

the micellar phase. This result is not particularly surprising, because aryl-aryl interactions between micelle and substrate in the initial state should also be present in the transition state for reaction in the micellar phase. In addition, for anion-molecule reactions, electrostatic interactions between the incoming nucleophile and the ammonium ions in the micelle are important in stabilizing the transition state, and a bulky aryl or benzyl group may hinder this interaction.

In many ion-molecule reactions catalyzed by ionic detergents, there are rate maxima with increasing detergent concentration,^{3,4,6,7} and it has been suggested that these maxima occur when all the substrate is incorporated into the micelle, so that additional micelles then merely deactivate the ionic reagent^{6,7} or, alternatively, that they result from a negative salt effect of the counterion.⁴ We observed no rate maxima with these aryl-substituted detergents because the substrates are incorporated into the micellar phase at very low detergent concentrations, so that neither of these deactivation factors should be present.

Analogies with Enzymic Catalysis.—Many workers have noted formal similarities between micellar- and

enzyme-catalyzed reactions,^{3-5,9,10,27} although in general it seems that micelles are best regarded as models for the binding between enzyme and substrate, except in the special cases in which active groups are built into the detergent.^{5,10,11} The present results support this view, because they show that it is possible to vary the detergent structure so as to enhance the micelle-substrate binding without materially changing the rate constant for the reaction in the micellar phase.

Registry No.—2,6-Dinitrophenyl phosphate, 15732-00-0; 2,4-dimethoxyphenylcetyldimethylammonium bromide, 22040-11-5; *p*-nitrophenyldiphenyl phosphate, 10359-36-1.

Acknowledgment.—We thank Dr. C. Smart of Unilever Research Laboratories for determination of the aggregation numbers and Dr. H. Morawetz for the communication of interesting comments on the nature of micellar catalysis.

(27) M. T. A. Behme, J. G. Fullington, R. Noel, and E. H. Cordes, *J. Amer. Chem. Soc.*, **87**, 266 (1965).

Ease of Homolytic Dissociation of Sulfur-Sulfur Bonds. II. The Thermal Decomposition of Aryl α -Disulfones¹

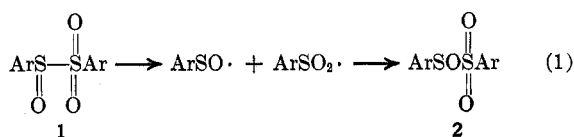
JOHN L. KICE AND NICOLAI A. FAVSTRITSKY

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

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The thermal decomposition of aryl α -disulfones (**5**) has been studied in diglyme and bromobenzene at 145–165°. The decomposition follows good first-order kinetics, although the final reaction products are very complex. However, given such observations as the formation of a high yield of *sym*-tetraphenylethane when the decomposition is carried out in the presence of diphenylmethane, and the fact that ΔS^\ddagger for the decomposition is large and positive (16.6 eu), the decomposition appears to involve initially the homolytic dissociation of the S-S bond in **5** (eq 2). Comparison of the rate and ΔH^\ddagger for the decomposition of **5** with the same parameters for the thermal decomposition of aryl sulfinyl sulfones (**1**) shows that the sulfinyl sulfone decomposes *ca.* 10^7 times faster and has *ca.* 13 kcal/mol smaller ΔH^\ddagger . This enormous difference in the ease of homolytic dissociation of **1** and **5** shows that the primary cause of the extremely facile radical dissociation of the sulfinyl sulfone is *not* destabilization of **1** due to repulsion between the two adjacent partially positively charged sulfur atoms. Comparison of the data for **1**, **5**, and other compounds containing a single S-S bond suggests that compounds in which a sulfinyl group is one of the partners in the S-S bond dissociate homolytically much more readily than those in which this feature is absent, and a likely reason for such behavior is suggested.

Aryl sulfinyl sulfones (**1**) undergo thermal decomposition very readily ($t_{1/2} = 30$ min at 50°) *via* a process (eq 1) that involves an initial homolytic dissociation of the S-S bond in **1**, followed by a head-to-tail recombination of the resulting radical fragments to give the sulfonyl sulfonate **2**.^{1a} The most striking thing about



the thermal decomposition of sulfinyl sulfones is the fact that homolytic dissociation of the S-S bond in **1** occurs orders of magnitude more readily than homolytic dissociation of the S-S bond in an aryl disulfide,

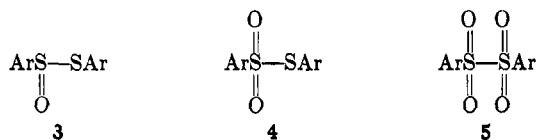
ArSSAr. Thus, 2,2'-dibenzothiazolyl disulfide, which apparently undergoes homolysis much more readily than most aryl disulfides, still dissociates into radicals at a rate² only 10^{-3} times that of *p*-tolyl *p*-toluenesulfinyl sulfone (**1a**, Ar = *p*-CH₃C₆H₄), and experiments in this laboratory³ indicate that the difference in the rates of homolytic dissociation of **1a** and *p*-tolyl disulfide is at least 10^7 at 100°. That merely changes in the oxidation state of the sulfur atoms participating in an S-S bond can lead to such profound changes in the ease of homolytic dissociation of that bond is most significant and would seem to be of great practical importance in sulfur chemistry. Before one can hope to know unequivocally the reasons for this behavior, one must have quantitative data on the ease of radical dissociation of the S-S bonds in all the other types of organic compounds containing a single sulfur-sulfur bond,

(1) (a) Paper I in this series: J. L. Kice and N. E. Pawlowski, *J. Amer. Chem. Soc.*, **86**, 4898 (1964). (b) This research was supported by the National Science Foundation, Grant GP-6952.

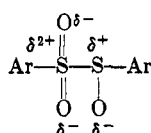
(2) R. E. Davis and C. Perrin, *J. Amer. Chem. Soc.*, **82**, 1590 (1960).

(3) M. Minch, unpublished results.

such as thiolsulfonates (3), thiol-sulfonates (4), and α -disulfones (5).



The present paper describes our efforts to obtain such information for **5** by studying their thermal decomposition in nonpolar, aprotic solvents. The selection of α -disulfones for our initial further work in this area was prompted by the fact that one reason for the great ease of dissociation of **1** could conceivably be the destabilization of the sulfinyl sulfone due to the unfavorable repulsion between the two adjacent partially positively charged sulfur atoms, *i.e.*



If this were the principal factor, α -disulfones ought also to be thermally very unstable. Although there were no indications that this was so in the literature, the chemistry of α -disulfones had been so little investigated that a specific study of this point was clearly necessary before a meaningful answer could be given.

Results

Rate of Thermal Decomposition of Aryl α -Disulfones in Diglyme.—Dioxane was the solvent used for most of the earlier studies of the thermal decomposition of sulfinyl sulfones.^{1a} Since temperatures considerably above 100° are required for the decomposition of the α -disulfones, it could not be used conveniently for the present work, and so the higher boiling, but structurally analogous solvent, diglyme, was employed instead. In diglyme the thermal decomposition of an aryl α -disulfone is accompanied by a significant decrease in the absorbance of the solution at the wavelength corresponding to the intense absorption maximum ($\log \epsilon$ 4.2–4.5) of the α -disulfone (257–284 $m\mu$, depending on the substituent in the Ar group). Plots of $\log (A_t - A_\infty)$ vs. time for the thermal decomposition of the α -disulfones in diglyme were nicely linear over at least 3 half-lives, showing that the reaction follows good first-order kinetics. The results of the various kinetic runs are summarized in Table I.

TABLE I

RATE OF THERMAL DECOMPOSITION OF ARYL α -DISULFONES (ArSO₂SO₂Ar) IN DIGLYME^a

Ar	Temp, °C	$k_1 \times 10^4, \text{sec}^{-1}$
<i>p</i> -CH ₃ C ₆ H ₄	163.5	1.3
	154.5	0.44 ($\Delta H^\ddagger = 40.9 \text{ kcal/mol}$)
	145.0	0.15 ($\Delta S^\ddagger = 16.6 \text{ eu}$)
<i>p</i> -BrC ₆ H ₄	163.5	1.8
<i>p</i> -ClC ₆ H ₄	163.5	1.6
<i>p</i> -CH ₃ OC ₆ H ₄	163.5	0.68

^a Initial concentration of **5**, 2.0–5.0 $\times 10^{-5} M$; all rate constants are the average of several runs.

A plot of $\log k_1$ vs. $1/T$ for *p*-tolyl α -disulfone (**5a**, Ar = *p*-CH₃C₆H₄) is nicely linear and indicates that

ΔH^\ddagger for the decomposition of this α -disulfone is 40.9 kcal/mol; ΔS^\ddagger is 16.6 eu.

From the data for the remaining α -disulfones it appears that electron-releasing substituents in the aromatic ring may in general retard the decomposition somewhat and electron-withdrawing ones accelerate it, but the effect is not very large.

Products of the Thermal Decomposition of *p*-Tolyl α -Disulfone.—The products of the thermal decomposition of **5a** in diglyme were investigated as follows. A $4 \times 10^{-3} M$ solution of the α -disulfone was heated at reflux for 20 hr (>13 half-lives). A slow stream of nitrogen was passed through the solution throughout the decomposition in order to remove any sulfur dioxide liberated in the decomposition, and the amount of sulfur dioxide was determined by subsequently passing the gas stream through a trap containing a mixture of barium chloride and hydrogen peroxide and weighing the amount of barium sulfate so produced at the end of the decomposition.

After the decomposition was complete, the solvent was removed under reduced pressure and the residue was taken up in a small amount of chloroform. The chloroform solution was washed with water several times and one half of the combined washings was then titrated with 0.10 *N* sodium hydroxide, while the other half was treated with S-benzylisothiuronium chloride in order to precipitate any *p*-toluenesulfonic acid as S-benzylisothiuronium *p*-toluenesulfonate. The amount of this salt isolated was comparable with the amount expected from the titration of the other half of the washings, assuming that all the acid being titrated was *p*-toluenesulfonic acid.

The dried chloroform solution was then evaporated and the residue was chromatographed on alumina in the usual way. Most of the chromatographic fractions consisted of oils which could not be identified. In particular, there was one large fraction eluted with 80:20 benzene-ether whose infrared spectrum showed clearly that it must possess a sulfonyl group (a pair of strong bands at 7.35 and 8.50 μ). The presence of a band of medium intensity at 3.4 μ suggested that this material also contains one or more solvent-derived fragments, but nothing more definitive of its exact structure could be learned. The products which were positively identified were *p*-tolyl sulfide and *p*-tolyl disulfide. The yields of the various identifiable products were as follows (mole/mole of **5a**): SO₂, 0.38; acid (ArSO₃H) in aqueous extract, 0.27; Ar₂S, 0.13; ArSSAr, 0.05.

We also examined the thermal decomposition of **5a** in two other solvents, diphenylmethane and bromobenzene. Our reason for employing diphenylmethane was the thought that, if free radicals were being produced in the decomposition of the α -disulfone, they would probably extract a hydrogen atom fairly readily from diphenylmethane, giving the relatively stable radical Ph₂CH·, and that the latter might then disappear chiefly by dimerization to *sym*-tetraphenylethane. A dilute solution of **5a** in diphenylmethane was heated at 156° for 20 hr under a nitrogen atmosphere. The final solution was washed with water and the water washings were titrated with 0.10 *N* NaOH. The titration showed that 0.95 mol of acid (ArSO₃H + ArSO₂H) was present in the aqueous extract per 1 mol

of **5a** decomposing. More important was the fact that, after removal of most of the diphenylmethane under reduced pressure, careful chromatography of the residue on alumina afforded 1.0 mol of *sym*-tetraphenylethane per 1 mol of **5a** decomposed.

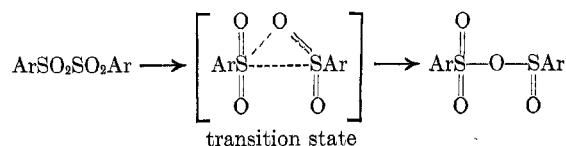
The decomposition products from the decomposition of **5a** in bromobenzene at reflux (156°), although interesting, were not particularly informative as to mechanism. Sulfur dioxide was estimated in the same manner as in the decomposition in diglyme. After removal of the solvent, the residue was extracted with water and the aqueous extracts were titrated with standard base to determine the amount of sulfonic acid in the aqueous extract. The other products were separated by chromatography of the residue on alumina. The yields of the various products were as follows (mole/mole of **5a**): SO₂, 0.23; acid (ArSO₃H) in aqueous extract, 0.84; Ar₂S, 0.25; ArSSAr, 0.05; ArSO₂Ph (phenyl *p*-tolyl sulfone), 0.28. The identity of the last product was unequivocally established by synthesis of a known sample of this sulfone⁴ and comparison of its properties with those of the material isolated from the decomposition.

Discussion

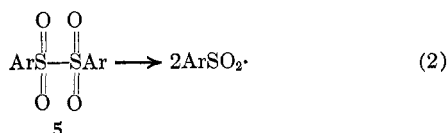
The thermal decomposition of aryl α -disulfones follows good first-order kinetics, suggesting that the rate-determining step is some unimolecular reaction of the α -disulfone. In principle, this might be (a) homolytic dissociation of the S-S bond in **5**, (b) heterolytic dissociation of the same bond, or (c) some sort of concerted rearrangement of the α -disulfone. The large positive ΔS^\ddagger (16.6 eu) for the thermal decomposition of **5a** hardly seems consistent with either rate-determining heterolytic dissociation or with a concerted rearrangement. Thus, in 90% dioxane, reactions of the type



generally have entropies of activation of the order of -20 eu,⁵ and ΔS^\ddagger would be expected to be even more negative for such a reaction in pure dioxane or diglyme. Also, a concerted rearrangement such as



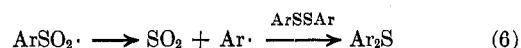
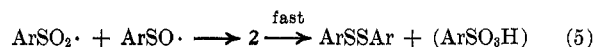
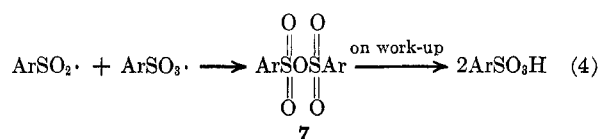
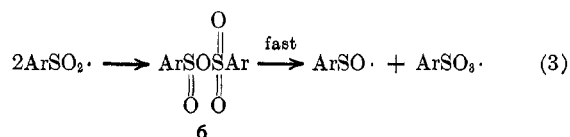
would also be unlikely to have a large positive ΔS^\ddagger .⁶ However, the large positive ΔS^\ddagger is consistent with the rate-determining step being homolytic dissociation of the S-S bond in **5** (eq 2), since a number of simple



homolytic dissociations such as those of the O-O bonds in *t*-butyl peroxide, benzoyl peroxide, or *t*-butyl peracetate are known⁷ to have ΔS^\ddagger values in the range of 13-17 eu. One might also note that dissociation of aryl sulfinyl sulfones into radicals (eq 1) has a ΔS^\ddagger of 11-14 eu in dioxane.^{1a} Further evidence that radical intermediates are involved in the thermal decomposition of α -disulfones is provided by the observation that the decomposition of **5a** in diphenylmethane leads to the formation of 1 mol of *sym*-tetraphenylethane per 1 mol of **5a** decomposing.

While the weight of the evidence therefore suggests that the initial step in the thermal decomposition of the α -disulfones is the homolysis of the S-S bond shown in eq 2, it is far from clear exactly how the various final products of the decomposition in solvents like diglyme or bromobenzene are subsequently formed. Although any lengthy speculation on this point is hardly in order, we do wish to suggest a few of the possible reactions that may be important for the decomposition in bromobenzene, because in that solvent we do have a reasonably good over-all material balance.

Head-to-tail recombination of two ArSO₂· radicals would give a sulfinyl sulfonate **6**. There is reason to believe that such a compound would be thermally much less stable than **5** and that under our reaction conditions it would quickly dissociate (eq 3) into an ArSO· and an ArSO₂· radical.⁸ Coupling of ArSO₂·



with ArSO₂· would give a sulfonic anhydride **7**. This would undergo hydrolysis to sulfonic acid very rapidly¹⁰ during the work-up procedure employed. Coupling of ArSO· with an ArSO₂· radical is known^{1a} to give **2**. The latter compound tends to decompose thermally to an aryl disulfide plus sulfonic acid (or its anhydride) by a mechanism as yet not understood,^{1a} but the reaction should be very rapid at these high temperatures. Desulfonylation of some of the ArSO₂· radicals could account for the sulfur dioxide liberated, and reaction of the resulting aryl radicals with the disulfide from the decomposition of **2** could account for the aryl sulfide (Ar₂S) formed (eq 6). The formation of a large amount of *p*-tolyl phenyl sulfone from the decomposition in

(7) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

(8) Oae and Ikura⁸ believe that they have prepared a sulfinyl sulfonate and have shown that it undergoes thermal decomposition readily at elevated temperatures. They feel that this thermal decomposition involves initial dissociation into ArSO· and ArSO₂·.

(9) S. Oae and K. Ikura, *Bull. Chem. Soc. Jap.*, **40**, 1420 (1967); **39**, 1306 (1966).

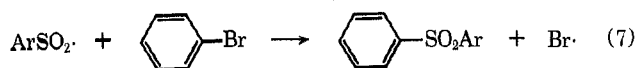
(10) N. H. Christensen, *Acta Chem. Scand.*, **20**, 1955 (1966); **21**, 899 (1967).

(4) C. A. Buehler and J. E. Masters, *J. Org. Chem.*, **4**, 262 (1939).

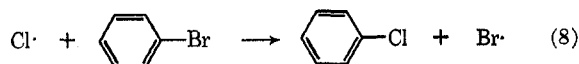
(5) (a) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1597, 1602, 5937 (1957); (b) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957).

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, pp 109-112.

bromobenzene is surprising. One possible suggestion to account for its origin is eq 7, which is analogous to the

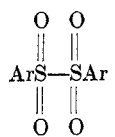
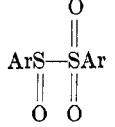


very rapid reaction of Cl \cdot free radicals with bromobenzene (eq 8) discovered by Miller and Walling.¹¹



Comparison of the Rate of Thermal Decomposition of α -Disulfones and Sulfinyl Sulfones.—Table II com-

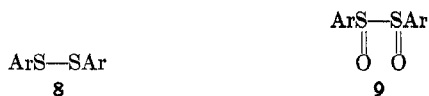
TABLE II
THERMAL DECOMPOSITION OF α -DISULFONES *vs.*
SULFINYL SULFONES^a

Compd Ar = <i>p</i> -tolyl	Solvent	k_{dec} at 100°, sec ⁻¹	ΔH^\ddagger , kcal/ mol	ΔS^\ddagger , eu
	Diglyme	3.3×10^{-8}	40.9	16.6
	Dioxane	1.6×10^{-1}	27.6	11.2

^a Data for the sulfinyl sulfone are from ref 1a.

pares the rates and activation parameters of the thermal decompositions of *p*-tolyl α -disulfone (**5a**) and *p*-tolyl *p*-toluenesulfinyl sulfone (**1a**). One sees that at 100° the rate of thermal decomposition of the sulfinyl sulfone is almost 10⁷ times faster than that of the α -disulfone and that ΔH^\ddagger for the decomposition of **1a** is a little over 13 kcal/mol smaller than for **5a**. These enormous differences show clearly that it is not an unfavorable repulsion between the partially positively charged sulfur atoms of **1a** which is primarily responsible for the ease of homolytic dissociation of the sulfinyl sulfone. What is the reason, then, that the S-S bond in **1** is so much weaker than that in **5**?

Consideration of the above data and what is known qualitatively^{3,12} or quantitatively¹³ about the rate of homolytic dissociation of the other possible compounds besides **1** and **5** which possess a single S-S bond, *i.e.*, **3**, **4**, **8**, and **9**, shows that **1**, **3**, and **9**, in which a sulfinyl



group is one of the partners in the S-S bond, all dissociate much more readily than those compounds (**4**, **5**, and **8**) in which this feature is absent. Of the three sulfinyl compounds, that in which both sulfurs are sulfinyl groups, **9**, is, in fact, so unstable that it cannot even be isolated.¹²

One possible explanation for the difference in behavior between **1**, **3**, and **9** and **4**, **5**, and **8** could be that

- (11) B. Miller and C. Walling, *J. Amer. Chem. Soc.*, **79**, 4187 (1957).
 (12) D. Barnard and E. J. Percy, *Chem. Ind. (London)*, 1332 (1960); U. Marangeli, G. Modena, and P. E. Todesco, *Gazz. Chim. Ital.*, **90**, 1 (1960).
 (13) P. Koch and A. Fava, *J. Amer. Chem. Soc.*, **90**, 3867 (1968).

ArSO \cdot radicals are notably more stable species than either ArS \cdot or ArSO₂ \cdot radicals. That ArSO \cdot could conceivably be more stable than these other radicals is suggested by the following considerations. An RSO \cdot radical is, in effect, isoelectronic with an RS₂ \cdot radical, and Kende, Pickering, and Tobolsky¹⁴ have shown that the latter species is apparently significantly less reactive than a thiyl radical, RS \cdot , in such reactions as addition to a carbon-carbon double bond, suggesting, as has been predicted¹⁵ by theoretical calculations, that RS₂ \cdot is a considerably more stable radical than RS \cdot . Kende, Pickering, and Tobolsky¹⁴ also determined that E_a for the dissociation of CH₃S₄CH₃ into two CH₃S₂ \cdot radicals was only 36.6 kcal/mol, or 25–30 kcal/mol less than the usual estimates of the bond dissociation energy for the reaction RSSR \rightarrow 2RS \cdot .

An alternative explanation for the behavior of **1**, **3**, and **9** is that the S-S bonds in those compounds where a sulfinyl group is part of the bond may be significantly longer, and therefore weaker, than the other S-S bonds. Unfortunately, the needed X-ray studies on **1** and **3** have never been done, and so one cannot at present say how the lengths of their S-S bonds compare with those in **4** or **8**. However, the fact that dithionite ion, -O₂SSO₂⁻, which is in essence the inorganic analog of **9**, has a very long S-S bond (2.39 Å)^{16a} and also dissociates into two SO₂ \cdot radicals extremely readily^{16b} suggests that this alternative explanation needs to be considered just as seriously as the first. Hopefully, future measurements of the S-S bond lengths in such compounds as **1**, **3**, and **5** will permit a decision between these two possible explanations.

Experimental Section

Preparation and Purification of α -Disulfones.—The preparation of the various α -disulfones has been described by Kice and Kasperk.¹⁷ They were purified by several recrystallizations from benzene–10% ethanol.

Purification of Solvents.—Diglyme (Ansul Chemical Co.) was twice refluxed over sodium and then fractionally distilled. Only the fraction boiling at 163–164° was collected. Bromobenzene (Matheson Coleman and Bell) was purified by shaking with concentrated sulfuric acid, washing with water, drying over anhydrous sodium sulfate, and finally carefully fractionally distilling at 156°. Diphenylmethane, mp 25–27°, was fractionally distilled under reduced pressure through a spinning-band column at 78° (1 mm).

Procedure for Kinetic Runs.—A 0.001 *M* stock solution of the α -disulfone in diglyme was made up and 2–5 ml of this solution was diluted to 100 ml with freshly distilled diglyme. This solution was then transferred to a reaction vessel of the type previously used in studying several other reactions.¹⁸ The construction of this vessel is such that the solution can be kept under nitrogen and an aliquot of the solution can be removed without exposing the solution to the atmosphere. The reaction vessel and its contents were then deaerated by passing a gentle stream of prepurified nitrogen through the solution at room temperature for 10–15 min. At that point the vessel was placed in the constant-temperature bath, and, once thermal equilibrium was achieved, an initial aliquot ($t = 0$) was removed and its absorbance was measured at the wavelength corresponding to the intense absorption maximum of the α -disulfone. The wavelengths

(14) I. Kende, T. L. Pickering, and A. V. Tobolsky, *ibid.*, **87**, 5582 (1965).

(15) G. Bergson, *Arkiv Kemi*, **18**, 409 (1961).

(16) (a) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 16–27; (b) S. Lynn, R. G. Rinker, and W. H. Corcoran, *J. Phys. Chem.*, **68**, 2363 (1964).

(17) J. L. Kice and G. J. Kasperk, *J. Amer. Chem. Soc.*, **91**, 5510 (1969).

(18) (a) J. L. Kice, C. G. Venier, and L. Heasley, *ibid.*, **89**, 3557 (1967); (b) J. L. Kice and K. W. Bowers, *ibid.*, **84**, 605 (1962).

used for the different α -disulfones were as follows: p -CH₃O, 284 m μ ; p -CH₃, 257 m μ ; p -Br, 266 m μ ; p -Cl, 259 m μ . At selected time intervals thereafter, additional aliquots were removed and their absorbance was measured in the same way.

Products of the Decomposition of 5a in Diglyme.— p -Tolyl α -disulfone (1.25 g, 0.004 mol) and 1 l. of freshly distilled diglyme were placed in a 2-l., three-necked flask fitted with a gas-inlet tube and a condenser. The top of the condenser was connected with a length of tubing to a trap that contained a solution of 2.5 g of BaCl₂·2H₂O and 10 ml of 30% hydrogen peroxide in 90 ml of water. A vigorous stream of nitrogen was passed through the solution and the rest of the system for 10 min at room temperature before the flask was warmed and gently swirled to dissolve the α -disulfone. Once the α -disulfone had dissolved, a sheet of aluminum foil was wrapped around the flask, the nitrogen stream was reduced to a gentle flow, and the solution was heated to reflux. After 20 hr at reflux, the solution was allowed to cool and trap was disconnected from the condenser. The amount of sulfur dioxide which had been liberated in the decomposition was determined from the amount of barium sulfate formed in the trap.

The solvent was removed from the final solution under reduced pressure and the residue was dissolved in chloroform. The chloroform solution was washed with several portions of water. The water washings were combined and one half was titrated with 0.10 *N* sodium hydroxide. The other half was treated with *S*-benzylisothiuronium chloride, using the procedure described by Donleavy¹⁹ and *S*-benzylisothiuronium *p*-toluenesulfonate, mp 179–180° (lit.¹⁹ mp 178°), was isolated in a yield equivalent to 94% of the amount expected from the titration results, assuming that all the acid being titrated was *p*-toluenesulfonic acid.

The chloroform solution was then evaporated and the residue was chromatographed on alumina in the usual way. Elution with hexane and 80:20 hexane–benzene gave fractions which were a mixture of *p*-tolyl disulfide and *p*-tolyl sulfide. A pure sample of each was isolated by repeated fractional crystallizations from ethanol of those fractions richest in each component. To determine quantitatively the relative amounts of sulfide and disulfide present, the combined fractions from a run were dissolved in alcohol, excess sodium borohydride was added, and the mixture was stirred for 10 hr at room temperature. Then dilute hydrochloric acid was added to decompose the excess borohydride, and an equal volume of a 50:50 pyridine–water solution

was added. The resulting solution was then titrated with standard iodine. Control runs with known mixtures of *p*-tolyl sulfide and disulfide showed that this method was quantitative for determining the amount of disulfide. The remainder of the material in the combined fractions was assumed to be *p*-tolyl sulfide.

A large amount of a dark oil was eluted with benzene. Its infrared spectrum in chloroform showed two strong bands at 7.35 and 8.50 μ , indicating the presence of a sulfonyl group. The presence of a wide band of medium intensity centered at 3.4 μ suggests that the oil possesses aliphatic protons and therefore contains one or more solvent-derived fragments.

Products of the Decomposition of 5a in Bromobenzene.—The same procedure as was used with diglyme was employed to investigate the products of the decomposition of 5a in bromobenzene. The decomposition was carried out at the reflux temperature (156°) in bromobenzene.

Besides the mixture of *p*-tolyl sulfide and disulfide, the chromatography on alumina gave a sizable fraction which was eluted with benzene. Recrystallization of this material from 95% ethanol gave pure phenyl *p*-tolyl sulfone, mp 126–127°, identical in all respects with a known sample of this compound prepared by the method of Buehler and Masters.⁴

Products of the Decomposition of 5a in Diphenylmethane.—The decomposition was carried out at 156° in the same general manner as the decompositions in diglyme or bromobenzene except that no estimate was made of whether any sulfur dioxide was evolved in the decomposition.

After removal of the solvent and extraction of the residue with water, the water washings were titrated with standard base, but, inadvertently, the experiment with *S*-benzylisothiuronium chloride to determine what fraction of the total acidity was due to sulfonic acid was not carried out, so that we do not know what fraction is due to sulfonic acid and what fraction to sulfinic acid.

Chromatography of the residue on alumina gave a large amount of *sym*-tetraphenylethane, eluted with 80:20 hexane–benzene, mp 210–212°, identical in all respects with a known sample²⁰ of this compound.

Registry No.—5a, 10409-07-1; 5 (Ar = *p*-BrC₆H₄), 14039-87-3; 5 (Ar = *p*-ClC₆H₄), 22040-25-1; 5 (Ar = *p*-CH₃OC₆H₄), 13603-79-7.

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Fluorinated Dialkyl Mono- and Polysulfates.

I. Preparation and Some Reactions¹

L. G. ANELLO AND R. F. SWEENEY

Specialty Chemicals Division, Allied Chemical Corporation, Morristown, New Jersey 07960

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Bis(1H,1H,2H,2H-perfluoroalkyl) and bis(1H,1H,2H,2H-perfluoroisopropoxyalkyl) polysulfates are prepared by the reaction of sulfur trioxide with the corresponding 1-iodo-1H,1H,2H,2H-perfluoro- and 1-iodo-1H,1H,2H,2H-perfluoroisopropoxyalkanes. Fluorinated dialkyl polysulfates, R_FCH₂CH₂O(SO₂O)_zCH₂CH₂R_F, where $z > 3$, have not been isolated owing to the instability of the longer sulfate chain length. The di- and trisulfates (where $z > 1$) are readily decomposed to the lower sulfates and sulfur trioxide when heated for extended periods above 80°. Reaction of the polysulfates with mineral or organic acids gave the corresponding alcohols or alkyl esters, respectively, whereas the monosulfates were unreactive under similar conditions.

The chemistry of fluorosulfur compounds has received an extensive amount of study during the last few years; yet fluorinated dialkyl sulfates are virtually unknown. Apparently, only a few such compounds have been reported: bis(difluorodiethyl) sulfate,² bis(trifluoromethyl) mono- and pyrosulfate,³ bis(hexafluoroisopropyl) pyrosulfate,⁴ bis(1H,1H, ω H-perfluoro-

alkyl) sulfates,⁵ and bis(1H,1H,2H,2H-perfluoroalkyl) sulfates.⁶

Related compounds such as fluorocarbon cyclic sulfonate–sulfate anhydrides as well as β -sulfones and novel fluorocarbon halosulfates have also been discussed by recent workers.^{7,8}

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