rium constant for the ionization of nitrous acid by sulfuric acid is much greater than the corresponding ionization of nitric acid by sulfuric acid. In our system the estimated concentration of NO^+ is about 0.01 M so the corresponding NO_2^+ concentration must be much less. The concentration of $H_2NO_2^+$ in sulfuric acid solution has been demonstrated spectrophotometrically to be zero within experimental error or at most to exist at very low fractions of the HONO and NO^+ concentrations.[23a] Nitrogen dioxide, though not detectable by us, must exist in some concentration since both N_2O_3 and HNO_3 can dissociate to give NO_2. However, the NO_2 concentration decreases from the start as indicated by the transition in color of the solution from green to blue. This behavior is contrary to observed rates, if NO_2 were the oxidizing agent. Nitrous acid by itself or in dilute acid solution readily forms nitrite esters with alcohols rather than act as an oxidizing agent. The nitrite ester can be considered a derivative of nitrous acid and, by itself, is sufficiently stable. Thus nitrous acid or the nitrite ester of methoxyethanol are probably not doing the oxidation. Dinitrogen trioxide in pentane acts as a nitrosating agent for alcohols so that species by itself is not an oxidizing agent.

Acknowledgment. We wish to thank R. A. Strojny and J. Crump for helpful discussions, R. A. Nyquist and V. B. Carter for infrared spectrophotometric interpretations and analyses, J. P. Heeschen and T. E. Evans for assistance in nmr interpretations, J. C. Tou and B. Hart for mass spectrometric analyses, and H. H. Grossman and B. I. Milner for computerized plotting of data.

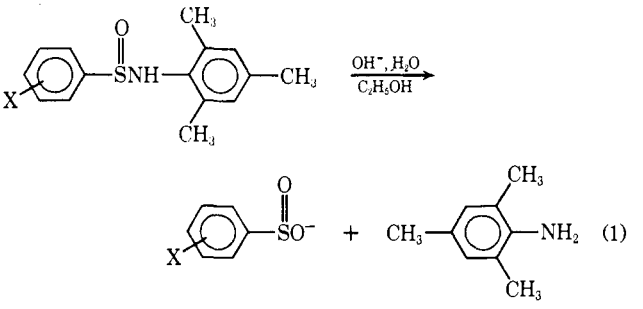
Hydrolysis of Arenesulfinamides in Basic Aqueous Ethanol. Nucleophilic Substitution at Tricoordinate Sulfur(IV)[1]

J. Brian Biasotti[2] and Kenneth K. Andersen*

Contribution from the Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824.
Received July 31, 1970

Abstract: Nine meta- and para-substituted *N*-mesitylbenzenesulfinamides were prepared and the kinetics of their reaction with hydroxide ion in aqueous ethanol studied. Second-order rate constants were obtained. The reaction was shown to be first order in base and first order in sulfinamide. Activation parameters were determined for the *p*-chlorobenzenesulfinamide as $\Delta H^{\pm} = +20.0$ kcal/mol and $\Delta S = -8.9$ eu. The rate constants gave a good correlation with Hammett's σ constants ($\rho = +1.3$). The procedure of Taft for determining specific resonance effects was applied to the data for the sulfinamides. A resonance value of -0.08 σ unit was obtained for *N*-mesityl-*p*-methoxybenzenesulfinamide indicating that the resonance contribution of the *p*-methoxyphenyl group to the resonance hybrid is slightly greater in the ground state than in the transition state. No significant resonance value (+0.03) was observed for the *p*-nitrophenyl substituent. The resonance contribution to the resonance hybrid for *N*-mesityl-*p*-nitrobenzenesulfinamide is of the same magnitude for both the ground state and the transition state. The lack of a significant resonance value for the *p*-nitrophenyl group argues against the formation of an addition intermediate. No incorporation of ^{18}O was found in unreacted *N*-mesityl-*p*-chlorobenzenesulfinamide isolated from a reaction mixture containing $H_2{}^{18}O$.

In recent years much attention has been given to the mechanistic aspects of nucleophilic substitution at di-, tri-, and tetracoordinate sulfur.[3] In hope of contributing to this general subject, we have investigated a specific case of substitution at tricoordinate sulfur(IV),[4] the basic hydrolysis of *N*-mesitylarenesulfinamides in aqueous ethanol (eq 1). Some other examples of tricoordinate sulfur(IV) compounds which undergo nucleophilic substitution at sulfur are sulfoxides (R_2SO), sulfinyl chlorides (RSOCl), sulfilimines (R_2SNR), sulfonium salts (R_3S^+), and sulfinate esters (RS(O)OR). The various aspects of the substitution reactions can be conveniently divided into four categories: (1) the influence of the nucleophile's structure on reactivity, (2) the stereochemistry of the reactions, (3) the influence of the sulfur compound's structure on reactivity, and (4)



(1)

(1) This work was supported by the National Science Foundation, Grants No. GP-5283 and GP-8136.
(2) This article is based on the Ph.D. Thesis of J. B. B., University of New Hampshire, 1968.
(3) For a discussion of nucleophilic substitution at sulfur as well as pertinent references, see (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 2731 (1970); (b) E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968); (c) E. Ciuffarin and G. Guaraldi, *J. Org. Chem.*, **35**, 2006 (1970); (d) J. L. Kice and G. J. Kasperek *J. Amer. Chem. Soc.*, **92**, 3393 (1970); (e) D. Landini, G. Modena, G. Scorrano, and F. Taddei, *ibid.*, **91**, 6703 (1969).
(4) The sulfur atom is named according to its coordination number (number of ligands not including unshared electrons) and its oxidation number (number of bonds to sulfur plus the formal charge on sulfur). See K. K. Andersen, S. A. Yeager, and N. B. Peynircioglu, *Tetrahedron Lett.*, 2485 (1970).

Table I. Rate Constants, Analytical Data, Melting Points, and Yields for the Arenesulfinamides

Compd no.	*N*-Mesityl-arene-sulfinamides	$k \times 10^4$, l. M^{-1} sec^{-1} [a]	Anal.[b] Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Mp,[c] °C	Yield, %
1	*p*-CH_3O	5.53 ± 0.17	66.41	6.62		66.55	6.72		143.5–145[d]	18
2	*p*-CH_3	6.82 ± 0.46	70.30	7.00		70.08	6.92		146–148[e]	55
3	*m*-CH_3	10.94 ± 0.14	70.30	7.00		70.38	7.13		121–122[d]	40
4	H	11.26 ± 0.12	69.46	6.61		69.54	6.77		134.5–136[e]	68
5	*p*-Cl	22.95 ± 0.40	61.32	5.49	4.77	61.51	5.63	4.86	161–162[f]	59
6	*m*-Cl	27.45 ± 0.14	61.32	5.49		61.15	5.59		152–153[d]	46
7	*m*-CF_3	48.59 ± 0.02	58.70	4.92		58.37	4.88		156–157[d]	37
8	*m*-NO_2	109.26 ± 0.16	59.19	5.30		59.07	5.34		176–177[d]	54
9	*p*-NO_2	143.61 ± 3.05	59.19	5.30	9.20	59.22	5.40	9.02	152–153.5[g]	73

[a] Determined at 49.80°. [b] Determined by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [c] With decomposition. [d] From petroleum ether–acetone. [e] From ethanol. [f] From acetone. [g] From methanol.

the possibility of intermediates of higher coordination number than that of the substrate.

It was the purpose of this work to examine the influence of the sulfur compound's structure on reactivity for one type of tricoordinate sulfur(IV) compound, the arenesulfinamides, in their reaction with hydroxide ion. A kinetic study on the rates of basic hydrolysis would provide rate constants for use in a Taft type of Hammett treatment. In this way, the electronic requirements of the reaction would be determined and information concerning the existence of an intermediate one coordination number higher than that of the substrate might be obtained.

A series of nine meta- and para-substituted *N*-mesitylbenzenesulfinamides were prepared and the kinetics of their reaction with hydroxide ion in aqueous ethanol studied. The sulfinamides are listed in Table I. The kinetics were run in 95% ethanol with the concentrations of base and sulfinamide approximately 10^{-2}–10^{-3} *M* depending upon the solubility of the sulfinamide. Second-order rate constants were obtained. The kinetics were followed by titrating the base with dilute acid. Generally, the reaction was followed for one half-life although good second-order plots could be obtained for two half-lives.

Several runs were carried out using *N*-mesityl-*p*-chlorobenzenesulfinamide in which the sulfinamide concentration was kept constant while the initial hydroxide concentration, kept in excess, was varied. The results presented in Table II indicate that the reaction is first order in sulfinamide and first order in base.

Table II. Dependence of Rate Constants for the Basic Hydrolysis of *N*-Mesityl-*p*-chlorobenzenesulfinamide on Hydroxide Ion Concentration at 49.80°

Sulfinamide, *M*	OH^-, *M*	$k_1 \times 10^5$, sec^{-1}	$k \times 10^4$, l. M^{-1} sec^{-1}
0.0075[a]	0.05	10.78 ± 0.24	22.95 ± 0.40
0.0075[b]	0.075	16.84 ± 0.30	23.58 ± 0.54
0.0075[a]	0.1125	24.75 ± 0.70	22.68 ± 0.60

[a] These runs in triplicate. [b] This run in duplicate; average deviations given.

Rates of hydrolysis were also measured at three temperatures for *N*-mesityl-*p*-chlorobenzenesulfinamide and the results are collected in Table III.

Log k/k_0 values for the substituted sulfinamides were plotted against σ (Figure 1). A good linear correlation

Table III. Rate Constants and Activation Parameters for the Hydrolysis of *N*-Mesityl-*p*-chlorobenzenesulfinamide

T, °C	$k \times 10^4$, l. M^{-1} sec^{-1}	Activation parameters[c]
30	2.85 ± 0.05[a]	$\Delta H^{\pm}$ = 20.0 ± 0.3 kcal/mol
40	8.62 ± 0.10[a]	
50	22.95 ± 0.40[b]	$\Delta S^{\pm}$ = −8.9 ± 1.2 eu

[a] These runs in duplicate. [b] This run in triplicate; average deviation given. [c] Errors calculated according to K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 378–379.

was obtained with $\rho = +1.3$, a correlation coefficient of 0.994, and a standard deviation of 0.061[5] (see Figure 1).

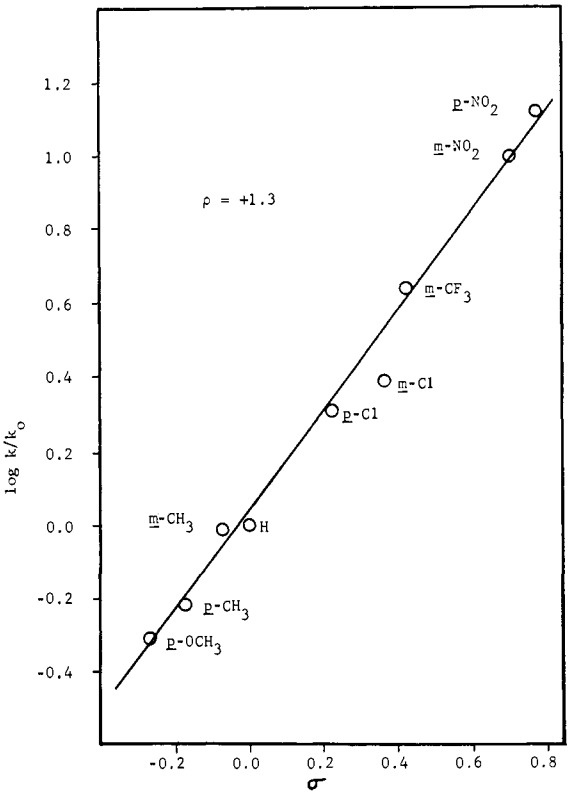


Figure 1. A plot of log k/k_0 *vs.* σ.

It is convenient to consider three transition states for a displacement reaction. The transition state may be one in which bond formation between hydroxide ion and

(5) H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

Table IV. Specific Resonance Effects ($\bar{\sigma} - \sigma^0$)

Subst	*N*-Mesityl-arenesulfinamides[a]	Ethyl benzoates[b]	Thiophenols[c]	Protonated acetophenones[d]	Protonated phenyl methyl sulfoxides[e]
p-CH_3O	−0.08	−0.11	+0.03	−0.59	−0.26
p-CH_3	−0.07	+0.02	+0.04	−0.24	−0.08
p-Cl	−0.03	−0.02	+0.02	−0.13	−0.06
p-NO_2	+0.03	−0.02	+0.14	+0.03	−0.07
	ρ = +1.32	+2.51	+3.06	+2.01	+3.61
	r = 0.983	0.998	0.986	0.981	0.983
	s = 0.346	0.005	0.108	0.128	0.22

[a] This work. [b] K. Kindler, *Ann.*, **450**, 1 (1926). [c] G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939). [d] R. Stewart and K. Yates, *J. Amer. Chem. Soc.*, **80**, 6355 (1958). [e] K. K. Andersen, W. H. Edmonds, J. B. Biasotti, and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966). The mathematical procedure used to determine ρ, and the definitions of the correlation coefficient, r, and the standard deviation, s, are given in ref 5.

sulfur has proceeded further than bond breaking between sulfur and nitrogen, it may be one in which bond breaking between sulfur and nitrogen has proceeded further than bond formation between hydroxide ion and sulfur, or a synchronous process may occur in which

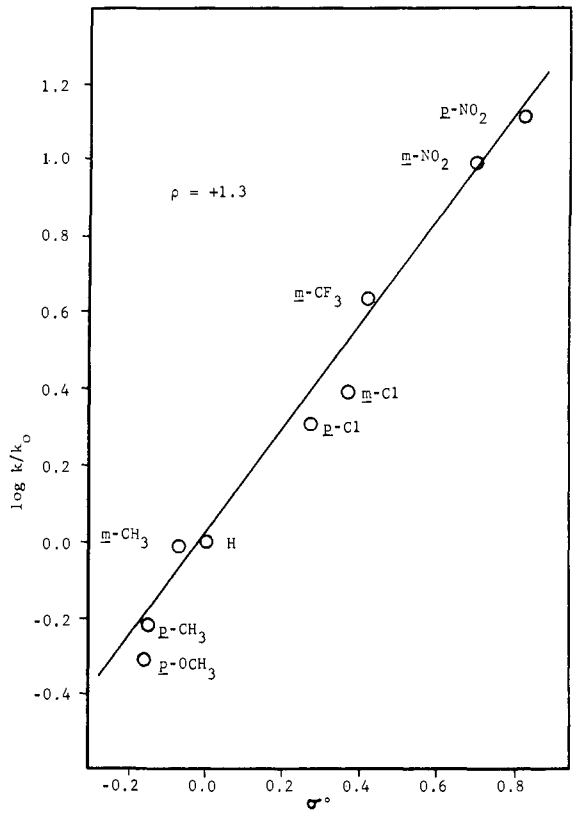


Figure 2. A plot of log k/k_0 *vs.* σ^0.

bond formation occurs to the same degree as bond breaking. Depending on which of these situations exists, the electron density at S in the transition state will be greater than, less than, or equal to that of S in the ground state, respectively. The ρ value obtained from a Hammett plot is a measure of the sensitivity of the reaction to substituent effects, and a measure of the change in electron density at the reaction site. Alkaline hydrolysis of sulfinamides yielded a positive ρ, indicating that the transition state is being stabilized by electron-withdrawing substituents and that bond formation is more advanced than bond breaking in this transition state.

In 1960, Taft[6] proposed a method for evaluating resonance effects between the substituted benzene ring and the reaction center bonded to it. In evaluating the effect of structure on reactivity for a given equilibrium or rate, the approach was taken that the substituent was considered to be the entire substituted benzene ring. A select group of meta substituents whose σ constants do not vary greatly for a large number of rate and equilibrium studies is used. These σ constants are defined as σ^0. The assumption was made that the resonance interaction between the meta-substituted benzene ring and the reaction center bonded to it is equal in the ground state and the transition state. If one uses the select group of meta σ values (σ^0) to define ρ for a given reaction series, then effective σ values for para substituents can be obtained from the relationship $\bar{\sigma} = 1/\rho(\log k/k_0)$ where log k refers to the rate constants for the para-substituted components. In order to obtain inductive σ constants (σ^0 values) for para-substituted phenyl substituents, several reactions involving compounds of the type $ArCH_2Y$ were selected. The assumption was made that the resonance effect could not be transmitted to the reaction center through the interposed methylene group. The difference ($\bar{\sigma} - \sigma^0$) is then a measure of the specific resonance interaction between the para-substituted phenyl ring and the reaction center.

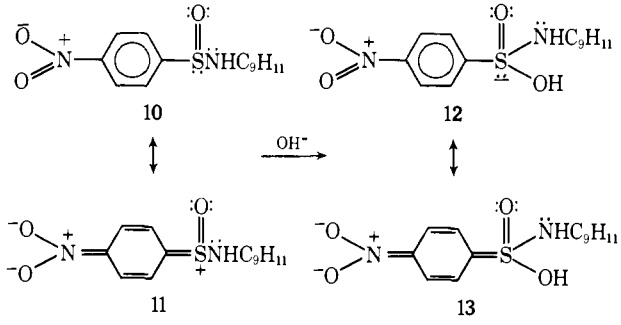
The Taft method has been applied to the meta- and para-substituted sulfinamides. In Figure 2, log (k/k_0) is plotted *vs.* σ^0 for the meta and para substituents; the line is determined by the meta σ^0 values only (ρ = +1.3). The data, with the unexplained exception of *N*-mesityl-*m*-chlorobenzenesulfinamide, fit the criteria proposed by Taft; at least four meta-substituted as well as the unsubstituted compound should be used to define ρ, no meta-substituted compound should deviate from the line by more than ± 0.07 σ unit, and the standard error for all the substituents should be ± 0.03 or less. This method has also been applied to the saponification of the benzoate esters, and to the ionization of a series of thiophenols, protonated acetophenones, and protonated phenyl methyl sulfoxides. These results, which are independent of ρ, are listed in Table IV.

The *p*-methoxy and *p*-nitrophenyl substituents can appreciably influence reaction rates and equilibria by direct conjugation with the reaction center. As can be seen in Table IV, with the exception of the *p*-methoxy substituent, no para resonance effects, within experimental error (± 0.07), are observed for the arenesul-

(6) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960). For a similar approach, see H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

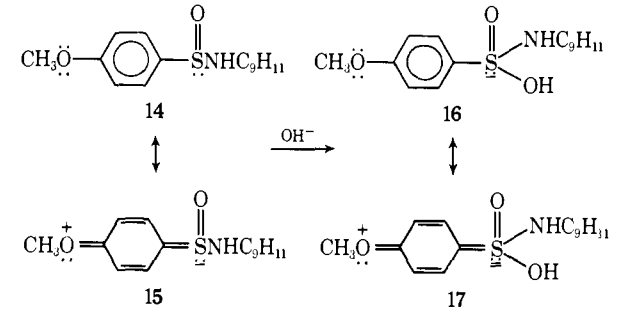
finamides. The lack of a resonance effect for *N*-mesityl-*p*-nitrobenzenesulfinamide is in direct contrast to that observed for the thiophenols. With *p*-nitrothiophenol a significant resonance value (0.14) is obtained. The sulfur atom is donating its nonbonding electrons to the benzene ring and this electron donation is greater in the conjugate base (ArS^-) than in the acid (ArSH). That is, there is a specific resonance effect involving the anion.

In contrast, no significant resonance effect is obtained for *N*-mesityl-*p*-nitrobenzenesulfinamide. This, of course, does not negate the possibility of sulfur exerting a stabilizing influence by donation of its nonbonding electrons. It does mean, however, that in the ground state the contribution of resonance structure **11** to the resonance hybrid is of the same magnitude as resonance structure **13** in the transition state.



Further examination of Table IV shows that for the ethyl benzoate esters, a resonance value of −0.11 is obtained for ethyl *p*-methoxybenzoate. This means that electron donation by the *p*-methoxy substituent is greater in the ground state than in the transition state.

In considering *N*-mesityl-*p*-methoxybenzenesulfinamide and its small value of −0.08, a similar argument may be applied. Here the reaction rate is decreased by a specific resonance effect. Resonance structure **15** contributes more to the resonance hybrid in the ground state than **17** does in the transition state. An intermediate is taken to approximate the transition state in this case as well as in the *p*-nitro case.



However, in view of the magnitude of the resonance effect (−0.08), which is small, the difference in contribution of resonance structures **15** and **17** is minimal.

Substitution reactions at sulfur may proceed by a direct displacement mechanism, or by an addition–elimination mechanism. While the formation of unstable addition intermediates occurs for carboxylic acid derivatives,[7] the existence of such intermediates is less well demonstrated for a tricoordinate sulfur(IV) compound.

(7) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969.

There is no question that tetracoordinate sulfur(IV) intermediates can exist because several such species do exist, *e.g.*, SF_4. The involvement of such species in various reactions has been postulated many times and, in some instances, documented by experimental evidence.[8]

Bunton and coworkers have studied the alkaline hydrolysis of sulfite esters.[9] No incorporation of ^{18}O into unhydrolyzed ester occurred when the hydrolysis was run in ^{18}O enriched water. Davis[10] has interpreted Bunton's results differently and feels a significant incorporation of ^{18}O did occur. The authors of the original do not agree with Davis' interpretation.[11] Strecker and Andersen[12] have argued against the presence of tetracoordinate S(IV) intermediates in the reduction of sulfoxides by iodide ion in acid solution.

When *N*-mesityl-*p*-toluenesulfinamide (**2**) was hydrolyzed for approximately 1 half-life in the presence of 20 atom % $H_2{}^{18}O$, 0.03 atom % excess ^{18}O incorporation was found in the recovered sulfinamide. If an intermediate did form, an appreciable amount of it did not revert to labeled starting material.

As mentioned previously, a positive ρ was obtained for the alkaline hydrolysis of the *N*-mesitylbenzenesulfinamides. The electron density at sulfur is greater in the transition state than in the ground state. Negative charge formation should be at its maximum when an addition intermediate is formed. A strong electron-withdrawing substituent, *i.e.*, *p*-NO_2, would be expected to exert a stabilizing influence. On examination of Table IV for the arenesulfinamides, the *p*-nitro substituent is seen to exert no exalted resonance effect. Models indicate that there is no steric inhibition of overlap of the lone pair of electrons on sulfur with the aromatic π system.

This resonance value is a measure of the charge present on the first atom from the benzene ring. For example, with the protonation of *p*-anisyl methyl ketone, a large resonance effect (−0.59) is observed reflecting the formation of a carbonium ion and its stabilization by the *p*-methoxy group.

In considering the formation of an intermediate for the hydrolysis of *N*-mesityl-*p*-nitrobenzenesulfinamide, the negative charge might reside predominantly on the sulfinyl oxygen atom. Even so, it would seem reasonable for the *p*-nitro substituent to stabilize an intermediate and a transition state leading to it. We conclude that the lack of a resonance effect for *N*-mesityl-*p*-nitrobenzenesulfinamide argues against the existence of an addition intermediate for the alkaline hydrolysis of arenesulfinamides.

Experimental Section

Procedure for Kinetic Runs. Fisher certified reagent grade sodium hydroxide was used to prepare the stock base solutions. Fisher hydrochloric acid solution (0.0333 *N*) was used as the titrant. Transferral of stock solutions to the reaction flasks was done by pipet. Best results were obtained when the pipet was washed with

(8) D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, **91**, 5239 (1969); C. R. Johnson and J. J. Rigan, *ibid.*, **91**, 5398 (1969); H. Kwart, E. N. Givens, and C. J. Collins, *ibid.*, **91**, 5532 (1969). For additional references, see ref 3.

(9) C. A. Bunton, P. B. D. de la Mare, P. M. Greaseley, D. R. Llewellyn, N. H. Pratt, and J. G. Tillett, *J. Chem. Soc.*, 4751 (1958).

(10) R. E. Davis, *J. Amer. Chem. Soc.*, **84**, 599 (1962).

(11) P. B. D. de la Mare, J. G. Tillett, and H. F. van Woerden, *J. Chem. Soc.*, 4888 (1962).

(12) R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, **33**, 2234 (1968).

acetone and then dried by flushing with nitrogen before each addition. The reaction vessels were 125-ml Erlenmeyer flasks sealed by rubber serum caps.

Sulfinamide dissolved in 95% ethanol was added to each of the flasks followed by the addition of sodium hydroxide solution. At the end of the appropriate time, each flask was cooled and crushed ice was added to quench the reaction. Phenolphthalein indicator was added and the solutions were titrated with hydrochloric acid. The time was recorded after an initial equilibration period of 5–15 min until removal of the reaction vessel from the temperature bath. Second-order and first-order rate constants were obtained from plots of log (sulfinamide/OH^-) *vs.* time, and log (sulfinamide) *vs.* time, respectively. An IBM 360 digital computer was used to perform the calculations.[13] All of the data were also plotted graphically in order to see if any deviation from linearity was present.

Sulfinamides **2**, **4**, **5**, **9**, and **8** were prepared by the addition of the sulfinyl chloride to mesidine. Sulfinamides **3**, **1**, **6**, and **7** were prepared according to the procedure of Klamann, Sass, and Zelenka,[14] by the addition of *N*-sulfinylmesidine to the substituted phenylmagnesium bromide. Representative preparations are given below.

***N*-Mesityl-*m*-toluenesulfinamide (3).** *m*-Bromotoluene (34.2 g, 0.20 mol) in anhydrous ether (50 ml) was added to magnesium turnings (4.9 g, 0.20 g-atom) in anhydrous ether (100 ml). Upon completing the addition, the mixture was stirred for 2 hr. The mixture was then brought to ice-bath temperature. *N*-Sulfinylmesidine (33.2 g, 0.194 mol) in anhydrous ether (50 ml) was added to the Grignard reagent. The solution was then stirred for 3 hr. Aqueous ammonium chloride (10%; 300 ml) was added slowly over a 1-hr period with stirring. The solid material which formed was filtered and washed with water (500 ml). Then the solid material was washed with petroleum ether, filtered, and recrystallized from ligroin (bp 65–70°) and acetone mixture giving 21 g (40% yield), mp 121–122° dec.

***N*-Mesityl-*p*-chlorobenzenesulfinamide (5).** Freshly distilled 2,4,6-trimethylaniline (86.4 g, 0.64 mol) was added to a 2-l. three-necked flask equipped with a stirrer, a calcium chloride drying tube, and containing anhydrous ether (500 ml). The flask was immersed in an ice bath in order to maintain a solution temperature below 10°. A solution of crude *p*-chlorobenzenesulfinyl chloride (62.1 g, 0.32 mol) in anhydrous ether (50 ml), contained in a pressure equalized addition funnel, was added dropwise over a 0.5-hr period. Stirring was continued for an additional 12 hr upon completing the addition. The solution was filtered under aspirator pressure. The white residue was swirled in 1 l. of cold water and then filtered. The white solid material remaining was recrystallized several times from methanol and finally from acetone giving 55.5 g (58.9% yield), mp 161–162° dec.

Reaction of *N*-Mesityl-*p*-chlorobenzenesulfinamide with Sodium Hydroxide. Analytical Grade sodium hydroxide (0.20 g, 0.005 mol) dissolved in 95% ethanol (150 ml) was added to a flask containing *N*-mesityl-*p*-chlorobenzenesulfinamide (1.465 g, 0.005 mol). The solution was brought to reflux for 3 days. The solution was cooled to room temperature, ether was added (200 ml), and the solution was swirled. The organic layer was washed with water (100 ml) and separated. The ether portion was washed once more with water and the aqueous portions combined and set aside. The ether solution was dried ($MgSO_4$), filtered, and evaporated, leaving a clear yellow liquid, 0.67 g (99.2%). A sample of the yellow liquid was gas chromatographed on an Aerograph A 90-P3 using a 5 ft × 1/8 in. 20% Carbowax 20 M on Chromosorb W 80–100 column. A single peak with a retention time of 100 sec was observed. A sample of 2,4,6-trimethylaniline was injected into the chromatograph and a single peak with a retention time of 100 sec was observed. An infrared spectrum of the yellow liquid proved to be identical with that of 2,4,6-trimethylaniline.

The aqueous solution was evaporated to dryness over a steam bath. A white powder remained, which was dissolved in approximately 50 ml of water. The solution was acidified with 5% hydrochloric acid. The solution was filtered to give a white solid, 0.87 g (98.9% yield), mp 98–99°. An infrared spectrum and the melting point of the white solid proved to be identical with an original sample of *p*-chlorobenzenesulfinic acid. A mixture melting point of the two substances was 98–99° (lit.[15] mp 92–93°).

Hydrolysis of *N*-Mesityl-*p*-toluenesulfinamide (2) in $H_2{}^{18}O$–Ethanol Solution. Sodium hydroxide (52 mg, 1.3 mmol) was dissolved in 1 g of 20% ^{18}O-labeled water. This solution was added to 190 ml of anhydrous ethanol containing sulfinamide **2** (111.6 mg, 0.41 mmol) in a serum capped 25-ml Erlenmeyer flask and was kept at 50 ± 0.02° for 4 hr and 45 min (roughly one half-life). The solution was removed, filtered, divided into two equal portions, and cooled in a Dry Ice–acetone bath. Water (4.0 ml) was added to each portion and the precipitates were recovered by centrifuging. Each precipitate was recrystallized from a solution of absolute ethanol (1.0 ml) and water (0.5 ml). The crystals were centrifuged, washed twice with 1.0-ml portions of water, and dried *in vacuo* over fresh phosphorus pentoxide (33.8 mg, 30% recovery). Upon conversion to carbon dioxide the sulfinamide sample showed a 46:44 mass ratio of 0.00550 compared to a ratio of 0.00511 for tank carbon dioxide.[16] This was calculated[17] to be 0.03 atom % excess ^{18}O which was considered to be no incorporation of ^{18}O into recovered sulfinamide **2**.[18]

---

(13) The authors wish to thank Professor J. J. Uebel for supplying the least-squares plot computer program.

(14) D. Klamann, C. Sass, and M. Zelenka, *Chem. Ber.*, **92**, 1910 (1959).

(15) I. B. Douglas, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961).

(16) We wish to thank Mr. Josef Nemeth for carrying out the ^{18}O analyses.

(17) J. C. Martin, J. W. Taylor, and E. H. Drew, *J. Amer. Chem. Soc.*, **89**, 129 (1967).

(18) NOTE ADDED IN PROOF. It should be pointed out that ^{18}O exchange experiments involving sulfinamides may in fact be quite different from those involving carbonyl compounds such as amides. If a tetracoordinate sulfur(IV), trigonally bipyramidal intermediate is formed with the labeled hydroxide nucleophile and nitrogen leaving group apically arranged, at least two pseudorotations around sulfur are required to interchange the labeled apical oxygen with the unlabeled sulfinyl oxygen (the other groups retaining their original or enantiomeric positions). The law of microscopic reversibility presumably requires this intermediate to be identical with the initially formed one except for labeling if it is to revert to sulfinamide (now labeled) by expulsion of the now unlabeled hydroxide ion. Pseudorotation has never been detected unambiguously at sulfur. Even if it can take place, at least one of the pseudorotations would be unfavorable, since groups of low electronegativity would be forced into apical positions. Thus, if a trigonally bipyramidal intermediate forms, it might revert to starting material without such a reversal being detectable by ^{18}O exchange (E. T. Kaiser and O. R. Zaborsky, *ibid.*, 90, 4626 (1968).