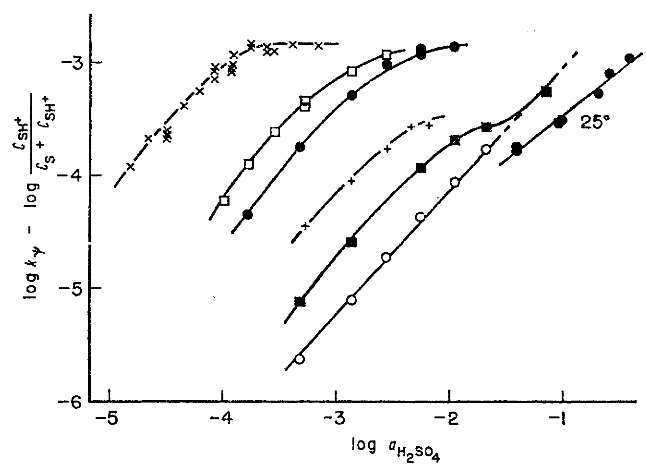
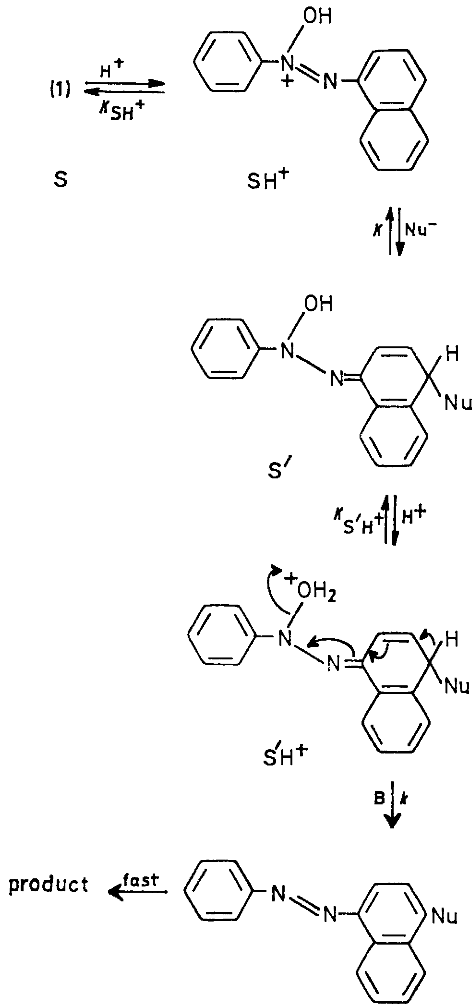


FIGURE 2 Graphs of log k_ψ − log ($C_{SH^+}/C_S + C_{SH^+}$) against log $a_{H_2SO_4}$, for the Wallach rearrangements of (1) (●); (2) (■); (3) (○); (4) (×); (5) (□); and (6) (+), all at 44·4°; and of (1) (●) at 25·0° in sulphuric acid

[8] R. A. Cox and E. Buncel, *Canad. J. Chem.*, 1973, **51**, 3143.
[9] E. B. Robertson and H. B. Dunford, *J. Amer. Chem. Soc.*, 1964, **86**, 5080.
[10] D. Duffey and E. C. Hendley, *J. Org. Chem.*, 1968, **33**, 1918; 1970, **35**, 3579.

in turn is protonated ($K_{S'H^+}$) on oxygen, yielding $S'H^+$, and the latter undergoes rate-determining attack



SCHEME 2

by base (again HSO_4^-) with concerted loss of H_2O. The resulting azoaryl hydrogen sulphate derivative will be rapidly hydrolysed [11] to yield the observed product (7).

Using the nomenclature of Scheme 2, it is possible to derive rate equations (1) and (2), as previously described.[1] These are applicable to the cases, where S' is essentially unprotonated, and fully protonated, respectively.

$$\log k_\psi - \log \frac{C_{SH^+}}{C_S + C_{SH^+}} = -H_0 + \log a_{Nu}a_{B:} + \log \frac{kK}{K_{S'H^+}} + \log \frac{f_{SH^+}f_{InH^+}}{f_\ddagger f_{In}} \quad (1)$$

$$\log k_\psi - \log \frac{C_{SH^+}}{C_S + C_{SH^+}} = \log a_{Nu}a_{B:} + \log kK + \log \frac{f_{SH^+}f_{S'H^+}}{f_\ddagger f_{S'}} \quad (2)$$

If it is assumed (a) that both B: and Nu^- are HSO_4^-, and (b) that the activity coefficient terms do not affect the linearity of the plots appreciably,[1,12] one can plot $\log k_\psi - \log [C_{SH^+}/(C_S + C_{SH^+})] - 2 \log a_{HSO_4^-}$ against $-H_0$; if the treatment holds these will be linear with unit slope if equation (1) applies, and zero slope if equation (2) applies. The relevant plots are shown in Figure 3; it is apparent that equations (1) and (2) apply at the extremes, since the initial slopes are all close to 1 and the final slopes all approach 0. It is also evident that the $pK_{S'H^+}$ values of all five S' compounds lie somewhere within the acidity range covered in Figure 3. Since this is so, it is necessary to use an equation which takes this into account; this is equation (3), which can be derived from equations (1) and (2) by standard procedures [13] [essentially equations (1) and (2) are added before taking logs], and involves the assumption that the protonation of S' follows the H_0 acidity function.

$$\log k_\psi - \log \frac{C_{SH^+}}{C_S + C_{SH^+}} = \log a_{Nu}a_{B:} + \log kK + \log \frac{C_{S'H^+}}{C_{S'} + C_{S'H^+}} + \log \frac{f_{SH^+}f_{S'H^+}}{f_\ddagger f_{S'}} \quad (3)$$

Now we have three equilibrium constants, K_{SH^+}, K, and $K_{S'H^+}$, describing reactions which occur before the slow step. Since K_{SH^+} is known, one can derive values of $C_{SH^+}/(C_S + C_{SH^+})$. K Need not be known as it is not involved in a variable term, but, in order

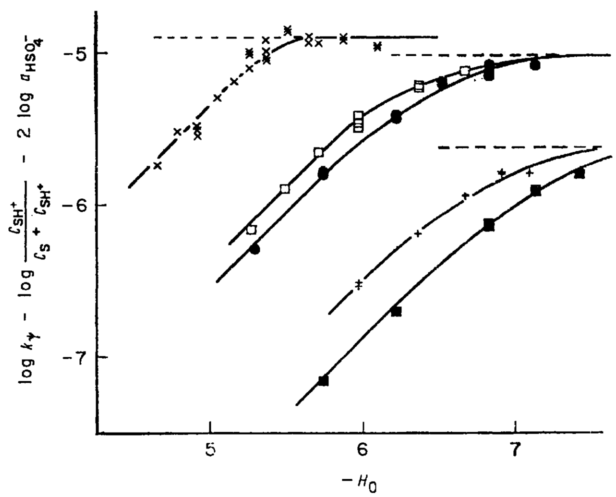


FIGURE 3 Graphs of $\log k_\psi - \log [C_{SH^+}/(C_S + C_{SH^+})] - 2 \log a_{HSO_4^-}$ against $-H_0$, for the Wallach rearrangements of (1) (●); (2) (■); (4) (×); (5) (□); and (6) (+) in sulphuric acid at 44·4°

to use equation (3), we need to know $K_{S'H^+}$ so that values of $C_{S'H^+}/(C_{S'}+C_{S'H^+})$ can be derived. We cannot measure $K_{S'H^+}$ directly, since K is apparently not large enough to allow appreciable quantities of S' to be present in the solutions orginally used to measure

[11] (a) C. S. Hahn, K. W. Lee, and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1967, **89**, 4975; (b) E. Buncel and W. M. J. Strachan, *Canad. J. Chem.*, 1969, **47**, 911.

[12] R. B. Moodie and R. Towill, *J.C.S. Perkin II*, 1972, 184.

[13] W. M. Schubert and H. K. Latourette, *J. Amer. Chem. Soc.*, 1952, **74**, 1829.

K_{SH^+};[6] otherwise standard methods[14] could be used to obtain both K_{SH^+} and $K_{S'H^+}$. However, one can obtain values of log $[C_{S'H^+}/(C_{S'} + C_{S'H^+})]$ from Figure 3

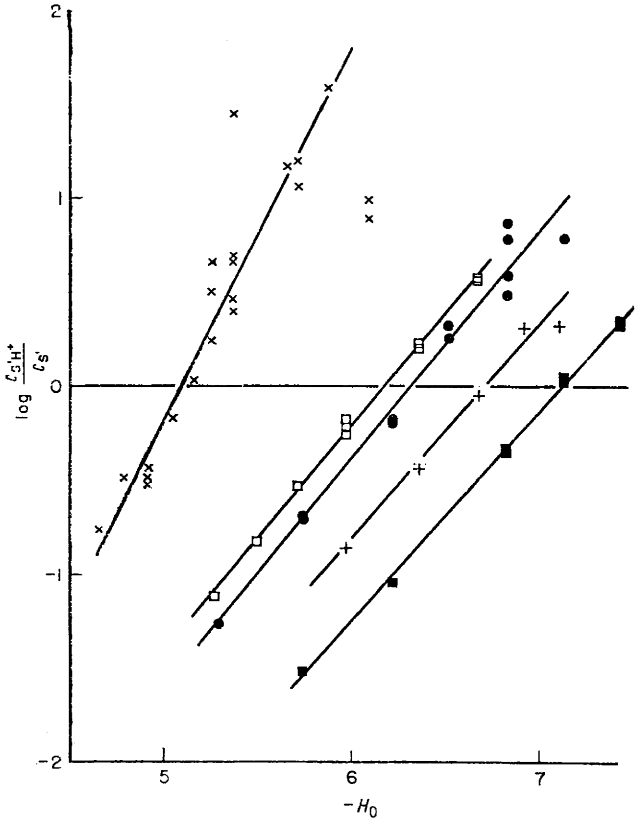


FIGURE 4 Graphs of log $(C_{S'H^+}/C_{S'})$ against $-H_0$, giving the $pK_{S'H^+}$ values of the quinonoid-type intermediates formed from (1) (●); (2) (■); (4) (×); (5) (□); and (6) (+), during their Wallach rearrangements in sulphuric acid at 44·4°

if it is assumed that equation (3) holds, *i.e.*, that the difference between the curves in Figure 3 and the acidity-independent lines parallel to the $-H_0$ axis (dashed lines in Figure 3) represent values of log $[C_{S'H^+}/(C_{S'} + C_{S'H^+})]$. One can then use these values to calculate log $(C_{S'H}/C_{S'})$, which is the log (ionization ratio) for S′. These data can be plotted against $-H_0$, and the intercepts on the *x*-axis yield the values of $pK_{S'H^+}$. The slopes of these plots indicate whether or not the different S′ compounds behave like Hammett bases. The result of this procedure is given in Figure 4, while in Table 7 the values of $pK_{S'H^+}$ are listed, with the Hammett slopes, standard deviations, and correlation coefficients. Values of the acidity-independent rate used in this treatment (dashed lines in Figure 3) were those which gave the best straight lines in the Figure 4 plots and were determined by inspection. Compound (3) is excluded from these treatments since this gives a linear plot in Figure 2; it reacts by another mechanism as will be seen in the subsequent discussion.

* Only numbers close to these give the best straight lines in the Figure 4 plots. Other values result in significant curvature.

Figure 4 and Table 7 show that the quinonoid-type intermediates from (1), (2), (5), and (6) approximate Hammett base behaviour, with slopes of *ca.* 1·2, and all give adequately linear plots. The exception seems to be the intermediate formed from (4); the experimental scatter for this compound is large, but the Hammett slope is reasonably well defined at *ca.* 2·0, and the $pK_{S'H^+}$ value at −5·1. This is the only compound with $pK_{S'H^+} > pK_{SH^+}$. Anomalous behaviour in this case can be attributed to the more stringent steric requirements in the 1,1′-dinaphthalene structure relative to the others in this series.

Now that $pK_{S'H^+}$ values for these compounds have been inferred, one can recalculate values of log $[C_{S'H^+}/(C_{S'} + C_{S'H^+})]$, and using equation (3) one can plot log k_ψ − log $[C_{SH^+}/(C_S + C_{SH^+})]$ − 2 log $a_{HSO_4^-}$ − log-$[C_{S'H^+}/(C_{S'} + C_{S'H^+})]$ against $-H_0$. This effectively removes all the acidity dependence; we should be left with straight lines of slope 0, and the only remaining variable is the experimental scatter. This is demonstrated in Figure 5, showing that the treatment is self-consistent.

In Figure 5, the intercepts on the *y*-axis * with their standard deviations are: (4), −4·898 ± 0·065; (5) and (1), −5·007 ± 0·022; (6) and (2), −5·622 ± 0·018. These values, which approximate to the term log *kK* in equation (3), lead to some interesting conclusions. It is apparent that compounds (1), (4), and (5), when the acidity dependence is factored out, all react at approximately the same rate. This is not surprising in itself, since these are reacting in the same way at the

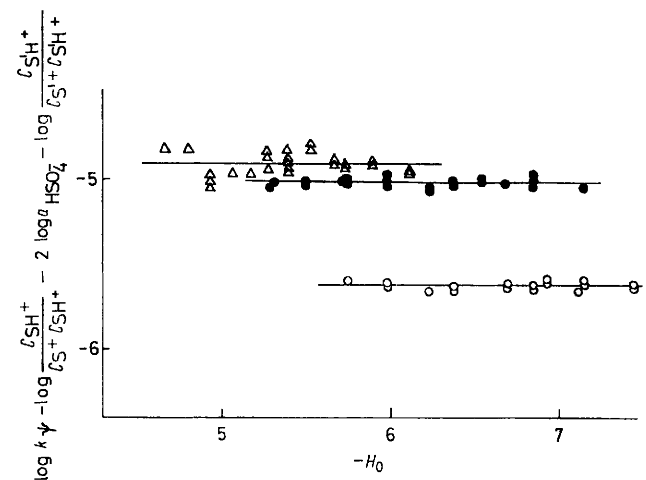


FIGURE 5 Graphs of log k_ψ − log $[C_{SH^+}/(C_S + C_{SH^+})]$ − 2 log $a_{HSO_4^-}$ − log $[C_{S'H^+}/(C_{S'} + C_{S'H^+})]$ against $-H_0$, illustrating the acidity-independent rates of the Wallach rearrangements of (4) (△); (1) and (5) (●); (2) and (6) (○) undergoing reaction *via* Scheme 1 in sulphuric acid at 44·4°

same site in closely similar molecules, according to Scheme 2, but it is surprising in terms of the ' normal ' Wallach rearrangement mechanism,[3] in which reaction

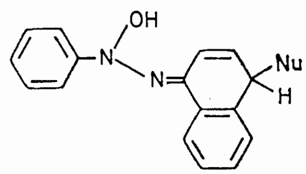
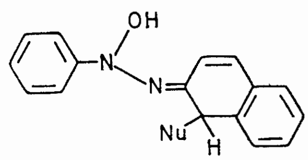
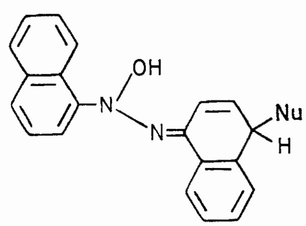
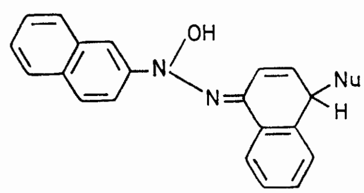
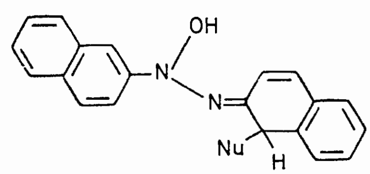
[14] B. Roth and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1965, **87**, 334.

occurs *via* a dicationic intermediate (see below). If this mechanism were to obtain then the symmetrical compound (4), with two identical reaction sites, would react *faster than* (1) and (5) by a symmetry factor of 2 (0·3 log units), which is not found. This also applies to compounds (2) and (6), of which only the latter is symmetrical. It is apparent that reaction at a 4-naphthyl position [(1), (4), and (5)] is easier than reaction at a 1-naphthyl position (2 and 6), which is what would be expected.[6] Both naphthyl substitutions involve partial retention of aromaticity in one of the naphthalene rings in the resulting quinonoid-type intermediates (S′ structures in Table 7). Reaction at phenyl does not have this energetically favourable feature; thus compound (3) does not react at the phenyl group; and in fact (3) does not react by this mechanism at all (see below) and one may conclude that reaction at phenyl is too unfavourable energetically to occur by this mechanism.

The mode of reaction of (3) is still to be explained. It will be recalled that log k_ψ − log $[C_{SH^+}/(C_S + C_{SH^+})]$ is a linear function of log $a_{H_2SO_4}$ for this compound (Figure 2). Behaviour of this type, previously found for hexamethylazoxybenzene at high acidity,[1] and for azoxybenzene itself at all acidities,[3a] has been shown to be consistent with the dicationic intermediate mechanism. This mechanism is shown in Scheme 3 for the case under discussion.

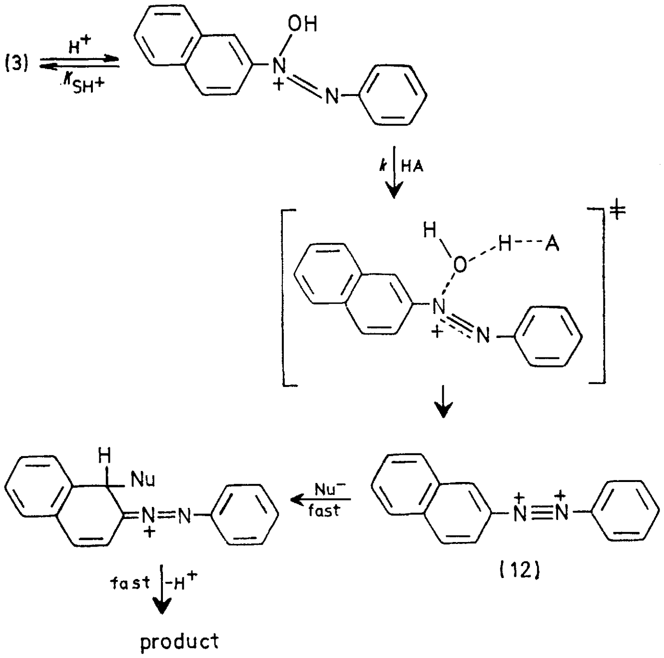
TABLE 7

Values of pK_{SH^+} for compounds (1)—(6) (S), and of $pK_{S'H^+}$ for the derivatives formed by nucleophilic attack of HSO_4^- on SH^+ (S′)

S	pK_{SH^+} [a]	S′	$pK_{S'H^+}$ [b]	Hammett slope [c]	Correlation coefficient
(1)	−5·71		−6·32	1·22 ± 0·06	0·986
(2)	−5·03		−7·12	1·12 ± 0·01	0·999
(3)	−5·00	*d*	*d*	*d*	*d*
(4)	−5·72		−5·09	2·00 ± 0·11	0·978
(5)	−5·82		−6·17	1·20 ± 0·02	0·998
(6)	−5·13		−6·71	1·15 ± 0·06	0·991

[a] From ref. 6. [b] Intercepts at log $(C_{S'H^+}/C_{S'}) = 0$ in Figure 4; error limit ±0·08 units. [c] Slope and standard deviation from computer least-squares line-fitting. [d] Compound (3) does not react by the quinonoid intermediate mechanism (see text).

In this Scheme, the protonated substrate SH^+ undergoes rate-determining proton transfer concertedly with loss of water (general acid catalysis, here by undissociated H_2SO_4) [1,3] to give the dicationic intermediate (12), which is subject to fast nucleophilic attack at the most favourable site, as shown, and subsequent fast reactions leading to (8). The contrast between the reaction of (3) and its isomer (2) is noteworthy. The latter can react by Scheme 2, since the 1-naphthyl site has the correct orientation with respect to the ^+N-OH group. However, if (3) were to react *via* Scheme 2,



SCHEME 3

it would have to react at phenyl; this is energetically unfavourable so (3) reacts by the pathway of Scheme 3 and the overall rate is some three times slower than that of (2). Thus we have the interesting phenomenon that the isomeric azoxy-substrates (2) and (3) react by different pathways in forming the same reaction product.[5c]

It can be seen from Figure 2 that the topmost point due to the reaction of (2) joins the line due to that of (3); this occurs at *ca.* 83% H_2SO_4, or H_0 *ca.* $-7{\cdot}8$. This type of behaviour is similar to that previously found for the reaction of hexamethylazoxybenzene,[1] for which reaction occurs by a pathway somewhat analogous (see above) to Scheme 2 below 80% H_2SO_4, and by a pathway like Scheme 3 in more concentrated acid. Thus both (2) and (3) are reacting *via* Scheme 3 in >83% H_2SO_4. As the acidity increases, Scheme 3 becomes relatively more favourable since log $a_{H_2SO_4}$ continues to increase while the Scheme 2 pathway reaches its terminal velocity. It is apparent that (1), and probably the other compounds also, react by the pathway of Scheme 2 above *ca.* 83% acid, since (1) at 25·0° shows a linear dependence on log $a_{H_2SO_4}$ above 83% H_2SO_4 (Figure 2).

Conclusions.—The mechanistic conclusions derived from this kinetic study are as follows. Reactions (1) ⟶ (7), (2) ⟶ (8), (4) ⟶ (9), (5) ⟶ (10), and (6) ⟶ (11), in H_2SO_4 solutions below 83% w/w proceed by the mechanism outlined in Scheme 2, involving quinonoid-type intermediates. Reaction (3) ⟶ (8), and the other reactions in H_2SO_4 solutions above 83% w/w, proceed by the mechanism of Scheme 3, which involves a dicationic intermediate similar to that previously postulated for the Wallach rearrangement of azoxybenzene. The latter mechanism requires rate-determining proton transfer from undissociated H_2SO_4 species, *i.e.* general acid catalysis in moderately concentrated sulphuric acid.[15]

Thus the kinetic study has made possible a delineation of the dichotomy in the reaction pathways (quinonoid *versus* dicationic intermediates) which were tentatively proposed as alternatives on the basis of the observed product orientation in this series and using simple HMO calculations.[5b]

We draw attention also to certain analogies between the Wallach and the benzidine [16] rearrangements. Both transformations can proceed by pathways involving intermediates with one or two positive charges. Within each pathway the reaction rate increases in the order phenyl < 2-naphthyl < 1-naphthyl, leading to an inverse pK_a-reactivity relationship for the substrates concerned. In both reaction series there is the requirement for substantial charge delocalization in the transition state of the reaction.

EXPERIMENTAL

The preparation of the azoxyarene substrates has been described previously.[6] The products from the reactions were identified spectrally under the kinetic conditions by comparison with the authentic compounds in neutral, acidic, and basic solutions.[5b] In the cases of reactions of (1) and (4) product identification was confirmed by actual isolation.

The reactions were studied over as wide an acidity range as possible, the lower acidity limit being the slowest rate conveniently measurable, or the limit of substrate solubility,[6] and the upper acidity limit being the onset of competing reactions, probably sulphonation [17] and/or ring protonation and decomposition, of either reactant or product. The reaction media were: (i) H_2SO_4 solutions containing 0·5% ethanol [(1)—(3) at 44·4°]; (ii) H_2SO_4 solutions containing 5% dioxan [(4)—(6) at 44·4°]; and (iii) aqueous H_2SO_4 [(1) at 25·0°]. The co-solvents were present to aid solubility; an appropriate acidity function

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was used for the H_2SO_4–5% dioxan medium.[18a] Acidity function and species activity data for H_2SO_4 solutions were from the sources previously cited.[3a]

The reactions of (1)—(6) in the H_2SO_4 media were followed by repeatedly scanning the u.v.–visible spectrum of reaction solutions, either directly in the cell, or indirectly after quenching portions in base, the ' direct ' and ' indirect ' methods previously described.[3c] A Unicam SP 800 spectrophotometer was used. Pseudo-first-order rate constants (k_ψ) were obtained from the slopes of log (OD_∞ − OD) against time plots, using the optical density at a suitable absorption maximum of either reactant or product.[5b] Values of OD_∞, where not obtainable directly (due to slow reaction in the weak acid solutions or to slight decomposition in the most strongly acid media), were theoretical values calculated from the known extinction coefficients of the known products in the medium; in some cases the Guggenheim procedure could be used advantageously. The rate constants recorded in Tables 1—7 represent the mean values of generally 2—4 determinations, as performed by a combination of the methods referred to above.

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