TABLE II

ENTROPIES AND ENTHALPIES OF HEXANE ISOMERIZATION

Conv. of hexane to	ΔH, cal./mole This work				ΔS, e.u. This work			
		Evering[1]	Condon[9]	Calcd.[5]		Evering[4]	Condon[1]	Calcd.[5]
n-C_6	0	0	0	0	0	0	0	0
2-MP	1100	1310	1740	1710	0.70	0.78	1.82	1.86
3-MP	850	820	1090	1020	1.4	1.12	2.00	1.59
2,3-DMB	2500	2500	2500	2500	6.5	6.07	5.48	5.13
2,2-DMB	4100	4620	4950	4390	8.4	8.93	6.89	6.74

substantially more 2,2-dimethylbutane and less 2-methylpentane than is actually found. Condon[9] indicates that this discrepancy is largely the result of differences in the heat content and entropy of 2,2-dimethylbutane and the entropy of 2,3-dimethylbutane.

Vapor phase equilibrium constants for the isomerization of n-hexane to each of its four isomers are plotted in Fig. 1 and compared with those calculated from thermodynamic data. Also shown in this figure are the experimental values of Evering and d'Ouville at 21–100°. The values repeated here are in good agreement with Evering and d'Ouville's indicating that the multitude of components in the virgin naphtha, used during the course of their work, did not affect equilibrium.[1]

The experimental entropies and enthalpies of isomerization are compared with the calculated values in Table II. Also shown are the experimental values of Evering[1] and the values calculated by Condon[9] from a best fit of the experimental data of several investigators. The values reported in the present work were obtained over a relatively narrow temperature range but agree well with those of Evering. They differ from the values calculated by Condon mainly in the entropy of 2-methylpentane. This might be due to the narrow temperature range investigated with a consequent decrease in the reliability of the isomerization heats.

Further work will be needed before definite conclusions can be reached. However, the work reported here, on pure hexane isomers, offers conclusive proof that thermodynamic values previously reported for hydrocarbons must be used with a degree of caution.

The data above hexane are very sparse, but limited heptane isomerization results indicate some disagreement between experimental and calculated equilibrium values.[9] The reason for these particular differences seems to be in the heat of combustion of 2,3-dimethylbutane. A re-evaluation of thermodynamic hydrocarbon values, and conditions under which they can be used with confidence, appears to be in order.

Acknowledgment.—The authors would like to acknowledge the help obtained in the Process Research Division of Esso Research & Engineering Co., and also to Esso Research & Engineering Co. for permission to publish this work. We would particularly like to acknowledge the analytical help provided by Messrs. W. A. Dietz and H. Pobiner, and the advice and encouragement of Messrs. D. L. Baeder and J. P. Longwell.

LINDEN, N. J.

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(9) F. E. Condon in "Catalysis," Vol. 6, Edited by P. H. Emmett, Reinhold Publ. Corp., New York, N. Y., 1958.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Thermal Decomposition of Thiolsulfonates[1]

BY JOHN L. KICE, FRED M. PARHAM AND ROBERT M. SIMONS

RECEIVED JUNE 3, 1959

The thiolsulfonates $RSO_2SCH_2C_6H_5$, where R = $(C_6H_5)_2CH$– or $C_6H_5CH_2$–, undergo thermal decomposition in inert solvents in the temperature range 130–200° with essentially quantitative evolution of sulfur dioxide and the formation of varying amounts of $RSCH_2C_6H_5$, RH, stilbene, dibenzyl disulfide and R–R. Investigation of the kinetics of the decomposition indicates that for both thiolsulfonates the reaction is a simple first-order process. Under comparable conditions the rate of decomposition of the benzhydryl compound is about 150 times greater than that of the α-toluenethiolsulfonate, providing evidence that the C–SO_2 bond is broken in the rate-determining step. For both thiolsulfonates the rate of decomposition is noticeably dependent on solvent, being considerably faster in relatively polar solvents (nitrobenzene, benzonitrile) than in non-polar solvents (1-chloronaphthalene, 2-methylnaphthalene, etc.). This fact, together with the complete failure of the diphenylmethanethiolsulfonate to initiate the polymerization of styrene, seems most consistent with a mechanism for the thiolsulfonate decomposition involving a rate-determining heterolytic fission of the C–SO_2 bond followed by recombination of the fragments with loss of sulfur dioxide. This recombination is believed to occur in two ways, one yielding $RSCH_2C_6H_5$, the other RH and $C_6H_5CH{=}S$. This last product then decomposes to yield the stilbene observed. The other minor products apparently result from subsequent reactions of some of the compounds initially formed.

Thiolsulfonates (RSO_2SR') represent a relatively little investigated class of organic sulfur compounds. Most studies of their chemistry have been concerned with their displacement reactions (eq. 1), which appear to involve nucleophilic attack on the sulfur–sulfur bond.

$$RSO_2SR' + A^- \longrightarrow RSO_2^- + R'S\text{–}A \qquad (1)$$

We, however, were more intrigued by an early report[2] that benzyl α-toluenethiolsulfonate ($C_6H_5CH_2SO_2SCH_2C_6H_5$) underwent thermal decomposition to afford at

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(1) Presented in part at the 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958.

(2) J. A. Smythe, *J. Chem. Soc.*, **121**, 1400 (1922).

least 70% of the theoretical amount of sulfur dioxide. The intervening years have brought no further study of the thermal decomposition of this or any other thiolsulfonate. In view of recent extensive study of such other desulfonylation reactions as the decomposition of chlorosulfites[3,4] and the pyrolysis of sulfites,[5] an investigation of the thermal decomposition of thiolsulfonates seemed worthwhile. The present paper reports the results of a mechanistic study of the thermal decomposition of α-phenyl substitute dmethanethiolsulfoates under a variety of conditions. The majority of this investigation has been concerned with the decomposition of benzyl diphenylmethanethiolsulfonate (I) [$(C_6H_5)_2CHSO_2SCH_2C_6H_5$], a substance easily prepared in good yield from diphenyldiazomethane, sulfur dioxide and benzyl mercaptan.[6] The decomposition of benzyl α-toluenethiolsulfonate (II) has also been studied, although somewhat less extensively.

Results

Products of the Decomposition of I and II.—In order to study the thermal decomposition of the thiolsulfonate under the simplest possible conditions we chose to employ a nitrogen atmosphere, inert solvents as the reaction medium, and provision for the removal of sulfur dioxide from the solution as rapidly as it was formed. (The apparatus used is shown in Fig. 3.) Under such conditions the yield of sulfur dioxide from the decomposition of I is essentially quantitative. The yields of this and the other products formed when 0.1 *M* solutions of I are decomposed in refluxing chloro- or bromobenzene and in nitrobenzene at 142° are shown in Table I. In nitrobenzene benzhydryl benzyl sulfide is the only organic product of importance. On the other hand, in either chloro- or bromobenzene the yield of the sulfide is considerably lower, and there are formed in its stead substantial amounts of diphenylmethane, stilbene, tetraphenylethane and dibenzyl disulfide, as well as a small amount of thiobenzophenone.

TABLE I

DECOMPOSITION PRODUCTS OF BENZYL DIPHENYLMETHANETHIOLSULFONATE

	Yield of product, mole % thiolsulfonate		
Reaction product	C_6H_5Br (b.p. 156°) reflux under N_2 1 day	C_6H_5Cl (b.p. 132°) reflux under N_2 7 days	$C_6H_5NO_2$ (142°) under N_2 11 hr.
Sulfur dioxide	98	92	97
$(C_6H_5)_2CHSCH_2C_6H_5$	51	56	84
Diphenylmethane	22	21	[b]
trans-Stilbene	8	5	1.5
sym-Tetraphenylethane	5	5	0
Dibenzyl disulfide	5	[a]	<1
Thiobenzophenone	1.5	[a]	0

[a] Not determined quantitatively; yield comparable to bromobenzene. [b] Small amount (~3%) found, not determined quantitatively; more may be formed since some could be lost on work-up.

In view of the known decomposition at more elevated temperatures of sulfides related to benzhydryl benzyl sulfide,[7,8] it is important to point out that the observed difference in product composition is not due to any thermal instability of initially formed benzhydryl benzyl sulfide during the longer reaction times required for the decomposition of I in chloro- or bromobenzene. This was shown by the fact that benzhydryl benzyl sulfide could be recovered uncharged in quantitative yield after being heated at reflux in bromobenzene for 24 hours.

The formation of a substantial amount of stilbene during the decomposition in the halobenzenes may at first sight seem somewhat surprising. However, when one remembers that thiobenzaldehyde decomposes under these conditions into stilbene and sulfur,[9,10] the origin of this product becomes fairly clear. The thioaldehyde could of course be formed by a number of routes from the original benzylthiyl group of the thiolsulfonate.

The crude reaction products had no trace of mercaptan odor, indicating the absence of benzyl mercaptan. However, this does not rule out mercaptan formation during the course of the reaction, because any which was formed might be subsequently consumed in a direct reaction between mercaptan and thiolsulfonate first reported by Smiles and Gibson[11] (eq. 2).

$$C_6H_5CH_2SH + RSO_2SCH_2C_6H_5 \longrightarrow C_6H_5CH_2SSCH_2C_6H_5 + RSO_2H \quad (2)$$

That this reaction can occur in the present case was shown by the fact that refluxing equimolar amounts of benzyl mercaptan and I in a dilute chlorobenzene solution for only one-fourth the time normally required for the decomposition of the thiolsulfonate resulted in the formation of dibenzyl disulfide in 89% yield, together with sulfur dioxide (93%), diphenylmethane (at least 45%) and tetraphenylethane (13%). In the present case the sulfinic acid formed in reaction 2 is not stable under the reaction conditions and apparently decomposes to give sulfur dioxide, diphenylmethane and tetraphenylethane (eq. 3). In any event, the low yields of dibenzyl disulfide in Table I show that reaction 2 is never of great importance in the decomposition of I.

$$(C_6H_5)_2CHSO_2H \longrightarrow SO_2 + (C_6H_5)_2CH_2 + (C_6H_5)_2CHCH(C_6H_5)_2 \quad (3)$$

We have not conducted extensive product studies on the thermal decomposition of benzyl α-toluenethiolsulfonate. However, in order to ensure that the thermal decomposition of this compound took a course similar to that shown by

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(3) E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 308 (1952); **75**, 3182 (1953); **76**, 794 (1954).

(4) S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak and W. G. Young, *ibid.*, **80**, 5965 (1958).

(5) C. C. Price and G. Berti, *ibid.*, **76**, 1207 (1954).

(6) H. J. Backer, J. S. Boerma and H. Kloosterzeil, *Rec. trav. chim.*, **72**, 612 (1953).

(7) E. Fromm and O. Achert, *Ber.*, **36**, 545 (1903).

(8) A. Schönberg, O. Schutz, V. Bruckner and J. Peter, *ibid.*, **62**, 2550 (1929).

(9) E. Baumann and M. Klett, *ibid.*, **24**, 3307 (1891); K. Kopp, *Ann.*, **277**, 339 (1893); J. H. Wood and R. W. Bost, THIS JOURNAL, **59**, 1721 (1937).

(10) We have confirmed that polymeric thiobenzaldehyde will undergo decomposition into stilbene and sulfur at a reasonable rate in refluxing bromobenzene. We find that the reaction appears to proceed more readily the more dilute the original solution. Thus, for a reaction time where Baumann and Klett[9] heating the molten polymer would have obtained only an 8% yield of stilbene, we obtained yields of 30% with a 0.1 *F* solution and 40% with a 0.05 *F* solution.

(11) S. Smiles and D. T. Gibson, *J. Chem. Soc.*, **125**, 176 (1924).

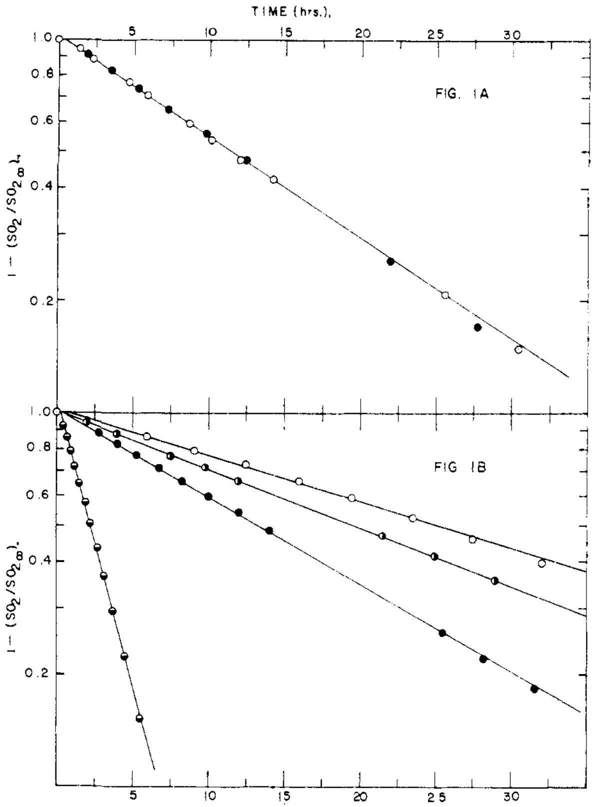

Fig. 1A.—Plot of log $(1 - SO_2/SO_{2\infty})$ *vs.* time for the decomposition of I in 1-chloronaphthalene at 142°: O, run with $[I]_0 = 0.102$ *M*; ●, run with $[I]_0 = 0.030$ *M*.

Fig. 1B.—Plot of log $(1 - SO_2/SO_{2\infty})$ *vs.* time for the decomposition of I in various solvents at 142°: O, bromobenzene; ◑, 2-methylnaphthalene; ●, methyl benzoate; ◒, nitrobenzene; time axis for bromobenzene run displaced 0.5 hr. for improved legibility.

I, we did study the products formed when a 0.1 *M* solution of II in *o*-dichlorobenzene was refluxed for 96 hours, this longer time and higher temperature being necessary to bring about essentially complete decomposition. The identified products and their yields (mole % thiolsulfonate) were sulfur dioxide (93%), benzyl sulfide (72%) and stilbene (13%). We did not find any bibenzyl; we did not attempt to determine if toluene was present. From this result it would appear that the decompositions of I and II take a similar course.

Kinetics of the Decomposition of I and II.—It is possible to study the kinetics of the decomposition of the thiolsulfonates by measuring the rate of evolution of sulfur dioxide. The method, described in detail in the Experimental section, consists of sweeping the sulfur dioxide out of the solution as it is formed with a steady nitrogen stream and through a chilled vessel containing an aliquot of standard iodine. The time required for the disappearance of the iodine color is recorded, another aliquot of iodine added, and the process repeated as many times as desired.[12] Finally an excess of iodine is added, and an "infinity" SO_2 yield is obtained from titration of the excess iodine with thiosulfate. For I these infinity values always agreed closely with those predicted from the weight of thiolsulfonate taken. In some solvents with II, however, they were as low as 85–90% of theory. All of the runs discussed in this section were carried out using carefully deaerated solutions, and air was rigorously excluded during the course of a run. It is important to emphasize this point since under some circumstances oxygen brings about a very pronounced change in the rate of decomposition (see Effect of Oxygen).

In all solvents studied to date the decomposition of I has been found to be first-order in thiolsulfonate. This is evident from Fig. 1A which shows the results of two runs at considerably different initial thiolsulfonate concentrations in 1-chloronaphthalene at 142°. These data, which are typical of the other solvents as well, clearly demonstrate that the experimental first-order rate constant does not show any significant change with changing initial thiolsulfonate concentration. This means that the decomposition is in fact a true first-order reaction without important contributions from higher order terms. On the basis of somewhat less extensive kinetic studies the same also appears to be true for the decomposition of II.

The rate of decomposition of I has been determined in a number of solvents at 142° (Fig. 1B), and in nitro- and bromobenzene the rate has also been measured at two additional temperatures, permitting the calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reaction in these solvents. The results of these studies are shown in Table II. In Table III are shown the corresponding kinetic data for the decomposition of the α-toluenethiolsulfonate.

TABLE II

RATE OF DECOMPOSITION OF BENZYL DIPHENYLMETHANETHIOLSULFONATE

Solvent	Temp., °C.	$[RSO_2SR]_0$, *M*	$k_1 \times 10^5$, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
Bromobenzene	134.1	0.033	0.420		
		.106	.425		
	142.1	.033	.80		
		.102	.87		
	150.0	.032	1.60	30.5	−8.9
		.101	1.81		
Nitrobenzene	125.1	.035	1.81		
		.101	1.78		
	134.1	.031	4.6		
		.103	4.4		
	142.1	.032	9.8	31.1	−2.6
		.102	10.2		
1-Chloronaphthalene	142.1	.030	1.74		
		.102	1.70		
Methyl benzoate	142.1	.109	1.48		
Benzonitrile	142.1	.106	14		
2-Methylnaphthalene	142.1	.108	1.01		

The kinetic results show that I decomposes much more rapidly than II and that the rate of decomposition of either thiolsulfonate is noticeably solvent dependent, being considerably faster in benzonitrile and nitrobenzene than in less polar

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[12] By avoiding reaction conditions with inconveniently short half-lives it was easily possible to pass nitrogen through the solutions at a rate which kept the time between the evolution of SO_2 and its absorption in the iodine sufficiently small that this factor did not interfere with the accurate determination of the rates.

TABLE III

RATE OF DECOMPOSITION OF BENZYL α-TOLUENETHIOLSULFONATE

Solvent	Temp., °C.	$[RSO_2SR]_0$, M	$k_1 \times 10^5$, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
1-Chloronaphthalene	185.2	0.032	0.92		
		.101	1.10		
	194.5	.030	2.06		
		.062	1.83		
		.101	2.04		
	200.5	.032	3.70	37.0	−1.6
		.100	3.62		
Benzonitrile	185.2	.032	5.05		
		.065	4.40		
Methyl benzoate	185.2	.066	0.98		
2-Methylnaphthalene	185.2	.065	1.32		

solvents such as bromobenzene or 2-methylnaphthalene. Since $\Delta H^{\ddagger}$ for the decomposition of I is the same within experimental error in both bromo- and nitrobenzene, the enhanced rate of decomposition in the latter solvent is due entirely to the more favorable entropy of activation.

For II $\Delta H^{\ddagger}$ in chloronaphthalene is 6.5 kcal. greater than $\Delta H^{\ddagger}$ for I in bromobenzene. Since for I there seems to be little dependence of $\Delta H^{\ddagger}$ on solvent, it seems reasonable to conclude that the larger $\Delta H^{\ddagger}$ for the α-toluenethiolsulfonate is the cause of this compound's generally much lower rates of decomposition.

Effect of I on the Polymerization of Styrene.—Deaerated solutions of styrene in bromobenzene containing varying amounts of I were heated at 142° for two hours. The amount of polystyrene formed is shown in Table IV. Measurement of the amount of sulfur dioxide evolved showed that the rate of decomposition of I under these conditions was not sensibly different from the rate in pure bromobenzene.

TABLE IV

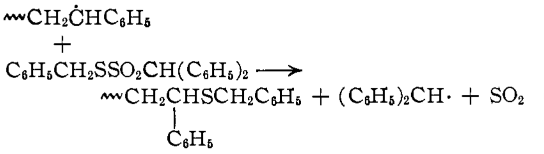
EFFECT OF I ON STYRENE POLYMERIZATION

Styrene taken, g.[a]	$[RSO_2SR]_0 \times 10^2$, M	Polystyrene, %
2.61	0.00	7.3
2.54	2.97[b]	6.5
2.38	10.6	4.8

[a] Amount of bromobenzene same in all runs. [b] k_{I} for I at 142° = 8.3×10^{-6} sec.$^{-1}$; even if rate of radical production is only $0.25k_1$, rate of styrene polymerization for 0.03 M thiolsulfonate should be 18%/hr.

The yield of polymer actually decreases slightly in the presence of the thiolsulfonate. Since Cohen and Wang[13] have shown in their studies of the decomposition of azo-bis-diphenylmethane that benzhydryl radicals are sufficiently reactive to initiate the polymerization of styrene (albeit less effectively than the more reactive radicals from benzoyl peroxide), the present results seem to provide clear evidence that no more than a very small fraction of the decomposition of I in bromobenzene proceeds through the formation of free benzhydryl and benzylthiyl radicals. Reconciliation of this fact with the observed formation of small amounts of such products as tetraphenylethane will be deferred until the Discussion.

It might be noted in passing that a reaction such as 4 would provide a plausible explanation for the decrease in polymer yield with increasing thiolsulfonate concentration. The benzhydryl radical being considerably less reactive toward addition



$$\sim\!\sim \mathrm{CH_2\dot{C}HC_6H_5} + \mathrm{C_6H_5CH_2SSO_2CH(C_6H_5)_2} \longrightarrow \sim\!\sim \mathrm{CH_2\underset{\underset{C_6H_5}{|}}{C}HSCH_2C_6H_5} + \mathrm{(C_6H_5)_2CH\cdot} + \mathrm{SO_2} \quad (4)$$

to monomer than the styryl radical, a chain transfer process such as 4 could also easily result in some retardation.

Acid Catalysis.—The effect of acids of varying strengths on the rate of decomposition of I was briefly studied. The results are shown in Table V.

TABLE V

EFFECT OF ACID ON THE RATE OF DECOMPOSITION OF I

$[RSO_2SR]_0 = 0.1$ M in all experiments

Solvent	Temp., °C.	Acid, concn., M	$k_1 \times 10^5$, sec.$^{-1}$
Bromobenzene	142.1	None	0.87
		Benzoic, 0.01	0.80
		o-Nitrobenzoic, 0.01	1.33
		p-Toluenesulfonic, 0.01	[a]
Nitrobenzene	125.1	None	1.78
		o-Nitrobenzoic, 0.01	2.40
		p-Toluenesulfonic, 0.0015	>58

[a] Too fast to measure.

Although benzoic acid (pK_a of 4.20 in H_2O at 25°) exerts no measurable catalytic effect at concentrations up to 0.01 M, stronger acids such as *o*-nitrobenzoic (pK_a 2.17) have a definite although small effect, and strong acids such as *p*-toluenesulfonic bring about very rapid decomposition of I even at concentrations as low as 10^{-3} M. (Investigation of the products of the *p*-toluenesulfonic acid catalyzed decomposition in nitrobenzene showed benzhydryl benzyl sulfide to be the only identifiable organic product. In nitrobenzene the products of the acid-catalyzed decomposition are thus the same as in the uncatalyzed decomposition.)

The decomposition of the α-toluenethiolsulfonate is also subject to acid catalysis. However, since at 185° the rate in chloronaphthalene containing 0.005 M *p*-toluenesulfonic acid is only eight times larger than the rate in the absence of acid, such catalysis is obviously less pronounced than in the case of I.

These findings raise the possibility of acid catalysis by the sulfur dioxide liberated in the reaction. Although this could be important where sulfur dioxide is not removed from contact with the solution as it is formed, *we have reasonably definitive proof that under our reaction conditions catalysis by sulfur dioxide is not a factor*, and that the data in Tables II and III represent the rate constants for the uncatalyzed decompositions of I and II under the conditions indicated. Some of the evidence leading to this conclusion is given in footnote 14.

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(13) S. G. Cohen and C. H. Wang, THIS JOURNAL, **77**, 2457 (1955).

(14) First, the rate constants do not appear to be measurably sensitive to the rate at which nitrogen is passed through the solution during the decomposition. An increased nitrogen flow should decrease

Effect of Oxygen.—When CO_2-free air, instead of nitrogen, was passed through the solution during the reaction the rate of decomposition of I in bromobenzene increased tremendously (Fig. 2). (In these experiments the rate of SO_2 evolution was determined by absorption of the gas in standard base rather than iodine. Experiments under nitrogen had shown both methods gave identical results.) The yield of sulfur dioxide, as in the absence of oxygen, was essentially quantitative, and the major organic product was benzhydryl benzyl sulfide (83%). The only other product which could be identified was benzophenone (3%). Although the rate of decomposition of I in chloronaphthalene showed similar acceleration in the presence of air, *the decomposition of II at 185° in the same solvent was not noticeably affected.*

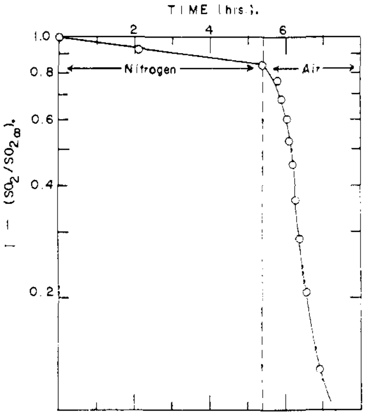
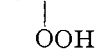


Fig. 2.—Plot of log $(1 - SO_2/SO_{2\infty})$ *vs.* time for the decomposition of I in bromobenzene showing the effect of oxygen on the rate; $[I]_0$, 0.106 *M;* temperature, 142°.

Since the matter is still under study, a definitive explanation of this oxygen effect cannot be given at present. However, we suspect it is due to the formation in the presence of oxygen of small amounts of an unstable or volatile strong acid, which markedly catalyzes the decomposition of I (*vide supra*). This would be consistent with the almost exclusive formation of benzhydryl benzyl sulfide from I (a reaction product not easily accounted for by any oxygen-initiated radical chain reaction), and the failure of II to show this marked oxygen effect, the decomposition of II being much less subject to acid catalysis. We believe the acid is unstable and/or volatile because upon resumption of the nitrogen flow the rate gradually decreases, and if the decomposition has not proceeded too far, eventually returns essentially to normal. A speculative possibility for such an unstable strong acid is $C_6H_5CH_2SSO_2OH$, which could be formed along with benzophenone by the decomposition of

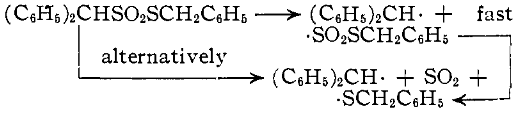


$$(C_6H_5)_2\underset{\displaystyle OOH}{\underset{|}{C}}{-}SO_2SCH_2C_6H_5.$$

Discussion

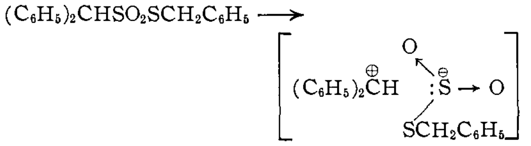
It seems desirable to point out at the outset that the following discussion is concerned only with those results obtained in the absence of oxygen.

At 142° in chloronaphthalene the diphenylmethanethiolsulfonate I decomposes about 150 times more rapidly than the α-toluenethiolsulfonate II. Furthermore, $\Delta H^{\ddagger}$ for the decomposition of II is 6.5 kcal./mole greater than $\Delta H^{\ddagger}$ for the decomposition of I. These facts clearly demonstrate that the rate-determining step of the thiolsulfonate decomposition involves the cleavage of the C–SO_2 bond. However, they do not tell us whether this bond is broken in a homolytic or heterolytic process. Homolytic decomposition of I (eq. 5) would lead to the formation of sulfur dioxide, a benzhydryl and a benzylthiyl radical.



(5)

On the other hand, heterolytic decomposition (eq. 6) would probably lead to the formation of an ion pair such as III as the first intermediate.



(6)

III

Although the rate of reaction 5 would not be expected to be noticeably dependent on the polarity of the solvent, the rate of reaction 6 should show a considerable dependence on solvent, proceeding the more rapidly the more polar the solvent. In this connection the rates of decomposition of I and II in the various solvents take on considerable significance. Thus the rate of decomposition of I is not greatly different in the four solvents bromobenzene, methyl benzoate, chloronaphthalene and methylnaphthalene, varying only over a factor of two. However, in the considerably more polar solvents nitrobenzene and benzonitrile the rate of decomposition of I is from six to fifteen times faster than in the other solvents. The decomposition of II shows similar behavior. This dependence of rate on solvent polarity and the failure of I to initiate the polymerization of styrene even under optimum conditions strongly suggest that in all solvents the decomposition of the thiolsulfonates occurs almost exclusively by ionic fission of the C–SO_2 bond (eq. 6). For I any contribution from a radical process cannot amount to more than a few per cent. of the over-all rate, even in bromobenzene.

Subsequent collapse of III by either of two plausible paths (eqs. 6a and 6b) can account for the principal products of the decomposition of I. Apparently 6a is the preferred path in nitrobenzene, while 6a and 6b compete about equally in the

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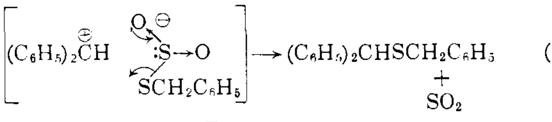
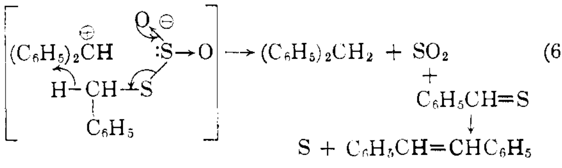
the concentration of SO_2 in the solution. Consequently, if SO_2 catalysis were actually a factor, an increase in the rate of nitrogen flow should decrease the rate of decomposition. Second, in any given run the rate of nitrogen flow through the solution (ml./min.) is constant. On the other hand, the rate of formation of sulfur dioxide (ml./hr.) is not constant but decreases as the concentration of thiolsulfonate decreases. Accordingly, the partial pressure of SO_2 above the solution decreases during the course of a run. If the kinetics of the decomposition were actually of the form $-d[RSO_2SR]/dt = (k_s + k_0[SO_2])[RSO_2SR]$, the apparent first-order rate constant should decrease noticeably during the course of a run. Examination of Figs. 1A and 1B shows this is not the case.

halobenzenes. The greater yield of sulfide in nitrobenzene may also result from the fact that in this more polar solvent the lifetimes of III and other ionic species are increased to the point that loss of sulfur dioxide (eq. 6c) competes effectively with 6a and 6b, with recombination of ion pair IV leading only to sulfide.



$$\left[(C_6H_5)_2\overset{\oplus}{C}H \quad \overset{O^{\ominus}}{:S\rightarrow O} \atop \quad SCH_2C_6H_5\right] \longrightarrow (C_6H_5)_2CHSCH_2C_6H_5 + SO_2 \qquad (6a)$$

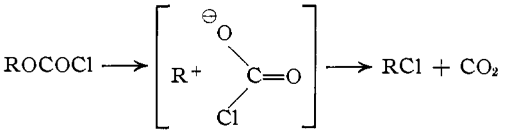


$$\left[(C_6H_5)_2\overset{\ominus}{C}H \quad \overset{O^{\ominus}}{:S\rightarrow O} \atop H\!-\!\underset{C_6H_5}{CH}\!-\!S\right] \longrightarrow (C_6H_5)_2CH_2 + SO_2 + C_6H_5CH{=}S \qquad (6b)$$

$$C_6H_5CH{=}S \longrightarrow S + C_6H_5CH{=}CHC_6H_5$$

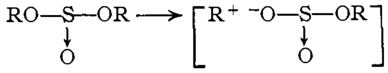
$$\mathrm{III} \longrightarrow SO_2 + [(C_6H_5)_2\overset{\oplus}{C}H \quad \overset{\ominus}{S}CH_2C_6H_5] \longrightarrow \underset{\mathrm{IV}}{} (C_6H_5)_2CHSCH_2C_6H_5 \qquad (6c)$$

Before considering possible paths for the formation of the small amounts of tetraphenylethane and dibenzyl disulfide found in the halobenzenes we should like to compare the mechanism proposed for the thiolsulfonate decomposition with those mechanisms which have previously been advanced for several other desulfonylation reactions[4,5] and for the related decomposition of chlorocarbonates.[15] In the latter case Wiberg and Shryne proposed a mechanism (eq. 7) based in part on these experimental observations: (1) α-Phenylethyl chlorocarbonate decomposes in dioxane at 90° about 450 times faster than benzyl chlorocarbonate. (2) The decomposition of p-substituted α-phenylethyl chlorocarbonates shows a ρ-value of about -3.6 in either toluene or dioxane. (3) Due to a larger negative entropy of activation in toluene, the reaction proceeds from four to six times faster in dioxane. We have already noted a similar observation concerning rates and $\Delta S^{\ddagger}$ for I in nitro and bromobenzene. Comparison of the 150-fold rate difference between I and II with the 450-fold difference between α-phenylethyl and benzyl chlorocarbonates suggests the aralkyl fragment in III has considerably less true carbonium ion character than the same moiety in the chlorocarbonate decomposition. For this reason we believe III is best represented as some type of tight ion pair.



$$ROCOCl \longrightarrow \left[R^+ \quad \overset{\ominus}{O}\!-\!\underset{Cl}{C}{=}O\right] \longrightarrow RCl + CO_2 \qquad (7)$$

Young and co-workers[4] propose a mechanism analogous to 7 for the decomposition of chlorosulfites, pointing out that the sum of the experimental evidence to date[3,4] requires a rate-determining ionization of the C–O bond. Price and Berti[5] postulate the pyrolysis of sulfites also involves an initial ionization of this type (eq. 8).[16]



$$RO\!-\!\underset{\substack{\downarrow\\ O}}{S}\!-\!OR \longrightarrow \left[R^+ \ {}^-O\!-\!\underset{\substack{\downarrow\\ O}}{S}\!-\!OR\right] \qquad (8)$$

Since the thermal decomposition of alkanesulfonyl chlorides is generally considered to be a free radical chain reaction,[17] the present decomposition appears to be the first recorded example of a desulfonylation reaction involving rate-determining heterolytic cleavage of a C–S bond. However, the present results suggest the previously reported rapid thermal decomposition of alkanesulfonyl chlorides having an α-phenyl substituent[18] may possibly involve ionic intermediates and might profitably be re-examined.

One should also note that thermal ionic decomposition of thiolsulfonates will probably be observed only when, due to the absence of a nucleophile, the usual S_N2 reactions of the thiolsulfonates (eq. 1) are excluded. This is evident from our observations that when I is decomposed in the presence of an equivalent of benzyl mercaptan one obtains an 89% yield of dibenzyl disulfide, the product expected from nucleophilic attack by mercaptan on the S–S bond, and that this reaction occurs in only one-fourth the time required for the ionic thermal decomposition of I.

Because it seems difficult to reconcile the formation of tetraphenylethane with other than radical intermediates, it was originally our belief that this product and the dibenzyl disulfide resulted from recombination of radicals formed by homolytic decomposition of I. However, the complete failure of I to initiate styrene polymerization rules out this route as the major source of these compounds and requires a search for an alternative explanation. One tentative possibility is the following: At somewhat more elevated temperatures (>200°) diphenylmethane and thiobenzophenone react to form, among other products, tetraphenylethane.[19] This reaction has been extensively studied by Moreau[19] who concludes that the initial step is the transfer of a hydrogen atom from hydrocarbon to thioketone (eq. 9). Consideration of the relative

$$(C_6H_5)_2CH_2 + (C_6H_5)_2C{=}S \longrightarrow (C_6H_5)_2CH\cdot + (C_6H_5)_2CHS\cdot \qquad (9)$$

stability of the C=S bond in thiobenzophenone and thiobenzaldehyde suggests such a reaction should happen much more readily with the thioaldehyde (eq. 10). Thiolsulfonate I seems to be a good chain

$$(C_6H_5)_2CH_2 + C_6H_5CH{=}S \longrightarrow (C_6H_5)_2CH\cdot + C_6H_5CH_2S\cdot \qquad (10)$$

transfer agent (see Effect of I on Styrene Poly-

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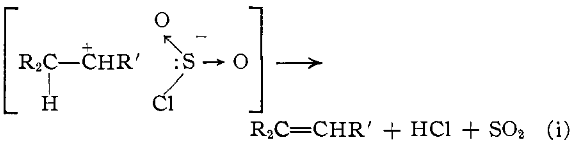
[15] K. B. Wiberg and T. M. Shryne, THIS JOURNAL, **77**, 2774 (1955).

[16] In the decomposition of secondary chlorosulfites there is often considerable olefin formation,[3] presumably due to the collapse of the ion pair by (i). With sulfites having β-hydrogen atoms elimination occurs to the exclusion of ether formation.[5] The behavior of thiolsulfonates having β-hydrogen atoms is currently under investigation.



$$\left[R_2\overset{+}{C}\!-\!CHR' \quad \overset{O^-}{:S\rightarrow O} \atop \quad H \qquad\quad Cl\right] \longrightarrow R_2C{=}CHR' + HCl + SO_2 \qquad (i)$$

[17] H. F. Herbrandson, W. S. Kelly and J. Versnel, THIS JOURNAL, **80**, 3301 (1958).

[18] H. Limpricht, *Ber.*, **6**, 532 (1873); M. S. Kharasch, E. M. May and F. R. Mayo, *J. Org. Chem.*, **3**, 189 (1938).

[19] R. C. Moreau, *Bull. soc. chim. France*, [5] **22**, 918, 922, 1044, 1049, 1064 (1955).

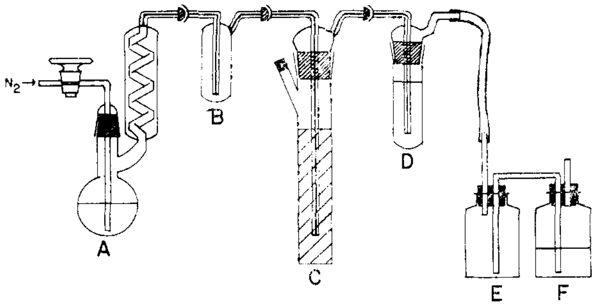


Fig. 3.—Apparatus for thiolsulfonate decomposition.

merization) and, accordingly, in the presence of I reaction 10 might well be followed by 11 and 12. The small amount of thiobenzophenone also formed could be explained by a sequence of reactions such as 13–15.

$$(C_6H_5)_2CHSO_2SCH_2C_6H_5 + C_6H_5CH_2S\cdot \longrightarrow (C_6H_5)_2CH\cdot + SO_2 + [C_6H_5CH_2S-]_2 \quad (11)$$

$$2(C_6H_5)_2CH\cdot \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2 \quad (12)$$

$$C_6H_5CH_2S\cdot + (C_6H_5)_2CHSCH_2C_6H_5 \longrightarrow C_6H_5CH_2SH + (C_6H_5)_2\dot{C}-SCH_2C_6H_5 \quad (13)$$

$$(C_6H_5)_2\dot{C}-SCH_2C_6H_5 \longrightarrow (C_6H_5)_2C{=}S + C_6H_5CH_2\cdot \quad (14)$$

$$C_6H_5CH_2\cdot + C_6H_5CH_2SH \longrightarrow C_6H_5CH_3 + C_6H_5CH_2S\cdot \quad (15)$$

As the thiolsulfonate decomposition proceeds and the concentration of diphenylmethane builds up reaction 10 should compete with the thioaldehyde–stilbene conversion with increasing effectiveness. Since the sequel to 10 involves the disappearance of a molecule of I, the over-all rate of decomposition of I should increase slightly during the latter portion of the decomposition. This is definitely observed in the bromobenzene kinetic runs (see Fig. 1B), a finding which perhaps lends some support to this highly tentative hypothesis. Naturally when only a few per cent. of I has decomposed, as in the styrene experiments, the concentration of diphenylmethane will still be so low that the rate of radical production from 9 will be considerably less than the thermal rate of initiation. Consequently the results of the styrene experiments are also compatible with this hypothesis.

Besides the above there are several other possible explanations for the formation of tetraphenylethane and the other minor products. For this reason we plan further study of this interesting sidelight of the decomposition of I, which it is hoped will permit decision between the various alternatives.

Acknowledgments.—We are deeply indebted to the Sloan Foundation for a grant used in support of this work.

Experimental

Benzyl diphenylmethanethiolsulfonate (I) was prepared from diphenyldiazomethane,[20] benzyl mercaptan and sulfur dioxide.[6] The crude product was recrystallized from ethanol to give fine needles, m.p. 143–145° dec.

Benzyl α-toluenethiolsulfonate (II) was prepared from dibenzyl disulfide by oxidation with the calculated amount of 30% hydrogen peroxide in glacial acetic acid.[21] Recrystallized from ethanol–ether it melted 106–108°.

Benzhydryl Benzyl Sulfide.—An authentic sample, m.p. 69–71°, was prepared by the method of Protiva, *et al.*,[22] and purified by recrystallization from hexane.

Thiobenzaldehyde Polymer.—Ten grams of undistilled benzaldehyde was dissolved in ethanol (50 ml.), and the solution was cooled to −3° in an ice–salt-bath. Hydrogen sulfide was passed into the solution slowly for 4 hours. The pinkish amorphous precipitate was removed by filtration and dissolved in a small amount of benzene. The benzene solution was then added slowly to a 10-fold excess of ethanol with good stirring. The finely divided solid which separated was filtered and dried. The material appeared to be similar to that previously described by Wood and Bost.[23]

Decomposition of I in Bromo and Chlorobenzene.—The apparatus used for the product studies is shown in Fig. 3. The desired amount (5.00 mmoles) of I was weighed into A, the requisite amount of solvent (50 ml.) added, and high purity nitrogen was slowly bubbled through the solution at room temperature for 1 to 2 hr. Trap B was cooled in ice and served to retain traces of solvent entrained by the gas stream. Trap C contained a known amount of standard iodine solution and was also cooled in ice to prevent entrainment of iodine. Trap D, which proved to be unnecessary, contained a 2% KI solution and was included to prevent the escape of any iodine which might be carried over by the nitrogen. Bottles E and F were partially filled with mineral oil and served to prevent back-diffusion of air into the system. After nitrogen had been bubbled through the solution at room temperature the thiolsulfonate solution was heated to reflux and maintained at that temperature for the desired length of time. Nitrogen was passed through at a slow rate throughout the decomposition. A blank run showed that in the absence of gases reducing iodine the iodine titer of C did not change with time. After decomposition, the reaction mixture was cooled to room temperature, and the iodine titer of C was determined. Since a separate experiment, in which C was filled with buffered cadmium acetate instead of iodine, showed that no hydrogen sulfide was formed in the decomposition, the change in iodine titer was ascribed only to the formation of sulfur dioxide. The yield of sulfur dioxide in all runs was close to quantitative.

Isolation and Identification of Non-volatile Products.—During the decompositions in the halobenzenes the solution became quite blue. The optical density at 595 mμ was determined at the end of the reaction, taking care to avoid exposure of the solution to oxygen. The thiobenzophenone yield was calculated using the molar extinction coefficient for the thioketone at this wave length.[24]

The solvent was then carefully removed by fractional distillation at reduced pressure (pot temp. below 70°), and the residue was chromatographed on alumina (Grade I, 65 g./g. original thiolsulfonate). The chromatographic column was eluted with successive 100-ml. portions of: hexane, 1:8 benzene–hexane, 1:6 benzene–hexane, 1:4 benzene–hexane, 1:2 benzene–hexane, benzene and ether. The products were collected in fractions of 20-ml. volume, the solvents removed, and the yield and identity of the various products was established as follows.

Diphenylmethane.—In the chlorobenzene decomposition the first fraction was a colorless oil whose infrared spectrum and melting behavior showed it to be rather pure diphenylmethane. In that case the amount of diphenylmethane was determined simply by weighing the fraction. In the bromobenzene runs, however, this initial fraction was contaminated with a small amount of bromobenzene as shown in the infrared by bands at 6.77, 9.80, 10.0 and 11.2 μ. Experiments with known mixtures of bromobenzene and diphenylmethane indicated the former could be determined quantitatively from the intensity of the 6.77 μ band. The amount of diphenylmethane was then determined from the total weight of the fraction and the amount of bromobenzene found by infrared analysis. Diphenylmethane could

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[20] "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 351.

[21] H. Breitschneider and W. Klotzer, *Monatsh.*, **81**, 593 (1950).

[22] M. Protiva, J. O. Jilek, O. Exner, M. Borovicka, J. Pliml, V. Simak and Z. Sedivy, *Chem. Listy*, **47**, 1038 (1953); *C. A.*, **49**, 248 (1955).

[23] J. H. Wood and R. W. Bost, THIS JOURNAL, **59**, 1011 (1937).

[24] R. H. Abeles, R. F. Hutton and F. H. Westheimer, *ibid.*, **79**, 712 (1957).

also be estimated directly from the intensity of its 3.4 μ absorption band. The amount of hydrocarbon found by the two methods agreed within ±2%.

trans-**Stilbene.**—The next two fractions consisted of a colorless oil (diphenylmethane + bromobenzene) containing varying amounts of colorless crystals (stilbene). In a preliminary experiment these crystals were separated by addition of a little cold hexane, filtration, and washing with cold hexane, m.p. 120–123°. An infrared spectrum and a mixed m.p. established that the substance was *trans*-stilbene. In subsequent experiments the amount of stilbene was determined quantitatively by dissolving the fractions in a known volume of carbon tetrachloride and measuring the intensity of the strong stilbene absorption band at 10.4 μ. The amount of bromobenzene, which was small, was determined from the strength of the 6.77 μ band, and the diphenylmethane was determined either by difference or from the optical density at 3.4 μ, the two methods again giving similar results.

Benzhydryl Benzyl Sulfide.—After several fractions containing only a small amount of unidentified pink oil we obtained several fractions consisting of a colorless oil, which partially solidified on standing. These fractions were combined, treated with a little cold hexane, cooled in ice, and the crystals filtered off, m.p. 69–71°, mixed m.p. with known benzhydryl benzyl sulfide 69.5–71°, mixed m.p. with dibenzyl disulfide, 52–60°. Evaporation of some of the hexane from the filtrate gave a second crop of sulfide, m.p. 68–71°. Removal of the remaining hexane left a viscous oil which infrared examination showed was chiefly a mixture of the sulfide and dibenzyl disulfide. After estimation of the amount of disulfide (*vide infra*) the amount of sulfide in this residue was taken as the difference between the total weight and the weight of disulfide, a procedure which somewhat overestimates the amount of sulfide. However, since the two crystalline crops always accounted for at least 80% of all the sulfide this error does not greatly influence our estimate of the total yield.

Dibenzyl Disulfide.—The infrared spectrum of dibenzyl disulfide differs from that of benzhydryl benzyl sulfide by the presence of a weak but sharp band at 8.40 μ. With known mixtures of sulfide and disulfide it was possible to estimate the disulfide content to about ±5% using this 8.4 μ band. Although the analysis is not as exact as desired, it nevertheless appears to give an approximately correct estimate of the disulfide content of such mixtures. The dibenzyl disulfide content of the residues (*vide supra*) was determined in this fashion. This was done because the usual disulfide analysis,[25] consisting of reduction with zinc to the mercaptan followed by titration with iodine, gave in the present case considerably higher results for dibenzyl disulfide content than was indicated by the infrared method. This suggests that some material of lower equivalent weight also reduced by zinc was present in the residues. Likely possibilities are sulfur or organic polysulfides formed from it.

sym-**Tetraphenylethane.**—After several fractions following the sulfide which contained nothing, we obtained a few fractions which on removal of the solvent gave feathery white crystals, which, recrystallized from hexane, melted at 208–211°; a mixed m.p. with authentic tetraphenylethane[26] showed no depression. The amount of tetraphenylethane was determined simply by weighing the fractions.

Thiobenzophenone (Benzophenone).—The blue color of the reaction mixture faded on exposure to light and air, suggesting the thiobenzophenone originally present had been oxidized all or in part to benzophenone.[27] In agreement with this expectation evaporation of the ether fractions of the chromatogram gave a residue with an infrared spectrum identical with that of benzophenone. The residue formed a 2,4-dinitrophenylhydrazone, m.p. 239–240°.

Decomposition of I in Nitrobenzene.—Fifty ml. of a 0.1 *M* solution of I in nitrobenzene was placed in A, nitrogen passed through the solution at room temperature for over an hour, and the solution subsequently heated at 142° for 11 hr. Nitrogen was passed through the solution during the decomposition. Titration of the excess iodine in C gave a sulfur dioxide yield of 97%. The solution in A was colorless at the end of the decomposition.

The products of the reaction were worked up as described above. The only chromatographic fractions containing significant amounts of material were those containing benzhydryl benzyl sulfide. The yield of crystalline sulfide, m.p. 70–71°, was 84%. No dibenzyl disulfide could be detected.

Reaction of I with Benzyl Mercaptan.—Fifty ml. of chlorobenzene containing 1.77 g. (5 mmoles) of I and 0.62 g. (5 mmoles) of benzyl mercaptan was deaerated with nitrogen at room temperature and was then heated at reflux for 42 hr. using the apparatus and procedure described above for the other decompositions of I. Titration of C showed the evolution of 93% of the theoretical amount of sulfur dioxide.

Chromatography of the residue after removal of the solvent gave 0.38 g. (45%) of diphenylmethane, no stilbene, 0.10 g. (12%) of tetraphenylethane, 1.09 g. (89%) of dibenzyl disulfide (isolated in this case as a pure crystalline compound and identified by m.p. and mixed m.p.) and 0.17 g. of benzhydryl benzyl sulfide (12%).

Decomposition of II in *o*-Dichlorobenzene.—The general procedure was that described for the decomposition of I. From 4.45 mmoles of II in 50 ml. of *o*-dichlorobenzene heated at reflux for 96 hours we obtained 4.15 mmoles (93%) of sulfur dioxide. The solvent was removed by fractional distillation under reduced pressure, and the residue was chromatographed on alumina. The first fractions, which did not appear to contain any bibenzyl, yielded 0.59 mmole (13%) of stilbene. Subsequent fractions consisted of slightly impure benzyl sulfide (72%), which was identified by its infrared spectrum, m.p. and mixed m.p. We did not attempt to determine if toluene was formed in the reaction.

Kinetic Studies of the Decomposition of I and II.—The apparatus used for the kinetic studies was a minor modification of that shown in Fig. 3. Traps B and D were omitted and C was connected directly to A by a length of capillary tubing. In addition a small magnetic stirring bar was placed in the bottom of C to permit gentle stirring of the solution. Weighed amounts of thiolsulfonate and solvent were placed in A, and nitrogen was passed through the solution at room temperature for at least one hour. At that time an aliquot of standard iodine solution was pipetted into C, and the flask was immersed in a silicone oil constant temperature bath regulated to ±0.05°. Nitrogen was passed through the solution during the decomposition at a rate of at least 200 ml./10 min. The iodine solution in C was cooled in ice. The time at which the solution in C became colorless was recorded, and a second aliquot of standard iodine was immediately added. The time at which the solution again became colorless was recorded, and the process was repeated until at least 75% of the expected sulfur dioxide had been liberated. Finally an excess of standard iodine was added, and after a suitable time an infinity value for the amount of sulfur dioxide liberated was obtained by titration of the excess iodine. With I the infinity value always agreed with that expected from the amount of thiolsulfonate taken within ±5%. With II in some solvents the infinity value was as low as 85–90% of the theoretical. The observed infinity values rather than the calculated ones were of course used in subsequent plotting of the data.

In those experiments in which CO_2-free air was passed through the solution during the decomposition standard base was used in trap C instead of iodine. Phenolphthalein was employed as the indicator. Experiments under nitrogen showed that this method gave identical results with the iodine method for both thiolsulfonates.

Decomposition of I in the Presence of Styrene.—In a control experiment a solution of styrene in bromobenzene was deaerated and heated at 142° for 2 hr., a slow stream of nitrogen being passed through the solution during the polymerization. At the end of this time most of the solvent was removed under reduced pressure at room temperature, and the polymer was precipitated by the slow addition of the remaining solution to a large volume of well-stirred methanol. In two otherwise identical experiments Compound I was present in the styrene–bromobenzene solutions at concentrations of 0.03 and 0.106 *M*. The amount of sulfur dioxide evolved showed that Compound I decomposed at essentially the same rate as in bromobenzene alone. The

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(25) H. G. Stone, "Determination of Organic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 194.

(26) J. F. Norris, R. Thomas and B. M. Brown, *Ber.*, **43**, 2959 (1910).

(27) A. Schonberg and A. Mustafa, *J. Chem. Soc.*, 275 (1943); H. Staudinger and H. Freudenberger, *Ber.*, **61**, 1582 (1928).

amount of polymer obtained in the various experiments is shown in Table IV.

Decomposition of Polymeric Thiobenzaldehyde.—A weighed amount (0.3 g.) of polymeric thiobenzaldehyde was dissolved in 25 ml. of bromobenzene and the solution deaerated with nitrogen at room temperature. It was then refluxed for 16 hr. under a nitrogen atmosphere. It was observed that the solution became blue soon after heat was applied. The blue color reached a maximum during the first hour of reflux and then faded rapidly, the solution finally becoming light brown. Infrared analysis of the products showed stilbene had been formed in 31% yield. Some trithiobenzaldehyde (0.07 g.) was also isolated. The other products were not identified.

In a second experiment using half as concentrated a solution of the polymeric thioaldehyde the stilbene yield was higher (40%).

Purification of Solvents. Bromobenzene and Chlorobenzene.—The highest grade commercial products were carefully fractionally distilled; bromobenzene, b.p. 155–156°; chlorobenzene, b.p. 131–132°. **1-Chloronaphthalene** (Eastman Kodak Co. white label) was washed with dilute sodium bicarbonate, dried over sodium sulfate, and fractionally distilled under reduced pressure, b.p. 152–153° (40 mm.).

The best grade commercial **2-methylnaphthalene** was fractionally crystallized four times, about half of the original material being discarded in the process. The remaining hydrocarbon was then fractionally distilled, b.p. 129–130° (25 mm.). **Benzonitrile** was steam distilled; the distillate was extracted with ether; the ether solution was washed with dilute sodium carbonate, dried overnight with calcium chloride, and the ether removed. The residue was fractionally distilled, b.p. 96° (40 mm.). **Methyl benzoate** (Eastman Kodak Co. white label) was washed with dilute sodium bicarbonate, then with water, dried over sodium sulfate and finally fractionally distilled under reduced pressure, b.p. 104–105° (39 mm.). **Nitrobenzene** (Eastman Kodak Co. white label) was fractionally distilled under reduced pressure, b.p. 115° (40 mm.). It gave no measurable acidity when tested in the fashion described by Rosin.[28]

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[28] J. Rosin, "Reagent Chemicals and Standards," 1st. ed., D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 285.

Columbia, S. C.

[Contribution from the Chemistry Division, Oak Ridge National Laboratory[1]]

Studies Involving Isotopically Labeled Formic Acid and its Derivatives.[1,2] V. Studies of the Decarbonylation of Formic, Benzoylformic and Triphenylacetic Acids in Sulfuric Acid

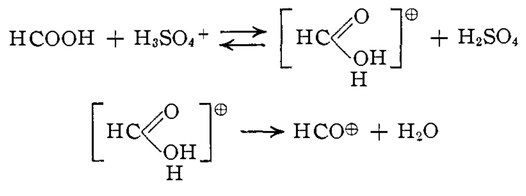
By Gus A. Ropp

Received May 20, 1959

By employing deuterium and carbon-14 isotope fractionation studies, carbon-14 tracer studies and oxygen-18 isotope exchange studies, definite information has been obtained about the mechanism of decarbonylation of formic acid, triphenylacetic acid and benzoylformic acid in concentrated sulfuric acid. The experimental results are in accord with previously proposed mechanisms of decarbonylation of formic and benzoylformic acids. In the case of the triphenylacetic acid decarbonylation, strong evidence is presented that a previously proposed mechanism is incorrect. A tentative mechanism for the decarbonylation of triphenylacetic acid which will account for the experimental observations has been suggested. An oxygen-18 exchange between carbon monoxide and concentrated sulfuric acid has been observed. A general discussion of isotopic methods which are applicable to the study of decarbonylation reactions and other similar reactions is included. Specific activity–per cent reaction curves that facilitate rapid computation of kinetic isotope effects are presented.

I. Introduction

The decarbonylation, or loss of carbon monoxide, by carboxylic acids in concentrated sulfuric acid occurs only with acids in which the group attached to the carboxyl group is one of a very few specific types. The principal acids which decarbonylate are formic,[3] oxalic[4] and triphenylacetic[5] acids, α-hydroxy acids,[6] α-keto acids[7] and acids in which a tertiary alkyl group is attached to the carboxyl group. In many instances the decarbonylation has been reported to proceed quantitatively. Little is known about the details of the mechanisms of any of these reactions. The relationship between log k, the logarithm of the pseudo-first-order rate constant, and the acidity function[7a,8] of the sulfuric acid used has been studied for several decarbonylations. In some instances the activation energies have been measured; in others the effects of various added chemicals on the specific reaction rates have been investigated. The usual view taken of the mechanism of these reactions is that they proceed in a manner similar to that proposed by Hammett[3c] for the decarbonylation of formic acid in excess concentrated sulfuric acid



$$\mathrm{HCOOH + H_3SO_4^+ \rightleftarrows \left[HC\begin{matrix}{\diagup}O\\ \diagdown OH\\ H\end{matrix}\right]^{\oplus} + H_2SO_4}$$

$$\mathrm{\left[HC\begin{matrix}{\diagup}O\\ \diagdown OH\\ H\end{matrix}\right]^{\oplus} \longrightarrow HCO^{\oplus} + H_2O}$$

$$\mathrm{HCO^{\oplus} + H_2SO_4 \longrightarrow CO + H_3SO_4^{\oplus}}$$

Hammett does not explain which is the rate-determining step except to state that if either the first or second steps determined the rate, the observed relation between the rate constant and the acidity function of the sulfuric acid should follow. Hammett also states, "whatever the detailed mechanism (of acid-catalyzed decarbonylation reactions) they necessarily involve the separation of the group attached to the carboxyl group in the form of a positive ion." Presumably,

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[1] Operated by Union Carbide Corp. for the U. S. Atomic Energy Commission.

[2] Preceding paper, C. E. Melton and Gus A. Ropp, This Journal, **80**, 5573 (1958).

[3] (a) E. Schierz, This Journal, **45**, 447 (1923); (b) R. De Right, *ibid.*, **55**, 4761 (1933); (c) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 283.

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