In terms of a direct partitioning model the rate ratio variation between vapor and condensed phase isomerizations may be explained by assuming that $\Delta\Delta \bar{V}^{\ddagger}$ for the two competitive processes and differences in solvent organization at the transition states may combine to cause the observed change.[12]

Either model may yet be demonstrated experimentally as the more correct, or each may be appropriate to some fraction of the total process. At present the issue remains unresolved, for neither the gas phase nor the solution phase kinetic findings are uniquely interpretable by a single mechanistic postulate.

(12) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, p 131.

(13) National Science Foundation Predoctoral Trainee, 1972–1973.

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The Chemistry of Alkyl Thiolsulfinate Esters. IV. A Mechanistic Study of the Disproportionation Reaction[1]

Sir:

Thiolsulfinate esters are an unusually unstable class of compounds known to disproportionate readily to disulfides and thiolsulfonate esters (eq 1); this reaction

$$2RS(O)SR \longrightarrow RSO_2SR + RSSR \qquad (1)$$

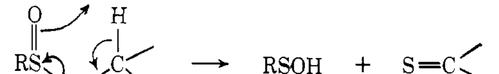
displays acid and sulfide catalysis and may be thermally as well as photochemically initiated.[2–4] Detailed studies of the mechanism of the thermal[2a] and catalyzed[4] disproportionation of diaryl thiolsulfinates have recently appeared; similar studies with dialkyl thiolsulfinates have not hitherto been described. We now report the preliminary results of a study of the thermal and photochemical disproportionation of a variety of symmetrical and unsymmetrical dialkyl thiolsulfinates and contrast these findings with those previously described for the diaryl esters. In a study of the disproportionation reaction, the dialkyl esters possess the advantage that they (and their decomposition products) are amenable to detailed gas chromatographic (gc) and coupled gas chromatographic–mass spectrometric (gc–ms) analysis under mild conditions. Furthermore the possibility exists for the diversion of intermediates through reactions involving the alkyl groups; the synthetic exploitation of this latter possibility is the subject of the accompanying communication.[5]

Table I. Relative Thermal Stability of Neat Dialkyl Thiolsulfinate Esters

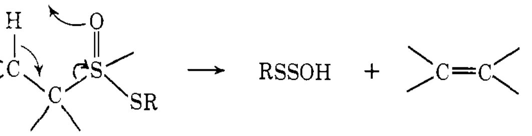
Thiolsulfinate esters	Time for 50% decomposition at 96° (min)[a]
MeS(O)SMe	7
MeS(O)SEt[6]	11
MeS(O)S-*i*-Pr[6]	32
EtS(O)SMe[6]	40
n-$C_{12}H_{25}S(O)SC_{12}H_{25}$-*n*[d]	52
t-BuS(O)S-*t*-Bu[e]	148
MeS(O)S-*t*-Bu[6]	~10^3
1-AdS(O)SAd-1[b,7]	>10^5 [c]

[a] Analysis by quantitative ir and/or quantitative gc. [b] 1-Adamantyl 1-adamantanethiolsulfinate.[7] [c] After 1.2 × 10^5 min, >70% remaining thiolsulfinate. [d] P. Allen, Jr., and J. W. Brook, *J. Org. Chem.*, **27**, 1019 (1972). [e] R. W. Murray, R. D. Smetana, and E. Block, *Tetrahedron Lett.*, 299 (1971).

The effect of structure on stability of the dialkyl esters is seen through a comparison of ease of disproportionation (indicated by time for 50% decomposition of *neat* thiolsulfinate at 96°) for the representative esters in Table I. The composition of the thiolsulfonate ester mixtures produced by disproportionation of several *unsymmetrical* thiolsulfinate esters[6] under a variety of conditions is indicated in Table II. Table I shows that thiolsulfinates are stabilized by alkyl substitution adjacent to *either* sulfur. Particular stability results when neither α-sulfenyl nor β-sulfinyl protons are available for β-elimination processes (eq 2[6b] and 3,[1b] respectively) as demonstrated by the remarkable stability of 1-adamantyl 1-adamantanethiolsulfinate.[7] Table II reveals that unsymmetrical thiolsulfonate is favored over symmetrical thiolsulfonate in pyrolysis of neat samples of thiolsulfinates (entries 1–5) by a factor of 4–15 with the singular exception of isopropyl methanethiolsulfinate. In none of the pyrolyses studied were we able to detect thiolsulfonates or thiolsulfinates derived from oxygen crossover (*i.e.*, $EtSO_2SMe$, $EtSO_2SEt$, or EtS(O)SMe from MeS(O)SEt, or $MeSO_2SEt$, $MeSO_2SMe$, or MeS(O)SEt from EtS(O)SMe) although our gc analytical method was capable of detecting as little as 0.1% of a crossover product in the presence of the noncrossover mixture of thiolsulfonates and thiolsulfinates. By way of comparison, Fava and coworkers found approximately 10% oxygen crossover in thiolsulfonates and thiolsulfinates recovered from pyrolysis of aryl thiolsulfinates specifically labelled (^{35}S) on the sulfinyl sulfur.[2a]



(2)



(3)

In order to minimize problems associated with different steric environments at the two thiolsulfinate sulfurs, we have examined the products from pyrolysis of the unsymmetrically deuteriated thiolsulfinates MeS(O)-SCD_3 and $EtS(O)SCD_2Me$ (Table II, entries 6 and 7). Here too we find a predominance of unsymmetrical

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(1) (a) Presented at the Vth Symposium on Organic Sulfur Chemistry, Lund, Sweden, June 5–9, 1972. (b) Paper III: E. Block, *J. Amer. Chem. Soc.*, **94**, 644 (1972).

(2) Thermal disproportionation: (a) P. Koch, E. Ciuffarin, and A. Fava, *ibid.*, **92**, 5971 (1970); (b) C. J. Cavallito, J. H. Bailey, J. S. Buck, and C. M. Suter, *ibid.*, **66**, 1950, 1952 (1944); (c) H. J. Backer and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **73**, 129 (1954); (d) D. Barnard, *J. Chem. Soc.*, 4675 (1957).

(3) Photochemical disproportionation: (a) W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965); (b) P. J. Berner, Ph.D. Thesis, Stevens Institute of Technology, 1964 (γ radiation).

(4) Catalyzed disproportionation: J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.*, **95**, 109 (1973).

(5) E. Block and J. O'Connor, *ibid.*, **95**, 5048 (1973).

(6) (a) Prepared by condensation of the appropriate sulfinyl chloride and mercaptan;[2c] satisfactory spectral and, where product stability permits, analytical data were obtained for all new compounds. (b) E. Block, *J. Amer. Chem. Soc.*, **94**, 642 (1972).

(7) Prepared in 53% overall yield by oxidation of 1-adamantanethiol;[8] ir 9.25 μ (S=O), uv λ_{max} (cyclohexane) 258 nm (ε 2300); mass spectrum *m/e* 350 ($C_{20}H_{30}S_2O$, parent). *Anal.* Calcd for $C_{20}H_{30}S_2O$: C, 68.52; H, 8.63; S, 18.29. Found: C, 68.61; H, 8.43; S, 18.52.

(8) H. Stetter, M. Krause, and W.-D. Last, *Chem. Ber.*, **102**, 3357 (1969).

Table II. Product Distribution from Disproportionation of Unsymmetrical Alkyl Thiolsulfinates

No.	Thiolsulfinate (% converted)	Conditions	Products (mol % in product)[c] Thiolsulfonates	Disulfides	Other
1	MeS(O)SEt (34)	Neat, 25°, dark, 4 days	MeSO$_2$SEt (14), MeSO$_2$SMe (3)	MeSSMe,[a] MeSSEt (9), EtSSEt (3)	MeS(O)SMe (5)
2	MeS(O)SEt (~100)	Neat, 25°, dark, 1 wk	MeSO$_2$SEt (44), MeSO$_2$SMe (11)	MeSSMe (7), MeSSEt (26), EtSSEt (12)	
3	MeS(O)S-*i*-Pr (~100)	Neat, 96°, dark, 75 min	MeSO$_2$S-*i*-Pr (10), MeSO$_2$SMe (22)	MeSSMe,[a] MeSS-*i*-Pr (32), *i*-PrSS-*i*-Pr (19)	H$_2$O (15), *i*-PrS$_3$-*i*-Pr
4	EtS(O)SMe (~27)	Neat, 25°, dark, 4 wk	EtSO$_2$SMe (9), EtSO$_2$SEt (0.6)	MeSSMe (4), MeSSEt (6), EtSSEt (0.7)	EtS(O)SEt (2.4), EtS(O)CH$_2$SSMe (maj),[4] EtS(O)CH$_2$SSEt (min)[4]
5	EtS(O)SMe (~98)	Neat, 25°, dark, 16 wk	EtSO$_2$SMe (54), EtSO$_2$SEt (9)	MeSSMe (6), MeSSEt (14), EtSSEt (5)	MeS$_3$Me (1), EtS$_3$Et (1), EtS(O)CH$_2$SSMe (maj),[7] EtS(O)CH$_2$SSEt (min)[7]
6	MeS(O)SCD$_3$[b] (~100)	Neat, 96°, dark, 15 min	MeSO$_2$SCD$_3$:MeSO$_2$SMe = 7:3[d]	Not determined	
7	EtS(O)SCD$_2$Me[e] (~75)	Neat, 100°, dark, 40 min	EtSO$_2$SCD$_2$Me:EtSO$_2$SEt = 2.6:1	C$_4$H$_6$D$_4$S$_2$:C$_4$H$_8$D$_2$S$_2$:C$_4$H$_{10}$S$_2$ = 3:3:1	
8	EtS(O)SMe (84)	0.163 *M* in C$_6$H$_6$, 96°, dark, 2600 min	EtSO$_2$SMe (17), EtSO$_2$SEt (5)	MeSSMe (11), MeSSEt (23), EtSSEt (5)	EtSO$_x$CHRSSR′ (17)
9	EtS(O)SMe (100)	0.905 *M* in C$_6$H$_6$, 25°[f]	EtSO$_2$SMe (35), EtSO$_2$SEt (10)	MeSSMe,[a] MeSSEt (42), EtSSEt (13)	
10	EtS(O)SMe (39)	*hν* in C$_6$H$_6$[g] at 25°, 11 min	EtSO$_2$SMe (5), EtSO$_2$SEt (10)	MeSSMe (16), MeSSEt (7), EtSSEt (<1)	

[a] Concentration not determined. [b] 98.2% d_3, 1.8% d_2. [c] Analyzed by gc (internal standard), gc–ms, and in several cases by prep tlc followed by ir and nmr; in most cases *ca.* 90% product was accounted for. [d] The isotopic composition follows from detailed mass spectral analysis (to be published elsewhere); upper limits of 0.2% and 2% of total thiolsulfonate concentration can be placed on the amounts of CD$_3$SO$_2$SCD$_3$ and CD$_3$SO$_2$SCH$_3$, respectively. [e] 95.1% d_2, 2.9% d_1, and 2.0% d_0. [f] Solution also 1 *M* in CF$_3$COOH and Et$_2$S; dark, 1 min. [g] A 0.163 *M* solution irradiated at 254 nm through quartz.

thiolsulfonate by a factor of 2.3–2.6. The product distribution from disproportionation in dilute solution is similar to that obtained from neat material (Table II, entry 8); in the concentration range 1–2 *M* in benzene, the initial rate of disappearance of EtS(O)SMe follows second-order kinetics with $k = 3.05 \times 10^{-5}$ l. mol^{-1} sec^{-1} at 96°. A modest increase in rate was observed in acetonitrile as solvent (at 96°, $k = 6.62 \times 10^{-5}$ l. mol^{-1} sec^{-1}); a substantial rate increase was seen with added trifluoroacetic acid and an even more dramatic increase noted with the added pair trifluoroacetic acid–diethyl sulfide. Under all of these conditions the product distribution was similar to that for neat pyrolysis (*cf.* Table II, entry 9). In no instance was there any evidence for the involvement of free radicals.[9] A deliberate effort to achieve disproportionation by a free radical pathway through the action of ultraviolet irradiation gave a product distribution totally different from that obtained thermally or under acid catalysis (Table II, entry 10). Control studies carried out under conditions somewhat more drastic than those used for the pyrolyses indicate that exchange processes involving the disproportionation products and the thiolsulfinates (or intermediates derived therefrom) are relatively unimportant.

The thermal decomposition of dialkyl thiolsulfinate esters is obviously quite a complex process, involving the formation of water (sometimes as a separate phase) and a variety of highly reactive intermediates, each capable of diverse reactions. Alkanesulfenic acids, with the potential to function as nucleophiles and electrophiles, reducing or oxidizing agents as well as hydrogen bonding acids, appear to have a prominent role in this process. The contrast in the thermal behavior of alkyl and aryl thiolsulfinates reflects the ability of the latter compounds to undergo elimination to afford sulfenic acids. Scheme I, analogous in a number of ways to the mechanism proposed by Kice[4] to explain the concomitant acid/nucleophile catalyzed disproportionation of aryl thiolsulfinates, accommodates our observations on the thermal disproportionation process involving an unsymmetrical dialkyl thiolsulfinate ester such as methyl ethanethiolsulfinate. We have previously documented steps a and b;[6b] steps c–f, i, and j have been presented by Kice[4] (in Kice's mechanism added sulfide functions as the attacking nucleophile in steps d and e rather than the thiolsulfinate sulfenyl sulfur as we propose), and the novel rearrangement in step g is considered in the following communication.[5] Step h is provided as one explanation for the preponderance of *unsymmetrical* disulfide in the early stages of the disproportionation (not fully explained by steps d–f); precedence is available for this proposed reaction.[10,11]

While further study of the *photochemical* disproportionation reaction would be desirable, it is not unreasonable to postulate initial homolysis of the S–S bond followed by radical recombination and displacement processes akin to those presented by Fava for the homolytic thermal disproportionation of aryl thiolsulfinates.[2a,12] In the latter studies,[2a] disproportiona-

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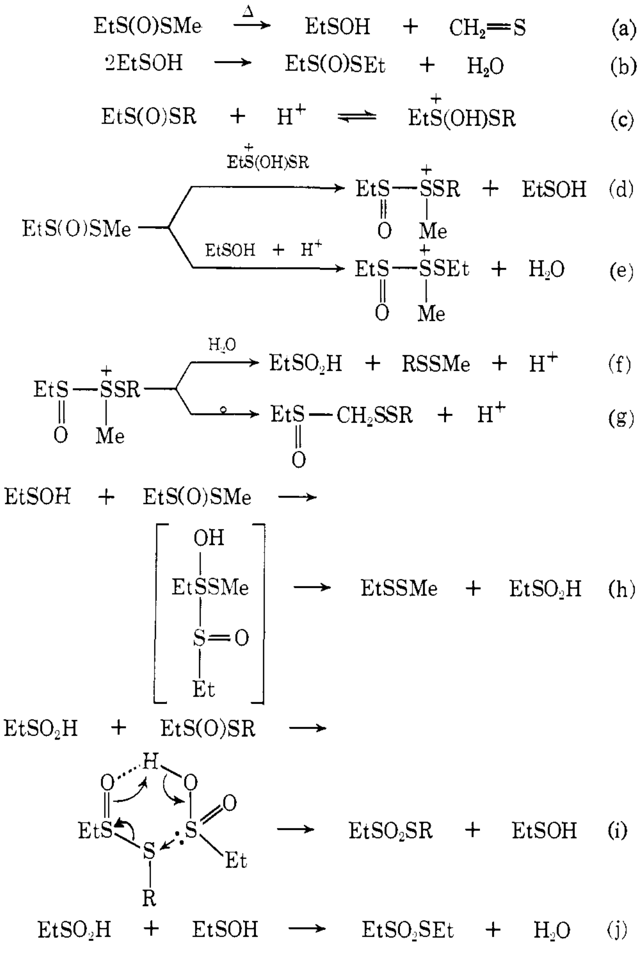
(9) We have unsuccessfully sought evidence for free radicals using esr, spin-trapping, and CIDNP methods; the presence of oxygen had no noticeable effect on the rate of disproportionation of neat thiolsulfinate.

(10) For discussion of reductions of sulfoxides by sulfenic and sulfinic acids see (a) M. E. C. Biffin, J. Miller, and D. B. Paul, *Tetrahedron Lett.*, 1015 (1969); (b) K. Gollnick and H.-U. Stracke, *Pure Appl. Chem.*, 33, 217 (1973), and references therein.

(11) An alternative possibility would involve direct oxygen transfer between two thiolsulfinate molecules. Arguing against this possibility is the fact that extended heating of dimethyl sulfoxide (which contains a more basic oxygen than alkyl thiolsulfinates[6b] and presumably should undergo oxygen transfer at least as easily) at 170–195° in the presence or absence of acid catalysts led only to trace amounts of dimethyl sulfone.[10a] Furthermore the direct oxygen transfer mechanism fails to account for the observed unreactivity of MeS(O)S-*t*-Bu and the product distribution from MeS(O)S-*i*-Pr.

(12) However, irradiation of solutions of dialkyl thiolsulfinate esters in an esr spectrometer did not give rise to observable alkanesulfinyl

Scheme I. Proposed Mechanism for the Thermal Disproportionation of Methyl Ethanethiolsulfinate



(In the above, R = Me or Et)

tion of an unsymmetrical diaryl thiolsulfinate was found to give a 2:1 mixture of unsymmetrical to symmetrical thiolsulfonate in addition to about 10% of the products resulting from oxygen crossover. The differences in product distribution between our photochemical example (*cf.* Table II, run 10) and the thermal studies of Fava (in our work, more symmetrical products and little oxygen crossover) could be attributable, in the present work, to more pronounced cage effects (lower temperature, more polar substrates) and possible multiplicity restrictions on oxygen crossover *via* a sulfenic anhydride.

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radical absorption. We thank Professor Kochi for performing this experiment.

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The Chemistry of Alkyl Thiolsulfinate Esters. V. A Novel Synthesis of α-Heteroatom Substituted Disulfides[1]

Sir:

In contrast to α-heteroatom substituted alkyl sulfides, the analogous α-substituted alkyl disulfides (**1**, X =

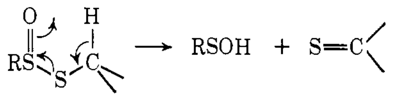
$$XCH_2SSR$$
1

RO, RS, R_2N, halogen, etc.) are a synthetically inaccessible class of compounds whose chemistry has hardly been explored.[2,3] We present here a novel, convenient route to a number of new structures of type **1** (in which X = RS, RS(O), RSO_2) discovered during an investigation of the chemistry of dialkyl thiolsulfinate esters.

Sulfinylsulfonium ions of type **2** have been postulated

$$RS(O)\overset{+}{S}R'R''$$
2

by Kice as intermediates in the reaction of sulfinic acids with disulfides[4a] and sulfides[4b] and in the catalyzed disproportionation of aryl thiolsulfinates.[4c] In view of our recent discovery of a facile intramolecular β-elimination process occurring during thermolysis of alkyl thiolsulfinates (eq 1),[5] it seemed possible that ion


(1)

3, postulated by us as an intermediate in the disproportionation of alkyl thiolsulfinates,[6] might undergo a similar intramolecular elimination process with even greater facility than the thiolsulfinate esters.[7] Sulfinylsulfonium ion **3** might fragment directly, or indirectly *via* ylide **4**, to alkylidenethiosulfonium ion **5** which could be trapped by a nucleophile (X^- or HX:) giving **6**. Another possibility would involve rearrangement of ylide **4** to α-sulfinyl disulfide **7** either in a concerted fashion or by recombination of RSOH and **5** within a solvent cage. In fact, these several possibilities, summarized in Scheme I, represent the options currently favored for the Pummerer rearrangement of an S heterosubstituted sufonium ion such as **3**.[8] We have found that, under the proper reaction conditions,

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(1) Presented in part at the 7th Midwest Regional Meeting of the American Chemical Society, St. Louis, Mo., Oct 27–29, 1971, and at the 5th Central Regional Meeting of the American Chemical Society, Cleveland, Ohio, May 13–15, 1973.

(2) Simple systems of type 1 which have been reported include bischloromethyl disulfide,[3a] α-chloromethylalkyl disulfides,[3b] α-alkylthioalkyl disulfides,[3c] 2,4,5,7-tetrathiaoctane,[3d] bismethoxymethyl disulfide,[3e] bishydroxymethyl disulfide[3f] and several N,N-disubstituted bisaminomethyl disulfides.[3f]

(3) (a) H. Brintzinger, K. Pfannstiel, H. Koddebusch, and K. E. Kling, *Chem. Ber.*, **83**, 87 (1950); (b) I. B. Douglass, F. T. Martin, and R. Addor, *J. Org. Chem.*, **16**, 1297 (1951); (c) H. Britzinger and H. Schmahl, *Chem. Ber.*, **87**, 314 (1954); (d) M. R. Altamura, T. Hasselstrom, and L. Long, Jr., *J. Org. Chem.*, **28**, 2438 (1963); (e) J. deLattre, *Bull. Soc. Chim. Belg.*, **26**, 323 (1913); (f) A. Binz, C. Räth, and E. Walter, *Chem. Ber.*, **57B**, 1398 (1924).

(4) (a) J. L. Kice and E. H. Morkved, *J. Amer. Chem. Soc.*, **86**, 2270 (1964); (b) J. L. Kice and E. H. Morkved, *ibid.*, **85**, 3472 (1963); (c) J. L. Kice and J. P. Cleveland, *ibid.*, **95**, 109 (1973).

(5) E. Block, *ibid.*, **94**, 642 (1972).

(6) E. Block and S. W. Weidman, *ibid.*, **95**, 5046 (1973).

(7) A similar possibility was considered by Kice in his study of the sulfinic acid–alkyl sulfide reaction to explain formation of alkyl sulfide derived carbonyl compounds.[4b]

(8) C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 632 (1969).