hydrochloride was refluxed for 8 hr. A large portion of the methanol was removed by distillation, then the portion of the residue at the retention time for methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate was isolated by gas chromatography. An infrared analysis indicated the presence of methyl α-methoxyisobutyrate and the absence of methyl α-chloroisobutyrate.

**Attempted Reaction of Hydrogen Chloride with 2-Chloro-1-methoxy-2-methylpropionaldehyde Oxime.**—Hydrogen chloride was passed into a solution of 6 g. (0.0396 mole) of 2-chloro-1-methoxy-2-methylpropionaldehyde oxime and 36 g. of benzene at room temperature for 1 hr. Very little absorption of hydrogen chloride occurred and no observable quantity of methyl chloride was formed during this treatment. A solution of 2 g. of ether and 2 drops of methanol was added, and hydrogen chloride was bubbled through the mixture at 70–75° for 4 hr. No methyl chloride formation was observed. The solvents were removed under reduced pressure to leave 5.9 g. of unchanged 2-chloro-1-methoxy-2-methylpropionaldehyde oxime.

**Preparation of Authentic 2-Chloro-1-methoxy-2-methylpropionaldehyde Oxime.**—This material was prepared by the reaction of α-chloroisobutyrohydroxamyl chloride with methanol in the presence of calcium carbonate as described by Ogloblin.[6]

**Hydrochloric Acid Hydrolysis of α-Chloroisobutyrohydroxamyl Chloride.**—A mixture of 20 g. (0.128 mole) of freshly distilled α-chloroisobutyrohydroxamyl chloride and 14 ml. (0.168 mole) of concentrated hydrochloric acid was stirred at 55–60° for 3 hr. During this time the two-phase system changed to a single phase. The solution was cooled to room temperature, an equal volume of ether was added, and the mixture was filtered to give 7.3 g. of hydroxylamine hydrochloride. The aqueous phase of the filtrate was extracted with several small portions of ether which were added to the organic phase; then the aqueous phase was evaporated to dryness to leave 2.7 g. of solid residue. This residue was triturated with ether to leave 0.5 g. of hydroxylamine hydrochloride. Evaporation of the ether extract gave 2 g. of α-hydroxyisobutyric acid.

The combined organic solutions were dried over magnesium sulfate, then distilled to give 9.3 g. (59% yield) of α-chloroisobutyric acid, b.p. 43–48° (1 mm.), and 1.8 g. of α-hydroxyisobuytric acid, b.p. 48–53° (1 mm.). In all, α-hydroxyisobutyric acid was obtained in 29% yield and hydroxylamine hydrochloride in 87% yield.

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[6] K. A. Ogloblin, *Zh. Obshch. Khim.*, **29**, 1752 (1959); *Chem. Abstr.*, **54**, 8617 (1960).

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# The Reaction of *sec*-Alkyl Sulfides with *p*-Toluenesulfinic Acid[1]

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The reaction of several *sec*-alkyl sulfides with *p*-toluenesulfinic acid has been investigated. As with their primary counterparts, the principal reaction involves cleavage of the sulfide, the products being *p*-tolyl *p*-toluenethiolsulfonate, the *sec*-alkyl *p*-toluenethiolsulfonate, and the ketone derived from oxidation of the *sec*-alkyl group. However, with 2-octyl sulfide the reaction appears to be somewhat more complex than usual, since some of the sulfide is also oxidized to the sulfoxide. The reactivity of *sec*-alkyl sulfides is distinctly lower than expected from the reactivity of primary alkyl sulfides. Evidence is presented that this is due to the influence of steric hindrance on the initial equilibrium (eq. 4) involving sulfinic acid and sulfide.

Previous papers[2,3] have described a new reaction between primary alkyl sulfides and *p*-toluenesulfinic acid, which leads to the cleavage of the sulfide and the oxidation of one of its alkyl groups to the corresponding aldehyde. The other products are the *p*-tolyl and alkyl *p*-toluenethiolsulfonates, the over-all stoichiometry presumably being as shown in eq. 1. Consideration of

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

the mechanism[3] of the reaction suggests no reason why secondary alkyl sulfides should not react in comparable fashion, one of their alkyl groups being oxidized to the corresponding ketone.

The present paper examines the reactions of several typical secondary alkyl sulfides with *p*-toluenesulfinic acid. In the main, the predictions above about the course of the reactions are borne out, although with 2-octyl sulfide one additional interesting new facet becomes apparent. Kinetic studies allow the reactivity of *sec*-alkyl sulfides to be compared with that of closely related primary alkyl sulfides.

## Results and Discussion

**Products of the Reaction of *sec*-Alkyl Sulfides with *p*-Toluenesulfinic Acid.**—The reaction was studied with two typical *sec*-alkyl sulfides—isopropyl sulfide and 2-octyl sulfide. In both cases the three products expected by analogy to eq. 1 were found: (1) the appropriate ketone (acetone or 2-octanone), (2) *p*-tolyl *p*-toluenethiolsulfonate, and (3) the *sec*-alkyl *p*-toluenethiolsulfonate. For both sulfides the yield of the *p*-tolyl ester was 0.29–0.30 mole/mole of sulfinic acid reacting, and that of the appropriate *sec*-alkyl *p*-toluenethiolsulfonate was 0.15–0.17 mole/mole of sulfinic acid. The yield of 2-octanone from the 2-octyl sulfide reaction, as determined by conversion of the crude 2-octanone fraction to the semicarbazone, was 0.10–0.11 mole/mole of sulfinic acid. In the isopropyl sulfide reaction, experimental difficulties precluded an accurate quantitative estimate of the amount of acetone formed.

In the 2-octyl sulfide reaction one further product was isolated, 2-octyl sulfoxide, in an amount equal to approximately 0.10 mole/mole of sulfinic acid consumed. On the other hand, no isopropyl sulfoxide was obtained from the isopropyl sulfide reaction, although it is conceivable the work-up procedure employed may have been responsible for its apparent absence. In this connection it is also worth noting that in our early studies[2] of the *n*-butyl sulfide–*p*-toluenesulfinic acid reaction we considered that *n*-butyl sulfoxide might be a possible product, and accordingly, made a careful search for it. None could be detected. The formation of sulfoxides would therefore appear to be limited to sulfide–sulfinic acid reactions involving secondary sulfides.

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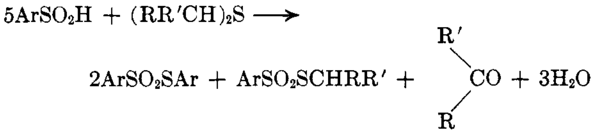
[1] Paper VII: Mechanisms of Reactions of Sulfinic Acids. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AFOSR-106-63.

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

[3] J. L. Kice and E. H. Morkved, *ibid.*, **85**, 3472 (1963).

At first glance, the simplest way to explain the formation of the sulfoxide seems to be to assume that in the case in question the reaction proceeds in part by the usual path (eq. 2) and in part by the path shown in eq. 3. One can even present some not unreasonable



$$5ArSO_2H + (RR'CH)_2S \longrightarrow 2ArSO_2SAr + ArSO_2SCHRR' + RR'CO + 3H_2O \quad (2)$$

$$2ArSO_2H + (RR'CH)_2S \longrightarrow ArSO_2SAr + (RR'CH)_2S{\rightarrow}O + H_2O \quad (3)$$

arguments[4] why reaction 3 should play a more important role in the 2-octyl sulfide case than in the other sulfide–sulfinic acid reactions so far examined. This explanation, however, also leads one to expect that the ratio of *p*-tolyl to alkyl *p*-toluenethiolsulfonate should be significantly larger than has been found[3] in the other alkyl sulfide–*p*-toluenesulfinic acid reactions. This is not the case. Indeed, if anything, the ratio (1.8:1) is slightly smaller than normally observed. This, coupled with the fact that the total yields of both thiolsulfonates, although a bit lower, are still closely comparable to those obtained in earlier[3] *p*-toluenesulfinic acid–primary alkyl sulfide reactions, tends to cast considerable doubt on this otherwise attractive explanation.

At present we have no simple alternative explanation for the formation of the sulfoxide. However, the results of some experiments we carried out to obtain further information relevant to this point are worth noting. Heating 2-octyl sulfide alone in the acetic acid–water–sulfuric acid medium used for the sulfide–sulfinic acid reactions yielded, as expected, no sulfoxide. However, heating it with 2-octanone in the same solvent, either in the presence or absence of *p*-tolyl *p*-toluenethiolsulfonate, led to the formation of a small amount of material, which from its infrared spectrum and point of elution from a chromatographic column must have consisted chiefly of 2-octyl sulfoxide. The amount of sulfoxide so formed was less than the amount isolated from the sulfide–sulfinic acid reaction, but the fact that some was formed raises the possibility that in the presence of sulfinic acid one might have a more efficient reaction involving ketone and sulfide, which would consume some of the ketone, oxidize some of the sulfide to the sulfoxide, and convert a small amount of sulfinic acid to indeterminate products.

We might then summarize the present state of our knowledge by saying that, although most of the reaction between *sec*-alkyl sulfides and the sulfinic acid seems to follow the expected course outlined in eq. 2, with at least some secondary sulfides additional complexities give rise to the formation of some *sec*-alkyl sulfoxide, apparently principally at the expense of some of the ketone expected from eq. 2.

**Reactivity of Secondary Alkyl Sulfides in the Sulfide–Sulfinic Acid Reaction.**—The kinetics of the reaction of several *sec*-alkyl sulfides with *p*-toluenesulfinic acid were examined in acetic acid–0.56 *M* water–0.6 *M* sulfuric acid using the techniques outlined in previous publications.[2,3] In each case the reactions were found to be first order in both sulfinic acid and sulfide. The rate contants, $k_s$, calculated from the equation

$$-d(ArSO_2H)dt = k_s(ArSO_2H)(R_2S)$$

are shown in Table I, along with selected data on primary alkyl sulfides from earlier work.[3]

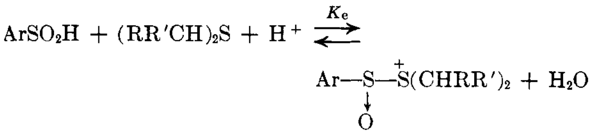
TABLE I

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

| Alkyl sulfide | $k_S \times 10^3$, $M^{-1}$ sec.$^{-1}$ |
|---|---|
| Isopropyl | 2.6 |
| *sec*-Butyl | 2.8 |
| 2-Octyl | 2.4 |
| *n*-Butyl[b] | 17.5 |
| Ethyl[b] | 10.2 |

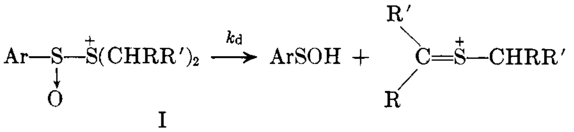
[a] All data are at 70° with acetic acid–0.56 *M* water–0.6 *M* sulfuric acid as the reaction medium. [b] Data of ref. 3.

The primary alkyl sulfides are seen to be four to seven times as reactive as the corresponding secondary alkyl sulfides. Since previous work[3] with selected primary alkyl sulfides has shown that the rate of the sulfide–sulfinic acid reaction is subject to inductive acceleration by an increase in the electron-donating character of the alkyl group ($\rho^* = -1.85$), the decreased reactivity of the *sec*-alkyl sulfides is certainly not due to an inductive effect. Consideration of the kinetically important steps[3] of the usual sulfide–sulfinic acid reaction (eq. 4 and 5) suggests two possible



$$ArSO_2H + (RR'CH)_2S + H^+ \overset{K_e}{\rightleftharpoons} Ar{-}\underset{\substack{\downarrow\\ O}}{S}{-}\overset{+}{S}(CHRR')_2 + H_2O \quad (4)$$

I



$$Ar{-}\underset{\substack{\downarrow\\ O}}{S}{-}\overset{+}{S}(CHRR')_2 \xrightarrow{k_d} ArSOH + RR'C{=}\overset{+}{S}{-}CHRR' \quad (5)$$

I

causes for the lower reactivity of the secondary sulfides. First, steric factors could cause the first equilibrium to be less favorable for the formation of I. Second, elimination of ArSOH from I might occur with greater difficulty than elimination of the same species from $ArS(O)S(CH_2R)_2$, the equivalent ion formed from a primary sulfide. Preliminary results[5] of a study of the preferred direction of elimination in unsymmetrical alkyl sulfides indicate that the first factor is the important one, since comparable amounts of ethyl and isopropyl *p*-toluenethiolsulfonates are formed in the reaction of ethyl isopropyl sulfide with *p*-toluenesulfinic acid. It thus appears that the increased steric require-

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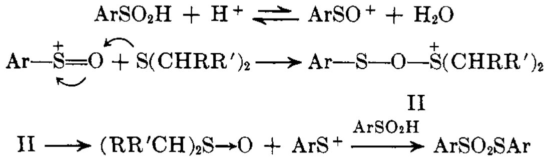
(4) The normal initial equilibrium between sulfinic acid and sulfide (eq. 4) leads to the ion I which then decomposes as shown in eq. 5.[3] One can argue that with increasing steric requirements of the alkyl groups of the sulfide an alternate equilibrium to give ion II may assume some importance, and that ion II will undergo decomposition as indicated below. This leads to the



$$ArSO_2H + H^+ \rightleftharpoons ArSO^+ + H_2O$$

$$Ar{-}\overset{+}{S}{=}O + S(CHRR')_2 \longrightarrow \underset{\text{II}}{Ar{-}S{-}O{-}\overset{+}{S}(CHRR')_2}$$

$$\text{II} \longrightarrow (RR'CH)_2S{\rightarrow}O + ArS^+ \xrightarrow{ArSO_2H} ArSO_2SAr$$

over-all stoichiometry shown in eq. 3. Clearly, if steric considerations tend to promote II at the expense of I, reaction 3 should be more important with 2-octyl sulfide than with the other sulfides that have been studied.

(5) B. Toth, unpublished results.

ments of the *sec*-alkyl sulfides cause the equilibrium in eq. 4 to be less favorable than for primary alkyl sulfides.

## Experimental

**Materials.**—*p*-Toluenesulfinic acid was prepared and purified as previously described.[3] Isopropyl and *sec*-butyl sulfides (Aldrich Chemical Co.) were purified by fractional distillation. Acetic acid–0 56 *M* water solutions and stock solutions of sulfuric acid in the same solvent were prepared from purified acetic acid in the manner outlined previously.[3]

**2-Octyl Sulfide.**—2-Octyl mercaptan[6] (10.4 g.), b.p. 87–89° (28 mm.), was dissolved in 30 ml. of methanol. The solution was kept under nitrogen, and 4 g. of potassium hydroxide in 25 ml. of methanol was added. To this was then added dropwise with good stirring 13.7 g. of 2-octyl bromide. The mixture was refluxed for 10 hr. After cooling the solution, the precipitated potassium bromide was filtered off, and the filtrate was poured into water and extracted with ether. The ether extracts were dried and the ether was removed by distillation. Distillation of the residue gave 11.2 g. (61%) of 2-octyl sulfide, b.p. 129–131° (2 mm.), lit.[7] b.p. 175° (20 mm.).

*Anal.* Calcd. for $C_{16}H_{34}S$: C, 74.45; H, 13.22. Found: C, 74.22; H, 13.22.

**Kinetic Runs.**—These were carried out using the methods described in an earlier paper.[3]

**Products of the *sec*-Alkyl Sulfide–*p*-Toluenesulfinic Acid Reactions.**—The same general procedure was used for both sulfides studied. A solution of 5.00 mmoles of *p*-toluenesulfinic acid and 15.0 mmoles of the *sec*-alkyl sulfide in 100 ml. of acetic acid–0.56 *M* water–0.6 *M* sulfuric acid was deaerated at room temperature and then heated under nitrogen at 70° for 2 hr. At the end of that time a small aliquot was removed, and the residual sulfinic acid content was determined by nitrite titration.[3] This was 0.28 mmole for the isopropyl sulfide reaction and 0.44 mmole in the 2-octyl sulfide case.

The reaction mixture was then poured into ten times its volume of water, and the mixture was extracted several times with ether. The ether extracts were washed with aqueous 5% sodium bicarbonate until neutral, then with water, and were finally dried over anhydrous sodium sulfate. The ether was removed by careful fractional distillation, and the residue was subjected to chromatography on acid-washed alumina.

In the isopropyl case successive elution with hexane and benzene allowed the separation of the unchanged sulfide from a mixture of *p*-tolyl and isopropyl[8] *p*-toluenethiolsulfonates. The relative amounts of the two thiolsulfonates in the mixture was then determined by an n.m.r. analytical method already outlined.[8] The results indicated the amounts of the two thiolsulfonates formed in the reaction were *p*-tolyl *p*-toluenethiolsulfonate, 1.37 mmoles, and isopropyl *p*-toluenethiolsulfonate, 0.74 mmole.

The formation of acetone as an additional reaction product was demonstrated in a separate experiment. In it the final reaction solution was distilled through a short Vigreux column until about 4 ml. of distillate was obtained. The distillate was treated with an alcohol solution of 2,4-dinitrophenylhydrazine in the usual manner, and the acetone 2,4-dinitrophenylhydrazone which precipitated was recrystallized and identified.

For the 2-octyl sulfide reaction, the chromatographic column was eluted much more gradually, using successively hexane, 10% benzene–hexane, 25% benzene–hexane, 50% benzene–hexane, pure benzene, and finally ether. After the unchanged sulfide there were eluted, in order, essentially pure fractions of 2-octanone, 2-octyl *p*-toluenethiolsulfonate, and *p*-tolyl *p*-toluenethiolsulfonate. The identity of the ketone was confirmed by comparison of the infrared spectrum of the crude product with that of a known sample of 2-octanone and by conversion of the crude ketone to its semicarbazone, m.p. 125–126°. The yield, as estimated from the amount of semicarbazone obtained, was 0.42 mmole. Experiments with pure 2-octanone samples indicated that under our conditions the formation of the semicarbazone from the ketone was only about 85% quantitative. On this basis the probable true yield of 2-octanone from the reaction would be about 0.49 mmole.

The yields of the two thiolsulfonates were determined from the weights of the respective fractions, n.m.r. analyses having shown that each was essentially uncontaminated by the other ester: *p*-tolyl *p*-toluenethiolsulfonate, 1.35 mmoles, and **2-octoyl *p*-toluenethiolsulfonate**, 0.76 mmole. The identity of the latter ester was established by elemental analysis and infrared and n.m.r. spectral data on the appropriate chromatographic fractions. It is a liquid, but too high boiling to allow distillation without decomposition.

*Anal.* Calcd. for $C_{15}H_{24}O_2S_2$: C, 59.95; H, 8.05. Found: C, 60.16; H, 7.94.

In the isopropyl sulfide runs, elution of the chromatographic column with ether gave no products. The ether fractions from the 2-octyl sulfide runs, on the other hand, contained a significant amount of material. Its principal component was shown to be 2-octyl sulfoxide.

**2-Octyl Sulfoxide.**—The ether fractions from the chromatogram were subjected to molecular distillation. The distillate had an infrared spectrum which showed a very strong band at 1025 cm.$^{-1}$, as would be expected for a sulfoxide.

*Anal.* Calcd. for $C_{16}H_{34}OS$: C, 70.01; H, 12.48; S, 11.68. Found: C, 70.12; H, 12.65; S, 11.78.

A known sample of 2-octyl sulfide was allowed to react in acetone solution with an equimolar amount of hydrogen peroxide for 1 week at room temperature. After standard work-up procedures there was isolated an 80% yield of a substance having an infrared spectrum identical with the compound isolated from the sulfide–sulfinic acid reaction.

**2-Octyl Sulfone.**—A sample of 2-octyl sulfide was oxidized in hot acetic acid with sufficient hydrogen peroxide to convert it to the sulfone. There was obtained a 98% yield of crude 2-octyl sulfone. Its infrared spectrum showed the expected strong absorption at 1300 and 1125 cm.$^{-1}$. It was further purified by molecular distillation at $10^{-4}$ mm. in a small Hickman still.

*Anal.* Calcd. for $C_{16}H_{34}O_2S$: C, 66.15; H, 11.80; S, 11.04. Found: C, 66.28; H, 12.04; S, 11.30.

A portion of the presumed 2-octyl sulfoxide from the sulfide–sulfinic acid reaction was treated with an equimolar amount of hydrogen peroxide in hot acetic acid. On work-up there was obtained an 80% yield of a substance having an infrared spectrum identical with that of the known 2-octyl sulfone, prepared above from the sulfide. There is thus no doubt that the compound formed in the 2-octyl sulfide-*p*-toluenesulfinic acid reaction is 2-octyl sulfoxide.

**Interaction of 2-Octanone and 2-Octyl Sulfide.**—2-Octyl sulfide (15 mmoles), 2-octanone (5 mmoles), and *p*-tolyl -*p*-toluenethiolsulfonate (2 mmoles) were heated at 70° for 2 hr. in 100 ml. of acetic acid–0.56 *M* water–0.6 *M* sulfuric acid. The reaction mixture was poured into water and worked up in just the same way as the 2-octyl sulfide–*p*-toluenesulfinic acid reaction. The ether fraction from the chromatography had an infrared spectrum which indicated it consisted chiefly of 2-octyl sulfoxide. It weighed 0.025 g. Similar results were obtained in the absence of *p*-tolyl *p*-toluenethiolsulfonate. However, heating the sulfide alone under the same conditions gave no detectable sulfoxide on work-up.

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[6] L. M. Ellis, Jr., and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 1674 (1932).

[7] S. O. Jones and E. E. Reid, *ibid.*, **60**, 2452 (1938).

[8] J. L. Kice and E. H. Morkved, *ibid.*, **86**, 2270 (1964).