AN ABSTRACT OF THE THESIS OF

RICHARD ALLEN BARTSCH for the ___M. S.___ in ___CHEMISTRY___
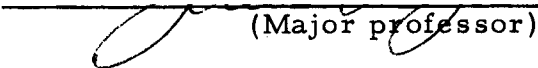(Name)   (Degree)

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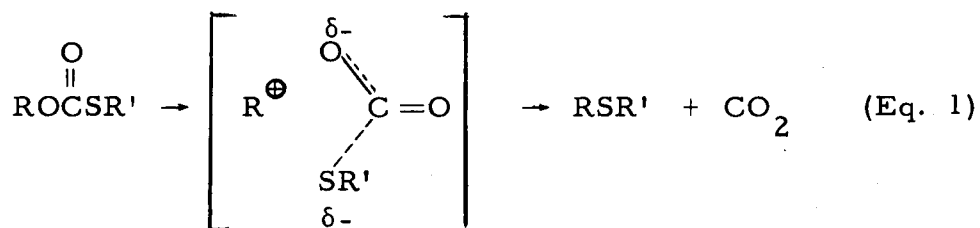Title _____THE THERMAL DECOMPOSITION OF_____

_____ARALKYL THIOCARBONATES_____

Abstract approved _____
(Major professor)

Benzhydryl S-phenyl thiocarbonate (I), benzhydryl S-methyl thiocarbonate (II), benzhydryl S-ethyl thiocarbonate (III), benzhydryl S-benzyl thiocarbonate (IV), benzyl S-phenyl thiocarbonate (V), p-chlorobenzhydryl S-phenyl thiocarbonate (VI), and p-chlorobenzhydryl S-methyl thiocarbonate (VII) were prepared by the reaction of the desired alcohol with the appropriate chlorothiolformate. Product studies of the decomposition of I in bromobenzene and benzonitrile and IV in benzonitrile showed that the only major products of the decomposition were the corresponding sulfide and carbon dioxide, which was obtained in nearly quantitative yield (See Equation 1). Solvent studies showed that the decomposition of I proceeded 26 times faster in benzonitrile than in bromobenzene. Kinetic studies of the reaction, by quantitative infrared analysis utilizing the disappearance of the C=O group absorption ($1705-1720$ cm.$^{-1}$) of the

thiocarbonates, showed that the decomposition of I in bromoben-

zene and of I, II, III, IV, V, VI, and VII in benzonitrile followed

good first-order kinetics. The solvent studies and the rela-

tive rates of decomposition of I, II, V, VI, and VII, provided evi-

dence for a rate-determining heterolysis of the R—O bond. Stud-

ies of the relative rates of decomposition of I, II, III, and IV

strongly indicated that the C—S bond was also weakened or broken

in the rate-determining step. Thus a mechanism such as shown in

Equation 1 was postulated for the thermal decomposition of

$$
\underset{\substack{\text{O} \\ \|}}{\text{ROCSR'}} \rightarrow
\left[
\begin{array}{c}
\overset{\delta-}{\text{O}} \\
\text{R}^{\oplus} \quad \text{C}=\text{O} \\
\underset{\delta-}{\text{SR'}}
\end{array}
\right]
\rightarrow \text{RSR'} + \text{CO}_2 \qquad \text{(Eq. 1)}
$$

thiocarbonates.

These results are of considerable significance for both the

detailed mechanism of the thermal decomposition of chlorocarbon-

ates and the mechanism of Sn_i processes in general.

THE THERMAL DECOMPOSITION OF
ARALKYL THIOCARBONATES

by

RICHARD ALLEN BARTSCH

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THE THERMAL DECOMPOSITION OF
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INTRODUCTION

One of the standard methods for converting alcohols to alkyl

chlorides is by treatment with thionyl chloride, $SOCl_2$. This reac-

tion has been shown to proceed through the isolable alkyl chlorosul-

fite, which decomposes upon heating to yield the alkyl chloride and

SO_2 (see Equation 1).

$$ROH + SOCl_2 \rightarrow RO-\overset{O}{\underset{}{S}}-Cl \xrightarrow{\text{heat}} RCl + SO_2 \qquad \text{(Eq. 1)}$$
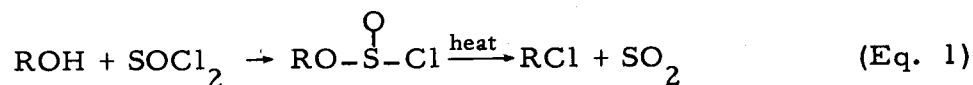
An analogous reaction between alcohols and phosgene,

$COCl_2$, produces alkyl chlorocarbonates. These chlorocarbonates

decompose upon heating with the formation of the corresponding

alkyl chloride and CO_2 (see Equation 2).

$$ROH + COCl_2 \rightarrow RO-\overset{O}{\underset{}{C}}-Cl \xrightarrow{\text{heat}} RCl + CO_2 \qquad \text{(Eq. 2)}$$
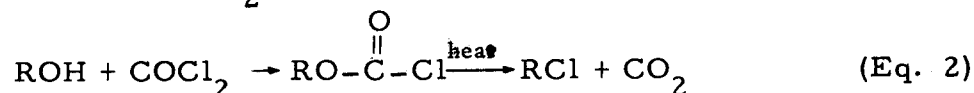
A mechanism (Equation 3) for the thermal decomposition of

chlorocarbonates has been proposed by Wiberg and Shryne (18).

$$RO\overset{O}{\underset{}{C}}Cl \rightarrow \left[R^{\oplus} \overset{\ominus O}{\underset{Cl}{}} C=O \right] \rightarrow RCl + CO_2 \qquad \text{(Eq. 3)}$$
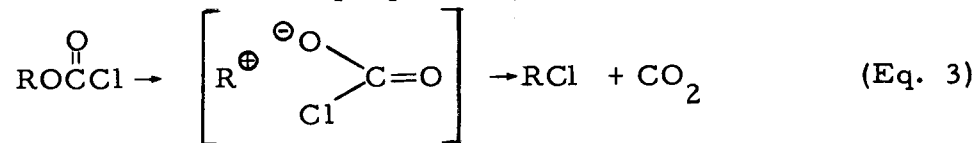
A carbonium ion intermediate was postulated due to the effects of

substitution on the rate of decomposition of a series of p-substi-

tuted α-phenylethyl chlorocarbonates and due to the observation

that α-phenylethyl chlorocarbonate decomposed at a rate which

was 450 times that of benzyl chlorocarbonate.

Olivier and Young (11) have studied the effect of solvent upon the chlorocarbonate decomposition. α-Methylallyl chloroformate decomposed 100 times faster in nitrobenzene (a polar solvent) than in toluene (a non-polar solvent).

It was also found by Wiberg and Shryne (18) that if the original chlorocarbonate were optically active, the resulting chloride usually exhibited a high degree of retention of configuration (Equation 4).

$$d-ROCOCl \xrightarrow{heat} d-RCl + CO_2 \qquad (Eq. 4)$$
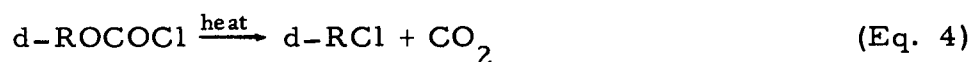
A group of compounds which are structurally related to chlorocarbonates, ROCOCl, are thiocarbonates, ROCOSR'. Relatively little is known about this class of organic sulfur compounds. However, due to their structural resemblance to chlorocarbonates, they might be expected to undergo a similar thermal decomposition reaction (see Equation 5).

$$ROCOSR' \xrightarrow{heat} RSR' + CO_2 \qquad (Eq. 5)$$

The purpose of the present research was to compare the thermal decomposition of thiocarbonates with the above cited thermal decomposition of chlorocarbonates.

Of first concern was whether or not the thermal decomposition of thiocarbonates, ROCOSR', followed the same course as that of

chlorocarbonates, ROCOCl. Product studies of the decomposition of the thiocarbonates could answer this question.

If the same general course were observed, the next concern would be whether or not the thiocarbonate decomposition was an ionic reaction as is the chlorocarbonate decomposition. Solvent studies would help illuminate this facet of the problem. If the rate of reaction were markedly faster in a polar solvent than in a non-polar one, this would probably mean that the decomposition involved ions or ion pairs as intermediates.

If there were agreement between the decompositions of thio-carbonates and chlorocarbonates on these first two points, two fur-ther areas of investigation should be considered.

First, how do R and R' influence the rate of decomposi-tion of thiocarbonates? In the chlorocarbonates, ROCOCl, where only the R group can be varied, one cannot determine, because of the invariance of the chloride group, whether the C—Cl bond is also broken or weakened in the rate-determining step. In thiocar-bonates, where both R and R' can be varied, one finds a system which potentially provides for additional information about the de-tailed mechanism of the decomposition. The variation of rate with R and R' would permit the determination of whether only the R—O bond, or alternatively both the R—O and C—S bonds are broken or weakened in the rate-determining step. If the

decomposition of thiocarbonates involves initial ionization of the

R—O bond, ROCOSR' → $\left[\text{R}^{\oplus} \;\; ^{\ominus}\text{OCOSR'} \right]$, as proposed for chloro-

carbonates (18), the rates of decomposition would be proportional

to the stability of the carbonium ion derived from the R group.

If the decomposition also involves the cleavage of the C—S bond

in the rate-determining step, the rate would be expected in addition

to be dependent upon the stability of SR'$^{\ominus}$.

A final area of interest is comparison of the stereochemis-

try of the decomposition of thiocarbonates with that of chlorocar-

bonates and other structurally related compounds (6, p. 294-296).

This research has entailed: (1) product studies of the thio-

carbonate decomposition, to determine if the thermal decomposi-

tions of thiocarbonates and chlorocarbonates follow the same gen-

eral course, (2) determination of the rate of decomposition as a

function of solvent, to see if the thiocarbonate decomposition re-

sponds in the same manner as the chlorocarbonate decomposition,

and (3) studies of the influence of R and R' upon the rate of re-

action, to gain insight into the detailed mechanism of the reaction

(vide supra).

An area of future research is the stereochemistry of the

thiocarbonate decomposition.

RESULTS

Preparation of Thiocarbonates. The various benzhydryl

thiocarbonates were all prepared by reaction of benzhydrol with the

appropriate chlorothiolformate in a benzene solution containing an

equivalent of pyridine (see Equation 6).

$$\text{Ph}_2\text{CHOH} + \text{RS}\underset{\text{O}}{\overset{\text{||}}{\text{C}}}\text{Cl} \xrightarrow{\text{pyridine}} \text{Ph}_2\text{CHO}\underset{\text{O}}{\overset{\text{||}}{\text{C}}}\text{SR} \qquad \text{(Eq. 6)}$$
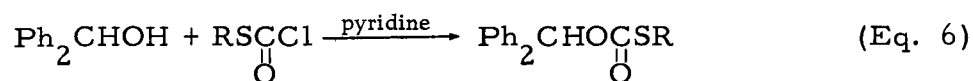
Yields generally were not high, however, and the thiocar-

bonate usually had to be separated from considerable unreacted al-

cohol and other by-products by chromatography. Table summa-

rizes the yields, and gives the physical constants of the various

benzhydryl thiocarbonates.

Table 1. Synthesis and Properties of Benzhydryl Thiocarbonates,
$\text{Ph}_2\text{CHO}\underset{\text{O}}{\overset{\text{||}}{\text{C}}}\text{SR}$

R		M. P. (° C)	Yield (%)	Analysis	
				Calculated (%)	Found (%)
Ph	(I)	87.5-88.5	55	C, 75.00 H, 5.04 S, 9.99	C, 75.08 H, 5.25 S, 10.19
CH$_3$	(II)	72-73	28	C, 69.74 H, 5.46	C, 69.77 H, 5.44
C$_2$H$_5$	(III)	37-38	22	C, 70.56 H, 5.92	C, 70.43 H, 5.92
CH$_2$Ph	(IV)	45-46	20	C, 75.41 H, 5.44	C, 75.51 H, 5.49

Benzyl S-phenyl thiocarbonate (V) and p-chlorobenzhydryl

S-phenyl thiocarbonate (VI) were prepared in similar fashion from

phenyl chlorothiolformate, and benzyl alcohol and p-chlorobenzhy-

drol, respectively.   p-Chlorobenzhydryl S-methyl thiocarbonate

(VII) was also similarly prepared from methyl chlorothiolformate

and p-chlorobenzhydrol.   Table 2 lists the yields and gives the

physical constants of these three thiocarbonates.

Table 2.   Synthesis and Properties of Thiocarbonates, $RO\overset{\overset{\textstyle O}{\|}}{C}SR'$

R	R'	M. P. (°C)	Yield (%)	Analysis	
				Calculated (%)	Found (%)
PhCH$_2$	Ph	59-60	20	C, 68.85 H, 4.92 S, 13.13	C, 69.05 H, 5.02 S, 12.89
PhCH $\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle$ Cl	Ph	95-96	26	C, 67.70 H, 4.26	C, 67.48 H, 4.36
PhCH $\langle\hspace{-0.3em}\bigcirc\hspace{-0.3em}\rangle$ Cl	CH$_3$	62-63	24	C, 61.53 H, 4.48	C,[a] H,

Products of the Decomposition of I in Bromobenzene.

Product studies of the decomposition of benzhydryl S-phenyl thio-

carbonate were conducted in earlier work (3, p. 15-17).   The ma-

jor products isolated consisted of carbon dioxide (100% yield) and

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[a] Analysis data not returned at time of printing.

benzhydryl phenyl sulfide (78% yield). There were also isolated

very small amounts (<2%) of phenyl disulfide and tetraphenylethane.

Thus, the thermal decomposition of I in bromobenzene

seems to occur almost entirely according to Equation 7.

$$Ph_2CHO\overset{O}{\overset{||}{C}}SPh \xrightarrow{heat} Ph_2CHSPh + CO_2 \qquad (Eq.\ 7)$$
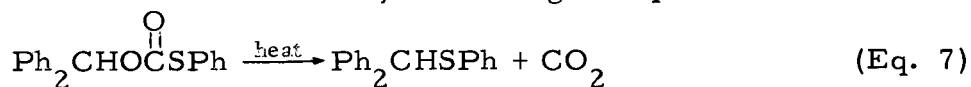
Products of the Decomposition of I in Benzonitrile. In

order to study the thermal decomposition of benzhydryl S-phenyl

thiocarbonate under the simplest possible conditions, the decompo-

sition was carried out in an inert solvent and under a nitrogen at-

mosphere. Means for rapid removal of carbon dioxide from the

solution were employed.

The apparatus employed is shown in Figure 1. The detailed

procedure is given in the Experimental section. In the procedure,

the carbon dioxide yield was estimated from the gain in weight of

the Ascarite tube.

Applying the above mentioned conditions, the change in

weight of the Ascarite tube during the decomposition corresponded

to a 101% theoretical yield of carbon dioxide. The one percent ex-

cess is considered to be within the experimental error of the tech-

niques involved.

In addition to carbon dioxide, the only other major product

was benzhydryl phenyl sulfide, which was found in 83% yield. Also

isolated were 7% of tetraphenylethane and approximately 2% of

phenyl disulfide.

The thermal decomposition of I in benzonitrile also appears

to proceed almost completely according to Equation 7.

Products of the Decomposition of IV in Benzonitrile. Pro-

duct studies of the decomposition reaction of benzhydryl S-benzyl

thiocarbonate in benzonitrile were carried out using methods simi-

lar to those described for the product studies of the decomposition

of I in benzonitrile. The estimated carbon dioxide yields were as

shown in Table 3.

Table 3. Carbon Dioxide Evolution in the Decomposition of IV in
Benzonitrile

Run	Duration (hrs.)	Amount of IV (g.)	$\dfrac{\text{Actual change (g.)}}{\text{Theoret. change (g.)}}$	Percent Yield (%)
1	4.0	1.197	$\dfrac{0.146}{0.157}$	93
2	4.5	1.037	$\dfrac{0.128}{0.136}$	93.5
3	20.0	0.950	$\dfrac{0.125}{0.125}$	100

Examination of kinetic data for the decomposition of IV in

benzonitrile in the temperature range of the decomposition (see

Kinetics of the Decomposition of I, II, III, IV, V, VI, and VII in Ben-

zonitrile in Results section) reveals that after 4.0 hrs. of reaction

time there should be less than two percent remaining thiocarbonate.

Thus, it appears that in the reaction some intermediate compound,

which later decomposes to yield carbon dioxide, is formed to a

small extent.

In addition to carbon dioxide, the only other major product

was benzhydryl benzyl sulfide, which was found in at least 67% yield.

Also, 7% of benzhydrol was isolated.

The decomposition of IV in benzonitrile seems to take place

primarily according to Equation 8, but clearly in this case

$$Ph_2CHOCSCH_2Ph \xrightarrow{heat} Ph_2CHSCH_2Ph + CO_2 \qquad (Eq. 8)$$
$$\underset{O}{\overset{\|}{}}$$
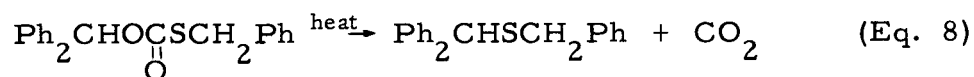
there is at least some side reaction which accounts

for the low yields of benzhydryl benzyl sulfide and carbon dioxide

and for the significant amount of benzhydrol which was isolated.

Kinetics of the Decomposition of Thiocarbonates. The kinet-

ics of the decomposition reactions of the thiocarbonates were fol-

lowed by an infrared method based on the disappearance of the car-

bonyl group absorption in the range 1705-1720 $cm.^{-1}$ (see Experi-

mental section for the approximate frequencies of the various

esters).

Standard solutions of the desired thiocarbonate and solvent

allowed for the construction of quantitative calibration curves,

such as those shown in Figure 3, by which the amount of

thiocarbonate in a sample could be determined. The straight line

relationships noted in Figure 3 show that the intensity of the car-

bonyl absorption follows the Lambert-Beer law (i. e. , $\log I_o/I$

varies directly with the concentration, where I_o is the incident

light and I is the transmitted light).

The apparatus employed is shown in Figure 2. The proce-

dure, described in detail in the Experimental section, consisted of

removing samples from the reaction mixture at various times and

determining the amount of unreacted thiocarbonate in the sample

by the quantitative infrared analytical method.

Kinetics of the Decomposition of I in Bromobenzene. The

kinetics of the decomposition of I in bromobenzene at 145° have

been studied in earlier work (3, p. 6-9). Selected examples of

these studies are presented in Table 20 (Runs 4, 5, and 7) and Fi-

gure 4.

The decomposition showed reasonably good first-order

kinetics, i. e. a graph of log of the percent of unreacted I versus

time gave a straight line over at least the first 60-70% of the reac-

tion (see Figure 4). The reaction accelerates in the later stages,

but the initial rates are easily determined, and more important,

are reproducible.

Comparison of Runs 4 and 5 (conducted at approximately

0.09 $\underline{M}$. concentration) with Run 7 (conducted at approximately

0.05 $\underline{M}$. concentration) shows that, as expected for a true first-

order reaction, the rate constant is independent of the initial thio-

carbonate concentration.

At 155° (Run 14), the decomposition exhibits good first-

order kinetics (see Figure 5), although there is still acceleration

in the later stages of the reaction.

Table 4 lists the kinetic data for the decomposition of I in

bromobenzene as derived from selected runs.

Table 4. Kinetics of the Decomposition of I in Bromobenzene

Run	Temp.,(°C)	Conc., ($\underline{M}$.)	$t_{\frac{1}{2}} \times 10^{-4}$,(sec.)	$k \times 10^{5}$,(sec.$^{-1}$)
5	145	0.088	3.96	1.75
7	145	0.048	3.56	1.94
14	155	0.088	1.53	4.53

Kinetics of the Decomposition of I, II, III, IV, V, VI, and VII

in Benzonitrile. Initial attempts to study the decompositions of

thiocarbonates in nitrobenzene were unsuccessful. Subsequent

trials with benzonitrile showed it to be an entirely satisfactory

polar solvent in which to follow the decomposition.

The decompositions of the various thiocarbonates (I, II,

III, IV, V, VI, and VII) in benzonitrile all followed good first-order

kinetics. Table 5 indexes the data and Figures which pertain to these decompositions.

Table 5. Decomposition of Thiocarbonates in Benzonitrile

Thiocarbonate	Temperature (°C)	Run (see Table 20)	Figure
I	134	21	6
	145	30	6
II	155	22	7
	155	23	7
	166	29	7
III	166	27	8
	166	28	8
IV	166	32	9
	166	33	9
V	166	31	10
VI	146	35	11
VII	166	36	12

Lack of dependence of the rate constant on initial thiocarbonate concentration, as expected for a true first-order reaction, is shown in Runs 27 and 28 (conducted at concentrations of 0.072 $\underline{M}$. and 0.050 $\underline{M}$., respectively) and in Runs 32 and 33 (conducted at concentrations of 0.072 $\underline{M}$. and 0.053 $\underline{M}$., respectively).

The decomposition of V was only followed to 25% completion

because of the slow rate of decomposition and high reaction tem-
perature required.

Table 6 lists the rate constant data for the decompositions of
I, II, III, IV, V, VI, and VII in benzonitrile. Tables 7, 8, 9, and
10 compare the relative rates of decomposition of the various thio-
carbonates. The relative rate of decomposition of benzhydryl S-
phenyl thiocarbonate in various solvents is shown in Table 11.

Table 6. Kinetics of the Decomposition of Thiocarbonates in
          Benzonitrile

Cmpd.	Temp.,(°C)	Conc.,($\underline{M}$.)	Run	$t_{\frac{1}{2}} \times 10^{-3}$ (sec.)	$k \times 10^4$, (sec.$^{-1}$)
I	134	0.081	21	3.87	1.79
	145	0.066	30	1.50	4.62
	146		calc.$^{b/}$	1.37	5.05
	166		calc.$^{b/}$	0.238	24.8
	186		calc.$^{b/}$	0.0648	107
II	155	0.083	23	14.7	0.470
	166	0.060	29	5.50	1.26
III	166	0.072	27	10.4	0.663
	166	0.050	28	10.4	0.663
IV	166	0.072	32	2.88	2.40
	166	0.053	33	2.88	2.40
V	186	0.072	31	1670	0.00415
VI	146	0.087	35	2.92	2.38
VII	166	0.068	36	12.1	0.575

$^{b/}$Since the values of the rate constant were known at two tempera-
tures, the rate constants at other temperatures could be calculated
from an integrated form of the Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{\Delta H^{\ddagger}}{2.3R} \frac{(T_2 - T_1)}{T_2 T_1}$$

where $\Delta H^{\ddagger}$ is the activation energy and k_2 and k_1 are the rate constants
at temperatures T_2 and T_1, respectively. See Table 12 for enthalpy
of activation.

Table 7. Relative Rates of Decomposition in Benzonitrile at 166° of Benzhydryl S-Aryl, Aralkyl, and Alkyl Thiocarbonates, $Ph_2CHOCSR'$ with C=O

R'		Relative Rate
Ph	(I)	(100)
CH_3	(II)	5.1
C_2H_5	(III)	2.7
$PhCh_2$	(IV)	9.6

Table 8. Relative Rates of Decomposition in Benzonitrile at 146° of Aralkyl S-Phenyl Thiocarbonates, $ROCSPh$ with C=O

R		Relative Rate
Ph_2CH	(I)	(1)
PhCH with Cl-phenyl	(VI)	0.47

Table 9. Relative Rates of Decomposition in Benzonitrile at 166° of Aralkyl S-Methyl Thiocarbonates, $ROCSCH_3$ with C=O

R		Relative Rate
Ph_2CH	(I)	(1)
PhCH with Cl-phenyl	(VII)	0.46

Table 10. Relative Rates of Decomposition in Benzonitrile at 186° of Aralkyl S-Phenyl Thiocarbonates, $ROCSPh$ with $\overset{\parallel}{O}$

R	Relative Rate
Ph_2CH (I)	(100)
$PhCH_2$ (V)	0.00388

Table 11. Relative Rates of Decomposition of Benzhydryl S-Phenyl Thiocarbonate in Various Solvents at 145°

Solvent	Relative Rate
Bromobenzene	(1)
Benzonitrile	26.4

Thus, the rate of decomposition of thiocarbonates is seen to depend upon the nature of both R' (Table 7) and R (Tables 8, 9, and 10). Table 11 shows that the decomposition proceeds at a faster rate in a more ionizing solvent than in a less ionizing solvent.

Table 12 gives the entropy and enthalpy of activation for the decomposition of benzhydryl S-phenyl thiocarbonate in benzonitrile. It should be emphasized that there is probably considerable error in these values, since the rate constants were only determined a limited number of times at temperatures which were not widely separated.

Table 12. Entropy and Enthalpy of Activation of Benzhydryl S-
Phenyl Thiocarbonate in Benzonitrile

$\Delta H_i^{\ddagger}$ (kcal./mole)	$\Delta S_i^{\ddagger}$ (e. u.)
29. 1	-3

DISCUSSION

That the thermal decomposition of thiocarbonates (see

Equation 9) occurs by an internal substitution reaction

$$ROCSR' \xrightarrow{heat} RSR' + CO_2 \qquad \text{(Eq. 9)}$$

which follows the same general course as the decomposition of chlo-

rocarbonates (see Equation 10) is evident from the product studies of the

$$ROCCl \xrightarrow{heat} RCl + CO_2 \qquad \text{(Eq. 10)}$$

decomposition of I in bromobenzene and benzonitrile and of IV in

benzonitrile. A summary of these product studies is given in

Table 13. The data presented in Table 13 show the appropriate

sulfide is always the only important organic product of the thiocar-

bonate decomposition and that yields of carbon dioxide are always

close to quantitative.

Table 13. Decomposition Products of Thiocarbonates, $ROCSR'$

Compound	Yields of Products, (%)				
	CO_2	RSR'	RR	R'SSR'	ROH
(I) (in bromobenzene)	100	78	< 2	< 2	
(I) (in benzonitrile)	100	83	7	2	
IV (in benzonitrile)	93	67			7

The effects upon the rate of reaction of (1) solvent and of (2) substitution on the carbon undergoing substitution are two common criteria for distinguishing between a reaction which is essentially covalent and one which is predominantly ionic. Both of these effects may be gaged by the magnitude of the rate ratios within a systematically varied series (13).

The differentiation of ion-pair processes and non-ionic processes by the use of rate response to solvent ionizing power has been advocated by Winstein (21, p. 169-181). Using this criterion in studying the decomposition of α-methylallyl chloroformate, Olivier and Young (11) found a rate increase of a factor of approximately 10,000 for a solvent change from decane to nitrobenzene and a rate increase of a factor of 100 for a solvent change from toluene to nitrobenzene.

Olivier and Young offer the large magnitude of the rate factors as evidence for a rate-determining heterolytic cleavage of the R—O bond in the chloroformates, ROCOCl (i.e. an ionic reaction would be assisted by an ionizing solvent). In contrast, Pegolotti and Young (12) found a rate increase of a factor of only seven for a solvent change from decane to nitrobenzene for the thermal decomposition of α-trifluoromethylallyl chlorosulfinate. From this, and the exclusive formation of rearranged chloride as product, they

concluded that the decomposition of this chlorosulfinate was of the

cyclic covalent type (see Equation 11). Insensitivity of rate of

$$CH_2=CHCHOSCl \rightarrow \left[CF_3-C \begin{smallmatrix} O-S \\ \\ C=CH_2 \\ H \end{smallmatrix} Cl \right] \rightarrow CF_3CH=CHCH_2Cl + SO_2$$
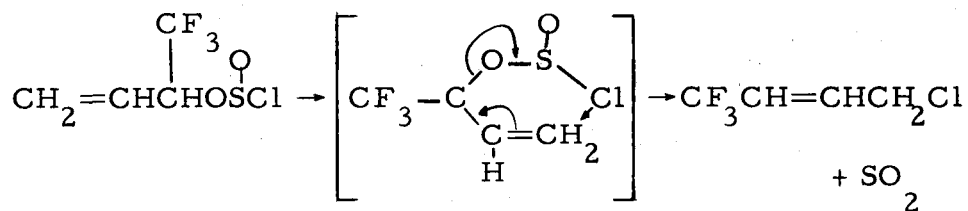
<div align="right">(Eq. 11)</div>

reaction to solvent ionizing power has also been taken as evidence

for the absence of truly ionic mechanisms in the thermal rearrange-

ments of allylic thiobenzoates (16) and allylic azides (5).

Solvent studies concerning the thermal decomposition of

benzhydryl S-phenyl thiocarbonate (see Table 11) showed that the

rate increased by a factor of 26 for a solvent change from bromo-

benzene to benzonitrile. Since there is less difference between

the relative ionizing power of bromobenzene and benzonitrile than

between toluene and nitrobenzene, this result suggests that the

thiocarbonate decomposition responds to solvent ionizing power in

a manner comparable to the chlorocarbonate decomposition. Thus,

it seems highly probable that the transition state of the thiocarbon-

ate decomposition involves solvated[c] ions or ion pairs, and the re-

action is therefore one of those normally considered to be ionic in

character.

[c] See reference 21 for a discussion of solvated ion pairs.

This ionic type of reaction seems very reasonable when the covalent mechanism which would be proposed for the thiocarbonate decomposition is examined (see Equation 12).

$$ROCSR' \quad \rightarrow \quad \left[\begin{array}{c} R{-}O \\ S{-}C{=}O \\ R' \end{array} \right] \rightarrow RSR' + CO_2 \qquad \text{(Eq. 12)}$$
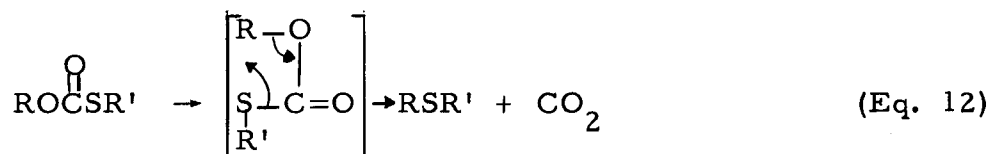
Unlike α-trifluoromethylallyl chlorosulfinate, which decomposes via a six-membered cyclic mechanism (see Equation 11), a comparable four-membered cyclic covalent mechanism seems unreasonable for the thiocarbonate decomposition because of the strain which would be involved in a four-membered ring.

Correlation of rate of reaction with the stability of the carbonium ion $R^{\oplus}$, which would be formed by heterolysis of the $R{-}O$ bond, has been advanced as evidence for a rate-determining ionization of the $R{-}O$ bond in alkyl chlorocarbonates, $ROCOCl$ (11 and 18), alkyl chlorosulfinates, $ROSOCl$ (15), and alkyl chloroglyoxalates, $ROCOCOCl$ (13).

Wilberg and Shryne (18) attributed a large negative ρ value in their $\rho\sigma$-correlation of the decomposition of p-substituted α-phenylethyl chlorocarbonates to an electron deficient migrating group, which suggests a carbonium ion intermediate. In addition, α-phenylethyl chlorocarbonate was found to decompose at a rate which was 450 times that of benzyl chlorocarbonate. This would also be expected of a carbonium ion intermediate.

In aralkyl S-phenyl thiocarbonates, the order of stability to thermal decomposition is benzyl >> p-chlorobenzhydryl > benzhydryl (see Tables 8, 10, and 14). Benzhydryl S-phenyl thiocarbonate was found to decompose at a rate which was 25,000 times faster than that of the benzyl S-phenyl thiocarbonate and 2.1 times faster than that of p-chlorobenzhydryl S-phenyl thiocarbonate. Similarly, with aralkyl S-methyl thiocarbonates, it was found that benzhydryl S-methyl thiocarbonate decomposed at a rate which was 2.2 times faster than that of p-chlorobenzhydryl S-methyl thiocarbonate (see Tables 9 and 15).

Table 14. Relative Rates of Decomposition of Aralkyl S-Phenyl Thiocarbonates, $RO\overset{O}{\overset{\|}{C}}SPh$

R	Relative Rate	
	at 146°C	at 186°C
PhCH$_2$		3.9×10^{-5}
PhCH$\overset{\bigcirc}{C1}$	0.47	
Ph$_2$CH	$(1)^{\underline{d/}}$	$(1)^{\underline{d/}}$

$\underline{d/}$ Calculated using $\Delta H^{\ddagger} = 29.1$ kcal./mole

Table 15. Relative Rates of Decomposition of Aralkyl S-Methyl

Thiocarbonates, $RO\overset{O}{\overset{\|}{C}}SCH_3$

R	Relative Rate
PhCH Cl	0. 46
Ph_2CH	(1)$\underline{e}/$

$\underline{e}/$ Calculated using $\Delta H^{\ddagger}= 29.1$ kcal./mole

The relative rates of decomposition of the aralkyl S-phenyl

and aralkyl S-methyl thiocarbonates correlate reasonably well with

the relative rates of solvolysis of the comparative aralkyl chlorides

(compare Tables 14 and 15 with Tables 16, 18 and 19). The ratios

of relative rates of solvolysis of benzyl chloride and benzhydryl

chloride in acetic acid at 186°, in methanol at 186°, and in 70%

ethanol at 80° are 1.2×10^{-4}: 1, 3.6×10^{-4}: 1 and 6.2×10^{-4}:1,

respectively; while the relative rate ratio for the decompositions

of benzyl S-phenyl thiocarbonate and benzhydryl S-phenyl thiocar-

bonate in benzonitrile at 186° is 3.9×10^{-5}:1. The relative rate

ratio for the solvolysis of p-chlorobenzhydryl chloride and benzhy-

dryl chloride in acetic acid at 25°, in methanol at 25°, and in 70%

ethanol at 146° are 0.34:1, 0.46:1, and 0.33:1, respectively;

whereas the ratio of the relative rates of decomposition of

p-chlorobenzhydryl S-phenyl thiocarbonate and benzhydryl S-phenyl

thiocarbonate in benzonitrile at 146° is 0.47:1 . Also the relative

rate ratio for the decomposition of p-chlorobenzhydryl S-methyl

thiocarbonate and benzhydryl S-methyl thiocarbonate in benzonitrile

at 166° is 0.46:1.

In recent work, Winstein and co-workers (22) found that

for p-chlorobenzhydryl chloride in acetic acid, k_i, the rate con-

stant for ionization, was 30-70 times k_s, the rate constant for

solvolysis. This means that in poorly nucleophilic solvents a giv-

en molecule will probably ionize and "internally return" to the

covalent state many times before the ions actually react with the

solvent to form solvolysis products (see Equation 13),

$$
\underset{\underset{C_6H_5}{|}}{\overset{\overset{H}{|}}{pClC_6H_4C}}-Cl \quad \underset{k_{-i}}{\overset{k_i}{\rightleftarrows}} \quad \left[\underset{\underset{C_6H_5}{|}}{\overset{\overset{H}{|}}{p\text{-}ClC_6H_4C}}{}^{\oplus} \quad {}^{\ominus}Cl \right] \overset{k_s}{\rightarrow} \text{ products} \qquad \text{(Eq. 13)}
$$
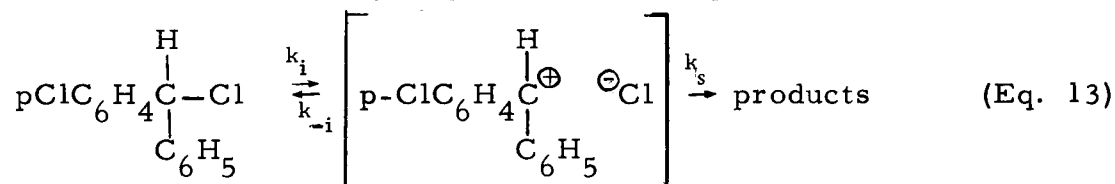
In comparing the behavior of the thiocarbonates and the chlorides,

what we really wish to do is to compare the relative rates of de-

composition of the thiocarbonates in benzonitrile with the actual

relative ionization rates of the various chlorides in a poorly nucle-

ophilic and yet moderately good ionizing solvent, such as acetic

acid. To do this the rate constants for the solvolysis of p-chloro-

benzhydryl and benzhydryl chlorides in acetic acid were increased

Table 16. Relative Rates of Solvolysis in Acetic Acid

Chloride	Relative Rate			Ref.
	at 25°C	at 50°C	at 186°C	
Ph_2CH	(1)	(1)[f]	(1)[f]	(20)
PhCH $\bigcirc$ Cl	0.34			(22)
$PhCH_2$	6.7×10^{-5}[g]	7.3×10^{-5}[g]	1.2×10^{-4}[g]	(14)

Table 17. Relative Rates of Ionization[h]

Chloride	Relative Rate			Ref.
	at 25°C	at 50°C	at 186°C	
Ph_2CH	(1)	(1)[f]	(1)[f]	(20)
PhCH $\bigcirc$ Cl	0.34			(22)
$PhCH_2$	2.2×10^{-6}[g]	2.4×10^{-6}[g]	4.1×10^{-6}[g]	(14)

[f] Calculated using $\Delta H^{\ddagger} = 23.5$ kcal. /mole.
[g] Calculated using $\Delta H^{\ddagger} = 22.45$ kcal. /mole.
[h] The rate constants for solvolysis of benzhydryl and p-chloro-benzhydryl chloride were increased by a factor of 30 to give estimated rate constants for the ionization of these two chlorides.

Table 18. Relative Rates of Solvolysis in 70% Ethanol

Chloride	Relative Rate			Ref.
	at 25°C	at 80°C	at 146°C	
Ph_2CH	(1)	(1)[i]	(1)[i]	(8)
PhCH (with Cl ring)	0.33	0.38[j]	0.41[j]	(8)
$PhCH_2$		6.2×10^{-4}		(7)

Table 19. Relative Rates of Solvolysis in Methanol

Chloride	Relative Rate			Ref.
	at 25°C	at 50°C	at 186°C	
Ph_2CH	(1)	(1)[k]	(1)[k]	(20)
PhCH (with Cl ring)	0.46			(2)
$PhCH_2$	8.0×10^{-5}	1.1×10^{-4}	3.6×10^{-4}[l]	(4) and (19)

[i] Calculated using $\Delta H^{\ddagger}$ = 20.6 kcal./mole.
[j] Calculated using $\Delta H^{\ddagger}$ = 21.1 kcal./mole.
[k] Calculated using $\Delta H^{\ddagger}$ = 19.8 kcal./mole.
[l] Calculated using $\Delta H^{\ddagger}$ = 22.4 kcal./mole.

by a factor of 30 to give estimated rate constants for the ionization
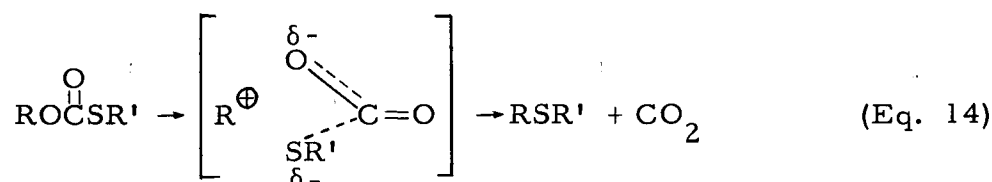
of these two chlorides. Table 17 gives the results of this operation.

Now, the relative rate ratio for solvolysis of benzyl chloride and

benzhydryl chloride in acetic acid at 186° is 4.1×10^{-6}:1. This is

compared to a relative rate ratio for the decomposition of benzyl

and benzhydryl S-phenyl thiocarbonate in benzonitrile at 186° of

3.9×10^{-5}:1. The relative ratio for the decomposition of benzyl

and benzhydryl S-phenyl thiocarbonate in benzonitrile appears to

be intermediate between the relative ratios of solvolysis and ioni-

zation of the corresponding chlorides in acetic acid.

Thus, the relative decomposition rates of the series of

aralkyl S-phenyl and aralkyl S-methyl thiocarbonates agree favor-

ably with the relative solvolysis rates of the corresponding aralkyl

chlorides. The solvolyses of these halides are known to involve

rate-determining ionization ($R-X \rightarrow R^{\oplus} + X^{\ominus}$) to a carbonium ion

intermediate.

From the solvent studies, which indicate that the decomposi-

tion of thiocarbonates responds to increased solvent ionizing power

in the same manner as the chlorocarbonate decomposition, and

from the effect upon the rate of reaction of substituents on the car-

bon undergoing substitution, it seems clear that the mechanism of

the thiocarbonate decomposition must involve the development of

appreciable positive charge on the R group in the rate-determining step. In other words, in the rate-determining step the R—O bond is heterolytically cleaved, and the R group becomes a carbonium ion. This being the case, we must now inquire whether or not the C—S bond is also affected in the rate-determining step.

If the decomposition of thiocarbonates involves both initial ionization of the R—O bond and initial cleavage or weakening of the C—S bond (see Equation 14), the rate of reaction would be expected to depend upon the stability of $SR'^{\ominus}$ as well as upon the stability of $R^{\oplus}$. That is, the rate of decomposition would be expected to parallel the pKa of the corresponding mercaptan, $R'SH$.

$$\underset{\substack{O \\ \| \\ ROCSR'}}{} \rightarrow \left[R^{\oplus} \quad \overset{\overset{\delta-}{O}}{\underset{\underset{\delta-}{SR'}}{}} C=O \right] \rightarrow RSR' + CO_2 \qquad \text{(Eq. 14)}$$

If, however, the decomposition of thiocarbonates involves a rate-determining heterolysis of only the R—O bond (see Equation 15), only the inductive properties of the R' group would have an effect upon the rate of decomposition. Since Taft's σ^* values (10, p. 587-589) are a measure of the inductive effect of a group, if there is an initial ionization of only the R—O bond (see Equation 15), one might well expect that there would be a good correlation

between the rate of decomposition of the thiocarbonates and the appropriate σ* values.

$$ROCSR' \rightarrow \left[R^{\oplus} \quad \begin{array}{c} {}^{\ominus}O \\ C=O \\ SR' \end{array} \right] \rightarrow RSR' + CO_2 \qquad (Eq. \ 15)$$
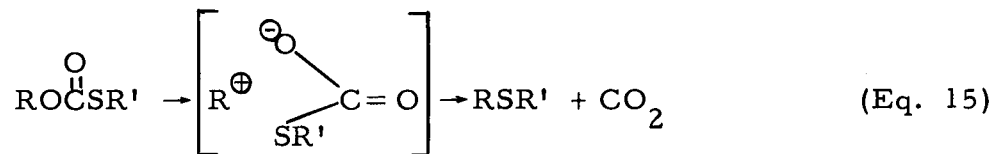
The critical test for distinguishing between these two mechanisms is when R' is a group which could stabilize, by resonance, a negative charge on the sulfur of the SR'$^{\ominus}$ anion. If, for instance, R' is a phenyl group, negative charge on the SR'$^{\ominus}$ anion could be distributed by resonance over the entire ion (see Equation 16).

$$\left[\quad \right] \qquad (Eq. \ 16)$$
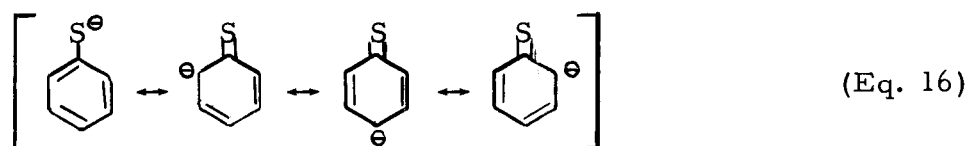
Now if the mechanism consists of initial heterolysis of only the R—O bond, resonance stabilization of the SPh$^{\ominus}$ ion could have no effect on the rate of reaction. The only consequence of the phenyl R' group would be its inductive effect. This means that a direct correlation between the rate of reaction and Taft's σ* values would be expected. However, if the mechanism entails in addition to a R—O bond cleavage, a rate-determining weakening or breaking of the C—S bond, the resonance stabilization of the SPh$^{\ominus}$ ion would have an effect on the rate of reaction of the thiocarbonate. Indeed, the reaction would proceed at a rate which would be faster than that which would be predicted from the inductive effect of the

phenyl group alone.

In order to provide for the differentiation between the two suggested mechanisms (see Equations 14 and 15), the kinetics of a series of benzhydryl S-aryl, aralkyl, and alkyl thiocarbonates were studied. The results of these kinetic studies are given in Tables 6 and 7.

Figure 13 is a plot of log k versus $\sigma*$ values for the series: benzhydryl S-phenyl thiocarbonate (I), benzhydryl S-methyl thiocarbonate (II), benzhydryl S-ethyl thiocarbonate (III), and benzhydryl S-benzyl thiocarbonate (IV). The log k versus $\sigma*$ correlation for members II, III, and IV of the series leads to a predicted rate of decomposition for benzhydryl S-phenyl thiocarbonate which is slower than that which is actually observed. In other words, the benzhydryl S-phenyl thiocarbonate decomposition proceeds at a rate which is faster than would be predicted from the purely inductive effect of the phenyl group (as measured by $\sigma*$). Thus, as would be expected if the thiocarbonate decomposition proceeded through a mechanism similar to the one shown in Equation 14, the ability of the R' group to stabilize the negative charge on the $SR'^{\ominus}$ anion by resonance does indeed seem to effect the rate of the thiocarbonate decomposition. This definitely suggests that in the rate-determining step both the R—O and C—S bonds are affected.

As mentioned earlier, if the mechanism shown in Equation 14 is the one involved in the thiocarbonate decomposition, the rate of reaction would be expected to depend upon the stability of $SR'^{\ominus}$. Figure 14 is a plot of the log of the rate constant of thermal decomposition for the thiocarbonate series cited above versus the pKa of the corresponding mercaptans (9). As can be seen, the points representing the various thiocarbonates of the series fall on a good straight line, as would be expected if, in addition to the R—O bond cleavage, the C—S bond is broken or weakened in the rate-determining step.

Thus, the thermal decomposition of thiocarbonates, ROCOSR', probably follows a mechanism in which there is multiple heterolysis of the R—O and C—S bonds in the rate-determining step (see Equation 14). In the transition state there is a positive charge on the R group and an appreciable negative charge on the sulfur. A rough estimate of the amount of negative charge which is on the sulfur may be made by the use of the slope of the plot of log k for the thiocarbonate decomposition versus pKa for the corresponding mercaptans (see Figure 14). If there were approximately a full negative charge on the sulfur, a direct correspondence (slope = 1) of log k versus pKa might be expected. Since the slope is in actuality only 0.4, one would estimate that there is 40% of a full

negative charge on the sulfur. The other 60% of the negative

charge would be distributed over the two oxygens, by resonance.

This mechanism is in contrast to that proposed by Wiberg

and Shryne (18) for the similar thermal decomposition of chloro-

carbonates (see Equation 3), in which it was suggested that only

the R—O bond is cleaved in the rate-determining step. Pending

an investigation of the stereochemistry of the thiocarbonate decom-

position, a new mechanism may be proposed for the thermal decom-

position of chlorocarbonates. The thermal decompositions of chlo-

rocarbonates, ROCOCl, and thiocarbonates, ROCOSR', have been

shown to be similar by product studies, solvent effects on reac-

tion rate, and effect of R on reaction rate. If the stereochemistry

of the two decompositions is similar (a high degree of retention in

both cases), then by analogy to the just investigated thiocarbonate

decomposition, it would appear in the chlorocarbonate decomposi-

tion that the C—Cl bond is weakened or broken in the rate deter-

mining step, in addition to the proposed R—O bond cleavage (see

Equation 17).

$$\text{RO}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{Cl} \rightarrow \left[R^{\oplus} \overset{\overset{\delta-}{\text{O}}}{\underset{\text{Cl }\delta-}{\diagdown}} C=O \right] \rightarrow \text{RCl} + \text{CO}_2 \qquad \text{(Eq. 17)}$$
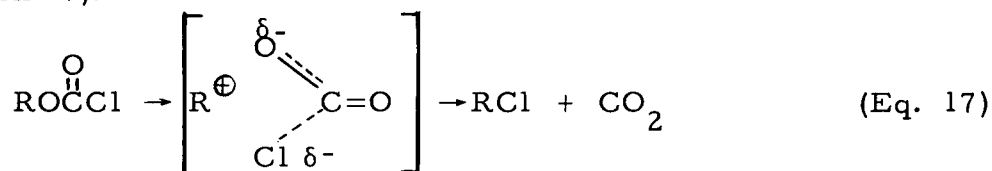
In a recent investigation of the thermal decomposition of

chloroglyoxalates, ROCOCOCl, Rhoads and Michel (13) also postu-

lated a rate-determining cleavage of both R—O and C—Cl bonds.

Thus, from the results of this study of the thermal decomposition of thiocarbonates and from the work of Rhoads and Michel concerning chloroglyoxalates, it is speculated that Sn_i reactions[m] may, in general, proceed by way of a multiple bond heterolysis in the rate-determining step.

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[m] See reference 6, p. 294-296 for a discussion of Sn_i reactions.

EXPERIMENTAL

Preparation of Benzhydryl S-Phenyl Thiocarbonate (I). Into
a three-necked flask, fitted with reflux condenser, dropping funnel,
and magnetic stirrer, were placed 18.4 g. (0.1 mole) of benzhydrol,
8 g. (0.1 mole) of pyridine, and 40 ml. of benzene. The resulting
solution was cooled with an ice bath for 15 minutes. Phenyl chloro-
thiolformate, 17.2 g. (0.1 mole), was added dropwise, giving the
previously colorless solution a yellow color, and producing a white
precipitate of pyridine hydrochloride. After refluxing for two hours
and cooling to room temperature, the mixture was washed three
times with water, discarding the aqueous layer each time. Fifty
milliliters of ether were added during the first washing to reduce
the tendency for emulsification of the organic layer. The yellow
benzene layer was dried over sodium sulfate. After filtering the
solution, the solvent was removed under reduced pressure. The
crude thiocarbonate was recrystallized twice from hexane giving
17.5 g. (55%) of purified thiocarbonate which had a melting point of
87.5 - 88.5°.

Analysis. Calculated for $C_{20}H_{16}O_2S$: C, 75.00; H, 5.04;
S, 9.99; Found: C, 75.08; H, 5.25; S, 10.19.

Preparation of Benzhydryl S-Methyl Thiocarbonate (II).

Utilizing the same procedure as stated for the preparation of I,

16.3 g. (0.09 mole) of benzhydrol, 7 g. (0.09 mole) of pyridine,

40 ml. of benzene, and 9.8 g. (0.09 mole) of methyl chlorothiol-

formate were combined to yield the crude product. Chromato-

graphy on alumina with benzene as eluent produced the purified

thiocarbonate. Recrystallization from hexane led to 7.3 g. (28%)

of II, m.p. 72-73°.

Analysis. Calculated for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46;

Found: C, 69.77; H, 5.44.

Preparation of Benzhydryl S-Ethyl Thiocarbonate (III).

Employing the same techniques indicated for the preparation of I

and II, 18.4 g. (0.1 mole) of benzhydrol, 8 g. (0.1 mole) of pyri-

dine, 40 ml. of benzene, and 12.5 g. (0.1 mole) of ethyl chlorothiol-

formate were combined to produce the crude thiocarbonate. The re-

sulting liquid product was chromatographed on alumina and eluted

with benzene. After evaporation of the benzene under reduced pres-

sure, the remaining oils were cooled in a refrigerator. Crystalli-

zation occurred after 6 hours, yielding 6.0 g. (22%) of III, m.p.

37-38°.

Analysis. Calculated for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92;

Found: C, 70.43; H, 5.92.

Preparation of Benzyl Chlorothiolformate. This was pre-
pared using a modification of Tilles' procedure (17, p. 727).
Phosgene (22. 8 g. , 0. 23 mole) was dissolved in 80 ml. of toluene.
To the mixture, which was kept -20-0° with a Dry Ice-isopropyl
alcohol bath, 20. 0 g. (0. 16 mole) of benzyl mercaptan was added
dropwise. The mixture was stirred for two hours at this tempera-
ture, warmed to room temperature, and left overnight. The mix-
ture was made basic to litmus with sodium hydroxide solution.
Following separation of the layers, the toluene fraction was frac-
tionally distilled. A yield of 23. 5 g. (78% yield) of benzyl chloro-
thiolformate, b. p. 128-129°/12 mm. , was obtained.

Preparation of Benzhydryl S-Benzyl Thiocarbonate (IV).
Again using the techniques described for the preparation of I, 16. 7
g. (0. 09 mole) of benzhydrol was reacted with 16. 9 g. (0. 09 mole)
of benzyl chlorothiolformate in 40 ml. of benzene containing 7 g.
(0. 09 mole) of pyridine to yield the crude thiocarbonate. The re-
sulting liquid was chromatographed on alumina with benzene as
eluent. Subsequent removal of the benzene from the fractions led
to oils. Crystallization was finally effected by cooling very dilute
hexane solutions of the thiocarbonate. A yield of 6. 6 g. (20%) of
IV, m. p. 45-46°, was realized.

<u>Analysis.</u> Calculated for $C_{21}H_{18}O_2S$: C, 75.41; H, 5.44;

Found: C, 75.51; H, 5.49.

<u>Preparation of Benzyl S-Phenyl Thiocarbonate (V).</u> Again

following the procedure given for the preparation of I, 11.0 g.

(0.1 mole) of benzyl alcohol, 8 g. (0.1 mole) of pyridine, 40

ml. of benzene, and 17.2 g. (0.1 mole) of phenyl chlorothiolformate

were reacted to give the crude thiocarbonate. The impure product

was chromatographed on alumina, with benzene as eluent. Removal

of the benzene from the fractions led to a white crystalline solid

which was subsequently recrystallized from hexane. A yield of

5.0 g. (20%) of pure thiocarbonate, m.p. 59-60°, was realized.

<u>Analysis.</u> Calculated for $C_{14}H_{12}O_2S$: C, 68.85; H, 4.92;

S, 13.13; Found: C, 69.05; H, 5.02; S, 12.89.

<u>Preparation of p-Chlorobenzhydrol.</u> This was prepared in

96% yield by reduction of p-chlorobenzophenone according to the

procedure given in Organic Reactions (1, p. 203) for the reduction

of benzophenone to benzhydrol.

<u>Preparation of p-Chlorobenzhydryl S-Phenyl Thiocarbonate</u>

<u>(VI).</u> Into a three-necked flask, fitted with a dropping funnel and

magnetic stirrer, was placed 21.9 g. (0.1 mole) of p-chlorobenzhy-

drol, 8 g. (0.1 mole) of pyridine, and 40 ml. of benzene. After

the resulting solution was cooled in an ice bath for 15 minutes,

17.2 g. (0.1 mole) of phenyl chlorothiolformate was added drop-wise, giving the solution a yellow tinge and producing a white precipitate of pyridine hydrochloride. The mixture was stirred overnight at room temperature. The mixture was then washed with water three times, discarding the aqueous layers. Fifty milliliters of ether was added during the first washing to prevent emulsification of the organic layer. The yellow benzene layer was dried over sodium sulfate. After filtering the solution and removing the solvent under reduced pressure, the crude product was chromatographed on 200 g. of alumina, using benzene as eluent. Removal of the benzene from the fractions led to oils which were crystallized and recrystallized from hexane, yielding 9.1 g. (26%) of pure VI, which had a melting point of 95-96°.

Analysis. Calculated for $C_{20}H_{15}ClO_2S$: C, 67.70; H, 4.26. Found: C, 67.48; H, 4.36.

Preparation of p-Chlorobenzhydryl S-Methyl Thio-Carbonate (VII). Employing the same techniques described for the preparation of VI, 11.1 g. (0.1 mole) of methyl chlorothiolformate was added to 40 ml. of benzene containing 8 g. (0.1 mole) of pyridine and 21.9 g. (0.1 mole) of p-chlorobenzhydrol. The impure product was chromatographed on alumina, with benzene as eluent. Removal of the benzene from the fractions yielded oils which were

crystallized and recrystallized from hexane. A yield of 6.8 g.

(24%) of pure VII, m.p. 62-63°, was realized.

Analysis. Calculated for $C_{15}H_{13}ClO_2S$: C, 61.53; H,

4.48; Found: C, 61.50; H, 4.48.

Thermal Decomposition of I in Benzonitrile. The apparatus

utilized is illustrated in Figure 1. Tubes A, B, and F were filled

with Drierite to absorb any water originating from the nitrogen (A

and B) or produced during the reaction (F). Tube C was filled with

Ascarite to remove any impurity from the nitrogen which might be

absorbed by Ascarite. D was the reaction flask. Trap E was filled

with glass wool and was cooled in an ice bath to prevent entrainment

of solvent. G, a U-tube with stopcocks, contained Ascarite for the

absorption of the CO_2 evolved. This U-tube was weighed after an

initial nitrogen flush and again after the desired decomposition

period. The yield of CO_2 was estimated by the difference in these

weights. Bottles H and I were partially filled with mineral oil to

prevent back diffusion of air into the system.

Benzhydryl S-phenyl thiocarbonate (1.351 g., 4.23 mmole.)

and 30 ml of benzonitrile were placed in reaction flask D. After high

purity nitrogen had been swept through the solution for one hour,

the U-tube was weighed and the reaction flask was immersed in a

silicone oil bath (140-150°). Nitrogen was passed through the

solution at a slow rate throughout the decomposition. After 3.5

hours, the U-tube was again weighed. The difference in weights

was 0.188 g. (101% yield of CO_2).

For the isolation and identification of non-volatile products

the solvent was removed under reduced pressure. The residue

was chromatographed on 35 g. of alumina with 100 ml. portions of

hexane, 1:8 benzene-hexane, 1:6 benzene-hexane, 1:4 benzene-hexane,

1:2 benzene-hexane, and benzene. Fractions of 25 ml. each were

collected. Material was found in fractions II-XVIII. Fraction II

(0.106 g.) was dissolved in hexane. Upon cooling, the separation

of a small crop (0.013 g.) of crystals which had a melting point of

79-80° and a mixed melting point of 79-80° with a known sample of

benzhydryl phenyl sulfide, was noted. After evaporation of the hex-

ane, the infrared spectra of the residue from II was compared with

spectra of prepared mixtures of 75:25, 50:50, and 25:75, benzhydryl

phenyl sulfide:phenyl disulfide. By this method the residue from II

appeared to be about 75% benzhydryl sulfide and 25% phenyl disulfide.

The infrared spectra of fractions III-IX (0.902 g.) showed them to be

benzhydryl phenyl sulfide. The white solid in III-IX had a melting

point of 79-79.5° and a mixed melting point of 79.5-80° with a known

benzhydryl phenyl sulfide sample. Fractions X-XVIII (0.076 g) were

recrystallized from hexane and were shown by infrared spectrum,

melting point (210°), and mixed melting point (210°) with a known sample, to be tetraphenylethane.

There was an overall product recovery of 1.084 g. (93%). Benzhydryl phenyl sulfide (0.968 g.) was found in 83% yield. Also, 0.076 g. of tetraphenylethane and an estimated 0.022 g. of diphenyl disulfide were isolated.

Thermal Decomposition of IV in Benzonitrile.

The apparatus employed was the same as that described in the thermal decomposition of I in benzonitrile and illustrated in Figure 1.

Benzhydryl S-benzyl thiocarbonate (1.197 g., 3.6 mmole.) and 30 ml. of benzonitrile were placed in reaction flask D. Following a one hour flush with high-purity nitrogen, the U-tube was weighed, and the reaction flask was immersed in a silicone oil bath (165-175°). Nitrogen was slowly swept through the solution throughout the decomposition. After 4.0 hours, the U-tube was again weighed. The weight of CO_2 evolved was 0.146 g. (93%). A second decomposition of 1.037 g. (3.0 mmole.) of IV yielded 0.128 g (93.5% yield) of CO_2 in 4.5 hours. At the finish of both decompositions, the solution possessed a light blue color, presumably due to the formation of small amounts of thiobenzophenone.

For the isolation and identification of non-volatile products, the solvent was removed under reduced pressure and the residue

was chromatographed on 35 g. of alumina with 100 ml. portions of:
hexane, 1:8 benzene-hexane, 1:6 benzene-hexane, 1:4 benzene-
hexane, 1:2 benzene-hexane, benzene, and ether. Fractions of 25
ml. each were collected. Material was isolated in fractions I-XXVII.
Fractions II and III were combined, dissolved in hexane, and cooled,
yielding a crop of white crystals. Successive partial evaporation of
solvent from the filtrate and cooling led to a second and third crop
of crystals. The three crops (0.191 g.) were identified as benzhy-
dryl benzyl sulfide by infrared spectrum, melting point (71-72°),
and mixed melting point (71.5-72°) with a known sample of benzhy-
dryl benzyl sulfide. Evaporation of the filtrate from the third
crystallization yielded 0.017 g. of residue which could not be identi-
fied. Fractions IV-X were combined and treated similarly. The
three crops of solid (0.501 g.) were again identified as benzhydryl
benzyl sulfide by infrared spectrum, melting point (70-71.5°), and
mixed melting point (70.5-72.5°) with a known sample of benzhydryl
benzyl sulfide. Again the residue (0.031 g.) could not be identified.
Fractions XXIII and XXIV (0.073 g.) were combined and identified
as benzhydrol by infrared spectrum, melting point (68-69°), and
mixed melting point (68-69°) with a known sample.

An overall product recovery of 0.939 g. (90% yield) was
realized. Benzhydryl benzyl sulfide (0.692 g.) was isolated in 67%

yield. A small amount of benzhydrol (0.073 g.) was also found.

Kinetic Studies of the Decomposition of I, II, III, IV, V,

VI, and VII. Advantage was taken of the fact that the carbonyl

group of thiocarbonates has a strong absorption peak in the infra-

red region. III and IV absorb at approximately 1705 cm.$^{-1}$; II and

VII, at 1710 cm.$^{-1}$; and I, V, and VI at 1720 cm.$^{-1}$.

Standard solutions of the appropriate ester in the desired

solvent were examined for infrared absorption in the range 1800-

1600 cm.$^{-1}$. By measuring the optical density of the carbonyl group

peaks of the standard solutions, at the frequencies given above,

quantitative calibration curves (as illustrated in Figure 3) were

constructed (i.e. optical density was plotted against concentration

in mg./ml.).

The apparatus used for the kinetic studies is shown in Figure

2. The bottles B and C were partially filled with mineral oil to

to prevent back diffusion of air into the system. D and E were dry-

ing tubes filled with Drierite.

The desired amounts of thiocarbonate and solvent (see

Results) were placed in A. After nitrogen had been bubbled through

the solution for one hour, the reaction flask A was immersed in a

silicone oil constant temperature bath (see Results for bath tem-

perature). A stream of nitrogen was bubbled through the solution

during the entire decomposition.

After the reaction flask had been in the constant temperature bath for five minutes, a t_o sample was taken. Other samples were removed at later desired times. At the end of each run a t_∞ sample was taken.

The infrared spectra of the samples were then examined for absorption over the region 1800-1600 cm.$^{-1}$. From the intensity of the carbonyl peaks of these samples and with the aid of the appropriate calibration curve (see Figure 3), a quantitative measure of the amount of unreacted thiocarbonate versus time was obtained (see Figures 4-12).

Purification of Compounds. Previous to their use, the chlorothiolformates supplied as experimental samples by Stauffer Chemical Company were fractionally distilled. Phenyl chlorothiolformate had a boiling point of 91°/6. 5 mm. ; methyl chlorothiolformate, 110-112. 5°; ethyl chlorothiolformate, 130°.

Purification of Solvents. Bromobenzene -- The highest grade commercial product was carefully fractionally distilled, b. p. 155-156? Benzonitrile-- Solvent of the highest purity was steam distilled and the distillate was extracted with ether. The ether solution was washed with five percent sodium carbonate and was dried for 24 hours over calcium chloride and for 24 hours over sodium sulfate. The

ether was removed and the benzonitrile was fractionally distilled,

b.p. 77°/16.5 mm.

Table 20. Table of Kinetic Data$\underline{n}/$

Run 4 (I, bromobenzene, 0.085 $\underline{M}$., 145°)

time, hours	4.0	8.0	13.3	16.0	20.0	21.5
% remaining	84	67	46	37	26	21

Run 5 (I, bromobenzene, 0.088 $\underline{M}$., 145°)

time, hours	4.7	8.0	12.0	16.0	20.0	23.0
% remaining	78	64	50	38	26	21

Run 7 (I, bromobenzene, 0.048 $\underline{M}$., 145°)

time, hours	1.3	2.3	4.6	6.5	9.4	12.3	14.2
% remaining	95	87	77	66	54	36	26

time, hours	15.8
% remaining	18

Run 14 (I, bromobenzene, 0.088 $\underline{M}$., 155°)

time, hours	1.0	2.0	3.0	4.0	6.0	7.0
% remaining	88	76	65	54	33	16

Run 21 (I, benzonitrile, 0.081 $\underline{M}$., 134°)

time, hours	0.25	0.5	1.0	1.5	2.0	2.5	3.0
% remaining	92	80	58	42	32	22	18

Run 22 (II, benzonitrile, 0.084 $\underline{M}$., 155°)

time, hours	2.3	4.9	7.5	9.8	12.1	15.3
% remaining	69	37	18	8	5	2

Run 23 (II, benzonitrile, 0.083 $\underline{M}$., 155°)

time, hours	0.5	1.0	1.8	2.5	3.2	4.2	5.2
% remaining	97	91	80	70	61	48	37

time, hours	6.2	7.2	8.2
% remaining	28	19	14

$\underline{n}/$ Conditions listed following the run number are identified as follows: (thiocarbonate, solvent, concentration of thiocarbonate, temperature).

Table 20 (Continued)

Run 27 (III, benzonitrile, 0.072 M., 166°)

time, hours	0.25	0.5	0.75	1.2	1.3	1.7	2.0
% remaining	94	88	84	76	72	67	63

time, hours	2.5	3.0	3.5	4.0	9.0
% remaining	56	48	42	38	10

Run 28 (III, benzonitrile, 0.050 M., 166°)

time, hours	0.5	1.0	1.5	2.0	2.5	3.0	3.5
% remaining	89	78	74	64	58	49	46

time, hours	4.0	5.0	7.0	9.0	11.0
% remaining	39	29	19	11	5

Run 29 (II, benzonitrile, 0.060 M., 166°)

time, hours	0.5	1.0	1.5	2.0	2.5	3.0	3.5
% remaining	81	65	52	41	33	26	17

time, hours	4.0	5.0
% remaining	16	8

Run 30 (I, benzonitrile, 0.066 M., 145°)

time, min.	5	10	15	20	25	30	35
% remaining	90	80	69	60	52	46	40

time, min.	40	50	60	70	80	90
% remaining	34	26	19	15	11	7

Run 31 (V, benzonitrile, 0.072 M., 186°)

time, hours	26	49	72	98	120	144	160
% remaining	97	93	91	90	84	81	79

Run 32 (IV, benzonitrile, 0.072 M., 166°)

time, hours	0.25	0.5	0.75	1.0	1.25	1.5	1.75
% remaining	85	69	55	46	36	30	25

time, hours	2.0
% remaining	20

Table 20 (Continued)

Run 33 (IV, benzonitrile, 0.053 $\underline{M}$., 166°)

time, hours	0.25	0.5	0.75	1.0	1.25	1.5	1.75
% remaining	83	68	53	44	35	27	21

time, hours	2.0
% remaining	17

Run 35 (VI, benzonitrile, 0.087 $\underline{M}$., 146°)

time, hours	0.25	0.50	0.75	1.0	1.25	1.5	1.75
% remaining	86	69	57	46	38	30	25

time, hours	2.0	2.25
% remaining	20	16

Run 36 (VII, benzonitrile, 0.068 $\underline{M}$., 166°)

time, hours	0.5	1.0	1.5	2.0	2.5	3.0	3.5
% remaining	94	87	77	67	64	57	50

time, hours	4.0	4.5	5.0
% remaining	46	42	39

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APPENDIX

Figure 1. Apparatus for Product Studies.
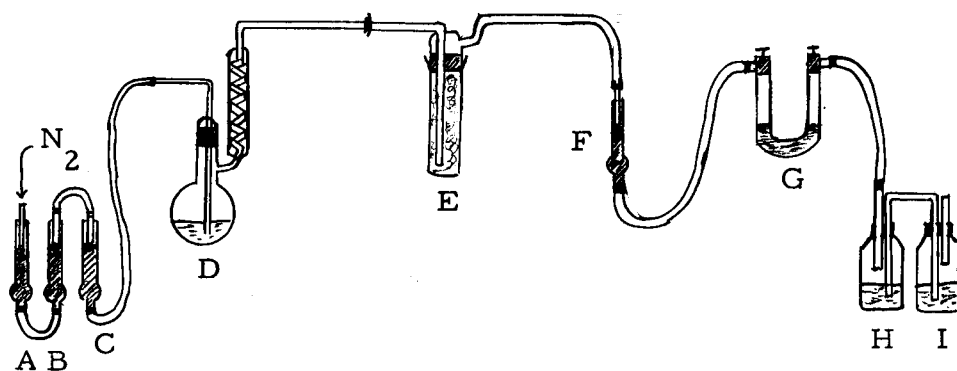
Figure 2. Apparatus for Kinetic Studies.
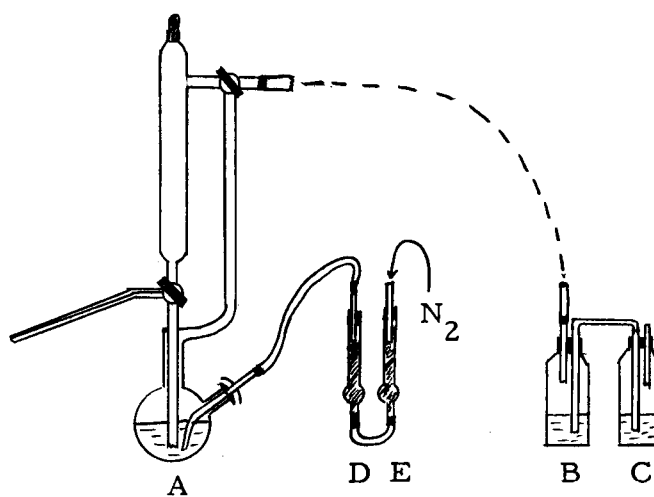
Figure 3. Sample Calibration Curves.

$\odot$ = I in Bromobenzene Solvent
$\boxdot$ = I in Benzonitrile Solvent
$\triangle$ = V in Benzonitrile Solvent
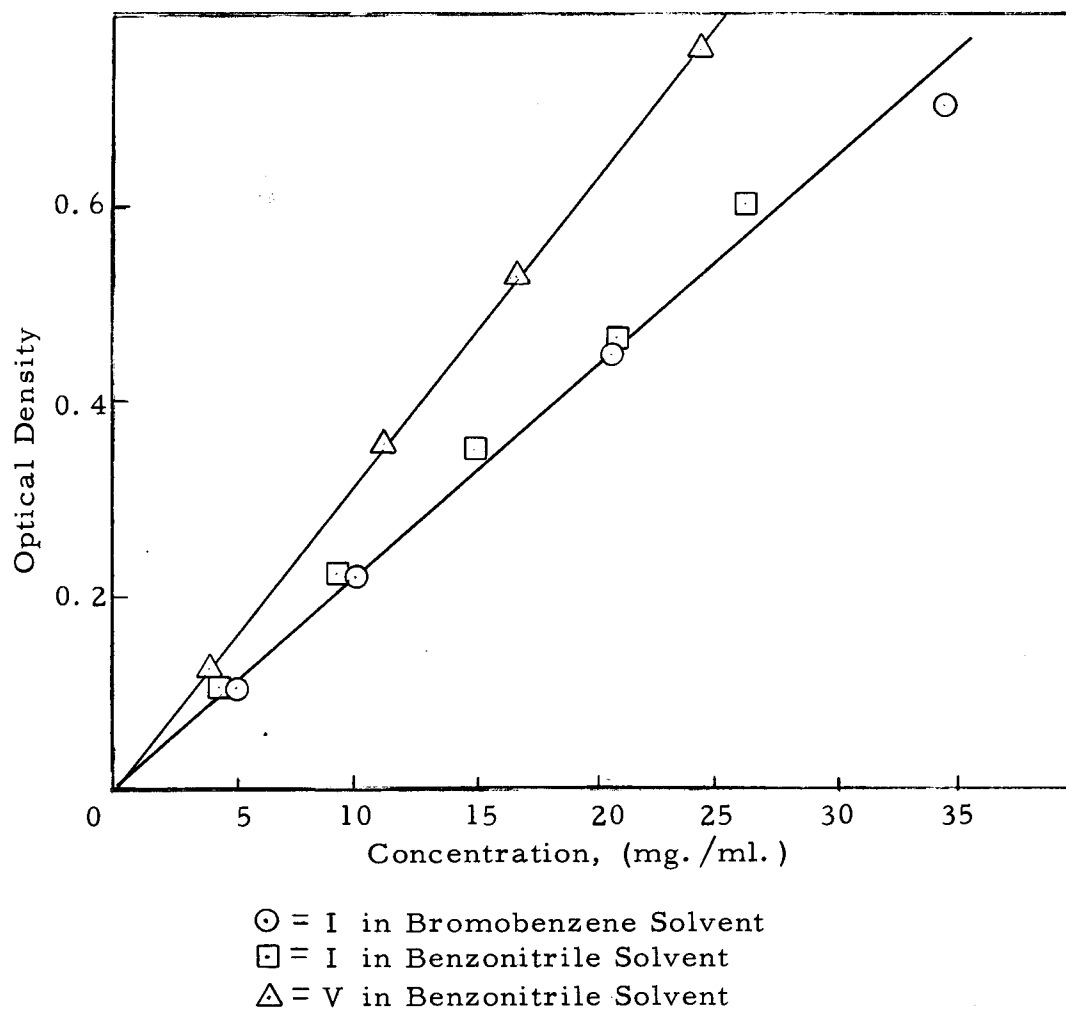
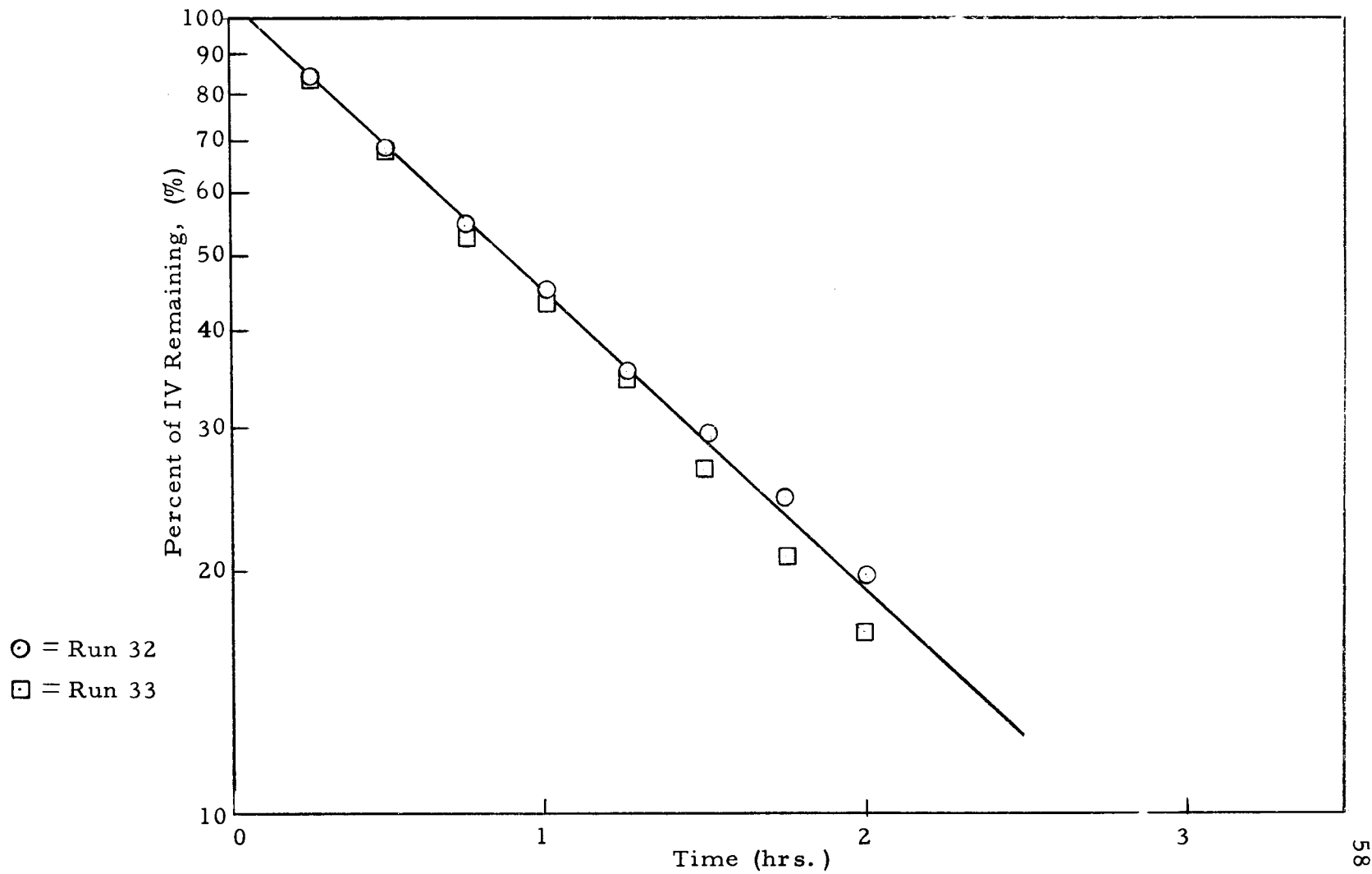Figure 4. Log of Percent I Remaining Unreacted vs. Time. (in Bromobenzene at 145°)
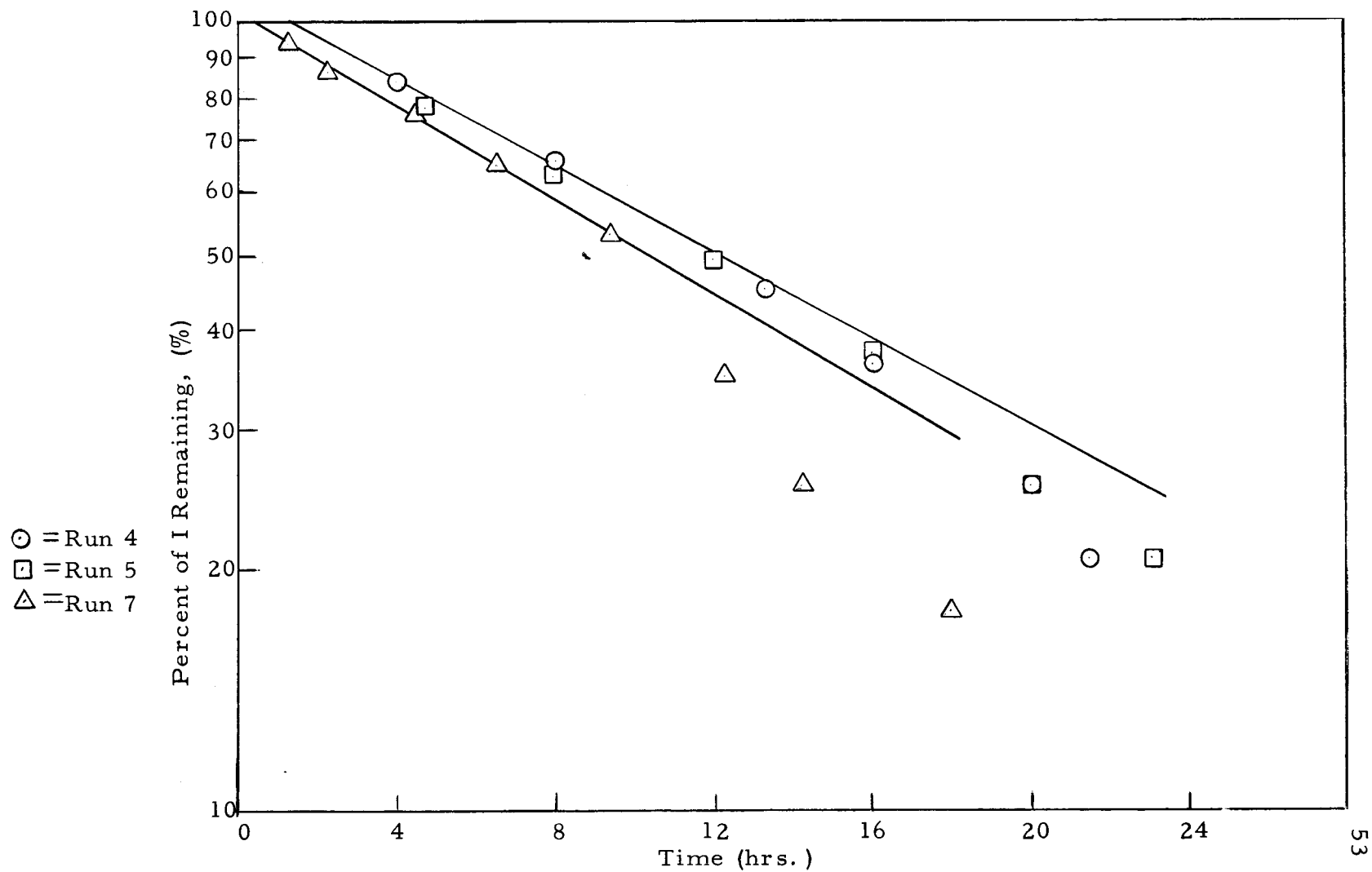
Figure 5.   Log of Percent I Remaining Unreacted vs. Time (in Bromobenzene at 155°)

⊙ = Run 14
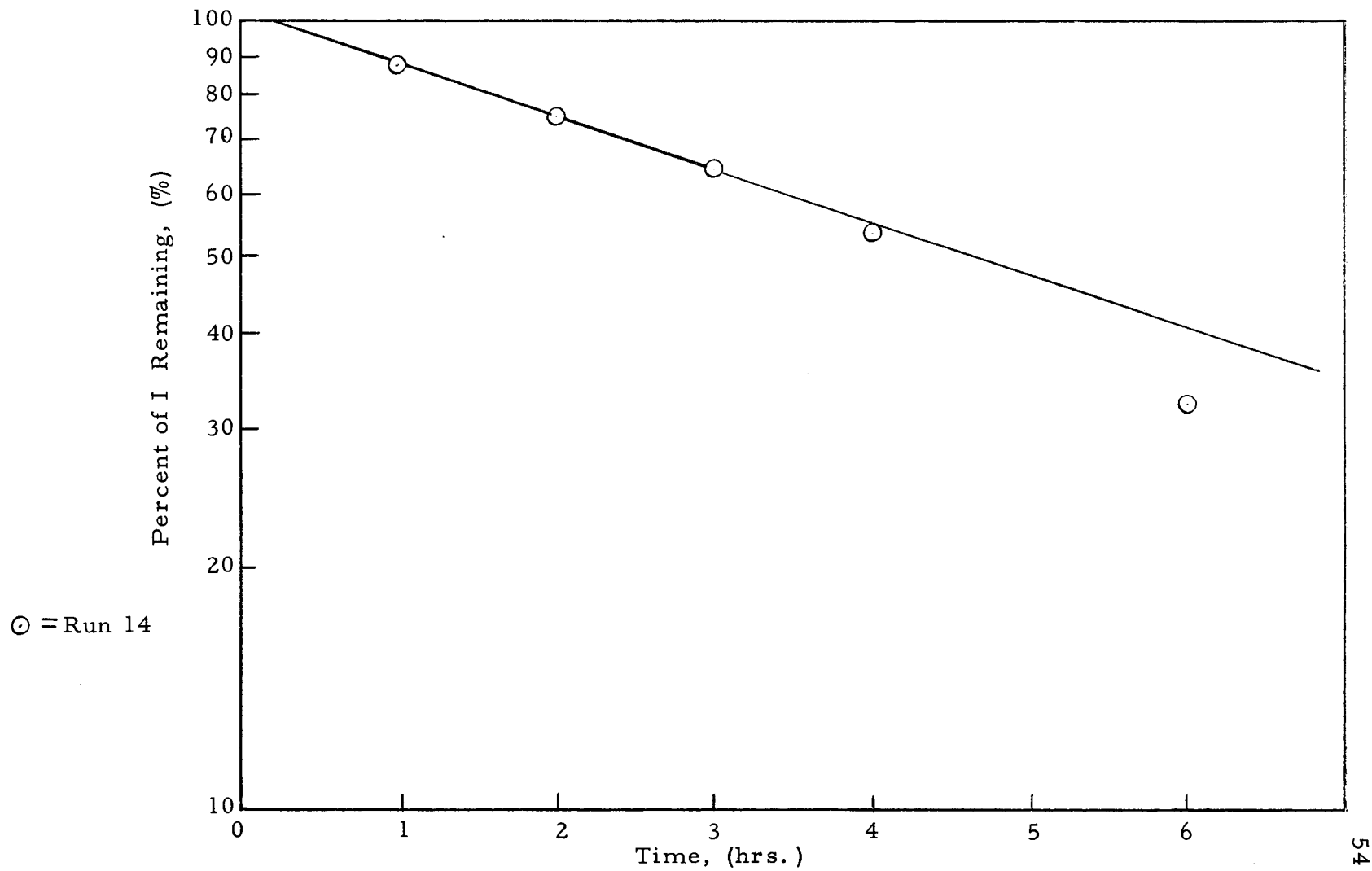
Figure 6. Log of Percent I Remaining Unreacted vs. Time (in Benzonitrile)

At 134°
⊙ = Run 21

At 145°
⊡ = Run 30

Percent of I Remaining, (%)

Time, (hrs.)
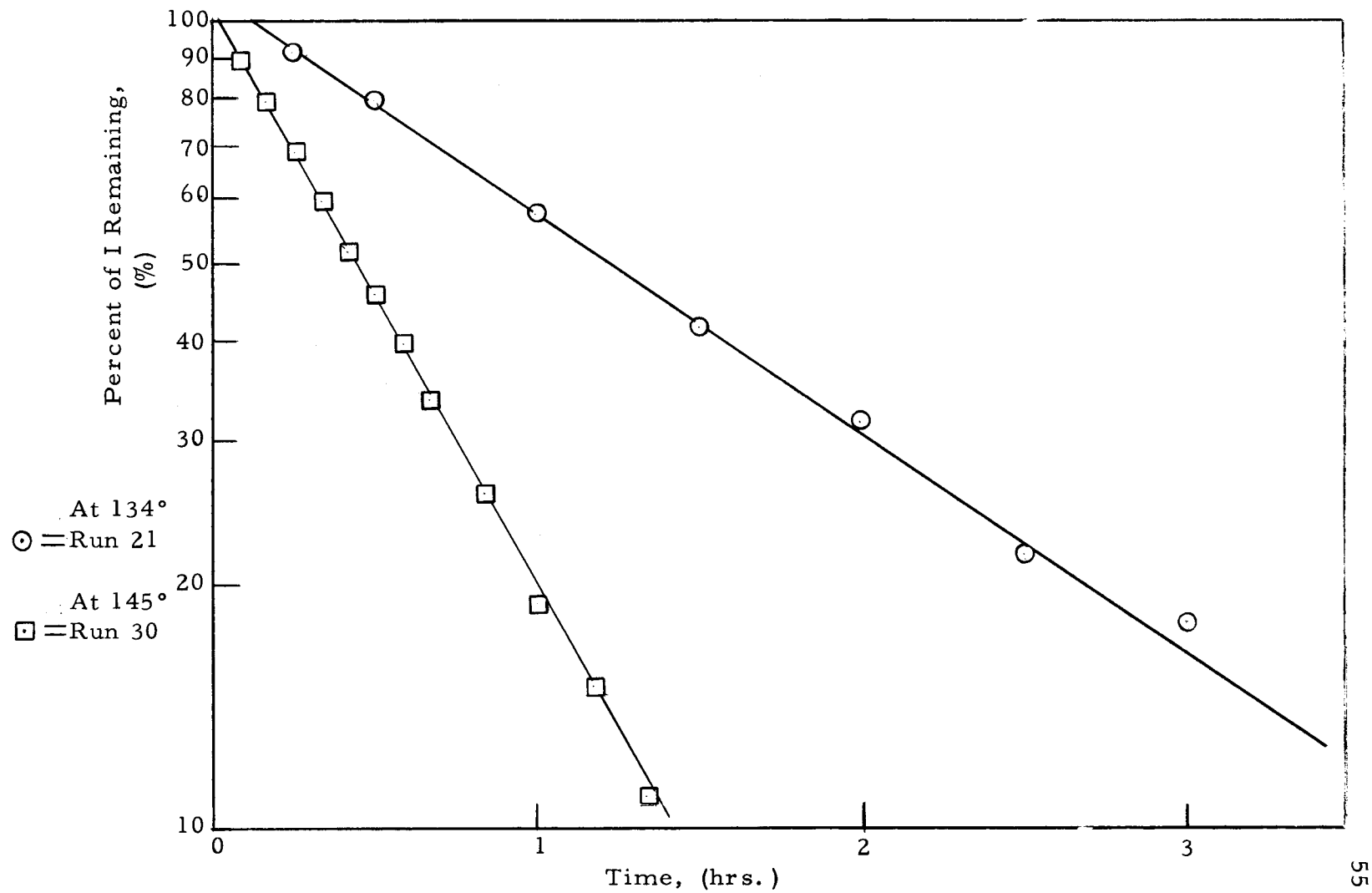
Figure 7. Log of Percent II Remaining Unreacted vs. Time (in Benzonitrile)
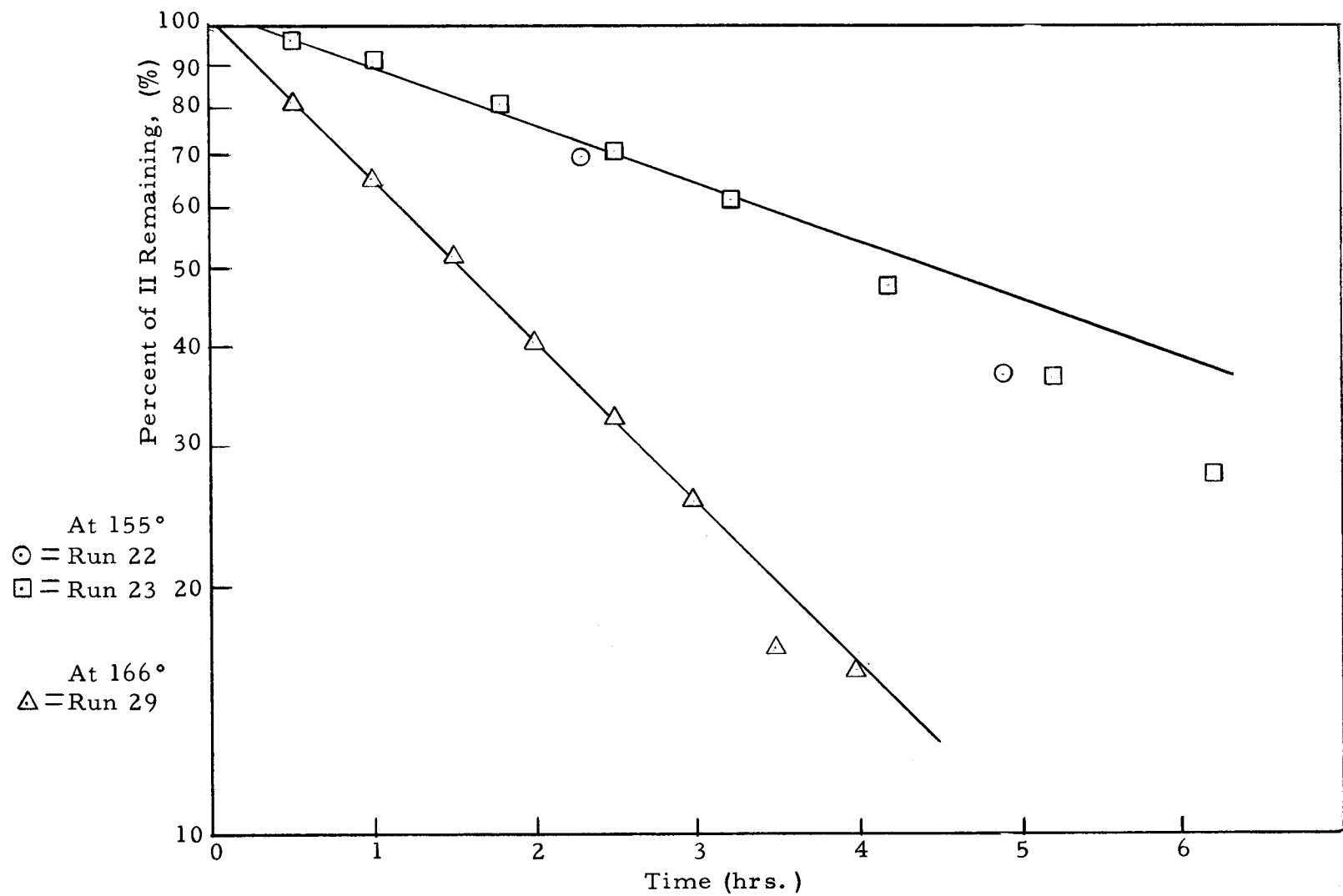
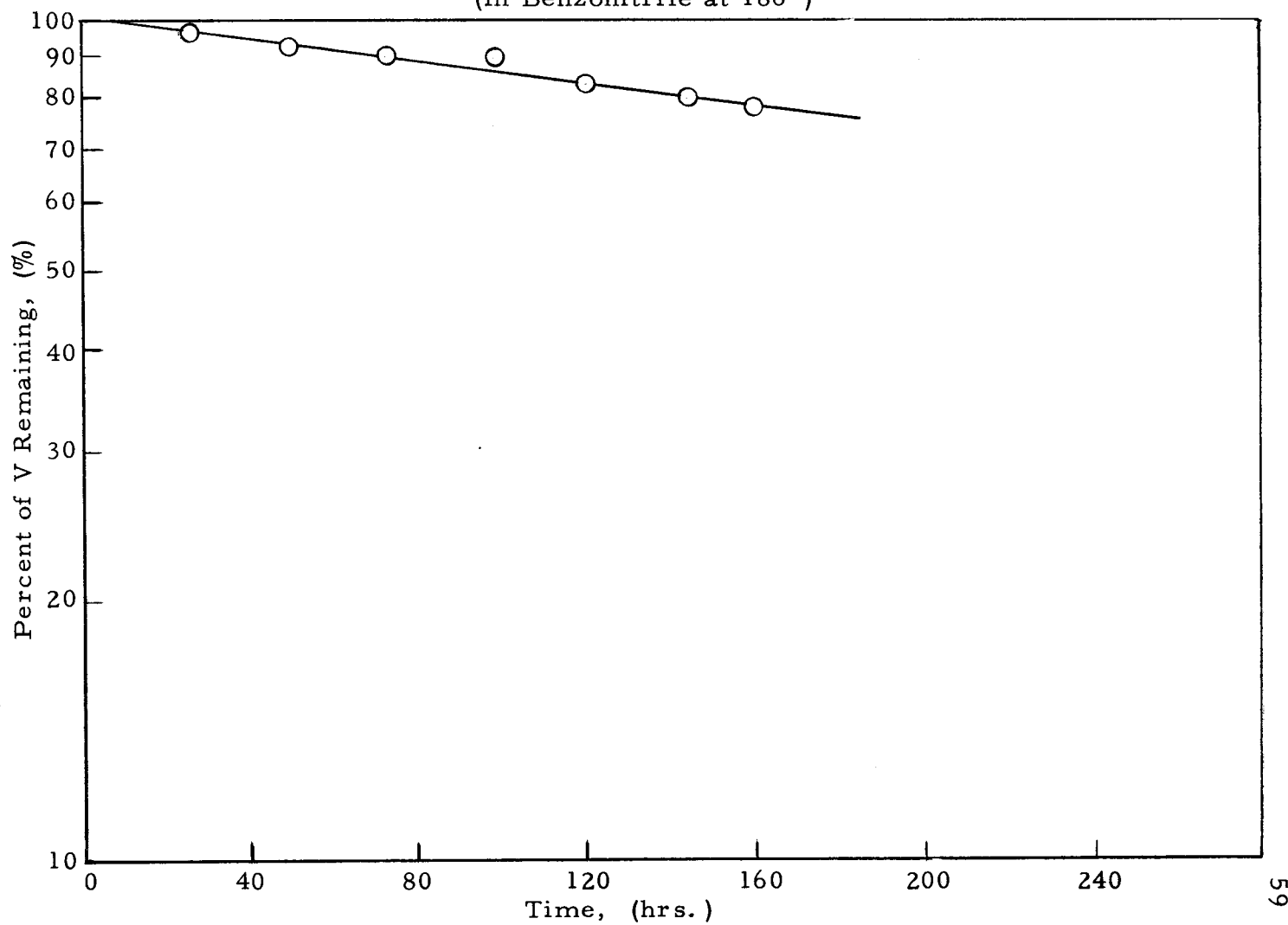Figure 8. Log of Percent III Remaining Unreacted vs. Time (in Benzonitrile at 166°)
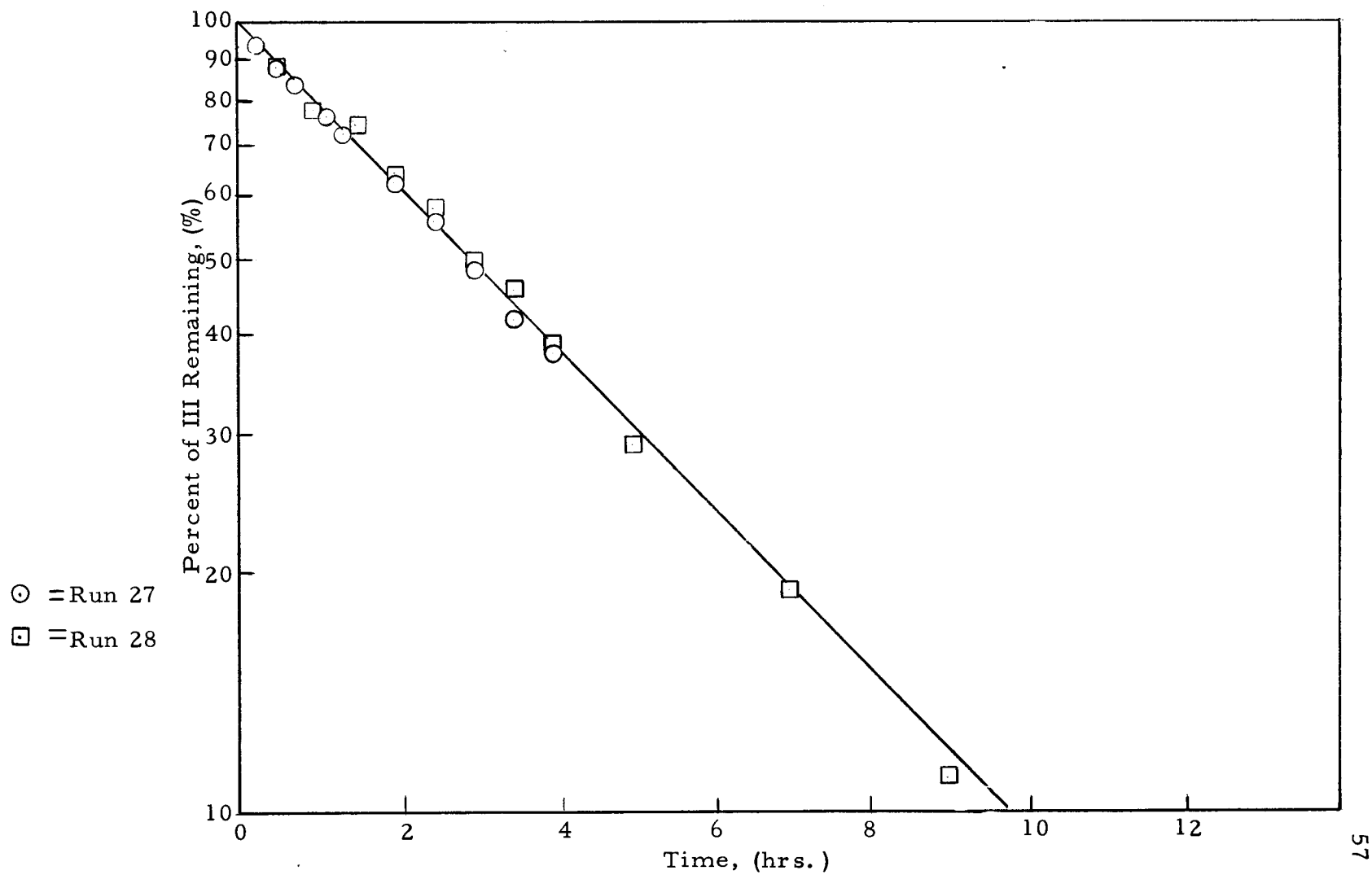
Figure 9.   Log of Percent IV Remaining Unreacted vs. Time
(in Benzonitrile at 166°)

○ = Run 32

□ = Run 33

Figure 10. Log of Percent V Remaining Unreacted vs. Time
(in Benzonitrile at 186°)

⊙ = Run 31

Figure 11. Log of Percent VI Remaining Unreacted vs. Time (in Benzonitrile at 146°)
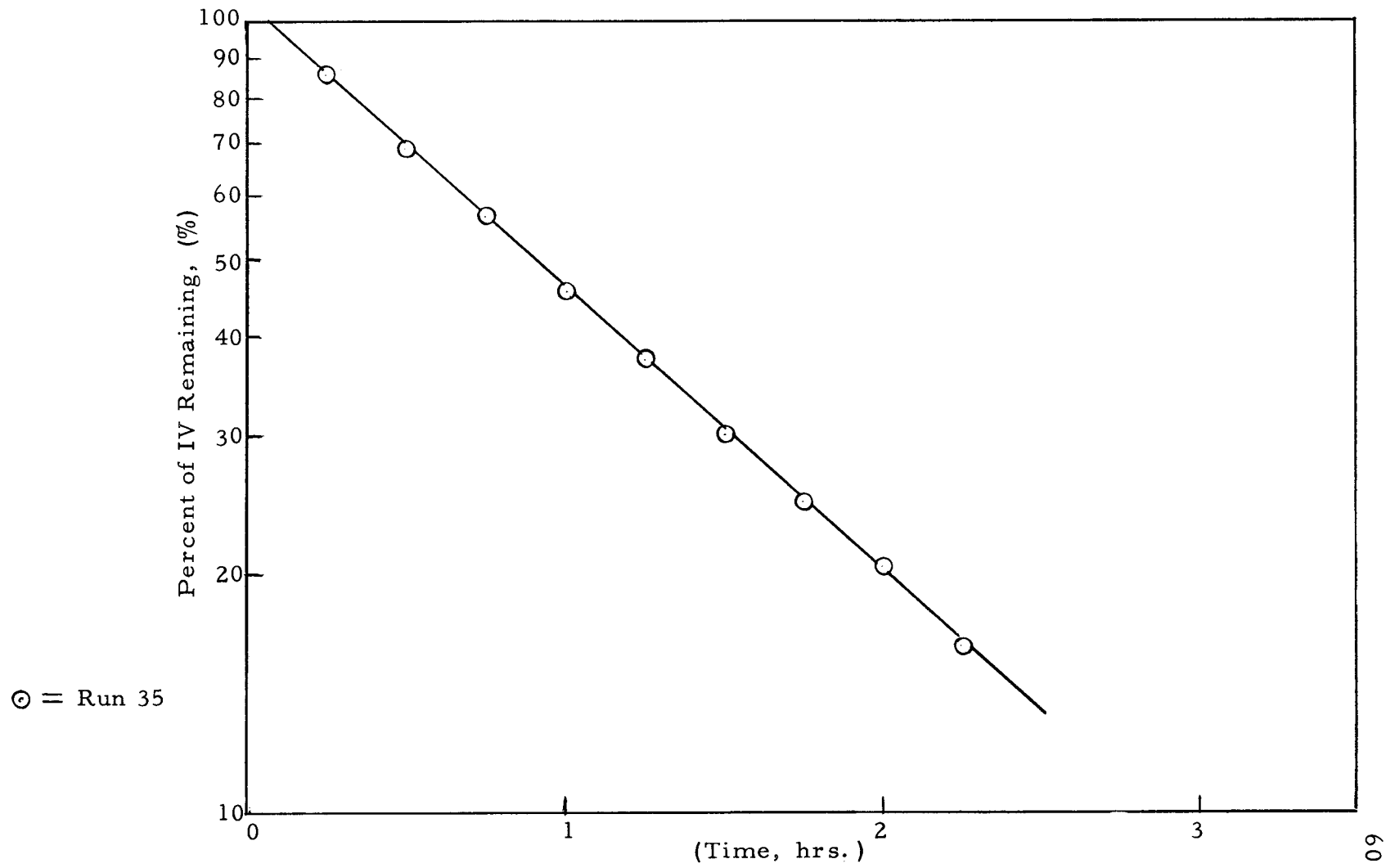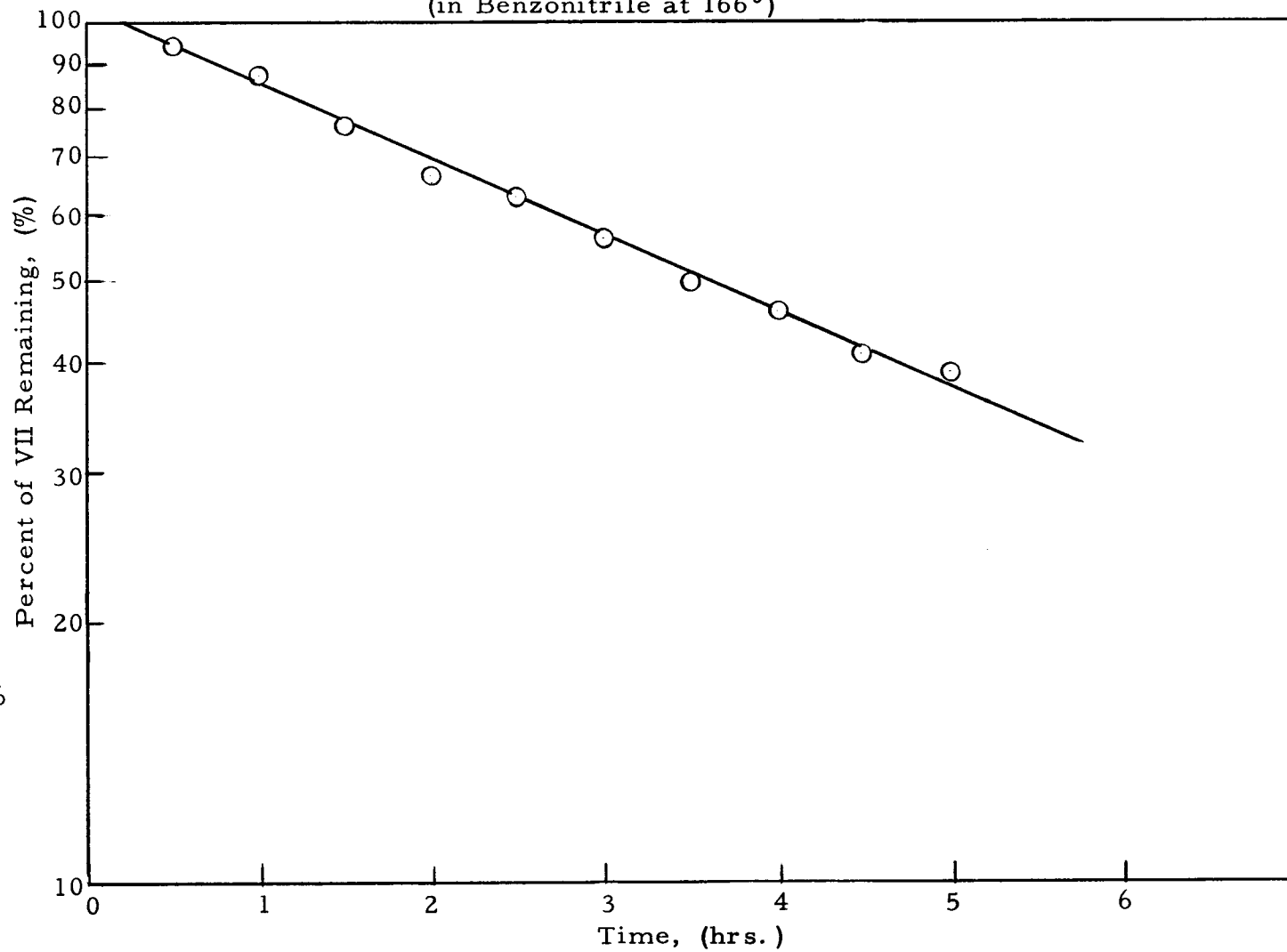
⊙ = Run 35

Figure 12. Log of Percent VII Remaining Unreacted vs. Time
(in Benzonitrile at 166°)

⊙ = Run 36

Percent of VII Remaining, (%)

Time, (hrs.)

Figure 13. Plot of Log k for Decomposition of I, II III, and IV versus Known σ* Values
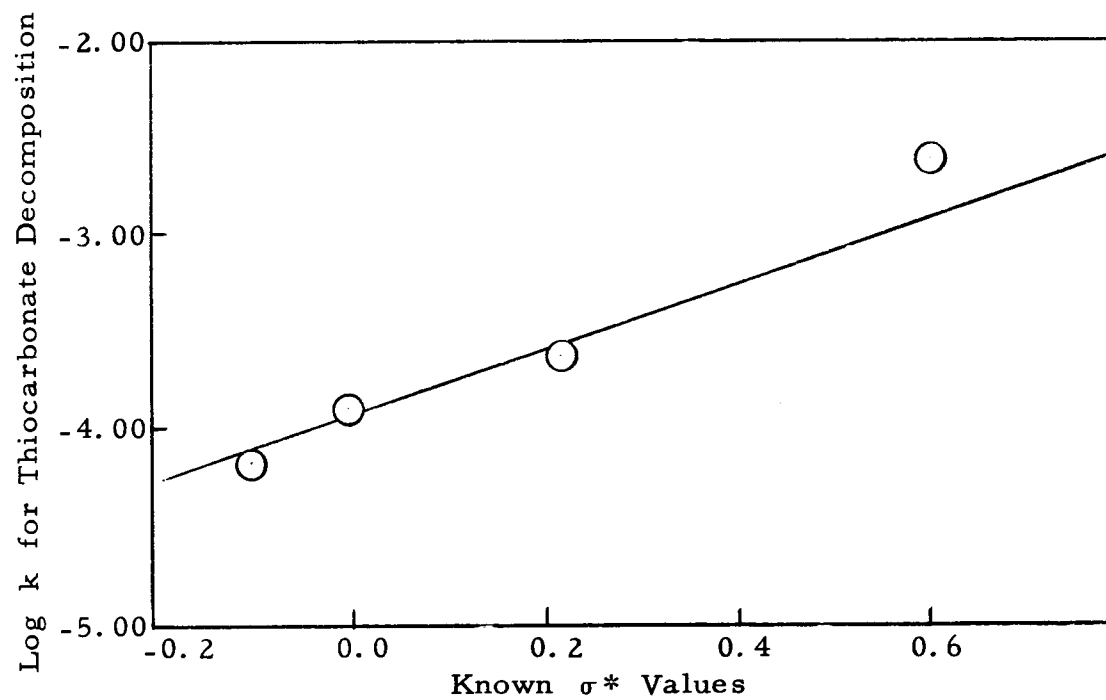
Figure 14. Plot of Log k for Decomposition of I, II, III, and IV versus pKa for the Corresponding Mercaptans