The ether filtrate was kept 66 hr. at −20°; it deposited crystals of *rac*-methyl (3,4-dimethyl-3,4-dihydroxyhexanedione-3,5) cyclic phosphate (IIIb, 10.1 g., 39%, crude m.p. 45–50°). Recrystallization from dry ether (*in the absence of moisture*) gave colorless crystals of racemic diketol phosphate IIIb, m.p. 54–56°. Analysis was performed immediately. The *solid* phosphate deteriorates on standing, even under nitrogen, but is conveniently stored under ether at 5°.

Anal. Calcd. for $C_9H_{15}O_6P$: C, 43.2; H, 6.0; P, 12.4. Found: C, 42.5; H, 6.0; P, 11.6.

The infrared spectrum was taken in dry CCl_4 (μ): 5.80 (1725 cm.$^{-1}$) (s) with shoulder at 5.83 [in CCl_4 the *meso* isomer shows a distinctly split carbonyl at 5.81, 5.84 μ]; 6.90 (w), 7.04 (w), 7.25 (m), 7.38 (m); 7.68 (1302 cm.$^{-1}$) (v. s.); 8.93 (m); 9.51 (1052 cm.$^{-1}$) (v. s.); 9.98 (m), 10.1 (shoulder), 10.4 (w). H^1 n.m.r. spectrum in $CDCl_3$ solution (τ): doublet at 6.00, J_{HP} 12 c.p.s., two singlets of equal intensities at 7.60 and 7.65 and two singlets of equal intensities at 8.43 and 8.53; see Fig. 6 (the spectrum does not change on standing, in the absence of moisture).

The ether filtrate from which the racemic diketol phosphate IIIb had separated was concentrated and cooled 24 hr. at −10°. Crystalline hemiketal cyclic phosphate IVa (2.4 g., 9%, m.p. 72–82°) separated out.

Hydrolysis of *meso*-Diketol Cyclic Phosphate (IIIa) to *meso*-3,4-Dimethyl-3,4-dihydroxyhexanedione-2,5 (Va).—A mixture of the *meso*-diketol phosphate IIIa (11.185 g., m.p. 105–110°), benzene (60 ml.), and water (4.02 ml., 5 mole equivalents) was kept 1.5 hr. at reflux temperature. The aqueous acid layer was separated, saturated with NaCl, and extracted with benzene. The combined benzene extracts and original layer were dried ($MgSO_4$) and evaporated *in vacuo*. Colorless needles of *meso*-3,4-dimethyl-3,4-dihydroxyhexanedione-2,5 (Va) (6.1 g., 80%, m.p. 89–92°) were obtained, analytical sample m.p. 95–96° (hexane).

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.2; H, 8.1; mol. wt., 174. Found: C, 54.6; H, 8.2; mol. wt., 215.

The infrared spectrum was obtained in CCl_4 (μ): 2.90 (3460 cm.$^{-1}$) (sharp) (m) (OH stretching); 3.34 (w), 3.40 (w), 5.86 (1707 cm.$^{-1}$) (s) (C = O stretching); 6.85 (w), 7.02 (w), 7.30 (s) (OH deformation); 8.23 (s), 8.76 (s) (C—O stretching); 9.35 (m); H^1 n.m.r. spectrum (in CCl_4, τ): singlets at 5.50, 7.64, and 8.75; intensities: 1:3:3; bis-2,4-dinitrophenyl-hydrazone m.p. 209–210° (chlorobenzene).

Anal. Calcd. for $C_{20}H_{22}O_{10}N_8$: C, 45.0; H, 4.1; N, 21.0. Found: C, 45.2; H, 4.0; N, 20.9.

Hydrolysis of *rac*-Diketol Cyclic Phosphate IIIb to *rac*-3,4-Dimethyl-3,4-dihydroxyhexanedione-2,5 (Vb).—A mixture of the *rac*-diketol phosphate IIIb (6.57 g., m.p. 50–52°), benzene (30 ml.), and water (1.9 ml., 4 mole equivalents) was kept 1.15 hr. at reflux temperature and worked up as for the *meso* isomer. A colorless oil (3.7 g., 80%) was obtained; this was stirred with 5 ml. of warm hexane and the mixture was kept 20 hr. at 5°. A small amount of crystalline *meso*-diketol Va (600 mg., 13%) was filtered off. The hexane was evaporated and the residue (2.72 g., 60%) was submitted to short-path distillation; *rac*-3,4-dimethyl-3,4-dihydroxyhexanedione-2,5 (Vb) (2.21 g., 48%) had b.p. *ca.* 45–50° (0.3 mm.), $n^{25}D$ 1.4495.

Anal. Found: C, 55.7; H, 8.2.

The infrared spectrum in CCl_4 had bands at (μ): 2.87 (3480 cm.$^{-1}$ (mw, broad) (OH stretching); 3.34 (w), 3.40 (w) 5.88 (1702 cm.$^{-1}$) (s) (C=O stretching); 6.90 (w), 7.02 (w), 7.18 (ms), and 7.32 (ms) (OH deformations); 7.96 (w), 8.10 (w), 8.26 (m), 8.47 (m), 8.76 (s) with shoulder at 8.93 (s) (C—O stretching); 9.22 (m); H^1 n.m.r. spectrum (in CCl_4, τ): singlets at 5.73, 7.77, and 8.70; bis-2,4-Dinitrophenylhydrazone, m.p. 200–202° (chlorobenzene). *Anal.* Found: C, 45.5; H, 4.3; N, 20.7.

Hydrolysis of the Crystalline *meso*-Oxyphosphorane (IIa) with an Excess of Water.—A solution of crystalline adduct IIa (10.08 g.) in benzene (50 ml.) containing some water (3 ml.) was kept 30 min. at reflux temperature under N_2. The layers were separated; the water–acid layer was saturated with NaCl and extracted with benzene; the dried benzene layer plus extracts were evaporated. The crystalline residue was recrystallized from hexane; first crop of diketol Va, 4.81 g.; second crop, 0.34 g. (yield 93%; both melting at 94–95%).

This hydrolysis of IIa was repeated using water enriched with 10.61 atom % O^{18}, 0.179 atom % O^{17}, and an unspecified amount of deuterium (YEDA, Research and Development Co., Israel), in order to establish possible incorporation of O^{18} into the diketol during the hydrolysis.

The *meso*-diketol of normal isotope content was kept in contact with O^{18}-enriched water, in refluxing benzene containing some phosphoric acid, as in the hydrolysis experiment, in order to determine possible incorporation of O^{18} into the diketol as a result of an exchange with the water. The three samples of diketol were submitted to mass spectrometric analysis, with results which will be described elsewhere.

Hydrolysis of the Original Mixture of Diastereomeric Oxyphosphoranes IIa and IIb with an Excess of Water.—The original distilled mixture of *meso* and racemic adducts IIa and IIb (66.84 g.) was dissolved in benzene (350 ml.), treated with water (about 12 ml.), and carefully warmed up to initiate a *vigorous* reaction. The mixture was kept 1 hr. at reflux temperature and worked up as for the *meso* isomer. Fractional crystallization from hexane gave crystalline diketol Va, m.p. 94–95°, in 63% yield. Distillation of the liquid residue gave the *rac*-diketol Vb, $n^{25}D$ 1.4491 in about 20% yield. It is difficult to obtain *rac*-Vb completely free from *meso*-Va by this procedure (*vide supra*).

Acknowledgment.—We are grateful to Dr. J. Lancaster of the American Cyanamid Co. (Stamford, Conn.) for the P^{31} n.m.r. spectra at 16 Mc./sec. and to Prof. E. Eliel of the University of Notre Dame and Dr. E. M. Banas of the American Oil Co. (Whiting, Ind.) for facilities and instruction in H^1 n.m.r. spectroscopy.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE UNIVERSITY, CORVALLIS, ORE.]

Mechanisms of Reactions of Sulfinic Acids. V. The Mechanism of the Alkyl Sulfide–Sulfinic Acid Reaction[1]

BY JOHN L. KICE AND EVA H. MORKVED

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The mechanism of the recently discovered[2] primary alkyl sulfide–*p*-toluenesulfinic acid reaction has now been determined. The relative reactivities of α,α-dideuteriobenzyl sulfide and its undeuterated analog show the reaction is subject to a large isotope effect (k_H/k_D = 5.2). This fact, combined with the variation of rate with sulfide structure for a series of sulfides $(RCH_2)_2S$ and the previously reported[2] dependence of rate on other reaction variables, requires that the rate-determining step be eq. 2B. Experiments with butyl α-acetoxybutyl sulfide show that the cation $RCH{=}S{-}CH_2R^+$ produced in reaction 2B will be immediately hydrolyzed to RCHO and RCH_2SH, and that the mercaptan will then react extremely rapidly with some of the remaining sulfinic acid. Other experiments show that under the present reaction conditions this mercaptan–sulfinic acid ($ArSO_2H$) reaction gives as products, almost exclusively, the two thiolsulfonates $ArSO_2SAr$ and $ArSO_2SCH_2R$. The course of the sulfide–sulfinic acid reaction subsequent to the rate-determining step is thus as shown in Chart I. Additional kinetic studies demonstrate that any small amount of disulfides produced along with the two thiolsulfonates in the mercaptan–sulfinic acid reaction will be rapidly consumed by further reaction with sulfinic acid, in a process which also yields the two thiolsulfonates above as products.

Kice and Bowers[2] recently described a new reaction between *p*-toluenesulfinic acid and primary alkyl sulfides, which leads to the cleavage of the sulfide and the oxidation of one of its alkyl groups to the corresponding aldehyde. Other reaction products are the

(1) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AFOSR-106-63.

(2) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 2390 (1962).

p-tolyl and alkyl *p*-toluenethiolsulfonates, the over-all stoichiometry being as shown in eq. 1.[3] Kinetic study

$$5ArSO_2H + (RCH_2)_2S \longrightarrow 2ArSO_2SAr + ArSO_2SCH_2R + RCHO + 3H_2O \quad (1)$$

Ar = *p*-$CH_3C_6H_4$–

of the reaction in moist acetic acid showed that it was first order in both sulfide and sulfinic acid. This, and the response of rate to such additional reaction variables as water and strong acid concentration, pointed clearly to a mechanism of the general form shown in eq. 2 but did not elucidate the exact nature of the change taking place in the rate-determining step.

$$ArSO_2H + (RCH_2)_2S + H^+ \rightleftharpoons Ar\text{–}\overset{+}{S}(CH_2R)_2 + H_2O \quad (2)$$

$$Ar\text{–}\overset{+}{S}(CH_2R)_2 \xrightarrow[\text{determining}]{\text{rate}} \text{final products after several steps}$$

The results described in the present paper now permit both determination of the course of the rate-determining step and also deduction of the complex reaction sequence by which the intermediates produced in this step are then converted to the final products.

Possibilities for the Rate-Determining Step.—The two reactions below seem the only possibilities worthy of serious consideration. Examination of the effect of

$$Ar\text{–}\overset{+}{S}(CH_2R)\text{–}S(O)CH_2R \xrightarrow[\text{detn.}]{\text{rate}} Ar\text{–}\overset{+}{S}\text{–}S(O)CHR\text{–}H \longrightarrow H^+ + RCHO + ArSSCH_2R \xrightarrow{ArSO_2H} \text{further reactions leading to final products} \quad (2A)$$

$$Ar\text{–}\overset{+}{S}(CH_2R)\text{–}S(O)CHR\text{–}H \xrightarrow[\text{detn.}]{\text{rate}} ArSOH + RCH{=}\overset{+}{S}\text{–}CH_2R \quad (2B)$$

I

isotopic substitution on reaction rate should allow distinction between them. Substitution of $(RCD_2)_2S$ for $(RCH_2)_2S$ should have little effect on either the initial equilibrium in eq. 2 or on the rate of reaction 2A. On the other hand, reaction 2B should be subject to a substantial primary isotope effect. Therefore, if the rate-determining step is actually 2B, the over-all rate of the sulfide-sulfinic acid reaction should be markedly lower for the deuteriosulfide. Conversely, if the rate-determining step is 2A, the over-all isotope effect will be small.

The Isotope Effect in the Benzyl Sulfide-Toluenesulfinic Acid Reaction.—α,α-Dideuteriobenzyl sulfide, $(PhCD_2)_2S$, deuterium content 3.82 atoms per molecule, was prepared from α,α-dideuteriobenzyl alcohol[4] by standard procedures. The kinetics of its reaction at 70° with *p*-toluenesulfinic acid in acetic acid–0.56 *M* water containing 0.6 *M* sulfuric acid are shown in Fig. 1 together with those for the undeuterated sulfide under the same reaction conditions.

Quantitative estimation of the clearly sizeable isotope effect was made as follows. As outlined previously,[2] sulfinic acid is consumed in such systems by both the alkyl sulfide–sulfinic acid reaction, which is first order in sulfinic acid, and by disproportionation to thiolsulfonate and sulfonic acid, a reaction which is second order in sulfinic acid.[5] Since the sulfide is present in considerable stoichiometric excess, $k_S(R_2S)$ remains effectively constant throughout a run. For the faster reacting undeuterated sulfide the k_S term in

$$-d(ArSO_2H)/dt = k_S(R_2S)(ArSO_2H) + k_2(ArSO_2H)^2 \quad (3)$$

eq. 3 is always enough the larger that the reaction follows good first-order kinetics. The procedure for correcting the experimental first-order rate constant in such cases for the small contribution from the $k_2(ArSO_2H)^2$ term in order to obtain $k_S(R_2S)$ has already been described.[2] For the slower reacting deuterated sulfide the $k_2(ArSO_2H)^2$ term contributes sufficiently to the over-all rate to cause curvature in the first-order plot. To evaluate $k_S(R_2S)$ in such cases one uses the procedure outlined by Frost and Pearson[6] for handling parallel first- and second-order reactions. The values of k_S obtained for the two sulfides are shown below. When account is taken of the fact the deuteriosulfide is only 95% deuterated, k_H/k_D is found to be 5.2 ± 0.4.

Undeuterated sulfide: $k_S = 3.5 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$

$(k_H/k_D) = 5.2 \pm 0.4$

Deuterated sulfide: $k_S = 0.8 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$ (3.8 atoms D/molecule)

An isotope effect of this magnitude requires that an α-CH bond in the sulfide be broken in the rate-determining step. Mechanism 2A is therefore ruled out. Alternatives to reaction 2B which also involve rate-determining fission of the C–H bond appear to be eliminated, either by their failure to fit the observed kinetics, particularly the dependence of rate on acid and water concentration, or by their incompatibility with the observed effects of changes in alkyl sulfide structure on rate. (The latter are discussed in the following section.) Reaction 2B is thus strongly indicated as the rate-determining step.

Effect of Sulfide Structure on the Rate of the Alkyl Sulfide-Sulfinic Acid Reaction.—If the reaction mechanism is as shown in eq. 2 and reaction 2B, consideration of the appreciable positive charge on the sulfide sulfur in the transition state of 2B leads one to expect that a systematic increase in the electron-withdrawing

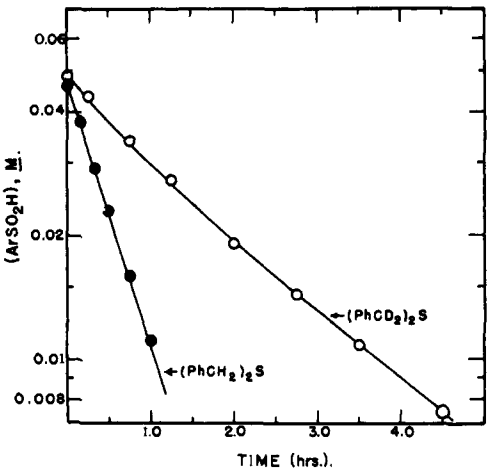


Fig. 1.—Deuterium isotope effect in the benzyl sulfide–toluenesulfinic acid reaction. Both runs in acetic acid–0.56 *M* H_2O–0.6 *M* H_2SO_4 at 70°: O, $(PhCD_2)_2S$, 0.1 *M*, $(ArSO_2H)_0$, 0.05 *M*; ●, $(PhCH_2)_2S$, 0.1 *M*, $(ArSO_2H)_0$, 0.05 *M*.

(3) The stoichiometry for *n*-butyl sulfide (R = *n*-Pr) was reported originally[2] to differ from that shown in eq. 1. In particular, *n*-butyl *p*-toluenethiolsulfonate was not thought to be formed. However, as described later in the present paper, a reinvestigation has shown that this thiolsulfonate is indeed formed, and in an amount commensurate with the requirements of eq. 1.

(4) J. L. Kice and F. M. Parham, *J. Am. Chem. Soc.*, **82**, 6168 (1960).

(5) J. L. Kice and K. W. Bowers, *ibid.*, **84**, 605 (1962).

(6) A. Frost and R. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 165.

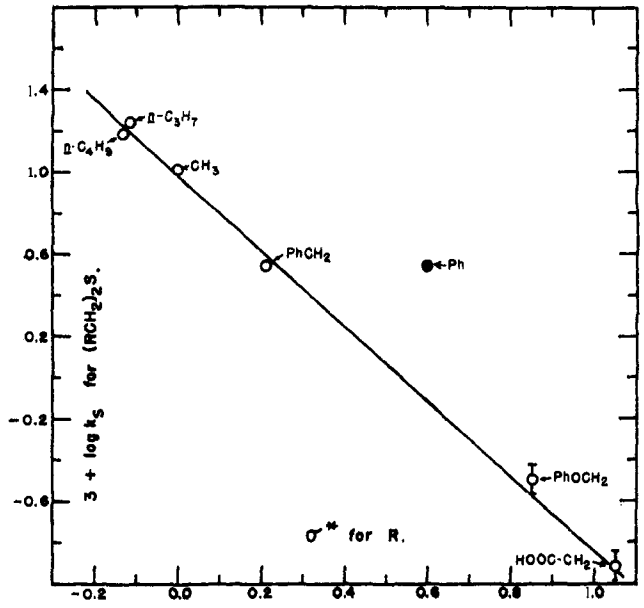


Fig. 2.—Effect of sulfide structure on rate of the $(RCH_2)_2S$–toluenesulfinic acid reaction. Plot of log k_S for $(RCH_2)_2S$ (see Table I) *vs.* σ^* for R.

character of the group R in a series of sulfides $(RCH_2)_2S$ should lead to a systematic decrease in the reactivity of the sulfides toward sulfinic acid.

The reactivity of a number of such sulfides toward *p*-toluenesulfinic acid was determined in acetic acid–0.56 *M* water–0.6 *M* sulfuric acid. The results, expressed as values of the rate constant k_S, are shown in Table I. (Experiments at different sulfide concentrations established that each reaction was first order in sulfide.) In most cases the k_S values were calculated from experimental first-order rate constants. For slower reacting sulfides, where indicated, the alternate procedure of ref. 6 was employed.

TABLE I

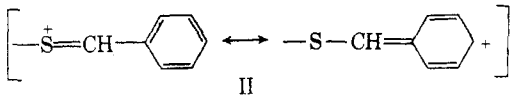
RATE CONSTANTS FOR REACTION OF *p*-TOLUENESULFINIC ACID WITH PRIMARY ALKYL SULFIDES

All data are at 70° with acetic acid–0.56 *M* water–0.6 *M* sulfuric acid as the reaction medium

Alkyl sulfide	$k_S \times 10^4$, M^{-1} sec.$^{-1}$[a]
n-Butyl	17.5[b]
n-Amyl	15.4
Ethyl	10.2
Isobutyl	9.0
Benzyl	3.5
2-Phenylethyl	3.4
2-Phenoxyethyl	0.28[c]
2-Carboxyethyl	0.12[d]
Carboxymethyl	Too small to measure

[a] Unless noted, k_S is determined from experimental first-order rate constant. [b] Calculated from data of ref. 2. [c] Determined from initial rates, corrected for rate of normal disproportionation, because sulfide undergoes slow solvolysis. [d] Determined by method of ref. 6

Inspection of Table I reveals that the expected decrease in reactivity with increasing electron-withdrawing character of R is indeed generally observed. A more quantitative examination of the results reveals one apparent, and we think, significant exception. Figure 2 shows a plot of log k_S for $(RCH_2)_2S$ *vs.* σ^* for R[7] for all sulfides except isobutyl. The data for six of the sulfides are well correlated ($\rho^* = -1.85$). That for benzyl sulfide (R = Ph) is not. The latter compound is about seven times more reactive than the $\rho^*\sigma^*$ correlation would predict. This, however, is not unexpected for reaction 2B as the rate-determining step. With benzyl sulfide, the incipient carbon–sulfur double bond in the transition state can be stabilized by resonance with the adjacent phenyl group. Such stabilization is not available to the other sulfides in Table I. The behavior of benzyl sulfide thus seems

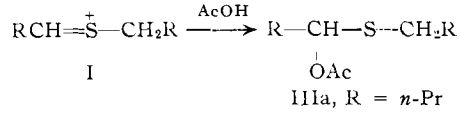


II

to provide additional support for reaction 2B as the rate-determining step.

The rate constant predicted for isobutyl sulfide (R = *i*-Pr, $\sigma^* = -0.19$) from Fig. 2 is about twice that actually observed. A high enough degree of branching at the β-carbon of the alkyl group thus results in lower reactivity than predicted from purely inductive considerations. A steric effect of this type is not surprising; its particular importance here is (1) to demonstrate that the increased reactivity of benzyl sulfide cannot be ascribed to increased branching at the β-carbon and (2) to suggest that the actual acceleration of rate due to resonance stabilization of the type shown in II may be somewhat greater than indicated by Fig. 2.

Reactions Subsequent to the Rate-Determining Step.—Reaction 2B having been established with reasonable certainty to be the rate-determining step, one must next determine, if possible, the manner in which the intermediates formed in this reaction, particularly I, are converted to the final products. Reaction of I with the acetic acid solvent would give the α-acetoxysulfide III. Since compounds of this type may be



I IIIa, R = *n*-Pr

synthesized independently by reaction of the alkyl sulfide and *t*-butyl peracetate,[8] the behavior of III under the conditions of the sulfide–sulfinic acid reaction can be examined directly.

The α-acetoxy derivative of *n*-butyl sulfide (IIIa) was selected for this study. Addition of 0.89 mmole of IIIa to a solution of 2.5 mmoles of *p*-toluenesulfinic acid in 50 ml. of the usual acetic acid–water–sulfuric acid mixture resulted in essentially instantaneous consumption of 0.60 mmole of the sulfinic acid. *The same amount of sulfinic acid was consumed if, instead of IIIa, one added 0.89 mmole of n-butyl mercaptan.* In both cases the extremely rapid initial reaction was followed by a slower disappearance of sulfinic acid, which may be shown (*vide infra*) to be due to reaction between the sulfinic acid and disulfides formed in the fast initial step.

From these results we can conclude that, under the reaction conditions employed, $RCH{=}\overset{+}{S}{-}CH_2R$, once formed, will effectively be immediately hydrolyzed to aldehyde and mercaptan, and that the mercaptan will then react extremely rapidly with some of the remaining sulfinic acid (eq. 4).

$$RCH{=}S^+{-}CH_2R + H_2O \xrightarrow[\text{fast}]{\text{very}} RCH{=}O + RCH_2SH + H^+ \qquad (4)$$

$$RCH_2SH + ArSO_2H \xrightarrow[\text{fast}]{\text{very}} \text{reaction stoichiometry dependent on reaction conditions; see text}$$

(7) R. W. Taft, Jr., Chapter 13 in "Steric Effects in Organic Chemistry," M. S. Newman, editor, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

(8) G. Sosnovsky, *Tetrahedron*, **18**, 15 (1962); *J. Org. Chem.*, **26**, 281 (1961).

The Mercaptan–Sulfinic Acid Reaction.—The next question which must be answered is the course and stoichiometry of the mercaptan–sulfinic acid reaction. A series of experiments was carried out in which a solution of *n*-butyl mercaptan was added with very efficient stirring to a solution containing a given amount of *p*-toluenesulfinic acid. Five minutes after the start of the addition the final solution was analyzed for sulfinic acid content. Both the rate of addition and the amount of mercaptan were varied independently. The results (Table II) show that the stoichiometry is

TABLE II

STOICHIOMETRY OF THE MERCAPTAN–SULFINIC ACID REACTION[a]

BuSH added, mmole	Time for addn. of BuSH, min.	$ArSO_2H$ remaining after 5 min., mmole	($ArSO_2H$ reacting/BuSH)
0.40	0.67	0.88	0.80
	1.5	.81	0.98
	3.3	.695	1.26
	5.0	.645	1.39
0.20	4.0	.85	1.75
.60	4.7	.56	1.07
.80	4.5	.465	0.92

[a] In all experiments 5 ml. of acetic acid–0.56 *M* water–0.6 *M* sulfuric acid, containing the amount of butyl mercaptan indicated, was added to 1.20 mmoles of *p*-toluenesulfinic acid dissolved in 20 ml. of the same acetic acid–water–sulfuric acid solution. The temp. was 70°.

variable: the lower the average concentration of mercaptan during the reaction, the greater the moles of sulfinic acid consumed per mole of mercaptan added. Product studies show the reaction yields four products: $ArSO_2SAr$, $ArSO_2SCH_2R$, $ArSSCH_2R$, and RCH_2SSCH_2R. As the data in Table III indicate, the larger

TABLE III

PRODUCTS OF THE MERCAPTAN–SULFINIC ACID REACTION

	Products, mole fraction			
$ArSO_2H$:BuSH	$ArSO_2SAr$	$ArSO_2SBu$	$ArSSBu$	$BuSSBu$
1.72:1	0.36	0.42	0.15	0.07
1.52:1	.33	.39	.18	.10
0.98:1	.25	.28	.26	.21

the $ArSO_2H$ reacting:BuSH ratio, the larger the mole fraction of thiolsulfonates in the products. Of particular significance is the fact that a variation in mercaptan concentration can lead to variations in stoichiometry and product composition *in a situation where sulfinic acid is always in excess.* This requires that the initial reaction of mercaptan with sulfinic acid be followed by an even faster reaction in which either mercaptan and sulfinic acid compete for an intermediate (or intermediates) produced in the initial reaction or, alternatively, the unimolecular decomposition of an intermediate competes with its capture by mercaptan. Naturally there are several general schemes of this sort which can accommodate the present results. With the limited information currently at hand no definitive choice between them is possible. One acceptable and reasonable scheme is that shown in eq. 5. In this,

$$\begin{array}{lccc} ArSO_2H & ArSO_2SAr & & ArSO_2SCH_2R \\ + & \uparrow ArSO_2H & & \uparrow ArSO_2H \\ RCH_2SH & & & \\ \longrightarrow & ArSOH \text{ (or } ArS^+) + & RCH_2SOH \text{ (or } RCH_2S^+) & \\ & \downarrow RCH_2SH & \downarrow RCH_2SH & \\ & ArSSCH_2R & RCH_2SSCH_2R & \end{array} \quad (5)$$

initial reaction of $ArSO_2H$ and RCH_2SH leads, probably by more than one step, to the sulfenic acids ArSOH and RCH_2SOH (or the equivalent sulfenium ions), and these latter intermediates then react rapidly with either sulfinic acid (giving thiolsulfonates) or mercaptan (giving disulfides).[9]

In any event, whatever the detailed mechanism of the mercaptan–sulfinic acid reaction, it is clear that under conditions where the mercaptan concentration is always low the principal reaction products will be the two thiolsulfonates $ArSO_2SAr$ and $ArSO_2SCH_2R$. Consideration of the relatively slow rate of formation of I (*via* 2 and 2B), as compared with the very rapid reaction of the mercaptan produced by its subsequent hydrolysis, suggests that the steady state concentration of mercaptan during an actual alkyl sulfide–toluenesulfinic acid reaction will be very low indeed, and, accordingly, reaction of mercaptan with sulfinic acid under these conditions should lead almost entirely to $ArSO_2SAr$ and $ArSO_2SCH_2R$.

Similarly, it seems reasonable to suppose that almost all the sulfenic acid (ArSOH) produced along with I in eq. 2B reacts with sulfinic acid rather than mercaptan, giving the thiolsulfonate $ArSO_2SAr$. We therefore suggest that the manner in which the great majority of the intermediates ArSOH and $RCH{=}\overset{+}{S}CH_2R$ produced in eq. 2B are converted to the final products is as shown in Chart I.

CHART I

$$Ar\text{–}\overset{+}{S}\text{–}S(CH_2R)_2 \quad (\overset{\|}{O})$$

$$\downarrow \text{rate determining}$$

$$ArSOH + RCH{=}\overset{+}{S}\text{–}CH_2R \xrightarrow{H_2O} RCH_2SH + RCH{=}O$$

$$\downarrow ArSO_2H \qquad \downarrow ArSO_2H \text{ (one or more steps)}$$

$$ArSO_2SAr \qquad [ArSOH + RCH_2SOH]$$

$$\downarrow ArSO_2H \quad \downarrow ArSO_2H$$

$$ArSO_2SAr \qquad ArSO_2SCH_2R$$

We should re-emphasize, however, that the results to date also permit formulation of the mercaptan–sulfinic acid reaction as proceeding through key intermediates other than ArSOH and RCH_2SOH, the only requirements being that such intermediates be able to explain the variation of reaction stoichiometry with mercaptan concentration, and that they lead in the limit of very low mercaptan concentration to the reaction stoichiometry

$$3ArSO_2H + RCH_2SH \longrightarrow ArSO_2SAr + ArSO_2SCH_2R + 2H_2O$$

Catalysis of the Disulfide–Sulfinic Acid Reaction by Alkyl Sulfides.—Even under the alkyl sulfide–toluenesulfinic acid reaction conditions, however, the two thiolsulfonates will not be the exclusive products of the mercaptan–sulfinic acid reaction, and to the extent they are not, one would expect small amounts of the two disulfides $ArSSCH_2R$ and $(RCH_2S)_2$ to be formed. At low concentration further reaction of these disulfides with the sulfinic acid would, in the absence of alkyl

(9) A referee has suggested an additional factor which might further complicate this and other schemes for the mercaptan–sulfinic acid reaction. This is the fact that thiolsulfonates can react very readily with mercaptans (eq. i).[10a] Although this reaction certainly cannot explain the formation of

$$ArSO_2SR + RCH_2SH \longrightarrow ArSO_2H + RCH_2SSR \quad (i)$$

thiolsulfonates in the mercaptan–sulfinic acid reaction, it might be responsible for some of the disulfides formed.

However, although Barnard and Cole[10a] found reaction i took place very rapidly in neutral ethanol, one should also note that Marvel and Johnson[10b] found no reaction took place on refluxing excess mercaptan with a thiolsulfonate in an ether solution containing added hydrochloric acid. Quite possibly the reactive nucleophile in eq. i is the mercaptide ion, rather than the mercaptan, and the reaction occurs readily only in those media which are not so acidic as to repress completely the formation of this ion.

(10) (a) D. Barnard and E. R. Cole, *Anal. Chim. Acta*, **20**, 540 (1959); (b) C. S. Marvel and R. S. Johnson, *J. Org. Chem.*, **13**, 822 (1948).

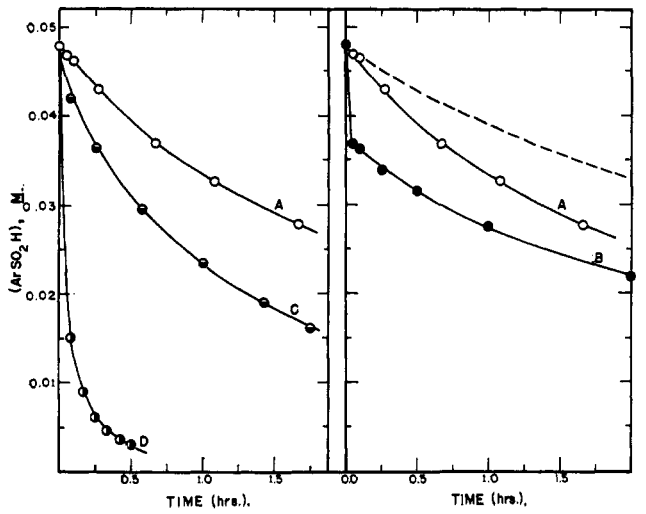
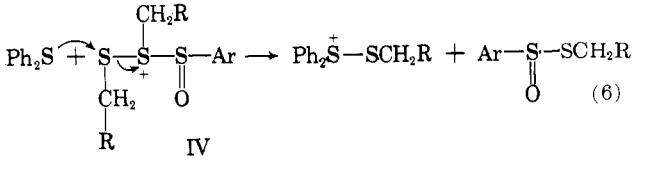


Fig. 3.—Rate of disappearance of *p*-toluenesulfinic acid in presence of butyl mercaptan or butyl disulfide. All runs in acetic acid–0.56 *M* H_2O–0.6 *M* H_2SO_4 at 70°; curve A, butyl disulfide, 0.0125 *M*; curve B, 0.018 *M* butyl mercaptan added at $t = 0$; curve C, butyl disulfide, 0.0125 *M*, phenyl sulfide, 0.1 *M*; curve D, 0.0125 *M* butyl disulfide, butyl sulfide, 0.01 *M*. All runs with $(ArSO_2H)_0$ approx. 0.05 *M*. Dashed line indicates rate of disappearance of sulfinic acid in absence of disulfides due to normal disproportionation.

sulfide, be quite slow. This is evident from curves A and B of Fig. 3. These show (1) the rate of disappearance of sulfinic acid in the presence of 0.0125 *M* butyl disulfide and (2) the similar slow disappearance of $ArSO_2H$ that follows the mercaptan–sulfinic acid reaction, when the stoichiometry of the latter process is such as to lead predominantly to disulfides as products.

However, the alkyl disulfide–toluenesulfinic acid reaction is subject to powerful catalysis by alkyl sulfides. This is not surprising, since catalysis of the tolyl disulfide–toluenesulfinic acid reaction by phenyl sulfide has already been observed.[11] Phenyl sulfide also catalyzes the reaction of *n*-butyl disulfide with *p*-toluenesulfinic acid (curve C of Fig. 3). Catalysis of these reactions presumably occurs because nucleophilic attack by the sulfide (eq. 6) increases the rate of decomposition of the intermediate ion IV.[11] The con-



siderably more nucleophilic alkyl sulfide- $(RCH_2)_2S$ would be expected to react much faster than phenyl sulfide in reaction 6, and it should therefore be a much more potent catalyst for the disulfide–sulfinic acid reaction. That this is indeed the case is evident from curve D of Fig. 3. This shows the dramatic catalytic effect of as little as 0.01 *M* *n*-butyl sulfide on the rate of the butyl disulfide–toluenesulfinic acid reaction.[12]

The usual conditions for the sulfide–sulfinic acid reactions involve sulfide concentrations from 0.075 to 0.20 *M*. Consequently, thanks to the powerful catalysis by the alkyl sulfide, any disulfides produced in the course of the sulfide–sulfinic acid reaction will react extremely rapidly with some of the remaining sulfinic acid. Reaction of the disulfides with *p*-toluenesulfinic acid should give the thiolsulfonates $ArSO_2SAr$ and $ArSO_2SCH_2R$,[11] probably with the approximate stoichiometries

$$4ArSO_2H + (RCH_2S-)_2 \longrightarrow ArSO_2SAr + 2ArSO_2SCH_2R + 2H_2O$$

and

$$4ArSO_2H + ArSSCH_2R \longrightarrow 2ArSO_2SAr + ArSO_2SCH_2R + 2H_2O$$

As a few calculations will show, if the disulfide reactions have the stoichiometry shown above, then no matter how little or how much disulfide is formed in the mercaptan–sulfinic acid reaction in competition with the reaction sequence leading to thiolsulfonates, the over-all stoichiometry of the $(RCH_2)_2S$–$ArSO_2H$ reaction will still be as shown in eq. 1. In other words, the over-all stoichiometry of the sulfide–sulfinic acid reaction should be essentially unaffected by changes in the stoichiometry of the mercaptan–sulfinic acid reaction. Equation 1 would thus be expected to be general for the reaction of primary alkyl sulfides with *p*-toluenesulfinic acid.

Reinvestigation of the Stoichiometry of the Butyl Sulfide–Toluenesulfinic Acid Reaction.—As mentioned earlier in a footnote,[3] reinvestigation of the *n*-butyl sulfide–toluenesulfinic acid reaction has shown: (1) contrary to the original report[2], *n*-butyl *p*-toluenethiolsulfonate is one of the principal reaction products; (2) the amount of *p*-tolyl *p*-toluenethiolsulfonate formed is actually only about 80% of that previously reported,[2] certain fractions containing appreciable amounts of the butyl ester having earlier erroneously been thought to consist only of the *p*-tolyl ester. (Probable reasons for the earlier confusion on these two points are outlined in the Experimental section.) Furthermore, since the v.p.c. method for quantitative estimation of butyraldehyde was never thought to be very accurate, it would seem, in view of the present results, that no significance should be attached to the yields reported for this aldehyde in the earlier paper. Rather, the relative yields of the butyl and *p*-tolyl *p*-toluenethiolsulfonate found in the present reinvestigation suggest that the stoichiometry for the butyl sulfide reaction is that shown in eq. 1, in agreement with expectations based on the mechanistic considerations outlined earlier, and in accord with that observed for benzyl sulfide.[2]

Further support for this view is provided by an investigation of the products of the ethyl sulfide–toluenesulfinic acid reaction.[13] Here too, reaction of the alkyl sulfide with the sulfinic acid leads to the alkyl and *p*-tolyl *p*-toluenethiolsulfonates, in a molar ratio of 1.0:2.03. As expected, acetaldehyde may also be identified as a reaction product.

Experimental

***p*-Toluenesulfinic acid** was prepared as previously described.[2] ***n*-Butyl α-acetoxybutyl sulfide** was prepared using Sosnovsky's[8] procedure. Its physical properties agreed with those previously reported.[8] Its n.m.r. spectrum was also consistent with the assigned structure. Samples were always fractionally redistilled immediately before use. **β-Phenoxyethyl sulfide** was synthesized from thiodiglycol as described by Reid, *et al.*[14]; m.p. 54–55°.

Commercial samples of the following compounds were purified either by fractional distillation or recrystallization: *n*-amyl sulfide, b.p. 45–47° (0.1 mm.); ethyl sulfide, b.p. 92°; isobutyl sulfide, b.p. 53–54° (10 mm.); β-phenylethyl sulfide, b.p. 151°

(11) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 2384 (1962).

(12) That the greatly enhanced rate of disappearance of sulfinic acid over that observed in the absence of added butyl sulfide cannot be due to the usual sulfide–sulfinic acid reaction may be demonstrated as follows. From Table I k_S (R_2S) for 0.01 *M* butyl sulfide should be 1.75×10^{-4} sec.$^{-1}$. Under these conditions the initial rate of consumption of sulfinic acid in the sulfide–sulfinic acid reaction would be 0.031 mole/l./hr. The observed initial rate of consumption of $ArSO_2H$ is 1.4 moles/l./hr., nearly 50 times this value.

(13) E. Morkved, unpublished results.

(14) F. Richter, F. B. Augustine, E. Koft, and E. E. Reid, *J. Am. Chem. Soc.*, **74**, 4076 (1952).

(0.25 mm.); *n*-butyl sulfide, b.p. 71° (13 mm.); phenyl sulfide, b.p. 155° (12 mm.); β-carboxyethyl sulfide, m.p. 130–131°; carboxymethyl sulfide, m.p. 129°; benzyl sulfide, m.p. 50°; *n*-butyl mercaptan, b.p. 97°; and *n*-butyl disulfide, b.p. 110° (14 mm.).

α,α-Dideuteriobenzyl Sulfide.—α,α-Dideuteriobenzyl alcohol[4] was converted in 65% yield to α,α-dideuteriobenzyl chloride, b.p. 70°(16 mm.), by refluxing it with thionyl chloride in benzene. A solution of 3.6 g. of sodium sulfide nonahydrate in 3 ml. of water was added to 3.8 g. of the chloride in 8 ml. of ethanol, and the mixture was refluxed for 14 hr. After work-up, recrystallization from ethanol gave 2.7 g. of α,α-dideuteriobenzyl sulfide, m.p. 50–51°; deuterium analysis[15]: 27.30 atom % excess D, corresponding to 3.82 atoms of D per molecule.

Procedure for Alkyl Sulfide Kinetic Runs.—A standard solution of acetic acid–0.56 *M* water was prepared by adding the proper amount of water to acetic acid purified by the method described previously.[5] The water content was checked by titration with Karl Fischer reagent. From a portion of this solution a 3 *M* stock solution of sulfuric acid in acetic acid–0.56 *M* water was prepared as follows. The sulfuric acid content of a sample of reagent grade sulfuric acid was determined, and the proper amount of acid, along with sufficient acetic anhydride to react with the excess water in the acid, were then made up to volume with acetic acid–0.56 *M* water solution. This stock solution was used as the source of sulfuric acid for all runs.

Samples of sulfide and sulfinic acid were weighed out separately, dissolved in acetic acid–0.56 *M* water, and mixed together in a volumetric flask. The proper amount of sulfuric acid stock solution was then added, and the solution was quickly made up to volume with acetic acid–0.56 *M* water. The solution was poured into the reaction vessel, whose construction has been described earlier,[5] and from this point on the procedure was exactly that outlined previously for following the kinetics of the disproportionation of *p*-toluenesulfinic acid.[5]

Behavior of Butyl α-Acetoxybutyl Sulfide under the Reaction Conditions.—The reaction vessel used for the kinetic runs was modified in such a way that a small glass bucket containing a weighed amount of the acetoxysulfide could be suspended above the solution in the flask. A solution of the sulfinic acid was placed in the flask, deaerated with nitrogen at room temperature, and then heated to 70° in a constant temperature bath. An aliquot of the solution was removed and analyzed for sulfinic acid content. As soon as this aliquot had been removed, the bucket containing the acetoxysulfide was dropped into the solution, and its contents was quickly mixed with the solution. One minute later another aliquot was removed and its sulfinic acid content determined. At selected intervals thereafter additional aliquots were removed and titrated. This allowed measurement of the slower disappearance of sulfinic acid which follows the extremely rapid hydrolysis of the acetoxysulfide and reaction of the resulting mercaptan with *p*-toluenesulfinic acid. The formation also under these conditions of *n*-butyraldehyde as a hydrolysis product of the acetoxysulfide was demonstrated in a separate experiment, by passing a rapid stream of nitrogen through the reaction mixture and thence through a 2,4-dinitrophenylhydrazine solution. *n*-Butyraldehyde 2,4-dinitrophenylhydrazone was precipitated; m.p. 120° after recrystallization.

In other runs using the same apparatus and technique, weighed amounts of *n*-butyl mercaptan were substituted for the acetoxysulfide. The kinetics observed were essentially identical with those obtained in the presence of an equimolar amount of the acetoxysulfide. In another set of experiments an amount of *n*-butyl disulfide approximately equivalent to the mmoles of disulfides that were thought to be formed under the reaction conditions above in the rapid sulfinic acid–mercaptan reaction was used in place of the mercaptan. In this case there was no rapid initial consumption of sulfinic acid. As is evident from Fig. 3, the kinetic behavior from the start closely paralleled that observed in the slow part of the mercaptan runs.

Sulfide Catalysis of the Disulfide–Toluenesulfinic Acid Reaction.—A series of runs was made, using the techniques employed for the acetoxysulfide studies, in which catalysis of the butyl disulfide–toluenesulfinic acid reaction by added phenyl or *n*-butyl sulfide was investigated. For the phenyl sulfide runs the sulfide was made up along with the sulfinic acid in the original solution, and the butyl disulfide was dropped in (*via* the bucket) and dissolved at zero time. For the runs with added *n*-butyl sulfide both the disulfide and the sulfide were placed in the bucket and dropped into the sulfinic acid solution at the start of the run.

Stoichiometry of the Sulfinic Acid–Mercaptan Reaction.—A 10-ml. pressure-equalizing separatory funnel was fitted to the reaction vessel used for the kinetic studies; 20 ml. of a solution of the sulfinic acid in the usual acetic acid–water–sulfuric acid mixture was placed in the flask, and a solution of the mercaptan in 5 ml. of the same solvent was placed in the separatory funnel. After deaerating the solution in the flask, the flask was heated to 70°, and the mercaptan solution was added at a steady rate over a measured period of time with very vigorous stirring. In each experiment, 5 min. after the start of the addition, an aliquot of the final solution was removed and analyzed for sulfinic acid content.

Products of the Butyl Mercaptan–Toluenesulfinic Acid Reaction.—The products of the *n*-butyl mercaptan–toluenesulfinic acid reaction were investigated in several larger scale runs carried out in the same manner as the stoichiometry studies. After determination of the residual sulfinic acid content, the final solution was poured into a large volume of water, and the water-insoluble products were extracted with ether. The ether extracts were washed with aqueous 5% bicarbonate until neutral, then with water, and finally were dried over anhydrous sodium sulfate. The ether was removed by careful fractional distillation. The residue was then easily separated by chromatography on acid-washed alumina into two fractions, the first a mixture of two disulfides, the second a mixture of two thiolsulfonates. Comparison of their infrared and n.m.r. spectra with those of known samples established that the disulfide mixture consisted of *n*-butyl and *n*-butyl *p*-tolyl disulfides and the thiolsulfonate mixture of *n*-butyl and *p*-tolyl *p*-toluenethiolsulfonates. The composition of the two mixtures could be determined by comparing the relative areas of selected n.m.r. peaks in the following manner. For the disulfides the area of the CH_2S triplet centered at 7.34 τ was compared to the area of the tolyl CH_3–singlet at 7.68 τ. For the thiolsulfonate mixture the intensity of the butyl ester's $-CH_2S-$ triplet at 7.05 τ was compared with the combined areas of the methyl group absorptions of the *p*-tolyl and *p*-toluenesulfonyl groups. These occur as two closely spaced singlets at 7.62 and 7.58 τ.

Naturally, authentic samples of *n*-butyl *p*-tolyl disulfide and *n*-butyl *p*-toluenethiolsulfonate were needed for comparison purposes in the above work. Neither appeared to have been reported before.

***n*-Butyl *p*-tolyl disulfide**[16] was prepared as follows. *n*-Butyl mercaptan (8.1 g., 90 mmoles), dissolved in an equal volume of acetic acid, was rapidly added (< 30 sec.) to a stirred solution of 4.67 g. of *p*-toluenesulfinic acid (30 mmoles) in 300 ml. of acetic acid–0.56 *M* water–0.6 *M* sulfuric acid at 70°. After 3 min., the solution was poured into water, the water-insoluble products were extracted with ether, and the ether solution was washed with aqueous bicarbonate until neutral. After drying over sodium sulfate, the ether was removed, and the residue was fractionally distilled. Two main fractions were obtained: *n*-butyl disulfide, 4.1 g., b.p. 60–64° (0.5 mm.), and *n*-butyl *p*-tolyl disulfide, 3.9 g., b.p. 102–104° (0.3 mm.).

Anal. Calcd. for $C_{11}H_{16}S_2$: C, 62.30; H, 7.59; mol. wt., 212. Found: C, 62.20; H, 7.72; mol. wt. (osmometric in $CHCl_3$), 210.

***n*-Butyl *p*-Toluenethiolsulfonate.**—A solution of potassium hydroxide (22.4 g.) in 32 ml. of water was saturated with hydrogen sulfide. To this was then added, in portions, 32 g. of *p*-toluenesulfonyl chloride. The reaction mixture was cooled in ice–water and the precipitate of crude potassium *p*-toluenethiolsulfonate[17] was filtered off. The salt was recrystallized from water following the directions of Foss and dried under vacuum; yield 22.5 g.

A portion of the purified potassium *p*-toluenethiolsulfonate (11.3 g., 0.05 mole) was dissolved in 45 ml. of acetone and 6 ml. of water. *n*-Butyl bromide (6.9 g., 0.05 mole) was added, and the solution was allowed to stand at room temperature for 6 days. The precipitated potassium bromide was filtered off, and the acetone was removed under reduced pressure. The water-insoluble portion of the residue was taken up in ether, and the ether solution was washed several times with water. After being dried over sodium sulfate, the ether was removed under reduced pressure, and the residue was subjected to distillation in a Hickman still (bath temp., 110°; pressure, 10^{-4} mm.). There was obtained 8.5 g. of *n*-butyl *p*-toluenethiolsulfonate. Both its infrared and n.m.r. spectra were in accord with the assigned structure.

Anal. Calcd. for $C_{11}H_{16}O_2S_2$: C, 54.09; H, 6.60. Found: C, 54.14; H, 6.74.

Reinvestigation of the Stoichiometry of the Butyl Sulfide–Toluenesulfinic Acid Reaction.—*p*-Toluenesulfinic acid (0.1 *M*) was allowed to react with butyl sulfide (0.2 *M*) in acetic acid–water–sulfuric acid solution in the same manner as described by Kice and Bowers.[2] The reaction solution was then worked up and the products separated from the unreacted sulfide by chromatography, again following previous procedures.[2] The chromatographic fractions containing thiolsulfonate were examined by n.m.r. and infrared. Comparison of their n.m.r. and infrared spectra with those for known samples and mixtures of *n*-butyl and *p*-tolyl *p*-toluenethiolsulfonates (*vide supra*) showed that without question the thiolsulfonate fractions were a mixture of these two thiolsulfonates, rather than consisting only

(15) Deuterium analysis by Mr. Josef Nemeth, Urbana, Ill.

(16) This preparation was carried out by Mr. Gary Bray.

(17) O. Foss, *Kgl. Norske Videnskab. Selsk. abs*, **1945**, No. 2 (1947).

of *p*-tolyl *p*-toluenethiolsulfonate, as was reported originally. The composition of the thiolsulfonate mixture was determined by the n.m.r. method outlined above. It was found to consist of 69 mole % *p*-tolyl *p*-toluenethiolsulfonate and 31 mole % *n*-butyl *p*-toluenethiolsulfonate, in reasonable agreement with the 2:1 mole ratio for the two thiolsulfonates required by eq. 1.

Except for a band of moderate intensity at 3000 cm.$^{-1}$ the infrared spectrum of the butyl ester is remarkably similar to that of the *p*-tolyl ester. This makes infrared a rather poor way of detecting the butyl ester in the presence of larger amounts of the *p*-tolyl ester, and this, combined with the fact that only *p*-tolyl *p*-toluenethiolsulfonate can be isolated as a crystalline product from such mixtures of the two esters, is presumably the reason the butyl compound was not detected in the earlier work. Further, since the yield of *p*-tolyl *p*-toluenethiolsulfonate reported in those studies[2] was based on the total weight of the thiolsulfonate fraction, now known to have been in part *n*-butyl *p*-toluenethiolsulfonate, it was naturally too high.

The n.m.r. spectra of the two esters, on the other hand, differ sufficiently to make it easy to detect and determine quite accurately small amounts of *n*-butyl *p*-toluenethiolsulfonate in the presence of larger amounts of the *p*-tolyl ester.

Acknowledgment.—The n.m.r. spectra described in this work were obtained on a Varian A-60 instrument whose purchase was made possible by a National Science Foundation grant to Oregon State University.

[CONTRIBUTION FROM THE CANCER RESEARCH INSTITUTE, NEW ENGLAND DEACONESS HOSPITAL, AND THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, HARVARD MEDICAL SCHOOL, BOSTON, MASS.]

Studies on the Mechanism of the Elbs Peroxydisulfate Oxidation[1a]

BY E. J. BEHRMAN

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Second-order rate constants have been measured for the reaction of a series of monosubstituted phenols with persulfate. Electron-releasing groups facilitate the reaction while electron-withdrawing groups retard it. Rate constants vary from 0.093 for *o*-nitrophenol to 21 for *p*-methoxyphenol (30°, l./mole-min.). Enthalpies and entropies of activation have been determined for some of these reactions. The values are in the ranges 12 to 16 kcal./mole ($\Delta H^{\pm}$) and −15 to −30 e.u. ($\Delta S^{\pm}$). A comparison of the rates of reaction of a series of 2,4- and 2,6-disubstituted phenols has shown that steric hindrance about the phenolic group increases the rate. The question of rate-limiting attack at oxygen or at carbon is considered in terms of the Hammett correlations and steric effects. Allyl alcohol, an inhibitor of the reaction of persulfate with 2-propanol, has no effect on the rate of the persulfate–phenol reaction.

Introduction

A previous investigation[1b] indicated that the rate-limiting step in the Elbs peroxydisulfate oxidation is an electrophilic attack by the persulfate ion on the phenolate ion. There was no evidence for a kinetically significant homolytic or heterolytic initiation step. The evidence was insufficient to draw conclusions as to the nature of the transition state. In particular, the question of whether the primary attack was at carbon or oxygen was undecided. In this paper, we shall consider some electronic and steric demands of the reaction.

Experimental

Materials.—Phenols were purchased from the Aldrich Chemical Co., Eastman, or Matheson Coleman and Bell and either recrystallized or redistilled before use. Distillation was carried out *in vacuo* (water-pump) under nitrogen. *o*-Cyanophenol was prepared according to the procedure of Bone[2] and recrystallized from benzene; m.p. 94.5 to 95.5°. *p*-Dioxane was purified according to the method of Hess and Frahm[3] as given by Fieser.[4] 2,6-Di-*t*-butylbenzoquinone was synthesized by oxidation of 2,6-di-*t*-butylphenol with trifluoroperacetic acid according to the procedure of Chambers, *et al.*,[5] for the dimethylphenol. A 60% yield of crude product was obtained after crystallization from 90% ethanol according to McClure.[6] The quinone was further purified by sublimation (m.p. 66–67°). 2,6-Di-*t*-butylhydroquinone was prepared by catalytic reduction of the quinone[7a] and gave m.p. 117.5 to 118° (lit.[7a] 110° dec.) after two crystallizations from *n*-hexane and one from methylcyclohexane; $\epsilon_{287\ m\mu}$ (95% EtOH) 3350. *Anal.* Calcd. for $C_{14}H_{22}O_2$: C, 75.6; H, 10.0. Found: C, 75.7; H, 10.0. Upon adding alkali to an ethanolic solution of the hydroquinone and shaking in air, the quinone, $\epsilon_{255\ m\mu}$ (95% EtOH) 17,000 (lit.[7b] $\epsilon_{256\ m}$ 15,400), is rapidly and quantitatively formed.

Methods.—The methods used have been described.[1]

Results

Further Evidence on the Lack of Free-Radical Participation.—A crucial finding in our previous study was the fact that allyl acetate, a sulfate-radical trap, had no detectable effect on the rate of disappearance of persulfate in the reaction with *o*-nitrophenol. This observation effectively eliminated mechanisms depending for their initiation on homolysis of persulfate. A mechanism involving the participation of sulfate radicals in a nonrate-limiting step was nevertheless possible,[7c] *e.g.*

$$ArO^- + S_2O_8^{-2} \xrightarrow{\text{slow}} ArO\cdot + SO_4^{-2} + SO_4^{-}$$

$$SO_4^{-} + ArO\cdot \xrightarrow{\text{fast}} \text{product}$$

The reaction of *o*-nitrophenol with persulfate in carbonate buffer was, therefore, repeated under the conditions previously described.[1] Allyl acetate had no effect on the rate or extent of product formation as measured by the appearance of Folin-positive material. The participation of sulfate radicals at any stage of the reaction thus seems unlikely.

The use of allyl acetate is, of course, limited by its rate of hydrolysis. Thus, the effect of allyl acetate on the rate of the reaction could be studied conveniently only with highly acidic phenols. It was desirable to generalize the lack of effect of allyl acetate on the disappearance of persulfate from which the kinetic nonparticipation of sulfate free radicals in the initiation step was concluded. Hence, a search was made for an alkali-stable free-radical trap. Allyl pivalate, N-allylpivalamide, and N,N-diallylpivalamide were found to be insufficiently water soluble. Allyl ethyl ether was found to accelerate the disappearance of persulfate in the presence of 2-propanol. Carr[8] (see also Bartlett and Cotman[9]) had already observed the relatively slow

(1) (a) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, Abstracts, p. 17O; (b) E. J. Behrman and P. P. Walker, *J. Am. Chem. Soc.*, **84**, 3454 (1962).

(2) W. A. Bone, *J. Chem. Soc.*, **63**, 1346 (1893).

(3) K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

(4) L. F. Fieser, "Experiments in Organic Chemistry," Third Ed., D. C. Heath and Co., Boston, Mass., 1957, p. 285.

(5) R. D. Chambers, P. Goggin, and W. K. R. Musgrave, *J. Chem. Soc.*, 1804 (1959).

(6) J. D. McClure, *J. Org. Chem.*, **28**, 69 (1963).

(7) (a) K. U. Ingold, *J. Phys. Chem.*, **64**, 1636 (1960); (b) S. J. Metro, *J. Am. Chem. Soc.*, **77**, 2901 (1955); W. K. Wilmarth and A. Haim, in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1962, p. 204.

(8) E. M. Carr, M.S. Thesis, University of Minnesota, 1952.

(9) P. D. Bartlett and J. D. Cotman, Jr., *J. Am. Chem. Soc.*, **71**, 1419 (1949).