Kinetics of sulfonation of 4-hydroxyazobenzene[1]

W. M. J. STRACHAN AND E. BUNCEL
Department of Chemistry, Queen's University, Kingston, Ontario

Received June 18, 1969

Spectral changes exhibited by 4-hydroxyazobenzene in the 90–100% H_2SO_4 region are shown to be the result of a sulfonation process, superimposed (above 98% H_2SO_4) on a second equilibrium protonation. The reaction product is 4-hydroxyazobenzene-4′-sulfonic acid. The rate of this sulfonation reaction increases by a factor of 500 over 91.7–100.0% H_2SO_4. The increase in rate is more gradual in acid media in which diprotonation of reactant is effective.

In 100% H_2SO_4 and above, a second, much slower, rate process is discerned from the spectral changes in this system and is probably the result of a further sulfonation of 4-hydroxyazobenzene-4′-sulfonic acid. Kinetic data for this reaction are reported for 99.99–100.76% H_2SO_4.

The results are in agreement with previous qualitative reports on the formation of sulfonation products from 4-hydroxyazobenzene or from azoxybenzene, its precursor in the Wallach rearrangement. The mechanism of the consecutive sulfonation reactions is discussed.

Canadian Journal of Chemistry, 47, 4011 (1969)

In early studies of the Wallach rearrangement (1) of azoxybenzene in the 100% H_2SO_4 region, in addition to the formation of 4-hydroxyazobenzene, sulfonic acid derivatives were also noted to be present (2,3). In particular, Wilsing in 1882 (2) obtained mono-, di-, tri-, and even tetrasulfonic acid derivatives of 4-hydroxyazobenzene upon treatment of azoxybenzene with fuming sulfuric acid of unspecified concentration at temperatures in excess of 100°. Of these only the monosulfonic acid was fully identified (3) as 4-hydroxyazobenzene-4′-sulfonic acid, though it was shown (2) that the second and third sulfonic acid groups entered the ring containing the hydroxyl substituent. More recent work, by Gore and Hughes (4) and by Newbold and Akhtar (5), has confirmed the formation of sulfonic acid derivatives in the rearrangement of azoxybenzene and of substituted azoxybenzenes even under less vigorous conditions.

In order to evaluate quantitatively the importance of the sulfonation process in Wallach rearrangement reactions in the 100% H_2SO_4 region, we embarked on a systematic study with 4-hydroxyazobenzene under controlled conditions of temperature and acid concentration. In our previous kinetic study with azoxybenzene in acids up to 96% H_2SO_4, it was noted that in the upper acid region 4-hydroxyazobenzene undergoes a further, relatively slow, reaction whose nature was not identified (6).

Results

4-Hydroxyazobenzene in Acids Below 100% H_2SO_4

Examination of 4-hydroxyazobenzene in the present work was carried out spectrally (substrate concentration 10^{-5}–10^{-4} *M*), for 90–100% H_2SO_4, at 25°. The spectral changes in the lower acid region are illustrated by the following experiment using 94.73% H_2SO_4 (Fig. 1). The initial

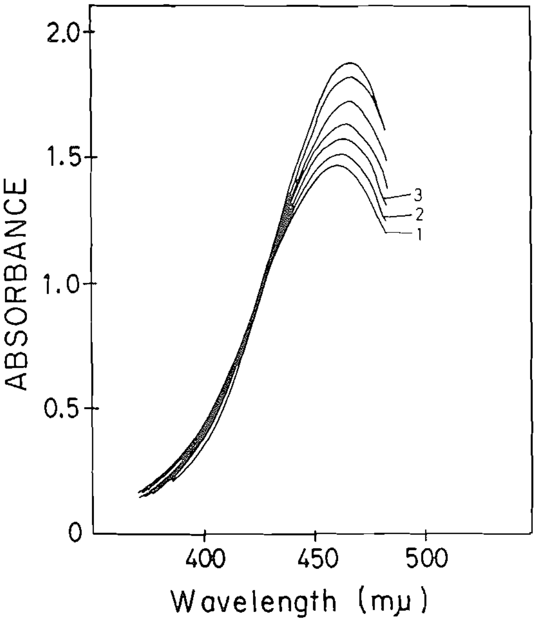

FIG. 1. 4-Hydroxyazobenzene in 94.73% H_2SO_4, 3.92×10^{-5} *M* substrate (25°, 1.00 cm cuvette). Scans noted are 1–0.1 h, 2–4 h, 3–9.5 h, last scan 120 h.

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[1] Part VII in series on the Wallach rearrangement.

spectrum of 4-hydroxyazobenzene in this medium shows absorption in the visible region at 460 mμ (ε = 3.78 × 10^4), which can be ascribed to the azo-protonated substrate (7). This absorption slowly grows in intensity and simultaneously shifts to slightly longer wavelengths. After 10 h the absorbance has increased by about 8% with the peak shifted to 462 mμ, while after 50 h the increase is about 25% (λ_{max} 465 mμ), and beyond 120 h (ε_{465} = 4.78 × 10^4) there is no further spectral change. The pseudo-first order rate constant for the growth of the absorption, calculated at 465 mμ by the log $(A_\infty - A_t)$ versus t plot where A_∞ is the final absorbance, is 1.16 × 10^{-5} s^{-1} ($T_{\frac{1}{2}}$ = 16.6 h). Using the Guggenheim method and absorbance changes at 460 mμ, a rate constant of 1.18 × 10^{-5} s^{-1} is obtained. In an analogous manner, examination of 4-hydroxyazobenzene was extended to about 100% H_2SO_4. Over this range of acid concentration there is a gradation in the spectral changes, as illustrated by Figs. 1–3 and discussed below.

It is seen from Figs. 1–3 that the initial spectrum of 4-hydroxyazobenzene shifts to shorter wavelengths as the acid concentration is increased; this has been ascribed to a second equilibrium protonation of the substrate (7). The rate process corresponding to the growth in absorbance, for which rate constants were obtained as previously (Table I), is characterized in each case by a sharp isosbestic point. The observed reaction is identified as sulfonation, to give 4-hydroxyazobenzene-4′-sulfonic acid; the shifts in λ_{max} of the product absorption with increasing acid concentration are ascribed to a second equilibrium protonation of this sulfonic acid (7).

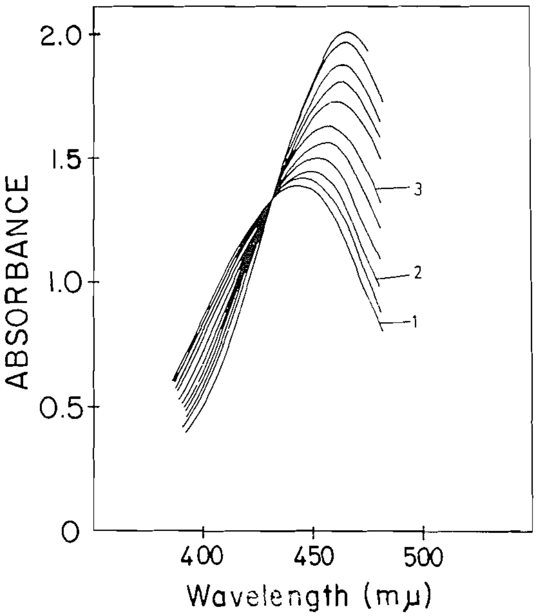

FIG. 2. 4-Hydroxyazobenzene in 99.72% H_2SO_4, 4.01 × 10^{-5} M substrate (25°, 1.00 cm cuvette). Scans noted are 1–1.5 min, 2–4 min, 3–12 min, last scan 60 min.

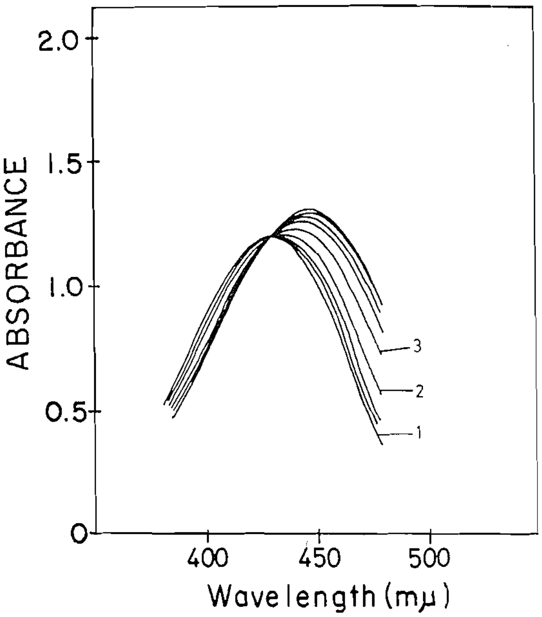

FIG. 3. 4-Hydroxyazobenzene in 99.96% H_2SO_4, 3.88 × 10^{-5} M substrate (25°, 1.00 cm cuvette). Scans noted are 1–1.5 min, 2–5 min, 3–9 min, last scan 55 min.

4-Hydroxyazobenzene-4′-sulfonic acid has spectral absorption in concentrated sulfuric acid solutions which agrees quantitatively with the final "infinity" spectra of 4-hydroxyazobenzene following reaction in 94.5–98.9% H_2SO_4 (see Experimental). Near the 100% H_2SO_4 region, spectral comparison is made more difficult as a result of extensive diprotonation, with accompanying changes in absorption (7), and also due to the advent of a second sulfonation (*vide infra*).

The total rate data for this sulfonation process are given in Table I. The kinetic methods are described in detail in the Experimental section.

4-Hydroxyazobenzene and 4-Hydroxyazobenzene-4′-sulfonic Acid in the 100% H_2SO_4 Region

The spectral behaviour of 4-hydroxyazobenzene takes on distinctly different character close

TABLE I

Kinetic data for sulfonation of 4-hydroxyazobenzene to 4-hydroxyazobenzene-4′-sulfonic acid at 25°

Weight (%) H_2SO_4	H_0	$10^5\ k_{obs}$ (s^{-1})	Kinetic method	(λ mμ)
91.66	−8.47	0.51	*	(460)
93.50	−8.68	1.08	*	(460)
94.52	−8.81	1.41	*	(460)
94.73	−8.83	1.18	*	(460)
—	—	1.16	†,*	(465)
94.73	−8.83	1.12	‡	(463)
96.18	−9.03	3.22	‡	(463)
97.33	−9.22	6.15	*	(460)
97.56	−9.28	6.63	*	(460)
97.78	−9.32	6.30	‡	(463)
97.80	−9.32	7.06	*	(460)
—	—	6.66	†,*	(463)
98.92	−9.68	26.0	‡	(460)
99.00	−9.74	28.2	‡	(463)
99.37	−9.93	50.8	*	(460)
99.37	−9.93	50.7	‡	(460)
99.59	−10.10	80.1	‡	(460)
99.59	−10.10	84.1	‡	(463)
99.72	−10.24	102	*	(460)
—	—	111	†,*	(465)
99.72	−10.24	152	‡	(463)
99.83	−10.42	164	‡	(460)
99.83	−10.42	211	‡	(463)
99.94	−10.82	246	‡	(460)
99.96	−10.94	250	*	(460)
99.96	−10.94	290	‡	(463)
99.99	−11.06	252	‡	(460)
99.99	−11.06	253	†,‡	(460)
100.01	−11.12	252	†,*	(480)
100.01	−11.12	265	†,*	(480)
100.02	−11.14	259	†,*	(480)
100.07	−11.25	238	†,*	(480)

*Reaction followed by periodic scanning. Rate constant calculated at wavelength indicated by Guggenheim method.

†Rate constant calculated using $A_\infty - A_t$ plot. Data obtained either as indicated under footnote * or as in footnote ‡. (When a rate constant was recalculated by the $A_\infty - A_t$ plot but using the raw data in a previous run, then the acid concentration is not re-stated in the first column.)

‡Reaction followed at constant wavelength shown. Rate constant calculated by Guggenheim method.

to 100% H_2SO_4 from that described hitherto. Figure 4 shows an illustrative run for 100.01% H_2SO_4. Two rate processes are reflected in Fig. 4, for which the corresponding spectra are drawn in dashed lines and in full lines for clarity. The two sets of curves correspond to different time scales, the former being taken minutes apart and representing an initial fast reaction and the latter taken hours apart and representing a subsequent slow reaction. The two processes were first observed on a scan of absorbance (460 mμ) versus time, as an initial rapid increase ($T_{\frac{1}{2}}$ = 4.5 min by the Guggenheim method) followed by a very slow increase ($T_{\frac{1}{2}}$ = 27.5 h) in absorbance. The fast reaction is identified as the sulfonation process discussed in the preceding section.

A further characteristic which differentiates the 4-hydroxyazobenzene runs near the 100% H_2SO_4 region is isosbestic point behaviour. Figure 4 shows that the initial dashed spectral curves do not pass through an isosbestic point but are nearly tangential on the short wavelength side of λ_{max} (426 mμ).[2] The isosbestic point that is observed (422 mμ) is common to the later full curves. It is shown below that the rate process corresponding to this isosbestic point is a second

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[2] The absence of an isosbestic point with respect to the first sulfonation process represented by the dashed curves in Fig. 4 is explained by the very close wavelength maxima of the absorptions due to the largely diprotonated 4-hydroxyazobenzene reactant ($\lambda^{BH_2{}^{2+}}$ 426 mμ) and the partly diprotonated 4-hydroxyazobenzene-4′-sulfonic acid product ($\lambda^{BH_2{}^{2+}}$ 420 mμ) in 100.01% H_2SO_4.

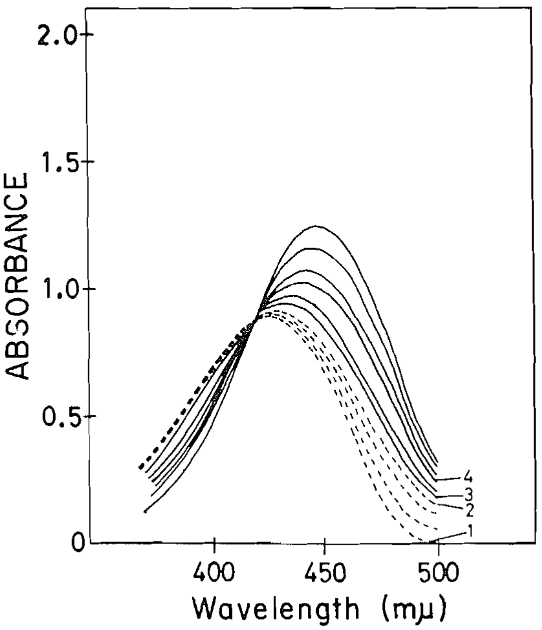


FIG. 4. 4-Hydroxyazobenzene (2.84×10^{-5} M) in 100.01% H_2SO_4 (25°, 1.00 cm cuvette). Scans noted are 1–1 min, 2–30 min, 3–4 h, 4–19 h, last scan 141 h.

sulfonation of 4-hydroxyazobenzene-4′-sulfonic acid. The positions of the maxima in Fig. 4 first need commenting on. The initial λ_{max} (426 mμ) corresponds to almost complete diprotonation in this medium of the reactant (pK_a^2 for 4-hydroxyazobenzene = −10.2 (7)). The first sulfonation is about complete with curve 2 (30 min, λ_{max} 429 mμ), which corresponds to about 50% diprotonation of the formed 4-hydroxyazobenzene-4′-sulfonic acid (pK_a^2 = −11.1). The final product spectrum (λ_{max} 449 mμ) is ascribed to a disulfonic acid derivative present essentially in monoprotonated form in this medium (see Experimental for an estimate of pK_a^2).

The reactivity of 4-hydroxyazobenzene-4′-sulfonic acid in the 100% H_2SO_4 region was confirmed by means of a kinetic run carried out with this substrate in 100.07% H_2SO_4, shown in Fig. 6. The spectral changes in Fig. 6 are typical of a rate process (isosbestic point at 422 mμ, $T_{\frac{1}{2}}$ = 15.0 h by the Guggenheim method). A kinetic run carried out with 4-hydroxyazobenzene in the same medium is shown in Fig. 5. The full curves in this 4-hydroxyazobenzene run show all the features (isosbestic point at 422 mμ, $T_{\frac{1}{2}}$ = 15.0 h) which characterized the reaction of 4-hydroxyazobenzene-4′-sulfonic acid (Fig. 6). However in addition Fig. 5 shows that 4-hydroxyazobenzene first undergoes a rapid rate process (dashed curves, $T_{\frac{1}{2}}$ = 4.5 min), which can clearly be ascribed to the first sulfonation reaction.

Rate data for the second reaction, as observed with 4-hydroxyazobenzene reactant, were obtained analogously over the region 99.99–100.76% H_2SO_4 and are given in Table II. Rate data for the first sulfonation process, which were obtained for part of this acid range from the initial fast increase in absorbance at 460/463 mμ, are included in Table I.

The product of the second process is tentatively identified as 4-hydroxyazobenzene-3,4′-disulfonic acid, though conclusive evidence is not available. The identification is made on the basis of the spectral absorptions in 100.79% H_2SO_4, 96% H_2SO_4, 0.2 N H_2SO_4, and 0.2 N KOH, in which media this product is expected to be present in several different ionization states (see Experimental). Also, this is the expected product on the basis of the directive effects of the substituents in 4-hydroxyazobenzene-4′-sulfonic acid toward electrophilic substitution (*vide infra*).

Independent evidence for the sulfonation pro-

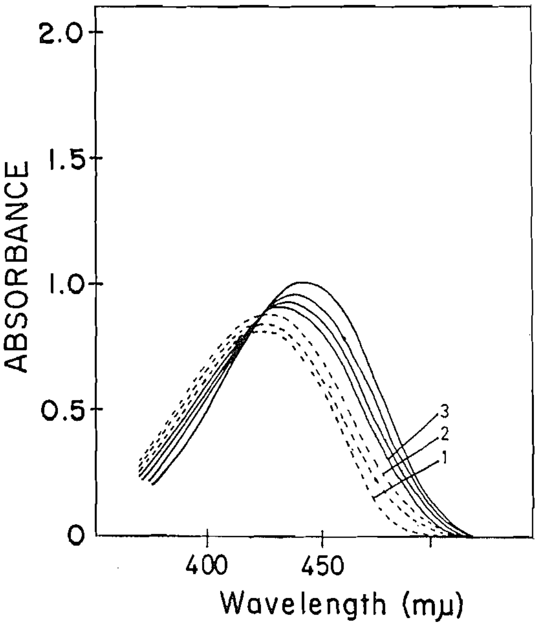


FIG. 5. 4-Hydroxyazobenzene (0.72×10^{-5} M) in 100.07% H_2SO_4 (25°, 4.00 cm cuvette). Scans noted are 1–1.5 min, 2–30 min, 3–9 h, last scan 36 h.

TABLE II

Kinetic data for sulfonation of 4-hydroxyazobenzene-4′-sulfonic acid observed with 4-hydroxyazobenzene as substrate

Weight (%) H_2SO_4	H_0	$10^5\ k_{obs}$ (s^{-1})	Kinetic method	(λ mμ)
99.99	−11.06	0.568	‡	(460)
100.00	−11.09	0.680	‡	(460)
100.01	−11.12	0.731	‡	(460)
100.01	−11.12	0.703	*	(460)
100.07	−11.25	1.04	*	(460)
—	—	1.32	†,*	(449)
100.07	−11.25	1.42	‡	(463)
100.07	−11.25	1.23§	*	(460)
100.22	−11.45	2.25	‡	(460)
100.76	−11.77	5.57	‡	(463)

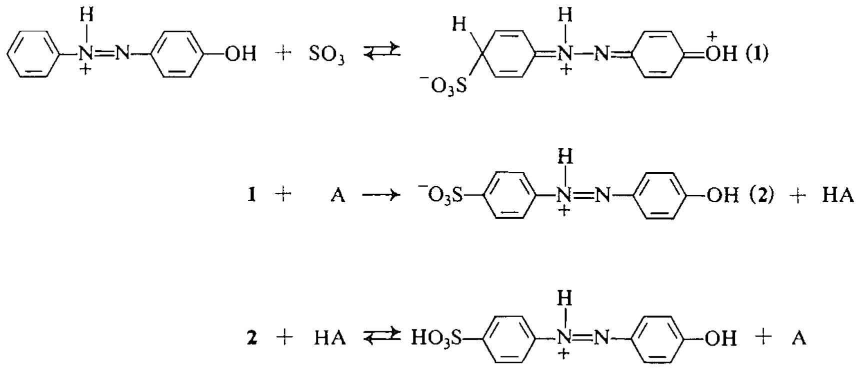
*,†,‡Kinetic methods as described for Table I.
§Rate constant using 4-hydroxyazobenzene-4′-sulfonic acid as substrate.

cesses described above derives from cryoscopic and conductivity measurements obtained with 4-hydroxyazobenzene in 100% H_2SO_4 (8).

Discussion

The results of the quantitative study of the sulfonation of 4-hydroxyazobenzene described above are in accord with previous qualitative reports in the literature on the conversion of 4-hydroxyazobenzene (or of azoxybenzene, its precursor in the Wallach rearrangement) to 4-hydroxyazobenzene-4′-sulfonic acid and to higher sulfonation products (2–5).

The acidity dependence of the sulfonation of 4-hydroxyazobenzene is in many ways comparable to that in the sulfonation of benzene (9–11), *p*-nitrotoluene (12,13), benzenesulfonic acid (14*a*), and other aromatic derivatives, in concentrated sulfuric acid–dilute oleum media. Such sulfonation processes are recognized to belong to the class of electrophilic aromatic substitution reactions (15,16). However differences have been expressed concerning the detailed nature of the sulfonation mechanism (9–16), partly as a result of the uncertainty as to the identity of the sulfonating species (17): H_2SO_4, SO_3, $H_2S_2O_7$, S_2O_6, SO_3H^+, $H_3SO_4{}^+$, and others. The statement (15*a*) "that monomeric sulfur trioxide, or, possibly, a sulfuric acid solvate of it, is the active species contained in sulfonating media of this type" forms the basis of the mechanism proposed for the sulfonation of 4-hydroxyazobenzene:



In this mechanism the 4-hydroxyphenylazo group is taken as activating toward electrophilic substitution but its effect should be considerably reduced by the deactivating nature of the protonated azonium function. In accord with this consideration, the reactivity of 4-hydroxyazobenzene is greater than of benzene derivatives containing the trimethylammonio or nitro substituents (12,13), though less than of benzene itself (9–11).

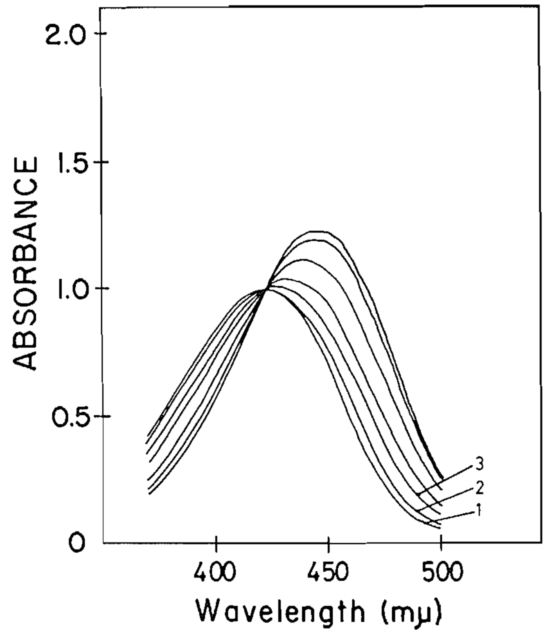


FIG. 6. 4-Hydroxyazobenzene-4′-sulfonic acid (2.97 × 10^{-5} *M*) in 100.07% H_2SO_4 (25°, 1.00 cm cuvette). Scans noted are 1-2.5 min, 2-2 h, 3-6 h, last scan 37 h.

The above scheme considers monoprotonated 4-hydroxyazobenzene to be the effective reactant on the ground that, with a pK_a^1 of -1.0 (reference 7 and others quoted therein) 4-hydroxyazobenzene is already 99.9% protonated in ca. 55% H_2SO_4. It is only in considerably more acidic media (ca. 90% H_2SO_4) that the sulfonating species reach effective concentration for reaction in this system.

It has been shown that above 98% H_2SO_4 a second equilibrium protonation of 4-hydroxyazobenzene becomes effective ($pK_a^2 = -10.2$ (7)) and that the site of the second protonation is the phenolic oxygen. The resulting diprotonated species should be very much less reactive toward sulfonation since *O*-protonation effectively negates the activating ability of the hydroxyphenylazo moiety. Some support for this view is given by the observation that the linearity range of the $\log k$ versus $-H_0$ plot is extended to higher acid concentrations when account is taken of the material present in diprotonated form by plotting $\log k - \log C_{SH^+}/(C_{SH^+} + C_{SH_2^{++}})$[3] versus H_0 (Fig. 7). The slope of the linear portion of this plot (1.50) is not readily interpretable but non-unit slopes appear to be general for reactions occurring in the concentrated sulfuric acid media (21,22).

The kinetic dependence of the second sulfonation is very similar to the first and requires little comment. The plot of $\log k - \log C_{SH^+}/(C_{SH^+} + C_{SH_2^{++}})$ versus H_0 is linear, which is analogously interpreted to mean that the reactive species is monoprotonated 4-hydroxyazobenzene-4′-sulfonic acid and that the diprotonated species is unreactive. It was shown previously (7) that for this substrate the second equilibrium protonation ($pK_a^2 = -11.1$) is also on phenolic oxygen. The above mentioned plot has a slope of 2.0

The observed orientation in these sulfonation reactions is of interest. The apparently exclusive first sulfonation in the 4′-position (rather than in the 3-position) is probably due in part to a steric factor, since it has been shown (15*b*) that *ortho* orientation is relatively disfavoured in aromatic sulfonation. However another factor (15*c*) influencing orientation in this system is the

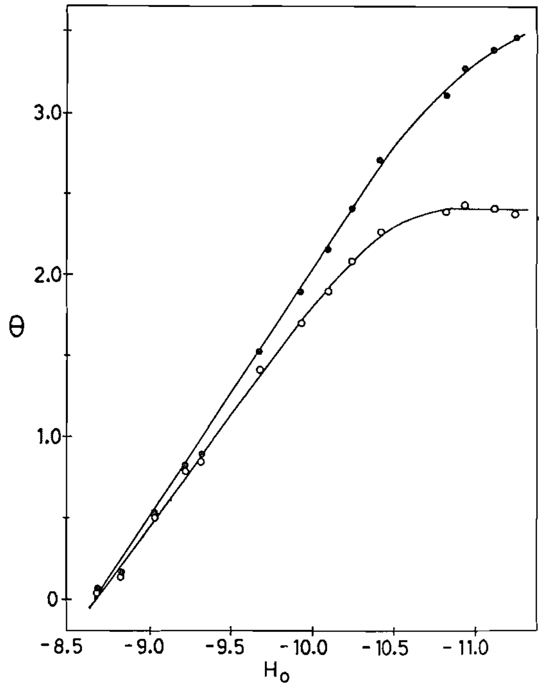


FIG. 7. Acidity function correlations for conversion of 4-hydroxyazobenzene to 4-hydroxyazobenzene-4′-sulfonic acid in sulfuric acid solutions at 25°.

O, $\Theta = 5 + \log k_{obs}$; ●, $\Theta = 5 + \log k_{obs} - \log C_{SH^+}/(C_{SH^+} + C_{SH_2^{++}})$

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[3] This term was evaluated by means of the expression $\log C_{SH_2^{++}}/C_{SH^+} = pK_a^2 - H_0$ using the H_0 values (18) in Table I. The possible application of an H_+ function (19,20) in this system was considered previously (7).

increased through-conjugation in the reaction product (and in the reaction intermediates and transition states) which results when sulfonation occurs in the 4-position. The second sulfonation should then be directed in the position *ortho* to the hydroxyl group, which will be more activating than the azo-nitrogen bonded to the second proton-bearing nitrogen.

Experimental

Materials

4-Hydroxyazobenzene and 4-hydroxyazobenzene-4′-sulfonic acid had physical properties as described previously (7). Sulfuric acid solutions were prepared by addition of fuming acid (30% SO_3) to 96% acid and analyzed conductimetrically (23). Acid concentrations are given as weight per cent.

Kinetic Measurements

The bulk of the kinetic data were obtained by following the reactions (10^{-4} to 10^{-5} *M* in substrate) spectrally *in situ* in thermostated cells mounted in a constant temperature holder in the spectrophotometer (the "direct method"). The substrate (0.1–1.0 mg, weighed on a Cahn-M10 Electrobalance in glass boats of tare less than 5 mg) was added to a pre-thermostated, weighed quantity of sulfuric acid (25–100 ml) and transferred to the thermostated 1 cm cells (25.00 ± 0.03°). The spectrophotometers used were either a Unicam SP800B or a Bausch and Lomb Spectronic 600 Spectrophotometer, the latter in conjunction with a Sargent SRL recorder. In kinetic runs carried out on the former instrument spectral sweeps were taken at various times over the region of interest and rate constants calculated from absorbance values read off these sweeps. The latter instrument was generally used for following the reaction at constant wavelength. A small variation (2–4 mμ) in absorption characteristics (peak or isosbestic point wavelengths) was observed between runs, presumably as the result of small differences in acid concentration (particularly in the 100% H_2SO_4 region) and in instrumental settings over a period of time.

The wavelength at which absorbance changes were computed was usually in the region 460–465 mμ, being close to, though not necessarily at λ_{max} for the product of reaction. In acid media over 100% H_2SO_4 the first sulfonation was also followed on occasion at 480 mμ, which gave more optimum changes in absorbance than was afforded at 460–465 mμ (cf. Fig. 4); the rate of the second sulfonation was also computed on occasion for ca. 450 mμ.

Most of the rate constants were calculated by the Guggenheim method since this removed the uncertainty with respect to "infinity" absorbance values current with the small sized substrate samples employed, the slow rates in the lower acid range, and the two consecutive sulfonation processes above the 100.0% H_2SO_4. Where "infinity" absorbance values could be obtained, some of the rate constants were also evaluated by means of log ($A_\infty - A_t$) versus t plots; in such cases experimental A_∞ values were used, which was deemed more accurate with the small sized samples.

Rate constants were calculated by means of a least square program using an IBM 360/–50 computer, with a Calcomp Digital Plotter 663 to plot the data. A correlation coefficient of 0.994 was taken as prepresentative of acceptable linearity. An illustrative plot is shown in Fig. 8.

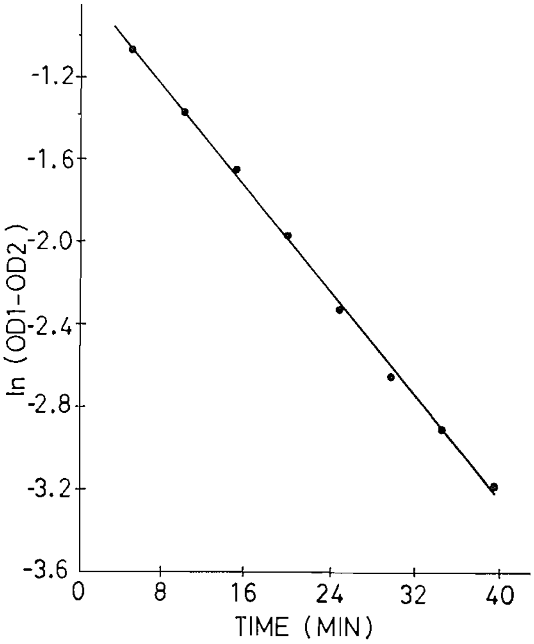

FIG. 8. Kinetic plot for sulfonation of 4-hydroxyazobenzene in 99.72% H_2SO_4. Data correspond to kinetic run illustrated in Fig. 2. Absorbance values at 460 mμ are plotted according to the Guggenheim method with $\Delta t = 15$ min and yield $k_{obs} = 102 \times 10^{-5}\ s^{-1}$.

One kinetic run in this series was carried out by the base-quenching procedure ("the indirect method" (24)). The reaction solution was prepared by adding 2.49 mg of 4-hydroxyazobenzene in 20 ml (36.6 g) of 97.80% H_2SO_4 in a constant temperature bath (25.00 ± 03°). Aliquots (0.991 ml) were periodically quenched with cold 1 *N* aqueous KOH, diluted to 50 ml at 25°, and the spectra taken in 4.00 cm cells. The rate constant was calculated from the absorbance changes at 440 mμ, being λ_{max} for 4-hydroxyazobenzene-4′-sulfonic acid in basic medium. Using the log ($A_\infty - A_t$) versus *t* plot, $k = 6.27 \times 10^{-5}\ s^{-1}$.

Identification of Product of First Sulfonation

Spectral characteristics of "infinity" solutions ($\geq$ 97% reaction) of 4-hydroxyazobenzene were compared with the spectrum of 4-hydroxyazobenzene-4′-sulfonic acid. For the range 94.52–98.92% H_2SO_4, the λ_{max} of the "infinity" solutions for 11 kinetic runs varied over 463–467 mμ, with molar extinctions taking the values 4.56×10^4–4.88×10^4. 4-Hydroxyazobenzene-4′-sulfonic acid in 89.3% H_2SO_4 showed λ_{max} 465 mμ ($\varepsilon = 4.61 \times 10^4$) and in 97.80% H_2SO_4, λ_{max} 463 mμ ($\varepsilon = 4.70 \times 10^4$). Below 94.5% H_2SO_4 "infinity" readings were not obtained due to the low reaction rate. Over 99% H_2SO_4, where the second equilibrium protonation of 4-hydroxyazobenzene-4′-sulfonic acid becomes important, the

TABLE III

Spectral characteristics of 4-hydroxyazobenzene and sulfonated derivatives in several states of ionization

	Basic (ArO^-)		Neutral (B)		Monoprotonated (BH^+)		Diprotonated (BH_2^{++})	
	λ(mμ)	$10^{-4}\varepsilon$	λ(mμ)	$10^{-4}\varepsilon$	λ(mμ)	$10^{-4}\varepsilon$	λ(mμ)	$10^{-4}\varepsilon$
4-Hydroxyazobenzene	440 402	2.18 2.16	348	2.50	460	3.81	426‡	3.30‡
4-Hydroxyazobenzene-4′-Sulfonic acid	448*	2.56	350	2.40	465	4.65	420	3.87
4-Hydroxyazobenzene-3,4′(?)-Disulfonic acid	440*	2.66	348	2.51	452	4.46	(436)†	(3.72)†

*The basic spectra have a broad shoulder in the 400–410 mμ region.
†Observed values in 100.79% H_2SO_4.
‡Observed values in 100.02% H_2SO_4.

"infinity" extinctions of the product solutions from the 4-hydroxyazobenzene reaction were found to fit well along the pK_a^2 curve of this sulfonic acid (see reference 7, footnote 6).

Partial Identification of Product of Second Sulfonation

4-Hydroxyazobenzene and 4-hydroxyazobenzene-4′-sulfonic acid were allowed to react in 100.79% at 25° (separate runs, substrate concentrations ca. 3×10^{-4} *M*) for periods of 24 and 65 h (corresponding to 6 and 16 half-lives). The spectra were then examined in that medium as well as in 96% H_2SO_4, 0.2 *N* H_2SO_4, and 0.2 *N* KOH, obtained by dilution (1:50) of the original 100.79% reaction solution with 96% H_2SO_4, 0.6 *N* KOH and 1.0 *N* KOH, respectively. The reaction solutions derived from 4-hydroxyazobenzene and from 4-hydroxyazobenzene-4′-sulfonic acid showed virtually identical absorption, for both reaction times, as expected on the basis of product identity, and average ε values are considered below. The spectrum in 0.2 *N* KOH is identified with the azophenolate anion (ArO^-); the spectrum in 0.2 *N* H_2SO_4 with the neutral species (B) with respect to the azo linkage; in 96% H_2SO_4 with the azo-protonated species (BH^+); and the 100.79% H_2SO_4 spectrum is ascribed to partial diprotonation.

In Table III the λ and ε values for the various ionized forms of 4-hydroxyazobenzene and 4-hydroxyazobenzene-4′-sulfonic acid are compared with corresponding values for this reaction product, tentatively identified as 4-hydroxyazobenzene-3,4′-disulfonic acid. This identification rests largely on the close similarity in these λ,ε data, since it is known that the introduction of a sulfonic acid group in the azobenzene system does not significantly alter the spectral characteristics of the parent compound (7).

The site of the second equilibrium protonation in the disulfonic acid product is probably the phenolic oxygen (7) and a λ_{max} in the region of 420 mμ for this species can be assumed. Since λ_{max} shifts from 452 to 436 mμ between 96% H_2SO_4 and 100.79% H_2SO_4, the extent of this shift would roughly correspond to ~50% diprotonation, with a pK_a^2 of ca. −12.

Acknowledgments

The award of an Ontario Graduate Fellowship to W.M.J.S. is gratefully acknowledged, as is continued financial support from the National Research Council of Canada.

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