

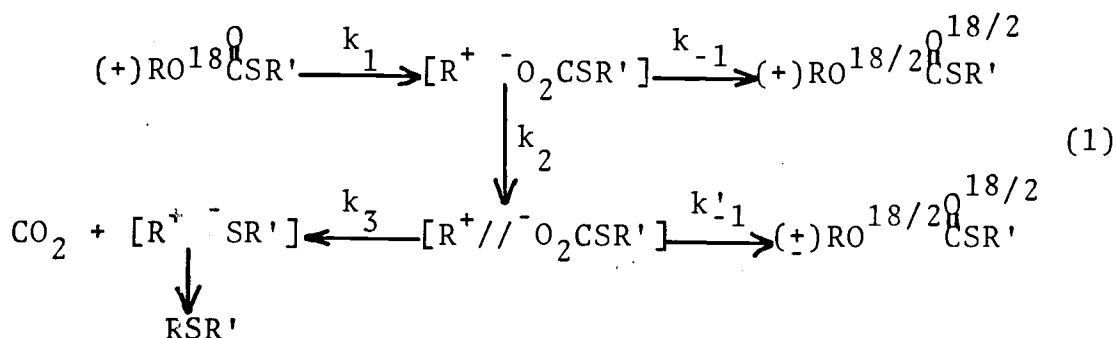
AN ABSTRACT OF THE THESIS OF

Gary Craig Hanson for the Doctor of Philosophy degree in
Chemistry presented on June 28, 1972

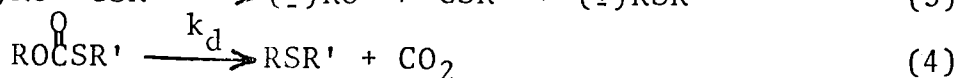
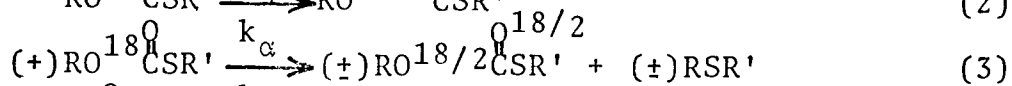
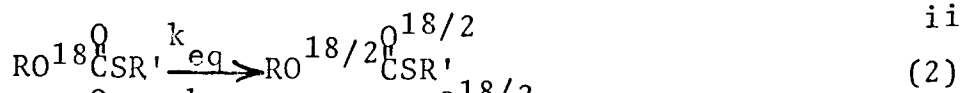
Title: Mechanistic Study of Some Internal Substitution
Reactions and a Substitution at Sulfenyl Sulfur

Abstract approved: Redacted for Privacy

Part A. The thermal decomposition of aralkyl thio-
carbonates is known to take place by an ion pair mechanism.
A mechanism consistent with the facts about this decomposi-
tion is shown in equation 1. One can investigate the



details of this ion pair process by observing the rate of
 O^{18} equilibration, k_{eq} (equation 2), the rate of loss of
optical activity, k_{α} (equation 3) and the rate of loss of
 CO_2 , k_d (equation 4).



In the present work a series of thiocarbonates where R was varied between *p*-methylbenzhydryl, α -naphthylphenylcarbinyl, and *p*-chlorobenzhydryl was studied. The rate data in benzonitrile for each of the compounds are given below.

| Cpd. | T°(C) | $k_d \times 10^5$ (sec ⁻¹) | $k_\alpha \times 10^5$ (sec ⁻¹) | $k_{eq} \times 10^5$ (sec ⁻¹) |
|----------------|-------|---|--|--|
| <i>p</i> -Me | 135 | 9.1 | 28.1 | 43.5 |
| α -Naph | 135 | 4.9 | 18.4 | 38.3 |
| <i>p</i> -Cl | 145 | 0.65 | 2.6 | 5.1 |

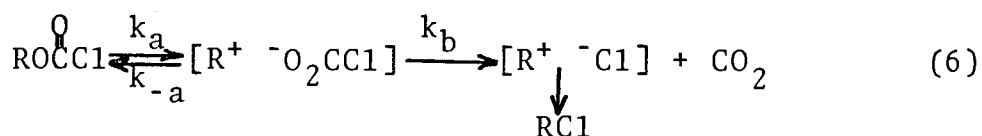
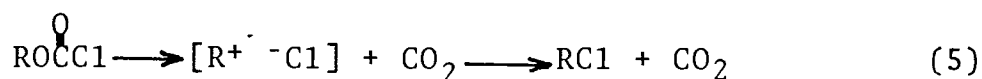
By suitable manipulation, these values may be expressed in terms of the rate constants in equation 1. The results of these calculations are:

| Cpd. | k_2/k_{-1} | k_3/k_{-1} |
|----------------|--------------|--------------|
| <i>p</i> -Me | 1.15 | 0.48 |
| α -Naph | 0.74 | 0.36 |
| <i>p</i> -Cl | 0.85 | 0.33 |

The increase in k_2/k_{-1} and k_3/k_{-1} for the *p*-methyl compound over the *p*-chloro compound is thought to arise from the fact that $\text{CH}_3\text{C}_6\text{H}_5\text{CHPh}^+$ is more stable than carbonium ion $\text{ClC}_6\text{H}_5\text{CHPh}^+$. The greater stability of the carbonium ion is thought to give the ion pair from the *p*-methyl compound a somewhat longer average lifetime and thereby increase the

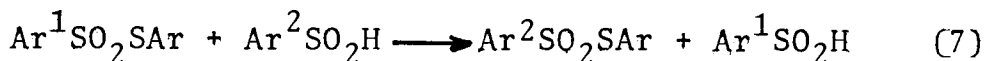
chance it will undergo either loss of CO_2 or racemization prior to recombination. The α -naph⁺CHPh ion is also thought to be a more stable carbonium ion than $\text{ClC}_6\text{H}_5\text{CHPh}^+$, although not as stable as $\text{CH}_3\text{C}_6\text{H}_5\text{CHPh}^+$. The α -naphthyl compound in this series would therefore be expected to exhibit a larger k_3/k_{-1} value than that for the *p*-chloro compound, which it does. However, it would also be expected on this basis to have a k_2/k_{-1} value somewhere between that for the *p*-methyl and *p*-chloro compounds. In actual fact the α -naphthyl compound has a k_2/k_{-1} value that is lower than the *p*-chloro compound. This lower k_2/k_{-1} value means that a larger number of ion pairs chose to return with retention relative to further dissociation for the α -naphthyl compound as compared to the *p*-chloro compound. In solvolysis reactions involving formation of a carbonium ion intermediate α -naphthyl compounds have been shown to behave differently compared to those aralkyl derivatives which do not have a peri hydrogen. The peri hydrogen is thought to force the aryl groups of the carbonium ion to be less coplanar than in other aralkyl carbonium ions. Arguments are presented that this non-coplanarity might lead to a marked increase in the tendency of the $[\text{R}^+ \text{ } ^-\text{O}_2\text{CSR}']$ ion pair to return with retention in the α -naphthyl case, and could possibly account for the low k_2/k_{-1} value observed for this compound.

Part B. The decomposition of chlorocarbonates has been a classic example of an S_Ni reaction. The previously available data are consistent with two possible mechanisms, (1) loss of CO_2 by a concerted mechanism (equation 5) or (2) by a two step cleavage mechanism (equation 6). Both mechanisms involve ion pair intermediates.



If one were to observe that equilibration of the O^{18} labeled oxygen in $RO^{18}\overset{O}{C}Cl$ accompanied decomposition of the chlorocarbonate into RCl and CO_2 , this would be evidence of ion pair return in this system and would show that one must have the mechanism shown in equation 6 with $k_b < k_{-a}$. After partial decomposition the reaction was stopped and the ester reduced with lithium aluminum hydride. The resulting alcohol was analyzed for O^{18} and it was found that no O^{18} had been lost from the alkyl oxygen in samples of chlorocarbonate recovered after 60% decomposition. This shows there is no detectable ion pair return in this system. The absence of any ion pair return accompanying decomposition indicates that if one has mechanism 6 then $k_b \gg k_{-a}$. On the other hand, it is also possible that decomposition proceeds by the concerted process shown in equation 5.

Part C. Nucleophilic cleavage of sulfur-sulfur bonds has been studied previously using reactions that involved attack of the nucleophile on, (1) $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \end{array}$ sulfonyl, (2) $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \end{array}$ sulfinyl and (3) $-\text{S}-$ sulfenyl sulfur. Nucleophilic attack on both the sulfonyl sulfur and sulfinyl sulfur was studied with an ArSO_2 leaving group. However, sulfenyl sulfur had not been studied with an ArSO_2 leaving group and it was thought that a study of the thiolsulfonate-sulfinic acid exchange (equation 7) and its possible catalysis by various nucleophiles might be an excellent way to do this. The



sulfinate anion is such a good nucleophile in this case that high concentrations of perchloric acid in 60% dioxane have to be added to slow this reaction down to conveniently measurable rates. Strong acid slows the reaction down by converting ArSO_2^- to the much less nucleophilic species ArSO_2H . It was found that added bromide did not greatly catalyze the exchange even at high added acid concentrations where the concentration of sulfinate anion was very low. The fact that the sulfinate anion exchanges extremely rapidly with the thiolsulfonate and that very high acid concentrations were necessary to slow down the exchange made this system unsuitable for the desired nucleophilic reactivity study.

Mechanistic Study of Some Internal Substitution Reactions
and a Substitution at Sulfenyl Sulfur

by

Gary Craig Hanson

A THESIS

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Typed by Joann H. Peckham for Gary Craig Hanson

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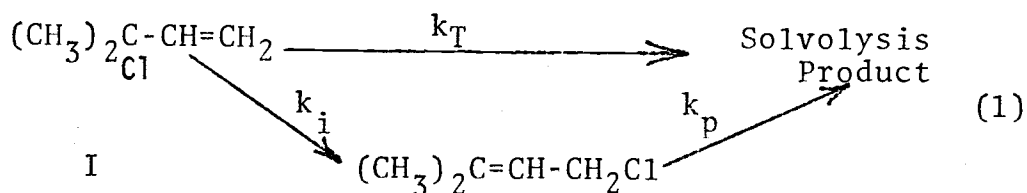
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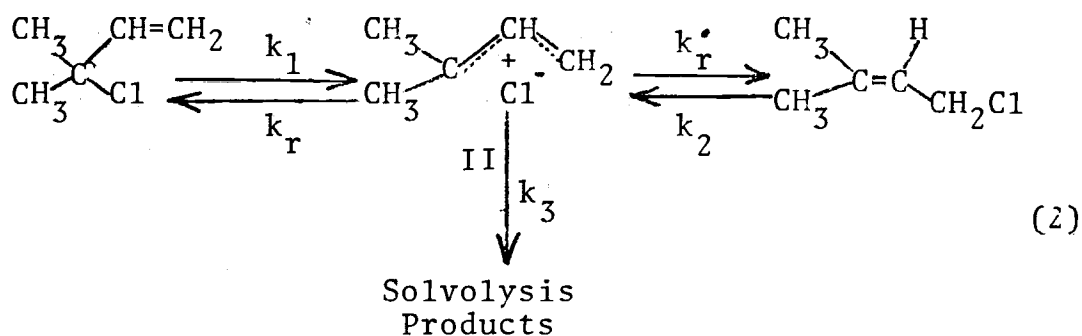
ION PAIR RETURN PHENOMENA IN THE THERMAL DECOMPOSITION OF ARALKYL THIOCARBONATES

INTRODUCTION

The carbonium ion has occupied a notable position in organic chemistry. Changes in both the character of the carbonium ion and the anion have led to many new reactions and a greater knowledge of reaction processes. Winstein and co-workers were first to postulate that an ion pair may be involved in reactions as an intermediate. Winstein and co-workers (48) reported that α,α -dimethylallyl chloride (I) isomerized faster than it solvolyzed (equation 1). Additional chloride anion had no common ion effect nor did radioactive chloride exchange appreciably into the unsolvolyzed product. It was found that $k_i = 2k_T = 16k_p$.

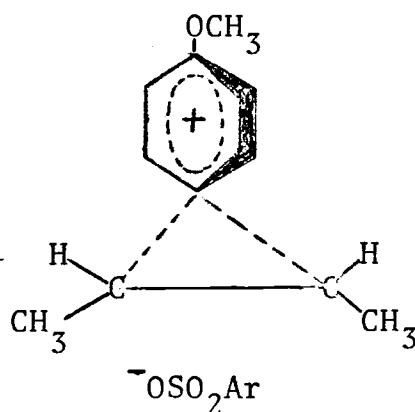


The fact that isomerization k_i occurs faster than solvolysis k_T was explained by assuming an ion pair intermediate which returned to covalent chloride product faster than it went on to solvolysis product. Such an ion pair would consist of an allylic stabilized carbonium ion (II) and a chloride anion which could return to either end of the allylic carbonium ion (equation 2)



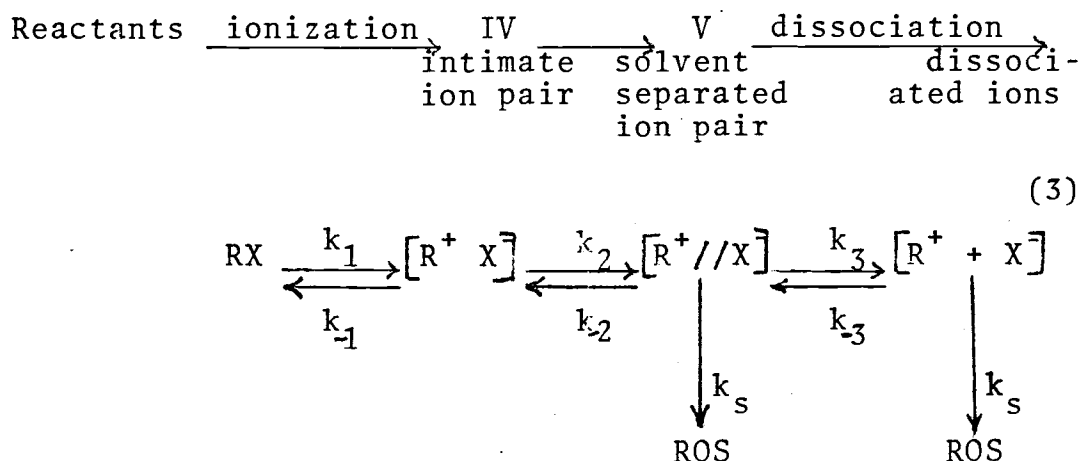
where k_r and $k'_r > k_3$.

Winstein and Robinson (47) in studying the solvolysis of threo-3-*p*-anisyl-2-butyl bromobenzenesulfonate found the polarimetric rate (k_α) to be four times the titrimetric rate (k_t) in acetic acid; k_α is larger than k_t because the bromobenzenesulfonate ester is undergoing racemization faster than it is undergoing solvolysis. Racemization accompanies each return of an ion pair to covalency in this case because of the special symmetrical nature of the bridged phenonium-type carbonium ion III that is formed. Ionization of this particular system is known to involve neighboring group participation by the *p*-anisyl group.



III

Lithium perchlorate had a normal linear salt effect on k_α , whereas with k_t there was a steep beginning which leveled off to a normal linear pattern with increased lithium perchlorate. This peculiar dependence of k_t on $[\text{LiClO}_4]$ they termed a "special salt effect" and they (46) ascribed it to the fact that addition of small amounts of lithium perchlorate could eliminate part of the ion pair return that otherwise occurred in its absence. However, since k_t never became equal to k_α no matter how much LiClO_4 was added, ion pair return is only partially eliminated by the special salt effect. The working hypothesis they put forward was that two kinds of carbonium ion pairs (equation 3), intimate, IV, and solvent-separated, V, were responding differently to the added LiClO_4 . The solvent separated ion pair V was presumed to be much more



reactive than the intimate ion pair IV towards added lithium perchlorate.

At the same time that Winstein postulated two types of

ion pairs in the previous example, Grunwald (16) had calculated the potential energy of ion pairs in a solvent with a moderate dielectric constant (ca. >10). His calculation showed two distinct minima in a plot of potential energy versus distance between the ions (Figure 1). These results agree with Winstein's hypothesis of two distinct ion pairs.

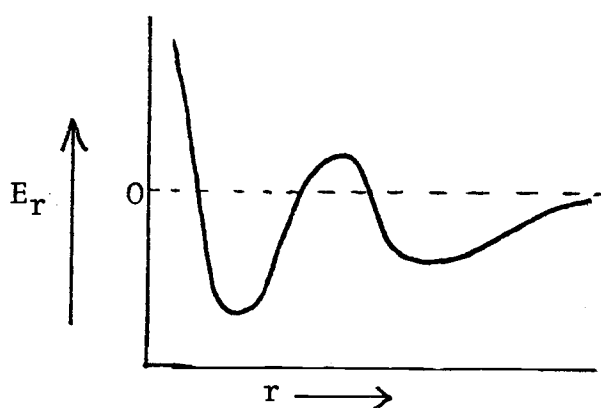
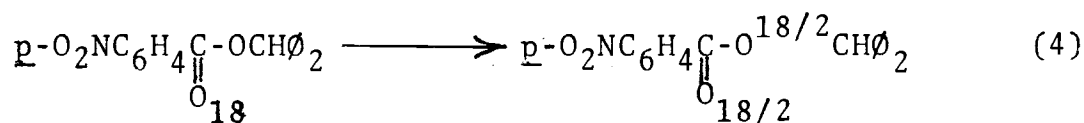


Figure 1

The allylic-stabilized carbonium ions are a special set of the greater class of carbonium ions to which Grunwald had referred. Allylic delocalization of the positive charge allows the anion to attach itself to a new carbon upon return from an ion pair, whereas many carbonium ions will not undergo rearrangement; rather return will be to the same carbon atom. The racemization of threo-3-p-anisyl-2-butyl bromobenzene-sulfonate may be a more sensitive measure of ionization, but this anchimerically assisted ionization creates an unusual carbonium ion. What one would like to have is some means of quantitatively measuring ion pair

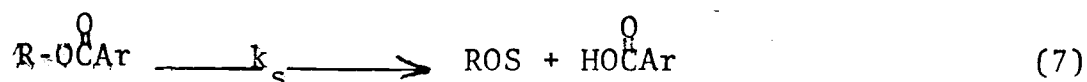
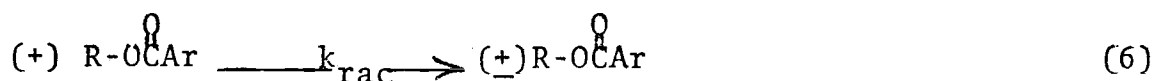
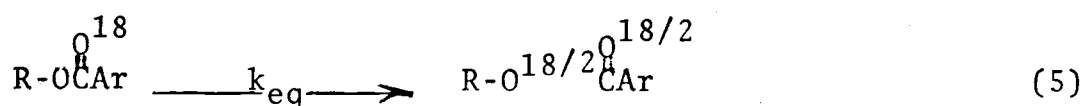
return in systems generally. One possibility, at first glance, would seem to be to use an optically active compound and measure the rate of loss of optical activity compared to the rate of solvolysis. However, since it is entirely likely that a sizable portion of the total return will occur with retention of configuration in the typical system being studied this is unlikely to prove an accurate measure of all ion pair return. It was for this reason that Goering and Levy (14) looked for and found a more accurate way of detecting total ion pair return. Goering's method was based on the fact that if one solvolyzes a carbonyl- O^{18} -labeled *p*-nitrobenzoate, such as $p-O_2NC_6H_4C(O^{18})-OCH_3$, and ion pairs $[p-O_2NC_6H_4CO_2^- + CH_3^+]$ are involved as intermediates, the ion pair return to ester should result in the equilibration of the oxygen-18 label between the acyl and alkyl oxygens of the ester, since in the anion $p-O_2NC_6H_4CO_2^-$ both carboxylate oxygens should hopefully be equivalent. Goering found that in 90% aqueous acetone the rate of equilibration, k_{eq} , (equation 4) as measured by the rate of equilibration of the O^{18} -label in samples of ester



recovered after various extents of partial solvolysis was about three times larger than the rate of solvolysis, k_s . Assuming that the oxygens become equivalent as soon as alkyl

oxygen cleavage takes place, k_{eq} then is a measure of the total ion pair return to the ester.

Goering and co-workers (11, 13) have studied the behavior of a series of optically active and O^{18} -labeled benzhydryl *p*-nitrobenzoate derivatives in aqueous acetone (80 and 90 percent). Three reactions of the ester may be observed during solvolysis, k_{eq} , the equilibration of the carboxyl oxygens (equation 5), k_{rac} , the racemization of the unsolvolyzed ester (equation 6) and k_s , the solvolysis of the ester (equation 7).



Assuming k_{eq} (equation 5) is indicative of total ion pair return, then k_{rac} (equation 6), which measures the return with racemization, will be some fraction of total return (k_{eq}). From the values of k_{eq} and k_{rac} the preference of ion pairs for return with retention to return with racemization can be compared. For the *p*-chlorobenzhydryl ester in 90% acetone, 62% of those ion pairs undergoing return do so with retention, and in 80% acetone 57% return with retention. In both solvents return with reten-

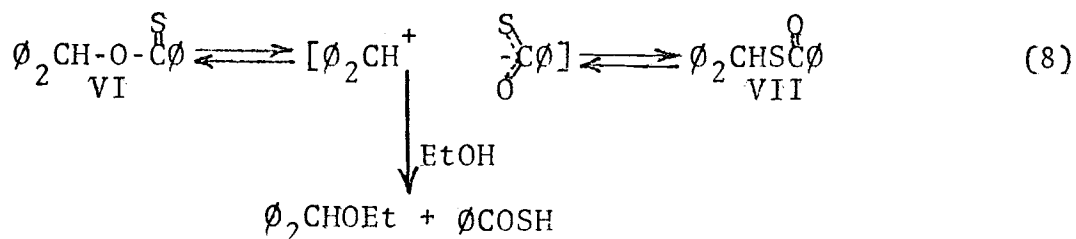
tion is predominant, and the better ionizing solvent (80% acetone) leads to a greater degree of racemization with respect to returning ion pairs.

The existence of a second ion pair was given greater substantiation by Goering and co-workers (15) when it was found that in the solvolysis of the *p*-chlorobenzhydryl *p*-nitrobenzoate in 80% acetone in the presence of 0.014 M sodium azide, the unsolvolyzed O^{18} equilibrated ester recovered had exclusively retained configuration. Thus addition of azide ion prevented all ion pair return that had been occurring with racemization, but did not prevent that portion of the return that involved retention. The simplest interpretation of these results is that there are two different kinds of ion pairs involved in the reaction, one in which return can occur with equilibration of oxygens, but without loss of configuration, and another where return occurs with both O^{18} equilibration and loss of configuration. This second ion pair can be effectively intercepted by azide ion in competition with return, but the first ion pair can not.

Goering and co-workers (13) have found that the amount of racemization associated with return (k_{rac}/k_{eq}) varies with structure and temperature. *p*-Chlorobenzhydryl and *p*-methylbenzhydryl esters at 99.5° have values of k_{rac}/k_{eq} of 0.35 and 0.60 respectively and the *p*-methylbenzhydryl and *p*-methoxybenzhydryl esters at 48° have k_{rac}/k_{eq} values of 0.17 and 0.28, respectively. This suggests that attractive

forces that preserve optical configuration in ion pair intermediates become weaker as delocalization of the charge in the cation increases. This pattern was observed (12) in the solvolysis of α -phenylethyl p-nitrobenzoate in 70% acetone where all return occurs with retention, while in the α -p-anisylethyl ester (>30,000 times more reactive) return results in considerable racemization, i.e. $k_{\text{rac}}/k_{\text{eq}}$ is 0.71 in 70% acetone at 60°.

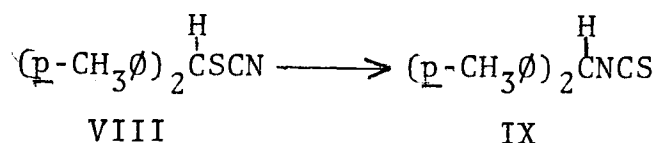
Other anions besides carboxylate ions can be used to detect the occurrence of ion pair return in reactions involving carbonium ion intermediates. Smith (38) has shown that solvolysis of benzhydryl thionbenzoate (VI) is accompanied by a faster isomerization of this ester to the corresponding thiobenzoate (VII). Since the solvolysis clearly involves a carbonium ion (ρ for $\text{C}_6\text{H}_5\overset{\text{Ar}}{\text{CH}}\text{O}-\overset{\text{S}}{\text{C}}\text{O} = -3.6$) the isomerization of VI \rightarrow VII presumably involves the mechanism shown in equation 8 and an ion pair



intermediate. The isomerization strongly favors the thiol ester VII. This is presumably due to the sulfur being a much better nucleophile than oxygen and the fact that the thiol ester is much more thermodynamically stable than the thion

ester. Because of the driving force of the reaction towards thiol ester, the rate of isomerization of VI \longrightarrow VII is thought to be a reasonably accurate measure of the total rate of ion pair return.

Fava (8) has made use of yet another ambident anion to investigate ion pair behavior. The isomerization of 4,4'-dimethylbenzhydryl thiocyanate VIII to the isothiocyanate IX proceeds

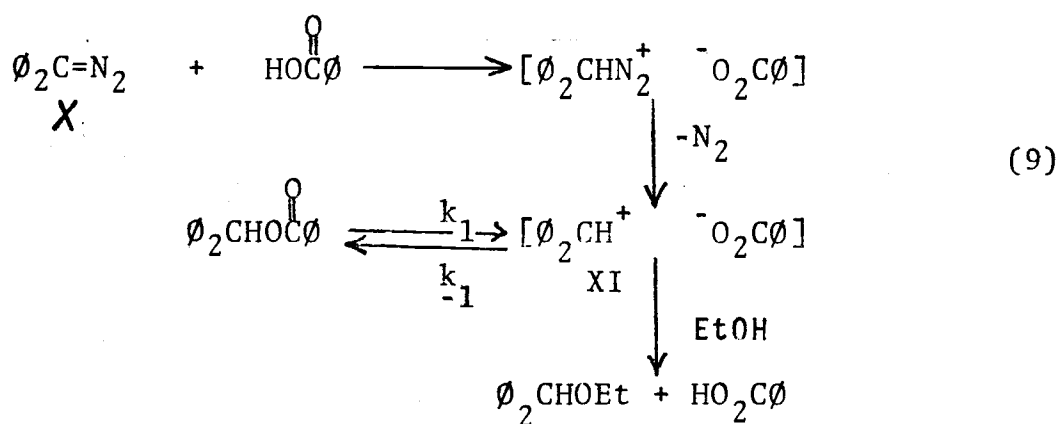


with only a small amount of S^{35} being picked up when run in the presence of NaS^{35}CN . The isomerization must therefore proceed via the intimate ion pair, since any isomerization going through the solvent separated ion pair or more dissociated ionic species would lead to incorporation of label from NaS^{35}CN . Using the incorporation of label as a lower limit to the amount of rearrangement proceeding through the more dissociated ion pair, it was found that 5.4 percent of the rearrangement proceeded through dissociated ion pair intermediates. Using optically active p-chlorobenzhydryl thicyanate, Fava and co-workers (41) showed that the isomerization occurred with net retention, which is consistent with the isomerization taking place via an intimate ion pair intermediate, since if isomerization were occurring via a

solvent-separated ion pair intermediate the isomerization should occur with racemization.

The use of ambident ions as an indication of ion pair return differs from Goering's carboxylate anion in that return is not to the same atom. Hence, one does not have an equal partitioning of return pathways. The partition of the ambident ion may be complicated by effects of temperature and solvent whereas, it would seem that the carboxylic anion must always partition equally. However, recent experiments now question whether the oxygens always become completely equivalent in Goering's carboxylate anion systems.

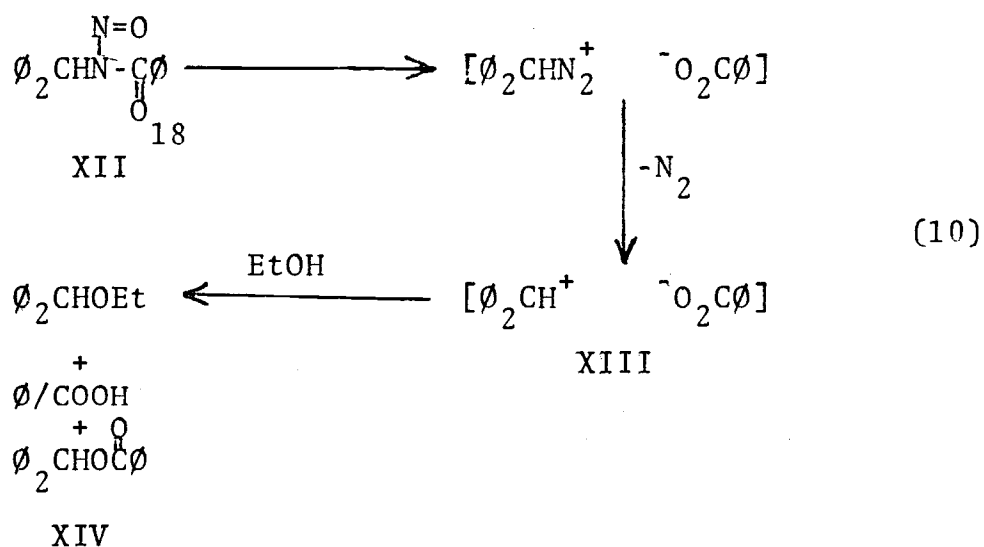
Diaz and Winstein (6) studied the reaction between diphenyldiazomethane X and benzoic acid in ethanol (equation 9). The behavior of the ion pair XI formed by loss of N₂ in



this system was compared to the behavior of the ion pair formed during the solvolysis of benzhydryl benzoate.

O¹⁸-Label equilibration (k_{eq}) was assumed to account for ion pair return in the solvolysis, whereas ester formation

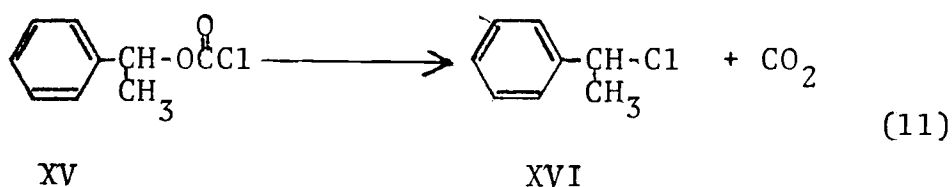
indicates return in the diphenyldiazomethane reaction. This was greater than in the corresponding solvolysis (0.588 and 0.47 respectively). Similar results were also observed for the p-nitrobenzoate system in 90% acetone (0.822 and 0.745 respectively). Considering the ion pairs to be the same in both cases, the lower value for return for ion pairs generated by ionization of the ester on solvolysis would arise from partial nonequivalence of the oxygens in the carboxylate anion. Some work of White and Elliger (44) tends to support this conclusion. They studied the decomposition of O^{18} labeled nitrosoamide XII in ethanol (equation 10), and



determined the distribution of the O^{18} -label in the ester XIV formed as one of the reaction products. 60% of the label was found in the carbonyl oxygen of the ester. Assuming that the ion pair XIII is the same as in previous cases, these results indicate a minimum of 20% of the ion pairs in the solvolysis reaction are undergoing return without the

oxygens becoming equivalent in the carboxylate anion. It could be that in the case of an ambident anion where a really larger driving force favors rearrangement one could have less undetected return than in the carboxylate anion case.

Ion pairs have also been proposed as intermediates in the thermal decomposition of compounds of the type $\text{RO}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{Y}$ (where $\text{Y} = \text{Cl}, \overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{Cl}$, etc.). The thermal decomposition of chlorocarbonates was studied by Wiberg (45). Using various substituted α -phenylethyl chlorocarbonates, XV, which were converted upon heating to the corresponding chloride XVI (equation 11), he found a large negative ρ value for the reaction, clearly indicative of a carbonium ion mechanism. Optically active

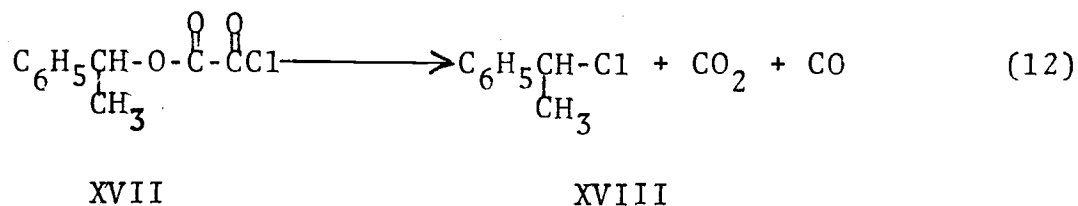


α -phenylethyl chlorocarbonate lost carbon dioxide to form the chloride with a high degree of retention. That racemization is not observed must be due to loss of CO_2 occurring before the ions dissociate. Interest in this ionic mechanism is pursued later on in the thesis.

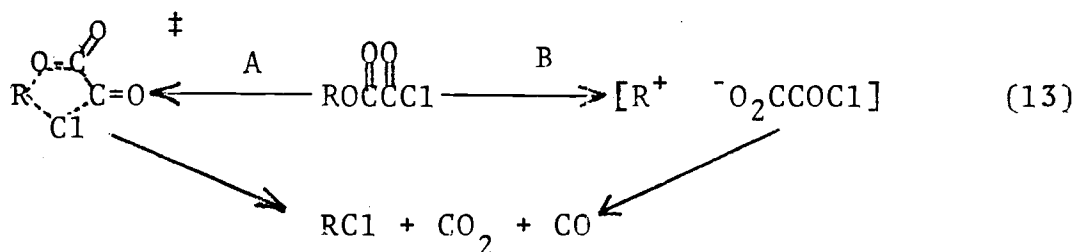
Young (48) studied the thermal decomposition of butenyl chlorocarbonates in even greater detail. Decomposition of optically active α -methylallyl chloride ($\text{CH}_2=\text{CH}-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{O}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{Cl}$)

gave the corresponding chloride ($\text{CH}_2=\text{CH}-\overset{\text{CH}_3}{\text{CH}}-\text{Cl}$) with varying degrees of retention depending upon the solvent used. It was reasoned that the loss of CO_2 occurs before the ion pair has a chance to dissociate.

Rhoads and Michel (34) studied the thermal decomposition of α -phenylethyl chloroglyoxalates, XVII, which have structural similarities to the corresponding chlorocarbonates. The thermal decomposition is characterized by loss of carbon dioxide and carbon monoxide to give α -phenylethyl chloride XVIII (equation 12).



The authors have proposed two possible mechanisms (equation 13). Mechanism A is a cyclic concerted process where ion-

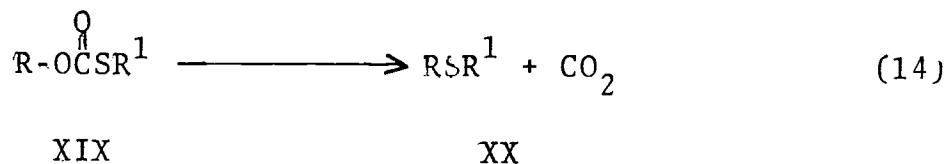


ization is at a minimum, whereas mechanism B proceeds via ion pairs. The rate of decomposition ratio of ca. 14:1 observed for the two solvents, nitrobenzene and toluene is in contrast to Oliver and Young's (32) rate ratio of ca. 100:1 for

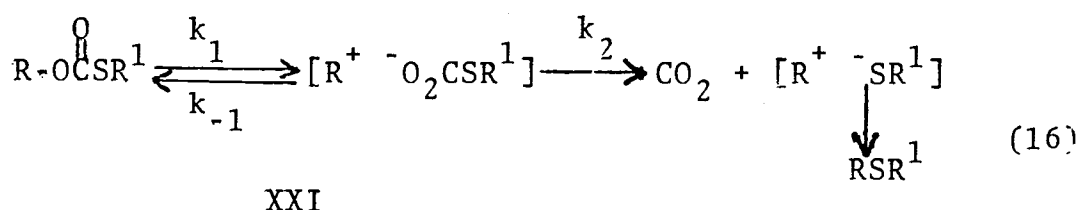
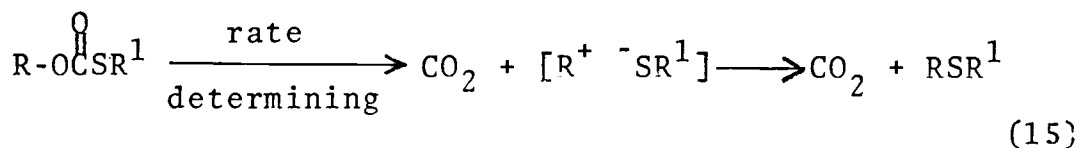
analogous chlorocarbonates in nitrobenzene versus toluene. Such a solvent effect, the ionic process of chlorocarbonates being relatively much faster in the more polar solvent, whereas the polar solvent does not affect the chloroglyoxalates as much, indicates a less polar transition state. Optically active α -phenylethyl chloroglyoxalate gave the corresponding chloride with about 70% retention which is consistent with a mechanism that does not allow the carbonium ion much freedom to racemize. It is also thought that $^-\text{O}_2\text{CCOCl}$ should be a slightly more stable anion than $^-\text{O}_2\text{CCl}$ (i.e. $K_{\text{aHCOOH}} = 1.8 \times 10^{-5}$ and $K_{\text{aHCOCOCH}} = 4.7 \times 10^{-5}$). Therefore, an ion pair mechanism should allow more time for racemization due to the greater stability of the $^-\text{O}_2\text{CCOCl}$ anion compared to the $^-\text{O}_2\text{CCl}$ anion. Since the chloroglyoxalates actually turn out to be more stable (α -phenylethyl chlorocarbonate decomposes ca. 1000 fold faster than α -phenylethyl chloroglyoxalate under similar conditions), more than just cleavage of the R-O bond is apparently involved in the rate-determining step. Rhoades and Michel accordingly favored mechanism A where an energy determining factor is the breaking of the C-Cl bond.

Thermal decompositions of ROCOY compounds may be studied in greater detail when $\text{Y} = \text{XR}^1$ so that the loss of carbon dioxide produces RXR^1 . This system can be studied with changes in both R and R^1 . Kice and co-workers (20) have shown that thiocarbonates XIX lose carbon dioxide to

form the corresponding sulfides XX upon thermal decomposition (equation 14).



Thiocarbonates demonstrate the same dependence of rate on the R group that was found for the chlorocarbonates. Further studies on the effect of the R¹ group on the rate demonstrated that the rate-determining step involved cleavage of the $\overset{\text{O}}{\parallel}\text{C}-\text{S}$ bond. Two mechanisms consistent with this fact and with other data on the dependence of rate on both structure of R and solvent can be proposed:

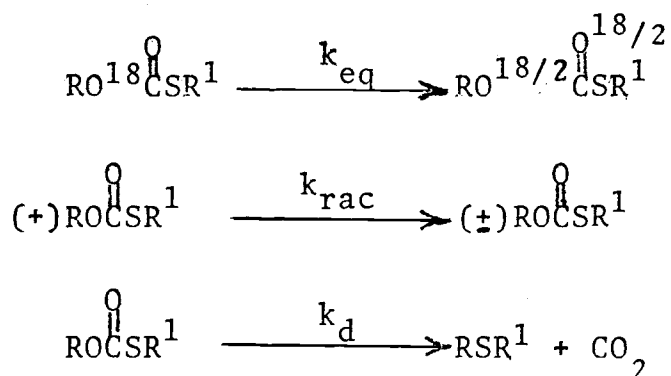


Mechanism 15 involves synchronous cleavage of the R-O bond and the $\overset{\text{O}}{\parallel}\text{C}-\text{S}$ bond to split out carbon dioxide. Mechanism 16 involves the formation of ion pair XXI before loss of carbon dioxide occurs. In this mechanism k_2 would be rate determining and $k_{-1} > k_2$.

Kice and Dankleff (22) resolved the problem of which

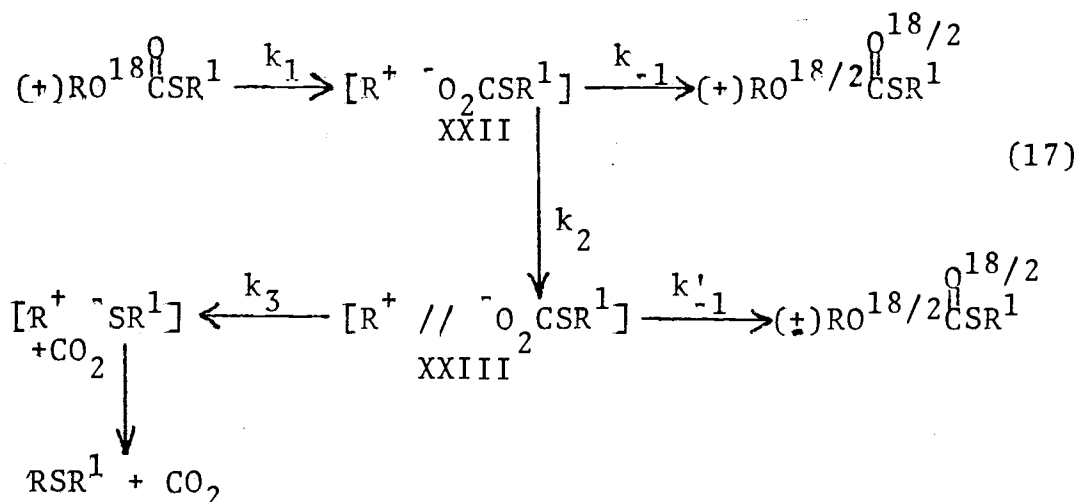
mechanism was correct by studying the thermal decomposition of optically active p-chlorobenzhydryl S-methyl thiocarbonate. They found that the optically active ester underwent racemization about four times faster than it underwent decomposition to sulfide and CO₂. Provided part of the return to thiocarbonate from XXI in mechanism 16 occurs with loss of configuration this result is of course consistent with mechanism 16, but there is no way to account for the occurrence of racemization of the thiocarbonate prior to decomposition in terms of the other mechanism in equation 15. Therefore, the mechanism in equation 16 is the correct one.

The total rate of return cannot of course be measured by measuring the rate of racemization. Therefore, Kice and co-workers (27) prepared O¹⁸-labeled thiocarbonates RO¹⁸^OCSR¹ and investigated their behavior. With these and the optically active thiocarbonates in hand three different processes can be followed:



Equilibration of the alkyl-acyl oxygens (k_{eq}) and the racemization of the R group (k_{rac}) accompany the decomposition of the ester to sulfide and carbon dioxide. Kice and

co-workers (27) using *p*-chlorobenzhydryl esters with various R^1 groups found $k_{eq} > k_{rac}$. A mechanism consistent with the above facts is shown in equation 17. The ester cleaves the

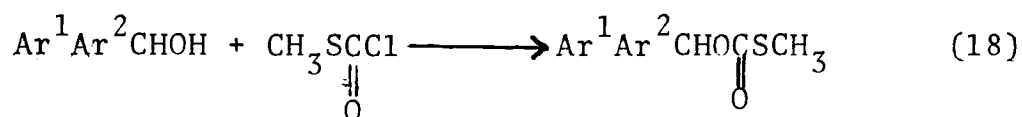


R-O bond first to form an intimate ion pair XXII which is assumed to have both oxygens equivalent in the anion. The intimate ion pair may collapse to ester k_{-1} or dissociate to the solvent separated ion pair XXIII which can either return with racemization to ester (k'_{-1}) or lose carbon dioxide (k_3) to form the sulfide product. The more stable the R^1S^- anion the greater the fraction of the solvent separated ion pairs which undergo loss of carbon dioxide.

The purpose of the work in this thesis was to investigate the thermal decomposition of thiocarbonates with specific respect to what effect changes in the carbonium ion portion of the ion pair would have on both k_2/k_{-1} and k_3/k'_{-1} . It was also of interest to see if the size of the carbonium ion's substituents would have any effect on the partitioning of the various ion pairs.

RESULTS

Preparation of Thiocarbonates. The various S-methyl thiocarbonates were all prepared by reaction of the desired alcohol with methyl chlorothiolformate in a benzene solution containing an equivalent amount of pyridine (equation 18). The alcohols chosen were



p-methylbenzhydrol and α-naphthylphenylcarbinol, and in the cases of the optically active and O¹⁸-labeled thiocarbonates, (-)-p-methylbenzhydrol, (+)-α-naphthylphenylcarbinol, p-methylbenzhydrol-O¹⁸, and α-naphthylphenylcarbinol-O¹⁸ were used.

In general, yields were not high and the thiocarbonates usually had to be purified by column chromatography.

Kice and co-workers (20) have previously studied the products of decomposition of benzhydryl S-phenylthiocarbonates in benzonitrile. They found that the major products consisted of carbon dioxide (100% yield) and benzhydryl phenyl sulfide (78 - 83% yield). A small amount of phenyl disulfide (ca. 2%) was also detected. Hence, the thermal decomposition proceeds primarily according to equation 14.

Kinetics of the Decomposition of p-Methylbenzhydrol,

and α -Naphthylphenylcarbinyl S-Methyl Thiocarbonates in Benzonitrile. The kinetics of the decompositions were studied by following the disappearance of the strong infrared absorption band due to the carbonyl group of the thiocarbonates, using the procedure previously described by Kice and co-workers (20). They (20) had previously demonstrated that the intensity of the carbonyl group absorption follows the Lambert-Beer Law. Plots of $\log [\text{thiocarbonate}]$ vs. time were satisfactorily linear as expected for a reaction following first-order kinetics (figures 2-3). In some runs there was a tendency for the rate to accelerate after about 40% decomposition. The rate constants for such runs were determined from the slope of the plot prior to the point where acceleration began. For each thiocarbonate at least five different kinetic runs were carried out, and the data shown in Table 1 for k_d represent the average value of k_d obtained for each thiocarbonate.

TABLE 1. Kinetics of Decomposition of S-Methyl Thiocarbonates in Benzonitrile at 135°

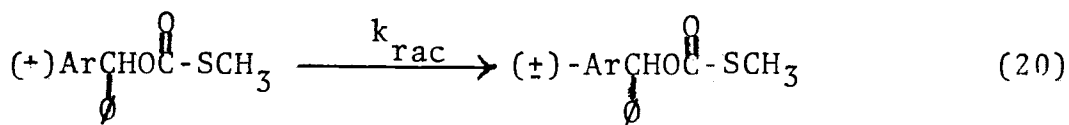
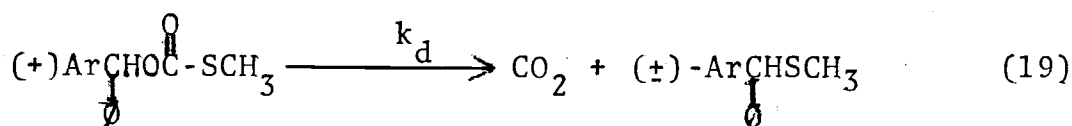
| S-Methyl Thiocarbonate | Conc. (M) | $t_{1/2} \times 10^{-3} \text{ sec}$ | $k_d \times 10^5 \text{ sec}^{-1}$ |
|-----------------------------------|-----------|--------------------------------------|------------------------------------|
| p-methylbenzhydryl | 0.122 | 7.61 | 9.1 \pm .7 * |
| α -naphthylphenyl-carbinyl | 0.117 | 14.12 | 4.9 \pm .5 |

* Average Deviation

Kinetics of Racemization of S-Methyl Thiocarbonates in Benzonitrile. In both systems studied in the present work the final solution from the decomposition of an initially

optically active thiocarbonate is optically inactive. In other words the products of the decomposition do not retain any optical activity.

During the decomposition the solution loses optical activity as a result of two processes: (1) decomposition of optically active thiocarbonate to give optically inactive aralkyl sulfide and CO_2 (equation 19) and (2) racemization of optically active thiocarbonate prior to its decomposition (equation 20).



The experimental first-order rate constant for the overall rate of loss of optical activity, k_α , is accordingly given by equation 21.

$$k_\alpha = k_{\text{rac}} + k_d \quad (21)$$

Plots of the logarithm of the observed rotation versus time at the chosen wavelength of maximum rotation for each thiocarbonate are shown in Figure 2,3. All plots were linear and from their slopes, the value of k_α for each thiocarbonate in benzonitrile was calculated. The results are shown in Table 2.

TABLE 2. Kinetics of Racemization of S-Methyl Thiocarbonates in Benzonitrile at 135°

| Thiocarbonate | Conc. (M) | λ | $t_{1/2} \times 10^{-3} (\text{sec})$ | $k \times 10^5 \text{sec}^{-1}$ |
|-----------------------------------|-----------|-----------|---------------------------------------|---------------------------------|
| p-methylbenzhydryl | .038 | 334 | 2.48 | 27.9 |
| | .038 | 334 | 2.45 | 28.3 |
| α -naphthylphenyl-carbinyl | .023 | 404 | 3.60 | 19.2 |
| | .023 | 404 | 3.96 | 17.5 |

Kinetics of Oxygen Equilibration of Alkyl-O¹⁸ Labeled S-Methyl Thiocarbonate in Benzonitrile. The rate of equilibration of O¹⁸ was measured by partially decomposing samples of thiocarbonate in benzonitrile, removing the solvent at a low temperature, and then reducing the residue with lithium aluminum hydride. The residue in ether was added dropwise to lithium aluminum hydride in ether and stirred overnight. Then with a few drops of water the salts were coagulated and the reduced residue filtered, dried, and crystallized from appropriate solvents. The crystalline product was sublimed before an analysis for O¹⁸ was performed on the alcohol using a mass spectrometer. The rate constants for O¹⁸ equilibration, k_{eq} , were determined by plotting the fraction of the label on the alkyl oxygen remaining versus time (Figure 2-3).

Kinetic data for p-methylbenzhydryl and α -naphthylphenyl carbinyl thiocarbonate are listed in Table 3.

TABLE 3, Kinetics of Equilibration of Acyl and Alkyl Oxygens
in S-Methyl Thiocarbonate in Benzonitrile at 135°

| Thiocarbonate | Conc. (M) | $t_{1/2} \times 10^{-3} \text{ sec}$ | $k_{eq} \times 10^5 \text{ sec}^{-1}$ |
|---------------------------------------|-----------|--------------------------------------|---------------------------------------|
| p-Methylbenzhydryl | .266 | 1.59 | 43.5 |
| α -Naphthylphenyl carbinyll | .295 | 1.81 | 38.3 |

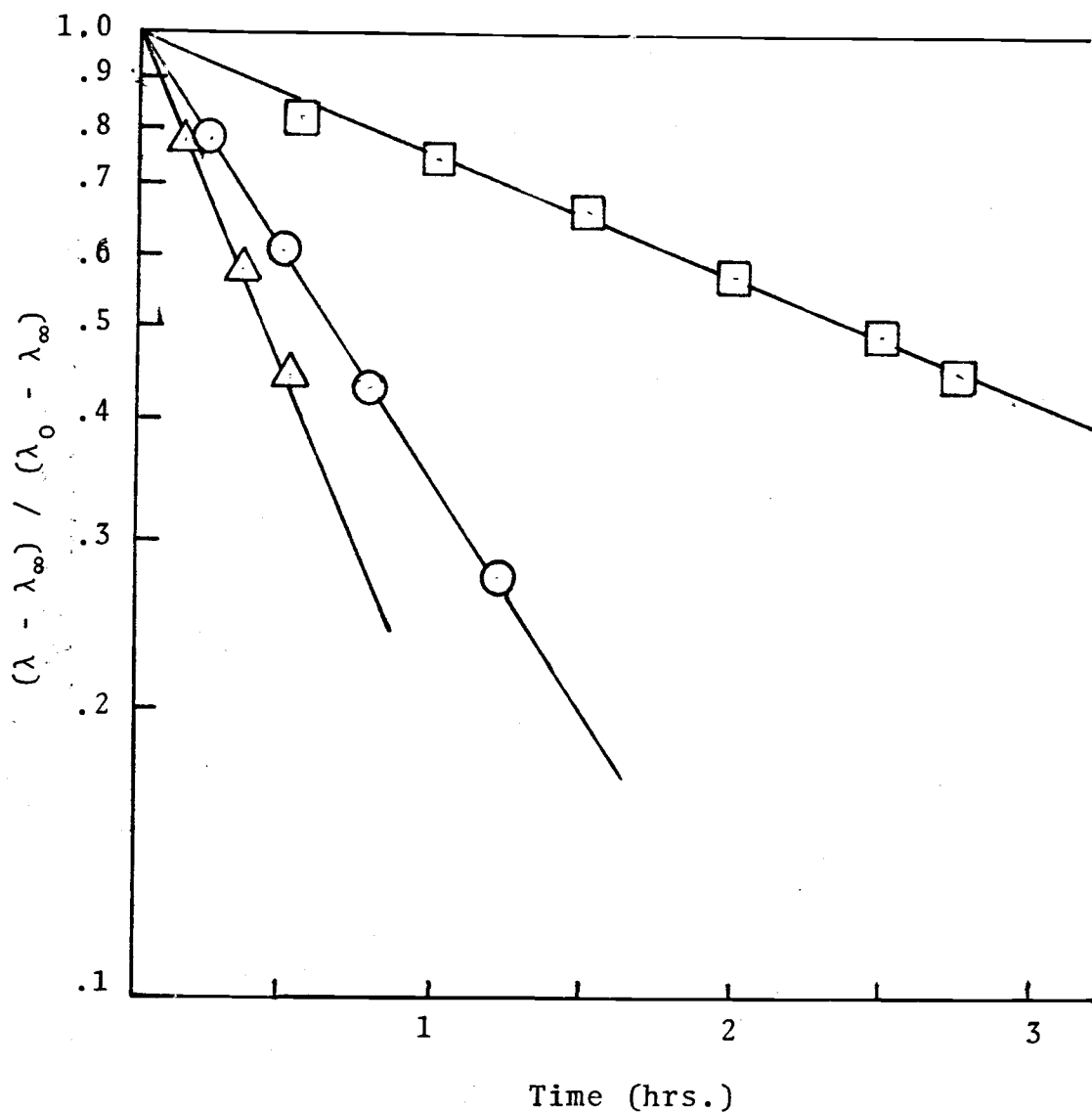


FIGURE 2. Rates of decomposition, O^{18} equilibration and loss of optical activity for *p*-methylbenzhydryl *S*-methyl thiocarbonate in benzonitrile at 135° :
 □, rate of decomposition, λ = (thiocarbonate);
 ○ rate of loss of optical activity, λ = rotation at $334\text{ m}\mu$; △ rate of O^{18} equilibration, λ = atom % O^{18} in alkyl oxygen of thiocarbonate.

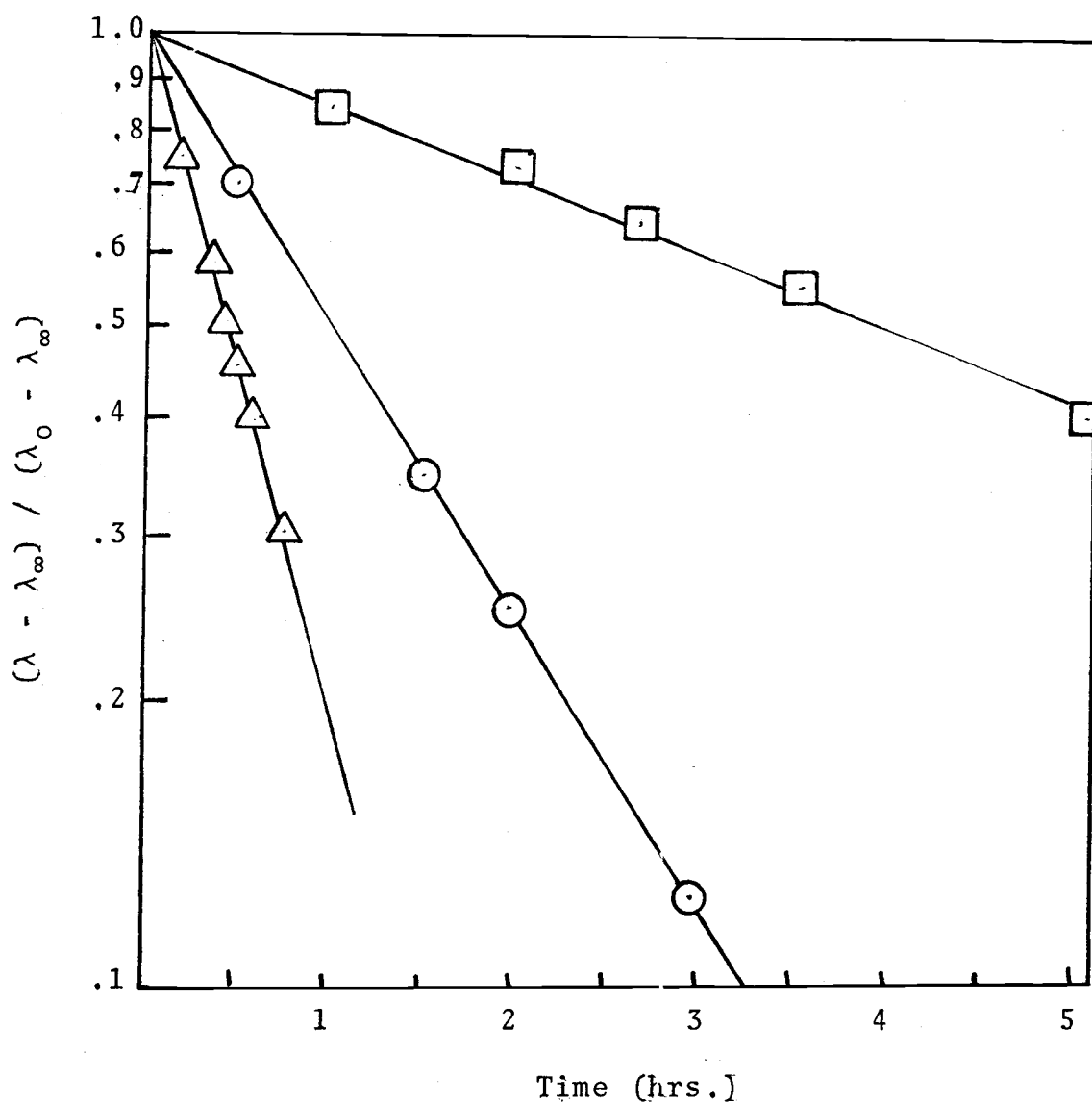
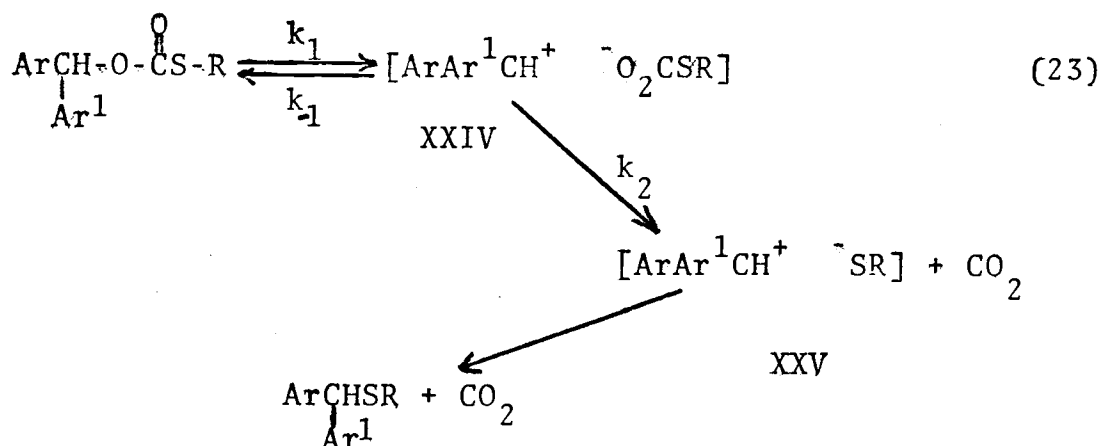


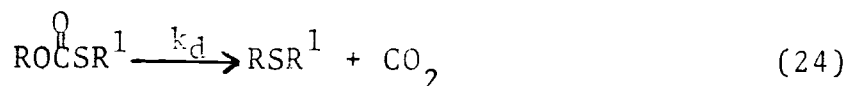
FIGURE 3. Rates of decomposition, O^{18} equilibration and loss of optical activity for α -naphthylphenylcarbonyl S-methyl thiocarbonate in benzonitrile at 135° : \square rate of decomposition, λ = (thiocarbonate); \bigcirc rate of loss of optical activity, λ = rotation at 404 m μ ; \triangle rate of O^{18} equilibration, λ = atom % O^{18} in alkyl oxygen of thiocarbonate.

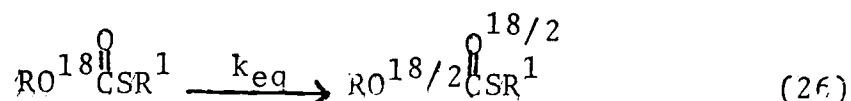
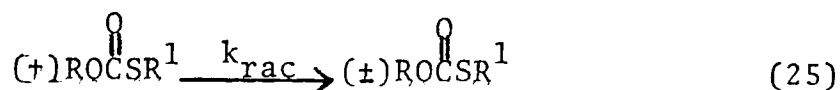
DISCUSSION

Earlier work by Kice and co-workers (26) established a two-step mechanism for the decomposition of aralkyl thiocarbonates. This mechanism involves the initial formation of ion pair XXIV. This ion pair then loses CO_2 to form a second ion pair XXV, which then collapses to the sulfide product (equation 23). The subtleties of bond cleavage can



be detected by four different experimental observations. One can measure (a) the rate of decomposition of the thiocarbonate, or loss of CO_2 , k_d (equation 24), (b) the rate of racemization of initially optically active thiocarbonate, k_{rac} (equation 25), (c) the rate of equilibration of an O^{18} label between the alkyl and acyl oxygens of the thiocarbonate prior to decomposition, k_{eq} , (equation 26), and (d) the stereochemistry of the sulfide product RSR^1 formed in the decomposition,





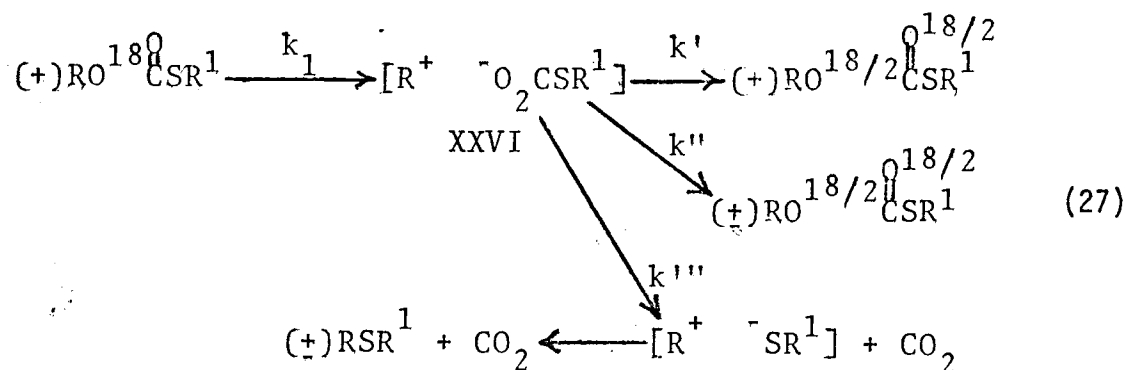
In the ion pair XXIV in equation 23, the two oxygen atoms should be equivalent and therefore return of this ion pair to thiocarbonate (step k_{-1} in equation 23) should lead to thiocarbonate containing equal amounts of label in both the alkyl and acyl oxygens. Thus to the extent that return of this ion pair to thiocarbonate competes with its loss of CO_2 (step k_2) one should observe equilibration of the oxygen-18 label in the thiocarbonate recovered after partial decomposition of the thiocarbonate (equation 26) and the relative magnitudes of k_d and k_{eq} should provide information about just what fraction of ion pairs lose CO_2 and what fraction return to thiocarbonate.

Return of the ion pair to thiocarbonate can occur with either loss or retention of configuration in the aralkyl group. Comparison of k_{eq} and k_{rac} provides a measurement of just what fraction of the return occurs with retention and what fraction with racemization.

In all of the aralkyl thiocarbonate decompositions studied so far, including the ones in the present work, the aralkyl sulfide formed as the decomposition product is optically inactive. Because of this, one can measure the rate at which a solution undergoing decomposition loses

optical activity, k_α , and equate this to the sum of $k_{rac} + k_d$ (i.e., $k_\alpha = k_{rac} + k_d$).

The experimentally measured rate constants, k_{eq} , k_α , and k_d can be related to the rate constants k_1 , k' , k'' and k''' in the general decomposition scheme shown in equation 27 in the



following manner. The rate of decomposition k_d is the rate of formation of the ion pair XXVI, k_1 , times the fraction of ion pairs losing CO_2 (equation 28). Likewise, the rate of loss of optical activity, k_α , is equal to k_1 times that fraction of ion pairs produced which either lose CO_2 or return to thiocarbonate with loss of configuration (equation 29). The return from ion pair to thiocarbonates leads to equilibration of the alkyl and acyl oxygens in both cases of return with retention and return with loss of configuration. Thus, both k' and k'' will be part of the fraction of ion pairs produced which equilibrate oxygens (equation 30),

$$k_d = k_1 \left(\frac{k'''}{k' + k'' + k'''} \right) \quad (28)$$

$$k_{\alpha} = k_1 \left(\frac{k'' + k'''}{k' + k'' + k'''} \right) \quad (29)$$

$$k_{eq} = k_1 \left(\frac{k' + k''}{k' + k'' + k'''} \right) \quad (30)$$

By suitable manipulation, the ratio k''/k''' can be expressed in terms of the experimentally measurable quantities k_{α} and k_d , as shown in equation 31.

$$\frac{k_{\alpha}}{k_d} = \frac{k_1 \left[\frac{k'' + k'''}{k' + k'' + k'''} \right]}{k_1 \left[\frac{k'''}{k' + k'' + k'''} \right]} \quad (31)$$

$$\frac{k_{\alpha} - k_d}{k_d} = \frac{k''}{k'''}$$

In a like manner, the ratio k'/k''' can also be expressed in terms of the experimentally measurable quantities k_{eq} , k_d , and k_{α} , as outlined in equation 32.

$$\frac{k_{eq}}{k_d} = \frac{k_1 \left[\frac{k' + k''}{k' + k'' + k'''} \right]}{k_1 \left[\frac{k'''}{k' + k'' + k'''} \right]} \quad (32)$$

$$\frac{k_{eq} + k_d - k_{\alpha}}{k_d} = \frac{k'}{k'''}$$

The percentage of ion pairs which will choose to follow one of the three paths (k' , k'' , k''') outlined in equation 27 can be determined by the use of the ratios k'/k''' and k''/k'''

in the following equations 33, 34, 35,

$$\begin{aligned} \text{fraction of return} &= \frac{k''}{k' + k'' + k'''} = \frac{k'/k'''}{k'/k''' + k''/k''' + 1} = \\ \text{with retention} & \end{aligned} \quad (33)$$

$$1 - \frac{k_{\alpha}}{k_{eq} + k_d}$$

$$\begin{aligned} \text{fraction of return} &= \frac{k''}{k' + k'' + k'''} = \frac{k''/k'''}{k'/k''' + k''/k''' + 1} = \\ \text{with racemization} & \end{aligned} \quad (34)$$

$$\frac{k_{\alpha} - k_d}{k_{eq} + k_d}$$

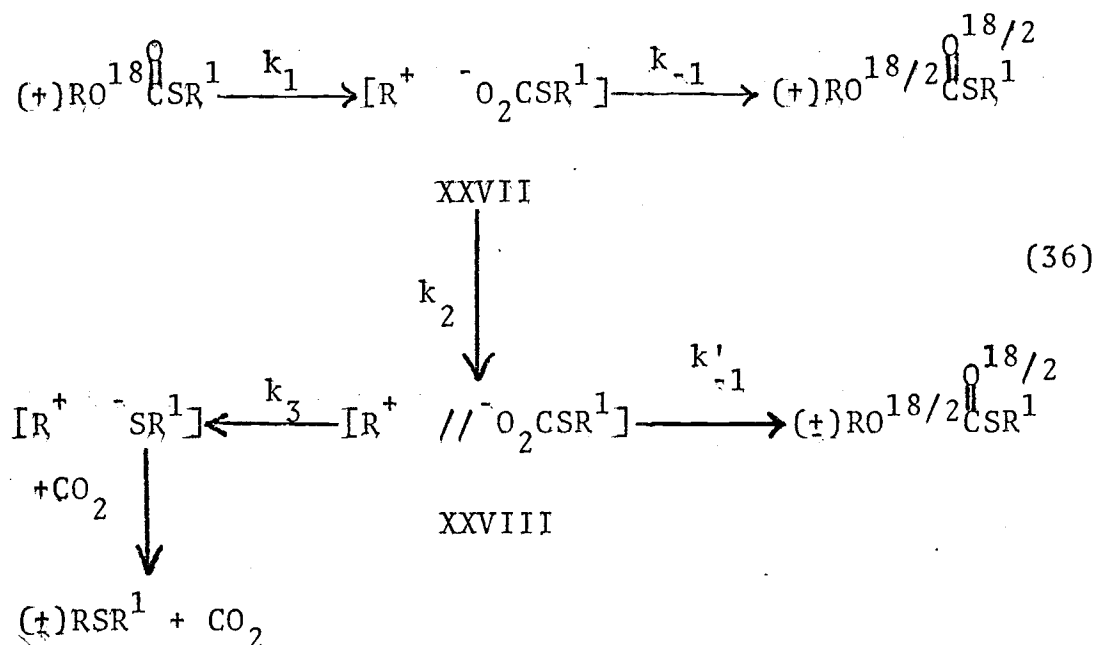
$$\begin{aligned} \text{fraction} & \\ \text{losing CO}_2 &= \frac{k'''}{k' + k'' + k'''} = \frac{1}{k'/k''' + k''/k''' + 1} = \\ & \end{aligned} \quad (35)$$

$$\frac{k_d}{k_{eq} + k_d}$$

In some related solvolysis reactions Goering (6) has postulated mechanisms involving two different types of ion pair intermediates. Studying ion pair return in the solvolysis of *p*-chlorobenzhydryl *p*-nitrobenzoate in aqueous acetone, he found that added azide ion (N_3^-) eliminated all return that occurred with racemization but did not eliminate that portion that occurred with retention of configuration. He postulated therefore that two distinct ion pair intermediates were involved in the solvolysis, one of which underwent return (measured by O^{18} equilibration) with

complete retention of configuration and a second, looser ion pair, which underwent return with racemization, but which could be intercepted and prevented from undergoing this return by having its carbonium ion trapped by the added azide ion. Azide is apparently not able to trap the carbonium ion in the tighter, first-formed ion pair before it undergoes return.

In terms of the decomposition of thiocarbonate Goering's scheme is outlined in equation 36.



The tight ion pair, or "intimate ion pair," XXVII, is formed first; then the ions continue to dissociate forming the looser, or "solvent separated ion pair," XXVIII. The experimentally measured rate constants in this mechanism are shown in equations 37, 38, and 39.

$$k_d = k_1 \left(\frac{k_2}{k_{-1} + k_2} \right) \left(\frac{k_3}{k_3 + k'_{-1}} \right) \quad (37)$$

$$k_a = k_1 \left(\frac{k_2}{k_{-1} + k_2} \right) \quad (38)$$

$$k_{eq} = k_1 \left(\frac{k_2}{k_{-1} + k_2} \right) \left(\frac{k'_{-1}}{k_3 + k'_{-1}} \right) + k_1 \left(\frac{k_{-1}}{k_{-1} + k_2} \right) \quad (39)$$

The fate of each ion pair, XXVII and XXVIII can then be determined by suitable manipulation of equations 37 - 39. In the case of the intimate ion pair, XXVII, one can determine the number of intimate ion pairs that go on to the solvent separated ion pair XXVIII, versus those that return with equilibration of oxygens as the ratio k_2/k_{-1} (equation 40). Likewise, the ratio k_3/k'_{-1} indicates what fraction of the solvent separated ion pairs XXVIII lose CO_2 as compared to undergoing ion pair return to give racemic thiocarbonate (equation 41).

$$k_2/k_{-1} = \frac{k_a}{k_{eq} + k_d - k_a} \quad (40)$$

$$k_3/k_{-1} = \frac{k_d}{k_\alpha + k_d} = \frac{k_d}{k_{\text{rac}}} \quad (41)$$

Ion Pair Behavior of p-Methylbenzhydryl and α -Naphthylphenylcarbinyl S-Methyl Thiocarbonates in Benzonitrile.

Using equations 33 - 35 the fraction of total ion pairs following the various pathways in equation 27 can be calculated. Table 4 lists the results for various S-methyl thiocarbonates including previous results on the p-chlorobenzhydryl S-methyl thiocarbonate obtained by Kice and Scriven (27).

TABLE 4. Ion Pair Behavior in Equation 27 for Various S-Methyl Thiocarbonates in Benzonitrile at 135°.

| R | Return with Retention | Return with Racemization | Loss of CO ₂ |
|---|-----------------------|--------------------------|-------------------------|
| p-CH ₃ - $\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$ -CH- | .47 | .36 | .17 |
| α -C ₁₀ H ₇ - $\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$ -CH- | .58 | .31 | .11 |
| p-Cl- $\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$ -CH-* | .54 | .35 | .11 |

*ref. (27) at 145°

The data in Table 4 shows that most of the ion pairs formed, XXVI, (equation 27) return to starting material, with only a small fraction (0.11 to 0.17 depending on the thiocarbonate) undergoing loss of CO₂. Of the ion pairs formed, XXVI, that return to starting material with equilibration of the O¹⁸-label, about 40% return with loss of configuration whereas 60% return without loss of configura-

tion,

The *p*-methylbenzhydryl cation is presumably a significantly more stable carbonium ion than the *p*-chlorobenzhydryl cation. This would be expected because of the electron-releasing inductive effect of *p*-methyl relative to *p*-chloro and is reflected in the fact that the rate of dissociation of the *p*-methyl thiocarbonate is over 40 times faster than that of the *p*-chloro compound. From Table 4 one sees that a significantly larger percent of the ion pairs in the *p*-methyl case undergo loss of CO₂ than in the *p*-chloro case. This seems consistent with the thought that the ion pair with the more stable carbonium ion should undergo return more slowly thereby increasing the chance that an ion pair will lose CO₂ rather than undergo recombination to the thiocarbonate. Also one sees that the fraction of the total return from the *p*-methyl compound that occurs with retention of configuration is somewhat less than for the *p*-chloro compound. This is also in line with the idea that return from the ion pair with the more stable carbonium ion should be somewhat slower than from the *p*-chloro compound ion pair, so that there should be a greater chance that the ion pair from the *p*-methyl compound will have lost configuration by the time it returns to thiocarbonate.

While the results with the *p*-methyl and the *p*-chloro compounds thus seem to be in line with expectations based on the fact that $p\text{-CH}_3\text{C}_6\text{H}_4\overset{+}{\text{CH}}\phi$ is a more stable carbonium ion

than $p\text{-ClC}_6\text{H}_4\text{CH}_2^+$, the results with the α -naphthyl compound are not so easy to account for. There is evidence (42,5) that an α -naphthyl group should also be considerably better at stabilizing a carbonium ion than a p -chlorophenyl group. Therefore based on such considerations one might have expected that the α -naphthyl compound would behave much the same as the p -methyl compound, particularly since its rate of dissociation is not too much slower than that of the p -methyl compound and considerably faster than that of the p -chloro compound. Instead the percent of ion pairs undergoing return is the same as for the p -chloro compound. In addition the fraction of return that occurs with retention is actually slightly greater than for the p -chloro compound rather than being somewhat less. Before attempting to see if one can come up with any reasonable explanation for the behavior of the α -naphthyl compound it will be helpful to discuss Goering's concept of two different types of ion pairs in carbonium ion reactions somewhat further.

As mentioned earlier Goering was able to trap all intermediates of the solvolysis of p -chlorobenzhydryl p -nitrobenzoate with azide ion, except for the first formed ion pair intermediate. This led Goering to assume that two different ion pairs were present. The experimental evidence, coupled with Grunwald's calculations (16) showing the potential energy of ion pair as a function of the distance of separation of the ions in a solvent with moderate dielectric

constant, suggested that in one type of ion pair (the intimate ion pair) XXVII of equation 36, the distance of separation between the ion is quite small so that there are strong electrostatic interactions between the ions. It is not at all unlikely that such an ion pair once formed would return essentially completely with retention of configuration. Should the ions move further apart a second type of ion pair could be formed (the solvent-separated ion pair), XXVIII in equation 36. The carbonium ion in the solvent-separated ion pair has a much greater chance of being trapped by a better nucleophile than the departing anion, such as is the case with an ionic scavenger like azide ion. The greater distance and less electrostatic interaction would allow the ions to return to covalency with essentially complete racemization.

If the results of the thiocarbonate studies are analyzed in terms of the scheme in equation 36 involving intimate and solvent-separated ion pairs, then from equations 40 and 41 one can arrive at values for k_2/k_{-1} and k_3/k_{-1}' . The results are listed for various S-methyl thiocarbonates in Table 5 below.

TABLE 5. Ion Pair Behavior in Equation 36 for Various S-Methyl Thiocarbonates in Benzonitrile at 135°

| R | k_2/k_{-1} | k_3/k'_{-1} |
|---|--------------|---------------|
| $\text{p-Me} \begin{array}{c} \text{O} \\ \\ \text{CH-} \end{array}$ | 1.15 | 0.48 |
| $\alpha\text{-C}_{10}\text{H}_7 \begin{array}{c} \text{O} \\ \\ \text{CH-} \end{array}$ | 0.74 | 0.36 |
| $\text{p-Cl} \begin{array}{c} \text{O} \\ \\ \text{CH-} \end{array} *$ | 0.85 | 0.33 |
| *ref. (27) at 145° | | |

The ratio of k_2/k_{-1} is the ratio for the fate of the intimate ion pair (XXVII, equation 36) as to whether it will separate further to the solvent-separated ion pairs or return to covalency with scrambling of O¹⁸, but with retention of configuration. The p-methyl compound has the largest k_2/k_{-1} value which is as one would expect from the reasoning that the more stable the carbonium the slower the rate of return relative to the other processes. On the basis of carbonium ion stability, while one would expect the α -naphthyl compound to have a lower k_2/k_{-1} value than the p-methyl compound, one would also on that basis expect k_2/k_{-1} for the α -naphthyl compound to be larger than for the p-chloro compound. However, as one can see from Table 5, the α -naphthyl compound actually has the lowest k_2/k_{-1} value of the three compounds.

The fate of the solvent-separated ion pair, XXVIII, is measured as the ratio of ion pairs losing CO₂ to ion pairs returning with racemization, or k_3/k'_{-1} . Our expectation is

that the more stable the carbonium ion the slower the rate of return, and since carbonium ion stability should have no effect on k_3 , the larger the value of k_3/k'_1 . In this instance the sequence of k_3/k'_1 values follow the pattern predicted on the basis of order of carbonium ion stability in that k_3/k'_1 is largest for the p-methyl compound, next largest for the α -naphthyl compound and smallest for the p-chloro compound. Here α -naphthylphenylcarbinyll S-methyl thiocarbonate follows the behavior expected on the basis of relative stability of the different carbonium ions whereas it has not in previous comparisons.

To better understand the character of the α -naphthyl compound, a more detailed analysis is in order. As noted earlier α -naphthyl should be better at stabilizing a carbonium ion than p-chlorophenyl. This is also suggested by comparing rates of thermal decomposition for the p-chloro and p-hydrogen compounds in benzonitrile from Kice and co-workers (20) and corrected to 135° C. with those determined in the present work. One finds the following: (p-Cl) k_d = $0.21 \times 10^{-5} \text{ sec}^{-1}$; (H) k_d = $0.38 \times 10^{-5} \text{ sec}^{-1}$; (α -naphthyl) k_d = $4.9 \times 10^{-5} \text{ sec}^{-1}$; (p-Me) k_d = $9.1 \times 10^{-5} \text{ sec}^{-1}$. Dewar and Sampson (5) find for the solvolysis of arylmethyl chlorides and 2-aryl-2-chloropropanes that the α -naphthyl compound solvolyzes 4.4 times faster than the phenyl compound. Clearly, these cases show that α -naphthyl group will stabilize a carbonium ion intermediate better than a p-chlorophenyl

or a phenyl group.

Verbit and Berliner (42) have determined the rate of solvolysis of arylphenylmethyl chlorides in 90% aqueous acetone at 25°. They also find the α -naphthyl compound to solvolyze 1.4 times faster than the β -naphthyl compound and 6.4 times faster than phenyl compound. The rate constants for different aryl groups correlated reasonably with Hückel molecular orbital reactivity parameters, but compounds with an α -naphthalene-like structure (i.e. a peri-hydrogen across from the methyl carbon bearing the halogen) fall on a separate line of lower reactivity. The difference between the higher and lower lines of reactivity has been ascribed to steric hindrance in the transition state for those compounds having the α -naphthalene-like structure, since coplanarity of the aryl group with the phenyl group will be more difficult to achieve. The lack of coplanarity of the diaryl carbonium ions has been measured as the difference in angle of twist between aromatic groups for the hindered compounds as compared to what twist might be in the unhindered compounds. It was found that hindered arylphenylmethyl carbonium ions have an average of 15° more twist between aryl groups than the unhindered carbonium ions. In considering the effect this might have on ion pair return phenomena, the out-of-coplanarity of the carbonium ion might well favor return to one side of the carbonium ion, of which the side of the leaving anion would remain more open for return to covalency.

It might also explain why the α -naphthyl ion pair is slower to lose configuration than the other ion pairs in which the aryl groups of the carbonium ion are more nearly coplanar with the central carbon. This, then is perhaps the explanation for why k_2/k_{-1} is smaller for the α -naphthyl compound than for the other two cases. In terms of the intimate ion pair XXVII, a greater amount of return with retention as compared to going to a solvent-separated ion pair XXVIII is indicative of a low k_2/k_{-1} ratio. It is also an explanation which would explain the high percentage of return with retention as seen in Table 4.

Once the ions have dissociated to the solvent-separated ion pair, then the carbonium ion should no longer be sensitive to any stereoselective return of the anion, but the stabilization factors of the carbonium ion should still be of influence on the rate of return of the ion pair relative to the loss of CO_2 . The trend for the k_3/k'_{-1} values is in accord with this reasoning.

Study of the behavior of carbonium ions in solution in systems where they may undergo several processes, all involving a small energy of activation compared to the initial energy of activation needed to create the carbonium ion is often a tricky business. The change from p-methyl, an electron-donating group, to a p-chloro, an electron-withdrawing group, depresses the rate of decomposition over 40 fold. The change in the ability to stabilize the carbonium ion thus

creates a significant change in the rate of decomposition. Yet when one looks at how this same change in phenyl substituent affects the partitioning of ion pair intermediates, only a small effect is noticed (i.e. $\frac{\text{p-Me}}{\text{p-Cl}}$ for the intimate

ion pair $k_2/k_{-1} = 1.35$ and $\frac{\text{p-Me}}{\text{p-Cl}}$ for the solvent-separated

ion pair $k_3/k'_{-1} = 1.45$). This is to be expected since the ion pair intermediates closely resemble the transition states as compared to covalent products and the energy of activation is going to be small between intermediate and transition state. These small energies of activation are not to be expected to exhibit large substituent effects as one would expect in the case of the activation energy of ionization.

Changing to an α -naphthyl group is not the simple change of electronic effects seen before, but also steric hindrance and relative size are additional effects to be dealt with. Certainly there is an effect beyond electronic stabilization which causes the α -naphthyl k_2/k_{-1} to be smaller than either of the others. The more complex situation has caused us to try and understand what is happening in terms of these additional effects. That we do not have many good examples for comparison makes the explanations given for the α -naphthyl case definitely very tentative ones. There is a need for more experimentation before the effect of the α -naphthyl group upon the carbonium half of the ion pair can be seen clearly, but the number of experiments per substituent and

especially the difficulty in obtaining necessary optically active compounds makes the solution to this problem an unenviable one.

EXPERIMENTAL

Preparation of Methylchlorothiolformate. Phosgene (120 ml., 1.69 moles) was collected in a trap immersed in dry ice-acetone and then distilled into a 2000 ml., 3-necked, round-bottom flask, fitted with both a dry ice condenser and a 500 ml. equilibrating addition funnel and containing 500 ml. anhydrous ether and a Teflon stirring bar. A solution of 54 ml. (0.98 moles) of methanethiol in 500 ml. anhydrous ether was added dropwise to the phosgene-ether solution over a half-hour interval. The reaction mixture was kept in an ice-salt bath throughout the addition. After the addition was complete the reaction mixture was allowed to stir overnight, the dry ice condenser being used to prevent the evaporation of any of the phosgene.

Then, at ice-bath temperature, about 300 ml. 6N NaOH was added slowly to the solution due to vigorous bubbling. As soon as a test with pH indicator paper showed the solution was basic, the addition of sodium hydroxide was stopped. The ethereal layer was then separated, washed twice with 300 ml. H_2O , and then once with 300 ml. saturated sodium chloride. The solution was concentrated to about 250 ml. volume. This was then cooled and dried over anhydrous magnesium sulfate. The dried solution was then fractionated through a 15 cm. Vigreux column (1 cm. diameter). There was obtained 75 ml. of methylchlorothiolformate, bp. $110 - 111^{\circ}$ (87% yield).

Preparation of p-Methylbenzhydrol. p-Methylbenzophenone, 137 g. (0.7 moles), in 200 ml. anhydrous ether was added dropwise to 15 g. lithium aluminum hydride (0.4 moles) in 200 ml. anhydrous ether. Stirring was continued overnight at room temperature, whereupon the remaining hydride was destroyed by the addition of saturated ammonium chloride solution. The organic layer was separated and was washed twice with water and once with saturated sodium chloride. It was then dried over magnesium sulfate. The solvent was removed under reduced pressure and the product was recrystallized from hexane, yielding 135 g. of p-methylbenzhydrol, mp. 51 - 53^o (lit.(4), 51 - 53^o).

Preparation of p-Methylbenzhydryl S-Methyl Thiocarbonate. p-Methylbenzhydrol (2.00 g., 0.01 moles) was dissolved in 10 ml. benzene, and 1.5 ml. dry pyridine was then added to this solution. Methylchlorothioformate, 2 ml. in 10 ml. benzene, was then added to this solution dropwise at room temperature with stirring. After the addition was complete the reaction was stirred for four more hours. Twenty ml. of ether was then added, the solution was washed with three portions of water, and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using benzene as an eluent. Recrystallization from hexane afforded 1.9 g. (72% yield) of p-methylbenzhydryl S-methyl thiocarbonate,

mp. 36 - 38° (Anal., Calc'd. for $C_{16}H_{16}O_2S$: C, 70.6; H, 5.93. Found: C, 70.66; H, 5.84).

Preparation of p-Methylbenzhydrol- O^{18} . p-Methylbenzophenone (69 g., 0.35 mole) was dissolved in a mixture of 350 ml. of dioxane, 35 ml. (1.7 mole) of oxygen-18 enriched water (1.59%), and 0.1 ml. of concentrated sulfuric acid. This mixture was heated under reflux conditions for 24 hours. The major portion of the solvent was distilled off and the residue was dissolved in 100 ml. of ether and dried over magnesium sulfate. After filtering, the solution was added dropwise with stirring to a three-necked flask fitted with a reflux condenser and containing 7.5 g. (0.2 mole) of lithium aluminum hydride and 100 ml. of anhydrous ether. The mixture was stirred overnight at room temperature. It was cooled in an ice-bath and saturated ammonium chloride was added. The organic layer was separated, washed twice with water, and then once with saturated sodium chloride; it was then dried over magnesium sulfate. The solvent was removed under reduced pressure and the product recrystallized from hexane, yielding 65 g. (94%) of the O^{18} -labeled alcohol mp. 51 - 53° (1.42% O^{18}).

Preparation of O^{18} -Labeled p-Methylbenzhydryl S-Methyl Thiocarbonate. The same general method was used as for all the thiocarbonates. A 2.0 g. sample of p-Methylbenzhydrol- O^{18} was dissolved in 10 ml. benzene and 1.5 ml. pyridine was

added. Then 2.0 ml. of methylchlorothioformate in 10 ml. of benzene was added dropwise with stirring, and stirring was continued for four hours at room temperature after the addition was complete. Then a 20 ml. portion of ether was added, and the organic phase was washed three times with water and once with saturated sodium chloride before drying over magnesium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel column using benzene as an eluent. The solvent was removed under reduced pressure and the resulting oil was recrystallized from hexane, yielding 0.9 g. (33%) of the O^{18} -labeled thiocarbonate, mp. $36 - 38^{\circ}$.

Preparation of p-Methylbenzhydryl Hydrogen Phthalate.

A mixture of phthalic anhydride (17 g., 0.115 moles), pyridine (9 g., 0.114 moles), and p-methylbenzhydrol (21 g., 0.106 moles) was stirred at $45 - 55^{\circ}$ for three hours. An equal volume of acetone was added and then the excess anhydride was decomposed by addition of a slight excess of dilute hydrochloric acid. Dilution with ice water gave p-methylbenzhydryl hydrogen phthalate (22 g., 59% yield) which separated from ether-pentane as clusters of needles, mp. $122 - 124^{\circ}$ (lit. (13), $121.5 - 123^{\circ}$).

Preparation of (+)-p-Methylbenzhydrol. Employing the procedure of Goering and Hopf (13), p-methylbenzhydrol acid phthalate (20 g., 0.0575 moles) was dissolved in 400 ml. of

distilled dry acetone. The solution was warmed on a steam bath at 50° - 60° and (+)quinidine (20.8 g., 0.065 mole) was added in small portions. The solution was filtered hot. Crystals appeared after cooling to room temperature, about a two hour period. After standing overnight the crystals were filtered off and the mother liquor was subsequently used to obtain the more soluble isomer as described later. The crystals were recrystallized from 230 ml. of dry acetone. A third recrystallization was carried out using 143 ml. of acetone. Crystallization was slower each time and longer needles were formed at the expense of the quantity of quinidine salt.

Only 2 g. of the quinidine salt was left after the 143 ml. acetone recrystallization. This salt was decomposed in a separatory funnel containing an excess of ice cold 10% hydrochloric acid and ether. The ethereal solution dried over magnesium sulfate, filtered, and then evaporated to leave behind the half-ester, 0.75 g., $[\alpha]_{589} = (-) 8.6^{\circ}$ (chloroform), $[\alpha]_{589} = (-) 11.3^{\circ}$ (benzene).

The mother liquor from which the first crop of crystals had been obtained was now used to obtain the more soluble diastereoisomer optically active. About 20 to 30 ml. of solvent was evaporated from the solution and set aside to allow material to crystallize out. The crystals which formed were filtered off and discarded and the procedure repeated. All told this procedure was repeated ten times until only 150 ml.

of solution remained. This solution was then completely evaporated and the quindine salt decomposed as above to the half-ester, 6.95 g., $[\alpha] = (+) 4.3^{\circ}$ (chloroform).

The (+) half-ester, 6.95 g., was dissolved in 50 ml. of hot methanol. To this was added 5 ml. of 40% sodium hydroxide and the solution was kept at 60° for 15 minutes. The solution was diluted with 150 ml. water and extracted twice with ether. The ether extracts were dried over magnesium sulfate, filtered, and the ether evaporated under reduced pressure to give 1 g. of p-methylbenzhydryl $[\alpha]_{589} = (+) 2.5^{\circ}$ (chloroform).

Preparation of (+)-p-Methylbenzhydryl S-Methyl Thiocarbonate. When subjected to the same procedure as used before for the synthesis of thiocarbonates, (+)-p-methylbenzhydryl (1 g. $[\alpha]_{589} = (+) 2.50$) gave 0.35 g. (25% yield) (+)-p-methylbenzhydryl S-methyl thiocarbonate $[\alpha]_{579} = (+) 8.2$, $[\alpha]_{334} = (+) 44.5$ (Benzonitrile).

Preparation of α -Naphthylphenylcarbinol. Magnesium turnings (18 g.) were placed in a 2000 ml. three-necked round bottom flask fitted with a 500 ml. equilibrating addition funnel, a Teflon stirring paddle, and reflux condensor connected to a mineral oil pressure trap, and the flask and contents were dried by flaming the outside of the flask briefly with a burner. A solution of 25 ml. of bromobenzene in 50 ml. ether was added to the magnesium turnings to start

the reaction, then 60 ml. of bromobenzene in 300 ml. ether was added dropwise while the reaction was controlled at reflux level with an ice-bath. The reaction was stirred until refluxing had stopped and then cooled with an ice-bath while 100 ml. of α -naphthylaldehyde in 200 ml. ether were added dropwise. The reaction was stirred one hour while being warmed in a hot water bath after all the reagents had been added. The reaction was worked up by addition of dilute sulfuric acid to dissolve the remaining magnesium turnings and washed with water before drying over magnesium sulfate. The dried solution was filtered and evaporated under reduced pressure. The residue was recrystallized from either benzene/hexane or carbon disulfide to give α -naphthylphenylcarbinol mp. 85.5° (lit. (36), 86.5°) (85 g., 45% yield).

Preparation of α -Naphthylphenylcarbiny l S-Methyl Thiocarbonate. Employing the same procedure as for other thiocarbonates, 2.5 g. α -naphthylphenylcarbinol (0.01 moles) was dissolved in 10 ml. dry benzene and 1.5 ml. pyridine. Then 2.2 ml. methylchlorothiolformate in 10 ml. benzene was added dropwise. After six hours 20 ml. ether was added and the reaction mixture was worked up as before. Recrystallization from methanol gave 1.2 g. of α -naphthylphenylcarbiny l S-methylthiocarbonate (40% yield), mp. $91 - 92^{\circ}$ (Anal., Calc'd. for $C_{19}H_{16}O_2S$: C, 73.99; H, 5.23. Found: C, 74.28; H, 5.01).

Preparation of α -Naphthyl Phenyl Ketone. Employing the method of J. Meinwald (30) 20 g. of α -naphthylphenylcarbinol was oxidized with Jones reagent. The crystals of the product as first obtained were red in color and had a rather broad melting point, 67 - 75°. They were then chromatographed on a Florosil column using benzene as an eluent. After this treatment recrystallization from benzene/hexane gave yellow crystals, mp. 74 - 75° (lit. (36), 75 - 75.5°) (15 g., yield 75%).

Preparation of α -Naphthylphenylcarbinol- O^{18} . The same type of procedure used to label *p*-methylbenzophenone with oxygen-18 was also used to label α -naphthyl phenyl ketone. α -Naphthyl phenyl ketone (15 g.) was dissolved in 60 ml. dioxane to which was added 4.5 ml. of 1.59%- O^{18} enriched water and a drop of concentrated sulfuric acid. The mixture was refluxed 24 hours and the solvent was then removed under reduced pressure. The oily residue was dissolved in 25 ml. ether and then reduced with 1.2 g. lithium aluminum hydride. Work up of product yielded 12 g. (80%) of O^{18} -labeled α -naphthylphenylcarbinol, mp. 85° (1.56% O^{18}).

Preparation of O^{18} -Labeled α -Naphthylphenylcarbiny
S-Methyl Thiocarbonate. Employing the same synthetic technique as used to make the other thiocarbonates, 2.5 g. α -naphthylphenylcarbinol- O^{18} was used to make 1.92 g. (60%

yield) of the O^{18} -labeled α -naphthylphenylcarbinyl S-methyl thiocarbonate, mp. 91 - 92 $^{\circ}$ (benzene/hexane).

Preparation of α -Naphthylphenylcarbinyl Hydrogen Succinate. Succinic anhydride (19 g. 0.2 moles) and α -naphthylphenylcarbinol (44.5 g., 0.19 moles) were placed in a three-necked, 100 ml., round bottom flask equipped with a Teflon stirring bar, reflux condenser, and thermometer. A solution of 19 ml. dry pyridine and 29 ml. of triethylamine was added and the mixture was stirred at 40 $^{\circ}$ for 30 minutes.

The solution was poured slowly into a beaker containing 200 g. ice and 48 ml. concentrated hydrochloric acid. Vigorous stirring caused the formation of a putty-like mass around the stirring rod. Upon warming to room temperature and stirring, this mass became a thick oil which was smeared onto the walls of the beaker and left overnight to harden. The crude succinate was dissolved in 80 ml. acetone and the above precipitation procedure repeated twice. The final white crystals were washed with water until neutral to litmus and then subjected to reduced pressure over a steam bath to remove any water. Recovery of the succinate was 49 g. (80% yield), mp. 118 - 120 $^{\circ}$ (lit. (36), 119 - 121 $^{\circ}$).

Preparation of (-)- α -Naphthylphenylcarbinol. Using the technique of Smetana (36) 15 g. dry brucine (Fisher Sci. Co. - Eimer and Amend Pure Crystals) in 20 ml. hot ethyl acetate were combined with a solution of 12.8 g. α -naphthylphenyl-

carbonyl hydrogen succinate in 40 ml. ethyl acetate. The solution was refluxed for two hours after which the heat was turned off but stirring was continued overnight. Next morning the solution was transferred to an Erlenmeyer flask and left in the refrigerator over the weekend. A crop of crystals had formed, 40 g., mp. $100 - 120^{\circ}$.

The 40 g. of crude brucine salt were combined with 40 ml. ethyl acetate and the mixture refluxed for two hours. The hot solution was filtered and allowed to stand at room temperature. The 30 g. of brucine salt which crystallized out was combined with 25 ml. ethyl acetate and the mixture refluxed for two hours. Again the hot solution was filtered and let stand at room temperature. A total of 20 g. of brucine salt crystallized out, mp. $114 - 118^{\circ}$. This 20 g. of brucine salt was combined with 40 ml. ethyl acetate and the mixture was refluxed. However, not all of the salt went into solution. The hot solution was filtered to remove the material which would not dissolve and the filtrate was allowed to stand at 55° until crystals had formed and then allowed to cool to room temperature in an attempt to have a slow rate of crystallization. From the filtrate a total of 12.24 g. of the brucine salt, m.p. $114 - 118^{\circ}$, crystallized.

Under a nitrogen atmosphere, in a 200 ml., round-bottom flask containing a Teflon stirring bar, a reflux condenser, and an equilibrating addition funnel were placed 2.42 g. lithium aluminum hydride and 52 ml. dry ether. A solution of

12.24 g. of the brucine salt in 42 ml. dry benzene was added dropwise over a half-hour period and stirring was continued for one hour at room temperature after the addition was complete. The mixture was then cooled in an ice-bath and water was added slowly until the inorganic salts coagulated. Then the solution was filtered and the salts were washed three times with small portions of ether. The organic filtrate was washed twice with 20 ml. portions of 2% HCl, once with water, and then dried over magnesium sulfate. After filtration the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column (20 g. mesh 70 - 325) using benzene as the eluent. The solvent was removed under reduced pressure and residual oil pumped on under vacuum over night. The residue had a rotation of $[\alpha]_{579} = (-)33.8^{\circ}$. Carbon tetrachloride, 5 ml., was added to the oil and the solution was kept in the refrigerator until the alcohol crystallized out. There was obtained 2.54 g. (53% yield from 12.24 g. brucine salt) of optically active α -naphthylphenylcarbinol, mp. $73 - 74^{\circ}$ $[\alpha]_{579} = (-)38.2^{\circ}$ (95% ethanol) (lit. (36), mp. $74 - 75^{\circ}$ $[\alpha]_D = (-)35.8$ 95% ethanol).

Preparation of (+)- α -Naphthylphenylcarbiny1 S-Methyl Thiocarbonate. Optically active (-)- α -naphthylphenylcarbinol, 2.5 g., was dissolved in 11 ml. dry benzene and 1.8 ml. dry pyridine was added. A solution of 2.2 ml. methylchlorothiol-

formate in 11 ml. dry benzene was added dropwise. The solution turned yellow immediately. The reaction was left stirring at room temperature for six hours. Then 20 ml. of ether was added and the solution was washed twice with water, once with saturated sodium chloride and then dried over anhydrous magnesium sulfate for five hours. The solvent was removed under reduced pressure leaving a light pink oil. The oil was chromatographed on a silica gel column (15 g.) using benzene as the eluent. Evaporation of the eluting solvent gave crystals melting $91 - 92^{\circ}$. Upon slow recrystallization from benzene/hexane one obtained first 0.4 g. of material having zero rotation; then another 0.2 g., also optically inactive, crystallized out. At this point the solvent was removed from the filtrate under reduced pressure and the residue was allowed to stand for four days in the refrigerator until crystals had formed. This material, 0.4 g., mp. $75 - 79^{\circ}$, was optically active, $[\alpha]_{579} = (+)17.3$, $[\alpha]_{404} = (+)28.6$, $[\alpha]_{366} = (+)20.0$, $[\alpha]_{334} = (-)24.4$ (benzonitrile). An infrared spectrum of the material was identical in all respects with the spectrum of sample of optically inactive thiocarbonate. A difference between the melting point of the racemic and partially resolved thiocarbonate has also been observed before by Kice et al. (20) in the case of an aralkyl thiocarbonate.

Purification of Benzonitrile. This was purified by the procedure previously described by Kice and co-workers (27).

Reagent grade benzonitrile was steam distilled and the distillate was extracted with ether. After washing with 5% sodium carbonate solution, the ethereal solution was dried over magnesium sulfate. The ether was removed and the benzonitrile was fractionally distilled under reduced pressure. The purified benzonitrile was then heated at 160° for 24 hours while a slow stream of nitrogen was bubbled through the solution. This removes certain volatile impurities that otherwise interfere with following the decomposition of the thiocarbonates by the infrared method. After this heating procedure the benzonitrile was again fractionally distilled bp. $75^{\circ}/10$ mm.

Kinetics Studies of the Thermal Decomposition of the Thiocarbonate. The apparatus used for the kinetic studies is shown in Figure 6. A solution of the desired amount of thiocarbonate in 10 ml. benzonitrile was placed in the reaction vessel. After nitrogen was bubbled through this solution for twenty minutes, the reaction vessel was immersed in a constant temperature bath at 135° . A very slow stream of nitrogen was bubbled through the solution during the entire reaction.

After the reaction vessel had been immersed in the constant temperature bath for five minutes, a t_0 sample was withdrawn. Other samples were withdrawn at later desired times. The sample containers were kept at ice temperature while

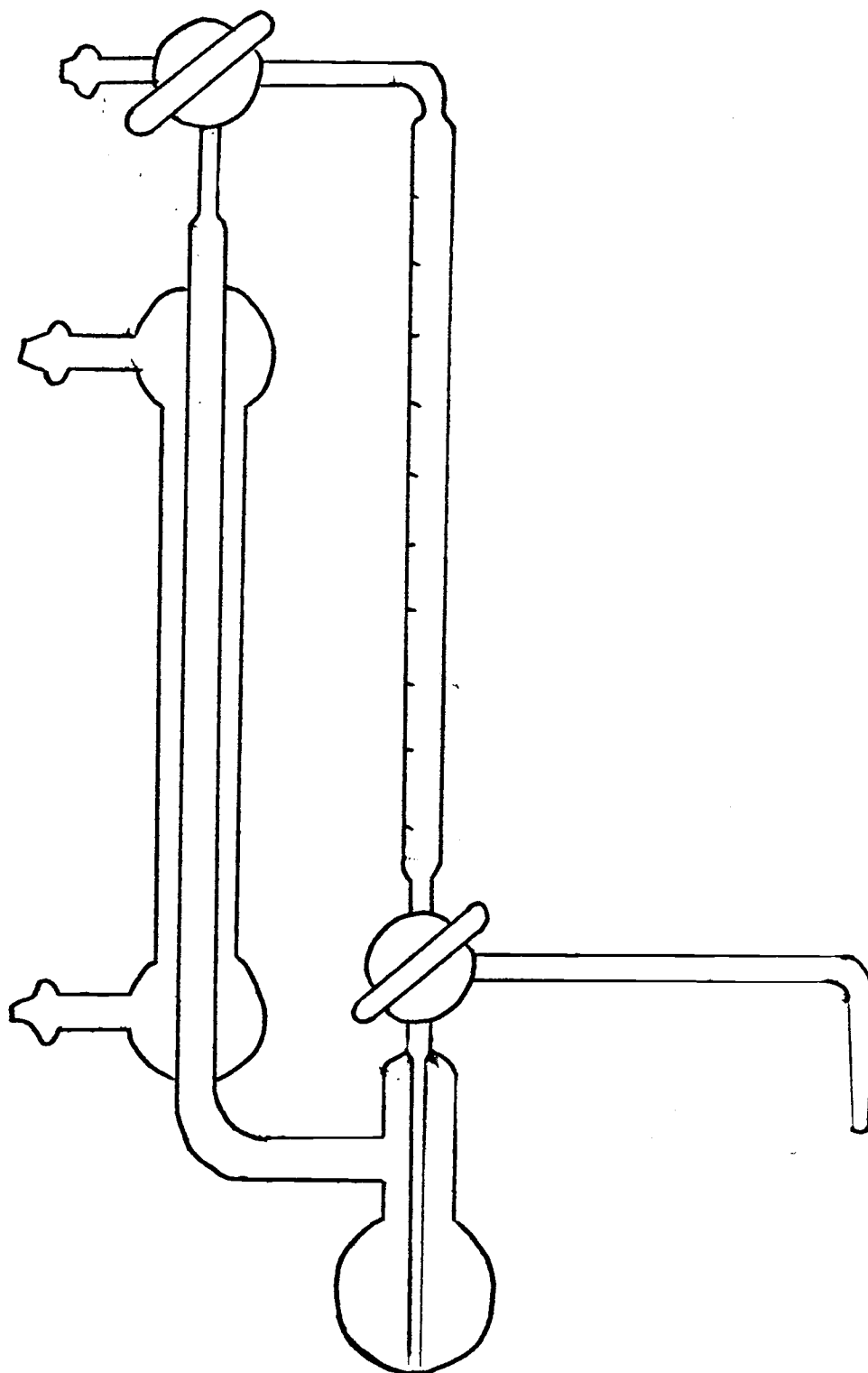


FIGURE 6. Apparatus used for kinetic studies.

being filled, in order to assist in quenching the reaction and the samples were stored in the refrigerator until all samples for a given run had been collected. They were then analyzed for thiocarbonate content by an infrared method. The infrared spectra were run in 0.1 mm. thick NaCl cells on a Perkin-Elmer Model 21 Double Beam Infrared Spectrophotometer. The absorption peak of the carbonyl group in the thiocarbonates occurs at approximately 1710 cm^{-1} and the spectra were run over the region $1800 - 1600\text{ cm}^{-1}$. Kice and co-workers (20) had previously shown that the intensity of the thiocarbonate ester carbonyl band followed Beer's Law and that a plot of optical density versus concentration of thiocarbonates was linear. Thus, the rate constants were obtained from a plot of the logarithm of optical density against time.

Kinetic Studies of the Equilibration of Alkyl and Acyl Oxygens in the Decomposition of Thiocarbonates. The same apparatus described in the kinetic studies of the thermal decomposition of the thiocarbonates was used for this study. A solution of the desired amount of thiocarbonate and 10 ml. benzonitrile was placed in the reaction vessel and deaerated as in the other study.

After removal of a sample at the desired time, the solvent was removed under reduced pressure at temperatures below 40° , and the residue was dissolved in ether. The ether

solution was added to a mixture of lithium aluminum hydride and ether, and the resulting mixture was allowed to stir overnight. A small amount of water was then added dropwise to coagulate the salts. The ether solution was filtered into a separatory funnel and was then washed once with water and dried over magnesium sulfate. The ether was removed under reduced pressure and the residue allowed to crystallize. In some cases, notably the more equilibrated samples, thick layer chromatograph on silica gel was necessary to separate the sulfide decomposition product from the alcohol. The crystals were then sublimed at $<10^{-4}$ mm. H_g to obtain samples of the alcohol suitable for analysis.

Oxygen-18 content of the samples of *p*-methylbenzhydryl and α -naphthylphenylcarbinol recovered in this way were then determined from mass spectra taken on a Hitachi RMU-6 Mass Spectrometer. Each sample was scanned several times at different intensities. The ratio of $\frac{M+1}{M+2}$, where M is the main molecular peak, was obtained by measuring peak heights. The top of the peaks were taken as $\frac{1}{2}$ the pen vibrational distance at peak maximum. Using the equations 42 and 43 the abundance of O¹⁸ was determined.

$$\frac{M+1}{M} = \frac{(nC^{13} \times P^{C^{13}})}{100} 100 + \frac{(nO^{17} \times P^{O^{17}})}{100} 100 + \frac{n(H^2 \times P^{H^2})}{100} 100 \quad (42)$$

$$\begin{aligned}
 \frac{M+2}{M} = & \left[\frac{nC^{13} \times (n-1)C^{13} \times (P^{C^{13}})^2}{2(100)^2} \right] 100 + \\
 & \left[\frac{(nC^{13} \times nH^2 \times P^{C^{13}} \times P^{H^2})}{2(100)^2} \right] 100 + \\
 & \left[\frac{(nC^{13} \times O^{17} \times P^{C^{13}} \times P^{O^{17}})}{2(100)^2} \right] 100 + P^{O^{18}}
 \end{aligned} \quad (43)$$

Taking the natural abundance of the isotopes to be as follows: $P^{C^{13}} = 1.112$; $P^{O^{17}} = 0.037$; $P^{H^2} = 0.015$, the percentages of O^{18} in *p*-methylbenzhydrol and α -naphthylphenylphenylcarbinol are given by equations 44 and 45 respectively.

$$P^{O^{18}} = \frac{19.144}{\frac{M+1}{M+2}} - 1.704 \quad (44)$$

$$P^{O^{18}} = \frac{15.808}{\frac{M+1}{M+2}} - 1.144 \quad (45)$$

The fraction of label on the alkyl oxygen X was calculated using equation 46.

$$X = \frac{P - P_{\infty}}{P_0 - P_{\infty}} \quad (46)$$

where P is the percent oxygen-18 in the alcohol sample, and P_0 is the percent of oxygen-18 at the alkyl oxygen at zero time. P_{∞} in the equation is given by

$$P_{\infty} = \frac{P_0 + 0.204}{2} \quad (47)$$

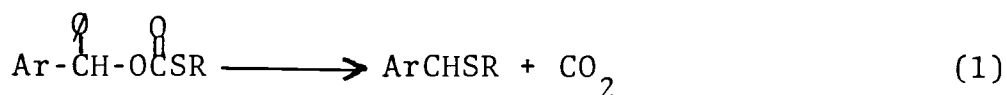
where equation 47 takes into consideration 0.204 natural abundance O^{18} in the acyl oxygen of the starting thiocarbonate. A plot of $\log X$ against time yielded the rate of equilibration, k_{eq} .

Kinetic Studies of the Loss of Optical Activity in the Decomposition of Thiocarbonates. The same apparatus was employed as described in the kinetic studies of the thermal decomposition of the thiocarbonates. A solution of the desired amount of thiocarbonate and 30 ml. benzonitrile was placed in the reaction vessel. To measure the rotation of samples they were placed in a 5 ml. water-jacketed polarimeter cell and rotations were measured while the temperature of the solution was held constant at 25° . Rotations were measured using a Perkin-Elmer Model 141 Spectropolarimeter. The rotations were measured at a wave length where the maximum possible rotation could be achieved. A plot $\log \alpha$ time was linear; its slope is equal to k_{α} .

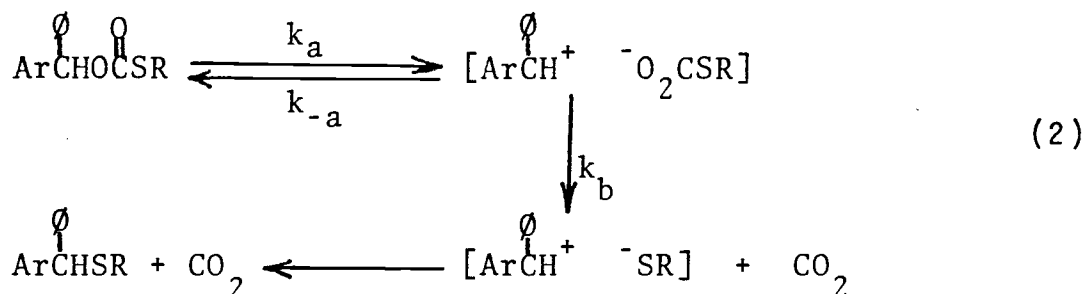
ION PAIR RETURN PHENOMENA IN THE THERMAL DECOMPOSITION
OF α -PHENYLETHYL CHLOROCARBONATE

INTRODUCTION

The thermal decomposition of thiocarbonates (equation 1) has been shown to proceed via an ion pair mechanism (20).

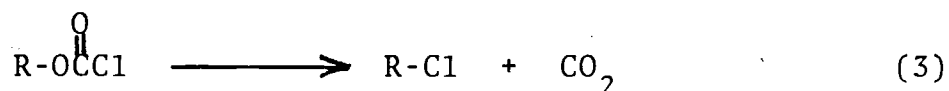


Subsequent studies (22, 27) have shown (equation 2) that alkyl-oxygen bond breaking is followed by rate determining cleavage of the carbonyl-sulfur bond ($k_{-a} > k_b$). This is

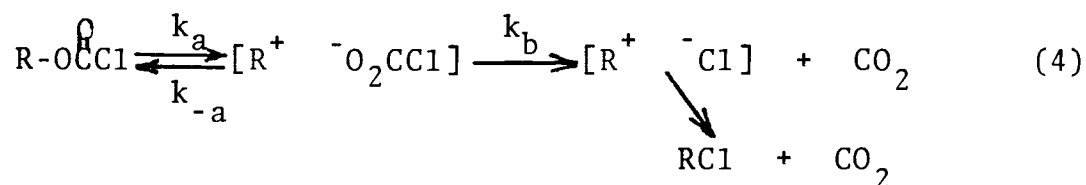


shown by the fact that optically active *p*-chlorobenzhydryl, *p*-methylbenzhydryl, and α -naphthylphenylcarbonyl thiocarbonates racemize faster than they lose carbon dioxide. It has also been shown that the alkyl oxygen-18 derivatives of these thiocarbonates equilibrate their alkyl and acyl oxygens considerably faster than they decompose. This can only be accounted for by a mechanism that allows ion pair return to reactants (step k_{-a}) to occur faster than loss of carbon dioxide from the anion RSCO_2^- (step k_b).

The unimolecular decomposition of chlorocarbonates (3) is one of the classic examples of an S_Ni reaction (45, 32). It is also known to involve ion pair intermediates (45, 32) and is clearly a reaction which is formally similar to the



thiocarbonate decomposition. Equation 4 shows a mechanism for the decomposition of the chlorocarbonate similar to that for the thiocarbonates in equation 2. However, since Cl^-



is presumably much more stable as an anion than any of the RS^- ions derived from the thiocarbonates it is entirely possible that in the chlorocarbonate decomposition k_b will be enough faster than k_{-a} that there will be no ion pair return to reactants.

The purpose of this study was to determine whether there was indeed any ion pair return to reactants from the ion pair $[R^+ \quad ^-O_2CCl]$. This was done by preparing α -phenylethyl chlorocarbonate labeled at the alkyl oxygen with O^{18} , partially decomposing samples of this chlorocarbonate, recovering the chlorocarbonate remaining after partial decomposition, and then determining whether or not there had been any equilibra-

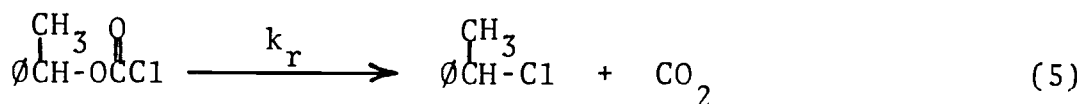
tion of oxygen-18 between the alkyl and acyl oxygens in this recovered chlorocarbonate. If there is any return of $[R^+ \text{ } ^-O_2CCl]$ to chlorocarbonate, this should lead to equilibration of the oxygen-18 label. On the other hand, if $k_b \gg k_{-a}$ so that there is no return, the recovered chlorocarbonate will have undergone no equilibration of oxygen-18 between the alkyl and acyl oxygens.

RESULTS

Preparation of the α -Phenylethyl Chlorocarbonate. The alcohol was reacted with sodium hydride to form the alkoxide. The alkoxide was used immediately to make the chlorocarbonate by dropwise addition of the alkoxide to phosgene at -60 to -78° C. The resulting product was an oil at 0° which consisted of nearly equal amounts of α -phenylethyl chlorocarbonate and α -phenylethyl chloride (45). The oil was stored in a freezer at -20° .

The O^{18} -labeled alcohol was prepared by exchanging O^{18} enriched water (1.59% enrichment) with acetophenone and then reducing to the alcohol. This alcohol was used as above to make the alkyl O^{18} -labeled α -phenylethyl chlorocarbonate.

Determination of the Amount of Equilibration of Alkyl and Acyl Oxygens During Thermal Decomposition. Wiberg and Shryne (45) had already studied the kinetics of the thermal decomposition of α -phenylethyl chlorocarbonate in several solvents. Determining the rate of decomposition, k_r (see equation 5) by the method of carbon dioxide evolution which has been used before by Kice and co-workers (20), it was found that k_r at 70° in dioxane was $1.84 \times 10^{-3} \text{ sec}^{-1}$, in



good agreement with the value of $k_r = 2.03 \times 10^{-3} \text{ sec}^{-1}$ at 70° in this same solvent measured by Wiberg and Shryne (45)

using a volumetric method for determining the amount of carbon dioxide liberated.

The alkyl- O^{18} -labeled α -phenylethyl chlorocarbonate was partially decomposed by heating in dioxane solution at 60° . The undecomposed chlorocarbonate was then reduced with lithium aluminum hydride and the oxygen-18 content of the α -phenylethyl alcohol formed by the reduction of the chlorocarbonate was determined and compared with that of the alcohol obtained by reduction of the starting chlorocarbonate. The results are shown in Table 1.

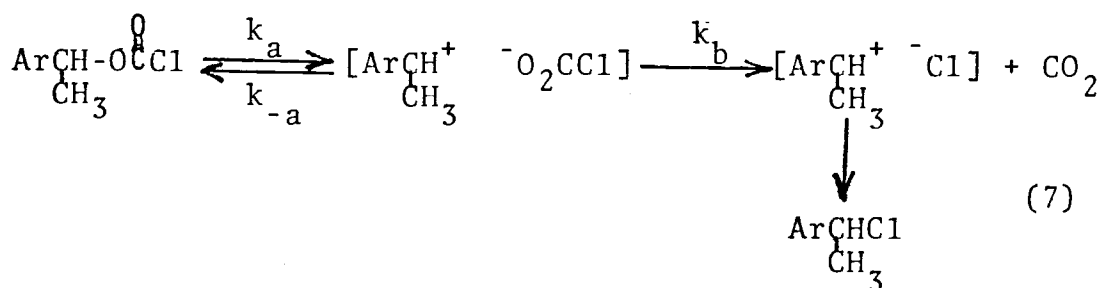
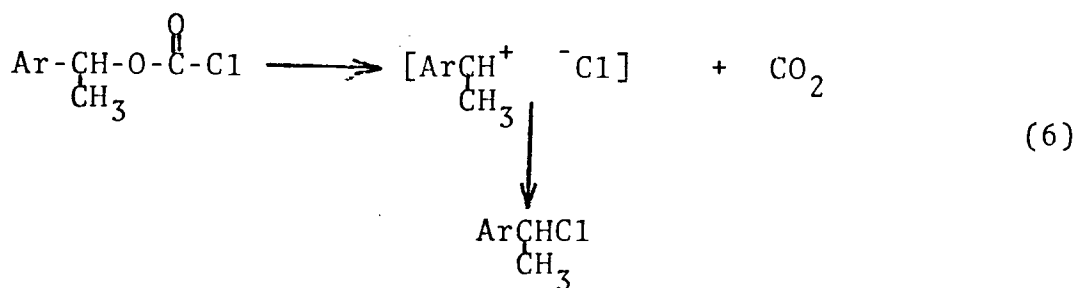
TABLE 1. Determination of the Equilibration of Alkyl- O^{18} During Decomposition at 60° in Dioxane.

| Time (min) | % O^{18} |
|------------|----------------|
| 0 | $1.43 \pm .03$ |
| 15 | $1.46 \pm .03$ |
| 20 | $1.46 \pm .03$ |

Even though the samples were removed after times corresponding to up to 60% decomposition of the original chlorocarbonate into α -phenylethyl chloride and CO_2 , one sees that there is no evidence of any equilibration of the oxygen-18 label between the alkyl and acyl oxygens of the undecomposed chlorocarbonate recovered after this length of time.

DISCUSSION

A detailed discussion of ion pairs was given in the thiocarbonate portion of this work. The lack of O^{18} equilibration accompanying the decomposition of α -phenylethyl chlorocarbonate rules out any return to chlorocarbonate from the ion pair involved in the chlorocarbonate decomposition. Therefore, the breaking of an O-C bond is either concerted with the C-Cl bond breaking (equation 6) or the initial anion formed, ^-O_2CCl , loses CO_2 (step k_b , equation 7) so much faster than recombination of R^+ and ^-O_2CCl (step k_{-a} , equation 7) that return is unable to compete with cleavage of ^-O_2CCl to CO_2 and Cl^- .



The similarities in the decomposition of thiocarbonates and chlorocarbonates were discussed earlier. Mechanistically the difference between the two is that the thiocarbonates

undergo return to starting ester from ion pair, k_{-a} , faster than they undergo loss of CO_2 , k_b , (equation 2), whereas chlorocarbonates show no ion pair return. Thus if equation 7 is the mechanism k_b is much faster than k_{-a} .

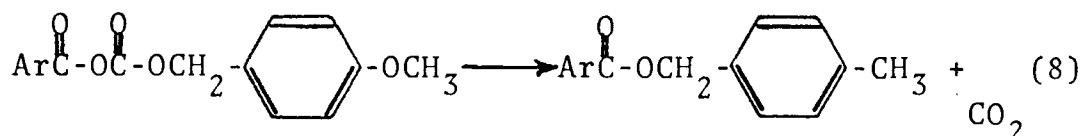
Comparison of the decomposition of *p*-chlorobenzhydryl S-methyl and *p*-chlorobenzhydryl S-phenyl thiocarbonates has shown (27) that going from the S-methyl to the S-phenyl compound leads to a substantial increase in the percentage of $[\text{R}^+ \text{ } ^-\text{O}_2\text{CSR}^1]$ ion pairs which undergo loss of CO_2 rather than return. Presumably the increase, which is from 11% to 23%, occurs because, OS^- being a significantly more stable anion than CH_3S^- , the rate of loss of CO_2 , k_b , is faster for the ion pair with the OSCO_2^- anion than for the one with the $\text{CH}_3\text{SCO}_2^-$ ion.

Since HCl is a much stronger acid than OSH , Cl^- is presumably a much more stable anion than OS^- . That being the case it would not be at all surprising if k_b for ClCO_2^- became so much faster than k_{-a} that no return should be observed in the chlorocarbonate case.

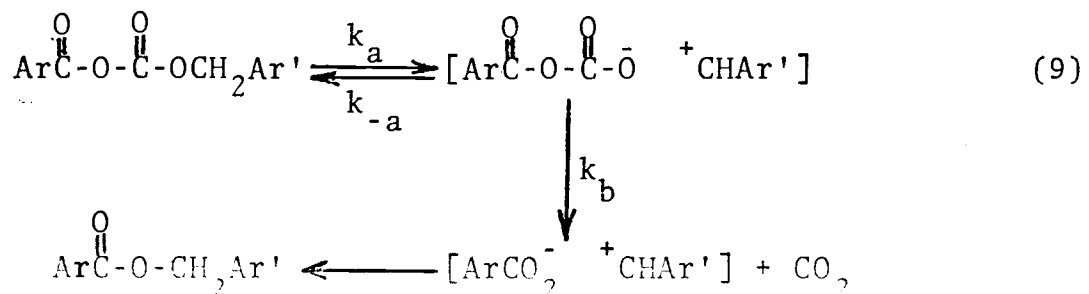
Presumably if one were to have as Y in YCO_2^- , a group which as Y^- would have a suitable intermediate stability between that of OS^- and Cl^- one ought to be able to achieve a situation where $k_b = k_{-a}$. One group that one might think would be of about the proper stability is $\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}^-$. Such compounds, $\text{Ar}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OR}$, have been studied by Tarbell and

co-workers (40).

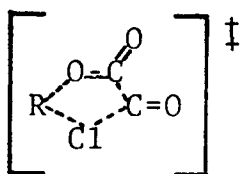
p-Methoxybenzyl carbonic anhydride (2) decomposed to form p-methoxybenzyl ester and CO_2 (equation 8). Experiments with O^{18} at the ester oxygen attached to the



p-methoxybenzyl group showed that the decomposition took place mainly via alkyl oxygen cleavage. Partial decomposition experiments showed no scrambling of the O^{18} label in the undecomposed carbonic anhydride. A change in solvents from O-dichlorobenzene to dimethylformamide increased the rate by 40 fold, which was reflected in a change in energy of activation from 18.7 ± 0.6 kcal/mole to 15.0 ± 0.3 kcal/mole. Since the rate of decomposition shows a large increase with an increase in the polarity of the solvent, an ion pair mechanism is presumably involved. Since O^{18} did not scramble this indicates that either one has a concerted cleavage or else that in equation 9 indicates k_b , the rate of loss of CO_2 , is greater than k_{-a} return to covalent starting anhydride.

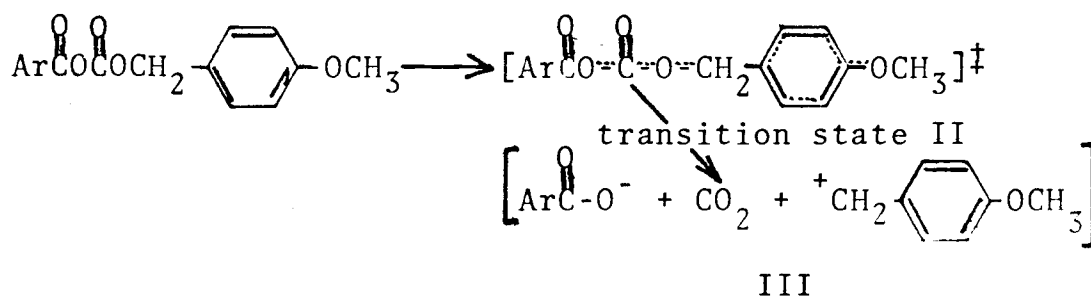


Though a compound with $k_{-a} = k_b$ has thus not yet been found, examples of $k_b \gg k_{-a}$ do present the problem as already suggested, of distinguishing between a mechanism of two independent bond cleavages where k_b is so much greater than k_{-a} that no return is detectable and a mechanism where both bonds break in a concerted fashion. Concerted mechanisms of the type proposed by Rhoads and Michel (34) for chloroglyoxalates where there is a cyclic concerted process, I, are known to show little enhancement in more polar solvents because the transition state is less polar than in the



I

highly ionic reactions we are now discussing. Tarbell has proposed a mechanism for the decomposition of *p*-methoxybenzyl carbonic anhydride where both $\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$ and $\text{O}-\text{CH}_2$ bonds are broken in a single step with the formation of ion pair III and a molecule of CO_2 . Tarbell favored a mechanism



involving transition state II because of the large negative entropy of activation ($\Delta S^\ddagger = -28.7 \pm 0.8$ in DMF) which means that there is either a high degree of solvation of the transition state, and/or a loss of considerable rotational freedom. If the concerted process proposed is correct for the carbonic anhydrides then a similar concerted process is probably also correct for the chlorocarbonates.

However, since it is also quite possible that ΔS^\ddagger would be large and negative for a mechanism of the type shown in equation 9, one can not really be sure whether Tarbell's case actually represents a concerted cleavage of both bonds in a single step or a case of equation 9 where $k_b > k_{-a}$. Clearly more experimentation designed to obtain reliable estimates of the type of ΔS^\ddagger expected from each of these two types of mechanism is needed, although it is also obvious that this may not be easy to obtain.

EXPERIMENTAL

Preparation of α -Methylbenzyl Alcohol. Acetophenone (81 ml., 0.7 moles) was dissolved in 200 ml. anhydrous ether. This was added dropwise with stirring to a three-necked flask fitted with a reflux condenser and containing 15 g. (0.4 moles) of lithium aluminum hydride and 200 ml. of anhydrous ether. The mixture was stirred overnight at room temperature. It was then cooled in an ice bath and saturated ammonium chloride solution was added very carefully. After no further reaction was observed, 300 ml. of 10% ammonium chloride solution was added to break up the emulsion. The organic layer was washed twice with water, once with saturated sodium chloride solution, and then dried over "Drierite." The ether was removed under reduced pressure. The residue was distilled at 91° (15 mm. Hg) to yield 75 g. (92% yield) α -methylbenzyl alcohol.

Preparation of α -Phenylethyl Chlorocarbonates. To a dry, 100 ml., three-necked flask equipped with a nitrogen inlet tube, a drying tube, addition funnel, and a stirring bar was added (0.04 moles) 1 g. of sodium hydride, which had been washed well with hexane to remove the packing oil, and 60 ml. of anhydrous ether. After dry nitrogen had been passed through the solution for ten minutes to flush out any oxygen, 0.04 moles of the α -methylbenzyl alcohol was added

and the flow of nitrogen continued for ten minutes. The solution was stirred at room temperature overnight. The ether was then removed on a steam-bath leaving a dry residue to which was added 60 ml. of pentane, giving a slurry.

Phosgene (10 ml.) was measured in a gas trap at dry-ice acetone bath temperatures and then distilled into 90 ml. of pentane in a 200 ml. three-necked flask fitted with stirrer and an addition funnel. The flask was cooled to -60° to -78° and the slurry of the alkoxide in pentane was added over a one-half hour period. The mixture was stirred for an additional half-hour and then allowed to warm to 0° . After cooling -60° the solution was quickly filtered away from the sodium chloride present in the mixture. The solvent was then removed under reduced pressure at 0° to give a few milliliters of oil which were placed in the freezer at -20° for storage. Kinetics of decomposition verified the similarity of the product to that reported by Wiberg and Shryne (45).

Preparation of O^{18} -Labeled α -Methylbenzyl Alcohol.

Acetophenone, 40 ml., was added to a solution of 500 ml. dioxane, 25 mls. water (1.59% O^{18} enrichment) and 0.1 ml. concentrated sulfuric acid. This was refluxed for 24 hours and then the solvent was distilled off. The remaining residue was added to 100 ml. of tetrahydrofuran. This solution was added dropwise to 7 g. (0.019 moles) lithium aluminum

hydride in 50 ml. tetrahydrofuran. The mixture was refluxed overnight. After cooling with an ice-bath the lithium aluminum hydride was destroyed with saturated ammonium chloride, and the organic layer was washed with water. The solution was dried with "Drierite" and then the solvent was removed under reduced pressure. The residue was distilled at 97° (about 15 mm. Hg) to give 30 g. (45% yield) α -methylbenzylalcohol- O^{18} (1.46% O^{18}).

Preparation of α -Phenylethyl Chlorocarbonate Labeled With O^{18} at the Alkyl Oxygen. The O^{18} -labeled alcohol was used in place of the unlabeled alcohol in the preparation of α -phenylethyl chlorocarbonate given earlier.

Kinetic Study of the Decomposition of α -Phenylethyl Chlorocarbonate. The carbon dioxide evolution method of determining the rate of decomposition was employed. The apparatus is shown in Figure 1. In this apparatus evolved CO_2 was carried by CO_2 -free nitrogen through a 50:50 pyridine ethanol trap and into an ethanol-dioxane-benzylamine solution (3:3:1) where it was determined by direct titration with a 0.102 N solution of sodium methoxide in methanol-benzene. Thymol blue (0.2% in dioxane) was used as an indicator. Ascarite tubes were placed before the reaction vessel and after the titration vessel to prevent any contaminating CO_2 from entering the system. A steady stream of nitrogen was passed through the system in order to get all

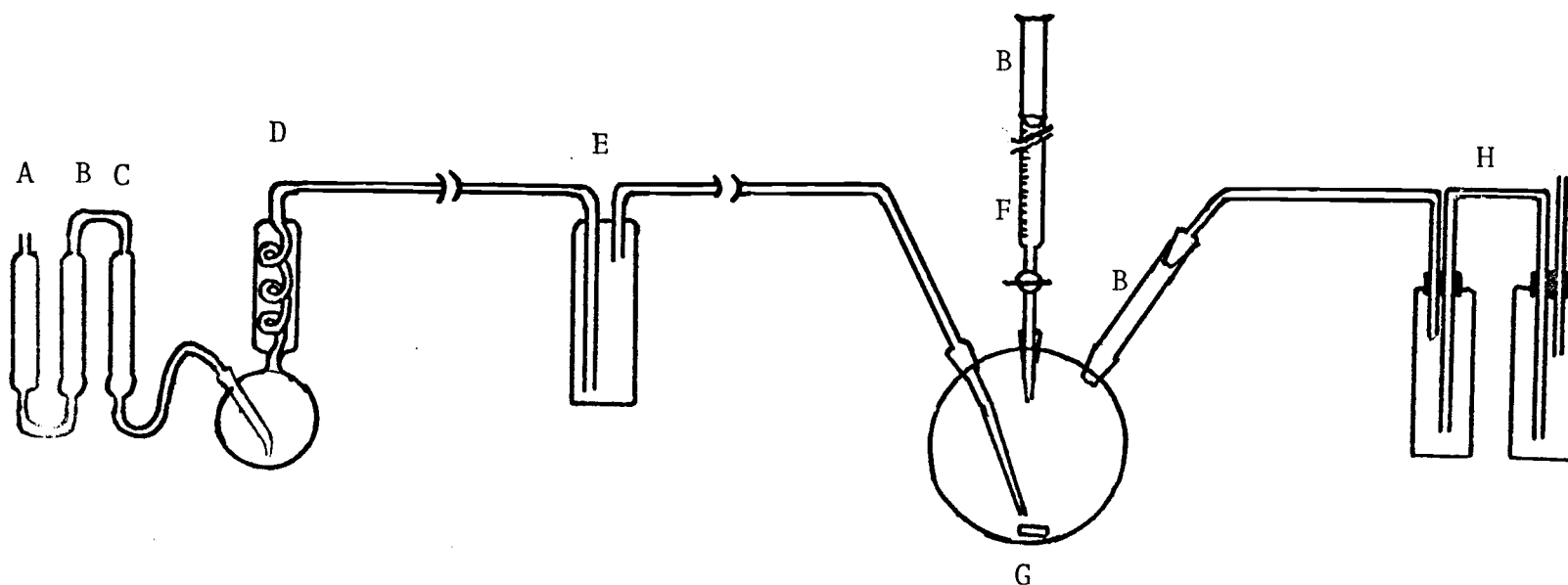


FIGURE 1: Carbon Dioxide Evolution Apparatus

- A. Drierite Tube
- B. Ascarite Tube
- C. Anhydron Tube
- D. Reaction Vessel
- E. Acid Trap
- F. Burette
- G. CO₂ Solution Trap
- H. Oil Pressure Trap

the evolved CO_2 quickly into the ethanol-dioxane-benzylamine solution.

In each run 0.2 ml. of α -phenethyl chlorocarbonate was placed in the reaction vessel, dissolved in dioxane, and then the solution was submerged into a 70° bath. The CO_2 trapping solution was slightly over titrated and t_0 was taken to be the first time the indicator changed color. Aliquots of base were added and the time of color change noted for each.

Investigation of the Possibility of Equilibration of Alkyl and Acyl Oxygens During the Thermal Decomposition of α -Phenethyl Chlorocarbonate. The same type of apparatus was used as described in the thermal decomposition of the thio-carbonates (Figure 6, page 55). Individual samples of about 3 μ moles of chlorocarbonate for each sample were run.

The samples were left in the 60° bath for the desired length of time and then removed and cooled. The solvent was removed at low temperature at 1 - 2 mm pressure, and the residue was dissolved in ether. The ether solution was added to lithium aluminum hydride in ether and left to stir overnight. After cooling in an ice-bath, saturated ammonium chloride solution was added. The ether layer was washed twice with water, once with saturated sodium chloride solution, and then dried over magnesium sulfate. The ether was removed and the alcohol was purified on a preparative gas chromatograph.

The α -methylbenzyl alcohol sample was pyrolyzed in Doering's (7) modified oxygen analysis train as shown in Figure 2. The flow of prepurified nitrogen was regulated by the needle valve A and measured with a flow meter (D). The nitrogen was purified further by passing it through a copper-copper oxide scrubber at 500° (B) and any water or carbon dioxide was absorbed in an ascarite-anhydride trap (C). The sample (15 - 20 mg.) was placed in a platinum boat and inserted into the pyrolysis tube (E) three inches from the furnace (F). After back-purging for fifteen minutes with a flow rate of 20 ml./min., the flow was reversed and the rate reduced to 10 ml./min. The tube behind the sample was slowly heated with a Bunsen burner. The sample was heated to red heat for five minutes and the flame was then moved forward at the rate of two inches per minute. After passing through the platinized carbon at 900° , the oxygen-18 labeled carbon monoxide was cleaned in an ascarite-anhydride trap (G) and oxidized to carbon dioxide by iodine pentoxide at 125° in oven (H). The other oxidation products were removed in an acetone-Dry Ice trap (I). The carbon-dioxide-oxygen O^{18} sample was frozen out in trap (J) with liquid nitrogen. Trap (J) was connected to another ascarite-anhydride trap (K) to prevent contamination by atmospheric carbon dioxide. Trap (J) was disconnected from the pyrolysis train and evacuated by use of a modified take-off

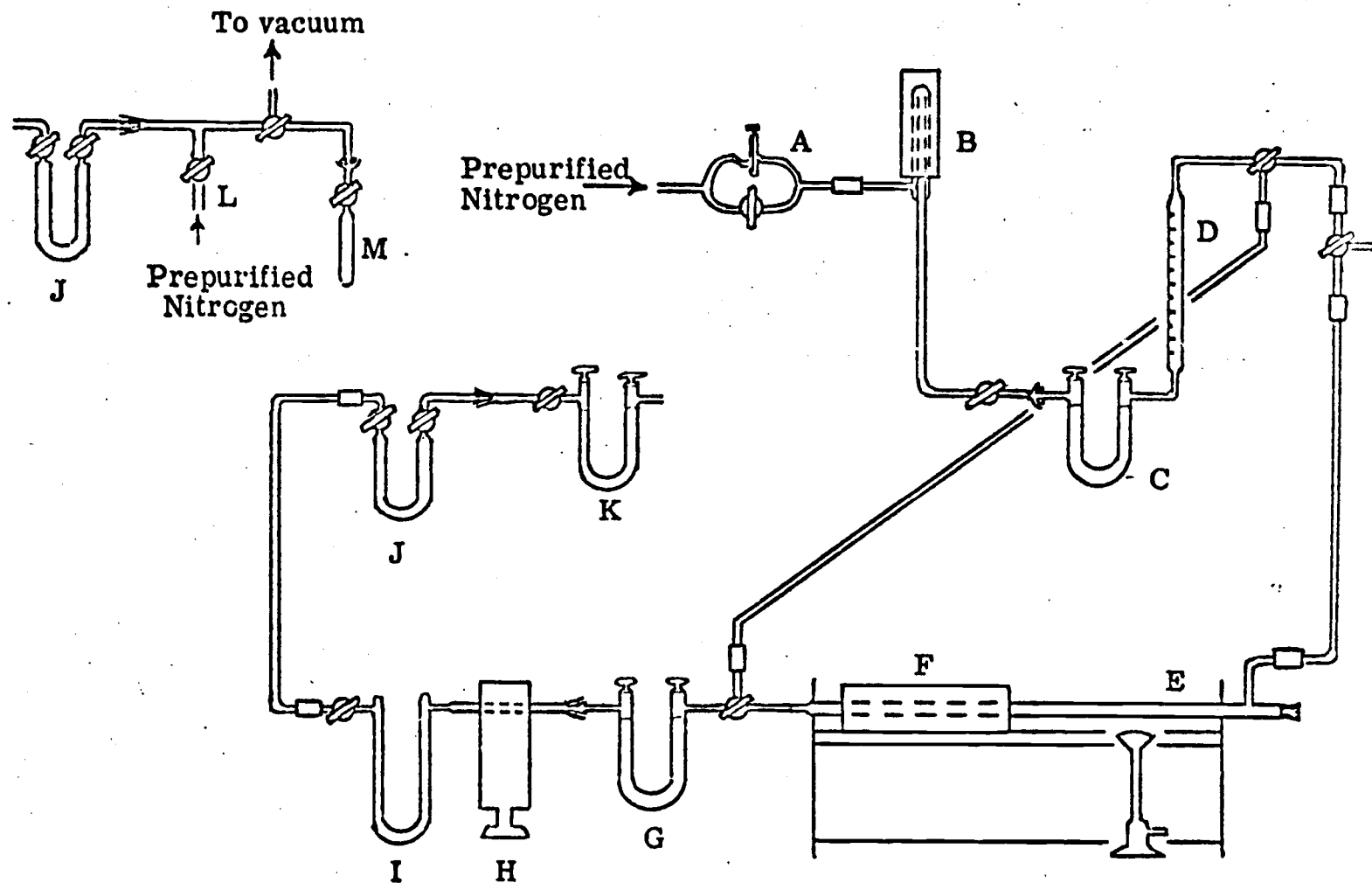


FIGURE 2. Oxygen Analysis Train.

system (L). The sample was allowed to warm up and then condensed in tube (M) with liquid nitrogen. Tube (M) was attached to the inlet system of a mass spectrometer and the desired amount of carbon dioxide removed.

It was necessary to pyrolyze three or four portions (15 - 20 mg.) of the sample before any degree of precision was obtained. Usually six portions were pyrolyzed, one following the other by 20 to 30 minutes, and only the last three portions of sample were collected for analysis. The samples of carbon dioxide enriched in oxygen-18 were analyzed on a CEC residual gas analyzer. The percentage of oxygen- O^{18} (P) in the sample was calculated by use of Doering's equation (10).

$$P = \frac{(0.00408)(R) - 0.00204}{0.9959 + (0.00408)R} \times 100 \quad (10)$$

where

$$R = \frac{I_{46}/I_{44}}{I_{46}^0/I_{44}^0}$$

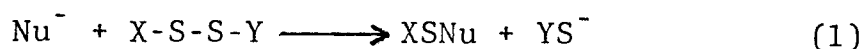
I^0 represents the intensity of the respective mass peaks of a standard carbon dioxide sample frozen from air and I the intensity of the sample peaks.

EXCHANGE OF AROMATIC SULFINIC ACIDS WITH AROMATIC THIOLSULFONATES

INTRODUCTION

The sulfur-sulfur bond, because of the frequency of occurrence of disulfide bridges in proteins and the use of S-S bonds for structural control of many proteins and enzymes, is of great importance biochemically. A greater knowledge of the properties of sulfur-sulfur bonds and the chemistry of reactions leading to their cleavage is therefore potentially very useful information.

A common way of breaking the S-S bond is by nucleophilic cleavage (equation 1). Nucleophilic attack may occur at sulfur in different oxidation states, i.e. the sulfenyl (-S-), sulfinyl ($-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-$), or sulfonyl ($-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-$), oxida-



tion states. Attack by most nucleophiles is faster at sulfenyl-sulfur as compared to sulfinyl-sulfur and at sulfinyl-sulfur as compared to sulfonyl-sulfur. One of the questions of interest about nucleophilic substitution at sulfur is how the relative reactivity of a series of nucleophiles varies with a change in the oxidation state of the sulfur being attacked by the nucleophile. An extensive study of this matter has been carried out by Kice and co-workers (19) using reactions of nucleophiles with a series

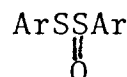
of different compounds possessing S-S bonds. All of these studies have been carried out in the same solvent, 60% aqueous dioxane. To study nucleophilic reactivity toward sulfonyl-sulfur they have used the reaction of nucleophiles with aryl α -disulfones I; for sulfinyl-sulfur they studied the rate of reaction of the same nucleophiles with sulfinyl sulfones II; to investigate reactivity toward sulfenyl-sulfur they used acid-catalyzed reactions of nucleophiles with thiolsulfinates III.



I



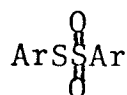
II



III

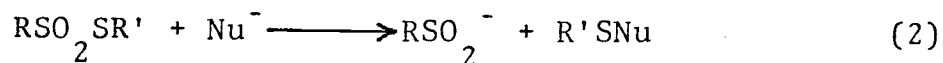
Kice and Kasperek (24) studied the nucleophile-catalyzed hydrolysis of α -disulfones. For the series of nucleophiles, Cl^- , Br^- , F^- and AcO^- they found that the order of reactivity toward sulfonyl-sulfur was $\text{F}^- \gg \text{AcO}^- \gg \text{Cl}^- \approx \text{Br}^-$. This is in marked contrast to the order of reactivity of the same nucleophiles toward sulfinyl-sulfur which was investigated by Kice and Guaraldi (23) by studying the nucleophile-catalyzed hydrolysis of sulfinyl sulfones. The order of reactivity toward sulfinyl-sulfur which they found is $\text{I}^- > \text{SCN}^- > \text{Br}^- > \text{Cl}^- \approx \text{AcO}^- > \text{F}^-$. Data on relative nucleophile reactivity toward sulfenyl-sulfur were obtained by studying the acid and nucleophile-catalyzed racemization of the optically active

thiolsulfinate. The order of reactivity of various nucleophiles at sulfenyl-sulfur was $I^- > SCN^- > Br^- > Cl^-$, which is the same general order as for sulfinyl-sulfur. A major difference in the comparison of these molecules is that in the case of the sulfenyl-sulfur the leaving group was $-\overset{+OH}{S}-Ar$ whereas $-\overset{O}{\underset{O}{S}}-Ar$ is the leaving group in the other two cases. A compound having both a potential sulfonyl-sulfur leaving group and a sulfenyl-sulfur is the thiolsulfonate IV.

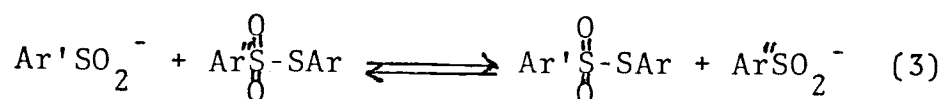


IV

Cymerman and Willis (3) gave spectral proof of the correct structure being one with both oxygens on one sulfur. Nucleophilic reactions (equation 2) of the thiolsulfonates had been known for half a century (37,38,39). Field and co-workers (47) have studied this reaction using different



reactions using different mercaptans where the mercaptide was the nucleophilic species. Gibson and Loudon (46) had looked at exchanges of the thiolsulfonate's sulfonyl-sulfur with various sodium sulfonates in cold aqueous ethanol (equation 3). They did not study the rates of exchange because under

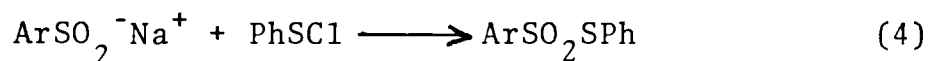


the conditions they employed, the reaction had proceeded to equilibrium before any measurement could be taken. Kice and co-workers (28) had previously reacted sulfinic acid with a thiolsulfinate in the strongly acidic medium of acetic acid - 1% water containing some sulfuric acid. Under these conditions all the sulfinic acid is present as ArSO_2H , which is much less nucleophilic than ArSO_2^- , and the reaction is relatively slow. Therefore, one might hope that in a sufficiently acidic medium the thiolsulfonate-sulfinic acid exchange might be slow enough to be easily studied, and that data on the relative reactivity of various nucleophiles toward sulfonyl-sulfur could be obtained by investigating their ability to catalyze this reaction.

The purpose of this work was then to look at the thiol-sulfonate-sulfinic acid exchange in a strongly acidic medium to observe the kinetics of this exchange. Secondly, since the nucleophilic-catalyzed cleavage of a S-S bond with attack at a sulfenyl-sulfur to expel an ArSO_2 group had not previously been studied, it was of interest to draw comparisons between the thiolsulfonate and the other S-S oxidative species already studied by Kice.

RESULTS

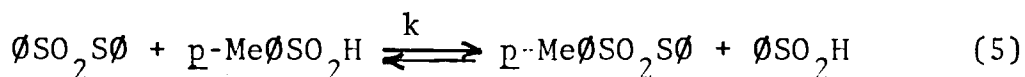
Preparation of the Thiolsulfonates. The thiolsulfonates were prepared by adding the appropriate amount of the sodium salt of the sulfinic acid in anhydrous ether to freshly generated benzenesulfonyl chloride (see equation 4). It was found best to generate the benzenesulfonyl



chloride using an excess of chlorine to assure the complete consumption of the disulfide. Small amounts of sulfide and disulfide in the crude thiolsulfonate were separated by chromatography on a silica gel column and the recrystallization.

Preparation of the Sulfinic Acid. The sulfinic acids were obtained and stored as the dry sodium salt. Just prior to their use they were converted to the acid using sulfuric acid.

Kinetic Studies of the Equilibration of Phenyl Benzene-thiolsulfonate with p-Toluenesulfinic Acid in 60% Dioxane. The equilibration under study was that of a sulfinic acid with a thiolsulfonate (see equation 5). Because of the



differences in solubility of sulfinic acid and thiolsulfonate, the thiolsulfonates were easily separated from the acids by partitioning between water and carbon tetrachloride. The carbon tetrachloride solution was then washed with water to assure the removal of any sulfinic acid. The ratio of the two thiolsulfonates was then determined by an NMR procedure. The hydrogens of the methyl group are shifted 2.4 δ and the aromatic-hydrogens are found as a series of peaks centered at 7.3 δ downfield from TMS. From the knowledge of the number of hydrogens on each molecule, the concentration of each thiolsulfonate was found as the function of the ratio of aromatic-hydrogens to methyl-hydrogens.

A concentration y of phenyl benzenethiolsulfonate contributes $10y$ aromatic hydrogens to the total number of hydrogens present, whereas a concentration x of phenyl *p*-toluenethiolsulfonate contributes $9x$ aromatic-hydrogens and $3x$ methyl-hydrogens. Therefore, in a solution of phenylbenzene-thiolsulfonate of concentration = $[y]$ and phenyl *p*-toluenethiolsulfonate of concentration = $[x]$, the total amount of aromatic-hydrogens present equals $10y + 9x$ and the number of methyl-hydrogens present equals $3x$. The ratio of hydrogens "R" is then defined to be the amount of aromatic-hydrogens per methyl-hydrogen (see equation 6)

$$R = \frac{[H]}{Me[H]} = \frac{10y + 9x}{3x} \quad (6)$$

The accuracy of the $\text{H}_2\text{O}-\text{CCl}_4$ work-up procedure was established with prepared mixtures of the two thiolsulfonates by determining the hydrogen ratios starting with different known ratios of the two thiolsulfonates. Table 1 shows that even with a large change in the ratios of thiolsulfonates the measured values of R agree well in each case with those expected from the known composition of the mixture.

TABLE 1. Determination of Accuracy of the NMR Technique

$p\text{-CH}_3\text{SO}_2\text{SO}$ and SO_2SO were mixed in reaction solutions and worked up to NMR samples.

| % $p\text{-CH}_3\text{SO}_2\text{SO}$ | Cal. R | Found R | % Error |
|---------------------------------------|--------|---------|---------|
| 92.5 | 3.27 | 3.17 | -3 |
| 90.5 | 3.36 | 3.25 | -3 |
| 89.5 | 3.39 | 3.52 | +4 |
| 79.0 | 3.72 | 3.36 | -9 |
| 75.0 | 4.09 | 4.03 | -1 |
| 74.0 | 4.18 | 4.26 | +2 |
| 48.8 | 6.50 | 6.45 | -1 |
| 48.2 | 6.59 | 6.40 | -3 |
| 10.5 | 35.2 | 34.4 | -2 |

The equilibrium for the reaction in equation 5 was determined in acidic 60% dioxane containing from 1 M to 2 M perchloric acid. The position of the equilibrium was measured in terms of the ratio R. As seen in Table 2 this ratio is not affected by changes in the perchloric acid concentration. The equilibrium was approached from both directions by starting with one set or the other set of sulfinic acid-thiolsulfonate combinations (see equation 5) -

no change in equilibrium was observed. An average value of $R = 5.09$ derived from the average of the various runs, was then used in all subsequent rate determinations. In terms of an equilibrium constant this value of R corresponds to a k_{eq} of 2.53.

TABLE 2. Equilibrium k_{eq} at 24.8° C. 60% Dioxane

| M HClO_4 | $\text{C}_6\text{H}_5\text{SO}_2\text{SC}_6\text{H}_5$ | $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}$ | $\text{C}_6\text{H}_5\text{H} / \text{MeH} = R$ |
|-------------------|---|--|---|
| 1.0 | .0497 g. | .0313 g. | 5.12 |
| 1.5 | .0501 | .0313 | 5.14 |
| 2.0 | .0505 | .0327 | 5.05 |
| | $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{SC}_6\text{H}_5$ | $\text{C}_6\text{H}_5\text{SO}_2\text{H}$ | |
| 1.0 | .0527 g. | .0288 g. | 5.05 |
| 1.5 | .0526 | .0280 | 5.05 |
| 2.0 | .0528 | .0288 | 5.13 |
| | | Ave | 5.09 |

The rate of equilibration was measured by following the appearance of phenyl *p*-toluenethiolsulfonate by the NMR method previously outlined. To simplify matters all runs were carried out using equal starting concentrations of phenyl benzenethiolsulfonate and *p*-toluenesulfinic acid. The kinetic data showed reasonably good reversible second-order kinetics. If the reaction follows reversible second-order kinetics a plot of $\ln \left(\frac{x(a-2x_e) + ax_e}{a(x_e-x)} \right)$ versus time should be linear. In this expression 'a' is the initial concentration of phenyl benzenethiolsulfonate or *p*-toluenesulfinic acid, x is the amount of phenyl *p*-toluenethiol-

sulfonate formed by time t , and x_e is the amount of the same thiolsulfonate formed at equilibrium. Figures 1 and 2 show plots of $\ln \left(\frac{x(a-2x_e) + ax_e}{a(x_e-x)} \right)$ vs. time for the various runs. These are seen to be satisfactorily linear.

Table 3 summarizes the kinetic data for the rate of equilibration of phenyl benzenethiolsulfonate with *p*-toluenesulfinic acid in 60% dioxane. One sees that the rate decreases markedly as the concentration of perchloric acid is increased.

TABLE 3. Rate k at 24.8°C 60% Dioxane

| $\text{C}_6\text{H}_5\text{SO}_2\text{S}\text{C}_6\text{H}_5$ | <i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}$ | HClO_4 | $k(\text{M}^{-1}\text{sec}^{-1}) \times 10^2$ | COR. |
|---|---|-----------------|---|------|
| .010M | .010M | 1.5M | 6.88 | .992 |
| .010 | .010 | 2.0 | 3.65 | .997 |
| .010 | .010 | 2.5 | 1.85 | .998 |
| .020 | .020 | 2.5 | 1.70 | .990 |

Attempted Catalysis by Added Bromide Ion. Bromide ion was added to the reaction to see if it would have any catalytic effect. Table 4 presents the kinetic results for 0.1 M and 0.2 M $[\text{Br}^-]$ at perchloric acid concentrations of 2.0 M and 2.5 M (see Figures 3 and 4). The rate of equilibration in 2.0 M HClO_4 was not detectably increased with 0.1 M and 0.2 M $[\text{Br}^-]$ added. When the rate of the uncatalyzed equilibration was decreased by increasing the the perchloric acid concentration to 2.5 M, then the addition of 0.1 M and 0.2 M $[\text{Br}^-]$ did increase the rate, but only modestly.

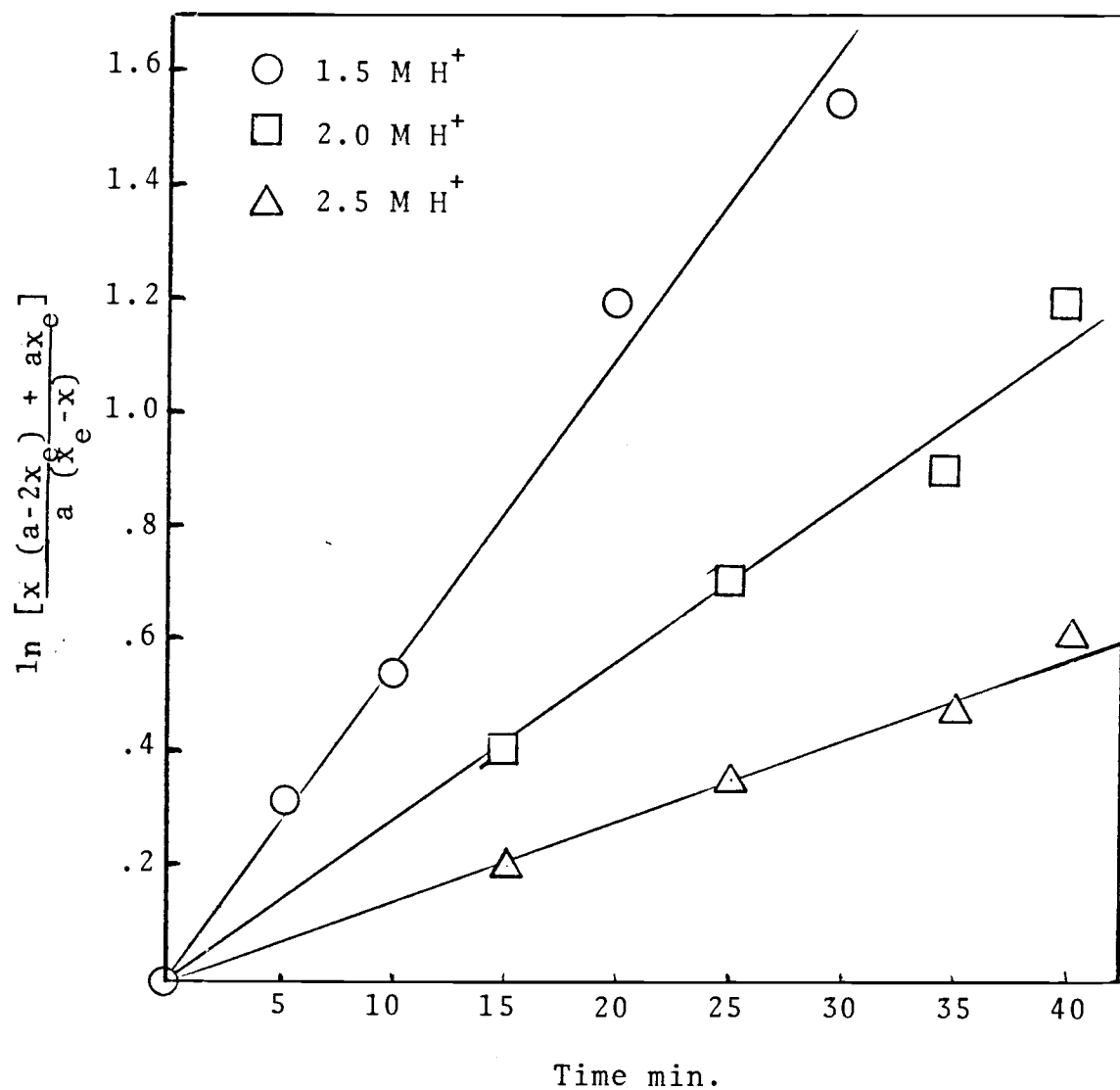


FIGURE 1. Change in concentration of perchloric acid for the phenyl benzene thiosulfate *p*-toluenesulfinic acid reaction in 60% dioxane at 24.8° C.

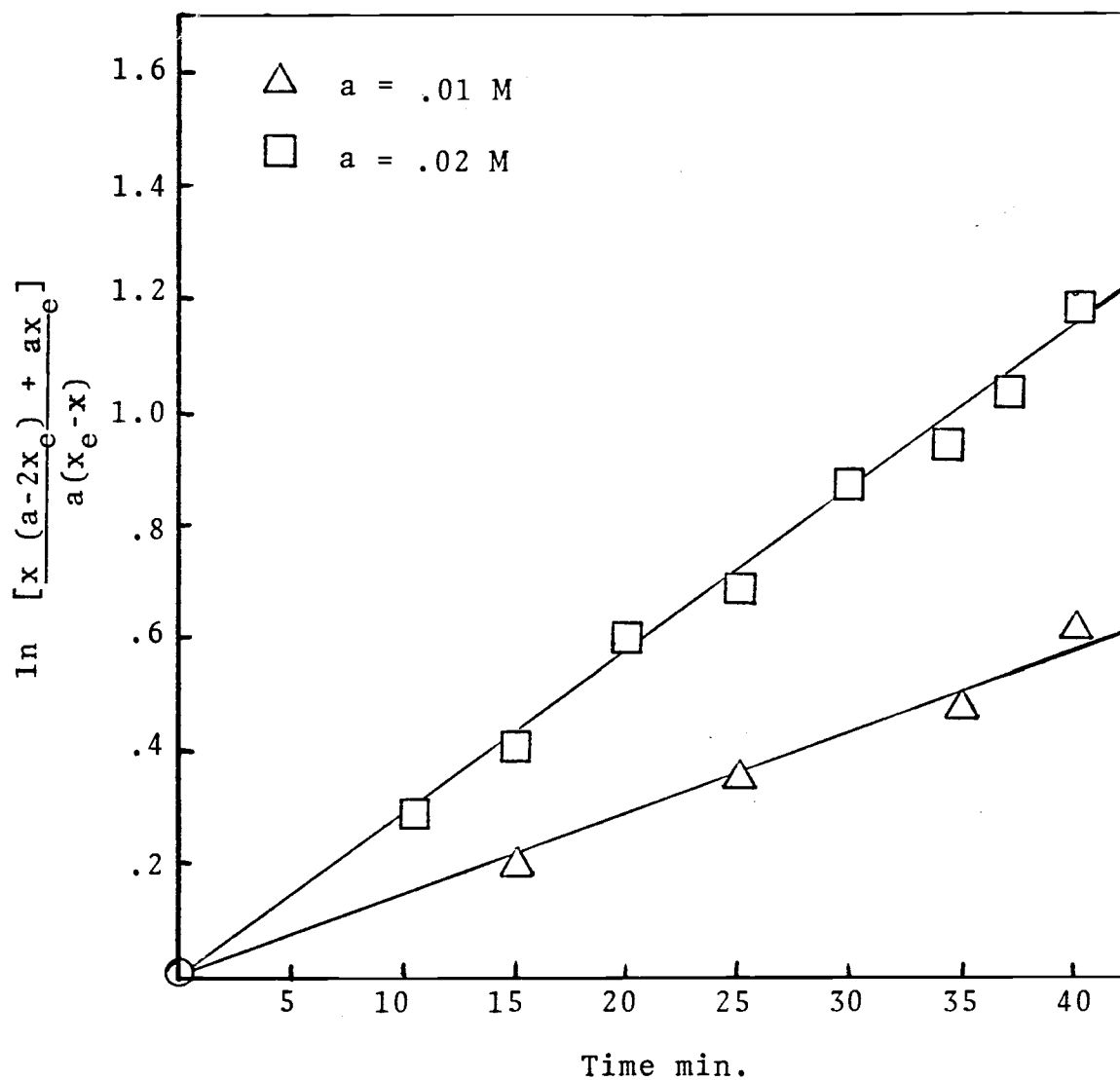


FIGURE 2. Change in concentration of starting reactants in 2.5 M perchloric acid 60% dioxane at 24.8°C .

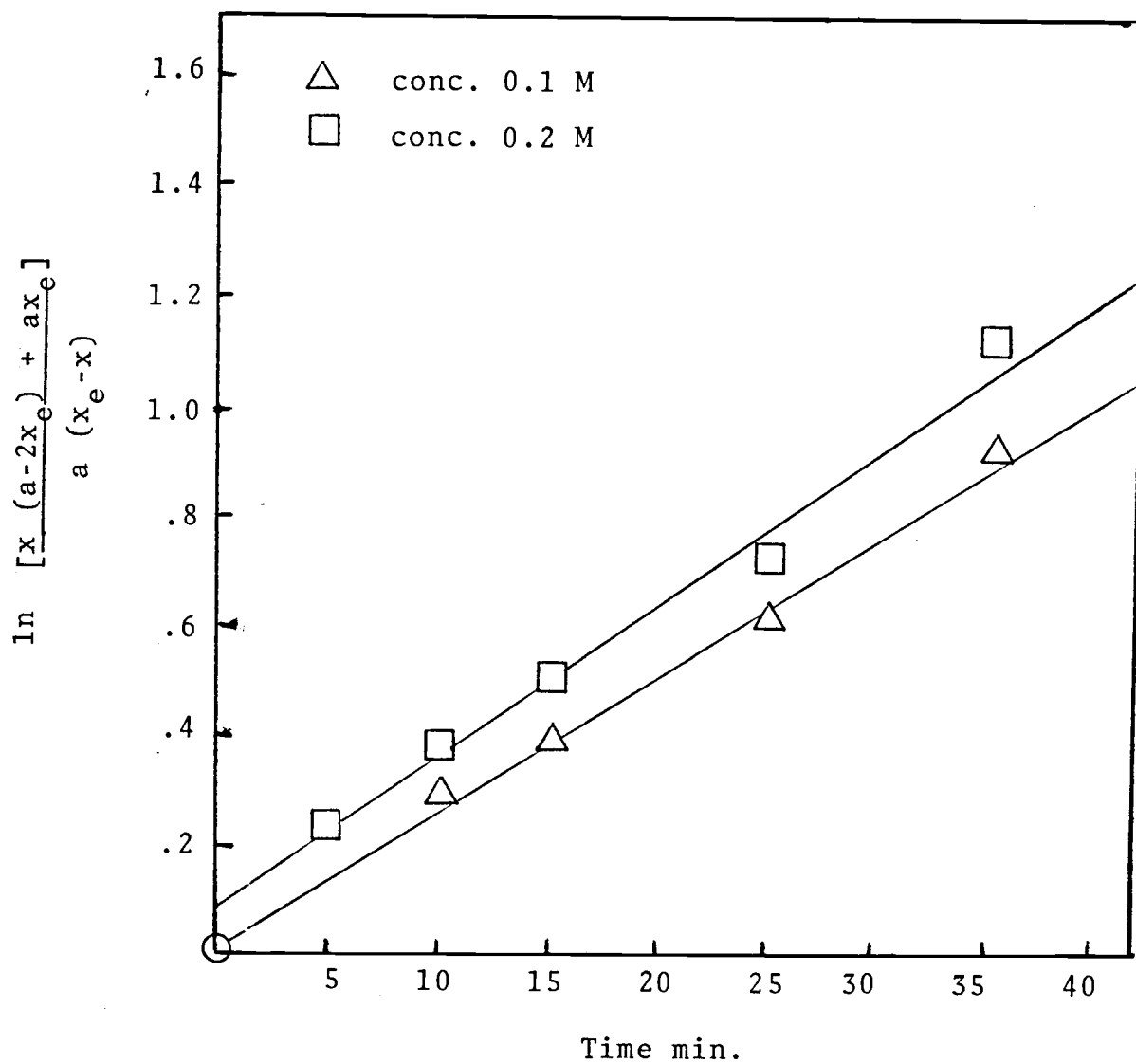


FIGURE 3.. Change in concentration of added Li Br for the reaction in 2.0 M perchloric acid 60% dioxane at 24.8°C.

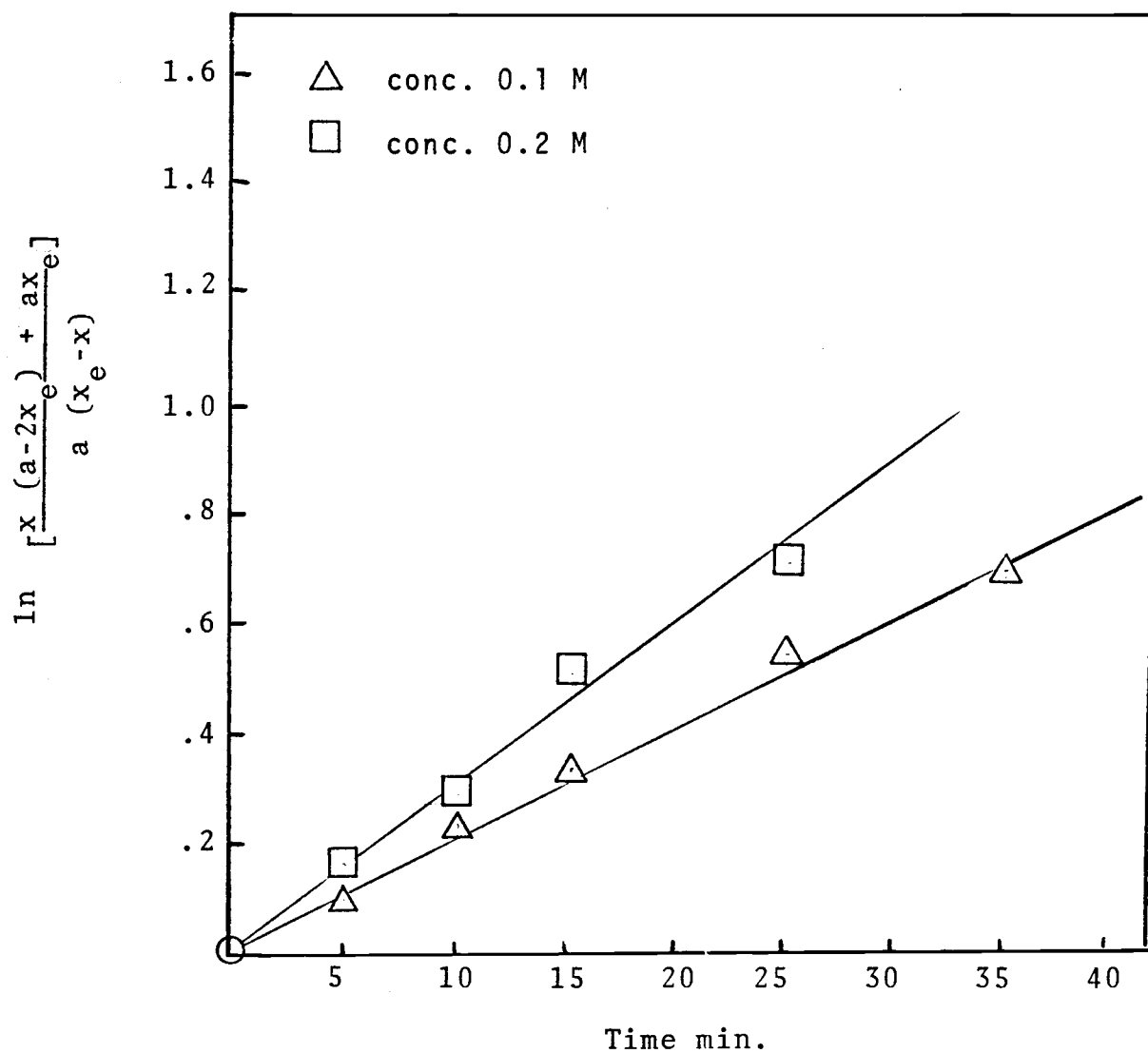
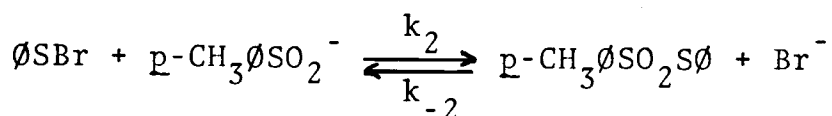
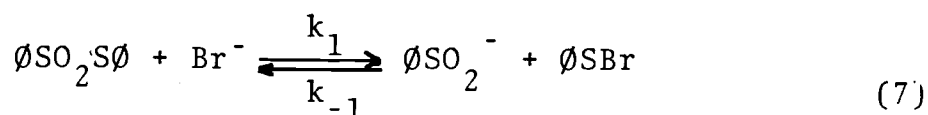


FIGURE 4. Change in concentration of added LiBr for the reaction in 2.5 M perchloric acid 60% dioxane 24.8°C.

TABLE 4. Rate k_{Br} at 24.8° C 60% Dioxane

| LiBr | $\phi\text{SO}_2\text{S}\phi$ | $p\text{-CH}_3\phi\text{SO}_2\text{H}$ | HClO_4 | $k(\text{M}^{-1}\text{sec}^{-1} \times 10^2)$ | COR |
|-------|-------------------------------|--|-----------------|---|------|
| 0.1 M | .010 M | .010 M | 2.0 M | 3.63 | .996 |
| 0.2 | .010 | .010 | 2.0 | 3.82 | .996 |
| 0.1 | .010 | .010 | 2.5 | 2.56 | .997 |
| 0.2 | .010 | .010 | 2.5 | 3.75 | .998 |

The kinetic data for these latter runs in which some acceleration of the rate by added bromide was detectable also gave satisfactory linear plots of $\ln \left(\frac{x(a-2x_e) + ax_e}{a(x_e-x)} \right)$ versus time (see Figure 4). This, at first seemed somewhat surprising, as the following discussion will make clear. The probable mechanism for any catalysis of the equilibration by added bromide is given in equation 7. Assuming that one has a steady state in the concentration of ϕSBr this



should lead to the rate expression shown in equation 8 where "x" is the amount phenyl p-toluenethiolsulfonate present at time t and "a" the initial concentration of both phenyl benzenethiolsulfonate and p-toluene sulfinic acid.

$$\frac{dx}{dt} = \frac{k_2[p\text{-CH}_3\phi\text{SO}_2^-] \left(k_1[a - x][\text{Br}^-] - k_{-2}[x][\text{Br}^-] \right)}{k_{-1}[\phi\text{SO}_2^-] + k_2[p\text{-CH}_3\phi\text{SO}_2^-]} \quad (8)$$

Since at equilibrium $\frac{dx}{dt} = 0$, one can also express k_{-2} as $k_1 \frac{(a - x_e)}{x_e}$ and when this is done the expression in equation 8 becomes the one shown in equation 9.

$$\frac{dx}{dt} = \frac{k_2[p\text{-CH}_3\phi\text{SO}_2^-] \left(k_1[a - x][\text{Br}^-] - k_1 \frac{(a - x_e)}{x_e} [x][\text{Br}^-] \right)}{k_{-1}[\phi\text{SO}_2^-] + k_2[p\text{-CH}_3\phi\text{SO}_2^-]} \quad (9)$$

in order to get the expression completely in terms of the variable x the following substitutions, $k'_{-1} = \frac{k_1 K_a \phi\text{SO}_2\text{H}}{[\text{H}^+]}$ and $k'_2 = k_2 \frac{p\text{-CH}_3\phi\text{SO}_2\text{H}}{[\text{H}^+]}$ are made, and after a few simple rearrangements this gives equation 10.

$$\frac{dx}{dt} = \frac{k_1[\text{Br}^-] \left(a^2 + a[x] \left(\frac{a - x_e}{x_e} - 2 \right) - [x]^2 \left(\frac{a - x_e}{x_e} - 1 \right) \right)}{[x] \left(\frac{k_{-1}}{k'_2} - 1 + a \right)} \quad (10)$$

Upon integration equation 10 gives equation 11.

$$\left[\frac{1 + 2 \left(\frac{k'_{-1}}{k'_2} - 1 \right) (a - x_e) x_e}{a(2x_e - a)} \right] \ln \left[\frac{x(a - x_e) + ax_e}{a(x_e - x)} \right] + \left[\frac{\left(\frac{k'_{-1}}{k'_2} - 1 \right) (a - x_e) x_e}{a(2x_e - a)} \right] \ln \left[\frac{\left(\frac{2x_e - a}{x_e^2} \right) x^2 - 2x + a}{a} \right] = \quad (11)$$

$$2k_1[\text{Br}^-] \left(\frac{a - x_e}{x_e} \right) t$$

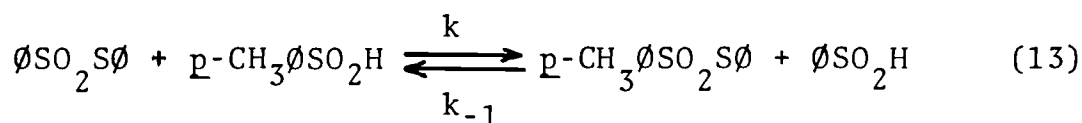
For the case where $\frac{k'_1}{k_2}$ is equal to one, equation 11 degenerates to a linear equation 12.

$$\ln \frac{x(a - 2x_e) + ax_e}{a(x_e - x)} = k_1[\text{Br}^-] 2 \left(\frac{a - x_e}{x_e} \right) t \quad (12)$$

Marked curvature is noticed when $\frac{k'_1}{k_2}$ is greater than 1.75 or less than 0.25. It should be noted that equation 11 is derived only for the catalyzed reaction and does not contain a function for the uncatalyzed reaction.

DISCUSSION

Method of Determining Rate of Exchange. For a second-order reversible reaction (equation 13) where the initial concentrations of the two reactants are taken as equal, the expected kinetics for the rate of formation of $p\text{-CH}_3\phi\text{SO}_2\text{S}\phi$



should be $dx/dt = k(a-x)^2 - k'x^2$. Integration of this yields $\ln \left(\frac{x(a-2x_e) + ax_e}{a(x_e - x)} \right) = k2a \left(\frac{a - x_e}{x_e} \right) t$, where a is the concentration of phenyl benzenethiolsulfonate and p -toluenesulfinic acid at zero time, x is the amount of phenyl p -toluenethiolsulfonate that has formed by time t , and x_e is the amount of the same thiolsulfonate once final equilibrium is reached.

The amount of $p\text{-CH}_3\phi\text{-SO}_2\text{S}\phi$ present at any time can be followed by an NMR method. The NMR data obtained is the ratio R of the number of aromatic hydrogens to the number of methyl hydrogens in the sample. By suitable manipulation it can be shown that $x = \frac{10a}{3R + 1}$.

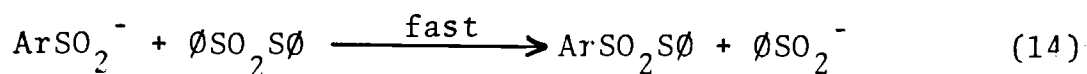
Magnitude of Equilibrium Constant. From the experimental data one finds that for the equilibrium in equation 13 to be

$$K_{eq} = \frac{[p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{SPh}][\text{C}_6\text{H}_5\text{SO}_2\text{H}]}{[\text{C}_6\text{H}_5\text{SO}_2\text{SPh}][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}]} = 2.53$$

This indicates that there is a small thermodynamic preference for the phenyl p-toluenethiolsulfonate + benzenesulfonic acid over phenyl benzenethiolsulfonate + p-toluenesulfonic acid. However, the preference is not a very large one and corresponds to a free energy difference of only about 0.5 kcal/mole between the substances on the left and right hand sides of the equilibrium above.

Effect of Perchloric Acid on Rate of Exchange. An increase in perchloric acid concentration from 1.0 to 2.0 M does not alter the equilibrium constant for the reaction. However this same increase in perchloric acid concentration does markedly decrease the rate at which equilibrium is obtained (see Table 3).

The fact that an increase in strong acid concentration decreases k but does not change K_{eq} shows us that equilibration must be achieved under these conditions principally via the reaction of the anion of the sulfinic acid with the thiolsulfonate (equation 14), rather than via a process



involving attack of the sulfinic acid itself on the thiolsulfonate (equation 15).

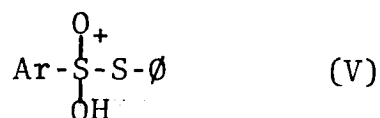


The pK_a of *p*-toluenesulfinic acid in water is 1.24 (35). For an acid like formic, of a charge type similar to the sulfinic acid, transfer from water to 60% dioxane increases the pK_a by 2.23 units. On that basis one would estimate that the pK_a of *p*-toluenesulfinic acid in 60% dioxane is probably about 3.47 (17). Presumably, therefore in 1.5 M to 2.5 M HClO_4 in this medium no more than 1 sulfinic acid molecule out of 4.4×10^3 is present as the anion. The fact that exchange still takes place predominantly with equation 14 as the rate-determining process shows that the sulfinic acid anion must be more than 8.4×10^3 times better nucleophile toward the thiol-sulfonate than is the sulfinic acid itself!

Actually it is not surprising to find that the sulfinate anion is a much more reactive nucleophile than the sulfinic acid. Sulfinic acid reacts with thiosulfates (28) in aqueous acidic acid via a mechanism which seems to require general base catalysis. Sulfinic acid has a much lower pK_a in aqueous dioxane, therefore the amount of sulfinate anion will be much greater allowing the sulfinate anion reaction (equation 14) to predominate. However, the magnitude of the effect appears to be even larger than might have been imagined from the earlier studies.

When the concentration of perchloric acid becomes large

enough, >2.5 M, the sulfinate anion will be at low enough concentration that the rate for the sulfinic acid reaction would predominate. A crude estimate of this rate is obtained from the plot of k_{obs} vs $\frac{1}{h_0}$ (1) and found to be $1.35 \times 10^{-2} \text{ M}^{-1}\text{sec}^{-1}$. The sulfinic acid reaction most likely is general base catalyzed as the low basicity associated with sulfonyl group would make an intermediate like V extremely unstable and it would presumably be formed only with great difficulty (28)



Catalysis of Exchange by Bromide. The sulfenyl sulfur being susceptible to nucleophilic attack, it was of interest to look at other common nucleophiles in comparison to sulfinic acid anion. Bromide was chosen because it showed promise of being a relatively fast nucleophile towards sulfenyl sulfur (25).

For the reaction run at 2.0 M perchloric acid no catalysis was detectable. Apparently even at very low concentrations sulfinic acid anion was a sufficiently better nucleophile than bromide, so that bromide catalysis was not able to make a contribution.

When the perchloric acid concentration was increased to 2.5 M, then catalysis by bromide could be detected. The rate in the presence of 0.20 M lithium bromide was about

double the rate in its absence. The catalyzed reaction still plots linearly for a second-order reversible reaction. If k'_{-1} in equation 11 does not have a value fairly close to $\frac{k'_{-1}}{k_2}$ one then the plot might be expected to curve. In equation 11 $\frac{k'_{-1}}{k_2}$ equaled $\frac{k_1 K_a^{\text{OSO}_2\text{H}}}{k_2 K_a^{\text{ArSO}_2\text{H}}}$ for OSO_2H and ArSO_2H ; this suggests using the $\text{p}K_a$ values by C. D. Ritchie, et al (35) that $\frac{k'_{-1}}{k_2}$ equals $\frac{k_{-1}}{k_2}$ (1.07). From the rates at which ArSO_2H and OSO_2H attack a protonated thiolsulfinate (28) one can make a rough estimate of $\frac{k_{-1}}{k_2}$. This turns out to be only 1.05. Therefore it is not at all unlikely that $\frac{k'_1}{k'_2}$ is probably quite close to unity (i.e. $1.07 \times 1.05 = 1.12$) and this is apparently the reason that a plot of $\ln \left(\frac{x(a - 2x)e^{-x}}{a(x_e - x)} + ax_e \right)$ versus t shows no detectable curvature.

A second point to note is that the catalyzed reaction is not really a great deal faster than the uncatalyzed reaction, so that a significant portion of the total reaction is going via the uncatalyzed route even with bromide added. This will also serve to diminish any curvature when the catalyzed portion follows a slightly different kinetic dependence.

Iodide should be a better nucleophile toward sulfenyl

sulfur than bromide (35). Accurate determination of the rate of exchange was found to be impossible in the presence of added iodide. Apparently this was due to the intervention of a side reaction between sulfinic acid and the nucleophile under these particular reaction conditions. When iodide was used, free iodine was liberated, so it could not be used as a catalyst at all. Sulfides, another potential nucleophilic catalyst, suffered from interference with the NMR technique. The α -hydrogens of sulfide absorb in the same region that the methyl hydrogens of *p*-tolyl group absorbed. Because the sulfides were soluble in carbon tetrachloride and therefore appeared in the NMR sample under the method previously described, the project was not pursued any further.

EXPERIMENTAL

Preparation of Benzenesulfonyl Chloride. Into a three-necked, 100 ml. flask, fitted with a gas inlet tube, calcium chloride drying tube, and Teflon stirring bar, was placed 7.0 g. (0.032 mole) of diphenyl disulfide and 50 ml. dry chloroform. After the diphenyl disulfide had dissolved, chlorine was bubbled through the solution for one hour. The solvent was then distilled off under a vacuum. The red oily residue, which was apparently reasonably pure PhSOCl , was used immediately.

Preparation of Phenyl Benzenethiolsulfonate. The benzenesulfonyl chloride was cooled in an ice bath and an ethereal slurry of the (0.04 mole) solid sodium benzene sulfinate, an amount roughly twice that of the (0.02 mole) diphenyldisulfide used to make the benzenesulfonyl chloride, was then added to the benzenesulfonyl chloride. The sodium benzene sulfinate suspension was added until the red color due to the benzene sulfonyl chloride was gone. The reaction was stirred for another ten minutes and then the ethereal solution was washed with 25 ml. saturated sodium bicarbonate and once with water; it was then dried over "Drierite." The ether was removed leaving an oil. Recrystallization from absolute ethanol at 15°C gave 5.0 g. (50% yield) of pure phenyl benzenethiolsulfonate, mp. $44 - 46^{\circ}$ (lit. (29), 45°).

Preparation of Phenyl p-Toluenethiolsulfonate. To the benzenesulfonyl chloride from 0.03 mole phenyl disulfide was added 0.06 mole of dried sodium p-toluenesulfinate in anhydrous ether. The reaction proceeded rapidly in an ice bath and more sodium p-toluenesulfinate was added until the red color from the benzenesulfonyl chloride was gone. The reaction was stirred another ten minutes before the ethereal solution was washed first with 25 ml. of saturated sodium bicarbonate, then with water, and finally dried over "Drierite." The ether was removed under reduced pressure and the oily residue recrystallized from absolute ethanol which gave 7.1 g. (45% yield) phenyl p-toluenethiolsulfonate, m.p. 75 - 77° (lit.(29), 78°).

Preparation of Benzenesulfinic Acid. Sodium benzenesulfinate that had been recrystallized from water was dissolved in water and filtered. The filtrate was acidified with 6 M sulfuric acid in an ice-bath with constant stirring until further addition of acid showed no new precipitate. The precipitate was removed by filtration, dried under vacuum. It was then dissolved in the minimum amount of ether and an equal amount of hexane was added. The benzenesulfuric acid which crystallized out in needles was filtered off, mp. 80 - 82° (lit.(13), 81-83°).

Preparation of p-Toluenesulfinic Acid. Sodium p-toluenesulfinate that had been recrystallized from water was

dissolved in water and filtered. The solution was acidified with 6N Sulfuric acid with constant stirring in an ice-bath until the further addition of acid showed no new precipitate forming. The precipitated sulfinic acid was dried under vacuum. The precipitate was dissolved in the minimum amount of ether and an equal volume of hexane was then added. The *p*-toluenesulfinic acid which crystallized out in long needles was filtered off, m.p. 85° (lit.(21), 85°).

Purification of Dioxane. In a five liter, three-neck flask, equipped with a gas inlet tube and condenser, was placed four liters of dioxane, 50 ml. of concentrated hydrochloric acid, and 400 ml. of water. This was refluxed for 12 hours, during which time a slow stream of nitrogen was bubbled through the solution. The solution was then cooled and potassium hydroxide pellets were slowly added with shaking until they no longer dissolved. The dioxane layer was then separated and fresh potassium hydroxide pellets were added and left to stand. The dioxane was again separated. The dioxane was then refluxed over sodium until the metal remained bright and shiny. It was then distilled into a storage flask containing benzophenone and fresh sodium and was stored in a stoppered flask. Whenever dioxane was needed a small amount was freshly fractionated from the storage vessel. As long as the blue color of the sodium ketyl of benzophenone remains in the storage flask

the dioxane is peroxide-free.

Kinetic Studies of the Equilibration of Phenyl Benzenethiolsulfonate with p-Toluenesulfinic Acid in 60% Dioxane. The apparatus used for the kinetic studies is shown in Figure 6, page 55). The solvent was prepared fresh by weighing out standardized 70% perchloric acid and adding this to the appropriate amount of dioxane. Then water was added after calculating how much was already in the 70% perchloric acid until the desired 60:40 dioxane:water ratio was achieved. The thiolsulfonate was dissolved in the reaction chamber in 80% of the total solvent. Nitrogen was bubbled through the solution. The sulfinic acid was dissolved in the remaining 20% of the solvent and this solution was then added to the reaction chamber. Where lithium bromide was used it was dissolved in 10% of the solvent and added to the sulfinic acid which had been dissolved in 10% of the solvent before combining with the thiolsulfonate in the reaction vessel. A slow stream of nitrogen was bubbled through the solution during the reaction.

After the reaction chamber had been immersed in the constant temperature bath for five minutes, sample t_0 was withdrawn. The samples were forced directly through the three-way stop cork and out the spout into a separatory funnel containing 10 ml. carbon tetrachloride. A stock

solution of carbon tetrachloride had been shaken with perchloric acid previously to assure the absence of any base which could catalyze the reaction prior to separation. The sample was immediately shaken and the carbon tetrachloride removed. An additional 5 ml. carbon tetrachloride was used to wash the aqueous solution. The carbon tetrachloride solutions were combined and washed with 5% sodium bicarbonate and then dried over magnesium sulfate. After concentrating the sample under reduced pressure it was mixed with an appropriate amount of carbon tetra-chloride - 1% TMS and the NMR spectrum run on the Varian A-60 NMR.

After the NMR was finely adjusted to give the best possible response a spectrum was taken over the 7.2 δ and 2.4 δ regions. Then integration was adjusted to get the maximum possible integral over the 7.2 δ (aromatic) region and then several integration runs were made over each area until a good average could be gotten. A peak at 3.5 δ due to dioxane was noted but the distance from the methyl hydrogen peaks was great enough to not cause any trouble.

The experimental ratio $R = \frac{\int [H]}{\int Me[H]}$ was then obtained as the average integral height of the aromatic hydrogens divided by the average integral height of the methyl-hydrogens. This R value was then used to obtain the rate of a second-order reversible reaction.

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