and P are imidazole, ester, laurate anion, and product, respectively; subscripts W, H, and I refer to water, heptane, and interface. No attempt will be made to analyze the system quantitatively such as we have previously done for less complicated micellar reactions.[19] The interfacial mechanism is consistent with the parabolic laurate inhibition curve (Figure 6) and with the saturation effect observed in the velocity *vs.* [*p*-nitrophenyl laurate] plot (Figure 2). Equation 9 represents nucleophilic attack by interfacial imidazole on the carbonyl group of interfacial ester.

$$IM_W \rightleftarrows IM_I \quad (6)$$

$$E_H \rightleftarrows E_I \quad (7)$$

$$L_W \rightleftarrows L_I \quad (8)$$

$$IM_I + E_I \longrightarrow P \quad (9)$$

An interfacial reaction may be viewed as a five-step process:[33] (a) transport of reactants to the interface, (b) adsorption of reactants onto the interface, (c) chemical reaction at the interface, (d) desorption of products from the interface, and (e) transport of products from the interface. The insensitivity of the initial reaction velocity to a 15° temperature change (Figure 4) suggests that the chemical reaction at the interface (eq 9) is not entirely rate determining. Interfacial reactions, of course, need not have the same activation parameters as the corresponding bulk phase reaction.[33] In micellar systems, for example, activation energies often differ from those for the same reaction in the water phase.[34,35] Yet there is no known case of a micellar reaction being independent of the temperature. Since small temperature coefficients are characteristic of diffusion-controlled reactions,[36] the migration of reactants into the interfacial region must be at least partially rate determining. If this conclusion is correct, then the laurate anion inhibition (Figure 6) may be the result of retarded transport of one or both of the reactants to the reaction site. Adsorbed gelatin is known to affect adversely the movement of diethyl phthalate across a hexadecane–water interface.[37]

In summary, we have determined the dependence of interfacial hydrolysis rates on stirring speed, concentration of reactants, temperature, viscosity of the hydrocarbon, volume of the heptane and water solutions, deuterium and salt content of the water, lauroylimidazole content of the heptane, presence of an amphiphile, and nature of the catalyst. Interesting differences were found between heterogeneous and homogeneous hydrolyses. The mode of imidazole catalysis and the nature of the rate-determining step were discussed. Most importantly perhaps, a methodology of interfacial bioorganic chemistry was developed.

Acknowledgment. I thank the Research Corporation and the National Science Foundation for financial support. I am also very grateful for a National Institutes of Health Career Development Award.

(33) Activation parameters for the homogeneous reaction of imidazole with *p*-nitrophenyl acetate in water are $\Delta H^{\ddagger} = 7.0$ kcal/mol and $\Delta S^{\ddagger} = -10.7$ eu: T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. 1, W. A. Benjamin, New York, N. Y., 1966, p 56.

(34) C. A. Bunton, E. J. Fendler, and J. H. Fendler, *J. Amer. Chem. Soc.*, **89**, 1221 (1967).

(35) C. A. Bunton and L. Robinson, *ibid.*, 90, 5972 (1968).

(36) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford University Press, London, 1933, p 267.

(37) A. Ghanem, W. I. Higuchi, and A. P. Simonelli, *J. Pharm. Sci.*, **58**, 165 (1969).

The Thermal Disproportionation of Aryl Arenethiolsulfinates. Kinetics and Mechanism[1a]

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Abstract: Aryl arenethiolsulfinates decompose thermally in inert solvents to give mainly the products of disproportionation, disulfide and thiolsulfonate. The rate of decomposition displays first-order kinetics within a run. However, massive changes of the initial concentration show that the first-order coefficient increases with increasing concentration. The rate law is $R = k_1[ArS(O)SAr] + k_2[ArS(O)SAr]^{1.5}$. Experiments in the presence of the stable radical DPPH show that DPPH disappears with zero-order kinetics within a run. In the presence of olefins or in the solvent acetonitrile the rate is independent of the initial concentration of thiolsulfinate. The overall effect of substituents on the phenyl rings is rather small. The above evidence and that which comes from tracer experiments is interpreted in terms of a radical process: a unimolecular decomposition along with an induced decomposition. The unimolecular initiation process is believed to be the homolytic fission of the S(O)–S bond, which appears to involve 34.5 kcal/mol. The induced decomposition is characterized by $\Delta H^{\ddagger} = 22.6$ kcal/mol. Various mechanistic paths are suggested which may be either radical displacement at sulfur or oxygen atom transfer reactions.

The recent discovery of an easy route to optically active thiolsulfinates[2,3] has revived the interest in the chemistry of this class of substances. Two papers already appeared dealing with their stereochemistry,[4,5]

(1) (a) The financial support of C.N.R., Rome, is gratefully acknowledged. (b) Address correspondence to this author at the Department of Chemistry, Louisiana State University, Baton Rouge, La. 70803.

(2) W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965).

(3) J. L. Kice and G. B. Large, *Tetrahedron Lett.*, 3537 (1965).

(4) P. Koch and A. Fava, *J. Amer. Chem. Soc.*, 90, 3867 (1968).

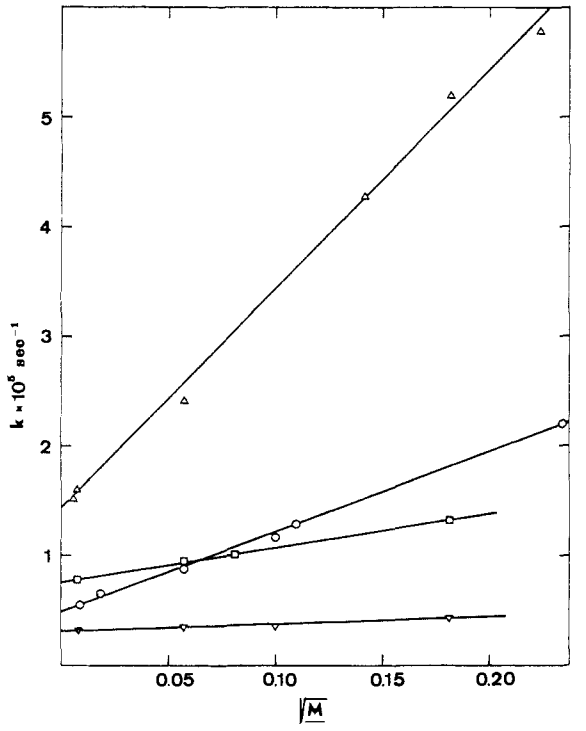


Figure 1. First-order rate constants for the thermal disproportionation of ArS(O)SAr in benzene at 80°. Ar: ▽, *m*-ClPh–; □, *p*-ClPh–; ○, Ph–; △, *p*-CH_3Ph–.

while investigations on various aspects of their chemical behavior are well under way in Kice's and our laboratory.

One particular aspect which has attracted attention of the investigators since the first successful synthesis[6a] was their instability toward disproportionation (eq 1).[6]

$$2RSOSR \longrightarrow RSO_2SR + RSSR \quad (1)$$

Although the evidence is scanty and unsystematic it appears that the reaction may be thermally as well as photochemically initiated, and Barnard has proposed that it may occur by a free-radical mechanism involving the homolytic fission of the SO—S bond.[6c] Very recently Kice has shown that a path for disproportionation is provided by concomitant acid and nucleophilic catalysis.[7]

A study of the purely thermal disproportionation reaction appeared to us particularly desirable in connection both with our investigation on the thermal racemization of a number of aromatic thiolsulfinates,[4] and with the recent investigation by Kice and Pawlowski on the thermal decomposition of sulfinyl sulfones, a closely related class of substances.[8] Such a study is the object of the present report.

The rate of decomposition of aromatic thiolsulfinate esters was measured in benzene at temperatures around 80°. The decomposition can be followed spectrophotometrically and the decrease in optical density in a single run follows a first-order law up to 90% reaction within experimental error. However, large variations in the initial concentration show that the first-order rate coefficient increases with increasing substrate concentration. The results are reported in Table I. In each case the rate follows very satisfactorily eq 2.

$$\text{rate} = k_1[ArS(O)SAr] + k_2[ArS(O)SAr]^{1.5} \quad (2)$$

The good fit of eq 2 can be visualized in Figure 1, where rate/[ArS(O)SAr] has been plotted against the square root of the concentration for a series of substrates in a 700-fold concentration range. The values of the rate constants, k_1 and k_2 (eq 2), are reported in Table II.

As is evident from Table I, k_1 changes only slightly with the substituents on the phenyl rings and the variations do not bear any correlation with the polar character of the substituent. On the other hand, k_2 decreases with the electron-withdrawing character of the substituent.

Table I. Rates of Thermal Decomposition of Aryl Arenethiolsulfinate Esters in Benzene

Run	Substituent	Solvent	Temp, °C	Concn × 10^3, *M*	$k \times 10^5$, sec^{-1}
1	H	C_6H_6	70	0.066	0.145
2	H	C_6H_6	70	3.3	0.160
3	H	C_6H_6	70	10.0	0.178
4	H	C_6H_6	80	0.081	0.55
5	H	C_6H_6	80	0.33	0.66
6	H	C_6H_6	80	3.3	0.88
7	H	C_6H_6	80	10.0	1.17
8	H	C_6H_6	80	12.0	1.28
9	H	C_6H_6	80	55.0	2.20
10	H	C_6H_6[a]	80	9.3	0.438
11	H	C_6H_6[a]	80	9.7	0.401
12	H	C_6H_6[a]	80	10.5	0.583
13	H	C_6H_6[b]	80	33.0	0.535
14	H	C_6H_6	80	10.5	0.409
15	H	C_6H_6	90	0.066	2.51
16	H	C_6H_6	90	3.3	3.50
17	H	C_6H_6	90	10.0	4.62
18	H	CH_3CN	80	0.33	0.56
19	H	CH_3CN	80	3.3	0.56
20	H	CH_3CN	80	10.0	0.52
21	H	CH_3CN	80	33.0	0.56
22	CH_3	C_6H_6	80	0.0317	1.53
23	CH_3	C_6H_6	80	0.053	1.60
24	CH_3	C_6H_6	80	3.3	2.41
25	CH_3	C_6H_6	80	20.0	4.27
26	CH_3	C_6H_6	80	33.0	5.20
27	CH_3	C_6H_6	80	50.0	5.78
28	CH_3	C_6H_6[a]	80	33.0	1.43
29	CH_3	C_6H_6[a]	80	10.0	1.53
30	CH_3	C_6H_6[a]	80	20.0	1.75
31	CH_3	C_6H_6[a]	80	33.0	1.54
32	CH_3	CH_3CN	80	1.2	1.73
33	CH_3	CH_3CN	80	3.3	1.75
34	CH_3	CH_3CN	80	10.0	1.65
35	CH_3	CH_3CN	80	33.0	1.57
36	CH_3	CH_3CN	80	66.0	1.60
37	CH_3	CH_3CN	80	120.0	1.60
38	*p*-Cl	C_6H_6	80	0.053	0.78
39	*p*-Cl	C_6H_6	80	3.3	0.94
40	*p*-Cl	C_6H_6	80	6.6	1.00
41	*p*-Cl	C_6H_6	80	33.0	1.32
42	*m*-Cl	C_6H_6	80	0.066	0.316
43	*m*-Cl	C_6H_6	80	3.3	0.35
44	*m*-Cl	C_6H_6	80	10.0	0.35
45	*m*-Cl	C_6H_6	80	33.0	0.43

[a] In the presence of styrene, 1 *M*. [b] In the presence of 1,1-diphenylethylene, 1 *M*.

(5) J. L. Kice and G. B. Large, *J. Amer. Chem. Soc.*, 90, 4067 (1968).
(6) (a) C. J. Cavallito, J. H. Bailey, J. S. Buck, and C. M. Suter, *ibid.*, 66, 1950, 1952 (1944); (b) H. J. Backer and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, 73, 129 (1954); (c) D. Barnard, *J. Chem. Soc.*, 4675 (1957).
(7) J. L. Kice, C. G. Venier, G. B. Large, and L. Heasley, *J. Amer. Chem. Soc.*, 91, 2028 (1969).
(8) J. L. Kice and N. E. Pawlowski, *ibid.*, 86, 4898 (1964).

Table II. Summary of the Rate Constants for the Thermal Disproportionation of ArS(O)SAr in Benzene

Ar	Temp, °C	$k_1 \times 10^5$, sec^{-1}	$k_2 \times 10^5$, $M^{-0.5}$ sec^{-1}	$k_2/\sqrt{k_1} \times 10^2$, $M^{-0.5}$ $sec^{-0.5}$
p-Tolyl	80	1.45	19.2	5.02
p-Chlorophenyl	80	0.77	2.6	0.94
m-Chlorophenyl	80	0.31	0.65	0.37
Phenyl	80	0.48	7.3	3.34
Phenyl	70	0.142	0.36	0.30
Phenyl	90	2.27	23.0	4.82

As can be seen from runs 10–13 and 28–31 the presence of olefins such as styrene and 1,1-diphenylethylene modifies the kinetic law in the sense that the second term of eq 2 vanishes and the specific rate constant is very close to the extrapolated value at zero substrate concentration. Similarly, in acetonitrile (runs 18–21 and 32–37) the kinetic law follows rigorously a first-order law in a large concentration interval and k_1 differs but slightly from the value in benzene.

From the runs 1–3 at 70°, 4–9 at 80°, and 15–17 at 90° it is possible to calculate the activation parameters for the k_1 and k_2 paths for the nonsubstituted substrate. The values of the activation parameters are $\Delta H^{\pm}$ = 34.5 kcal/mol and $\Delta S^{\pm}$ = 12.1 eu at 80° for k_1; $\Delta H^{\pm}$ = 22.6 kcal/mol and ΔS = −5.8 eu at 80° for k_2.

Decomposition experiments were carried out in the presence of the radical scavenger diphenylpicrylhydrazyl, DPPH. The disappearance of DPPH was followed spectrophotometrically, the substrate's concentration being much higher than that of DPPH. Under these conditions zero-order kinetics were observed as can be seen from Table III.

Table III. Rate of Disappearance of DPPH during Decomposition of *p*-Tolyl *p*-Toluenethiolsulfinate in Benzene at 50°

[ArSOSAr] × 10^2, *M*	[DPPH] × 10^4, *M*	$k \times 10^8$, *M* sec^{-1}	k/[ArSOSAr] × 10^7, sec^{-1}
4.64	1.035	1.65	3.56
4.64	2.05	1.635	3.52
4.64	4.1	1.79	3.86
2.28	4.1	0.835	3.66
0.93	4.1	0.35	3.76

Tracer Experiments. *p*-Chlorophenyl *p*-chlorobenzenethiolsulfinate specifically labeled (^{35}S) on the sulfinyl sulfur was synthesized and partially decomposed. Starting materials and products were separated by elution chromatography and subjected to reactions allowing for the separation of nonequivalent sulfur atoms (see Experimental Section) which were then counted. The results are collected in Table IV.

Table IV. Decomposition of *p*-Chlorophenyl *p*-Chlorobenzenethiol[^{35}S]sulfinate.[a] Specific Activities[b] of Sulfur Atoms

Solvent	% reaction	ArSO—SAr		$ArSO_2$—SAr		ArSSAr
Benzene	56	89	29.5	85.5	35.2	24.2
Acetonitrile	30.6	93	24.4	90.5	35.2	15.7

[a] At 80°. [b] Setting equal to 100, the specific activity of sulfinyl sulfur at zero time.

Products. The stoichiometry of the disproportionation reaction is not given simply by eq 1. Gas-chromatographic analysis shows a disulfide–thiolsulfonate ratio greater than 1. For example, a typical analysis at 100% decomposition of phenyl benzenethiolsulfinate gave 58.3 mol of disulfide and 39.8 mol of thiolsulfonate for 100 mol of initial ester. The greater percentage of disulfide was already noticed by Barnard in the decomposition which occurs on drying the solid under vacuum.[6a] Barnard has also identified arenesulfonic acid in the products of the water work-up.[6c] The presence of nonreducing strong acid has been confirmed by us. For the aforementioned experiment it amounted to about 8 equiv/100 mol of initial thiosulfinic ester. Thus the main product which explains the lack of equimolarity between disulfide and thiolsulfonate is very likely sulfonic anhydride.

In the presence of styrene, the effect of this additive on the kinetics notwithstanding, the percentage of disulfide and thiolsulfonate were not greatly diminished: disulfide 43%, thiolsulfonate 34%. Gas-chromatographic analysis showed the presence of at least six more minor products the identification of which was not attempted.

Discussion

The form of the rate equation, the lack of solvent effect and of any important structural effect on the first-order term of the rate equation (eq 2), and the experiments in the presence of the radical scavenger DPPH all agree with some kind of radical mechanism presiding over the disproportionation of thiolsulfinates. Let us first examine the rate equation (eq 2). This contains one first-order and one three-halves-order term. This particular form strongly suggests a unimolecular decomposition along with an induced decomposition.[9a] The first-order path may simply be the homolytic fission of the S(O)—S bond to give one sulfinyl and one thiyl radical which by dimerization yield the observed products

$$\underset{\text{I}}{\text{ArSOSAr}} \xrightarrow{k_1} \text{ArSO}\cdot + \text{ArS}\cdot$$

$$2\text{ArSO}\cdot \longrightarrow \underset{\text{II}}{\text{ArSO}_2\text{SAr}} \qquad (3)$$

$$2\text{ArS}\cdot \longrightarrow \underset{\text{III}}{\text{ArSSAr}}$$

Recombination of the two primary radicals would lead to no net reaction. This sequence is entirely reasonable as it is self-evident that thiyl radicals will dimerize to disulfide and it is well established that sulfinyl radicals dimerize to thiolsulfonate, perhaps through the intermediacy of a sulfenic–sulfinic mixed anhydride.[10,11]

$$2\text{ArSO}\cdot \longrightarrow \underset{\text{O}}{\text{ArSOSAr}} \longrightarrow \text{ArSO}_2\text{SAr}$$

This mechanism in its simplest form predicts that in tracer experiments both sulfur atoms of thiolsulfonate will have the same specific activity, equal to the activity

(9) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966; (a) p 94; (b) p 15 and p 315; (c) p 89.

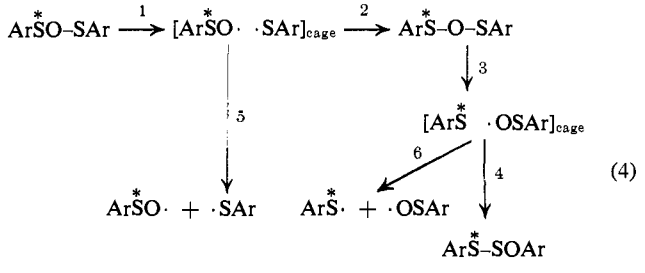
(10) (a) D. Barnard, *J. Chem. Soc.*, 4673 (1957); (b) R. M. Topping and N. Kharasch, *J. Org. Chem.*, **27**, 4353 (1962).

(11) C. M. M. da Silva Corrêa and W. Waters, *J. Chem. Soc. C*, 1874 (1968).

of the sulfinyl sulfur in the starting material, while the disulfide will have the activity of the sulfenyl sulfur in the starting material. Moreover, in experiments with unsymmetrically substituted thiolsulfinate, Ar'SOSAr'', the mechanism predicts formation of Ar'SO_2SAr' and Ar''SSAr'' without cross-products. None of these expectations is fulfilled by experiment. In fact, Barnard[6c] has found that in the spontaneous decomposition of *p*-tolyl benzenethiolsulfinate in the pure solid the aromatic disulfide contains only 64% *p*-tolyl groups indicating that there must be an oxygen transfer at some stage of the disproportionation.[6c] Our tracer experiments also bear out the same conclusion since from thiolsulfinate labeled on the sulfinyl sulfur the disulfide product is substantially radioactive and the sulfur atoms of the thiolsulfonate have not the same specific activity (Table IV).

Since it was proved that neither of the products exchange with the starting material nor between themselves, the tracer data are not vitiated by reactions which may have occurred *after* disproportionation. It must be observed, however, that the data provide a "still picture" of the situation after the decomposition has progressed to a certain extent. Therefore their analysis cannot provide a quantitative description of the phenomena for which data would be required on the change of tracer distribution at various decomposition fractions and extrapolation of such distributions down to zero decomposition. In spite of this important limitation we believe it is still possible to gather insight into the details of the disproportionation mechanism from our limited data.

Let us examine the distribution of radioactivity in the experiment in acetonitrile where the three-halves-order term vanishes. Since activity appears to be, though partially transferred, from the sulfinyl function sulfur, –SO–, to the sulfenyl function sulfur, –S–, one must analyze the possible ways this may take place. Let us first focus attention on the starting material: –SO– appears to lose activity and –S– to acquire activity. A simple way this may happen is through an oxygen transfer between ArSO· and ArS· radicals, within the solvent cage or after diffusion. This may involve the intermediate formation of a metastable sulfenic anhydride from which scrambling of oxygen would follow inevitably (eq 4). The formation of the



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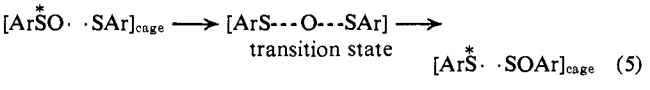
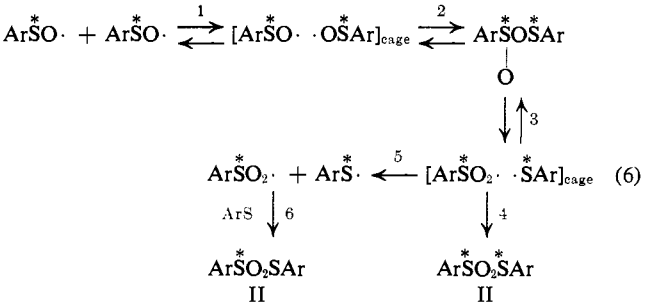
sulfenic anhydride may not be a necessary requirement for oxygen transfer since this may be envisioned as a one-step process within the solvent cage (eq 5). Since



(5)

oxygen scrambling in the starting material is not very extensive with respect to net reaction (–SO– of I has preserved 93% of the original activity after 31% decomposition), diffusion out of the cage must compete favorably with cage return accompanied by oxygen scrambling.

Reasonable as the above sequence may be, it cannot be the whole story since it does not account for the observation that the *overall* activity (*i.e.*, taking into account both sulfur atoms) of I isolated after 31% decomposition is *greater* than at the start. Clearly there must be another reaction which transfers an oxygen atom from ArSO· to give ArS·. A clue to what this additional reaction may be is provided by the observation that the two sulfur atoms of II have very unequal activities, that of the sulfonyl function sulfur, $-SO_2-$, being much higher. Obviously the dimerization of ArSO· radicals to give II is not as simple as it has been depicted in eq 3 for this would imply equal activities of the two sulfurs. A very reasonable explanation is that in the recombination of two ArSO· radicals an oxygen transfer occurs which may involve, but not necessarily, a mixed sulfinic–sulfenic anhydride, leading to sulfonyl and thiyl radicals. The fraction of



(6)

II which obtains by cage recombination (step 4) will have equal activities on the two sulfur atoms, while the rest will preserve the original activity of the ArSO· radical on $-SO_2-$, but a lower one on –S– since the ArS· radical will have equilibrated its activity with that of thiyl radicals in solution, the largest fraction of which comes from the fission of I (eq 4, steps 1 and 5). This obvious particularization of the ArSO· dimerization mechanism qualitatively rationalizes the tracer distribution. The fact that –S– of II has higher activity than all other –S–'s indicates that a nonnegligible fraction of II is formed in the cage recombination (step 4 of eq 6). On the other hand the apparent "accumulation" of activity of I indicates that recombination of ArSO· and ArS· radicals to give I occurs at least partially from radicals which have diffused out of the solvent cage.

The data at hand, if they strongly point to the sequences above, cannot exclude that other reactions may contribute to the actual tracer distribution, nor allow to assess the relative importance of the reactions depicted in eq 4 and 6. Therefore our analysis of the data is better not pursued further.

The idea that emerged from the previous discussion, that sulfonyl radicals are present as discrete intermediates, reasonably accounts for the finding that other products are formed which contain more than two oxygen atoms per molecule thus yielding a disulfide to thiolsulfonate ratio greater than unity. The evidence that these products consist mainly of sulfonic anhydride is consistent with available information in the literature.[11] The formation of sulfonic anhydride must arise from recombination of one $ArSO_3$· and one

$ArSO_2\cdot$ radical. The for mermay conceivably arise both from reaction of $ArSO_2\cdot$ and $ArSO\cdot$ radicals, probably *via* a sulfonic–sulfenic mixed anhydride as depicted by eq 7 where we neglect possible cage re-

$$ArSO_2\cdot + ArSO\cdot \longrightarrow ArSO_2OSAr \longrightarrow ArSO_3\cdot + ArS\cdot \quad (7)$$

actions, and by reaction of two $ArSO_2\cdot$ radicals probably *via* a sulfonic–sulfinic mixed anhydride (eq 8).

$$2ArSO_2\cdot \longrightarrow ArSO_2OSOAr \longrightarrow ArSO_3\cdot + ArSO\cdot \quad (8)$$

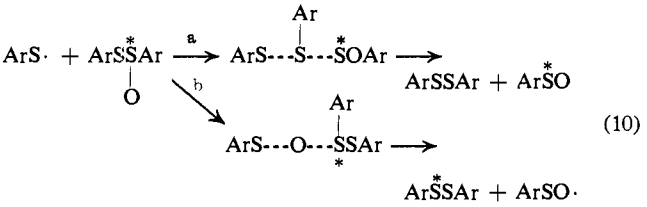
The combination of $ArSO_2\cdot$ radicals with either $ArSO\cdot$ or $ArSO_2\cdot$ to give products containing the S—S bond are not important in our system. In the first case this is obvious since a product would be obtained, the sulfinyl sulfone, which contains a very labile S—S bond (27 kcal/mol)[8] and would immediately decompose to the starting radicals. In the second case a product could be obtained stable under our experimental conditions, the α-disulfone (D = 40.9 kcal/mol).[12] The fact that it is not produced in an appreciable amount means that recombination *via* oxygen bridge (eq 8) competes very favorably with recombination *via* S—S bond formation.[13] This particular finding is substantiated by the recent work of Waters, who finds recombination of $ArSO_2\cdot$ radicals variously produced that yields mainly the products of disproportionation (sulfonic anhydride and thiolsulfonate), but including very minor amounts of α-disulfone.[11]

Let us now consider the induced decomposition reaction which gives rise to the three-halves-order term in the rate equation. A reaction sequence which appears to satisfy the requirements of the rate law is

$$ArS\cdot + ArSOSAr \longrightarrow ArSO\cdot + ArSSAr \quad (9a)$$

$$ArSO\cdot + ArSOSAr \longrightarrow ArS\cdot + ArSO_2SAr \quad (9b)$$

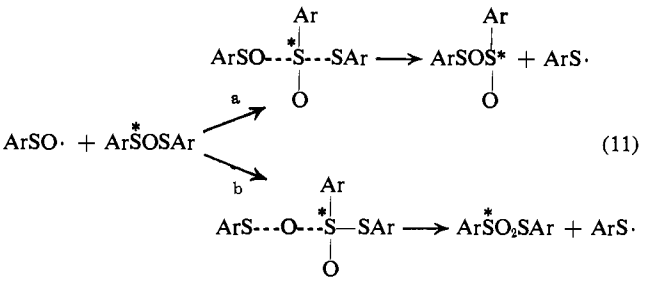
Each of these reactions can be envisioned to occur in two basically different ways, *i.e.*, as a radical displacement at one sulfur atom or as an oxygen transfer. Let us consider reaction 9a. It may occur either by route a (eq 10), radical displacement at –S–, or by route b (eq 10), oxygen transfer. In either case the energetics of the change are the same and a choice



(10)

between them cannot be made on this ground. However, (10b) may be the preferred route due to the less stringent steric requirements for attack at sulfoxide oxygen with respect to dicoordinated sulfur.

For reaction 9b the possible routes are as in eq 11, where in (11a) the anhydride eventually leads to thiolsulfonate as discussed above for the first-order decomposition. The energetics of either reaction 11a and 11b are unknown. However, the fact that thiolsulfonates are quite stable compounds, while the sulfenic–sulfinic mixed anhydrides could never be isolated



(11)

and are most likely to be unstable, make us favor the oxygen transfer (11b) as the more likely route.[14]

An additional reaction that may contribute to the induced decomposition is an oxygen transfer from the substrate to the $ArSO\cdot$ radical (eq 12). A choice

$$ArSO\cdot + ArSOSAr \longrightarrow ArS(O)-O-SSAr \longrightarrow ArSO_2\cdot + ArSSAr \quad (12)$$

between displacement at sulfur (eq 10a and 11a) and oxygen abstraction (eq 10b, 11b, and 12) could be made on the basis of the tracer distribution resulting from the induced decomposition. It is obvious from the equation that the oxygen transfer reactions would lead to an increased activity of the disulfide (eq 10b and 12) and to high activity on $-SO_2-$ and low activity on –S– (eq 11b) of the thiolsulfonate. Unfortunately our data (Table IV, experiment in benzene) are not adequate for such a choice. It may be calculated that under the conditions of our experiment only 15% of the total reaction occurred by the induced decomposition route, too small a fraction for changing appreciably the tracer distribution with respect to that due to the first-order decomposition. The small changes observed with respect to the experiment in acetonitrile, however, are in the expected direction.

An argument in favor of the oxygen-transfer reactions might be worked out on the basis of the structural effect which is observed on the induced decomposition. No matter what the detailed mechanism is, the values of $k_2/(k_1)^{1/2}$ (Table II) are proportional to the rate constant of the propagation steps for induced decomposition. This is true if all rate constants for termination are equal, an assumption which appears to be very reasonable in the case at hand.[9b] The ratio k_2/k_1 for various substrates displays a structural effect roughly corresponding to a Hammett reaction constant of -2. Such a relatively high value can hardly result from radical displacement at sulfur, but could be more easily accommodated within the framework of oxygen transfers of the type depicted in eq 10b, 11b, and 12. In fact, the pertinent transition states involve very considerable stretching of the S—O bond. The direction of the S—O dipole makes it quite reasonable that such stretching be facilitated by electron-releasing substituents, a notion which is substantiated by the effect that *para* substituents have on the S—O stretching frequencies of aromatic thiolsulfinates.[15]

(12) J. L. Kice and N. A. Favstritsky, *J. Org. Chem.*, **35**, 114 (1970).

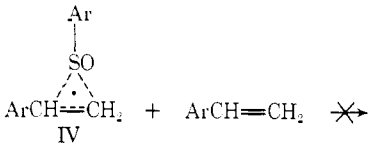
(13) Merely on statistical grounds S–O bond formation is favored over S—S bond formation by a factor of 4. Moreover, formation of the S—S bond is likely to have a substantial barrier to recombination due to steric crowding.

(14) The sulfenic–sulfinic mixed anhydride is isomeric with the disulfoxide, ArS(O)–S(O)Ar. Also these compounds have never been isolated and attempts to prepare them led to the more stable isomeric thiolsulfonate. If, as it appears well substantiated,[12] the special lability of the S—S bond of sulfoxides is due to the relatively great stability of $ArSO\cdot$ radicals, it is clear that the sulfenic–sulfinic mixed anhydride must be very unstable as well.

(15) S. Ghersetti and G. Modena, *Spectrochim. Acta*, **19**, 1809 (1963); *Ann. Chim. (Rome)*, **53**, 1083 (1963).

Decomposition Mechanism in the Presence of Olefins. It has been shown above that, although the induced decomposition is entirely suppressed in the presence of olefins, the reaction product is not substantially changed insofar as disulfide and thiolsulfonate still remain the major components. In the more significant experiment, phenyl benzenethiolsulfinate, 0.1 *M* in benzene, was completely decomposed in the presence of 1 *M* styrene. Disulfide and thiolsulfonate were formed in the ratio 1.4:1 and accounted for 77% of the total product. If it is considered that at a concentration 0.1 *M* the induced decomposition accounts for about 80% of the total initial rate (as it may be computed from the rate constants in Table II) it is clear that the olefin has the peculiar property of suppressing the induced decomposition largely through a mechanism which does not yield stable products of radical addition to the olefin itself.

This unexpected result requires some novel hypothesis on the mechanism of radical trapping by olefin. To account for the product distribution in the presence of olefin we suggest that addition of the primary radicals, ArS· and ArSO·, to the olefin does indeed take place. The radical adducts, likely a cyclic species,[16-18] are probably too stable to act as the chain carrier in a polymerization reaction (eq 13).[19] Rather it may



$$\xrightarrow{} \underset{\text{ArCHCH}_2\text{CHCH}_2\text{SOAr}}{\overset{\text{Ar}}{|}} \quad (13)$$

undergo a radical attack on the sulfur (or on the oxygen) atom to give the product of coupling of two primary radicals and the original olefin. Obviously the attacking radical could itself be a radical adduct.

$$\text{IV} + \cdot\text{OSAr} \longrightarrow \text{ArSO}_2\text{SAr} + \text{ArCH=CH}_2 \quad (14)$$

If a mechanism such as eq 14 is required to account for our results (the same equation may be written for the ArS· radical), it could very well be operative also in the cases described by Kice[8] and Waters.[11] Similarly, the fact that in acetonitrile solvent we find no kinetic evidence of induced decomposition may be due to the nitrile function playing the role we have attributed to the olefin.

If our hypothesis is correct, a word of caution appears to be in order concerning the use of styrene, or other unsaturated material, as a radical trap to gauge the extent of cage *vs.* noncage reaction.[9c]

However, the mechanism depicted in eq 14 cannot be the whole story since in our experiments in the presence of olefins several other unidentified products (at least six) were formed. It seems obvious to assume that these are products of radical reaction with the olefin, so that reactions of the radical adduct other than that of eq 14 may be occurring though to a minor extent. Conceivably these can be hydrogen-transfer reactions (as observed by Kice[8] and by Waters[11]) and radical addition (as observed also by Waters[11]). Our present efforts are directed toward the identification of these minor products with the aim of clarifying the detailed role of the olefin in determining the product distribution.

(16) (a) P. S. Skell and R. R. Pavlis, *J. Amer. Chem. Soc.*, **86**, 2956 (1964); (b) P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964).

(17) P. Krusic, private communication.

(18) The radical adduct IV has been written in eq 13 as a symmetrically bonded bridged species, sulfur being the bridging atom. While it is not at all certain that such a species is symmetrically bonded,[17] it must be kept in mind that the bridging atom could also be the oxygen atom.

(19) The fact that styrene does not polymerize during decomposition of thiolsulfinates (under conditions which would otherwise give polymerization) is in itself evidence that thiolsulfinates are effective polymerization inhibitors.[20]

(20) D. Barnard, L. Bateman, E. R. Cole, and J. I. Cunneen, *Chem. Ind. (London)*, 918 (1958).

Experimental Section

Materials. Reagent grade benzene was refluxed over Na–K alloy for 1 day and fractionated. Acetonitrile was dried over Drierite, refluxed over phosphorus pentoxide, and distilled. From the redistillation over anhydrous potassium carbonate the fraction boiling at 81.5–81.6° was collected. Styrene and 1,1-diphenylethylene were stored over Drierite for 24 hr to remove inhibitor,[21] then distilled.

All thiolsulfinates have been prepared by condensation of the corresponding thiols and sulfinyl chlorides in dry ether in the presence of pyridine.[6b] Phenyl benzene-, *p*-chlorophenyl *p*-chlorobenzene-, and *p*-tolyl *p*-toluenethiolsulfinates have been already described and had good elemental analysis. *m*-Chlorophenyl *m*-chlorobenzenethiolsulfinate was obtained as an oil which was dissolved with a small amount of ethyl ether. Addition of petroleum ether and cooling at −25° afforded a yellow precipitate which was recrystallized in the same way, mp 55°. The purity of the product was checked by thin layer chromatography which yielded only a single spot. *Anal.* Calcd for $C_{12}H_8OS_2Cl$: C, 47.53; H, 2.66; S, 21.15; Cl, 23.38. Found: C, 47.18; H, 2.54; S, 20.77; Cl, 23.89.

Decomposition of *p*-Chlorophenyl *p*-Chlorobenzenethiol[^{35}S]-sulfinate. Determination of the Specific Activity of the Various Sulfur Atoms in the Decomposed Mixture. [^{35}S]*p*-Chlorothiophenol was converted to sulfinyl chloride by the method of Douglass and Farah[22] and thence condensed with unlabeled thiophenol in the presence of pyridine.[23] The ester (3.3×10^{-2} *M*) was partially decomposed at 80° in benzene or acetonitrile. The per cent decomposition was determined by uv. The mixture containing disulfide, thiolsulfonate, and undecomposed thiolsulfinate was separated into its components by elution chromatography by using cyclohexane–benzene 80–20, benzene–cyclohexane 60–40, and benzene in order to separate disulfide, thiolsulfonate, and thiolsulfinate in this order.

The disulfide was reduced by zinc powder in refluxing dilute sulfuric acid for 8 hr. The resulting thiol was extracted with cyclohexane, reextracted with NaOH (1 *M*), acidified, extracted again with cyclohexane, and precipitated with $Hg(CN)_2$. The mercury mercaptide was counted as a solid of infinite thickness with a Geiger counter.[24]

The total radioactivity of the thiolsulfinate was determined by reduction of the ester with KI in acetic acid. Water was added and after extraction with cyclohexane the organic extract was washed with a solution of KI until disappearance of iodine. After evaporation of the solvent the disulfide was reduced, converted, and counted as before.

The specific activity of the sulfenyl sulfur of the thiolsulfinate was obtained as that of the thiol produced by Grignard[25] reaction of the ester with magnesiumbenzyl chloride, after purification as described above. The specific activity of the sulfinyl sulfur was computed from the total activity and the activity of sulfenyl sulfur.

The thiolsulfonate, upon reaction for about 4 hr with an excess (three times) of morpholine, yielded the corresponding sulfenamide and a white precipitate of morpholinium sulfinate which was filtered off. The precipitate was dissolved in water, washed with ethyl ether, and reduced for about 8 hr with $Zn–H_2SO_4$ at reflux. The

(21) P. H. Boundy, R. F. Boyer, and S. M. Stoesser, "Styrene," Reinhold, New York, N. Y., 1952, p 208.

(22) I. B. Douglass and B. S. Farah, *J. Org. Chem.*, 23, 330 (1958).

(23) D. Barnard and E. J. Percy, *J. Chem. Soc.*, 1667 (1962).

(24) A. Fava, G. Reichenbach, and U. Peron, *J. Amer. Chem. Soc.*, **89**, 6696 (1967).

(25) E. Vinkler, F. Klivényi, and E. Klivényi, *Acta Chim. Acad. Sci. Hung.*, **16**, 247 (1958).

resulting thiol was purified and counted as before. The ether layer containing the sulfenamide was washed several times and dried over anhydrous sodium sulfate. After evaporation of the solvent the solid was reduced with $Zn-H_2SO_4$ at reflux. The thiol was purified and counted.

In check experiments it was proved that these methods of separation of the unequivalent sulfur atoms for both thiolsulfinate and thiolsulfonate do not induce any appreciable scrambling.

Kinetic Procedure. Aliquots of the reaction mixture were sealed under nitrogen in glass ampoules and placed in a thermostated bath from which they were withdrawn at time intervals. Temperature control was ±0.05°. The reaction was followed by uv spectroscopy at 300 mμ with a Unicam SP 800 or a Beckman DU spectrophotometer. The runs in the presence of DPPH were followed between 350 and 520 mμ according to the concentration of DPPH. All the solutions containing DPPH were prepared, sealed in ampoules, and decomposed in the dark due to the instability of DPPH in the presence of light in solutions of thiolsulfinates.

Quantitative Analysis of the Disproportionation Products. The decomposition products of phenyl benzenethiolsulfinite were identified and quantitatively assessed by glc analysis of the reaction mixture. In the presence of styrene the formation of about 30% of at least six addition products with styrene made impossible a clean separation of disulfide and thiolsulfonate by column chromatography. The gas chromatographic analysis was critical and required carefully controlled conditions. A 50-cm column filled with 2.5% XE 60 (Perkin-Elmer) on Chromosorb 80–100 mesh was used. The disulfide was determined at 165° with tetracosane (C_{24}) as internal standard. The thiolsulfonate was determined at 180° without any internal standard by carefully controlling the amount of solution injected using a special Hamilton syringe.

The decomposition mixture of phenyl benzenethiolsulfinate in benzene was checked for acidity by stirring with water with a magnetic stirrer and titrating with 0.01 *N* NaOH. The mixture was also checked for the presence of sulfinic acid with a standard solution of KNO_2. The test was negative.

The Role of Solvent in the Solvolysis of *t*-Alkyl Halides[1]

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Abstract: In the Winstein–Grunwald relationship for solvolysis reactions, $\log k/k_0 = mY$, Y is a parameter taken to represent "solvent ionizing power" and not the nucleophilicity of the solvent or its ability to promote rate-determining elimination. Using *t*-butyl chloride, the reference compound chosen by Winstein and Grunwald to evaluate Y, it is impossible to rule out these other mechanistic contributions. In order to assess the role of solvent, rate constants for solvolysis of 1-adamantyl bromide in fourteen solvents were determined; data for eight additional solvents were obtained from the literature. In such a bridgehead substrate, backside nucleophilic solvent attack and elimination are both impossible. In general, an excellent correlation between data for *t*-butyl chloride and 1-adamantyl bromide is found indicating that *t*-butyl chloride, in most instances, solvolyzes by a limiting mechanism, free from nucleophilic solvent participation and from rate-determining elimination. Significant dispersion is found for aqueous trifluoroethanol solvent systems; this deviation is discussed in terms of specific substrate and leaving group effects.

The Winstein–Grunwald relationship for solvolysis reactions, $\log k/k_0 = mY$, affords a useful although not entirely precise tool for the calculation of solvolysis rates.[3] The parameter m is taken to be a measure of the susceptibility of a substrate to changes in Y, "the measure of the ionizing power of the solvent";[3c] k and k_0 are rate constants for solvolysis in the solvent in question and the standard solvent, respectively. While there are many possible modes of solvent interaction during solvolysis,[4] these are generalized into two factors of overriding importance: solvent nucleophilicity and ionizing power. "Solvent nucleophilicity" refers to the ability of the solvent acting as nucleophile to displace the leaving group, while "solvent ionizing power" concerns the ability of the medium to solvate ions and thus to facilitate their separation.[5] Since tertiary compounds have been assumed to solvolyze by a limiting mechanism free from nucleophilic solvent participation, Winstein and Grunwald[3] chose *t*-butyl chloride as the reference compound for the mY relationship and defined its m value as unity. Y values were then assigned by measuring the solvolysis rates of *t*-butyl chloride in various solvents. It was reasoned that the Y values thus obtained should be a function of solvent ionizing power only. The good agreement between Y and other measures of solvent polarity[6] (*e.g.*, Z,[7] a parameter determined from the effect of solvent on charge-transfer absorptions, which is presumably independent of solvent nucleophilicity) lends support to this contention.

Recently, however, we have shown that large rate enhancements may be ascribed to solvent participation in the solvolysis of secondary derivatives.[8,9] In the

(1) This work was supported by grants from the National Institutes of Health (AI-07766), the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society.

(2) National Institutes of Health Fellows: (a) Postdoctoral, 1968–1970; (b) Predoctoral, 1967–1970; (c) Postdoctoral, 1969–1970; (d) Postdoctoral, 1967–1969.

(3) (a) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 70, 846 (1948); (b) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, 78, 2770 (1956).

(4) (a) C. D. Ritchie in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969; (b) S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Amer. Chem. Soc.*, 79, 4146 (1957).

(5) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

(6) For a recent review of the various solvent parameters see: C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 4, 29 (1965).

(7) E. M. Kosower, *J. Amer. Chem. Soc.*, 80, 3253 (1958).

(8) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, 91, 4291 (1969); C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, 91, 4294 (1969); C. J. Lancelot and P. v. R. Schleyer, *ibid.*, 91, 4296 (1969); P. v. R. Schleyer and C. J. Lancelot, *ibid.*, 91, 4297 (1969).