

AN ABSTRACT OF THE THESIS OF

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(Major) (Date)

Title THE THERMAL DECOMPOSITION OF ALKYL BENZENE-
DIAZO SULFONES

Abstract approved: Redacted for privacy
John L. Kice

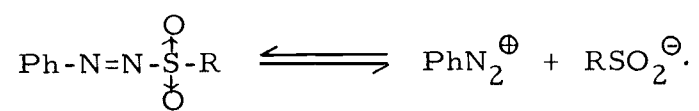
The thermal decomposition of methyl and benzyl benzenediazo sulfones in various solvents has been studied. In benzene, the decomposition of benzenediazo methyl sulfone ($\text{Ph-N=N-SO}_2\text{CH}_3$) produced biphenyl (0.32 mole/mole BMS), azobenzene (0.03 mole/mole BMS) and sulfur dioxide (0.14 mole/mole BMS). In cumene, the decomposition led to the formation of considerable benzene and bicumyl, while the decomposition in diphenylmethane produced benzene, benzhydryl methyl sulfone and tetraphenylethane. These products indicate that decomposition of the methyl diazosulfone in hydrocarbon solvents proceeds in considerable measure by a free radical route. Experiments using the Koelsch radical as a radical scavenger in benzene and measurements of the overall rate of decomposition of the diazosulfone in the same solvent showed that only about one-third of the molecules of the methyl diazosulfone decomposing yield scavengable

free radicals. Possible reasons for this relative low efficiency of radical production are discussed.

In contrast to the behavior of the methyl compound, the decomposition of benzenediazo benzyl sulfone ($\text{Ph-N=N-SO}_2\text{CH}_2\text{Ph}$) in either benzene, cumene or diphenylmethane produced benzaldehyde phenylhydrazone (0.55-0.34 mole/mole BBS), N-benzyl benzaldehyde phenylhydrazone (0.06-0.16 mole/mole BBS) and sulfur dioxide (0.57-0.80 mole/mole BBS) as the principal products. The rate of decomposition of benzyl diazosulfone in benzene solution could be dramatically reduced by the addition of Koelsch radical, the rate of evolution of sulfur dioxide being reduced to approximately the rate at which scavengable free radicals appeared to be produced in the decomposition as measured by the rate of disappearance of Koelsch radical. From this data one concludes that the decomposition of the benzyl diazosulfone in hydrocarbon solvents most likely proceeds by a free radical chain induced decomposition. Some possible chain initiation, propagation and termination steps are proposed and discussed.

In the polar, ionizing solvent acetonitrile, acetanilide is the only important product from the decomposition of either the methyl diazosulfone (0.71 mole/mole BMS) or the benzyl diazosulfone (0.42 mole/mole BBS). A mechanism is proposed which involves as the key intermediate the phenyldiazonium ion produced by the following

dissociation of the diazosulfone:



The Thermal Decomposition of
Alkyl Benzenediazo Sulfones

by

Rolf Steven Gabrielsen

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Date thesis is presented

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Typed by Nancy Kerley for

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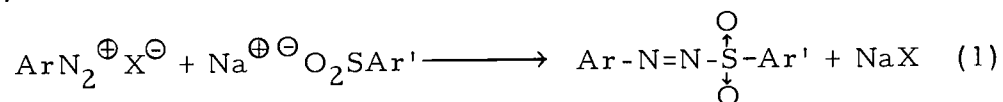
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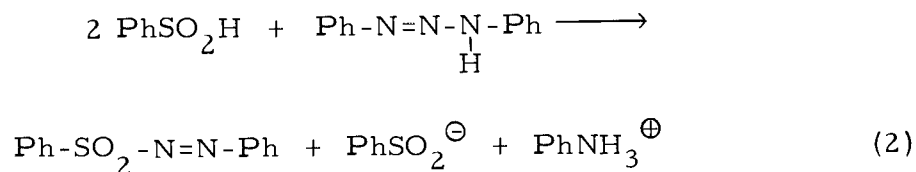
THE THERMAL DECOMPOSITION OF ALKYL BENZENEDIAZO SULFONES

INTRODUCTION

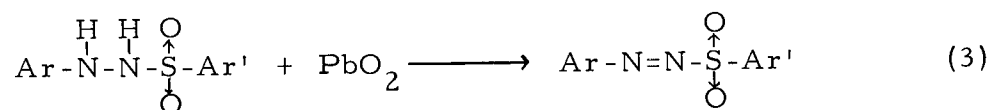
Little chemistry of the diazosulfones ($\text{Ar-N=N-SO}_2\text{R}$) has been accomplished since their first reported synthesis by W. Koenigs (46) in 1877. The preparation of the original diazosulfone was achieved by coupling an aromatic diazonium salt with an aryl sodium sulfinate (eq. 1).



Variations in diazosulfone synthesis include reactions of diazo compounds with sulfinic acids. Hantzsch has described one of these (28) as the reaction of eq. 2.



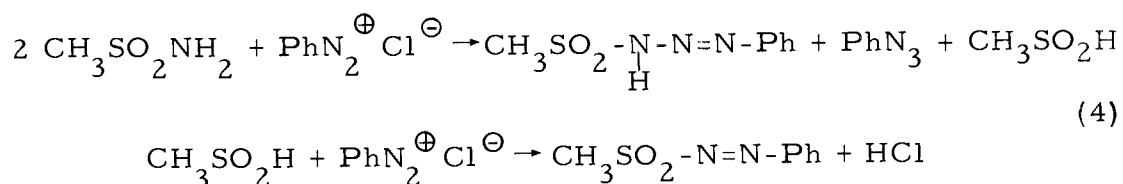
Diazosulfones can also be prepared by oxidation of diaryl sulfonyl hydrazines with mild oxidizing agents (12) such as PbO_2 (eq. 3). This oxidation demonstrates the existence of a sulfone



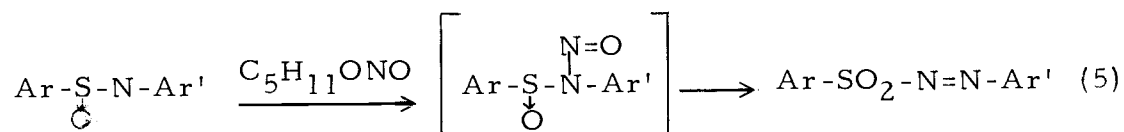
group with an S-N bond, rather than the O-N bond that would be present if these compounds had a diazosulfinate structure,

$\text{Ar}-\text{N}=\text{N}-\text{O}-\overset{\text{O}}{\underset{|}{\text{S}}}-\text{Ar}'$. This is important because the usual method of formation of diazosulfones (eq. 1) could have just as easily resulted in a diazosulfinate as in a diazosulfone.

An aliphatic benzenediazo sulfone was prepared by Dutt (19) by the reaction of diazonium salts with methanesulfonamide. He formulated the reaction according to eq. 4.

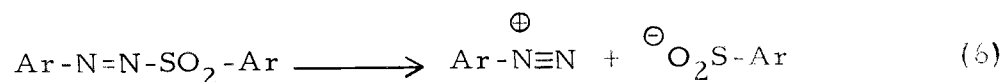


Meerwein (54) achieved a novel preparation of diazosulfones by the reaction of amyl nitrite with aryl sulfinimides (eq. 5).



However, he was unable to isolate the probable N-nitroso intermediate.

Ionization of diazosulfones to salt-like diazonium sulfinates, assumed by Claasz (12) (eq. 6) does not take place according to



Meerwein (54), who was able to isolate true solid ionic diazonium sulfinates only in special cases.

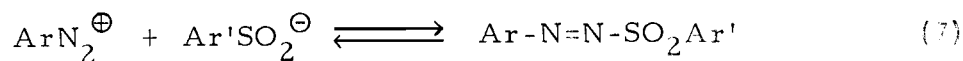
The question of geometrical isomerism of diazosulfones about the $-\text{N}=\text{N}-$ linkage was partially resolved in 1952 by Le Fèvre and

co-workers (22), when they noticed that a reversible change may have been occurring upon irradiation of the diazosulfone in solution. They assigned the trans structure, $\text{Ar}\backslash\text{N}=\text{N}\backslash\text{SO}_2\text{Ar}'$, to the known, isolable isomer but, due to irreversible photodecomposition, were unable to isolate the labile photoisomer, which they assumed was in the cis configuration, $\text{Ar}/\text{N}=\text{N}/\text{SO}_2\text{Ar}'$.

Diazosulfones have found some utility as initiators in the solution polymerization of vinyl compounds (72) and as initiators for the emulsion polymerization of styrene-butadiene mixtures (8). These applications indicate the decomposition of diazosulfones can proceed with the formation of radical intermediates.

The spectral properties of various diazosulfones have been recorded (17, 22, 26, 49).

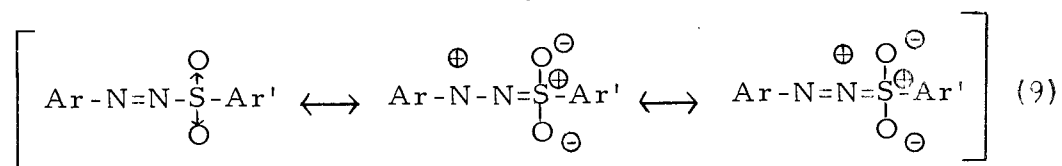
Ritchie, Saltiel and Lewis (64) measured the rate and equilibrium constants for the reaction between substituted diazonium ions and substituted benzenesulfinic acids in buffered methanol (eq. 7). They applied the Hammett equation to their data and



calculated ρ for the equilibrium ($\text{Ar}' = \text{Ph}$) to be +3.8. They suggested that possibly the reason this ρ value is smaller than the ρ observed for the equilibrium of other anions with aryldiazonium ions (eq. 8, $\rho = +4.7$) (50) is due to expanded octet structures

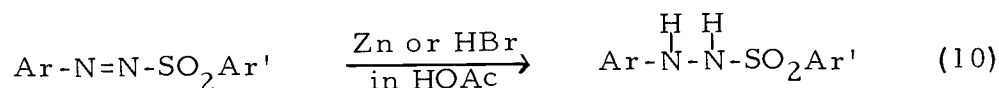


which can be written as contributing forms for the diazosulfone (eq. 9)

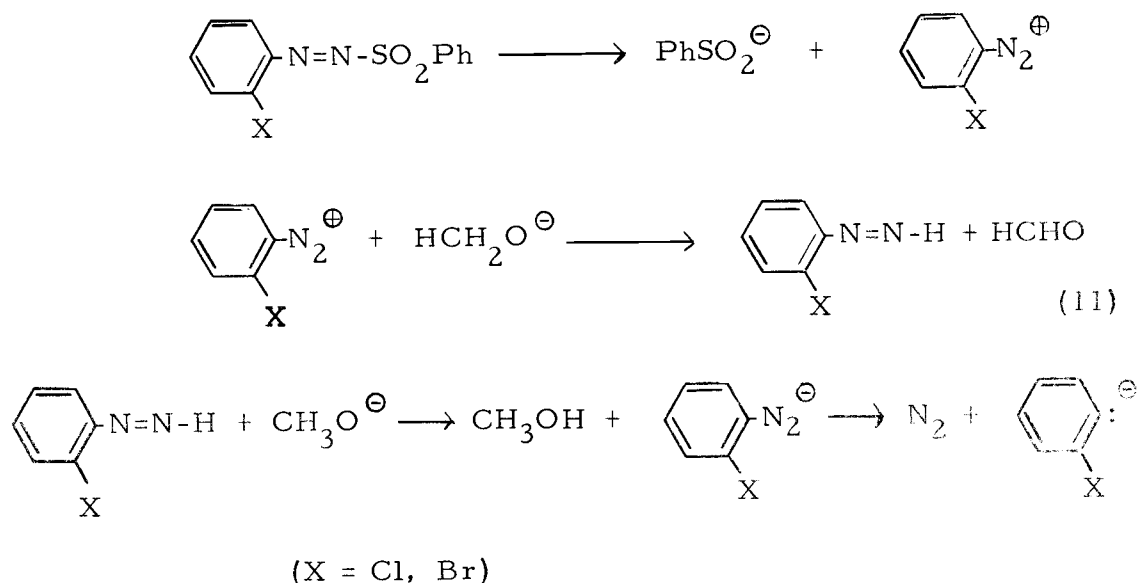


These expanded octet structures could also contribute to lowering the barrier of rotation about the -N=N- bond, consistent with the apparent lack of easily isolated geometrical isomers (22).

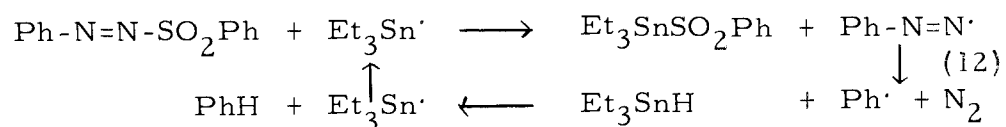
Reduction of the azo group can be accomplished with zinc and acetic acid (10) or hydrobromic acid and acetic acid (43) (eq. 10)



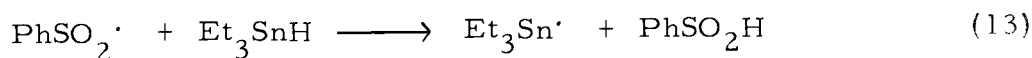
Ionic reactions of o-halophenylazo phenyl sulfones (9) in concentrated base generate, in part, o-halophenyl anions, possibly by the mechanism shown in eq. 11.



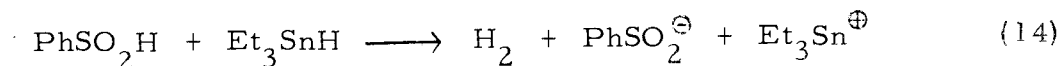
Radical decomposition of benzenediazo phenyl sulfone induced by organotin hydrides has been reported recently (58). The free radical decomposition of this diazosulfone was accelerated ten-fold by the addition of an organotin hydride, with a bimolecular homolytic substitution (S_H2) mechanism being invoked to explain the induced decomposition (eq. 12).



The products of the induced decomposition reaction are benzene, nitrogen and triethylstannyl phenyl sulfone ($\text{Et}_3\text{SnSO}_2\text{Ph}$), all found in equimolar amounts. The stannyl radicals are suggested to induce the decomposition by covalent attachment to the sulfonyl group, synchronous with loss of the phenylazo radical. Free phenylsulfonyl radicals may be precluded for, if formed, they would abstract a hydrogen atom from the tin hydride to give benzenesulfinic acid (eq. 13). With further hydride, the sulfinic acid would give



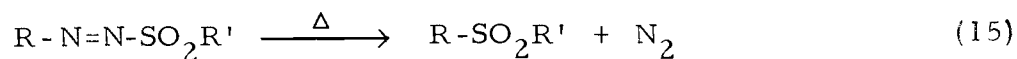
hydrogen and the stannyl sulfinic acid (eq. 14).



Although S_H2 mechanisms are rare, such a mechanism could possibly be operative in this case.

A review of sulfur chemistry through 1955 found in Volume 9 of Methoden der Organischen Chemie (Houben-Weyl) (56) explains the

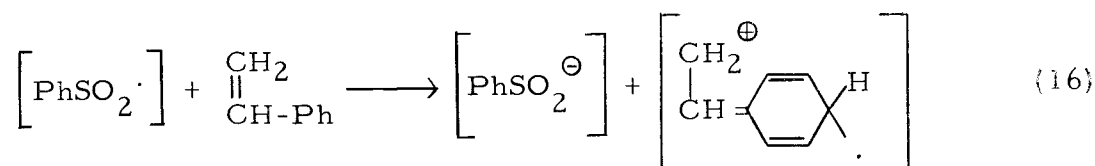
chemistry of diazosulfones in a brief paragraph. The references cited (28, 46) claim that diazosulfones decompose thermally to sulfones with loss of nitrogen (eq. 15). In none of these references do



the investigators, however, actually confirm this behavior.

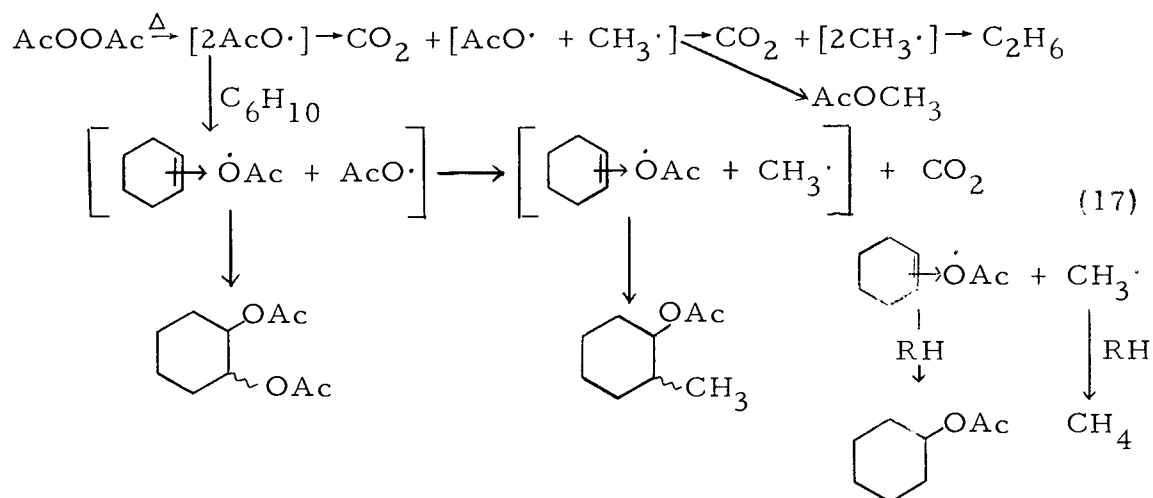
Straightforward thermal decomposition of benzenediazo phenyl sulfone in hydrocarbon solvents has been studied extensively by Overberger and Rosenthal (61, 65). The kinetics of this decomposition (65) in toluene were followed by nitrogen evolution, and an autocatalyzed first order decomposition was observed. Linear first order kinetics could be obtained, however, by suspending calcium oxide in solution, indicating that the autocatalysis was due to an acidic product produced in the decomposition. Solvent radical induced decomposition complicated the decomposition also, with the order of induced decomposition being two in toluene under a nitrogen atmosphere and with calcium oxide suspended in the solvent. Surprisingly, the addition of free radical scavengers (trinitrobenzene, iodine, chloranil, styrene) accelerated the decomposition instead of the anticipated inhibition of radical induced decomposition. Overberger and Rosenthal attempted to explain this anomalous behavior in an unusual way. Specifically, in the case of the decomposition of benzenediazo phenyl sulfone in benzene with added styrene, they suggested that styrene interacted with the caged radical pairs $(\text{PhSO}_2' \cdot \text{N}=\text{N}-\text{Ph})$

to form a loose π -complex species, which they wrote as shown in eq. 16. The formation of this complex effectively removed the



$\text{PhSO}_2 \cdot$ radicals from the caged pairs and thereby accelerated the decomposition rate by preventing the cage recombination of $[\text{PhSO}_2 \cdot \cdot \text{N}=\text{N-Ph}]$ radical pairs. They also suggested that the other scavengers might interact in an analogous fashion with caged radical pairs. Thus, their view was that the added scavengers accelerated the rate of decomposition by reducing the amount of cage recombination of initially formed radical pairs to diazosulfone. In view of what is known about the ability of low concentrations of radical scavengers to prevent cage recombination in other systems, this explanation certainly seems questionable. For example, although Hammond and Trapp (74) were able to eliminate the cage recombination product tetramethylsuccinonitrile from the decomposition of azobisisobutyronitrile (AIBN) by thermally decomposing the azo compound in liquid bromine, Hammond and co-workers (27) found a substantial amount of tetramethylsuccinonitrile formed by the decomposition of AIBN in a dilute solution of bromine in carbon tetrachloride. Since the cage recombination reaction disappears in liquid bromine, Hammond suggested that the cage reaction must involve an intermediate that is scavengable only by reactive species present in high

concentration in direct contact with the azo compound. Bevington (3) has investigated the decomposition of AIBN in benzene with added styrene as a scavenger and found only a two-fold decrease in the yield of the cage recombination product, tetramethylsuccinonitrile, for a corresponding 280-fold increase in styrene concentration. Also, the decomposition of benzoyl peroxide in cyclohexane with added styrene, studied by Swain and co-workers (70), shows only a minor decrease (eight percent) in cage recombination products (phenylbenzoate and biphenyl) with an increase of styrene concentration from 0.015 M to 0.120 M. Formation of a π -complex from a phenylsulfonyl radical and styrene proposed by Overberger and Rosenthal is perhaps made more attractive, however, in view of a suggestion by Martin, Taylor and Drew (53), who studied the thermal decomposition of acetyl peroxide in cyclohexene, both in the absence and presence of the radical scavenger, galvinoxyl. The yields of the following products: carbon dioxide, ethane, methyl acetate, 2-methylcyclohexyl acetate and 1,2, -diacetoxycyclohexane, were unaltered by the addition of an 11.1 molar excess of galvinoxyl. Since their yield is not altered by a large excess of galvinoxyl these various products must all arise by cage recombination reactions. The yield of cyclohexyl acetate, however, was greatly depressed by the addition of galvinoxyl. The formation of the various products may be accounted for by the reaction scheme in eq. 17, proposed by Martin. This scheme is consistent

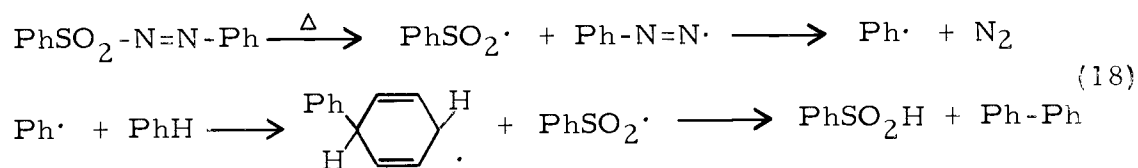


with their observation that the presence of galvinoxyl was unable to intercept the caged radical pairs (in brackets) and alter the amounts of products formed by cage recombination. The decrease yield of cyclohexyl acetate in the presence of galvinoxyl suggests that its formation occurs through an intermediate radical with a lifetime long enough to allow its escape from the solvent cage. Martin proposed that the radical leaves the solvent cage in which it is formed as a π -complexed radical species, denoted by the arrow from the cyclohexene double bond to the acetoxy radical. Thus, cyclohexene is able to confer some degree of stability to the acetoxy radical which would, without π -complex formation, decarboxylate rapidly to methyl radical. Moreover, the decomposition of acetyl peroxide in isooctane yields 1.25 times as much carbon dioxide as does the decomposition in cyclohexene, again illustrating the stabilization of the acetoxy radical by solvents which can form π -complexes with it.

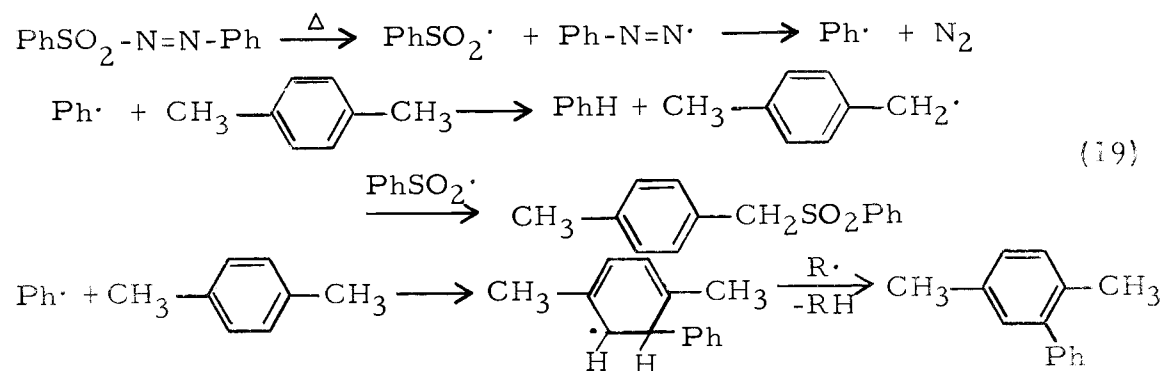
In this same manner then, the π -complex formation between

a free radical scavenger and a phenylsulfonyl radical, postulated by Overberger and Rosenthal, may explain why the decomposition of benzenediazophenylsulfone is accelerated in the presence of free radical scavengers such as styrene.

The products of the decomposition of benzenediazo phenyl sulfone (61) in benzene and p-xylene in a nitrogen atmosphere with calcium oxide suspended in the solvent are indicative of a radical reaction. The principal products in benzene are biphenyl, nitrogen and benzenesulfinic acid. These products can be accounted for on the basis that the diazosulfone initially cleaves to phenylazo and phenylsulfonyl radicals; this is then followed by the reaction of these radicals with the solvent (eq. 18) to give the observed products. In p-xylene, the major products are benzene, nitrogen,

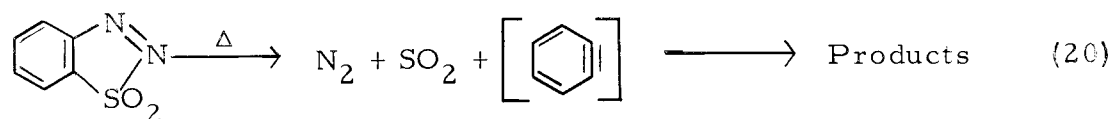


2, 5-dimethylbiphenyl and p-methylbenzyl phenyl sulfone. A similar mechanism was advanced to account for these products (eq. 19).



The possibility of radical recombination reactions involving both the initial and solvent derived radicals accounts for the numerous minor products isolated in both decompositions. Clearly, this is not the clean decomposition suggested in Houben-Weyl.

Recently, the decomposition of 1,2,3, -benzothiadiazole-1,1-dioxide in a variety of solvents was investigated (31). The author favored a one-step mechanism to generate benzyne (eq. 20), with



little, if any, decomposition occurring from an ionic or radical pathway.

A preliminary study of the thermal decomposition of benzyl and methyl benzenediazo sulfones in this laboratory by R. Engebrecht (20) indicated a complex and intriguing mechanistic problem. The methyl and benzyl diazosulfones differ from each other in the rate and manner of evolution of sulfur dioxide and in the decomposition products isolated.

The principal difference in products was that the methyl diazosulfone decomposed in benzene solution with the loss of only a small amount (17 percent) of sulfur dioxide and the formation of 0.31 mole biphenyl/mole of methyl benzenediazo sulfone. The large yield of biphenyl is reminiscent of Overberger and Rosenthal's results with benzenediazo phenyl sulfone and suggests that the methyl diazosulfone

is decomposing by an analogous mechanism. On the other hand, benzenediazo benzyl sulfone decomposed in benzene solution with the evolution of 75 percent of the theoretical amount of sulfur dioxide, and the principal organic products were benzaldehyde phenylhydrazone (0.26 mole/mole diazosulfone), and N-benzyl benzaldehyde phenylhydrazone (0.15 mole/mole), both of which retain the nitrogen of the original diazosulfone. Only a trace amount of biphenyl was found.

The gross difference in products between the methyl and benzyl benzenediazo sulfone indicates that there must be significant differences in their modes of decomposition.

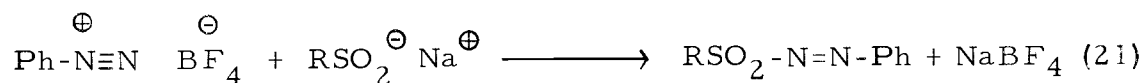
Moreover, the methyl diazosulfone evolved sulfur dioxide in a smooth first order manner, while the benzyl diazosulfone showed a long induction period, followed by a relatively rapid and approximately first order evolution of sulfur dioxide.

Although benzenediazo methyl sulfone apparently decomposed by a straightforward free radical reaction, the benzyl diazosulfone decomposition reaction merited further study because of the nitrogen-containing products formed and the manner in which sulfur dioxide was evolved. This work was begun to determine the mechanisms of the thermal decomposition reactions of these aliphatic benzenediazo sulfones.

RESULTS

Synthesis of Alkyl Benzenediazo Sulfones

The alkyl benzenediazosulfones, $R-SO_2-N=N-Ph$, used in this work were prepared by adding an aqueous solution of benzenediazonium fluoborate to a cold, stirred solution of the appropriate sodium alkylsulfinate (eq. 21). This is the method that was used for the first



reported preparation of a diazosulfone (46). The methyl and t-butyl diazosulfones [$R = CH_3-$ and $(CH_3)_3C-$] were easily purified but the benzyl diazosulfone ($R = PhCH_2-$) was much more difficult to obtain pure. The purity of the sodium α -toluenesulfinate used in the preparation is apparently the factor which determines the purity of this diazosulfone, for carefully prepared and purified sodium α -toluenesulfinate gave benzenediazo benzyl sulfone with a melting point eight degrees higher than the previously reported value of $92-94^{\circ}$ (dec.) (20). All of the benzyl diazosulfone used in this work with the exception of that used to obtain Curve A of Figure 3 had the lower melting point of $94-95^{\circ}$ (dec.), because it was not until almost all of the work had been completed that the benzyl diazosulfone of m. p. $100-101^{\circ}$ (dec.) was prepared.

Product Studies

The thermal decomposition of the alkyl benzenediazo sulfones was studied in several different solvents under various conditions. The thermal decompositions were carried out under nitrogen in a vessel provided with a gas inlet tube and a condenser (39). The sulfur dioxide liberated during the decomposition was swept out with a slow stream of nitrogen and oxidized with aliquots of standard iodine solution in a trap connected by a length of tubing to the top of the condenser. In this manner both the rate at which sulfur dioxide was evolved, and the total amount of sulfur dioxide evolved could be determined. After about five half-lives, the vessel was removed from the constant temperature bath and the solvent was removed under reduced pressure. The residue was then chromatographed on alumina and the identity of the various chromatographic fractions was determined.

Benzenediazo Methyl Sulfone (BMS)

The thermal decomposition of the diazosulfone was studied in four different solvents. The results are summarized in Table 1.

Products in benzene. The products of the decomposition of BMS (0.135 M) in benzene at 80.1° are tabulated in the first column of Table 1. A total of 0.14 mole of sulfur dioxide was evolved per

Table 1. Products of the thermal decomposition of BMS in various solvents.

Product	Run:	Product Recovered (mole/mole BMS)				
		1	2	3	4	5
Biphenyl		0.26	0.32			
Azobenzene		0.14	0.032			
Phenyl methanesulfonate		0.069		0.074		
1,2- (or 2,2) Bismethane-sulfonyl phenylhydrazine		0.05				
Sulfur dioxide		0.14	0.14	0.033	0.11	0.03
<u>p</u> -Phenylazobenzene			0.02			
Benzene				0.24	0.23	
Bicumyl				0.12		
<u>o</u> -Phenyldiphenylmethane					0.04	
<u>p</u> -Phenyldiphenylmethane					0.04	
1,1,2,2-Tetraphenylethane					0.065	
Benzhydryl methyl sulfone					0.11	
Acetanilide						0.71

Run 1 - 0.135 M BMS in benzene, Temp. = 80.1°

Run 2 - 0.10 M BMS in benzene with 1.8 M excess calcium oxide suspended in solvent, Temp. = 80.1°

Run 3 - 0.135 M BMS in cumene, Temp. = 79.6°

Run 4 - 0.10 M BMS in diphenylmethane, Temp. = 80.1°

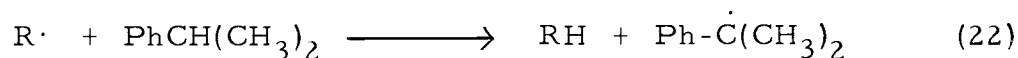
Run 5 - 0.10 M BMS in acetonitrile, Temp. = 82°

mole of BMS decomposing. Chromatography of the decomposition residue gave four identifiable compounds, biphenyl (0.26 mole), azobenzene (0.14 mole), phenyl methanesulfonate (0.069 mole) and either 1,2- or 2,2-bismethanesulfonyl phenylhydrazine (0.05 mole), all yields in mole/mole BMS decomposing. The isolation and purification of these compounds was made more difficult by the formation of a large amount of intractable tar, apparently a characteristic of the thermal decomposition of azo compounds in general (77, p. 34). The four products isolated and identified account for only a modest fraction of the functional groups originally present in the diazosulfone. Thus in this decomposition in benzene only 31 percent of the sulfone groups and 45 percent of the phenyl groups initially present in the diazosulfone are accounted for in the products. Infrared spectra of the intractable tars isolated indicate that the tars contain sulfone, phenyl and N-H groups. Small quantities of more complex products than those identified are no doubt also formed, but these could not be identified in the present work.

Products in benzene with added calcium oxide. Because Overberger and Rosenthal had observed that calcium oxide suspended in the solvent influenced both the rate and products in the decomposition of benzenediazo phenyl sulfone (65), we investigated its effect on the decomposition of BMS in benzene. The results are shown in Column 2 of Table 1. The yield of sulfur dioxide (0.14 mole/mole

BMS) was unchanged. The yield of biphenyl was somewhat larger (0.32 mole/mole BMS) than in the absence of calcium oxide, and the yield of azobenzene was significantly lower (0.032 mole/mole BMS). No phenyl methanesulfonate or bismethanesulfonyl phenylhydrazine was found, but a small quantity of p-phenylazobenzene was isolated (0.02 mole/mole BMS).

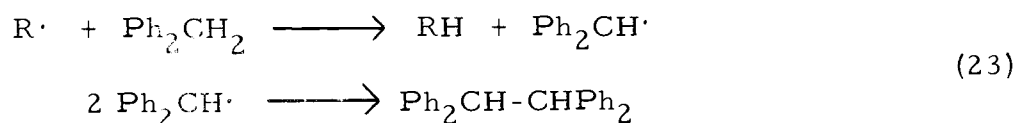
Products in cumene. Cumene (isopropylbenzene) is known to be quite reactive toward many free radicals in reactions of the type shown in eq. 22.



The cumyl radicals formed in eq. 22 often dimerize to bicumyl (14, 30, 62). It was of interest therefore to see what effect the use of cumene as the solvent might have on the thermal decomposition products of BMS. The results are shown in Table 1, Column 3. One sees that only 0.033 mole sulfur dioxide was evolved per mole of BMS decomposing. The principal organic products which could be identified were benzene, (0.24 mole/mole BMS) bicumyl or 2,3-dimethyl-2,3-diphenylbutane (0.12 mole/mole BMS), and phenyl methanesulfonate (0.074 mole/mole BMS).

Products in diphenylmethane. Diphenylmethane is an even better hydrogen atom transfer agent toward free radicals than cumene (6). It was therefore also studied as the solvent for the thermal decomposition of BMS. In diphenylmethane (Table 1, Column 4), the

decomposition evolved 0.11 mole of sulfur dioxide per mole of BMS decomposing. The organic products which could be identified included benzene (0.23 mole/mole BMS), o- and p-phenyldiphenyl methane (each 0.04 mole/mole BMS), 1,1,2,2-tetraphenylethane (0.065 mole/mole BMS) and diphenylmethyl methyl sulfone (0.11 mole/mole BMS). Tetraphenylethane has been observed in other systems as a product of free radical reactions in diphenylmethane (13, 34) and presumably results from coupling of two diphenylmethyl radicals formed by hydrogen atom transfer from the solvent to free radicals (eq. 23).



Products in acetonitrile. We also studied the decomposition of BMS in a highly polar, ionizing solvent, acetonitrile. Under those conditions, the sole organic product which could be isolated and identified from the thermal decomposition of a 0.10 M solution of BMS was acetanilide (0.71 mole/mole BMS). Only 0.03 mole of sulfur dioxide was evolved per mole BMS during the decomposition in acetonitrile (Table 1, Column 5).

Benzenediazo Benzyl Sulfone (BBS)

The products of the thermal decomposition of benzenediazo benzyl sulfone were determined in the same solvents and in the same manner as the products of the decomposition of benzenediazo

methyl sulfone. However, the products recovered and identified in the thermal decomposition of BBS account for a greater percentage of the groups initially present in the diazosulfone than do the products of the decomposition of benzenediazo methyl sulfone. Here, as in the methyl diazosulfone decomposition, a considerable amount of interactable tar is also formed. The results of the various product studies with the benzyl diazosulfone are summarized in Table 2.

In the decomposition of benzenediazo benzyl sulfone the amount of sulfur dioxide evolved in the decomposition in benzene (Run 1), cumene (Run 2), or diphenylmethane (Run 3) was much larger (90.57-0.80 mole/mole BBS) than the amount of sulfur dioxide evolved in the decomposition of the methyl diazosulfone in these same solvents (0.03-0.14 mole/mole BMS). The major organic products isolated from the decomposition of BBS in these three solvents were in each case the same, benzaldehyde phenylhydrazone and N-benzyl benzaldehyde phenylhydrazone. The yield of benzaldehyde phenylhydrazone ranges from 0.34 to 0.55 mole/mole BBS, being highest in benzene and lowest in diphenylmethane. The yield of N-benzyl benzaldehyde phenylhydrazone is lower (0.06 to 0.16 mole/mole BBS) and, conversely, is largest in diphenylmethane and smallest in benzene. Traces of azobenzene (0.01 mole/mole BBS) and biphenyl (0.03 mole/mole BBS) were formed in the decomposition of the benzyl diazosulfone in benzene. In cumene as solvent, the decomposition produced

Table 2. Products of the thermal decomposition of BBS in various solvents.

Product	Run:	Product Recovered (mole/mole BBS)			
		1	2	3	4
Sulfur dioxide		0.66	0.57	0.80	0.33
Benzaldehyde phenylhydrazone		0.55	0.46	0.34	
N-Benzyl benzaldehyde phenyl- hydrazone		0.06	0.12	0.16	0.03
Biphenyl		0.02			
Azobenzene		0.01			
Toluene			0.01	0.05	
Benzene			0.11	0.15	
Acetanilide					0.42

Run 1 - 0.078 M BBS in benzene, Temp. = 54.8°

Run 2 - 0.08 M BBS in cumene, Temp. = 79.6°

Run 3 - 0.10 M BBS in diphenylmethane, Temp. = 80.1°

Run 4 - 0.10 M BBS in acetonitrile, Temp. = 82°

some benzene (0.11 mole/mole BBS) and a small amount of toluene (0.01 mole/mole BBS). No bicumyl could be detected in the products. With diphenylmethane as solvent, there was both more benzene (0.15 mole/mole BBS) and more toluene (0.05 mole/mole BBS) formed. No tetraphenylethane could be isolated.

As was also true with BMS, the use of the highly ionizing solvent acetonitrile (Run 4) led to an entirely different set of products than those formed in benzene, cumene or diphenylmethane. As with the methyl diazosulfone, acetanilide was the major organic product (0.42 mole/mole BBS), although a very small amount of N-benzyl benzaldehyde phenylhydrazone (0.03 mole/mole BBS) was also formed. The amount of sulfur dioxide evolved (0.33 mole/mole BBS) was considerably lower than in any of the hydrocarbon solvents. No benzaldehyde phenylhydrazone could be isolated.

Benzenediazo t-Butyl Sulfone (BtBuS)

A less extensive study was made of the thermal decomposition of benzenediazo t-butyl sulfone. This involved the use of only benzene as the solvent. Since only a small quantity of the t-butyl diazosulfone was available, the yields of most of the various decomposition products were determined in only semi-quantitative fashion. The decomposition of t-butyl benzenediazosulfone (0.07 M) in benzene evolved 0.36 mole of sulfur dioxide per mole BtBuS decomposing.

This is lower than the amount of sulfur dioxide evolved from BBS in benzene (0.66 mole/mole BBS) but considerably more than the amount evolved from the methyl diazosulfone (0.14 mole/mole BMS). The major organic products isolated and identified were 1', 1'-dimethyl benzeneazoethane (tBu-N=N-Ph) (about 0.25 mole/mole diazosulfone) and biphenyl (0.10 mole/mole diazosulfone). Two other products were isolated in smaller yield, but were not conclusively identified.

Kinetic Studies of the Thermal Decomposition of Alkyl Benzenediazo Sulfones

Because the alkyl benzenediazo sulfones exhibit well defined visible and ultraviolet absorption spectra, one might have hoped to follow the disappearance of the diazosulfone by observing the change in the visible absorption of the solution with respect to time. This was attempted with the benzyl diazosulfone, but no reasonable kinetics could be obtained because the decomposition resulted in a deep red solution. Since the decomposition of the methyl diazosulfone also forms a deep red solution, and some precipitate is deposited, no attempt was made to investigate it kinetically using this procedure.

NMR Kinetic Method

The NMR spectrum of benzenediazo methyl sulfone shows a sharp singlet at 7.52τ due to the methyl protons of the CH_3SO_2^-

group. During the course of the decomposition this signal disappears. This suggested that one might be able to use the rate of disappearance of this signal as a means of measuring the rate of decomposition of the diazosulfone. A similar situation exists with BBS. Here the CH_2 protons of the benzyl group give a sharp singlet at 5.75 τ which disappears completely during the course of the decomposition.

The exact procedure used was as follows. A solution of the diazosulfone was made up in benzene and a small amount of cyclohexane was added to serve as an internal proton standard. The solution was transferred to an NMR tube, the contents of the tube were deoxygenated, and the tube was sealed under reduced pressure. At appropriate time intervals the relative strengths of the CH_3SO_2^- (or $-\text{CH}_2\text{SO}_2^-$) singlet and the cyclohexane singlet were determined, and from such measurements the change in the concentration of the diazosulfone with time was determined.

The method has certain disadvantages, however. For one thing, the NMR tube is sealed so that the sulfur dioxide evolved during the decomposition cannot escape as it could in the decomposition for product studies. Also, the concentrations necessary to obtain a good signal to noise ratio are 0.20 M, approximately twice as concentrated as the solutions used for product studies, and twenty times as concentrated as the solutions used for the sulfur dioxide kinetic method.

Sulfur Dioxide Evolution Kinetic Method

We have seen that some sulfur dioxide is evolved in all the diazosulfone decompositions. The rate at which this gas is evolved can be followed by sweeping it out of the reaction vessel as it is produced with a slow stream of nitrogen and observing the time necessary for the sulfur dioxide evolved to reduce an aliquot of standardized iodine solution in a trap attached to the reaction vessel.

As will be seen shortly, in some cases, the rate of evolution of sulfur dioxide parallels closely the rate of disappearance of the diazosulfone as measured by the NMR method. In other cases, however, it does not, a result that is thought to have considerable significance in terms of the possible mechanisms allowed for those particular diazosulfone decompositions.

Benzenediazo Methyl Sulfone Kinetics

Sulfur dioxide evolution method. A plot of $\log (1 - \text{SO}_2/\text{SO}_{2\infty})$ vs. time for the thermal decomposition of the methyl diazosulfone in benzene at 80.0° showed good first order kinetics for the first half-life (Figure 1, Curve A); then the rate of evolution of sulfur dioxide accelerated for the remainder of the decomposition. Suspending a 1.8 M excess of calcium oxide in a solution of the methyl diazosulfone in benzene slowed the initial rate of evolution of sulfur dioxide slightly

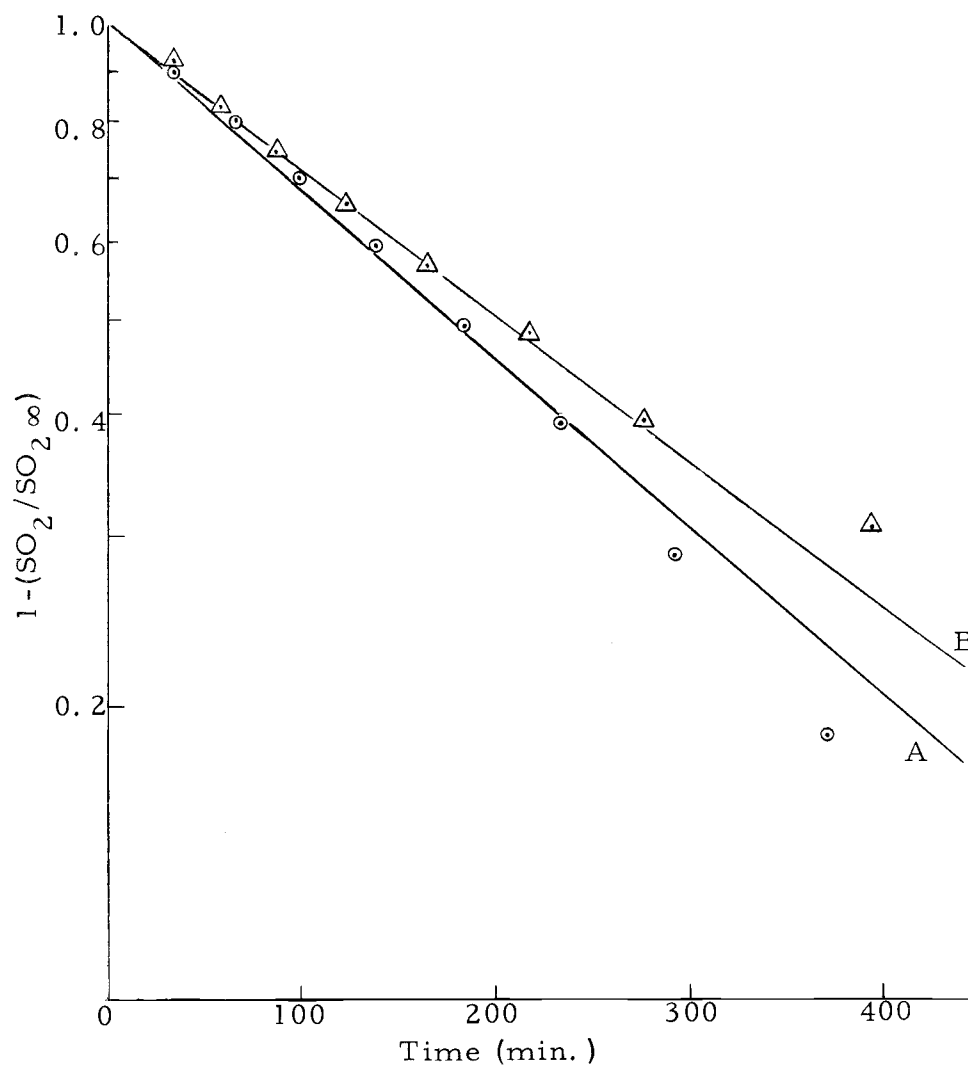


Figure 1. Plot of $\log (1 - \text{SO}_2 / \text{SO}_{2\infty})$ vs. time for the decomposition of 0.10 M BMS at 80.0° in benzene (Curve A, ○) and with 0.18 M CaO in benzene (Curve B, Δ).

(Figure 1, Curve B), and stopped the accelerated rate of evolution of sulfur dioxide after the first half-life. The initial slope of the run (Curve A) in the absence of suspended calcium oxide indicates a rate constant for diazosulfone decomposition of $6.5 \times 10^{-5} \text{ sec}^{-1}$. That for the run in the presence of suspended calcium oxide gives a rate constant of $5.5 \times 10^{-5} \text{ sec}^{-1}$.

NMR method. The disappearance of the methyl diazosulfone itself, as measured by the NMR method using the methyl singlet at 7.52τ also followed good first order kinetics (Figure 2), but the first order rate constant obtained from the slope of Figure 2, $9.3 \times 10^{-5} \text{ sec}^{-1}$, is about 50 percent faster than those estimated from the SO_2 evolution experiments. The probable reason for this apparent discrepancy would appear to be as follows. The results of the sulfur dioxide evolution experiments in the presence and absence of suspended calcium oxide indicate clearly that acidic materials are capable of accelerating the decomposition of the diazosulfone. If not removed from the solution as formed, sulfur dioxide can presumably act as an acid catalyst for the decomposition. Since the conditions of the NMR experiments necessarily preclude the removal of sulfur dioxide as it is formed, this could easily be the reason that the decomposition, when followed by the NMR procedure, appears to proceed somewhat more rapidly than in either of the runs followed by the sulfur dioxide evolution method.

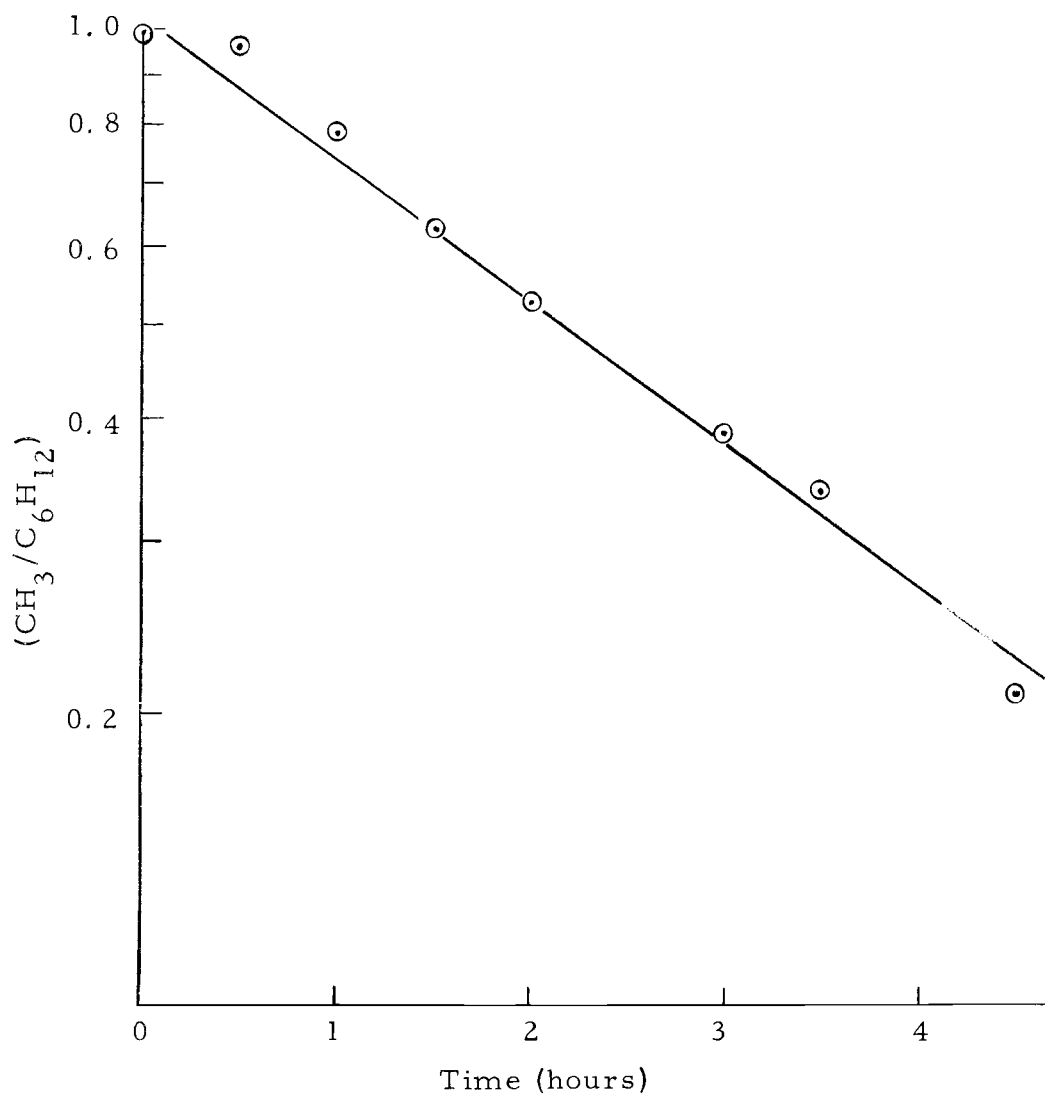


Figure 2. Plot of the log of the ratio of the area of the methyl proton resonance of BMS to the area of cyclohexane (internal proton standard), $(\text{CH}_3/\text{C}_6\text{H}_{12})$ vs. time for the decomposition of 0.20 M BMS in benzene at 80.1°.

Benzenediazo Benzyl Sulfone Kinetics

Sulfur dioxide evolution method. Plots of $\log (1 - \text{SO}_2/\text{SO}_2 \infty)$ vs. time for the thermal decomposition of 0.01 M solutions of BBS in benzene at 55.0° are shown in Figure 3. An approximate two hour induction period is followed by a rapid first order evolution of sulfur dioxide. The slope of the plot after the induction period, although not the length of the induction period itself, appeared to depend upon the purity of the benzyl diazosulfone used. The slope of the linear portion of the plot for the decomposition of a sample of BBS having a melting point of 100-101° (dec.) (Curve A, Figure 3) gives a "rate constant," k_{SO_2} of $0.57 \times 10^{-4} \text{ sec}^{-1}$, while the run using BBS with a melting point of 94-95° (dec.) (Curve B, Figure 3) gives a "rate constant" almost twice as great, $1.13 \times 10^{-4} \text{ sec}^{-1}$.

Kinetic studies of the rate of sulfur dioxide evolutions were also carried out for the decomposition of BBS in cumene, diphenylmethane, and acetonitrile. In all of these solvents, the length of the induction period preceding sulfur dioxide evolution was much shorter than that observed for the decomposition of BBS in benzene at 55°, and the "rate constant," as measured from the slope of the linear $\log (1 - \text{SO}_2/\text{SO}_2 \infty)$ vs. time plot after the induction period, was considerably smaller than the "rate constant" from the slope of the same portion of plots for the decomposition of BBS in benzene at the same

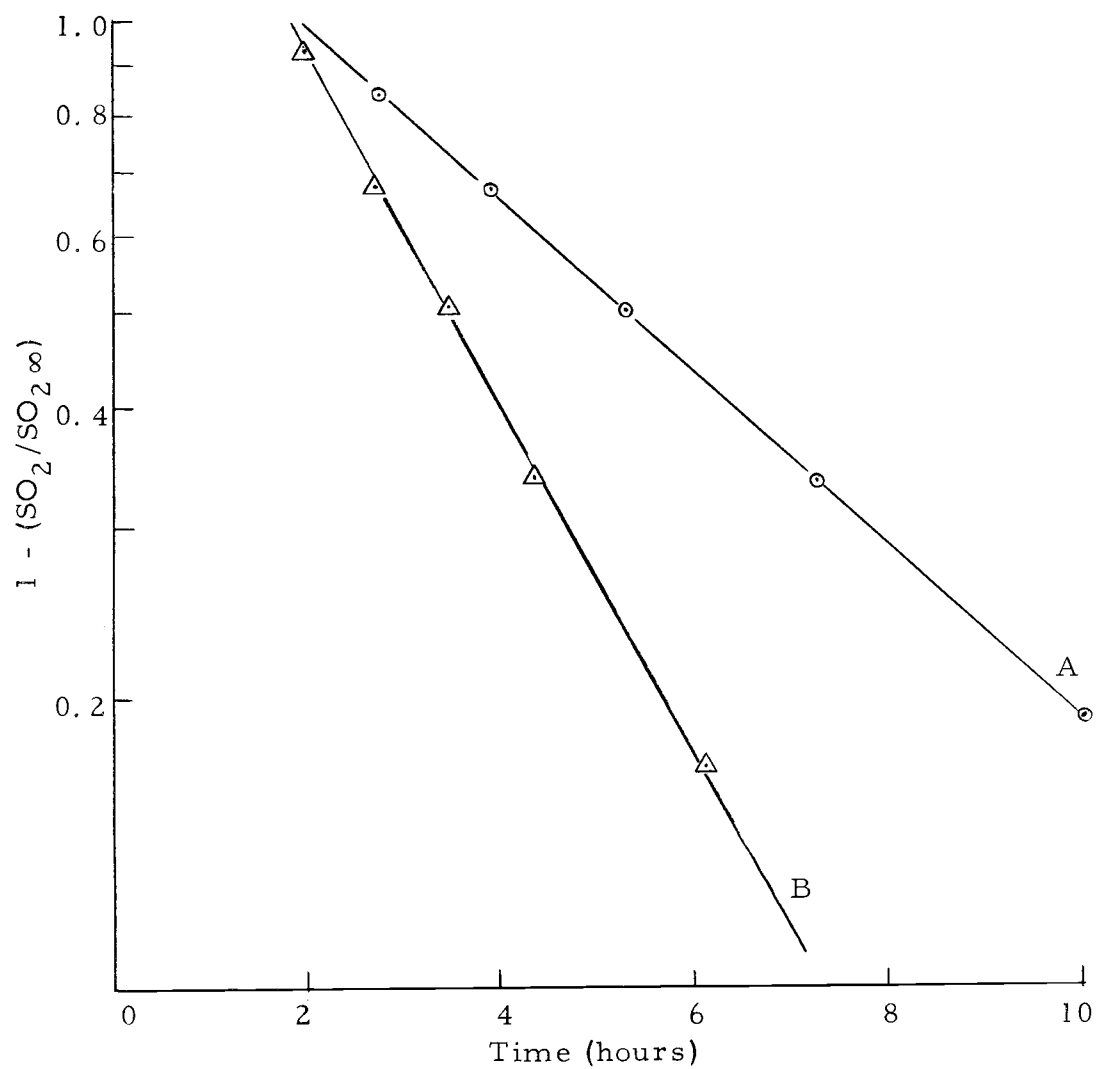


Figure 3. Plot of $\log (1 - \text{SO}_2/\text{SO}_{2\infty})$ vs. time for the decomposition of 0.01 M BBS in benzene at 55.0° . Curve A, with BBS m.p. $100-101^\circ$ (dec.); Curve B, with BBS m.p. $94-95^\circ$ (dec.).

temperatures. The results for cumene are shown in Figure 4, those for diphenylmethane in Figure 5, and those for acetonitrile in Figure 6. The data for the various kinetic runs on the decomposition of BBS using the sulfur dioxide evolution method are summarized in Table 3.

Table 3. BBS decomposition. Sulfur dioxide evolution method.

Solvent	(BBS), <u>M</u>	Temperature	Induction Period	"k _{SO₂} ", "sec ⁻¹ " ¹
PhH	0.01 ²	55.0°	2 hr.	0.57 x 10 ⁻⁴
PhH	0.01	55.0°	2 hr.	1.13 x 10 ⁻⁴
PhCH(CH ₃) ₂	0.08	79.5°	45 min.	0.66 x 10 ⁻⁴
Ph ₂ CH ₂	0.10	80.1°	10 min.	1.5 x 10 ⁻⁴
CH ₃ CN	0.10	82°	10 min.	2.0 x 10 ⁻⁴

¹The first order rate constant obtained from the linear slope of the plot of $\log (1 - \text{SO}_2/\text{SO}_{2\infty})$ vs. time.

²Determined using BBS, m. p. 100-101° (dec.). All other kinetics obtained using BBS, m. p. 94-95° (dec.).

The rate of evolution of sulfur dioxide from a benzene solution of the benzyl diazosulfone at the same concentration of diazosulfone as was used for the NMR kinetic method (0.20 M) is seen in Figure 7. The plot of $\log (1 - \text{SO}_2/\text{SO}_{2\infty})$ vs. time shows neither a well defined induction period nor a reasonable fit to a first order evolution of sulfur dioxide in the "linear" portion of the curve, as was observed in the decomposition of 0.01 M BBS in benzene (Figure 3). The

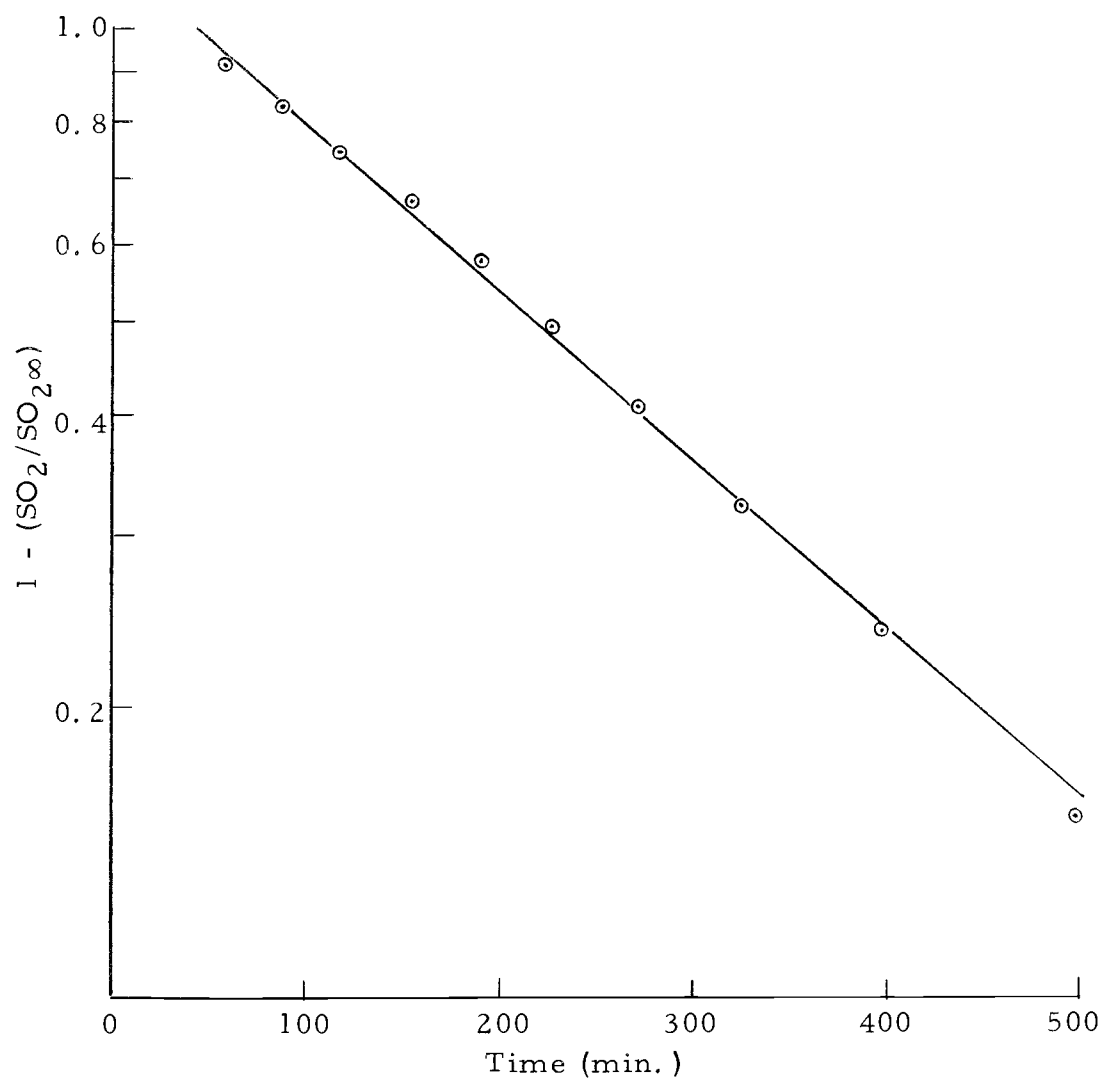


Figure 4. Plot of $\log (1 - \text{SO}_2/\text{SO}_{2\infty})$ vs. time for the decomposition of 0.080 M BBS in cumene at 79.6°.

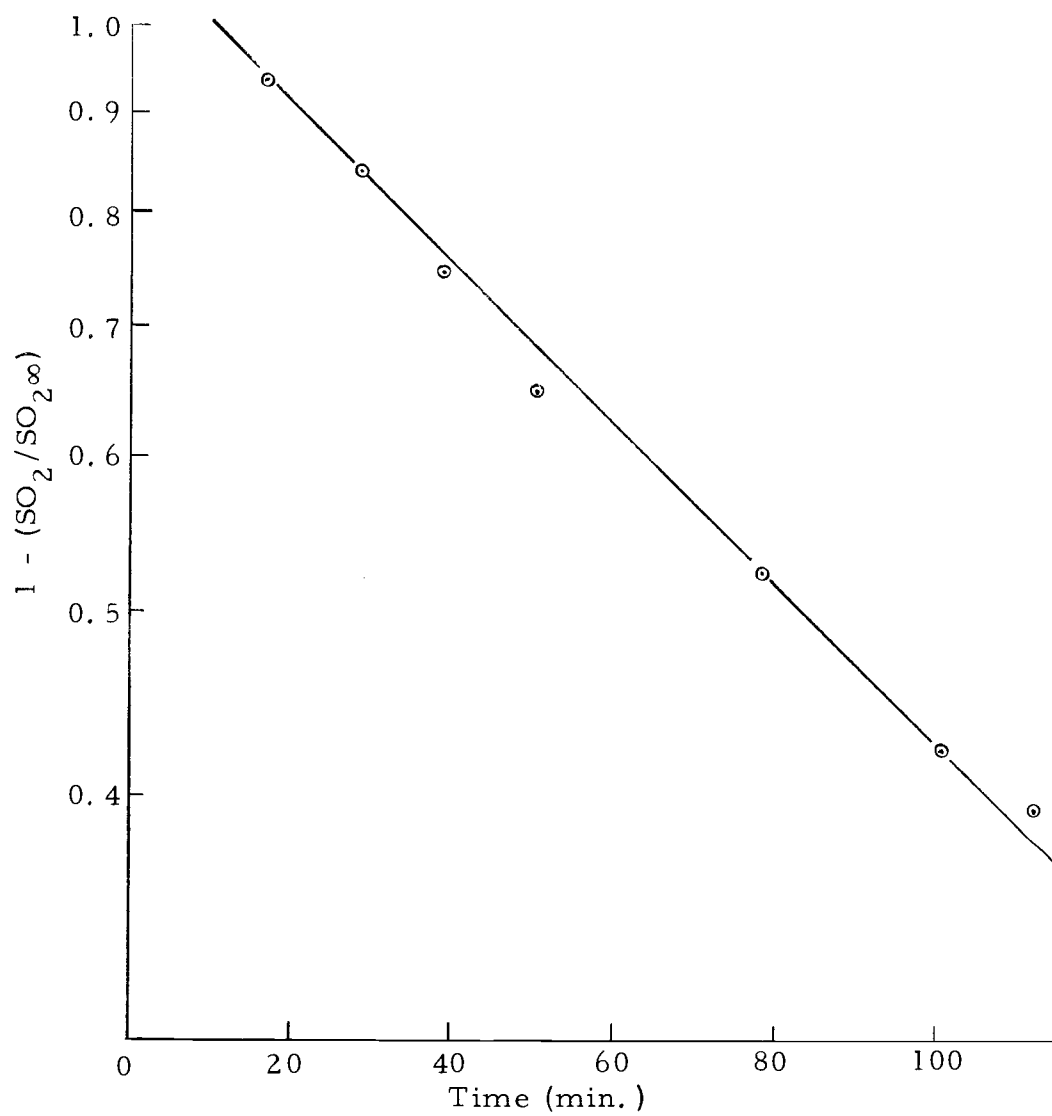


Figure 5. Plot of $\log (1 - \text{SO}_2/\text{SO}_{2\infty})$ vs. time for the decomposition of 0.10 M BBS in diphenylmethane at 80.1°.

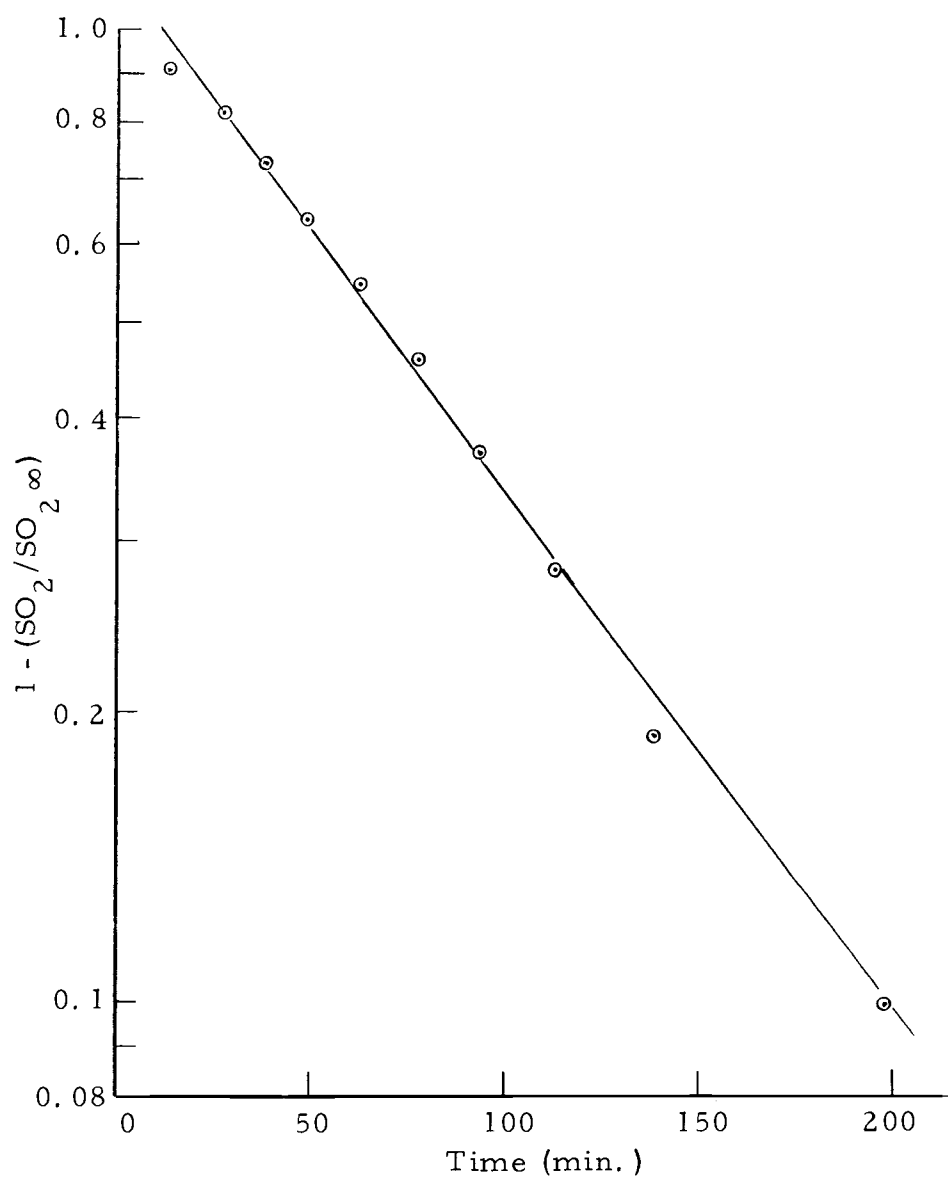


Figure 6. Plot of $\log (1 - \text{SO}_2/\text{SO}_{2\infty})$ vs. time for the decomposition of 0.10 M BBS in acetonitrile at 82°.

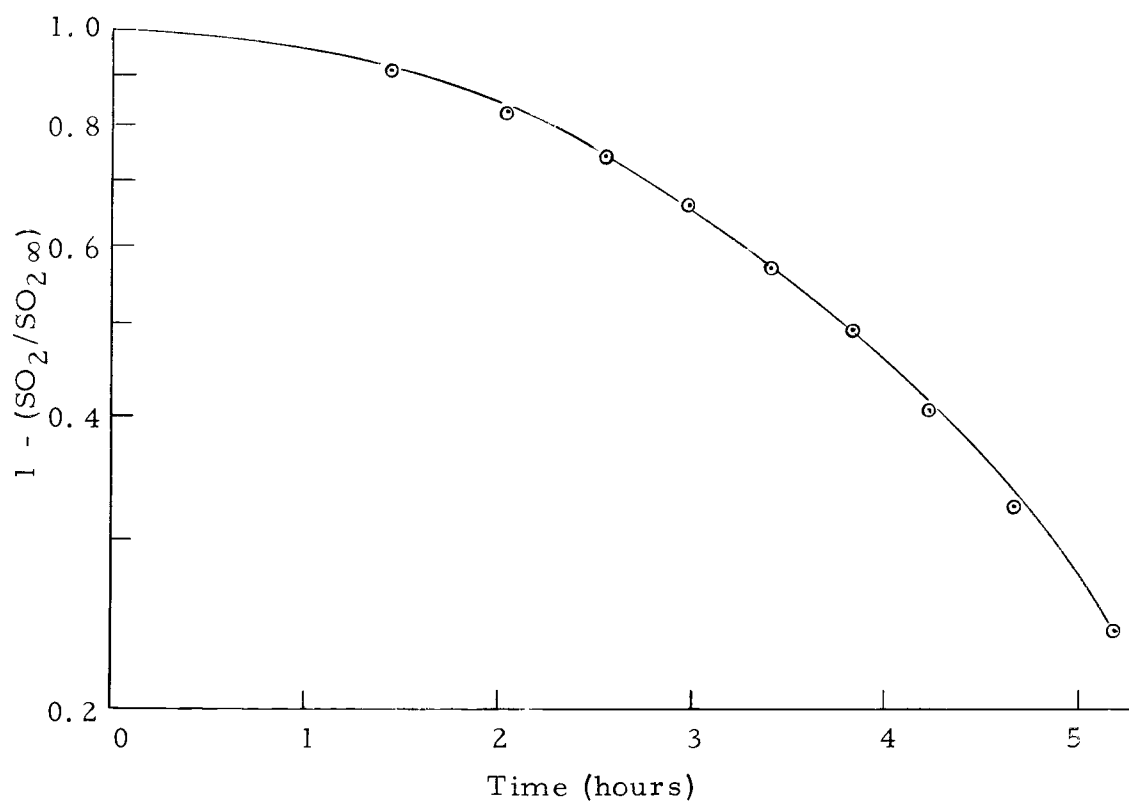


Figure 7. Plot of $\log (1 - \text{SO}_2/\text{SO}_{2\infty})$ vs. time for the decomposition of 0.20 M BBS in benzene at 55.0°.

appearance of this plot suggests that at this higher concentration a significant amount of autocatalyzed decomposition may be occurring because the decomposition of BMS in pure benzene showed accelerated evolution of sulfur dioxide relative to its decomposition in the presence of calcium oxide (Figure 1).

NMR kinetic method. The disappearance of BBS in benzene at 55° was measured by the NMR method. The ratio of the area of the sharp benzyl proton signal at 5.75τ relative to the area of the protons of the internal standard decreased steadily with time. The first order plots of the ratio of benzyl protons to internal standard protons vs. time are shown in Figure 8. Although at first glance some of these plots may appear to follow first order kinetics, comparison with Figure 7 suggests that the disappearance of the diazosulfone protons under these conditions follows much the same pattern as does SO_2 evolution. Why there is no induction period as there is in the decomposition of the much more dilute solutions is not entirely clear, although as noted above the acceleration of the rate toward the end of the decomposition may be due to autocatalysis by acidic products produced during the decomposition.

The intermediate observed by NMR during the decomposition of BBS. During the decomposition of benzenediazo benzyl sulfone in benzene at 55° , the NMR singlet of the benzyl protons at 5.75τ steadily decreased in intensity. Another sharp singlet appeared,

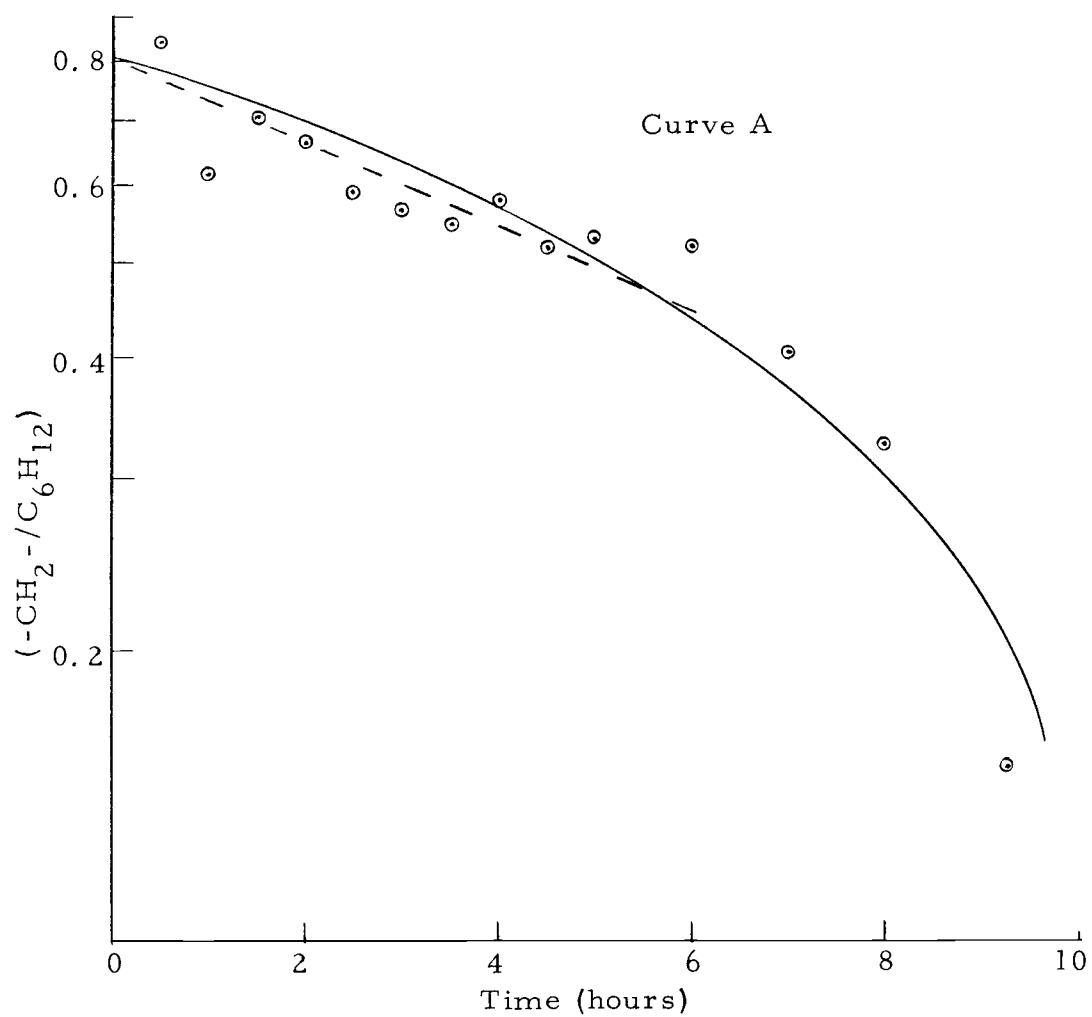


Figure 8. Plot of (log BBS benzyl proton area/cyclohexane proton area) vs. time for the decomposition of 0.20 M BBS in benzene at 55°.

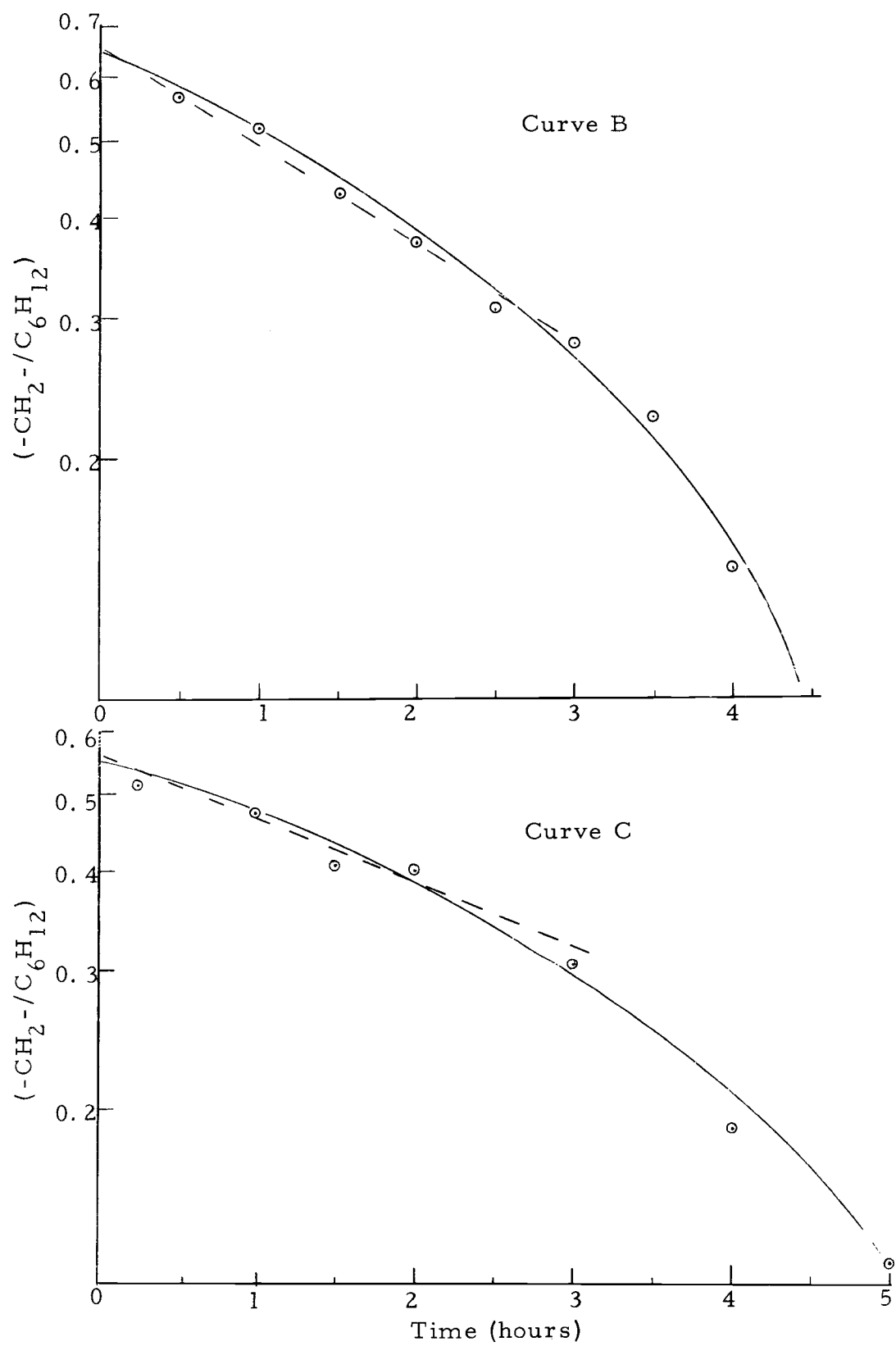


Figure 8. (continued)

whose absorbance was at 4.92τ . For the three runs, the new signal was first detectable from one to two hours after the beginning of the decomposition; the signal then increased to its maximum intensity from four and one-half to eleven hours after the beginning of the decomposition and then disappeared swiftly. The appearance of one set of these spectra over a period of time is recorded in Figure 9. This new signal could possibly be due to the absorption of a proton (or protons) in an unstable intermediate formed during the decomposition of BBS. The amount of this intermediate relative to the amount of BBS initially present in the experiment can be determined in the following way. The integrated area of the benzyl protons of BBS, the protons of the intermediate and the protons of the internal standard is measured at appropriate time intervals. From these values, the ratio of BBS protons/internal standard and intermediate protons/internal standard can be calculated. Each value obtained is then multiplied by the number necessary to make the initial ratio of BBS benzyl protons/internal standard equal 1.00. In this fashion, both the disappearance of the benzyl protons of BBS and the appearance and disappearance of the intermediate protons with respect to time can be determined.

Figure 10 shows the relative proton areas of BBS and the intermediate vs. time for three runs. Figure 10 also shows that the maximum concentration of the intermediate is 0.89, 0.83 and 0.82 mole/mole BBS if the intermediate's signal represents a one proton-containing

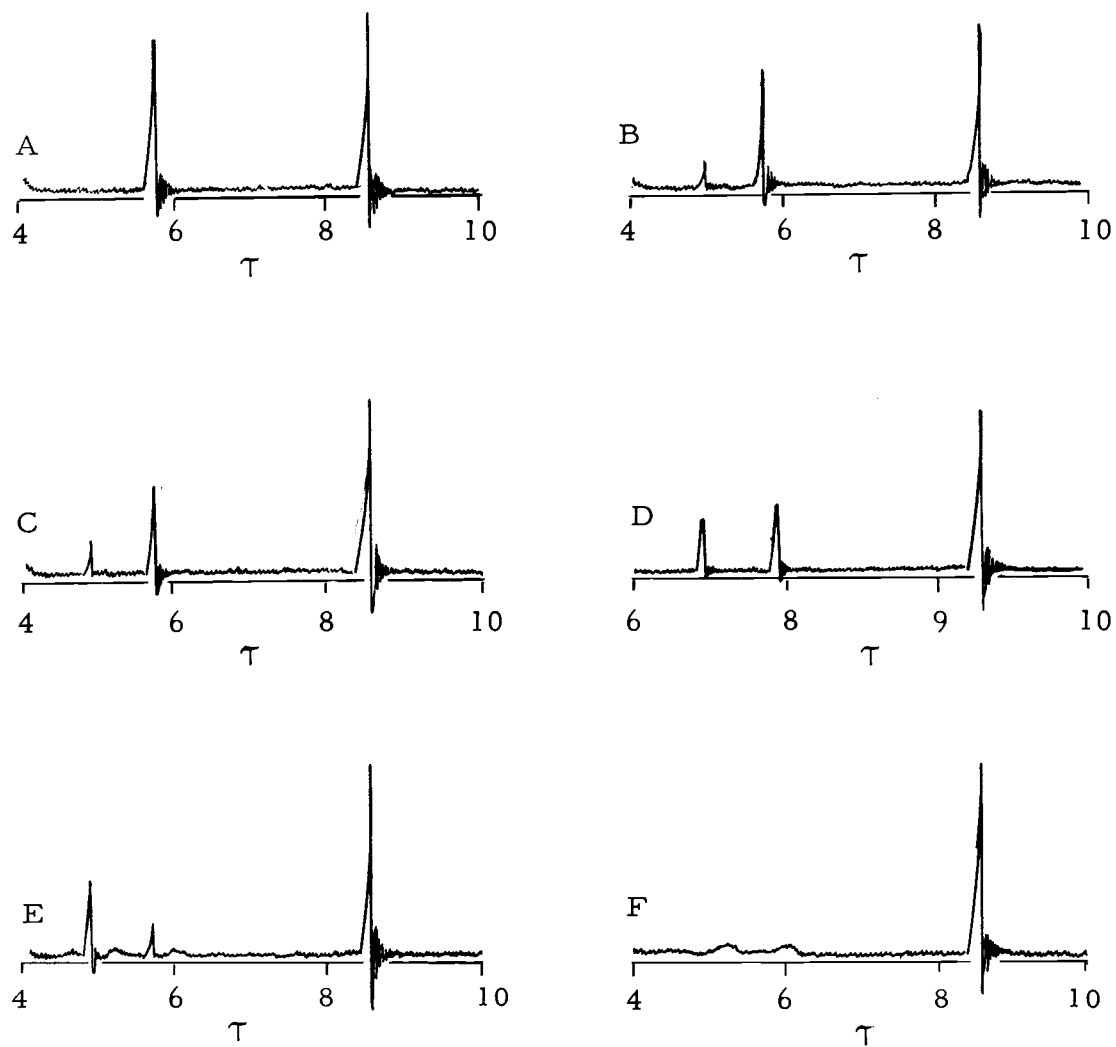


Figure 9. NMR spectra of reaction solution during the course of the decomposition of BBS in benzene at 55°. Curve A, initial solution. Curve B, after two hours. Curve C, after three hours. Curve D, after four hours. Curve E, after five hours. Curve F, after eight hours.

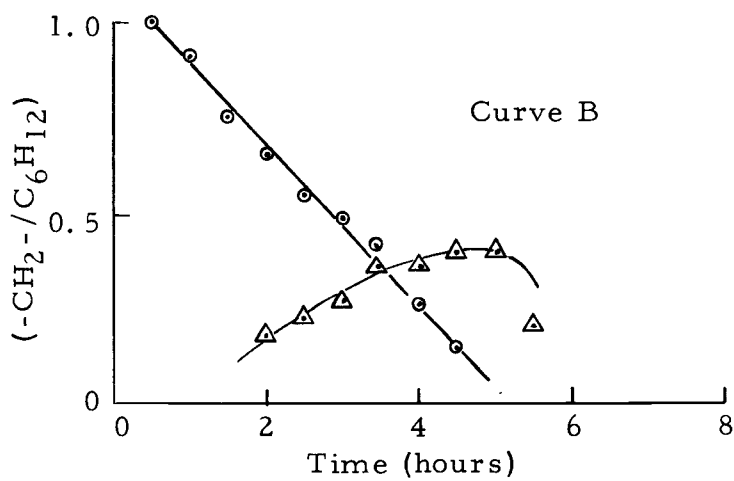
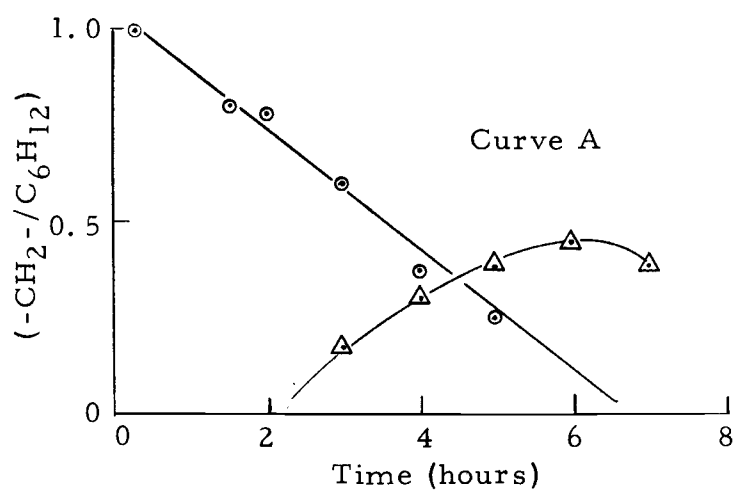


Figure 10. Plot of (BBS benzyl proton area/cyclohexane proton area) vs. time for the decomposition of 0.20 M BBS in benzene at 55°. BBS protons, \odot ; intermediate protons, Δ .

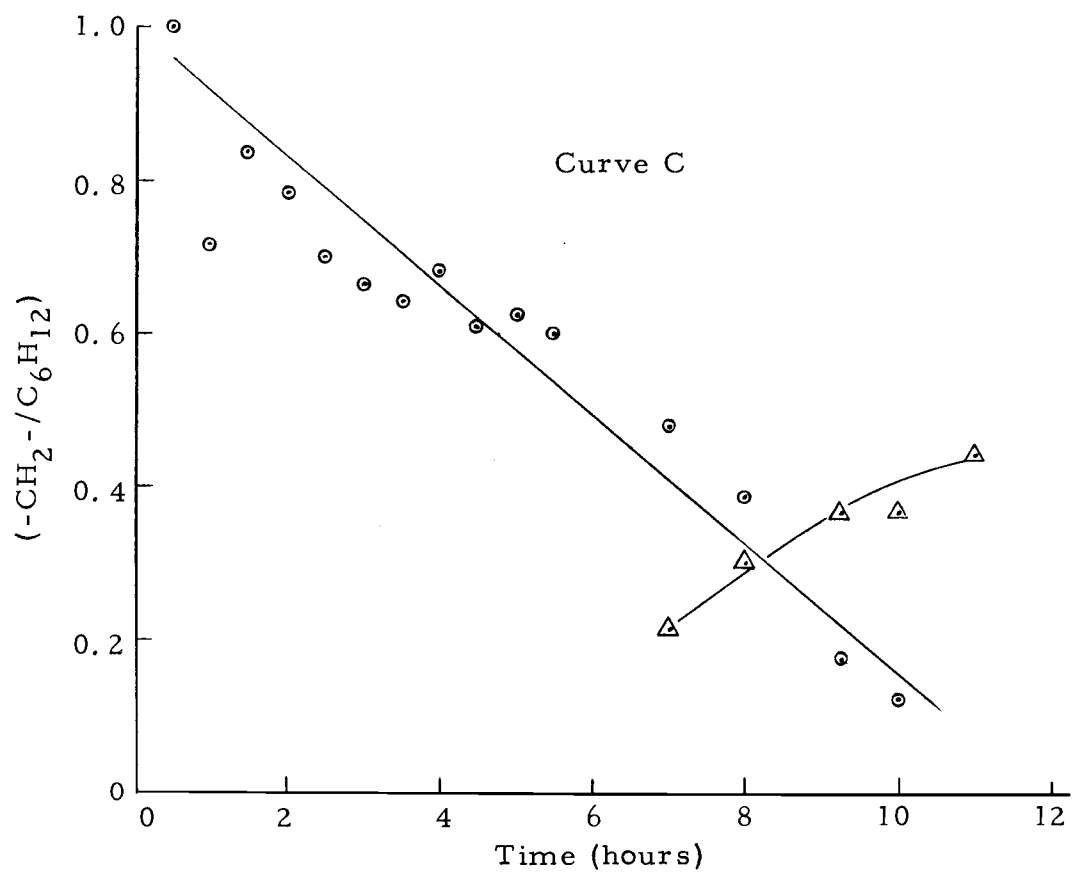


Figure 10. (continued).

intermediate, or a corresponding conversion of 0.44, 0.41 and 0.41 mole/mole BBS if the intermediate's signal represents a two proton-containing intermediate.

Attempted IR and UV spectroscopy of the NMR observable intermediate. Because the NMR experiments indicated that the concentration of the unstable intermediate becomes quite large during the decomposition of the benzyl diazosulfone in benzene, it was of interest to see if UV or IR spectroscopy could aid in determining the structure of this intermediate.

First, solutions of 0.20 M BBS in benzene were prepared, put into Pyrex tubes, degassed and sealed. They were heated at 55° and removed after 1.0, 1.5 and 2.0 hours. The infrared spectrum of these benzene solutions (vs. benzene) showed decreasing amounts of BBS and increasing amounts of benzaldehyde phenylhydrazone. No absorption due to any other compound could be discerned. For comparison purposes the spectra of 0.20 M BBS in benzene (vs. benzene) and 0.20 M benzaldehyde phenylhydrazone in benzene (vs. benzene) were recorded.

In a second experiment, two identical solutions of 0.20 M BBS in benzene, one contained in an NMR tube and the other in a small flask fitted with a vacuum stopcock, were degassed and sealed. After heating both samples at 55°, the flask was removed from the constant temperature bath when the NMR measurements on the sealed tube

showed a minimum amount of BBS remaining and a maximum amount of the intermediate. The contents of the flask were frozen, and the benzene was removed under reduced pressure from the frozen solution. Part of the remaining residue was then dissolved in chloroform and an infrared spectrum was taken of the chloroform solution. Another portion was dissolved in cyclohexane and the UV spectrum of the cyclohexane solution was recorded. The IR spectrum of the chloroform solution of the residue showed no important absorptions other than those present in the spectrum of synthetic benzaldehyde phenylhydrazone in chloroform. The visible spectrum of the decomposition residue showed a very weak absorption at 405 m μ ($A = 0.11$ for 16 mg. residue/25 ml. cyclohexane). O'Connor (59) has shown that alkyl benzeneazo compounds, $R-N=N-Ph$, show absorptions in this region (400-407 m μ) and are characterized by small molar extinction coefficients ($\epsilon = 128-156$). The ultraviolet spectrum of the residue showed a well defined band at 335 m μ ($A = 1.78$ for 16 mg. / 25 ml. cyclohexane). The ultraviolet spectrum of the fully decomposed diazosulfone showed λ_{\max} 235 m μ ($A = 0.90$), 300 m μ (shoulder) ($A = 0.50$) and 337 m μ ($A = 1.03$) for 1.68×10^{-2} mg. residue/ml. cyclohexane. The literature values for the λ_{\max} (ϵ) of benzaldehyde phenylhydrazone are 346 m μ (2×10^4), 300 m μ (shoulder) (10^4) and 243 m μ (1.3×10^4) (68). The UV spectrum of the fully decomposed diazosulfone has the appearance of the spectrum of

benzaldehyde phenylhydrazone, but one can see from the above data that the λ_{\max} of the decomposed diazosulfone do not coincide with the reported λ_{\max} for benzaldehyde phenylhydrazone. The absorption at 405 m μ in the solution of the intermediate is absent in the visible spectrum of the fully decomposed diazosulfone. The intermediate was shown to be in the residue used for IR and UV analysis since a solution of the residue redissolved in benzene showed the NMR absorbance at 4.92 τ characteristic of the intermediate. Thus, these attempts to obtain other definitive spectroscopic evidence on the intermediate observable in the NMR spectrum during the decomposition of BBS were indeterminate.

Benzenediazo t-Butyl Sulfone Decomposition Kinetics

Sulfur dioxide evolution method. The evolution of sulfur dioxide from the thermal decomposition of benzenediazo t-butyl sulfone in benzene showed the same sort of behavior as that of the decomposition of benzenediazo benzyl sulfone. At 55°, with benzene solutions of the t-butyl diazosulfone, there is an induction period of about one hour during which essentially no sulfur dioxide is evolved. This is followed by a relatively rapid evolution of the gas. A plot of $\log (1 - \text{SO}_2/\text{SO}_2^\infty)$ vs. time (Figure 11) for a run is linear after the induction period. As in the benzyl diazosulfone decomposition, the rate of evolution of sulfur dioxide is dependent upon the melting point

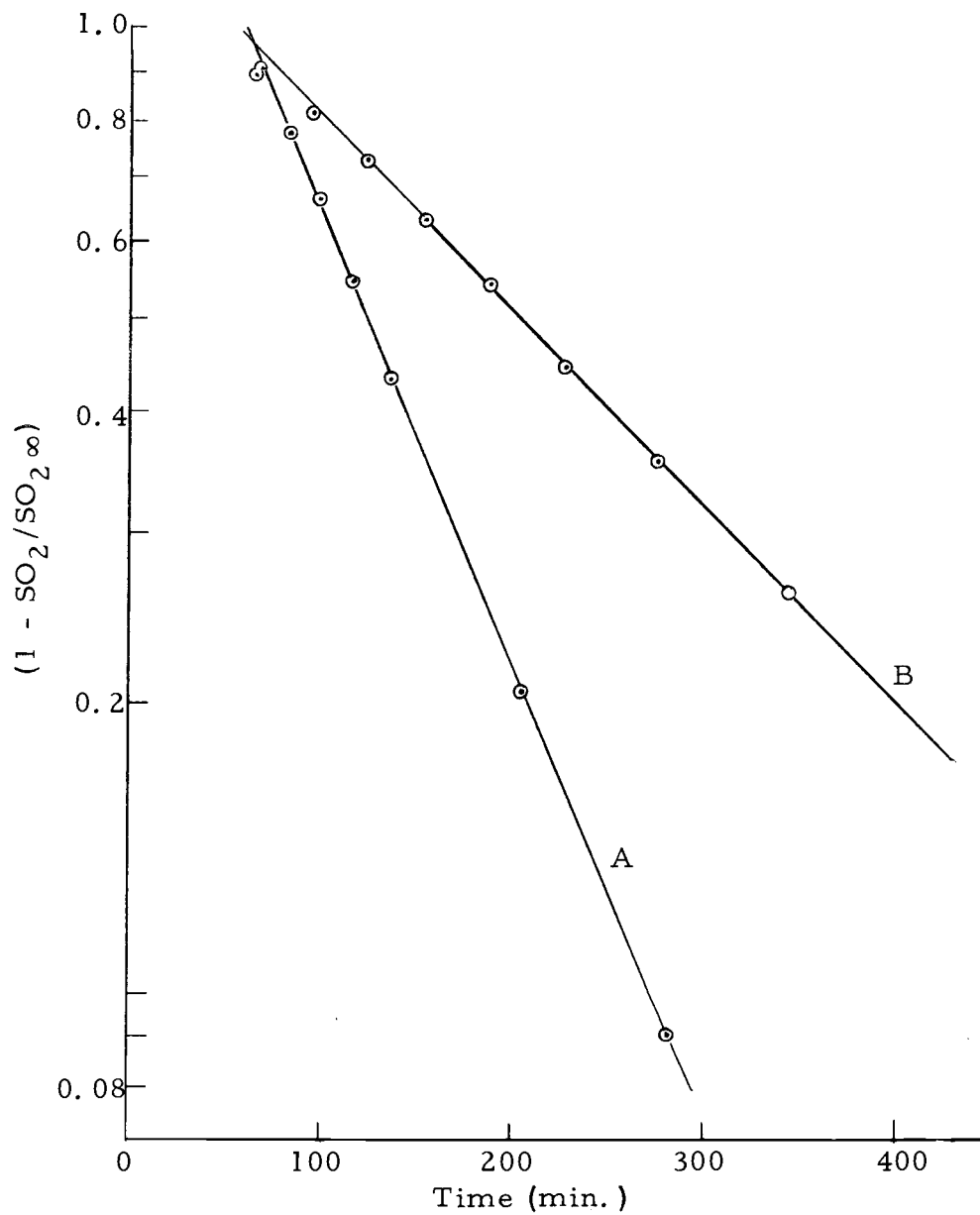


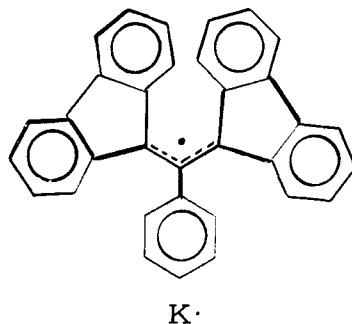
Figure 11. Plot of $\log (1 - \text{SO}_2/\text{SO}_{2\infty})$ vs. time for the decomposition of BtBuS in benzene at 55° . Curve A, $4.68 \times 10^{-2} \text{ M}$ BtBuS , m.p. $63-64.5^\circ$ (dec.). Curve B, $7.0 \times 10^{-2} \text{ M}$ BtBuS , m.p. $65-66.5^\circ$ (dec.).

of the t-butyl diazosulfone. Figure 11, Curve A shows the rate of evolution of sulfur dioxide from a 4.68×10^{-2} M solution of a sample of benzenediazo t-butyl sulfone of melting point 63-64.5° (dec.). The slope of the linear portion of the plot corresponds to a "rate constant" of $k_{\text{SO}_2} = 1.83 \times 10^{-4} \text{ sec}^{-1}$. Curve B shows the rate of evolution of sulfur dioxide from a 7.0×10^{-2} M solution of a sample of the same diazosulfone of melting point 65-66.5° (dec.). The "rate constant" for sulfur dioxide evolution is seen to be appreciably slower, $k_{\text{SO}_2} = 0.77 \times 10^{-4} \text{ sec}^{-1}$.

Scavenging of Radicals Produced in the Decomposition of Alkyl Benzenediazo Sulfones

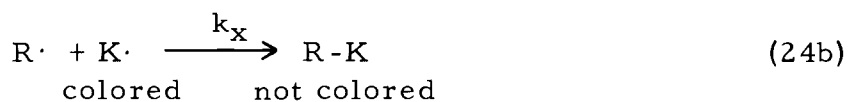
One common method for measuring the rate of production of free radicals in a solution is to add to the solution a highly colored stable free radical which can trap or scavenge reactive free radicals and which in doing so will be converted to some much less strongly colored product (1, 47, 48). The rate of production of radicals in the solution can then be determined from the rate of fading of the color of the radical.

The radical prepared for use as the scavenger in this study was the Koelsch radical, α , γ -bisdiphenylene- β -phenylallyl, $K\cdot$ (45).



In studies of this type it is most convenient to have the suspected radical source present in large molar excess over the stable free radical, the so-called "excess initiator technique," because, under such conditions the fading of the color of the stable radical follows simple zero-order kinetics, as the following derivation will show (eq. 24).

For the scheme



provided that $k_x(K\cdot) \gg k_t(R\cdot)$, i.e. all $R\cdot$ is trapped by $K\cdot$, one can show that

$$\frac{-d(K\cdot)}{dt} = 2 k_d f(I) \quad (24d)$$

At 489 mμ the optical density of the solution is entirely due to the Koelsch radical so that

$$A_{489} = \epsilon (K\cdot) \quad (24e)$$

and therefore

$$\frac{-dA_{489}}{dt} = \epsilon \frac{-d(K\cdot)}{dt} \quad (24f)$$

and

$$- \frac{1}{\epsilon} \frac{dA_{489}}{dt} = 2 k_{df}(I) . \quad (24g)$$

Since I is taken in large molar excess over $K\cdot$, its concentration will not change appreciably during the period required for the complete disappearance of $K\cdot$. As a result,

$$\frac{-dA_{489}}{dt} = 2 k_{df}(I)_0 \epsilon = \text{constant} \quad (24h)$$

$$A_{489} = A_{489}^0 - 2 k_{df}(I)_0 \epsilon t \quad (24i)$$

Thus a plot of A_{489} vs. time should be linear; and, since $(I)_0$ and ϵ are known, from its slope one should be able to calculate k_{df} , the rate constant for the production of scavengable free radicals. This can then be compared with other estimates of the rate of decomposition of I , and an estimate made of the fraction, f , of the total decomposition of I which yields trappable free radicals.

The rates of production of free radicals in the decompositions of both BMS and BBS were investigated by this technique. As expected from eq. 24i, plots of the absorption due to the Koelsch radical vs. time during the decomposition of both the methyl and benzyl diazosulfones followed excellent zero-order kinetics (Figures 12 and 13) and were reproducible. Values of k_{df} for the two diazosulfones

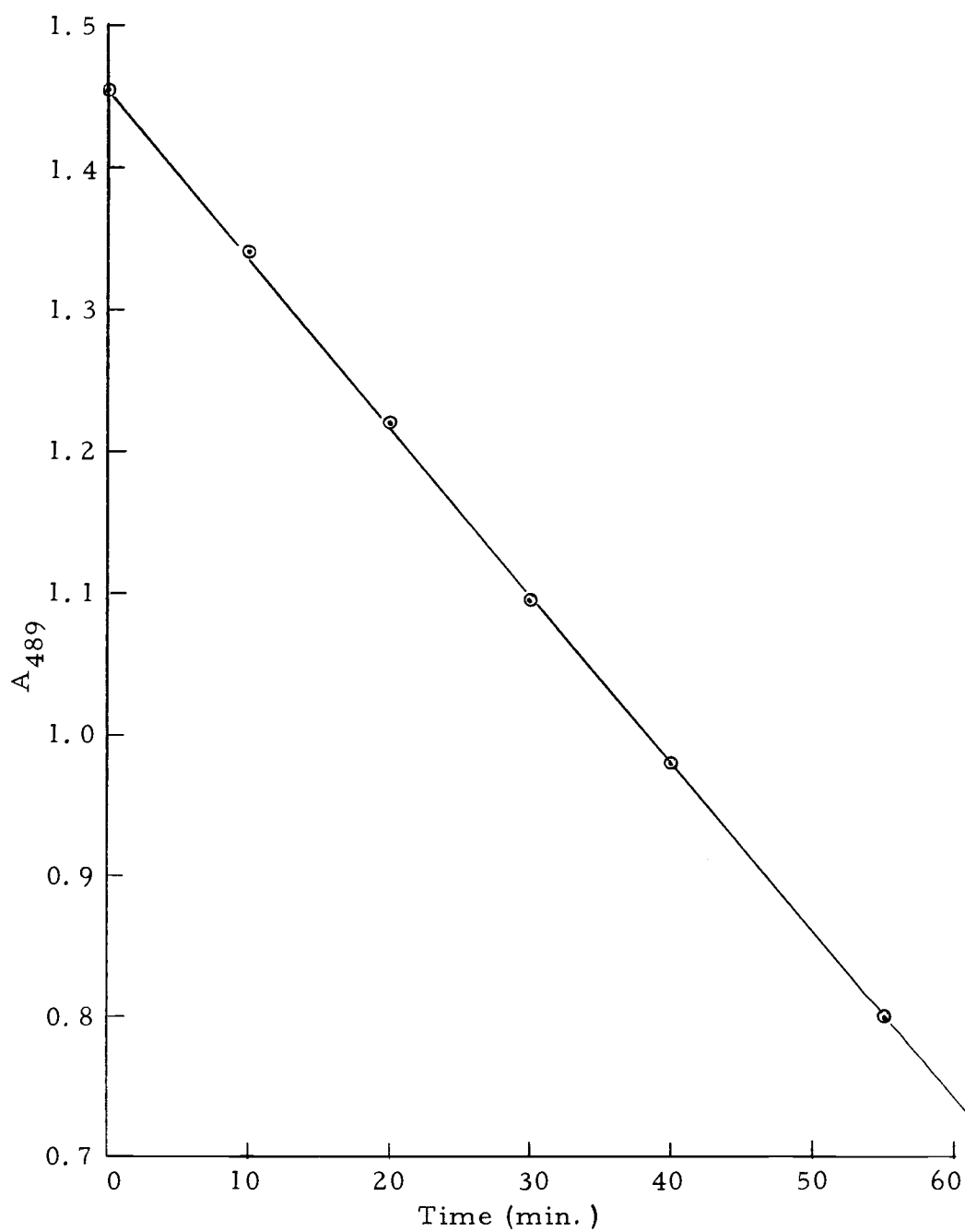


Figure 12. Plot of A_{489} vs. time for the decomposition of 5.30×10^{-4} M BMS with 5.04×10^{-5} M K^{\cdot} in benzene at 70.0° .

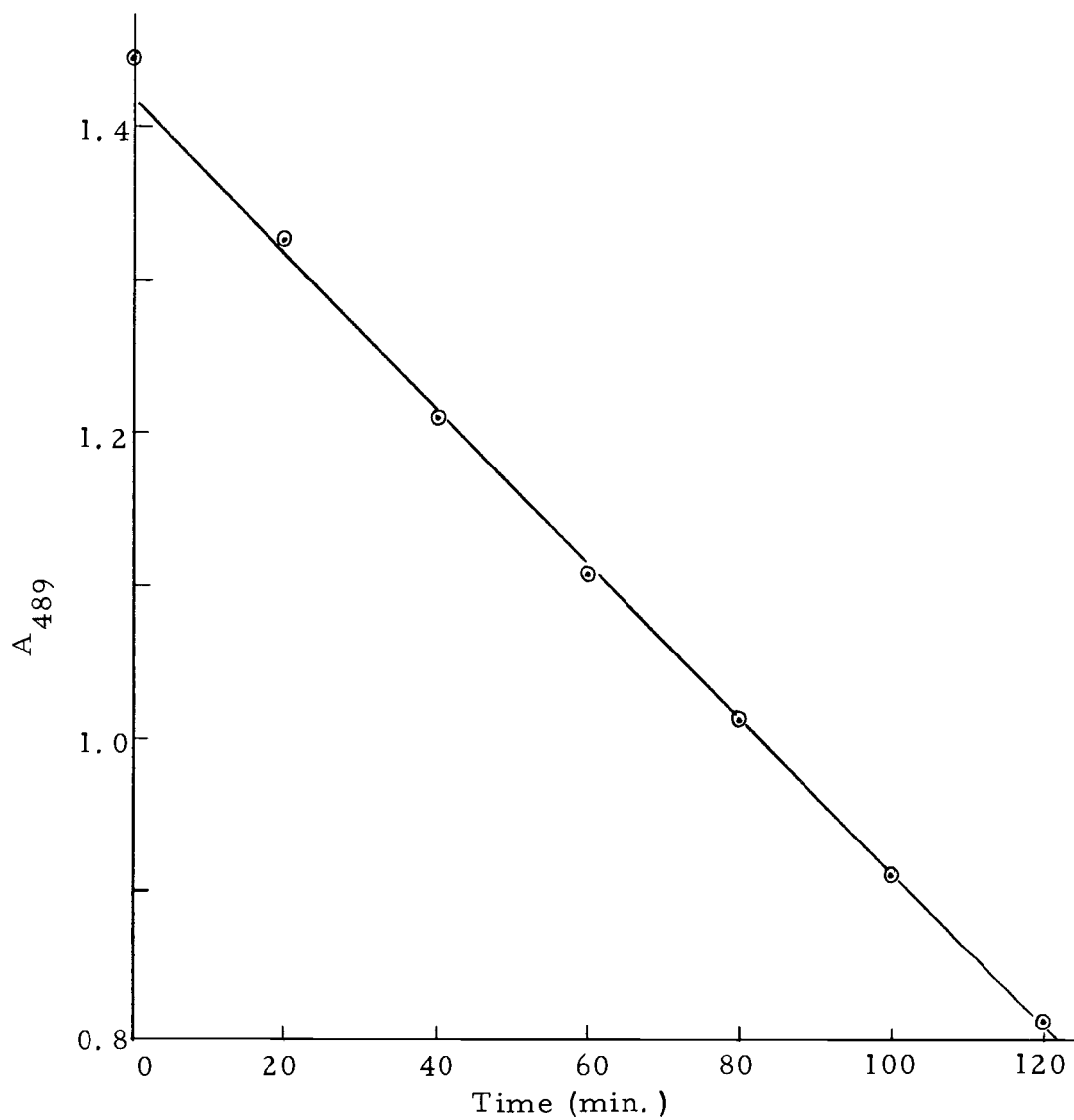


Figure 13. Plot of A_{489} vs. time for the decomposition of $1.02 \times 10^{-4} \text{ M}$ BBS with $5.10 \times 10^{-5} \text{ M}$ K^\cdot in benzene at 60.0° .

as evaluated from the slopes of these plots are presented in Tables 4 and 5.

The value of $k_d f$ for the decomposition of the methyl diazo-sulfone in benzene at 80.0° is $1.87 \times 10^{-5} \text{ sec}^{-1}$, which is significantly slower than the overall rate of decomposition of this diazo-sulfone at 80° ($k_{\text{SO}_2} = 5.5 \times 10^{-5} \text{ sec}^{-1}$) as estimated by what we think is our most reliable kinetic experiment, the measurement of the rate of evolution of sulfur dioxide in the presence of suspended calcium oxide. If this rate is assumed to be the most reliable estimate of the actual decomposition rate of BMS, then the fraction, f , of the decomposition which produces scavengable free radicals is equal to the rate at which scavengable free radicals are produced divided by the "actual" decomposition rate (eq. 25), and is equal to

$$f = \frac{k_d f}{k_{\text{SO}_2}} \quad (25)$$

$1.87 \times 10^{-5} \text{ sec}^{-1} / 5.5 \times 10^{-5} \text{ sec}^{-1} = 0.34$, which indicates that only about one-third of the decomposition produces scavengable free radicals. Lamb and Pacifici (47) found an f value of 0.24 or less in the decomposition of cyclohexanecarbonyl peroxide in benzene. They ascribed the low efficiency to a predominating cage recombination and disproportionation of the radicals produced in the decomposition. Significantly, similar results for the f values were obtained using either galvinoxyl, diphenylpicrylhydrazyl, or the Koelsch radical as

Table 4. Benzenediazo methyl sulfone. Rate of radical production ($\frac{dR\cdot}{dt}$) and rate of decomposition of BMS decomposition (k_{df}) in benzene measured by radical scavenging with the Koelsch radical ($K\cdot$).

Temp. (°C)	[BMS] ₀ × 10 ⁻⁴	[K·] × 10 ⁻⁵	$\frac{dR\cdot}{dt}$ (M hr. ⁻¹)	k_{df} (sec. ⁻¹)
54.8	4.98	5.05	3.10 × 10 ⁻⁶	8.63 × 10 ⁻⁷
59.9	5.03	5.15	6.52 × 10 ⁻⁶	1.80 × 10 ⁻⁶
59.9	5.03	5.15	7.22 × 10 ⁻⁶	2.00 × 10 ⁻⁶
70.0	5.30	5.04	2.46 × 10 ⁻⁵	6.44 × 10 ⁻⁶
70.0	5.02	5.20	2.62 × 10 ⁻⁵	7.27 × 10 ⁻⁶
70.0	5.00	5.05	2.54 × 10 ⁻⁵	7.08 × 10 ⁻⁶
80.0	5.02	5.20	6.83 × 10 ⁻⁵	1.88 × 10 ⁻⁵
80.0	5.00	5.05	6.71 × 10 ⁻⁵	1.86 × 10 ⁻⁵

Table 5. Rate of radical production ($\frac{dR\cdot}{dt}$) and rate of decomposition of BBS ($k_d f$) in benzene measured by radical scavenging with the Koelsch radical ($K\cdot$).

Temp. ($^{\circ}C$)	[BBS] $\times 10^{-4}$	[$K\cdot$] $\times 10^{-5}$	$\frac{dR\cdot}{dt}$ (\underline{M} hr. $^{-1}$)	$k_d f$ (sec. $^{-1}$)
54.8	1.00	4.90	4.31×10^{-6}	6.00×10^{-6}
60.0	1.02	5.10	10.95×10^{-6}	1.50×10^{-5}
60.0	1.01	4.98	8.52×10^{-6}	1.17×10^{-5}
60.1	0.996	5.03	9.39×10^{-6}	1.31×10^{-5}
65.0	1.02	5.10	2.25×10^{-5}	3.08×10^{-5}
70.0	1.02	5.00	4.46×10^{-5}	6.08×10^{-5}
70.0	1.01	5.07	3.94×10^{-5}	5.42×10^{-5}
70.0	1.02	5.13	4.63×10^{-5}	6.31×10^{-5}
70.0	1.02	5.10	4.46×10^{-5}	6.07×10^{-5}
80.0	1.00	5.15	8.57×10^{-5}	1.19×10^{-4}

the free radical scavenger. In another study, Lamb and co-workers (48) found f values in the range of 0.42 to 0.45 for the thermal decomposition of γ -benzylidenebutyl peroxide in a number of solvents and proposed that both cage recombination and radical induced decomposition contributed to the fraction of the decomposition occurring without the formation of scavengable free radicals. Thus it appears that our f value of 0.34 may be due to some fraction of the decomposition proceeding by either cage recombination and induced decomposition, or both.

The value of $k_d f$ determined by radical scavenging experiments with the benzyl diazosulfone is seen to be $6.0 \times 10^{-6} \text{ sec}^{-1}$ at 54.8° . This value is considerably smaller than the average apparent initial "first-order" rate constants for the disappearance of the benzyl diazosulfone at 55° evaluated from the initial stages of the plots in Figure 8, $5.5 \times 10^{-5} \text{ sec}^{-1}$. If the rate at which the diazosulfone disappears is assumed to be valid, then the fraction f is equal to $6.0 \times 10^{-6} \text{ sec}^{-1} / 5.5 \times 10^{-5} \text{ sec}^{-1} = 0.11$. Also, if the "rate" of evolution of sulfur dioxide from the decomposing diazosulfone is assumed to represent the rate at which most of the diazosulfone disappears, then the f value is even smaller, $6.0 \times 10^{-6} \text{ sec}^{-1} / 1.13 \times 10^{-4} \text{ sec}^{-1} = 0.053$. Both these f values are quite small and could be interpreted to mean that a significant fraction of the decomposition of the benzyl diazosulfone is occurring by a free radical

induced chain decomposition, in which a small number of free radicals can cause the disappearance of a substantial amount of the diazosulfone.

From the rates of scavengable radical production over a range of temperatures, the activation energies necessary for the decompositions to produce scavengable free radicals were calculated (Figures 14 and 15) (25, p. 23). The activation value for the decomposition of the methyl diazosulfone into scavengable free radicals is $E_a = 30$ Kcal/mole and for the benzyl diazosulfone, $E_a = 32$ Kcal/mole. It must be emphasized that these values reflect only the activation energy necessary for the decomposition to produce scavengable free radicals.

The Effect of Koelsch Radical on Sulfur Dioxide Evolution from BBS

The very small f value observed in the decomposition of BBS in benzene raised the question of whether a significant amount of the decomposition might be occurring by a radical chain decomposition. If this is correct, then the addition of Koelsch radical to solutions of the diazosulfone should inhibit this chain decomposition, provided, of course, that it traps the radicals which initiate the induced decomposition. We measured the rate of evolution of sulfur dioxide at 55° from a benzene solution of benzyl diazosulfone containing the Koelsch radical. A plot of $\log (1 - SO_2/SO_{2\infty})$ vs. time is shown in Figure 16.

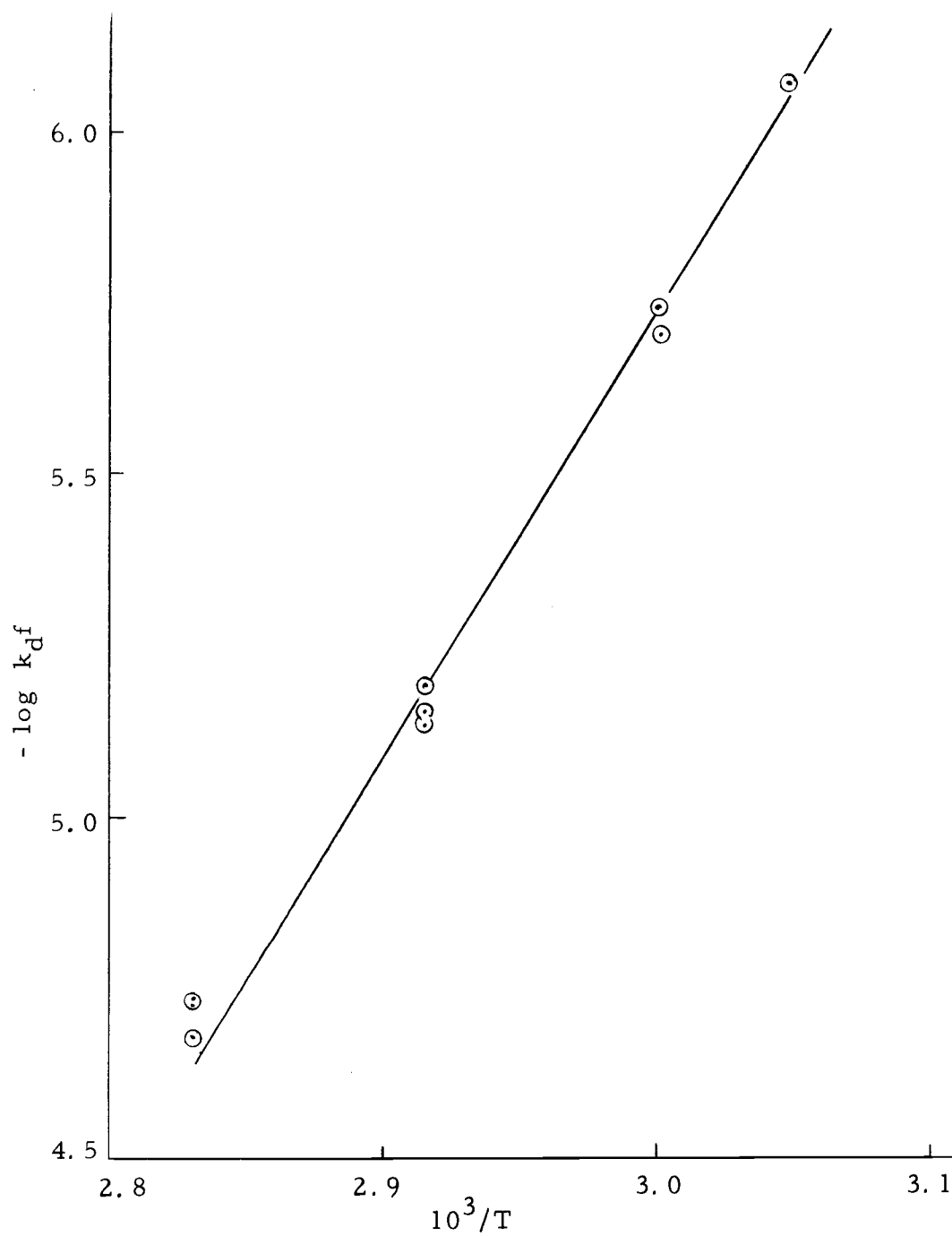


Figure 14. Arrhenius plot of $-\log k_d^f$ vs. $10^3/T$ for BMS decomposition in benzene.

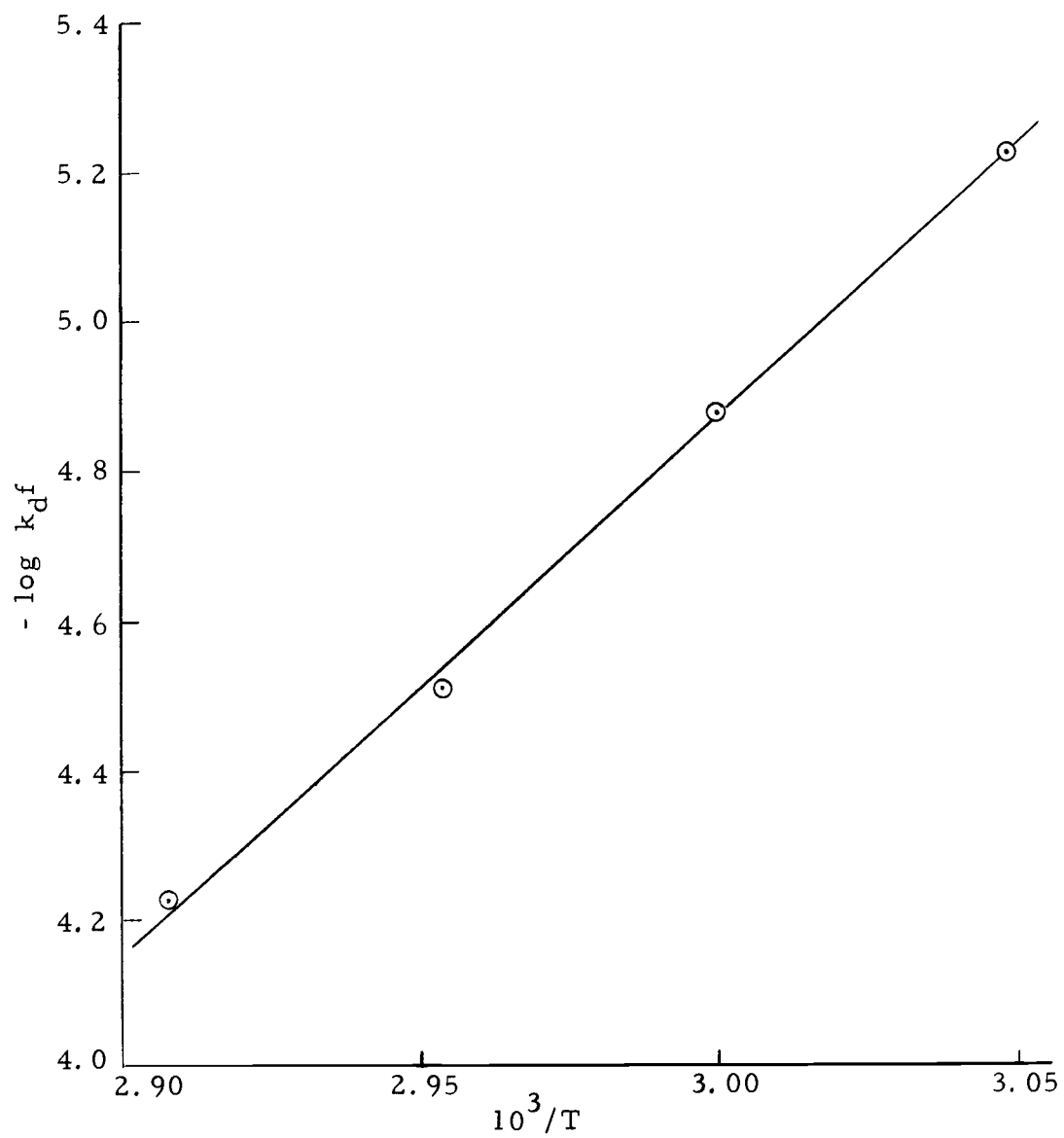


Figure 15. Arrhenius plot of $-\log k_d^f$ vs. $10^3/T$ for BBS decomposition in benzene.

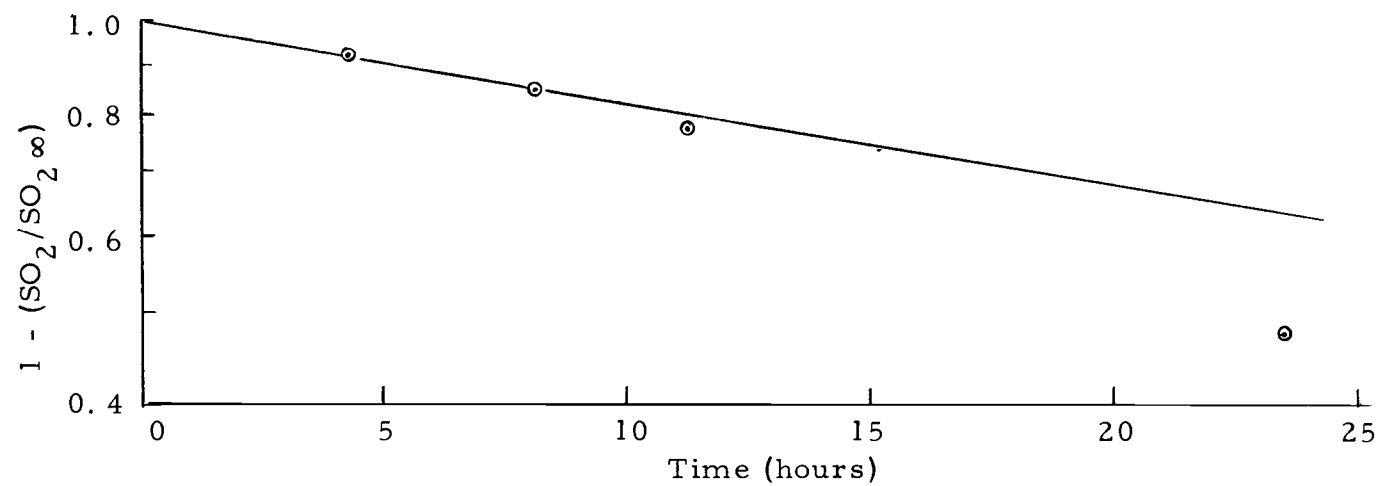


Figure 16. Plot of $\log (1 - \text{SO}_2/\text{SO}_2\infty)$ vs. time for the decomposition of 1×10^{-2} M BBS and 4×10^{-3} M K \cdot in benzene at 55° .

The first order rate of evolution of sulfur dioxide determined from the slope of the plot is $5.4 \times 10^{-6} \text{ sec}^{-1}$, and the plot is seen to show neither an induction period nor any rapid evolution of the gas as was observed in the decomposition of BBS in pure benzene (Figure 3).

The value of the first order rate of appearance of sulfur dioxide from decomposing BBS in the presence of the Koelsch radical ($5.4 \times 10^{-6} \text{ sec}^{-1}$) is seen to be about equal to k_{df} , the measured rate for the decomposition of BBS into scavengable free radicals ($6.0 \times 10^{-6} \text{ sec}^{-1}$).

Thus one interpretation is that the effect of adding the free radical trap, the Koelsch radical, is to completely inhibit a usual induced chain decomposition and that the decomposition in the presence of the Koelsch radical evolves sulfur dioxide at a rate comparable to the rate at which scavengable radicals are produced. It must be pointed out that the rate constant was evaluated by assuming that 100 percent sulfur dioxide evolution would occur. If it was assumed that only 66 percent of the theoretical amount were to be evolved, the amount of sulfur dioxide evolved during the decomposition in pure benzene, then the rate constant for evolution of the gas would be about $1 \times 10^{-5} \text{ sec}^{-1}$, still considerably slower than the evolution of sulfur dioxide in pure benzene, and yet still close to the rate at which scavengable radicals are produced. The rate of evolution of sulfur dioxide is seen to increase as the decomposition progresses, probably due to

the decrease in the concentration of the Koelsch radical. Thus, radicals produced in the presence of a lower concentration of the Koelsch radical would perhaps not be completely scavenged, and could induce the decomposition of BBS.

The Effect of Koelsch Radical on the Disappearance of BBS

We have just seen that the addition of the Koelsch radical inhibits the fast evolution of sulfur dioxide normally observed in the decomposition of BBS. It was thus of interest to see what effect the addition of Koelsch radical would have on the rate at which the diazosulfone itself disappeared. If the decomposition is a radical chain, then by trapping out the radicals which initiate the chain decomposition (by coupling them with the Koelsch radical), the swift disappearance of the diazosulfone should be halted. What should be observed then is the very slow decomposition of the diazosulfone into scavengable free radicals.

The rate of production of scavengable free radicals at 54.8° from a 1×10^{-4} M solution of BBS in benzene is 4.31×10^{-6} moles of scavengable radicals/hour (Table 5). Therefore, in the concentration necessary for the NMR experiments (0.20 M) the rate of production of scavengable free radicals should be

$$\frac{2 \times 10^{-1} \underline{\text{M}}}{1 \times 10^{-4} \underline{\text{M}}} (4.31 \times 10^{-6} \underline{\text{M}} \text{ radicals/hr.}) = 8.62 \times 10^{-3} \underline{\text{M}} \text{ radicals/hr.}$$

Thus, if each free radical produced is scavenged, the addition of $8.6 \times 10^{-3} \underline{\text{M}}$ Koelsch radical should inhibit the chain decomposition for

$$\frac{8.6 \times 10^{-3} \underline{\text{M}}}{8.6 \times 10^{-3} \underline{\text{M}} \text{ radicals/hr.}} = 1 \text{ hour .}$$

Addition of Koelsch radical does inhibit the disappearance of BBS (Figure 17). For the solution $8.6 \times 10^{-3} \underline{\text{M}}$ in Koelsch radical, the actual inhibition period determined by the NMR method is seen to be two hours (Figure 17, Curve A), this being the period of time in which essentially no diazosulfone decomposes. In the same manner, the addition of twice this amount of Koelsch radical, $17.2 \times 10^{-3} \underline{\text{M}}$, should inhibit the decomposition of BBS twice as long. However, the period in which no decomposition occurs is again about two hours (Figure 17, Curve B). It is not clear why doubling the amount of Koelsch radical present does not double the length of time in which no decomposition of BBS occurs, nor is it apparent why the diazosulfone should disappear so rapidly after this two hour period. However, since kinetics of the disappearance of the diazosulfone under these conditions in the absence of the Koelsch radical are rather peculiar anyway (Figure 8), one should perhaps not be surprised by this type of behavior.

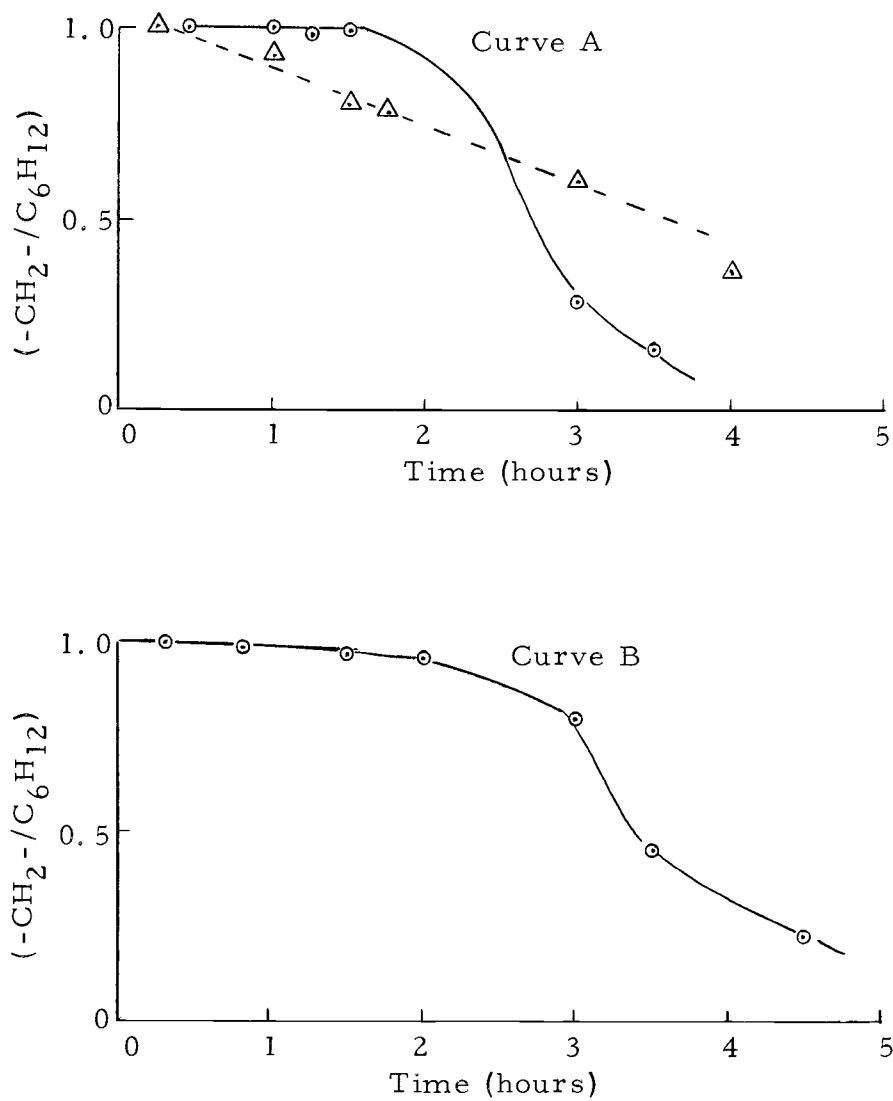


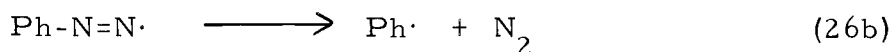
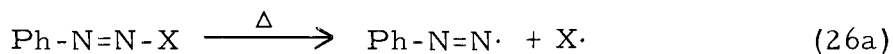
Figure 17. Plot of (BBS benzyl proton area/cyclohexane proton area) vs. time for the decomposition of 0.20 M BBS in benzene with 8.6×10^{-3} M K^\cdot (Curve A) and 1.72×10^{-2} M K^\cdot (Curve B).

It is, however, apparent from this experiment that the addition of the free radical scavenger, the Koelsch radical, does indeed inhibit the decomposition of BBS, which in the absence of the Koelsch radical shows a substantial degree of decomposition after a two hour period, shown by the dotted line of Figure 17, Curve A.

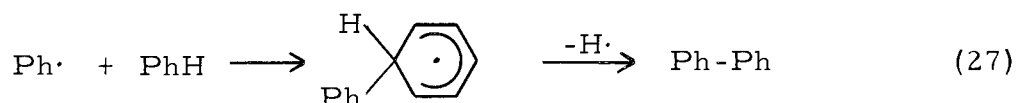
DISCUSSION

The Thermal Decomposition of Benzenediazo Methyl Sulfone

Earlier work (77) has shown that the thermal decomposition of benzenediazo compounds, Ph-N=N-X , can provide a source of phenyl radicals. This occurs by initial cleavage of the N-X bond to give a phenylazo and X^\cdot radical pair (eq. 26a). The phenylazo radical can



then lose nitrogen to form the phenyl radical (eq. 26b). In benzene, the phenyl radical can attack the solvent, and after hydrogen atom loss, give biphenyl (eq. 27). The thermal decomposition of a variety

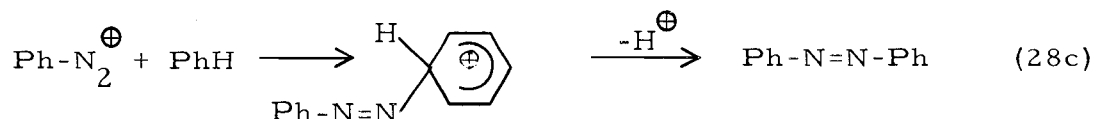
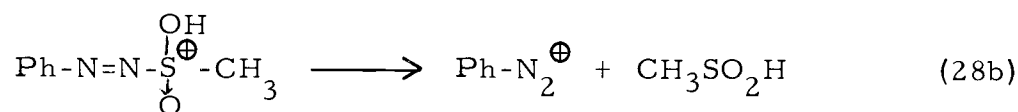
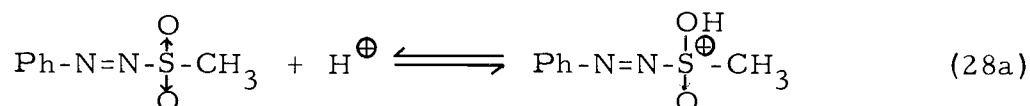


of phenylazo compounds [$\text{X} = -\text{OAc}$, $-\text{CN}$, $-\text{NHAr}$, $-\text{NR}_2$, $-\text{CAr}_3$, (77, p. 27), $-\text{SAr}$ (76), and $-\text{OSO}_2\text{Ar}$ (2)] in aromatic solvents do give biphenyls as major products.

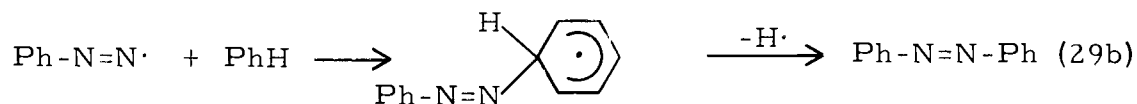
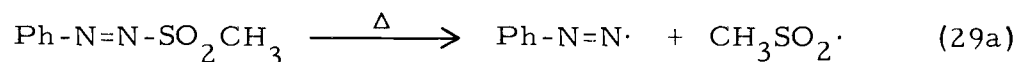
Products in benzene. The thermal decomposition of benzenediazo methyl sulfone in benzene is no different in this regard since biphenyl is the principal identifiable organic product (0.32 mole/mole BMS) (Table 1, Column 1). In the present system, biphenyl can, of course, arise from the cleavage of the S-N bond of the diazosulfone to form a methanesulfonyl and phenylazo radical pair (eq. 26a,

X = CH₃SO₂-), followed by loss of nitrogen from the phenylazo radical to form the phenyl radical (eq. 26b), and reaction of the phenyl radical with the solvent to give the observed product (eq. 27).

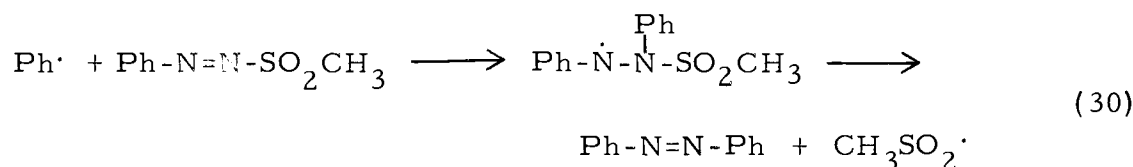
The yield of azobenzene formed in the thermal decomposition of the methyl diazosulfone in pure benzene (0.14 mole/mole BMS) compared to its yield in the decomposition of BMS in benzene with calcium oxide suspended in the solvent (0.032 mole/mole BMS) would seem to suggest that the presence of calcium oxide inhibits the formation of azobenzene. It is possible that in the absence of calcium oxide the principal mechanism for the formation of azobenzene is by an acid catalyzed route (eq. 28). Phenyldiazonium ion could be formed by the



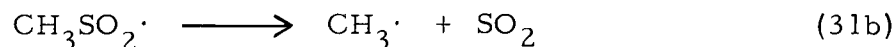
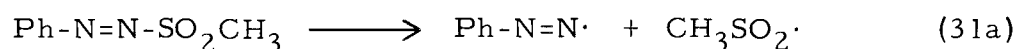
loss of methanesulfinic acid from the protonated diazosulfone (eq. 28b). The diazonium ion could then react with the solvent by electrophilic aromatic substitution (eq. 28c). In the presence of calcium oxide, acid catalyzed decomposition could be suppressed and the principal mode of formation of azobenzene could be by homolytic aromatic substitution by the phenylazo radical (eq. 29).



Another way that azobenzene could be formed would be by the attack of a phenyl radical on the azo group of a molecule of BMS, with subsequent loss of a methanesulfonyl radical (eq. 30).



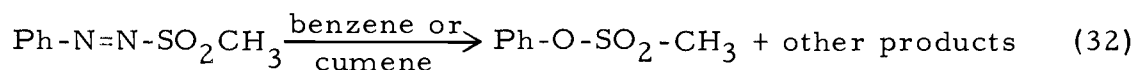
The amount of sulfur dioxide evolved during the decomposition of BMS is rather small (0.03-0.14 mole/mole BMS). This sulfur dioxide is presumably formed by desulfonylation of methanesulfonyl radicals (eq. 31b) formed in the initial homolysis of the diazosulfone (eq. 31a).



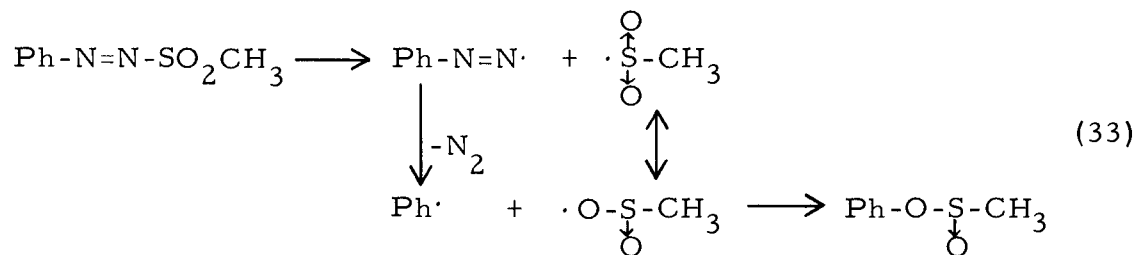
The dissociation energy for the R-SO_2 bond in $\text{R-SO}_2\cdot$ has been estimated to be 23.3 kcal for $\text{R} = \text{CH}_3$, 18.2 kcal for $\text{R} = \text{t-Bu}$, and only 12.0 kcal when $\text{R} = \text{Ph-CH}_2$ - (11). Thus, alkanesulfonyl radicals which would give a reasonably stable free radical by loss of sulfur dioxide, such as a benzyl radical formed from an α -toluene-sulfonyl radical, would be expected to lose sulfur dioxide readily at room temperature, while the methanesulfonyl radical should do so

with reluctance (37, p. 118). The small amount of sulfur dioxide evolved from the decomposition of BMS is in accord with this prediction. Another possible explanation for the low yield of sulfur dioxide observed is that the methanesulfonyl radical could react with the solvent, or another molecule of diazosulfone before loss of sulfur dioxide occurred.

The small yield of phenyl methanesulfonate found in the decomposition of BMS in benzene (0.069 mole/mole BMS) and in cumene (0.074 mole/mole BMS) was quite unexpected because the methanesulfonate contains three oxygen atoms, while the diazosulfone contains two (eq. 32). A number of mechanisms can be proposed to account

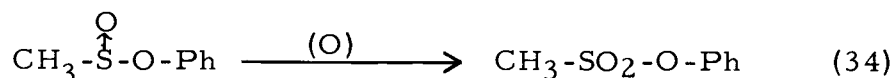


for the formation of this product, although all of them are at this stage highly speculative. The first is a cage recombination of a methanesulfonyl radical with a phenyl radical, the latter formed by loss of nitrogen from the phenylazo radical (eq. 33). If the radicals

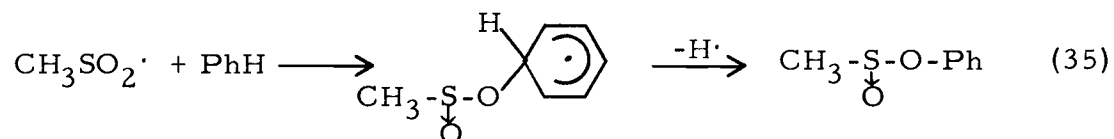


couple carbon to oxygen, this would give phenyl methanesulfinate as the product. The intermediate sulfinate ester could then be oxidized

by some product present in the reaction mixture, or possibly on work-up of the reaction mixture (eq. 34).

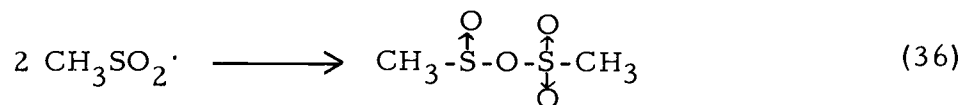


A second possible mode of formation of phenyl methanesulfonate is by attack of a methanesulfonyl radical on the solvent, with subsequent hydrogen atom loss (eq. 35). Again, this intermediate

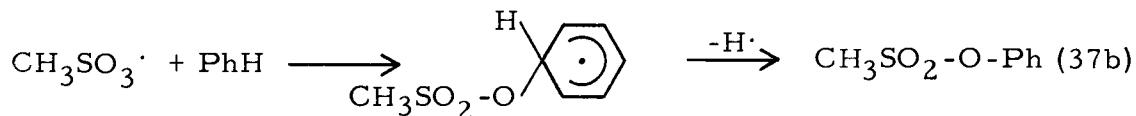
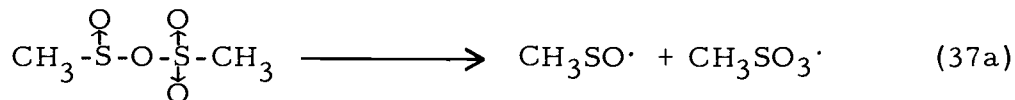


sulfinate ester could be oxidized as in eq. 34.

A third possible way the ester could be formed would be by head to tail recombination of two methanesulfonyl radicals (eq. 36).

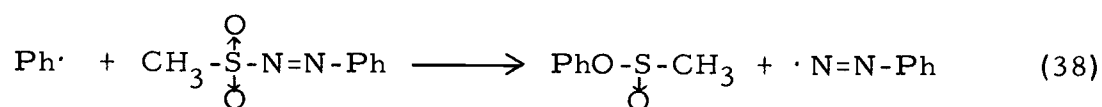


The product of eq. 36 could then decompose thermally to a $\text{CH}_3\text{SO}_3\cdot$ radical (eq. 37a) which then reacted with the solvent (eq. 37b).



Unpublished results from this laboratory indicate that eqs. 36 and 37 quite probably occur for the case where the sulfonyl radical is $\text{ArSO}_2\cdot$.

Another possible route for the formation of phenyl methanesulfonate is by the attack of a phenyl radical on a diazosulfone oxygen (eq. 38) to give a phenylazo radical and an intermediate sulfinate

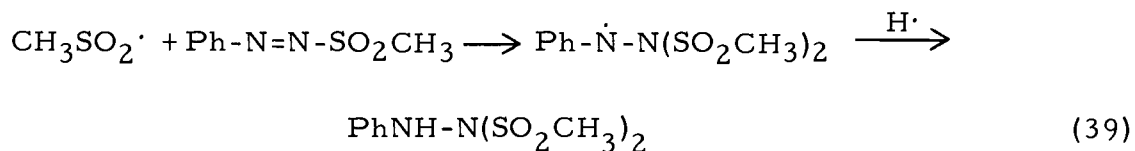


ester which could be oxidized in the manner proposed previously (eq. 34).

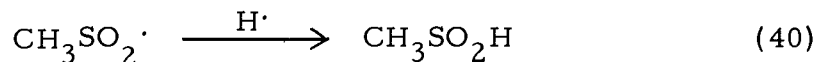
The first route for the formation of phenyl methanesulfonate (eqs. 33 and 34) is perhaps the most attractive one at present. The reason is as follows. One will recall that thermal decomposition of BMS in cumene also gave about 0.07 mole/mole BMS of the phenyl ester. With cumene as the solvent, the amount of free benzene is negligible and hence the probability of eqs. 35 or 37b being able to occur successfully in competition with other reactions of the methanesulfonyl radical is exceedingly small. Equation 38, however, cannot be excluded by such an argument, although precedent for a reaction of this type is difficult to find. It is clear then that phenyl methanesulfonate could be formed in one or more of many possible schemes but there is no way to distinguish the correct mechanism for its formation.

Two mechanisms can be postulated to account for the formation of either the 1,2- or 2,2-bismethanesulfonyl phenylhydrazine isomer isolated in low yield from the decomposition of BMS in

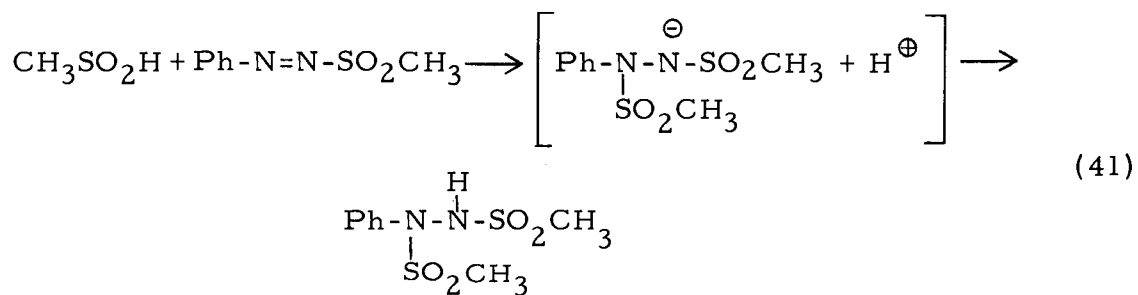
benzene. To form the 2,2- isomer, a methanesulfonyl radical could add to the diazo group of another molecule of BMS and the resulting radical could subsequently abstract a hydrogen atom to form the product (eq. 39). To account for the possible formation of the 1,2-



isomer, methanesulfinic acid could be formed in the decomposition by hydrogen atom abstraction by a methanesulfonyl radical (eq. 40). The



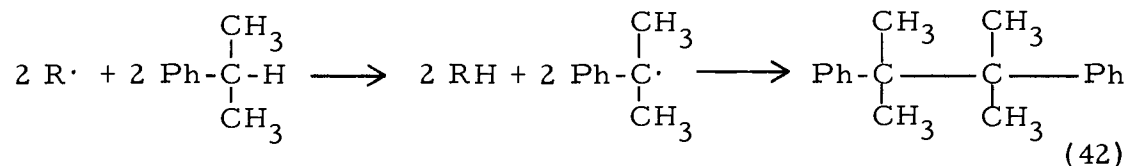
acid could then add across the diazo group of a molecule of BMS to form the 1,2-isomer (eq. 41).



Products in Cumene and Diphenylmethane

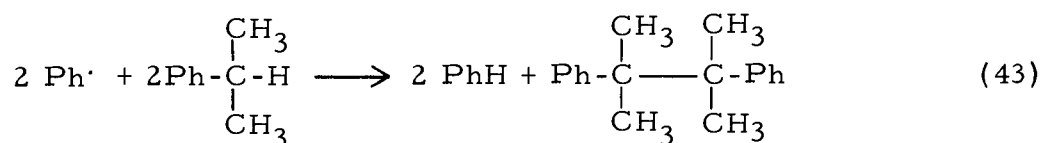
It was thought that a greater proportion of tractable products could be isolated and a more meaningful mechanism postulated if the decomposition of BMS were carried out in solvents with easily abstracted hydrogen atoms. Cumene is a good solvent in this respect because abstraction of its labile α -hydrogen atom forms a reasonably

stable free radical which can undergo dimerization to give bicumyl (eq. 42). Hey, Pengilly and Williams (30) demonstrated that



α -hydrogen abstraction by radicals produced in the thermal decomposition of benzoyl peroxide predominates 3:2 over homolytic aromatic substitution on the cumene aromatic ring, and that the rate of nuclear phenylation of cumene relative to benzene is 0.87.

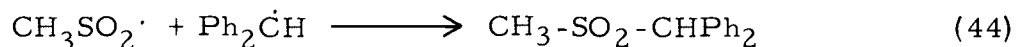
The isolated products from the thermal decomposition of BMS in cumene (Table 1, Column 3) were those corresponding only to an α -hydrogen atom abstraction reaction, with no product of phenylation of the cumene aromatic ring being detected. The observed 2:1 molar ratio of benzene to bicumyl formed is what would be expected if phenyl radicals from the diazosulfone were to abstract the α -hydrogen atom from cumene, and the cumyl radicals thus formed were to dimerize (eq. 43). As already noted, the formation of phenyl methanesulfonate



in cumene suggests that either a cage recombination reaction of phenyl and $\text{CH}_3\text{SO}_2^\cdot$ radicals may be occurring (eq. 33) or that a phenyl radical could displace a phenylazo radical from a molecule of BMS (eq. 38). Subsequent oxidation of the intermediate sulfinic ester

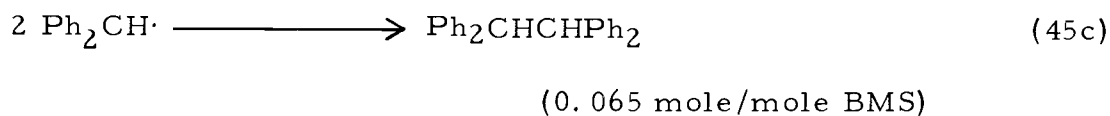
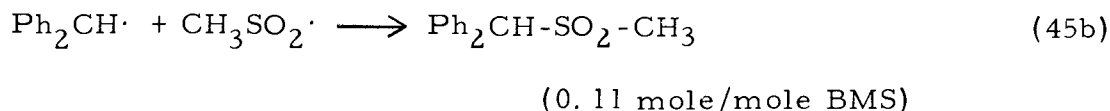
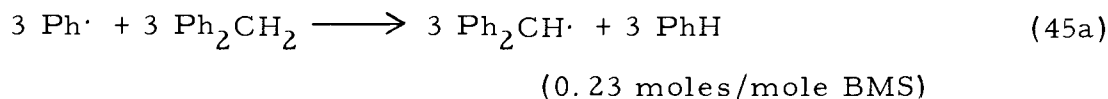
(eq. 34) formed by these reactions could occur to produce the observed product.

Decomposition of BMS in diphenylmethane was expected to be analogous to the decomposition in cumene since diphenylmethane has two easily abstracted α -hydrogen atoms, and the diphenylmethyl radical formed by an abstraction reaction would be highly stabilized by resonance and likely to dimerize to tetraphenylethane. Tetraphenylethane was indeed observed as one of the products of the decomposition (Table 1, Column 4), being formed in the ratio 0.065 mole/mole BMS. In this decomposition, however, some of the phenyl radicals formed do phenylate the solvent, since approximately equimolar amounts (0.04 mole/mole BMS) of o- and p-phenyldiphenylmethane were observed as products. Diphenylmethyl methyl sulfone was isolated in relatively large yield (0.11 mole/mole BMS). This is the only sulfone isolated from the decomposition in any solvent, and its formation is most easily explained by assuming that a methanesulfonyl radical couples with a diphenylmethyl radical (eq. 44). The amount

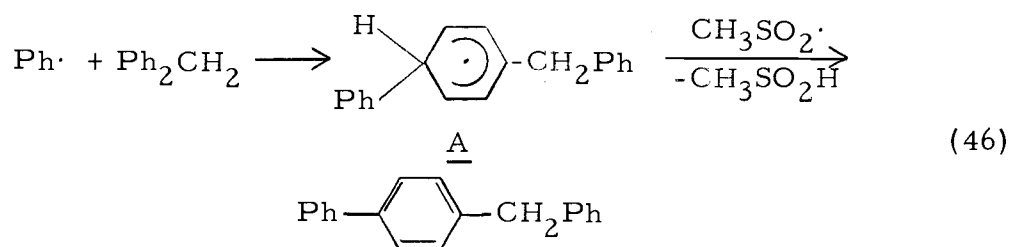


of benzene formed in the decomposition can be related to the number of phenyl radicals necessary to abstract an α -hydrogen atom from diphenylmethane, assuming the diphenylmethyl radicals thus formed either dimerize to tetraphenylethane or couple with a methanesulfonyl radical to form the benzhydryl sulfone. This can be seen as follows.

If all 0.23 mole benzene/mole BMS is assumed to arise from eq. 45a,



one should get 0.23 moles of $\text{Ph}_2\text{CH}\cdot$ radicals. Formation of 0.11 mole methyl benzhydryl sulfone/mole BMS (eq. 45b) accounts for the fate of 0.11 mole of these radicals. Formation of 0.065 mole tetraphenylethane/mole BMS (eq. 45c) accounts for the fate of the remaining 0.12 moles of $\text{Ph}_2\text{CH}\cdot$ radicals. The observed phenylation of the solvent, however, would also require hydrogen loss from intermediate A (eq. 46). Here perhaps the abstraction of the hydrogen

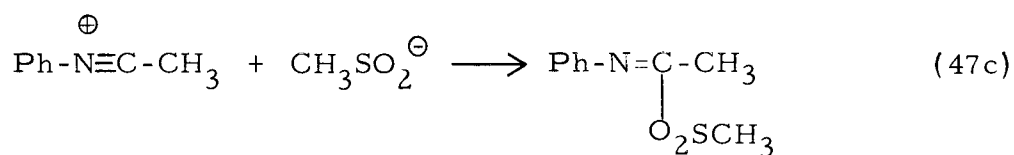
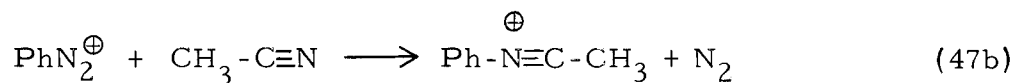
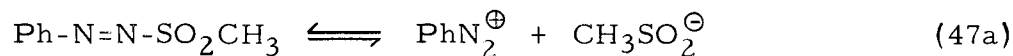


atom involves some other radical than phenyl such as $\text{CH}_3\text{SO}_2\cdot$.

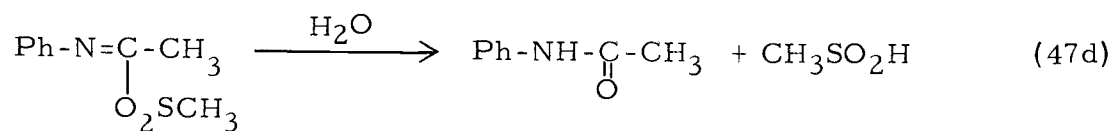
Products in Acetonitrile

In order to see if a change in the polarity of the solvent would have any effect on the products of the decomposition of benzenediazo

methyl sulfone, acetonitrile was used as a solvent (Table 1, Column 5). The only product isolated from this decomposition was acetanilide, which was formed in a yield of 0.71 mole/mole BMS, an excellent conversion to product when compared to the yields of tractable products isolated from the decomposition of BMS in hydrocarbon solvents. The mechanism for its formation is most likely ionic, since Lewis and co-workers (64) have demonstrated that ionization of phenyl diazosulfones to PhN_2^{\oplus} and RSO_2^{\ominus} occurs in methanol, another polar solvent. Moreover, since Makarova and Nesmeyanov (52) have shown that the decomposition of $\text{PhN}_2^{\oplus} \text{BF}_4^{\ominus}$ in acetonitrile results in the formation of acetanilide in 29 percent yield, a mechanism for the decomposition of BMS in acetonitrile which involves a diazonium ion as an intermediate is certainly in accord with the products formed under such conditions. One can thus satisfactorily accommodate the behavior of BMS in acetonitrile on the basis of the following mechanistic scheme (eq. 47).



on work-up



(There is no mechanism implied in eq. 47b).

Thus it appears that changing the polarity of the solvent in which the diazosulfone is decomposed likewise changes the mechanism of its decomposition, because the formation of products in hydrocarbon solvents is most easily explained by assuming a homolytic decomposition, while the product formed in acetonitrile is most easily explained by invoking an ionic decomposition.

Kinetics of the Decomposition of Benzenediazo Methyl Sulfone

Kinetic studies in benzene. A first order plot of the rate of evolution of sulfur dioxide from decomposing BMS in benzene (Figure 1, Curve A) shows that the rate accelerates after about the first half-life. This perhaps is due to acidic products formed during the decomposition, since suspending calcium oxide in the solvent during the decomposition (Curve B) entirely stops the accelerated rate of evolution of sulfur dioxide seen in the absence of calcium oxide. The first order rate of evolution of sulfur dioxide from BMS in benzene with calcium oxide present is seen to be slightly slower than the initial first order rate for BMS in pure benzene. Calcium oxide could possibly inhibit any acid catalyzed decomposition which occurs in its

absence.

Table 6 shows the first order rate constants for the three methods of following the decomposition reaction.

Table 6. First order rate constants for the decomposition of BMS at 80°.

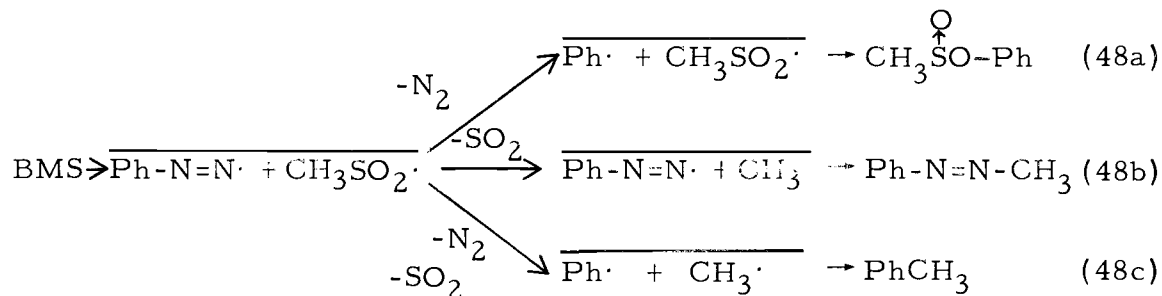
Measured by	SO ₂ Evolution	NMR Method	Radical Scavenging
k, sec ⁻¹	5.5 x 10 ⁻⁵	9.3 x 10 ⁻⁵	1.87 x 10 ⁻⁵
(BMS), <u>M</u>	0.10	0.20	5 x 10 ⁻⁴

For the rate of evolution of sulfur dioxide, that from decomposing BMS in benzene with added calcium oxide (Figure 1, Curve B) was chosen since this value represents the rate of evolution of the gas in the assumed absence of any acid catalyzed or ionic decomposition. It is also assumed, as mentioned previously, that this value reflects the most accurate rate of decomposition of the diazosulfone, since there is no indication that sulfur dioxide evolution is faster or slower than the true rate of decomposition of BMS. The rate of disappearance of BMS, determined by recording the disappearance of the methyl protons of BMS in the NMR method, is faster than sulfur dioxide evolution. The behavior of the rate of sulfur dioxide evolution in the presence and absence of calcium oxide suggests that this faster rate may well be due to autocatalysis of the decomposition by acidic

impurities such as sulfur dioxide trapped in the sealed NMR tube.

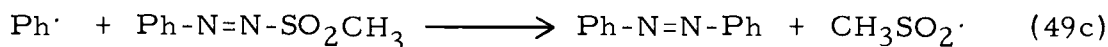
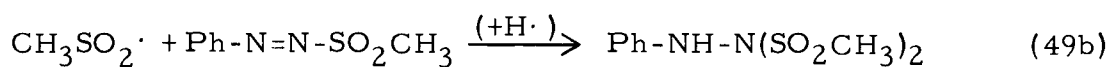
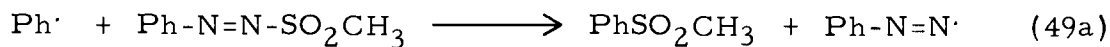
The rate of production of scavengable free radicals during the decomposition of BMS in benzene, k_{df} , is significantly smaller than what we feel to be the most accurate rate of decomposition of the diazosulfone, k_{SO_2} . The ratio of the values of k_{df}/k_{SO_2} is 0.34, which indicates that only about one-third of the molecules of BMS decomposing produce scavengable free radicals. This value of f is fairly low, but not significantly smaller than the f values found in certain other radical decompositions (47, 48); in those other studies, free radical induced decomposition and cage recombination was invoked to explain the low f values.

There are several possible processes in the decomposition of BMS which might result in approximately two-thirds of the decomposition occurring without the formation of scavengable free radicals. First, decomposition of BMS could occur with some cage recombination of the initially formed pairs of radicals. Some possible cage recombination pathways are shown in eq. 48 (where the caged pair of radicals is represented by a line above the radical pairs). Product



studies have previously been interpreted to show that phenyl methane-sulfonate could be formed in the manner of eq. 48a. There was no effort made to determine if any toluene was formed in the decomposition. The isolation and identification of the cage product of eq. 48b might have been obscured by the large amounts of intractable tars formed. The only product isolated then that may indicate that cage recombination could be occurring is phenyl methanesulfonate, but one should remember that the mechanism for its formation is highly speculative.

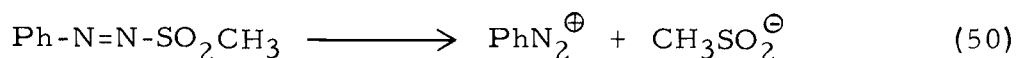
Free radical induced decomposition of BMS is a second possible process which could contribute toward k_d being smaller than k_{SO_2} . Some possible induced decomposition reactions which could occur are presented in eq. 49. It will be remembered that these



same induced decomposition reactions were postulated to account for some of the observed products of the decompositions, but the fraction of induced decomposition occurring, if based on the yields of these products, would not be large.

A third way in which at least part of the low efficiency can presumably be explained is to assume that some fraction of the

decomposition occurs by an ionic pathway in which the intermediates would not be scavengable by the Koelsch radical (eq. 50). This could



conceivably occur since it was shown that the decomposition in acetonitrile was most likely ionic. Therefore, it appears that cage recombination, induced decomposition and heterolytic decomposition could possibly be occurring, and that the occurrence of these processes may be reflected by the low value of f observed.

This study of the thermal decomposition of BMS has shown that in the ionizing solvent acetonitrile, the decomposition proceeds by a heterolytic pathway. In hydrocarbon solvents a fair part of the decomposition apparently proceeds via a free radical route. It is not clear why the decomposition in benzene does not give a larger f value although the three factors discussed above might contribute.

The free radical decomposition of benzenediazo methyl sulfone in hydrocarbon solvents appears similar to the decomposition of benzenediazo phenyl sulfone studied by Overberger and Rosenthal (61, 65) but, as we shall see, it is quite different than the decomposition of benzenediazo benzyl sulfone.

The Thermal Decomposition of Benzenediazo Benzyl Sulfone

A comparison of the thermal decomposition of BBS with the decomposition of other benzenediazo compounds. The principal organic products of the decomposition of BBS in benzene, cumene or diphenylmethane are benzaldehyde phenylhydrazone and N-benzyl benzaldehyde phenylhydrazone, both of which contain the two nitrogen atoms of the parent diazo group. The thermal decompositions of benzenediazo methyl sulfone and a number of other benzenediazo compounds in aromatic solvents give major products which do not contain the nitrogen atoms of the diazo group (2, 61, 76, 77). Moreover, BBS decomposes in benzene to produce only a very small amount of biphenyl, a result quite different than that observed in the thermal decompositions of benzenediazo methyl sulfone and other benzenediazo compounds (2, 61, 76, 77). Decomposition of BBS in solvents with easily abstracted hydrogen atoms such as cumene and diphenylmethane had a noticeable effect on the yield of the products of the decomposition (Table 7) but no products were isolated which contained a solvent derived group, in contrast to the products of the decomposition of benzenediazo methyl sulfone in these solvents (Table 1, Columns 3 and 4).

The amount of sulfur dioxide evolved from decomposing BBS in benzene was much greater (0.66 mole/mole BBS) than the amounts

Table 7. Major organic products from the thermal decomposition of BBS in benzene, cumene and diphenylmethane.

Product	Mole Product/Mole BBS Decomposed in		
	Benzene ¹	Cumene ²	Diphenylmethane ³
Benzaldehyde Phenyl-hydrazone	0.55	0.46	0.34
N-Benzyl Benzaldehyde Phenylhydrazone	0.06	0.118	0.16
Benzene	----	0.11	0.15
Toluene	None	Trace	0.049

¹0.078 M BBS, Temp. = 54.8°

²0.080 M BBS, Temp. = 79.5°

³0.100 M BBS, Temp. = 80.1°

evolved from the decompositions in benzene of benzenediazo t-butyl sulfone (0.36-0.46 mole/mole BtBuS), benzenediazo methyl sulfone (0.14 mole/mole BMS), or from benzenediazo phenyl sulfone (none). Also, a two hour induction period preceded the evolution of sulfur dioxide from dilute solutions of the benzyl diazosulfone in benzene (Figure 3) while a one hour induction period was observed prior to the evolution of sulfur dioxide from similar solutions of decomposing t-butyl diazosulfone (Figure 11). A reasonably smooth first order evolution of sulfur dioxide with no induction period was observed for the decomposition of benzenediazo methyl sulfone in benzene (Figure 1).

The Effect of Added Koelsch Radical on the Decomposition of BBS

The effect of added Koelsch radical on the rate of evolution of sulfur dioxide from decomposing BBS and its effect on the rate of disappearance of BBS as determined by the NMR method is striking. A comparison of Figures 3 and 16 show that the Koelsch radical effectively stops the swift evolution of sulfur dioxide observed in the decomposition of BBS in pure benzene, and that the rate at which sulfur dioxide is evolved from the decomposing benzyl diazosulfone in benzene with Koelsch radical present is comparable to the rate at which scavengable radicals are produced.

The effect of added Koelsch radical on the disappearance of BBS in benzene is seen in Figure 17. The apparent effect of adding the free radical is to stop the decomposition of the benzyl diazosulfone. Thus, the presence of the Koelsch radical certainly inhibits the decomposition of BBS. We have remarked previously that the results of these experiments are in accord with an interpretation that the effect of the Koelsch radical is to inhibit the usual free radical chain induced decomposition of BBS. The Koelsch radical could possibly do this by scavenging free radicals which initiate this chain process.

Tentative Identification of the Intermediate

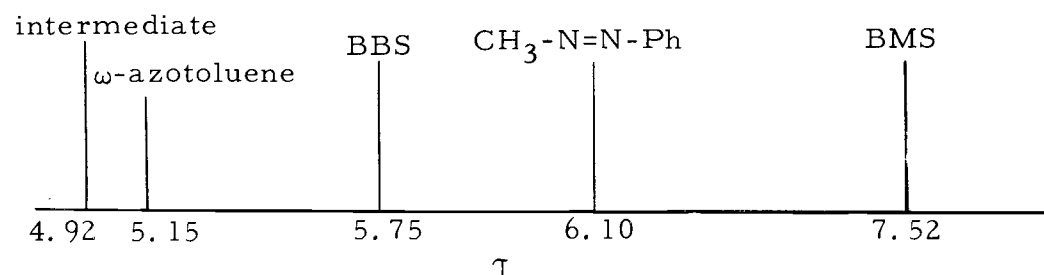
The thermal decomposition of BBS in benzene proceeds with the formation of a short-lived compound which subsequently disappears in the course of the reaction. In order to develop a reasonable mechanism for the decomposition of BBS it was of principal importance to identify this elusive intermediate. As we have shown, the only clear spectroscopic evidence for the identification of the intermediate is its singlet NMR signal at 4.92 τ , shifted 50 c. p. s. downfield from the NMR absorbance of the benzylic protons of BBS. Little definitive evidence about this intermediate could be obtained from either UV or IR spectroscopy of solutions of the reaction mixture containing the intermediate.

Measurements of the rate of formation of the intermediate relative to the rate of disappearance of the diazosulfone indicate that the intermediate reaches its maximum concentration when little, if any, diazosulfone remains (Figure 10). A qualitative comparison of the rate of sulfur dioxide evolution from a benzene solution of the diazosulfone in the same concentration as that used for the NMR experiments shows that the evolution of sulfur dioxide from the decomposing diazosulfone is approximately concurrent with the formation of the intermediate (Figures 7 and 10). This suggests that the intermediate is formed from some precursor by the evolution of sulfur

dioxide and that the intermediate most likely does not contain a sulfone group. The NMR experiments also indicate that the concentration of the unstable intermediate becomes quite large during the decomposition of the diazosulfone in benzene and thus it is most likely related to one of the major products of the decomposition.

We propose that this intermediate is 1'-phenyl benzeneazomethane ($\text{PhCH}_2\text{-N=N-Ph}$) (7, 73, 75). The evidence is as follows. Figure 18 shows τ values for the alkyl protons of the intermediate and other compounds. The NMR spectrum of the intermediate in benzene solution is a sharp singlet at 4.92 τ . The reported NMR

Figure 18. τ - Values for the alkyl protons of

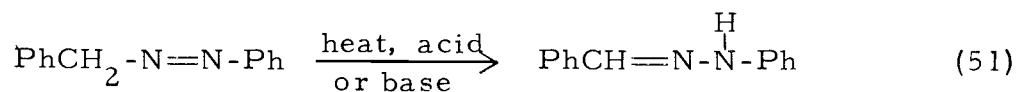


spectrum of a solution of ω -azotoluene ($\text{PhCH}_2\text{-N=N-CH}_2\text{Ph}$) in carbon tetrachloride shows a sharp singlet due to the benzyl protons at 5.15 τ (23). The benzyl proton signal of BBS in benzene is a sharp singlet at 5.75 τ . The methyl proton signal of benzenediazo methyl sulfone in benzene is a singlet at 7.52 τ while the methyl proton signal of benzeneazomethane in carbon tetrachloride is reported to be at

6.10 τ (23). The difference in the chemical shifts of the benzyl protons of 1'-phenyl benzeneazomethane, the proposed intermediate, and the benzyl protons of ω -azotoluene may be due to the inclusion of the benzyl protons of the former in the deshielding cone generated by the phenyl ring of the benzeneazo group. The benzyl protons of ω -azotoluene are further from the opposite phenyl ring which presumably results in their higher upfield position relative to the alkyl protons of the intermediate.

If benzenediazo methyl sulfone were to decompose to an intermediate analogous to the one we propose for the decomposition of BBS it would be benzeneazomethane. Figure 18 shows that the resonance of the methyl protons of benzeneazomethane is downfield from that of the methyl protons of BMS, similar to the downfield absorptions of the alkyl protons of the intermediate relative to the alkyl protons of BBS.

The NMR experiments have shown that the maximum concentration of a two alkyl proton containing intermediate is 0.42 mole/mole of BBS initially present. This requires that a major product of the decomposition be derived from the intermediate. Since benzaldehyde phenylhydrazone, the major organic product isolated from the decomposition of BBS in hydrocarbon solvents, would be formed by tautomerization of 1'-phenyl benzeneazomethane, this is in accord with the results of our products studies. The facile tautomerization of 1'-phenyl benzeneazomethane has indeed been observed (eq. 51)



(16, 73). The yield of benzaldehyde phenylhydrazone isolated from the products of the decomposition of BBS in benzene is 0.55 mole/mole BBS, while the amount of the intermediate present at its maximum concentration is 0.42 mole/mole BBS, another fact which certainly seems to indicate that the proposal that the intermediate is 1'-phenyl benzeneazomethane and that it tautomerizes to benzaldehyde phenylhydrazone during the course of the decomposition is a most reasonable one.

The visible absorption spectrum of a solution of the decomposition residue containing the intermediate showed a weak absorption band at 405 mμ which was absent in the spectrum of the fully decomposed diazosulfone. This absorption could quite reasonably be due to 1'-phenyl benzeneazomethane since O'Connor (59) has shown that alkyl benzenediazo compounds have visible absorption maxima in the region of 400 to 407 mμ which are characterized by small molar extinction coefficients.

The ultraviolet absorption spectrum of 1'-phenyl benzeneazomethane is characterized by an extinction coefficient of approximately 1000 at its 344 mμ shoulder (75) while the tautomer, benzaldehyde phenylhydrazone effectively masks this absorption with an extinction coefficient of 20,000 at its 344 mμ λ_{max} (68). Besides the

344 m μ shoulder, no other UV absorption characteristics of 1'-phenyl benzeneazomethane have been reported. Therefore it is not difficult to understand why no useful information could be obtained from the UV spectrum of a solution of the reaction mixture containing the intermediate. The infrared spectrum of 1'-phenyl benzeneazomethane has never been reported, but Le Fèvre and co-workers (49) believe that relatively weak absorption bands at $1579 \pm 9 \text{ cm}^{-1}$ and $1406 \pm 14 \text{ cm}^{-1}$ are characteristic of compounds containing an azo group. Since infrared absorption spectra of both the reaction mixture containing the intermediate and the fully decomposed diazosulfone exhibit strong absorption bands at these wavelengths one would not expect to be able to see any specific absorption due to the intermediate in the infrared. Any absorption due to the intermediate would be masked by the stronger absorption of the phenylhydrazone present in the reaction mixture.

We feel that 1'-phenyl benzeneazomethane most adequately represents the structure of the intermediate observed in the NMR spectrum during the decomposition of the benzyl diazosulfone, and that much of the major organic product, benzaldehyde phenylhydrazone, is formed by the tautomerization of initially formed 1'-phenyl benzeneazomethane.

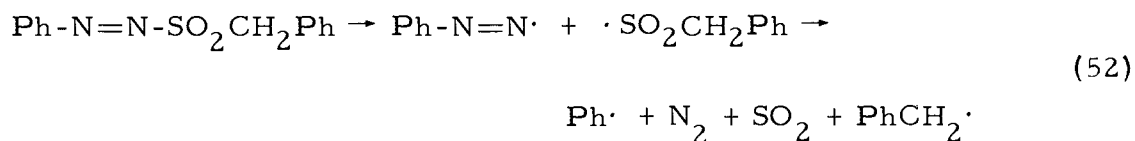
Proposed Mechanisms for the Thermal Decomposition of BBS

To be consistent with the experimental results obtained in this study, any mechanism proposed for the thermal decomposition of dilute solutions of BBS in hydrocarbon solvents should account for:

1) the induction period prior to the evolution of sulfur dioxide; 2) the types of products isolated and the dependence of their yields on the solvent in which the diazosulfone is decomposed; 3) the gross difference between the rate at which scavengable radicals are produced and both the apparent rate at which the diazosulfone disappears and the rate of evolution of sulfur dioxide; 4) the ability of the Koelsch radical to inhibit both the fast evolution of sulfur dioxide and to substantially decrease the rate at which the benzyl diazosulfone disappears; and 5) the formation of 1'-phenyl benzeneazomethane as the metastable intermediate observed in the decomposition.

We believe that the majority of our results are best explained in terms of a free radical chain induced decomposition of the diazosulfone, which, like any free radical chain mechanism must have three fundamental features; initiation, propagation and termination.

Initiation of the decomposition. The thermal decomposition of BBS could possibly be initiated by free radicals produced by the decomposition of BBS (eq. 52). Hey and co-workers (17) postulated that

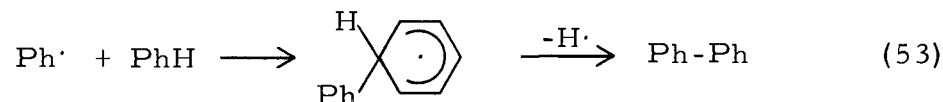


nitrogen loss from a phenylazo radical is most likely fast, and Kice (37) pointed out that the loss of sulfur dioxide from an alkanesulfonyl radical can occur readily if the resulting alkyl radical is stable.

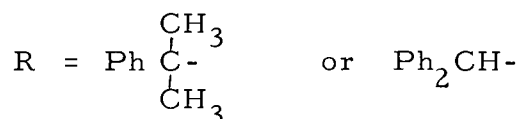
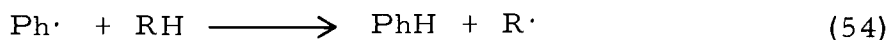
If a free benzyl radical is involved in the decomposition of BBS in benzene, one would not expect it to abstract a hydrogen atom from the solvent, and indeed no detectable amount of toluene was formed in the decomposition of BBS in benzene. However, for the decomposition of BBS in cumene and diphenylmethane, one would expect a free benzyl radical to abstract a hydrogen atom from diphenylmethane and possibly from cumene. A greater proportion of toluene should be formed in diphenylmethane than in cumene since diphenylmethane has a larger hydrogen atom transfer constant than does cumene. This, too, is observed since the decomposition of BBS in diphenylmethane resulted in the formation of 0.049 mole toluene/mole BBS while the decomposition of BBS in cumene gave only a trace of toluene (less than 0.01 mole/mole BBS). It appears then that free benzyl radicals might be formed during the decomposition of BBS, and that they could possibly abstract a hydrogen atom from suitable solvents.

The phenyl radical formed by the decomposition of the diazo-sulfone (eq. 52) could also react with the solvent. In benzene, the

reaction of the phenyl radical with the solvent would give biphenyl (eq. 53) which is observed in low yield in the products of the



decomposition of BBS in benzene (0.02 mole/mole BBS). In cumene and diphenylmethane, phenyl radicals produced by the decomposition of BBS could abstract a hydrogen atom from the solvent to form benzene and the corresponding cumyl or diphenylmethyl radical (eq. 54).



The ratio of the amount of benzene formed in the decomposition of BBS in cumene as the solvent to the amount formed with diphenylmethane as the solvent is $0.11/0.15 = 0.73$. Bridger and Russell (6) showed that free phenyl radicals produced by the decomposition of phenylazotriphenylmethane in cumene and diphenylmethane form benzene in the ratio of $0.93/1.4 = 0.67$ respectively. Thus, the similarity of these two ratios may indicate that benzene is formed in the decomposition of BBS in cumene and diphenylmethane by hydrogen atom abstraction from the solvent by a free phenyl radical.

The fate of the cumyl and diphenylmethyl radicals (eq. 54) is possibly more complex since the coupling products of the two radicals,

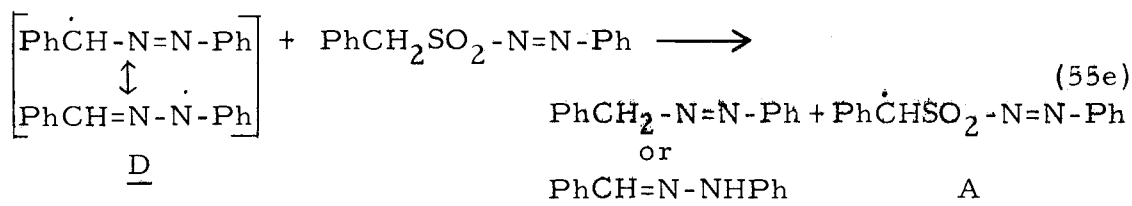
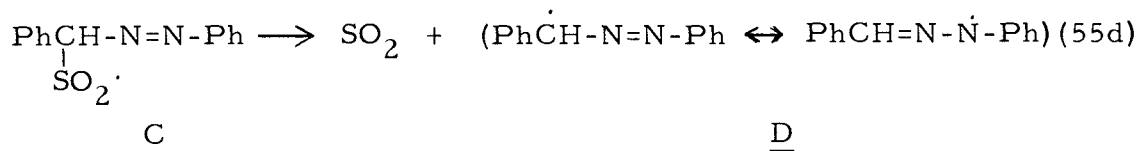
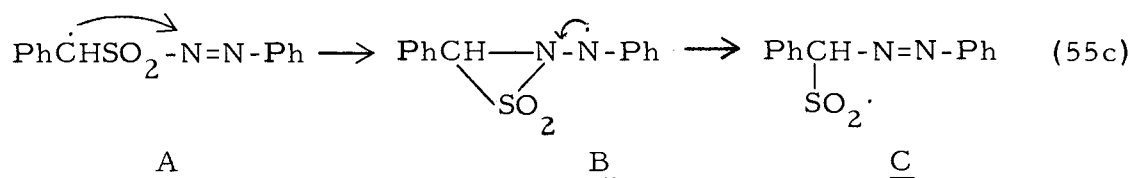
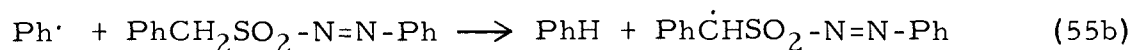
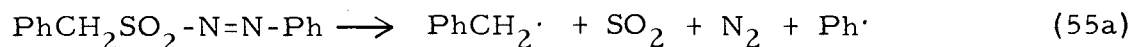
bicumyl and tetraphenylethane, were not observed as products of the decomposition of BBS in cumene or diphenylmethane, respectively. Their possible reactions will be discussed later. Thus, both the phenyl and benzyl radicals could be formed by the initial decomposition of the diazosulfone and both could conceivably initiate a chain decomposition.

Propagation of the decomposition. If a free radical induced decomposition of BBS is occurring, the presence of a free radical scavenger such as the Koelsch radical might be expected to inhibit the decomposition by trapping the free radicals before they can induce the decomposition. Thus, under such conditions the rate of decomposition of BBS should be much slower and close to the rate at which scavengable free radicals are produced. Indeed, we have shown that the decomposition of BBS in benzene solution in the presence of the Koelsch radical evolves sulfur dioxide at a rate comparable to the rate of production of scavengable free radicals, and that the relatively fast evolution of sulfur dioxide observed in the decomposition of BBS in pure benzene can be eliminated (compare Figures 3 and 16). Also we have shown that the disappearance of BBS in benzene in the presence of the Koelsch radical is negligible over the period of time in which pure benzene solutions of BBS show substantial decomposition (Figure 17). This might indicate that the decomposition of BBS is induced by free radicals which, in the presence of

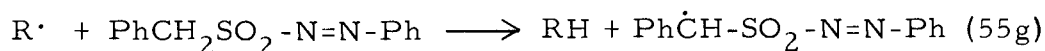
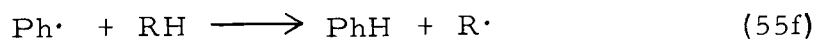
the Koelsch radical, are trapped and cannot react further.

The free radical chain propagation step of the decomposition should presumably form either 1'-phenyl benzeneazomethane and/or its tautomer benzaldehyde phenylhydrazone, the principal final organic product of the decomposition. Either of these products requires a mechanism for the propagation step which effectively involves the migration of the benzyl group from its original attachment to the sulfone group of BBS to a nitrogen of the benzeneazo group. Two possible mechanisms for the propagation step of the decomposition of BBS follow.

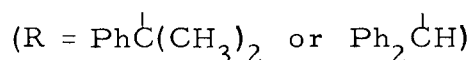
Mechanism I (intramolecular propagation). The induced decomposition of BBS could occur in the following fashion (eq. 55). In this case,



in benzene, chain decomposition of BBS is initiated by the abstraction of a benzylic hydrogen atom of BBS by a phenyl radical (eq. 55b) produced by the initial decomposition of the diazosulfone (eq. 55a). The intermediate radical A thus formed could rearrange intermolecularly through radical B to form radical C (eq. 35c). Radical C would be expected to lose sulfur dioxide rapidly to form the resonance stabilized radical D (eq. 55d) which could then abstract a benzylic hydrogen atom from another molecule of BBS to form the proposed intermediate 1'-phenyl benzeneazomethane (or benzaldehyde phenylhydrazone) and the chain carrying radical A. The steps of eqs. 55 c, d and e however would most likely be fast since there was no product isolated from the decomposition of BBS in hydrocarbon solvents that would correspond to a radical coupling product of any of the intermediate radicals A, B or C. In cumene or diphenylmethane, the decomposition of BBS could possibly be initiated by the alternate sequence shown in eq. 55 f and g. Radical A could then react in the



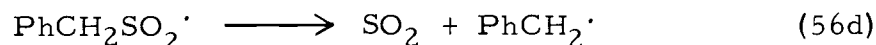
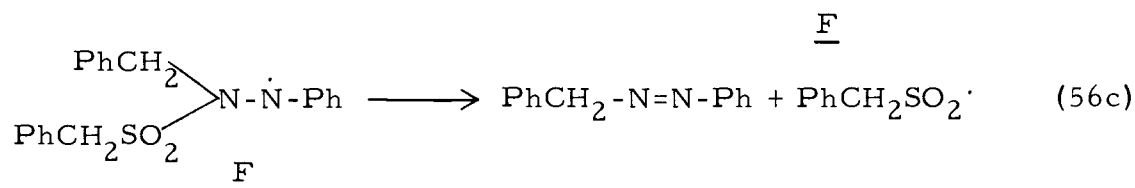
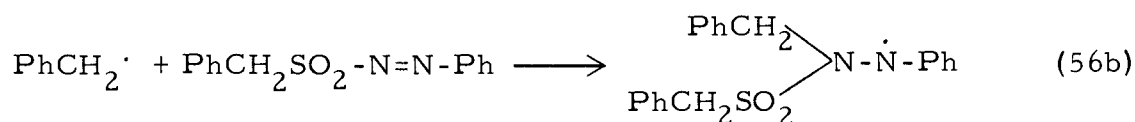
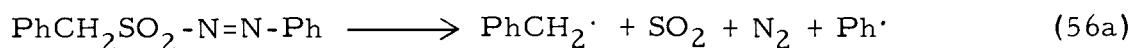
A



fashion proposed in eq. 55 c, d and e. Precedent for a scheme such as we propose in eq. 55 is in some ways difficult to find, however.

Mechanism II (intermolecular propagation). An intermolecular

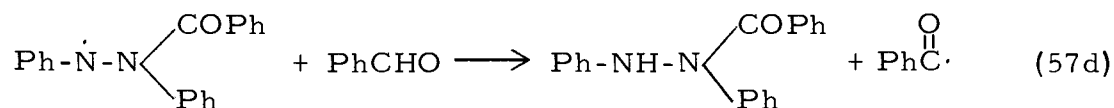
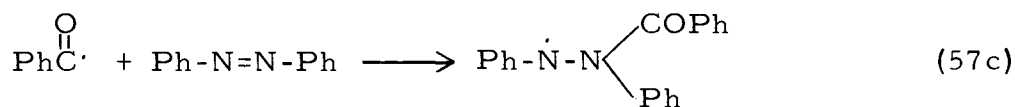
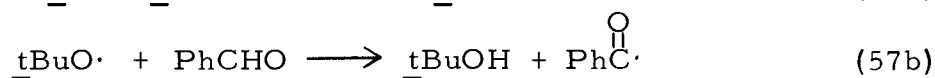
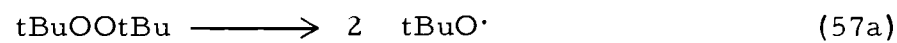
propagation step for the decomposition of BBS in hydrocarbon solvents can also account for the formation of the principal decomposition products (eq. 56). In this case, propagation is envisaged to



occur by the initial attack of a benzyl radical [produced in the initial decomposition of BBS (eq. 56a)] on the azo group of another molecule of BBS could give radical F. The intermediate radical F could then form the proposed intermediate 1'-phenyl benzeneazomethane by the β -elimination of an α -toluenesulfonyl radical (eq. 56c). The chain carrying benzyl radical could then be regenerated by desulfonylation of the α -toluenesulfonyl radical (eq. 56d). Equations 56 b, c and d could continue as a chain until the chain carrying benzyl radical is removed from further reaction presumably by coupling with another radical. Although the lifetime of radical F appears to be short since there is no product isolated from the decomposition of BBS in hydrocarbon solvents which would indicate that it couples with another

radical, a possible chain termination step involving the coupling of a benzyl radical with radical F will be proposed in the Chain Termination discussion.

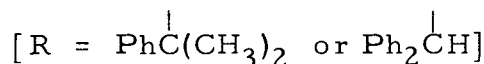
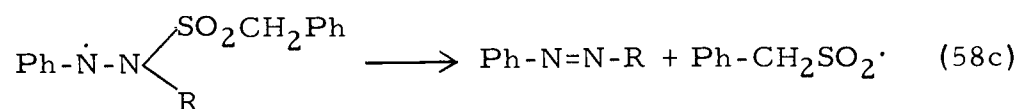
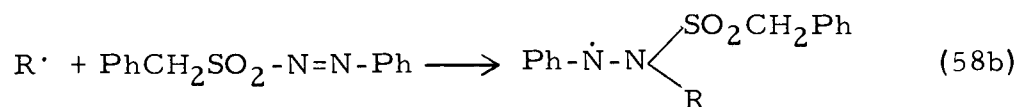
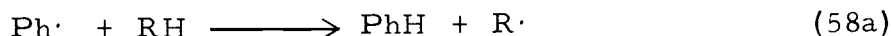
Free radical additions to the azo group, such as we propose in either eq. 55c or eq. 56b have received little study, but one reported free radical addition to the azo group is thought to involve the following sequence (eq. 57) (36). This mechanism was proposed to



account for the observation that decomposition of as little as 0.05 mole t-butyl peroxide/mole azobenzene in benzaldehyde solvent produced an 80 percent yield of 1-benzoyl-1,2-diphenyl hydrazine, presumably by the chain mechanism shown in eq. 57c and d. Moreover, Pryor has remarked (63) how efficient phenylazotriphenylmethane appears to be as a phenyl free radical trap and advanced the hypothesis that "the addition of a phenyl radical to phenylazotriphenylmethane might be expected to be fast since it produces a stabilized radical with a structure reminiscent of that of diphenylpicrylhydrazyl."

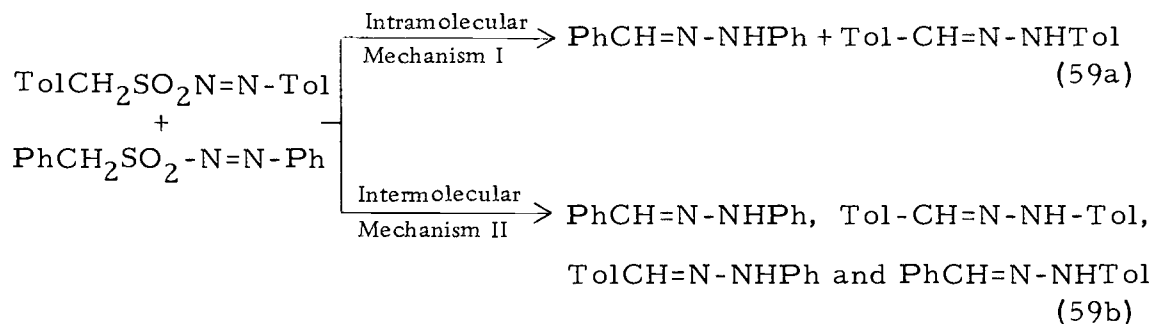
Elimination of a substituent β to the radical center, similar to what we propose in eq. 55c and 56c, has considerable precedent in free radical chemistry. Halogen atoms (66), thiyl radicals (35, 71), and even alkyl radicals (33, 60) can be eliminated in this manner. Thus, the loss of an alkanesulfonyl radical such as we propose in these reactions appears feasible.

In cumene or diphenylmethane as the solvent for the decomposition of BBS, chain propagation could quite possibly be initiated in a slightly different manner (eq. 58) than in benzene. The azo



compound formed by eq. 58c (or the tautomer $\text{Ph}_2\text{C=N-NHPh}$ for $\text{R} = \text{Ph}_2\overset{|}{\text{C}}\text{H}$) could possibly have been overlooked in the product studies of the decomposition in cumene and diphenylmethane.

Differentiation between an intermolecular and intramolecular propagation step could be determined conveniently by the following method (eq. 59). A mixture of benzenediazo benzyl sulfone and an



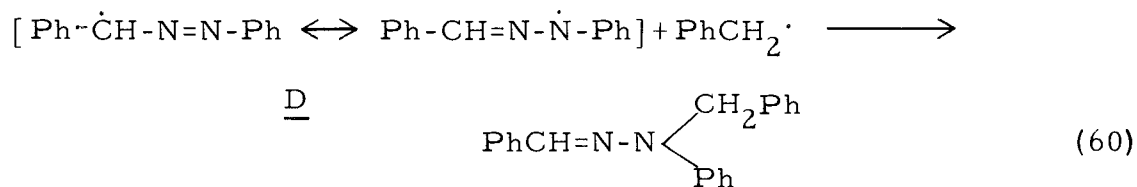
appropriately "labeled" benzyl diazosulfone (here for example, p-tolyl diazo p-methylbenzyl sulfone) could be decomposed in benzene solution. An intramolecular reaction (Mechanism I) would form only PhCH=N-NHPh and Tol-CH=N-NH-Tol (eq. 59a), while an intermolecular mechanism such as we propose in Mechanism II should form all possible combinations of the two diazosulfones; Tol-CH=N-NH-Tol , PhCH=N-NHPh , Tol-CH=N-NHPh and PhCH=N-NHTol (eq. 59b). This "crossover" experiment could cleanly differentiate between the two possible propagation pathways we have postulated.

Termination of the Decomposition

The possible termination mechanisms presented in the following discussion are schemes which seem to be supported or suggested by certain of the experimental evidence, yet at the same time are seemingly at variance with other pieces of experimental data. For example, in the decomposition of BBS in cumene or diphenylmethane one might have expected that the chain decomposition would

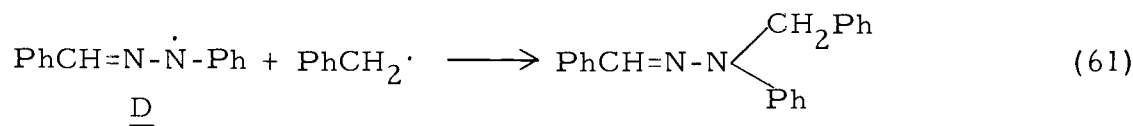
be terminated by the coupling of the chain carrying radical with a solvent derived free radical, yet no such products were found in the product studies. Other examples of this type could be given. For this reason, critical discussion of each possible termination step seems unwarranted with the evidence at hand because obviously some piece of our experimental data is misleading us. Accordingly, no attempt will be made either to support or to detract from the proposed termination schemes. It is assumed, however, that the ultimate product of one of the important termination steps in N-benzyl benzaldehyde phenylhydrazone.

Mechanism I termination. A reasonable way to terminate the chain propagation sequence proposed in Mechanism I would be to couple the chain carrying radical D with a "leftover" benzyl radical (eq. 60). Provided chain transfer of benzyl radicals with cumene or



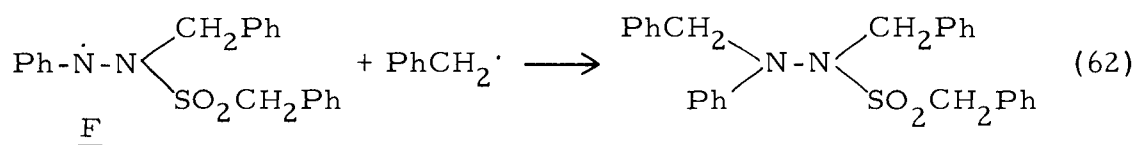
diphenylmethane is not too facile, one can then explain why products of the coupling of these radicals with D are not important.

Mechanism II termination. Scheme A. One possible way in which Mechanism II could be terminated is shown in the following reaction sequence (eq. 61). One of the radicals participating in the

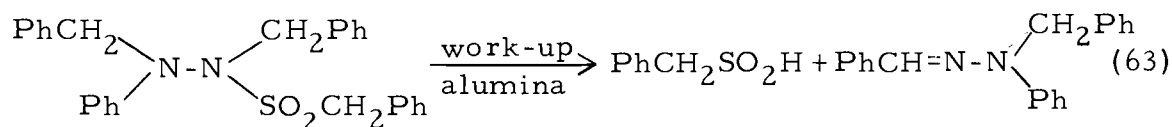


chain terminating reaction is again D, presumably formed as was shown in eq. 55b, c and d. It couples with the chain carrying benzyl radical in the same manner proposed for the termination of Mechanism I. Once again one must assume that benzyl radicals are sluggish about undergoing transfer with cumene or diphenylmethane (RH) in order to explain why products of the type $\text{PhCH=N-N} \begin{array}{l} \text{R} \\ \text{Ph} \end{array}$ are not formed. Note that the same assumption is required to explain why the principal product of the propagation sequence in Mechanism II is $\text{PhCH}_2\text{-N=N-Ph}$ rather than R-N=N-Ph .

Scheme B. A second possible mode of termination of Mechanism II involves coupling of the intermediate radical F of Mechanism II with the chain carrying benzyl radical (eq. 62). Upon work-up by



chromatography over alumina, the initial termination product could possibly decompose to form α -toluenesulfinic acid and N-benzyl benzaldehyde phenylhydrazone (eq. 63).



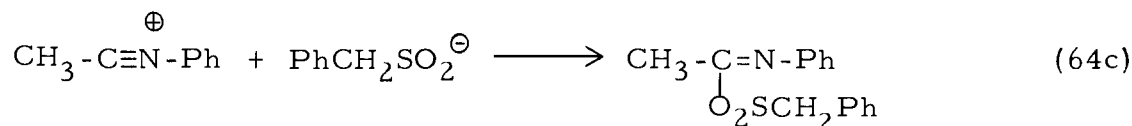
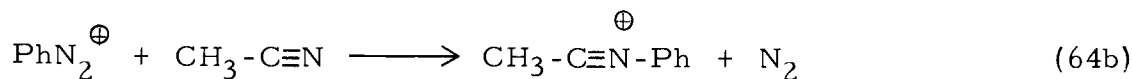
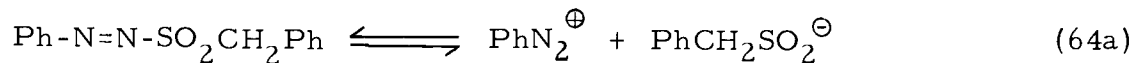
The Induction Period

Both mechanisms which have been suggested to account for the propagation step of the apparent chain decomposition of BBS would evolve sulfur dioxide from the beginning of the decomposition. Experimentally, there is a well defined induction period observed prior to the evolution of sulfur dioxide from dilute solutions of BBS in hydrocarbon solvents (Figures 3, 4, 5 and 6). It is possible that there is some impurity present which traps a chain propagating radical before the radical can induce the decomposition of an appreciable amount of the diazosulfone. When this inhibitor is consumed, the induction period ends and the reaction proceeds at a much more rapid rate with the evolution of sulfur dioxide. Added inhibitors like the Koelsch radical, of course, do have just this effect on the behavior of the system.

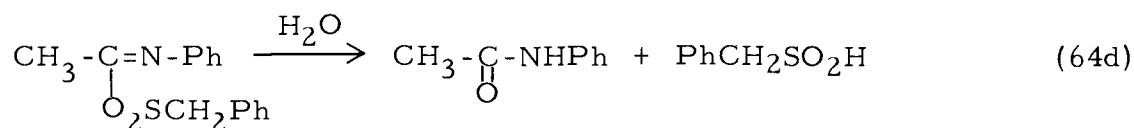
In more concentrated solutions, however, no well defined induction period is observed. Instead, we observe sulfur dioxide being evolved at an increasing rate from the beginning of the decomposition which suggests that under these conditions perhaps part of the decomposition is occurring by some autocatalyzed route, perhaps catalyzed by acidic products produced in the decomposition.

The Decomposition of BBS in Acetonitrile

The thermal decomposition of BBS in acetonitrile produced acetanilide as the major organic product (0.42 mole/mole BBS), and a small amount of N-benzyl benzaldehyde phenylhydrazone (0.03 mole/mole BBS). The decomposition at 82° evolved 0.33 mole sulfur dioxide/mole BBS at a first order rate of $2 \times 10^{-4} \text{ sec}^{-1}$ following a brief induction period of ten minutes (Figure 6). We have previously discussed the mechanism for the formation of acetanilide produced by the decomposition of the methyl diazosulfone in acetonitrile and a brief summary follows. The methyl diazosulfone most likely decomposes heterolytically in the ionizing solvent acetonitrile to provide phenyldiazonium ions since Lewis and co-workers (64) have demonstrated that the ionization of phenyl diazosulfones to PhN_2^{\oplus} and RSO_2^{\ominus} occurs in another polar solvent, methanol. Makarova and Nesmeyanov (52) have shown that phenyldiazonium ions from $\text{PhN}_2^{\oplus} \text{BF}_4^{\ominus}$ decomposed in acetonitrile produce acetanilide as the major product. Thus the analogous benzyl diazosulfone could decompose in acetonitrile to form acetanilide as outlined in the following mechanism (eq. 64).

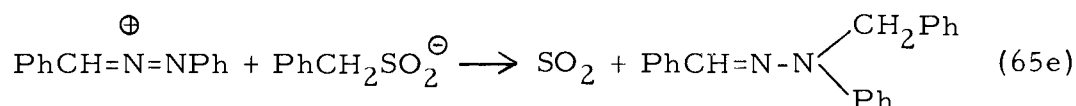
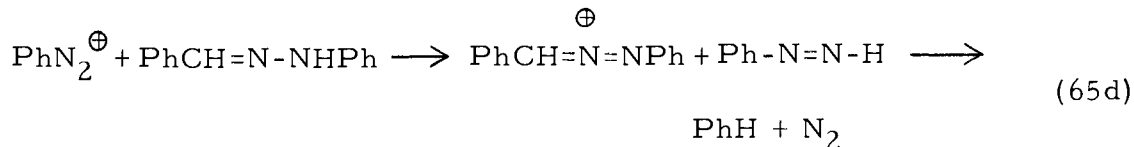
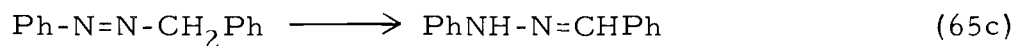
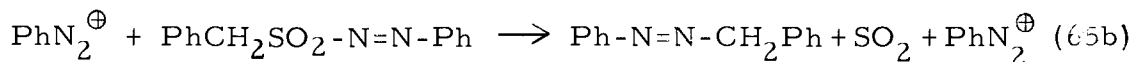
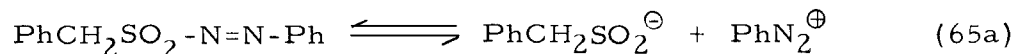


On work-up,



Changing the polarity of the solvent in which the diazosulfone is decomposed most likely changes the mechanism of the decomposition just as we concluded it did in the decomposition of BMS in various solvents.

At first glance, the isolation of a small amount of N-benzyl benzaldehyde phenylhydrazone appears unusual, but its formation can be rationalized by the following ionic scheme (eq. 65). Except for the



tautomerization of 1'-phenyl benzeneazomethane in eq. 65c (73) and the decomposition of phenyldiazene to benzene and nitrogen in eq. 65d (32), there is no specific precedent for a reaction sequence such as we postulate here. Moreover, the steps of eq. 65 d and e would have to occur much more rapidly than the other steps since no benzaldehyde phenylhydrazone was observed as a product of the decomposition. Sulfur dioxide formed in the decomposition could presumably be formed in a process such as eq. 65 b and e.

The rate at which sulfur dioxide is evolved from the decomposing diazosulfone in acetonitrile at 82° is comparable to the rate at which sulfur dioxide is evolved from solutions of the diazosulfone in diphenylmethane at 80.1° (Table 3). This would seem to indicate that although the diazosulfone decomposes heterolytically in good ionizing solvents such as acetonitrile, the amount of heterolytic decomposition via PhN_2^{\oplus} and $\text{PhCH}_2\text{SO}_2^{\ominus}$ occurring in non-polar solvents such as diphenylmethane is probably quite small since the rate of this process should be much slower in lower dielectric media. However, this does not mean that some acid catalyzed decomposition, such as we suggested occurs in the decomposition of BMS in benzene, is not occurring in the decomposition of BBS in hydrocarbon solvents.

Further study of the mechanism of the decomposition of alkyl benzenediazo sulfones in acetonitrile should perhaps include a careful product analysis in order to determine if the intermediate we

propose, $\text{Ph}-\text{N}=\underset{\text{O}_2\text{SR}}{\text{C}}-\text{CH}_3$, can indeed be isolated. Such an isolable product would be clinching evidence to support the mechanism postulated here for the decomposition of the benzyl and methyl diazosulfones in acetonitrile.

EXPERIMENTAL

The following instruments were used in the experimental work:

The ultraviolet spectra were recorded on a Cary 15 spectrophotometer and the infrared spectra on a Beckman IR 8 infrared spectrophotometer. Vapor phase chromatograms were obtained from an Aerograph Model A-90-P using a 15 ft. XF 1150 (15 percent on 40/60 Firebrick) column. Nuclear magnetic resonance spectra were recorded on a Varian Model A-60 analytical NMR spectrometer with a V-6057 variable temperature accessory. Molecular weight determinations were made with a Vapor Pressure Osmometer, model 301, Mechrolab, Inc. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Synthesis of Alkyl Benzenediazo Sulfones

Benzenediazo Benzyl Sulfone (BBS). Crude α -toluenesulfinic acid (20, p. 47) (7.10 gm., 45.5 moles) was dissolved in 150 ml. of anhydrous methanol. To this solution was added 5 ml. of water, then 38.2 gm. (45.5 mmoles) of sodium bicarbonate. This solution was stirred until evolution of carbon dioxide ceased; then the solution was filtered and the filtrate was evaporated to dryness at room temperature under reduced pressure. The sodium α -toluenesulfinate obtained (6.76 gm., 38.0 mmoles) was dissolved in 40 ml. of cold

water. This solution was extracted with one 20-ml. portion of ether, the ether layer discarded, and the aqueous layer swirled in an ice-water bath while a solution of benzenediazonium fluoborate (18) (7.25 gm., 38.0 mmoles) in 250 ml. of cold water was dripped in. Ten minutes after the addition was complete the yellow precipitate which had formed was filtered and washed with two 50-ml. portions of cold water. The precipitate was pressed dry with a rubber dam, then dissolved in 70 ml. of benzene, filtered through anhydrous magnesium sulfate, and 210 ml. of hexane was added to the benzene filtrate. The bright yellow precipitate was filtered off after cooling the solution, and the crystals were again recrystallized from benzene-hexane, yielding 6.0 gm. (62 percent) of benzenediazo benzyl sulfone, m.p. 97-99° (dec.).

This was further purified by column chromatography. A concentrated solution of BBS in benzene was passed through a column of silica gel (100 mesh, 20 gm./gm. BBS) under pressure. The benzene eluant was reduced to one-half its original volume on a rotary evaporator, and three volumes of hexane were slowly added to precipitate the BBS. Then the diazosulfone was filtered off and washed with a small volume of cold hexane and dried, giving bright yellow crystals of BBS, m.p. 100-101° (dec.), lit. (20) m.p. 92-94° (dec.).

The ultraviolet absorption spectrum of BBS showed λ_{\max} at 438 m μ (ϵ , 129) and 290 m μ (ϵ , 14,200) in cyclohexane. The infrared

spectrum (chloroform) showed intense sulfone absorption at 1350 cm^{-1} and a doublet at 1145 cm^{-1} and 1162 cm^{-1} .

Benzenediazo methyl sulfone (BMS). Benzenediazonium fluoroborate (3.64 gm., 19.1 mmoles) in 50 ml. of water was added dropwise to a stirred cold solution of sodium methanesulfinate (20, p. 97) (2.42 gm., 19.1 mmoles) in 40 ml. of cold water. The solution was stirred in the ice bath for an additional 15 minutes. The crystals which had formed were filtered off and washed with 100 ml. of cold water. The yellow BMS was dissolved in 30 ml. of warm benzene, the solution filtered through anhydrous magnesium sulfate, the magnesium sulfate washed with a little hot benzene, and the filtrates combined. Two volumes of hexane were added slowly to the benzene solution, and then the mixture was placed in a refrigerator overnight. The yellow needles of the diazosulfone were filtered off, washed with cold hexane and dried, giving 1.60 gm. (46 percent) of BMS, m.p. $73-74.5^\circ$, lit (19) m.p., $70-71^\circ$.

Benzenediazo phenyl sulfone (BPS). Benzenediazonium fluoroborate (7.5 gm., 39.1 mmoles), dissolved in a minimum amount of water, was added dropwise to a cold, stirred solution of the sodium salt of benzenesulfinic acid (Aldrich Chemical Co., Inc.) (6.4 gm., 39.1 mmoles) in a minimum amount of water. Stirring was continued for ten minutes after the addition was completed, and then the precipitate was filtered off, washed with two 40-ml. portions of cold water

and pressed dry. The yellow solid was recrystallized from ethanol, filtered off, washed with cold ethanol, and dried, yielding 6.3 gm. (66 percent) yellow crystalline BPS, m.p. 78-79° (dec.), lit. (65) m.p. 77.0-77.5°.

Benzenediazo t-butyl sulfone (BtBuS). Benzenediazonium fluoborate (9.6 gm., 50 mmoles), dissolved in a minimum amount of water was added dropwise to a cold, stirred solution of sodium t-butylsulfinate (7.2 gm., 50 mmoles) (generously provided by Dr. K. Ikura) dissolved in a minimum amount of water. Stirring was continued for five minutes after the addition was completed. The yellow crystals were filtered off and were washed with two 50-ml. portions of cold water and pressed dry. The yellow solid was dissolved in hexane at room temperature, the hexane solution was filtered through anhydrous magnesium sulfate, and the filtrate left overnight in the refrigerator. The yellow crystals were filtered off and the crystals were washed with a little cold hexane and dried, yielding 3.4 gm. (30 percent) yellow crystalline BtBuS, m.p. 65-66.5° (dec.). The infrared spectrum of a carbon tetrachloride solution of the diazo-sulfone corresponded closely to the spectrum of benzenediazo n-butyl sulfone. The NMR spectrum of BtBuS in carbon tetrachloride showed a singlet at 8.43 τ and a multiplet centered at 2.5 τ . Anal. Calc'd. for $C_{10}H_{14}N_2O_2S$: C, 53.2; H, 6.2. Found: C, 53.4; H, 5.97.

Procedure for Kinetic Runs

Reagent-grade solvents (benzene and cumene) were refluxed over lithium aluminum hydride and distilled through a 60 cm. glass helices-packed column, the middle one-half fraction being collected. Diphenylmethane was fractionally distilled twice under vacuum on a 40 cm. Nester-Faust spinning band column. Reagent-grade acetonitrile was refluxed over calcium oxide for 24 hours, then distilled through a 60 cm. glass helices-packed column, collecting only a fraction corresponding to the middle two-thirds of the distillate. This was then refluxed over and distilled from phosphorus pentoxide through a 60 cm. glass helices-packed column. The middle two-thirds of the distillate was retained for use.

The thermal decomposition reactions were carried out in an apparatus previously described by Kice, Parham and Simons (39). The desired amount of diazosulfone was placed in the decomposition vessel, the solvent was pipetted in, and the vessel was covered with aluminum foil to prevent photodecomposition of the diazosulfone. The solution was deoxygenated with prepurified nitrogen for one hour, the foil was then removed and then the vessel was immersed in a thermostatted oil bath. The decomposition was allowed to proceed through eight to ten half-lives.

Sulfur dioxide evolution rates were measured by the method of

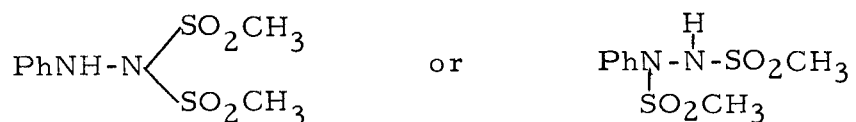
Kice, Parham and Simons (39).

Identification of the Decomposition Products

Generally, the solvent was removed from the solution remaining at the end of the decomposition, and the residue was column chromatographed on acid washed alumina (25 gm./gm. residue). The column was eluted successively with hexane, hexane-benzene, benzene, benzene-ether, ether, ether-methanol and methanol. Small fractions were collected, the solvent was removed and the identity of the residue was investigated. Only solvent mixtures eluting tractable decomposition products are reported.

BMS Decomposition Products

BMS in benzene. To the final solution from the decomposition of 9.93 gm. (53.8 mmoles) of BMS in benzene (400 ml.) was added 600 ml. of hexane; the mixture was cooled and the crystals which formed were filtered off. The crystals were dissolved in benzene, treated with decolorizing carbon, filtered hot, and the benzene was removed on a rotary evaporator. Recrystallization of the residue from benzene-hexane gave light tan crystals, m.p. 155-156°. Spectroscopic evidence indicated two possible isomeric structures,



Anal. Calc'd. for $C_8H_{12}N_2O_4S_2$: C, 36.35; H, 4.58; N, 10.60; mol. wt. 264. Found: C, 36.57; H, 4.49; N, 10.68; mol. wt. 267 ± 3 . The amount recovered corresponded to 0.05 mole/mole diazosulfone.

The hexane-benzene filtrate was distilled under reduced pressure, and the tarry residue was chromatographed. Elution with pure hexane gave a mixture of biphenyl and azobenzene. The amount of azobenzene was determined by dissolving this mixture in 95 percent ethanol, measuring the absorbance at 314 m μ and calculating the amount present from the published extinction coefficient for azobenzene (67, p. 102). The calculated weight of azobenzene was subtracted from the total weight of this fraction to give the weight of biphenyl. The amount of azobenzene formed was 0.14 mole/mole BMS. The biphenyl isolated (0.26 mole/mole BMS) was further characterized by melting point (69-71°), mixed melting point and comparison of its infrared spectrum with a known sample.

Elution with 2:1 ether-methanol gave phenyl methanesulfonate, 0.069 mole/mole BMS, identified by its melting point (60-61°) [lit. (29) m. p. 59-61°] and mixed melting point (60-61°) with a prepared sample (29). The infrared spectra of the recovered and synthetic phenyl methanesulfonate were identical.

The amount of sulfur dioxide evolved was 0.14 mole/mole BMS.

BMS in benzene with added calcium oxide. After the decomposition of BMS in benzene (1.842 gm., 10 mmoles in 100 ml. of benzene) with added calcium oxide (1.2625 gm., 18 mmoles) the final solution was filtered through a tared medium porosity fritted funnel, and the solid on the filter was washed with benzene until colorless. A total of 1.0867 gm. (80 percent) of calcium oxide was recovered. The calcium oxide was dried at room temperature overnight, and dissolved in a minimum amount of dilute aqueous hydrochloric acid; the pH was then adjusted to 6 by the addition of ten percent aqueous sodium bicarbonate. The solution was cooled in an ice bath and aqueous benzenediazonium fluoborate was added, giving a pale yellow solution but no precipitate of BMS, corresponding to little, if any $\text{Ca}(\text{SO}_2\text{CH}_3)_2$. To the benzene filtrate was added 6 gm. of alumina. The solvent was removed on the rotary evaporator and the coated alumina added to a prepared alumina chromatography column overlaid with sand. Elution was then begun. Elution with hexane gave biphenyl, 0.32 mole/mole BMS. Elution with 80:20 hexane-benzene gave azobenzene, 0.032 mole/mole BMS. The recovered azobenzene had an infrared spectrum identical with that of a known sample. Elution with 50:50 hexane-benzene gave a product tentatively identified as p-phenylazobenzene, less than 0.02 mole/mole BMS, characterized by its infrared spectrum and melting point, 148-150°. lit. (51) m.p., 154-155°. The amount of sulfur dioxide evolved was 0.141 mole/mole

BMS.

BMS in cumene. After the decomposition was complete, a 5 ml. aliquote of the final solution was withdrawn and was subjected to VPC analysis. The chromatogram showed two peaks with retention times identical to those of a prepared sample of benzene and cumene. The remainder of the final solution was carefully fractionally distilled under vacuum to remove cumene and other volatiles, leaving a tarry residue. This residue was dissolved in a minimum amount of chloroform, 15 gm. of alumina was added, and the chloroform was removed under reduced pressure. The coated alumina was placed on top of a prepared alumina column and elution was begun. Elution with hexane gave white crystals, whose infrared spectrum indicated it was 2,3-dimethyl-2,3-diphenylbutane (bicumyl), m.p. 117-118°, lit. (41) m.p., 119-120°. The yield of bicumyl was 0.12 mole/mole BMS. Elution with 2:1 ether-methanol gave phenyl methanesulfonate, 0.074 mole/mole BMS. The yield of sulfur dioxide was 0.033 mole/mole BMS.

BMS in diphenylmethane. After the decomposition was complete, a 5 ml. aliquot of the solution was withdrawn and subjected to VPC analysis. The chromatogram showed two peaks with retention times identical to those of a prepared sample of benzene and diphenylmethane. A ratio of peak areas showed 0.23 mole benzene/mole BMS. The remaining solution was carefully fractionally distilled under

vacuum to remove diphenylmethane and other volatiles, leaving a residue. This residue was dissolved in a minimum amount of benzene, 5 gm. of alumina added, and the benzene removed under reduced pressure. This coated alumina was placed on top of a prepared alumina column and elution was begun. The fraction eluting with hexane was identified as o-phenyldiphenylmethane, 0.044 mole/mole BMS, characterized by its infrared spectrum and melting point (55-56°), [lit. (24) m.p., 54-56°]. Elution with 95:5 hexane-benzene gave p-phenyldiphenylmethane, 0.043 mole/mole BMS, identified by its melting point (85-86°), [lit. (21) m.p., 84-85°] and mixed m.p. with a prepared sample (21). Elution with 80:20 hexane-benzene gave 1,1,2,2-tetraphenylethane, 0.065 mole/mole BMS, identified by its infrared spectrum, melting point (210-212°), [lit. (4) m.p., 211°] and mixed melting point with an authentic sample. Elution with 80:20 benzene-ether gave diphenylmethyl methyl sulfone, 0.11 mole/mole BMS, identified by its infrared spectrum, melting point (129-133°), [lit. (42) m.p., 127-128.5°] and mixed melting point with a prepared sample (42). The amount of sulfur dioxide evolved was 0.11 mole/mole BMS.

BMS in acetonitrile. After the decomposition was complete, a 5 ml. aliquot of the solution was withdrawn and subjected to VPC analysis. The chromatogram showed acetonitrile to be the only volatile component. The remaining solution was distilled under reduced

pressure, and the residue remaining after removal of the solvent was dissolved in methanol. Seven gm. of alumina was added, and the methanol was removed under reduced pressure. The coated alumina was added to a prepared column and then the column was eluted. Elution with 80:20 benzene-ether gave acetanilide, 0.71 mole/mole BMS, identified by its infrared spectrum, melting point (112-113°), [lit. (69) m. p., 114.4-114.9°] and mixed melting point. The amount of sulfur dioxide evolved was 0.03 mole/mole BMS.

BPS in benzene with added calcium oxide. This experiment was run as a check on technique, since the products of the decomposition of this diazosulfone in benzene had already been reported by Overberger and Rosenthal (61). The conditions and procedures used by Overberger and Rosenthal were followed exactly. The result was:

<u>Compound</u>	<u>(Yields in mole/mole BPS)</u>	
	<u>Ref. 61</u>	<u>Experimental</u>
Biphenyl	0.45	0.444
Azobenzene	0.02	0.008
<u>p</u> -Phenylazobenzene	0.005	0.011
Diphenyl sulfone	0.05	None
Benzenesulfinic acid	0.27	0.33
Nitrogen	0.85	Not measured

BBS in benzene. After the decomposition was complete, a 3 ml. aliquot of the solution was withdrawn and subjected to VPC

analysis. The chromatogram showed benzene to be the only volatile component. Seven gm. of alumina was added to the remaining solution, and the benzene was removed under vacuum. The coated alumina was added to a prepared column and the column was then eluted. Elution with hexane gave biphenyl, 0.02 mole/mole BBS. Elution with 80:20 hexanebenzene gave azobenzene, less than 0.01 mole/mole BBS. Elution with 50:50 hexane-benzene gave N-benzylbenzaldehyde phenylhydrazone, 0.06 mole/mole BBS, identified by its melting point, 108.5-109°, [lit. (55) m.p., 111°], mixed melting point and comparison of its infrared spectrum with a known sample. Elution with benzene gave benzaldehyde phenylhydrazone, 0.55 mole/mole BBS, identified by its melting point, 156-158°, [lit. (15) m.p., 156°] mixed melting point, and comparison of its infrared spectrum with a known sample. The amount of sulfur dioxide evolved was 0.66 mole/mole BBS.

BBS in cumene. After the decomposition was completed, a 5 ml. aliquot of the solution was withdrawn and subjected to VPC analysis. The chromatogram showed three peaks with retention times identical to those of a prepared sample of benzene, toluene and cumene. The ratio of peak areas corresponded to 0.11 mole benzene/mole BBS and less than 0.01 mole toluene/mole BBS. The cumene and other volatiles was removed from the remaining solution by vacuum distillation, leaving a dark residue. The residue was dissolved in

a minimum amount of ether. Three gm. of alumina was added to the ether solution and the ether was removed under reduced pressure. The coated alumina was added to a prepared column and the column was then eluted. Elution with 75:25 hexane-benzene gave N-benzyl benzaldehyde phenylhydrazine, 0.118 mole/mole BBS. Elution with 20:80 hexane-benzene gave benzaldehyde phenylhydrazine, 0.46 mole/mole BBS. The yield of sulfur dioxide was 0.57 mole/mole BBS.

BBS in diphenylmethane. After the decomposition was complete, a 5 ml. aliquot of the solution was withdrawn and subjected to VPC analysis. With the conditions of column temperature 160°, injector temperature 218°, detector temperature 260° and helium carrier gas flow rate of 80 ml./min., the chromatogram showed four peaks, three of which had retention times identical to a prepared sample of benzene, toluene, and diphenylmethane. Relative peak areas on the chromatogram showed 0.149 mole benzene/mole BBS (retention time one minute), 0.049 mole toluene/mole BBS (retention time 1.5 minutes) and a compound with a retention time of eight minutes, whose peak area corresponded to 61 mg./2.6 gm. BBS. The remaining solution was carefully vacuum distilled to remove the solvent and other volatiles. The residue was dissolved in a minimum amount of benzene, 4 gm. of alumina was added and the benzene was removed at reduced pressure. The coated alumina was placed on top of a prepared column and the column was then eluted. Elution with

80:20 hexane-benzene gave N-benzyl benzaldehyde phenylhydrazone, 0.164 mole/mole BBS. Elution with 25:75 hexane-benzene gave benzaldehyde phenylhydrazone, 0.341 mole/mole BBS. The amount of sulfur dioxide evolved was 0.795 mole/mole BBS.

BBS in acetonitrile. After the decomposition was complete, the solution was vacuum distilled to remove the solvent and the remaining black viscous liquid partially crystallized. The crystals were filtered off, washed with hexane, and dried. The hexane was removed from the filtrate under reduced pressure, and the residue was chromatographed. Elution with 80:20 hexane-benzene gave N-benzyl benzaldehyde phenylhydrazone, 0.034 mole/mole BBS. The crystals isolated by filtration were combined with the product eluting with ether and was identified as acetanilide, 0.425 mole/mole BBS. The amount of sulfur dioxide was 0.328 mole/mole BBS.

Benzenediazo t-butyl sulfone in benzene. After the decomposition was complete, 3 gm. of alumina was added to the benzene solution and the benzene was removed under vacuum. The coated alumina was placed on top of a prepared column and the column was eluted. Elution with hexane gave a mixture of biphenyl and 1'1'-dimethyl benzeneazoethane. The amount of 1'1'-dimethyl benzeneazoethane was determined in the following way. The mixture was quantitatively diluted with hexane and the visible absorbance of 1'1'-dimethyl benzeneazoethane was measured at its λ_{\max} , 411 m μ [lit. (16) λ_{\max}

415 m μ (ϵ , 151)]. The amount of the azo compound found was 0.24 mole/mole BtBuS. The NMR spectrum of the hexane eluant was recorded and integrated and the ratio of t-butyl protons in 1'1'-dimethyl benzeneazoethane in the aromatic protons of the mixture showed 0.10 mole biphenyl/mole BtBuS formed in the decomposition. Elution with benzene gave an oil which could not be conclusively identified. Elution with ether gave a white solid which was recrystallized from hexane, m.p. 115-116° (dec.). This compound melted with the evolution of copious quantities of gas. The infrared spectrum of this solid in chloroform was characteristic of a sulfonate, and the NMR spectrum showed only aromatic and alkyl (τ = 8.43, singlet) protons, in a ratio of 5.1:3.0, respectively. Elution with methanol gave a white solid which was recrystallized from hexane, m.p. 147-149° (dec.). The infrared spectrum of this compound was also characteristic of a sulfonate. The NMR spectrum of this compound indicated phenyl and alkyl (τ = 8.91) protons in a ratio of 5:4 respectively. The decomposition evolved 0.36 mole sulfur dioxide/mole BtBuS.

Synthesis of the Koelsch radical. The Koelsch radical was prepared by the method of Koelsch (44, 45) with the modification of Kice (38) used in the preparation of 9-benzylidenefluorene, and the improvement of Nelsen and Bartlett (57) used for the preparation of α , γ -bis-(diphenylene)- β -phenylallyl alcohol. The crude radical was recrystallized from 95 percent ethanol giving lustrous green plates,

m.p. 186-188° [lit. (45) m.p., 187.5-189.5°]. The visible absorption spectrum of the radical in benzene showed a λ_{\max} at 489 m μ (ϵ , 2.71×10^4) [lit. (47) λ_{\max} 490 m μ (ϵ , 2.6289×10^4)].

Measurements of the rate of scavengable radical production by scavenging with the Koelsch radical. The rate at which the diazosulfone decomposed into free radicals which were then scavenged by the Koelsch radical was measured by the method of Bartlett and Funahashi (1) in a self-contained reaction cell previously described by Kice and Pawlowski (40). In a typical kinetic run, 2.0 ml. of a 5×10^{-5} M solution of the Koelsch radical in benzene was transferred to the B compartment of the cell, and 2.0 ml. of a 5.1×10^{-4} M solution of BBS in benzene was transferred to the A compartment. The apparatus was connected to a vacuum line through D; then the solutions in compartments A and B were frozen in a Dry Ice-acetone bath. Stopcock E was opened and the cell was evacuated on the vacuum line. Pre-purified nitrogen was then introduced into the cell to atmospheric pressure, stopcock E was closed, and the frozen solutions were thawed. After three of these freeze-pump-thaw cycles, about 400 mm. of nitrogen pressure was introduced into the cell and stopcock E was closed. The solutions were thawed, were then mixed thoroughly, and the final solution was poured into cell C. The absorbance of the solution was then measured at 489 m μ . Compartment C was then immersed into a thermostatted oil bath and withdrawn after a suitable

time interval. The oil was carefully rinsed from the cell with chloroform and the absorbance at 489 m μ was remeasured. Care was taken to insure that cell C was always at the same temperature during the absorbance measurements. The process was repeated until the Koelsch radical had been consumed. The Koelsch radical in benzene was shown to be stable under these same conditions. As anticipated, excellent kinetics were obtained.

Diazosulfone decomposition rates followed by UV spectroscopy.

A measured amount of solid BBS was placed in the A compartment of the self-contained reaction cell (40, Figure 2) and a measured amount of diphenylmethane was transferred to compartment B. The contents were deoxygenated seven times as described previously (see above). The cell was shaken to dissolve the BBS in the solvent and the cell was warmed quickly in a water bath kept at the same temperature as the thermostatted cell compartment of the Cary spectrophotometer. After 30 seconds, the cell was dried and quickly transferred to the thermostatted cell compartment. The machine recorded the decrease in absorbance at 438 m μ , the λ_{max} of BBS. The kinetics obtained in this manner did not correspond to a first-order disappearance of the diazosulfone.

Diazosulfone decomposition rates followed by NMR spectroscopy. A solution of diazosulfone in benzene, to which one drop of cyclohexane per ml. of solution had been added as an internal proton

standard, was transferred by a capillary dropper to an NMR tube with a constricted neck. The contents of the tube were deoxygenated with pre-purified nitrogen in the manner described previously, with the modification that the tube was frozen in an ice-salt bath. The tube was sealed at the constriction under about 100 mm. of nitrogen pressure. The tube was heated in a thermostatted oil bath for a brief period to insure that the tube would not rupture in the thermostatted NMR probe. The tube was then transferred to the thermostatted NMR probe and the spectrum recorded and integrated at appropriate intervals. Alternatively, the tube was heated in the oil bath for the desired period of time, was then removed, the oil rinsed off, and the tube cooled. The NMR spectrum was then recorded and integrated. The tube was then replaced in the oil bath until time for the next measurement.

BIBLIOGRAPHY

1. Bartlett, Paul D. and Toshio Funahashi. Galvinoxyl (2,6-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolyl-oxyl) as a scavenger of shorter-lived free radicals. *Journal of the American Chemical Society* 84:2596-2601. 1962.
2. Benati, L., M. Tiecco and A. Tundo. Thermal decomposition of some diazoaryl sulfonates. *Bollettino Scientifico della Facolta di Chimica Industriale di Bologna* 24:219-212. 1966. (Abstracted in *Chemical Abstracts* 67:2847p. 1967)
3. Bevington, J. C. The sensitized polymerization of styrene. The rate and efficiency of initiator. *Transactions of The Faraday Society* 51:1392-1397. 1955.
4. Biltz, Heinrich. Phenylirte Aethan- und Aethylenderivate. *Justus Liebig's Annalen Der Chemie* 296:219-260. 1897.
5. Bock, H. Farbe und Konstitution bei Azoverbindungen. *Ange-wandte Chemie* 77:469-489. 1965.
6. Bridger, Robert F. and Glen A. Russell. Directive effects in the attack of phenyl radicals on carbon-hydrogen bonds. *Journal of the American Chemical Society* 85:3754-3765. 1963.
7. Brough, J. N., B. Lythgoe and P. Waterhouse. Macrozamin. Part IV. Positional and geometrical isomerism in mixed aliphatic-aromatic azoxy-compounds. *Journal of The Chemical Society*, 1956, p. 4069-4079.
8. Brown, Robert W. Initiators for emulsion polymerization. U.S. patent 2,527,393. Oct. 24, 1950. (Abstracted in *Chemical Abstracts* 45:383a. 1951)
9. Bunnett, J. F. and D. A. R. Happer. Reactions of o-halophenyl-azo phenyl sulfones and of (o-chlorophenyl) triphenylphosphonium iodide with sodium methoxide in methanol. *Journal of Organic Chemistry* 32:2701-2704. 1967.

10. Bunnett, J. F. and D. A. R. Happer. Substituent effects on the ratio of proton capture to bromide ion loss by o-bromophenyl anions in methanol. *Journal of Organic Chemistry* 31:2369-2372. 1966.
11. Busfield, W. K. et al. Studies in the thermochemistry of sulphones. Part IV. *Transactions of the Faraday Society* 57: 1064-1069. 1961.
12. Claasz, Max. Über das Sulfinsäure Diazonium. *Berichte der Deutschen Chemischen Gesellschaft* 44:1415-1419. 1911.
13. Cohen, Saul G. and Chi Hua Wand. Phenyl-azo-diphenylmethane and the decomposition of azo compounds. *Journal of the American Chemical Society* 77:3628-3631. 1955.
14. Corbett, G. E. and G. H. Williams. Homolytic aromatic methylation. *Proceedings of The Chemical Society*, 1961, p. 240-241.
15. Cowley, Eric G. and James R. Partington. Studies in dielectric polarisation. Parts VIII, IX, X and XI. *Journal of The Chemical Society*, 1933, p. 1252-1259.
16. Curtin, David Y. and Joanne Arnheim Ursprung. Reaction of organometallic compounds with diazonium salts. Synthesis of arylazoalkanes. *Journal of Organic Chemistry* 21:1221-1225. 1956.
17. Davies, G. L., D. H. Hey and Gareth H. Williams. The decomposition of arylazotriarylmethanes. *Journal of The Chemical Society*, 1956, p. 4397-4408.
18. Dunker, Melvin F. W., Edgar B. Starkey and Glenn L. Jenkins. The preparation of some organic mercurials from diazonium borofluorides. *Journal of the American Chemical Society* 58: 2308-2309. 1936.
19. Dutt, Pavitra Kumar. Action of diazo-salts on methanesulphonamide. *Journal of The Chemical Society* 125:1463-1465. 1924.
20. Engebrecht, Ronald Henry. Mechanism of internal substitution reactions. Ph.D. thesis. Corvallis, Oregon State University, 1964. 112 numb. leaves.

21. Etlis, V. S. and G. A. Razuvaev. Preparation and properties of some aryl derivatives of thioxanthen-5-ol dioxide having indicator properties. *Zhurnal Obshchei Khimii* 28:1225-1227. 1958. (Abstracted in Chemical Abstracts 52:20075g. 1958)
22. Freeman, H. C. et al. The possible occurrence of geometrical isomerism among the diazosulphones. *Journal of The Chemical Society*, 1952, p. 3381-3384.
23. Freeman, Jeremiah P. The nuclear magnetic resonance spectra and structure of aliphatic azoxy compounds. *Journal of Organic Chemistry* 28:2508-2511. 1963.
24. _____. The reaction of enolic β -ketoesters and β -diketones with phenylmagnesium bromide. *Journal of the American Chemical Society* 80:1926-1930. 1958.
25. Frost, Arthur A. and Ralph G. Pearson. Kinetics and mechanism. 2d ed. New York, Wiley, 1961. 405 p.
26. Grammaticakis, P. Contribution à l'étude de l'absorption dans l'ultra-violet moyen et le visible de quelques hydrazines. α , β -disubstituées et de leurs produits d'oxydation. *Bulletin de la Société Chimique de France* 20:86-93. 1953.
27. Hammond, George S. et al. The mechanism of decomposition of azo compounds. II. Cage effects in the decomposition of α , α' -azoisobutyronitrile and related compounds. *Journal of the American Chemical Society* 82:5394-5399. 1960.
28. Hantzsch, A. Notizen über Diazocyanide und die Reaction von Diazokörpern mit Benzolsulfinsäure. *Berichte der Deutschen Chemischen Gesellschaft* 31:636-642. 1898.
29. Helferich, Burckhardt and Panayotis Papalambrou. Die Maskierung phenolischer Hydroxylgruppen durch Veresterung an Methansulfonsäure. *Justus Liebig's Annalen der Chemie* 551:235-241. 1942.
30. Hey, D. H., B. W. Pengilly and Gareth H. Williams. Homolytic aromatic substitution. Part XI. The phenylation of toluene, ethylbenzene and isopropylbenzene. *Journal of The Chemical Society*, 1956, p. 1463-1475.

31. Hoffmann, Reinhard W., Wolfgang Sieber and Gabriele Guhn. Über den Zerfall des 1,2,3-Benzothiadiazole-1,1-dioxyds. *Chemische Berichte* 98:3470-3478. 1965.
32. Huang, Pih-kuei C. and Edward M. Kosower. Diazenes. III. Properties of phenyldiazene. *Journal of the American Chemical Society* 90:2367-2376. 1968.
33. Huyser, Earl S. The free radical induced rearrangement of 2-methoxytetrahydropyran to methyl valerate. *Journal of Organic Chemistry* 25:1820-1822. 1960.
34. Johnston, K. M. and Gareth H. Williams. Homolytic reactions of aromatic side chains. Part I. Reactions of t-butyl peroxide with aromatic compounds. *Journal of The Chemical Society*, 1960, p. 1168-1171.
35. Kampmeier, J. A. et al. Free-radical elimination reactions. The reaction of phenyl radicals with t-butyl sulfide and phenyl t-butyl sulfide. *Journal of the American Chemical Society* 88: 1257-1265. 1966.
36. Kharasch, M. S. et al. Reactions of atoms and free radicals in solution. XXXI. Reactions of free benzoyl radicals with azo compounds. (Preliminary paper). *Journal of Organic Chemistry* 18:1045-1050. 1953.
37. Kharasch, Norman and Cal Y. Meyers (eds.) The chemistry of organic sulfur compounds. Vol. 2. Norwich, Pergamon, 1966. 465 p.
38. Kice, John L. A kinetic study of the reactivity of some dibenzofulvenes toward free radicals. *Journal of the American Chemical Society* 80:348-352. 1958.
39. Kice, John L., Fred M. Parham and Robert M. Simons. The thermal decomposition of thiolsulfonates. *Journal of the American Chemical Society* 82:834-842. 1960.
40. Kice, John L. and Norman E. Pawlowski. The decomposition of aromatic sulfinyl sulfones (sulfinic anhydrides). The facile homolysis of a sulfur-sulfur bond. *Journal of the American Chemical Society* 86:4898-4904. 1964.

41. Klages, August. Zur Kenntniss der Styrole. Berichte der Deutschen Chemischen Gesellschaft 35:2633-2646. 1902.
42. Klenk, Mabel M., C. M. Suter and S. Archer. The preparation and properties of some benzohydril sulfones. Journal of the American Chemical Society 70:3846-3850. 1948.
43. Kobayashi, Michio. The reduction of the azo linkage with hydrogen bromide. Nippon Kagaku Zasshi 74:968-970. 1953. (Abstracted in Chemical Abstracts 49:2989g. 1955)
44. Koelsch, C. Frederick. Syntheses with triarylvinylmagnesium bromides. Pentaarylallyl alcohols. Journal of the American Chemical Society 54:3384-3389. 1932.
45. _____. Syntheses with triarylvinylmagnesium bromides. α - γ -bis-diphenylene- β -phenylallyl, a stable free radical. Journal of the American Chemical Society 79:4439-4441. 1957.
46. Königs, W. Einwirkung von schwefliger Säure und von Sulfinssäure auf Diazoverbindung. Berichte der Deutschen Chemischen Gesellschaft 10:1531-1534. 1877.
47. Lamb, Robert C. and Jas. Grady Pacifici. Organic peroxides. III. The behavior of cyclohexanecarbonyl peroxide in the presence of excess stable radicals. The simultaneous determination of kinetic and free radical efficiencies in the thermal decomposition of free radical initiators. Journal of the American Chemical Society 86:914-918. 1964.
48. Lamb, Robert C. et al. Organic peroxides. I. The intramolecular reaction between the olefinic double bond and the peroxide linkage in the decomposition of trans- γ -benzylidenebutyryl peroxide. Journal of the American Chemical Society 84:2635-2640. 1962.
49. Le Fèvre, R. J. W., M. F. O'Dwyer and R. L. Werner. Infra-red spectra of compounds containing the azo-group. Australian Journal of Chemistry 6:341-359. 1953.
50. Lewis, Edward S. and Harold Suhr. Untersuchungen über die Reaktion von Diazoniumsalzen mit Cyanide. Chemische Berichte 92:3043-3049. 1959.

51. Little, William F. and Allen K. Clark. Ferrocenylazobenzenes. Resonance interaction of ferrocene with substrates. *Journal of Organic Chemistry* 25:1979-1982. 1960.
52. Makarova, L. G. and A. N. Nesmeyanov. Decomposition and formation of onium salts and the synthesis of heteroorganic compounds. VIII. Decomposition of phenyldiazonium fluoborate in nitriles of acids. *Izvestiya Akademii Nauk S. S. S. R. Otdelenie Khimicheskikh Nauk*, 1954, p. 1019-1023. (Abstracted in *Chemical Abstracts* 50:240i. 1956)
53. Martin, J. C., James W. Taylor and E. H. Drew. The decomposition of acetyl peroxide in olefinic solvents. The acetyl peroxide-cyclohexene reaction. *Journal of the American Chemical Society* 89:129-135. 1967.
54. Meerwein, Hans et al. Über die Isomerie zwischen Diazosulfonen und Diazonium-Sulfinaten. *Chemische Berichte* 90:853-862. 1957.
55. Michaelis, A. Ueber synthesen vermittelt Natriumphenylhydrazines. *Justus Liebig's Annalen der Chemie* 252:260-317. 1889.
56. Müller, Eugene (ed.). *Methoden der organischen Chemie* (Houben-Weyl). Stuttgart, George Thieme Verlag, 1955. 1337 p.
57. Nelsen, Stephen F. and Paul D. Bartlett. Azocumene. II. Cage effects and the question of spin coupling in radical pairs. *Journal of the American Chemical Society* 88:143-149. 1966.
58. Neumann, W. P. and H. Lind. Free-radical decomposition of azo compounds induced by organotin hydrides. *Angewandte Chemie, International ed., in English*, 6:76-77. 1967.
59. O'Connor, Rod. Tautomerism in phenylhydrazones. *Journal of Organic Chemistry* 26:4375-4380. 1961.
60. Oldroyd, Dorothy M., G. S. Fisher and L. A. Goldblatt. The peroxide-catalyzed addition of carbon tetrachloride to β -pinene. *Journal of the American Chemical Society* 72:2407-2410. 1950.

61. Overberger, C. G. and A. J. Rosenthal. Azo compounds. XXXIII. Products of the thermal decomposition of phenylphenyl-sulfonyl diimide. *Journal of the American Chemical Society* 82:117-119. 1960.
62. Pines, Herman and C. N. Pillai. Phenyl migration during decomposition of peroxides in alkylbenzenes. *Journal of the American Chemical Society* 82:2921-2925. 1960.
63. Pryor, William A. and Harold Guard. Walden inversion by radicals. The reaction of phenyl radicals with disulfides. *Journal of the American Chemical Society* 86:1150-1152. 1964.
64. Ritchie, C. D., J. D. Saltiel and E. S. Lewis. The reaction of diazonium salts with nucleophiles. VIII. The formation of diazosulfones and the application of linear free energy equations to diazonium salt reactions. *Journal of the American Chemical Society* 83:4601-4605. 1961.
65. Rosenthal, Arnold J. and C. G. Overberger. Azo compounds. XXXII. Kinetics of the thermal decomposition of phenylphenyl-sulfonyl diimide. *Journal of the American Chemical Society* 82:108-117. 1960.
66. Russell, Glen A. and Akihiko Ito. Photochlorination of bromocyclopentane and chlorocyclopentane. *Journal of the American Chemical Society* 85:2983-2988. 1963.
67. Silverstein, Robert M. and G. Clayton Bassler. Spectrometric identification of organic compounds. New York, Wiley, 1963. 177 p.
68. Stevens, Harold Robert and Fred Wilbert Ward. Tautomerism of the mesoxalic acid and pyruvic acid phenylhydrazones. Evidence for the hydrazone structure of the tautomerides. *Journal of The Chemical Society* 125:1324-1329. 1924.
69. Sugihara, J. M. and Stanley R. Newman. Recrystallization of organic compounds from detergent-water systems. *Journal of Organic Chemistry* 21:1445-1447. 1956.
70. Swain, C. Gardner, Lawrence J. Schaad and A. Jerry Kresge. The mechanism of decomposition of benzoyl peroxide in cyclohexane solution. *Journal of the American Chemical Society* 80: 5313-5319. 1958.

71. Terent'ev, A. B. and R. G. Petrova. Homolytic rearrangement with the migration of an alkylthio or arylthio group. Bulletin of the Academy of Sciences of the U.S.S.R., Division of Chemical Sciences, 1963, p. 1984-1986.
72. Theobald, Clement W. Solution polymerization of vinyl compounds. U. S. patent 2,584,306. Feb. 5, 1952. (Abstracted in Chemical Abstracts 46:3798i. 1952)
73. Thiele, Johannes. Über Nitrosohydrazine, Isoazotate und Azoverbindungen der Fettreihe. Justus Liebig's Annalen der Chemie 376:239-268. 1910.
74. Trapp, Orlin D. and George S. Hammond. The decomposition of α, α' -azoisobutyronitrile in liquid bromine. Journal of the American Chemical Society 81:4876-4878. 1959.
75. Uémura, Taku and Yasuo Inamura. Les spectres d'absorption des composés azoïques mixtes et ceux de leurs isomeres. Bulletin of the Chemical Society of Japan 10:169-182. 1935.
76. van Zwet, H. and E. C. Kooyman. Sulfur compounds in free radical reactions. Part II. Thermal decomposition of arenediazothiolates. Recueil des Travaux Chimiques des Pays-Bas 86:1143-1152. 1967.
77. Williams, Gareth H. Homolytic aromatic substitution. Norwich, Pergamon, 1960. 133 p.