

kcal./mole corresponding to half the bond dissociation enthalpy of iodine.

The ion-pair<sup>3,4</sup> and molecular<sup>5,6</sup> mechanisms exhibit similar concentration dependence for the rates; they differ chiefly in the extent of charge separation in the transition state. For runs in dichloroethane, the pre-exponential factors in eq. 3 and 4 are about ten orders of magnitude smaller than would be expected for a reaction of neutral molecules; this very large effect seems inexplicable unless the transition state is so polar as to be virtually an ion pair.

An ion-pair transition state should lead to very different rates in dichloroethane (dielectric constant 10.1) and in hexane (dielectric constant 1.9). Thus the ratio of  $k_1$  values in these two solvents is 60 for exchange of benzoyl iodide<sup>4</sup> and 2000 for *t*-butyl iodide.<sup>3</sup> The apparent factor for iodoacetone seems to be much smaller and is more like the ratio of about 6 observed for allyl iodide.<sup>6</sup>

Although the mechanistic conclusion must be somewhat equivocal, we believe that the very low entropy of activation in dichloroethane requires that the transition state in that solvent has charge separation approaching that of an ion pair. The observed rates in

hexane are too rapid to accommodate to the same model. The difference may reflect a change in mechanism on going to this solvent. The unsatisfactory kinetics may also reflect side effects. Thus, when mercury was used to remove iodine, the peculiar accelerations suggest formation of a catalyst during each run. Such a catalyst might be HI formed from hydrolysis of iodoacetone by atmospheric moisture. The runs in which iodine was removed by sulfite were faster than those in which mercury was used, although the true rate of exchange could not possibly be influenced by a choice between separation procedures that did not induce exchange in the initial solution and that were not applied until *after* the period of exchange. The discrepancies strongly suggest that the experiments in hexane were influenced by trace impurities probably associated with the action of atmospheric moisture. Other work in these laboratories<sup>9</sup> has indicated the great difficulty of getting reproducible rates for exchange by apparently ion-pair mechanisms in this solvent.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER, N. Y.]

## Mechanisms of Elimination Reactions. V. Sulfur Isotope Effects in Some Reactions of *t*-Butyldimethylsulfonium Iodide<sup>1</sup>

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The E2 reaction of *t*-butyldimethylsulfonium ion with ethoxide ion in 97% ethanol at 24° shows a <sup>32</sup>S/<sup>34</sup>S isotope effect of 0.72%. The SN1-E1 solvolysis of the same compound in 97% ethanol at 40° shows a <sup>32</sup>S/<sup>34</sup>S isotope effect of 1.03%. These results are compared with earlier work, and their mechanistic significance is discussed.

Some time ago, we showed that the E2 reaction of 2-phenylethyldimethylsulfonium ion with hydroxide ion at 59° occurs with a very small sulfur isotope effect (0.15%).<sup>3</sup> We took this result as evidence for a high degree of carbanion character in the transition state, a conclusion supported by data on substituent effects<sup>4</sup> and deuterium isotope effects.<sup>5</sup> At that time there was no evidence on whether low sulfur isotope effects were general for E2 reactions of sulfonium salts, or only to be expected when the β-hydrogens were activated by some group such as phenyl. The present research was an effort to settle this problem.

The reactant chosen was the *t*-butyldimethylsulfonium ion. We had used the isotope effect in its SN1-E1 reaction in water as an experimental "upper limit" in our previous work,<sup>3</sup> and hoped to study its E2 reaction with hydroxide ion in water. Unfortunately, we could not attain conditions under which the first-order reaction was not an important fraction of the total reaction. Both the first- and second-order reactions of *t*-butyldimethylsulfonium ion have been

studied in 97% ethanol,<sup>6</sup> and the rate constants shown to be sufficiently different to permit isolation of the second-order reaction

We determined the kinetics of both reactions in 97% ethanol under conditions feasible for the isotope-effect studies. No special effort to attain high precision was made for the rate constants given in Table I, though on the one comparison possible with the literature,<sup>6</sup> the E2 reaction at 24°, agreement is excellent (8.0 *vs.* 7.97 × 10<sup>-4</sup>) in spite of slight differences in the ionic strength and the method of making up solvent. From these constants, times for 5% completion of the E2 reaction at 24° and of the SN1-E1 reaction at 40° were calculated to be 5.5 min. and 3.8 hr., respectively. Similar calculations for 99% reaction gave 2.8 hr. at 75° for the E1-SN1 and 1.0 hr. at 35° for the E2 reactions.<sup>7</sup> The isotope-effect runs were carried out and the isotopic ratios of the resulting dimethyl sulfide

(6) E. D. Hughes, C. K. Ingold, and L. I. Woolf, *J. Chem. Soc.*, 2084 (1948).

(7) Calculations based on an equation given by Melander<sup>8</sup> show that the isotope ratio of <sup>32</sup>S to <sup>34</sup>S in the dimethyl sulfide collected should be the same within experimental error for samples taken at 2 and 5% completion assuming an isotope effect of 1.8%; so 5% completion was chosen so as to permit smaller reaction mixtures. Similarly, the isotopic composition of samples taken after 99% reaction can be shown to be within experimental error of the isotopic composition of the original reactant.

(8) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960, eq. 3-3, p. 49.

(1) This work was supported by the National Science Foundation.

(2) Alfred P. Sloan Foundation Fellow.

(3) W. H. Saunders, Jr., and S. Asperger, *J. Am. Chem. Soc.*, **79**, 1612 (1957).

(4) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).

(5) W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960).

samples determined as detailed under Experimental. The results and the calculated isotope effects are given in Tables II and III.

TABLE I  
RATE CONSTANTS FOR THE REACTIONS OF  
*t*-BUTYLDIMETHYLSULFONIUM IODIDE IN 97% ETHANOL

Reaction type	<i>t</i> , °C. <sup>a</sup>	<i>k</i> × 10 <sup>4</sup>
SN1-E1	35.00	0.021 <sup>b</sup>
SN1-E1	40.00	0.039 <sup>b</sup>
SN1-E1	75.00	4.9 <sup>b</sup>
E2	24.00	8.0 <sup>c</sup>
E2	35.00	34 <sup>c</sup>

<sup>a</sup> Temperature constant to ±0.05°. <sup>b</sup> Units are sec.<sup>-1</sup>.  
<sup>c</sup> Units are l.-mole<sup>-1</sup> sec.<sup>-1</sup>.

TABLE II  
<sup>32</sup>S/<sup>34</sup>S ISOTOPE RATIOS AND ISOTOPE EFFECTS IN THE E2  
REACTION OF *t*-BUTYLDIMETHYLSULFONIUM IODIDE WITH  
SODIUM ETHOXIDE IN 97% ETHANOL AT 24°

<sup>32</sup> S/ <sup>34</sup> S, 100% completion <sup>a</sup>	<sup>32</sup> S/ <sup>34</sup> S, 5% completion <sup>a</sup>	Isotope effect, <sup>b</sup> %
24.432	24.621	0.75
24.441		
25.420	25.553	.73
25.432		
25.301	25.499	.79
25.294		
<i>c</i>	<i>c</i>	.62
Mean value of isotope effect		.72 <sup>d</sup>

<sup>a</sup> Ratio of ion current at mass 62 to ion current at mass 64.  
<sup>b</sup> % isotope effect ( $k_2/k_4 - 1$ ) × 100. <sup>c</sup> Isotope effect is the average of five runs on the mass spectrometer at four different sample pressures of the same pair of samples; standard deviation of the mean, 0.04. <sup>d</sup> Standard deviation of the mean, 0.04; 95% confidence limit, 0.12.

TABLE III  
<sup>32</sup>S/<sup>34</sup>S ISOTOPE RATIOS AND ISOTOPE EFFECTS IN THE  
SN1-E1 REACTION OF *t*-BUTYLDIMETHYLSULFONIUM IODIDE  
WITH 97% ETHANOL AT 40°

<sup>32</sup> S/ <sup>34</sup> S, 100% completion <sup>a</sup>	<sup>32</sup> S/ <sup>34</sup> S, 5% completion <sup>a</sup>	Isotope effect, <sup>b</sup> %
25.176	25.406	0.87
25.197		
25.918	26.230	1.23
25.904		
25.845	26.092	0.98
25.831		
Mean value of isotope effect		1.03 <sup>c</sup>

<sup>a</sup> See corresponding footnotes in Table II. <sup>c</sup> Standard deviation of the mean, 0.11; 95% confidence limit, 0.47.

Precision is excellent on the E2 reaction. The last value in Table II is the average of four runs over a range of sample pressures on a single pair of samples, and shows that change in the sample pressure does not cause any noticeable change in the isotope effect, even though the apparent isotopic ratio varied somewhat with sample pressure for each sample taken individually. Precision is distinctly poorer on the SN1-E1 reaction, though this is partly the result of one run fewer than was done on the E2 reaction. Application of the "t" test<sup>9</sup> showed a greater than 95% probability that the value of 1.03% for the SN1-E1 reaction is significantly different from the 0.72% for the E2 reaction.

These results are qualitatively very reasonable. The *t*-butyldimethylsulfonium ion has a tertiary α-carbon and lacks any activating groups on the β-

(9) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 25.

carbons, so the transition state for its E2 reaction would be expected to possess less carbanion character than that for the 2-phenylethyldimethylsulfonium ion. In agreement with our results, the <sup>14</sup>N/<sup>15</sup>N isotope effect is greater for ethyltrimethylammonium ion than for 2-phenylethyltrimethylammonium ion in the E2 reaction,<sup>10</sup> the isotope effect for which should still be less than that for the SN1-E1 reaction, as some carbanion character is needed to explain the adherence of *t*-alkyldimethylsulfonium salts to the Hofmann rule.<sup>6</sup>

Both of our isotope effects are significantly below the values calculated from theoretical models, which range from 1.34% for the simple diatomic C-S to 1.86% for a tetratomic Me<sub>3</sub>S<sup>11</sup> at 59° (at our lower temperatures, these effects should be higher—by 0.1–0.2% at 24°). More recent calculations using a tetratomic model for the E2 transition state (H-CH<sub>2</sub>-CH<sub>2</sub>-S)<sup>12</sup> do not change this picture significantly. They do point to the comforting conclusion that the magnitude of the isotope effect is primarily determined by the extent of C-S bond weakening. Incidentally, the temperature differences between our two results and between them and the earlier work<sup>3</sup> should not make any qualitative difference in the picture. If all were brought to a common temperature—say 40°—the difference in isotope effect between our two results might be increased by about 0.1%, while the difference in isotope effect between the E2 reactions of 2-phenylethyl- and *t*-butyldimethylsulfonium ions might be narrowed by 0.1–0.2%. No change in order could result from any reasonable temperature dependence.

One rather puzzling matter remains. Why should the isotope effect for the SN1-E1 reaction of *t*-butyldimethylsulfonium ion change from 1.0 to 1.8% merely on changing solvent from ethanol to water? Though *ad hoc* explanations can be adduced, the phenomenon is certainly neither obvious nor expected. More work is needed before detailed discussion will be worthwhile. It will be particularly important to see what effect solvent may have on comparisons of different E2 reactions.

## Experimental

*t*-Butyldimethylsulfonium iodide was prepared as before.<sup>3,13</sup> Its purity was verified by analysis.

*Anal.* Calcd. for C<sub>6</sub>H<sub>16</sub>SI: C, 29.27; H, 6.14. Found: C, 29.41; H, 6.33.

**Preparation of Samples for Measurement of Mass Spectra.**  
1. **The E2 Reaction.**—The apparatus was a gas-washing bottle with an inlet, a side arm, and an outlet connected to a small condenser. To the top of the condenser was connected a drying tube containing calcium chloride and phosphorus pentoxide, followed by a double U-tube collection trap cooled in liquid nitrogen. The side arm was normally closed with a rubber ampule stopper, but could be connected to an addition funnel for introduction of solvent or reagents in solution. A stream of nitrogen previously purified by passage through an Ascarite tower and a Dry Ice trap was admitted through the inlet. The system could be used under partial vacuum by means of an aspirator pump attached to the outlet of the collection trap. For the large reaction mixtures used for the 5% samples, a 1-l. flask with an appropriate adapter replaced the gas-washing bottle.

Both the 5 and 100% reactions were conducted on aliquots of the same 0.1 M solution of *t*-butyldimethylsulfonium iodide in

(10) G. Ayrey, A. N. Bourns, and V. A. Vyas, *Can. J. Chem.*, **41**, 1759 (1963).

(11) W. H. Saunders, Jr., *Chem. Ind. (London)*, 1661 (1963).

(12) Unpublished results.

(13) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1571 (1933).

94% ethanol (prepared by diluting 6% of water by volume with absolute ethanol to the mark). The reaction mixture for the 5% reaction was prepared by diluting 250 ml. of the solution with 250 ml. of 0.4 *M* sodium ethoxide in absolute ethanol; that for the 100% reaction was prepared by diluting 15 ml. of the solution with 15 ml. of 1 *M* sodium ethoxide in absolute ethanol. Solutions were equilibrated in the constant-temperature bath prior to mixing, and addition of base was done with the apparatus completely connected to prevent loss of any methyl sulfide. The system was maintained at a pressure of ca. 100 mm., and the reaction bottle at 24° in the 5% reaction. After 5.5 min. the reaction was quenched with 110 ml. of 1 *M* aqueous HCl, and nitrogen passed through the mixture for another hour to expel products. The 100% reaction was run in a similar fashion for 1.5 hr. at ca. 170-mm. pressure and 35°.

**2. The E1 Reaction.**—The apparatus was the same as for the E2 reaction. Solutions were prepared in the same manner, except the 0.1 *M* solutions in 94% ethanol were diluted with equal values of absolute ethanol to give the final reaction mixtures. The 5% reaction was conducted at 40° for 3.8 hr. and a partial vacuum of 170 mm. The 100% reaction was conducted at 75° for 3 hr. at atmospheric pressure.

**Purification of Dimethyl Sulfide Samples.**—The collection trap was connected to a vacuum line and the sample distilled through a tube containing phosphorus pentoxide into a small sample tube. The material collected in this tube was transferred with a chilled hypodermic syringe to a gas chromatograph (Wilkins Aerograph Model A-90C) fitted with a 5-ft. column of 20% tri-*o*-cresyl phosphate on Chromosorb. At room temperature and a flow rate of 25 ml. per min. the retention time for isobutylene was 1.5 min. and for dimethyl sulfide 17 min. The latter peak was

collected in a trap immersed in liquid nitrogen. In the SN1-E1 reactions another peak followed shortly after the dimethyl sulfide (probably *t*-butyl alcohol or *t*-butyl ethyl ether) but could be separated from it satisfactorily. The dimethyl sulfide was then distilled into the sample bulb and carefully degassed as described before.<sup>3</sup>

**Mass Spectrometry.**—A Consolidated Model 21-620 instrument was used. The procedure was similar to that used before.<sup>3</sup> Sample pressure was normally 300  $\mu$ . Some dependence of the apparent mass 62:mass 64 ratio on sample pressure was noted. A set of runs on the same pair of 100 and 5% samples over the range 150–300  $\mu$  showed no significant variation in the isotope effect, provided the two samples of a pair were measured at the same pressure. This was accomplished by starting each series of runs at the same scale deflection on the recorder, and carrying out the 20 consecutive scans on a rigidly timed schedule. The 100% sample was run both before and after the 5% sample. The standard deviations from the mean of the averages of 20 scans usually were less than 0.2%.

**Kinetic Measurements.**—Apparatus and sampling techniques were similar to those used by Williams.<sup>4</sup> Solvents and solutions were prepared as described above (Preparation of Samples for Measurement of Mass Spectra). Temperature control was good to  $\pm 0.05^\circ$ , and temperatures were checked against an N.B.S. thermometer. Chilled aliquots from the SN1-E1 reaction were titrated with standard base. Aliquots from the E2 reaction were quenched in 0.1 *N* hydrochloric acid and back titrated with standard base. No particular effort was made to attain maximum precision. Most of the rate constants are good to  $\pm 5\%$  or better, but those for the faster reactions may be as poor as  $\pm 10\%$ .

[CONTRIBUTION FROM THE CENTRAL BASIC RESEARCH LABORATORY, ESSO RESEARCH AND ENGINEERING COMPANY, LINDEN, N. J.]

## Organic Sulfur Compounds. XIV.<sup>1</sup> Oxidative Addition of Thiol Acids to Unsaturated Hydrocarbons. Cooxidation of Thiolacetic Acid and Indene by Molecular Oxygen

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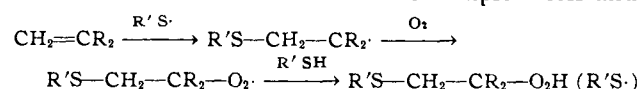
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The mechanism of oxidative addition of thiol acids to unsaturated hydrocarbons was studied with thiolacetic acid and indene as model reactants. While the free-radical addition of thiolacetic acid to indene is a rather slow process, a rapid chain reaction occurs when solutions containing thiolacetic acid and indene are oxygenated at room temperature. In the cooxidation reaction, the 2-acetylmercaptoindanyl radical (V) resulting from addition of the acetylmercapto radical to indene combines with  $\cdot O_2$  to form a peroxy radical (VII). This then abstracts hydrogen from thiolacetic acid to yield the unstable 2-acetylmercapto-1-indanyl hydroperoxide (VIII), a new type of peroxide compound, as the primary cooxidation product. The hydroperoxide VIII is slowly reduced by thiolacetic acid or thiols to the corresponding alcohol IX. Aliphatic amines catalyze this reduction. The structures of the new addition and cooxidation products (VI, VIII, and IX) were established by n.m.r. and infrared spectroscopy. An analogous cooxidation mechanism seems applicable to the oxidative addition of thiolcarboxylic and thiophosphoric acids to olefinic hydrocarbons and anthracenes and opens a new synthetic route to  $\beta$ -acylmercaptoalknols.

### Introduction

The cooxidation of thiolacetic acid and hydrocarbons—anthracenes<sup>3,4</sup> and fluorenes<sup>4</sup>—with molecular oxygen was first described by Mikhailov and Blokhina in 1951. Ten years later, Beckwith and Beng See<sup>5</sup> re-examined the reaction of thiolacetic acid with anthracene and oxygen. On cooxidation with anthracene, Mikhailov and Blokhina<sup>3,4</sup> obtained diacetyl disulfide and the two isomeric 9,10-dihydro-9,10-bis(acetylmercapto)anthracenes (IV) as the main products. Beckwith and Beng See found<sup>5</sup> that 9-acetylmercapto-

anthracene (III) and some sulfur were also formed. Each group proposed a different reaction mechanism. We believe that the chain mechanism proposed by the second group is the more probable one. This mechanism postulates 9,10-dihydro-9-acetylmercapto-10-hydroperoxyanthracene (I) as the primary and 9,10-dihydro-9-acetylmercapto-10-hydroxyanthracene (II) as the secondary unstable reaction products. This mechanism for thiolacetic acid cooxidation is analogous to the mechanism of cooxidation of simple thiols and



(1) Previous paper of this series, *J. Am. Chem. Soc.*, **86**, 2877 (1964).

(2) Central Basic Research Laboratory, Esso Research and Engineering Co., Esso Research Center, P. O. Box 45, Linden, N. J.

(3) B. M. Mikhailov and A. N. Blokhina, *Dokl. Akad. Nauk, S.S.S.R.*, **80**, 373 (1951).

(4) B. M. Mikhailov and A. N. Blokhina, *Problemy Mekhanizma Org. Reaktsii, Akad. Nauk, Ukr. S.S.R.; Otdel. Fiz.-Mat. i Khim. Nauk*, 215 (1953); *Chem. Abstr.*, **50**, 16,735f (1956).

(5) A. L. J. Beckwith and Low Beng See, *J. Chem. Soc.*, 1304 (1961).

(6) A. A. Oswald, *J. Org. Chem.*, **24**, 443 (1959); **26**, 842 (1961); A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *ibid.*, **27**, 2439 (1962).

(7) A. A. Oswald, F. Noel, and G. Fisk, *ibid.*, **26**, 842 (1961).

(8) For a more detailed treatment of this subject, see A. A. Oswald and T. J. Wallace, "Anionic Oxidation of Thiols and Co-oxidation of Thiols and Olefins by Molecular Oxygen," chapter in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press, London, in press.