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FREE RADICAL REACTIONS AND MASS SPECTRAL STUDIES OF 2-ARYL-1,3-DIOXOLANES, 2-ARYL-1,3-OXATHIOLANES, 2-ARYL-1,3-DITHIOLANES, AND 2-ARYL-N,N'-DIMETHYL-1,3-IMIDAZOLIDINES

by

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A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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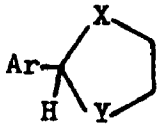
ABSTRACT

Di-t-butyl peroxide has been decomposed in the presence of compounds of structure:



I. X=Y=O; 2-aryl-1,3-dioxolanes

II. X=O, Y=S; 2-aryl-1,3-oxathiolanes

III. X=Y=S; 2-aryl-1,3-dithiolanes

IV. X=Y= NCH_3; 2-aryl-N,N'-dimethyl-1,3-imidazolidines

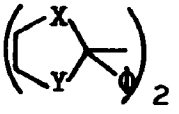
in the temperature range 100-140°C. Chlorobenzene was used as solvent. t-Butyl alcohol to acetone ratios have been obtained by gas chromatography for several members of each series whose aromatic portions were m- and p-NO_2-, m- and p-Cl-, m- and p-OCH_3-, p-CH_3-, and unsubstituted phenyl in an effort to study the sensitivity of the benzylic hydrogen to several kinds of substituents. Corrections for hydrogen abstraction reactions from non-benzylic positions were made by measuring t-butyl alcohol to acetone ratios on appropriate model compounds (e.g., 1,4-dioxanes and hetero-atomic analogues). Members of series IV all gave t-butyl alcohol to the exclusion of acetone.

The t-butyl alcohol to acetone ratios obtained in this work are compared to other t-butoxy radical reactions in a wide variety of substrates. The reactivity of benzylic positions toward t-butoxy radicals reported here all stand near the top of the list of previously studied compounds and are in the order I > II > III for the unsubstituted phenyl compounds. These values are extrapolated to lower temperatures in order to make fair comparisons with literature values.

In another set of experiments compounds of series I, II, and III were added pairwise to di-t-butyl peroxide and permitted to react.

Disappearance of benzylic hydrogen was measured directly by NMR spectroscopy for pairs whose resonance lines did not overlap. Excellent agreement was obtained between the direct and the indirect methods of determining relative reactivities.

Members of series I and IV were subjected to mass spectral fragmentation (70 ev source potential) in the absence of peroxide. A fragmentation pattern has been postulated for series IV. The fragmentation patterns for both series can be fitted to Hammett $\sigma - f$ plots, which indicate that the dioxolane series is more sensitive to substituent effects than the imidazolidine series.

Product studies from the reaction di-t-butyl peroxide and 2-phenyl-1,3-dioxolane have been reported. The main products (ethyl benzoate, benzaldehyde), require dioxolane ring opening. We have verified these experiments and also find that for 2-phenyl-1,3-dithiolane and 2-phenyl-1,3-oxathiolane the main products formed are dimeric bis-2-phenyl-1,3-dithiolane and bis-2-phenyl-1,3-oxathiolane: 

Activation parameters, Hammett $\sigma - f$ plots, and isokinetic temperature plots for hydrogen abstraction reactions and mass spectral fragmentation patterns have been discussed. Polar contributions to the transition states for hydrogen abstraction by t-butoxy radical in the several reaction series are indicated.

I. INTRODUCTION

In this section a brief survey of the literature of the chemistry of tertiary alkoxy radicals is presented. Tertiary alkoxy radicals are compared with other free radicals, especially in hydrogen abstraction reactions in solution. Some effects of structure on the reactivity of the substrate (substance undergoing hydrogen abstraction) are discussed briefly.

The reactions between free radicals and a large variety of hydrocarbons has been extensively studied in recent years. The relative reactivity of various types of hydrogens, polar and resonance contribution to hydrogen abstraction and factors which lead to radical rearrangement or decomposition have been exceptionally active areas of research. Tertiary alkoxy radicals have been studied in all these areas.[1,2] Tertiary butoxy radicals can be generated from a large variety of sources thermally or photochemically using alkyl peroxides,[3] hydroperoxides,[4,5] hyponitrites,[6] peresters,[7] nitrites,[8,9] and hypochlorites.[2]

Tertiary butoxy radicals, once they are formed, either abstract a hydrogen or decompose to acetone and methyl radicals as their predominant reactions. Williams[10] made use of these two reactions to determine the relative reactivity of hydrogens by combining the kinetic equations of the following reactions:

1) $(CH_3)_3CO^{\bullet} + RH \xrightarrow{k_a} (CH_3)_3COH + R^{\bullet}$

2) $(CH_3)_3CO^{\bullet} \xrightarrow{k_d} \text{Acetone} + {}^{\bullet}CH_3$

3) $$\frac{[(CH_3)_3COH]}{[\text{Acetone}]} = k_a/k_d\,[RH]$$

with excellent results. Brook[11] also measured the reactivity of hydrocarbons in the absence of solvent. Russell,[12] however, found that t-butyl alcohol to acetone ratios were sensitive to solvent.

Walling et al[13-16] investigated the factors which influence the β scission (Step 2) and hydrogen abstraction by tertiary alkoxy radicals.

Walling and Padwa[13] found that β scission (scission of bond β to radical site) from tertiary alkoxy radicals $RC(CH_3)_2O^{\bullet}$ were in the order R = methyl < chloromethyl < ethyl < benzyl < isopropyl < t-butyl. These results paralleled the resonance stabilization of the resulting radical. The β scission of R = benzyl appeared to be anomalously low because of the small PZ factor in the Arrhenius equation; however its activation energy of decomposition was the lowest of the series. The small PZ factor for benzyl scission was attributed to the small range of conformation which permit delocalization of the incipient radical.

Solvent effects on free radical reactions are well known in the literature. Russell[17-19] postulated a large complexing effect of the chlorine radical with aromatic solvents. Subsequently Walling[23] cast doubts on this complexing effect of chlorine radicals with aromatic solvents. The solvent order for increasing chlorine radical selectivity was t-butyl benzene > benzene > chlorobenzene, and polar solvents and olefins did not effect the selectivity of photoinitiated chlorinations. The decomposition of o-iodo-p'-nitrobenzoyl peroxide[20] and trans-γ-benzylidene butyryl peroxides[21] were found to have large solvent effects, while those for bis (β-iodopropionyl) peroxide[22] were smaller. Hendry and Russell[63] found that solvents of high polarity favored the propagation over termination reaction in the autoxidation of cyclohexene.

Raley, Rust and Vaughan[31] noticed that the activation energy for di-t-butyl peroxide decomposition changed with solvent. A more complete study showed the activation energy range to be from 30-40 kcal, and was lowest in polar solvents.[29]

Walling and Wagner[14,16] have studied the solvent effect on t-butoxy radicals in detail. The decomposition of the t-butoxy radical to acetone and methyl radicals was found to be very sensitive to solvent effects. The E_d-E_a (activation energy of decomposition minus activation energy of abstraction) was found to vary from 10.5-5.9 kcal, with polar solvents lowering the activation energy. This effect on E_d-E_a was due predominantly to changes in E_d. Hershenson and Benson[23] found the β scission (E_d) process to have an activation energy of 13 kcal in the gas phase.

The hydrogen abstraction process was found to be much less sensitive than t-butoxy radical decomposition to solvent polarity. The ρ value[26] of the reaction between t-butoxy radicals and substituted toluenes was not affected by solvent polarity. Also there was no evidence of a t-butoxy radical complex with aromatic solvents. All aromatic solvents produced hydrogen abstraction selectivities which were similar.

Discrepancies were found in relative reactivity measurements made by direct competition and measurements using t-butyl alcohol/acetone ratios using t-butyl hypochlorite as a radical source.[15] Sakurai and Hosomi[26] found that the ρ value for the reaction of t-butoxy radicals from di-t-butyl peroxyoxalate with substituted toluenes was -0.32 to -0.39 at 45°C, and was -0.75[27] at 40°C and -0.83[25] at 40°C when t-butyl hypochlorite was used. Sakuri and Hosmi[26] postulated that the difference in ρ value was due to the chlorine radical participation. Walling and

McGuinness[28] have shown that the difference in reactivities determined by t-butyl alcohol/acetone ratios and direct competition was due to interference by the chlorine radicals when t-butyl hypochlorite was used as a t-butoxy radical source.

Other sources of t-butoxy radicals avoid complication of the chlorine radical, but are not entirely free of side reactions. Di-t-butyl peroxyoxalate reacts bimolecularly with ethers producing anomalous t-butyl alcohol/acetone ratios[131] and di-t-butyl peroxide undergoes induced decomposition with alcohols.[30]

A normal sequence of hydrogen abstraction reactivities in hydrocarbon was found for the t-butoxy radical, which increases in the order primary < secondary < tertiary[24] for hydrocarbons. The same reactivity sequence was found in the allylic photochlorination of olefins.[32] Long alkyl chain hypochlorites undergo an intramolecular hydrogen abstraction which proceeds through a six member transition state producing chloroalcohols.[33] In the reaction between small ring cycloparaffins and t-butyl hypochlorite the reactivity of the C-H bond decreased with ring size.[34]

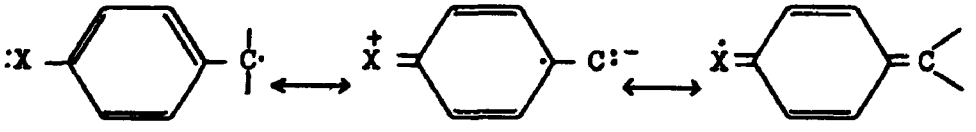
The study of polar and resonance effects in the transition state of hydrogen abstraction reactions for free radicals has been reported. Polar effects are usually measured by reacting the radical with substituted toluenes or some other series of compounds containing benzylic hydrogens. Examples of free radicals used in these studies are t-butoxy,[25,26,36-39,74] bromo,[39-45,59] chloro,[46-49,60] trichloromethyl[39,45,50-56] methyl[57,58] peroxy,[60-62,64] perbenzoate,[68] phenyl,[65,66] benzoyloxy[69] diphenylpicrylhydrydrazyl,[67] benzyl,[70] and piperidinium.[71]

The transition state of the abstraction of a hydrogen by a radical has been regarded as a resonance hybrid of the forms shown below, with electron transfer taking place in II.[72]

$$\underset{\text{I}}{R{:}H{\cdot}X} \longleftrightarrow \underset{\text{II}}{R^{+}{\cdot}H{:}X^{-}} \longleftrightarrow \underset{\text{III}}{R{\cdot}H{:}X}$$

Polar effects would be most important in II, and Russell[73] has argued that they should be more important in I than in III. In I the transition state resembles reactants and charge stabilization would not be expected to be important. As the transition state starts to resemble products charge stabilization becomes more important and the Hammett function obeys σ^{+} rather than σ values.

Polar effects observed in benzylic hydrogen abstraction reactions depend on electron affinities of radicals and the amount of bond breaking in the transition state. As the electronegativity of the radical or the bond breaking in the transition state increases, polar effects for the incipient radical become more important.[60] The resonance forms of a substituted benzyl free radical involve at least one important polar contributor.



Electronegativities of five common radicals lie in the following order chloro $>$ bromo $>$ t-butoxy $>$ trichloromethyl $>$ phenyl. The magnitude of the polar effects observed in hydrogen abstraction reactions is bromo $\sim$ trichloromethyl $>$ t-butoxy $>$ chloro $>$ phenyl, and the

discrepancy between the electronegativity order and the order of the actually observed polar effect is explained by the amount of bond breaking in the transition state.[60]

The relative reactivity of hydrogens do not always increase when phenyl groups are placed α to them. When methyl groups are replaced by phenyl the following changes take place. The substitution produces an activation which decreases in magnitude as the reactivity of the alkane increases. The benzylic hydrogen in toluene is 64,000 times as reactive as ethane, while cumene is only 130 times as reactive as isobutane.[61] As the phenyl alkanes become more reactive the increase in resonance stabilization is apparently not as important as the change in electron density. The benzylic hydrogens of 1,1-diphenyl ethane are twice as reactive as triphenyl methane, while ethyl benzene's benzylic hydrogens are more reactive than those of diphenylethane. These relative reactivities apply to phenyl, polystyrenyl and bromo radicals but not to t-butoxy and peroxy radicals.[61]

The relative reactivity of benzylic hydrogens has an inverse relationship to the f° value. The sequence of reactivity per benzylic hydrogen for benzylic hydrogen abstraction at 80°C by bromine radicals is $\phi CH_2OCH_3 > \phi CH(OCH_3)_2 >$ cumene $>$ allyl benzene $>$ ethyl benzene $>$ toluene, but the absolute value of f from each series Ar CH_2OCH_3, Ar $CH(OCH_3)_2$, cumene etc. is generally reversed.[42,44]

Gleicher[41] found that the reactivity for α, α-dimethoxy toluene is about 50 times as great as toluene at 80°C for the bromo and trichloromethyl radical, while the f values are approximately 1/3 and 1/2 as great for each radical respectively. The smaller change in f value for the trichloromethyl radical is attributed to greater bond

breaking in the transition state due to steric interaction between the reacting species. Brook[11] found similar interaction between t-butoxy radicals and aromatic hydrocarbons.

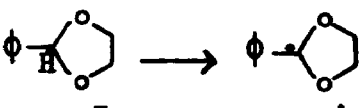
Polar effects and reactivity of ∝ substituted toluenes with trichloromethyl radicals at 80°C parallel those of the corresponding reaction with bromine radicals.[44,50] The sequence of ρ values for Ar $CHOCH_3$, Ar $CH_2OCH_2\phi$ etc. is also generally opposite that of benzylic hydrogen reactivity which is $\phi_2CHOCH_3 > \phi CH_2OCH_2\phi > \phi CH_2OCH_3 > \phi CH(OCH_3)_2$ > cumene > allyl benzene > ethyl benzene > toluene.

Russell[62] found the following relative reactivities of arylalkane and arylalkenes to peroxyradicals: 2-phenyl-1,3-dioxolane > p-methylstyrene > p-methoxystyrene > styrene > p-nitrostyrene > benzylethyl ether > dibenzyl ether > tetralin > cumeme > bibenzyl > cis decalin.

It is well known that free radicals abstract hydrogens adjacent to ethers preferentially.[68,74,76-79] The reaction of 1,1-diethoxybutane with t-butoxy radical involves the initial abstractions of the methine hydrogen followed by scission of the resultant radical.[75]

Huyser and Garcia[80] described the mechansim of the free radical reaction between di-t-butyl peroxide and 2-phenyl-1,3-dioxolane. The complete mechanism proposed by Huyser[80] is shown below:

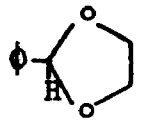
4) $(t\text{-BuO})_2 \longrightarrow 2\ t\text{-BuO}\cdot$

5) $t\text{-BuO}\cdot +$  $+\ t\text{-BuOH}$

I A

6) A ⟶ ϕ-C(=O)-O-CH_2CH_2·
B

7) B + I ⟶ ϕ-C(=O)-O-CH_2CH_3 + A

8) I + R· ⟶ 
C

9) C ⟶ ϕCHO + ·CH_2CHO
D

10) D + I ⟶ CH_3CHO + A or C

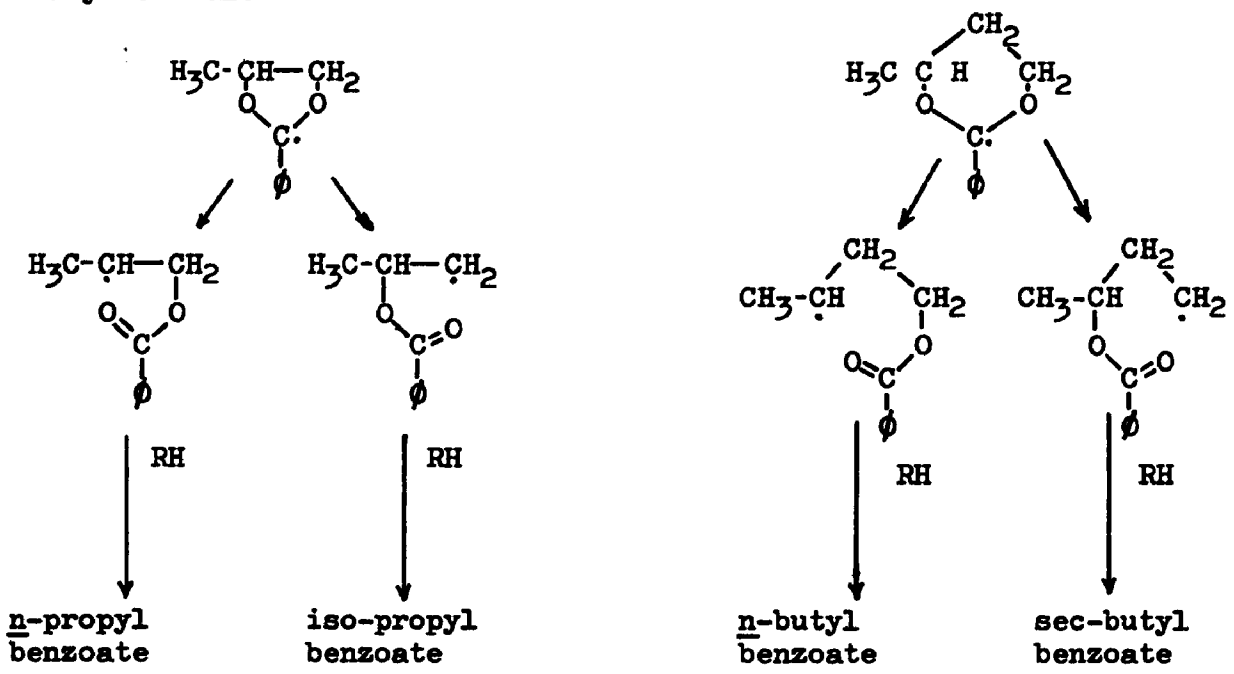
11) 2A ⟶ Termination products
2B ⟶ " "
A + B ⟶ " "

The molecular weight of the termination product was found to be almost exactly twice the weight of 2-phenyl-1,3-dioxolane. The chain lengths for the reaction between di-t-butylperoxide and 2-phenyl-1, 3-dioxolane varied from 2.0 for a 5:1 substrate peroxide ratio to 3.2 for a 21.5:1 ratio at 132°C. Reactions under similar conditions using 2-phenyl-1,3-dioxane as the substrate produced chain lengths which were shorter than those of the 2-phenyl-1,3-dioxolane. This is due to the lower reactivity of the benzylic hydrogen in a 2-phenyl-1,3-dioxane.

The reaction mechanism for the 2-phenyl-1,3-dioxane is similar to that for 2-phenyl-1,3-dioxolane shown above. Abstraction of the benzylic hydrogen leads to the formation of n-propyl benzoate, while hydrogen abstraction from a methylene adjacent to an oxygen yields benzaldehyde and propionaldehyde. There is a greater amount of carbonyl

containing termination products in dioxane reaction than the dioxolanes, 40% as compared to 30%. The chain lengths for this reaction varied from 1.03 for a 4.9:1 substrate peroxide ratio to 1.9 for a 20:1 ratio at 132°C.

Reaction between di-t-butylperoxide and 2-phenyl-4-methyl-1, 3-dioxolane and 2-phenyl-4-methyl-1,3-dioxane produced two esters for each reaction. The formation of the n-alkyl ester proceeds through a secondary radical intermediate and the branched chain ester through a primary radical.



For both of these reactions the beta scission to the secondary radical was favored by approximately 5 to one over that of the primary radical. The preferential formation of the secondary radical is due to radical stability. These two reactions had chain lengths which were longer than for the corresponding compound without the methyl group in the 4 position. The chain lengths for reactions of 2-phenyl-4-

methyl-1,3-dioxolane were longer than for reactions of 2-phenyl-4-methyl-1,3-dioxane under similar substrate to peroxide ratios. Prugh and McCarthy found that in the reaction between 2-phenyl-4-methyl-1,3-dioxolane with N-bromo succinimide (NBS) at 35-45°C the dioxolane ring opened to form the primary radical preferentially.[82]

In the reaction of mixed acetals ($CH_3C(OR)(H)(OR')$) with di-t-butyl peroxide at 135°C the relative amount of R versus R' scission correlated with radical stability, charge stabilization of the transition state and relief of steric strain.[81] The methine hydrogen of formyl ortho esters was found to be extremely unreactive, unlike the corresponding hydrogens of acetals.[83]

Benzaldehyde[84,85] reacts with t-butoxy radicals to form esters by the following mechanism:

12) $(t\text{-BuO})_2 \longrightarrow 2\ t\text{-BuO}\cdot$

13) $t\text{-BuO}\cdot + \phi CHO \longrightarrow t\ BuOH + \phi\dot{C}{=}O$

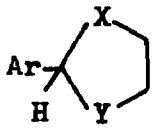
14) $\phi\dot{C}O + \phi CHO \longrightarrow \phi C(=O)\text{-}O\text{-}\dot{C}H\phi$

15) $2\ \phi C(=O)\dot{C}OCH\phi \longrightarrow$ Dimer

In a related reaction, the autoxidation of araldehydes Walling and McElhill[68] found the abstraction of the aldehydic hydrogen to be sensitive to substituent effect. A ρ value of -0.74 at 30°C was found for the hydrogen abstraction reaction by perbenzoate radicals.

In the work of this thesis attempts have been made to extend the information describing influences of structural features on hydrogen abstraction reactions at benzylic positions. The effects of heteroatoms

substituted ∝ to the benzylic hydrogen have been investigated and comparisons between heteroatom stabilization and aryl stabilization are made. The series of compounds chosen for this work were:



I. X=Y=O; 2-aryl-1,3-dioxolanes

II. X=O, Y=S; 2-aryl-1,3-oxathiolanes

III. X=Y=S; 2-aryl-1,3-dithiolanes

IV. X=Y= NCH_3; 2-aryl-1,3-N,N'-dimethyl-1,3-imidazolidines

Di-t-butylperoxide was used as a source of t-butoxy radicals and reactivities were measured in two different ways: indirectly (by the method of comparing alcohol/acetone ratios resulting from peroxide decomposition) and directly from NMR data observing the disappearance of benzylic hydrogen resonance.

Series I and IV of the above compounds were also subjected to mass spectral fragmentation (70 ev source potential) in the absence of peroxide. These results are compared with the hydrogen abstraction reactions.

II. MASS SPECTRA

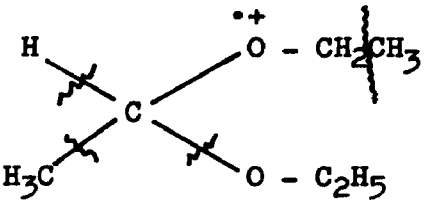
A. Decomposition patterns of 1,3-dioxolanes and 1,3-dithiolanes

Early in the course of measuring hydrogen abstraction reactions by indirect methods, it was noted that 2-aryl-N,N'-dimethyl-1,3-imidazolidines invariably gave only alcohol (no acetone) from the decomposition of di-t-butylperoxide. With such results it is possible to make only the most qualitative comparison between the imidazolidine series and the other series involving sulfur and oxygen analogs. It was decided that these several series of compounds could yield intercomparisons if subjected to mass spectral fragmentation. In part A of this section a review of the literature of mass spectral fragmentation patterns for acetals, ketals and thio analogs is presented. In part B fragmentation patterns of the imidazolidines are presented and pathways accounting for the patterns are suggested. In parts C and D data are presented for dioxolane fragmentation patterns and intercomparisons between the dioxolane and imidazolidine series of compounds are made by fitting the data to Hammett $\sigma - \rho$ plots.

The mass spectra of a large variety of acetals and ketals have been extensively studied, while information on the dithio analogues is not as abundant.[86]

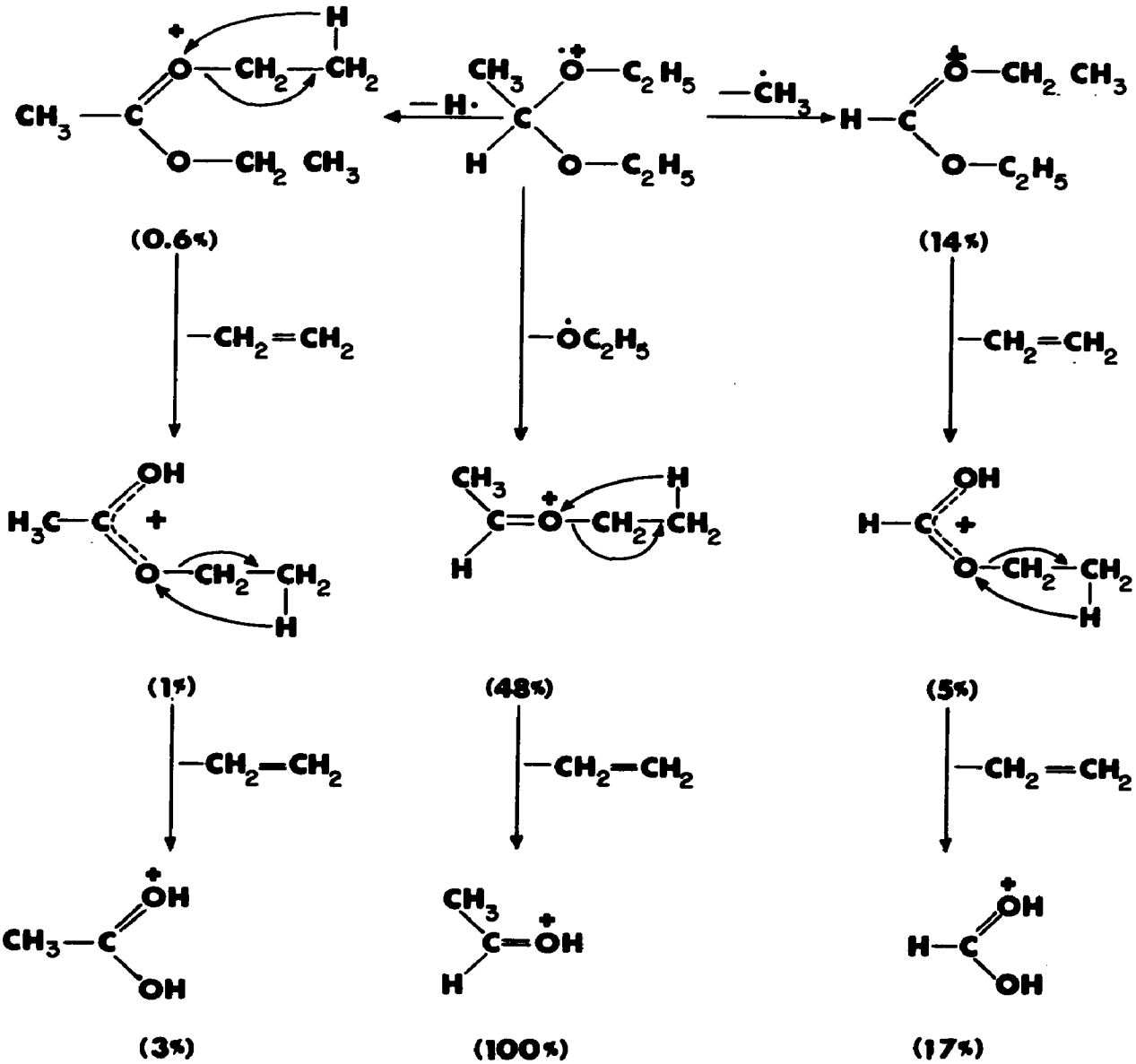
Mass spectra of acyclic acetals such as $R_1CH(OR_2)_2$ have been examined in detail.[87,88] Acetals such as these have negligible molecular ion intensities with high intensity (p-1) and (p-R_1) peaks. Where R_1 is H,CH_3 or C_2H_5 and R_2 was also an alkyl group.

The decomposition pattern of 1,1-diethoxyethane is given in Scheme I. The molecular ion can undergo cleavage at four different sites:



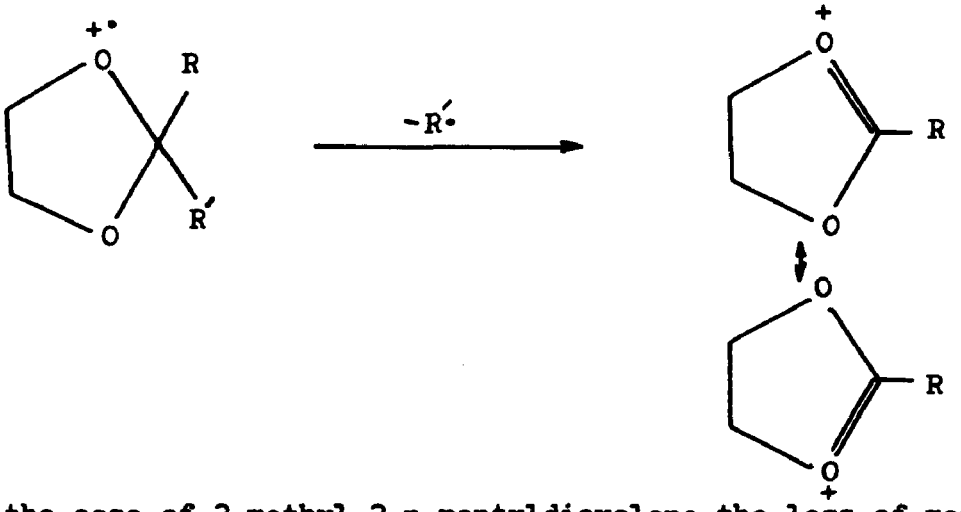
but evidence for only three of them were found (p-R_1), (p-OR_2), and (p-1).

Scheme 1



The relative abundance of these primary scissions depends on R_1 and R_2. For example an ethoxy radical is lost in preference to a methyl radical in 1,1-diethoxy ethane while in 1,1-diethoxy heptane the base peak of the spectrum corresponds to the loss of a hexyl radical.

The mass spectra of 2-alkyl or 2,2-dialkyl-1,3-dioxolanes show strong similarities to their acyclic analogues.[90,91] The molecular ion is absent and strong peaks which correspond to the loss of C-2 substituents is observed. The resulting ion is a resonance stabilized oxonium ion.

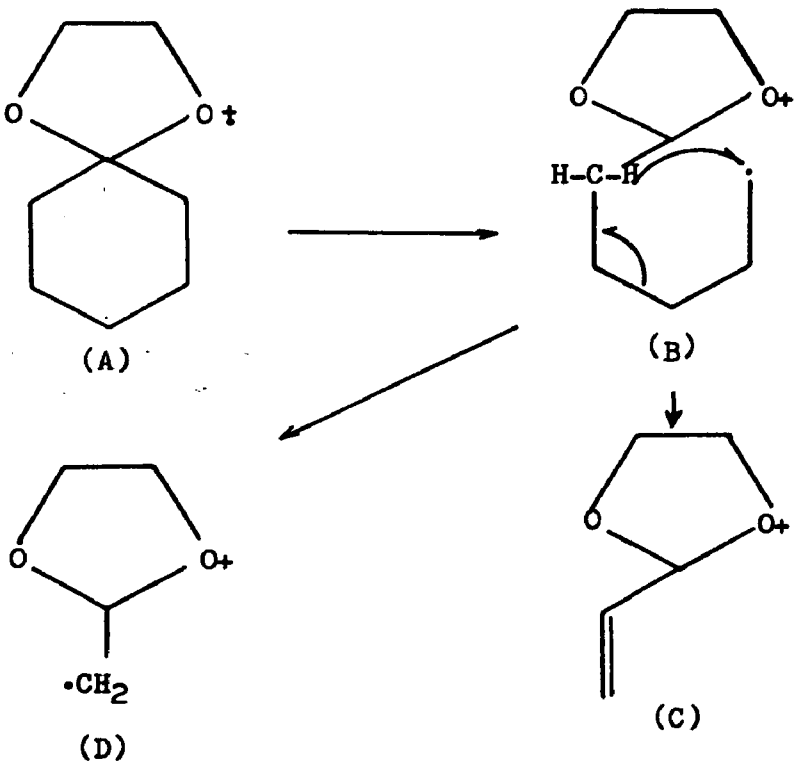


In the case of 2-methyl-2-n-pentyldioxolane the loss of methyl and n-pentyl radicals accounted for 59% of the ion current at 70 ev and 83% at 15 ev, with the loss of n-pentyl predominating.

In general[90] for 2-alkyl substituted-1,3-dioxolanes it is found that: (1) alkyl groups are lost in preference to hydrogen; (2) increased chain length facilitates alkyl elimination; (3) radical loss follows the sequence tertiary > secondary > primary; (4) branching further from the site of bond breaking is less important; (5) steric requirements (e.g. tertiary groups) may affect the correlation.

In fragmentation of spiro-1,3-dioxolanes intense peaks containing the dioxolane ring are found. Products containing unsaturated residues in the 2-position are very intense. The most important decomposition pathways for the ethylene ketal of cyclohexanone is shown below (Scheme II).[89]

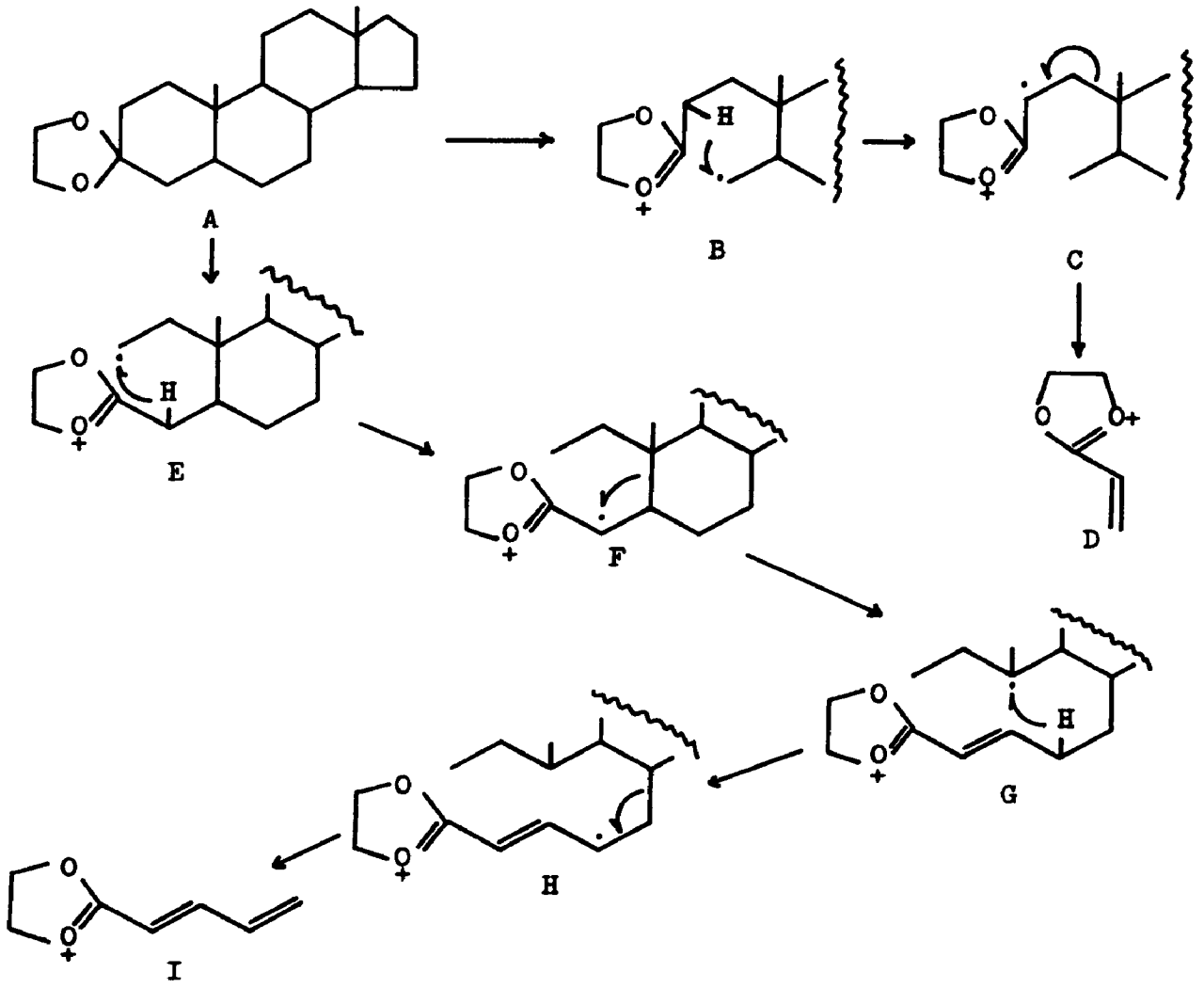
Scheme II



Fragment C (Scheme II) is the base peak in the spectrum and this peak is generally an intense peak for any compound containing a spiro -1,3-dioxolane.

The sequence of steps is similar in bicyclic and polycyclic compounds containing the spiro 1,3-dioxolane moiety.[91] Scheme III contains the mass spectra of 5α - androstan-3-one ethylene ketal and α -scission is seen to occur at both sides of the 3 position.

Scheme III



The most abundant peak in the spectrum is D followed by I in Scheme III. These ions show the importance of resonance stabilization on the oxonium ion by the unsaturated residues in the 2 position of the 1,3-dioxolane ring.

The decomposition of ethylene thioketals are analogous to ethylene ketals, except that the molecular ion is usually of greater intensity. Fragmentation pathways are identical for ethylene ketal and ethylene thioketal derivatives of steriods, but the intensity of diagnostically significant ions is lower for the sulfur analog.[92]

B. Mass spectra of 2-aryl-N,N'-dimethyl-1,3-imidaxolidines

The mass spectra of 2-aryl-N,N'-dimethyl-1,3-imidazolidines shows similarities to those of the 2-aryl-1,3-dioxolanes. The P-1 peak and the imidazolidines or dioxolane ring are very prominent peaks in these spectra. In the imidazolidine series this ring was always the base peak of the spectrum. When the imidazolidine series was run at a lower voltage (12 - 15 ev) the major peaks were the imidazolidine ring (still the base peak), and P-1 peak with ion C (Scheme IV, p. 19) and the molecular ion showing as the only other peaks of importance.

Scheme IV

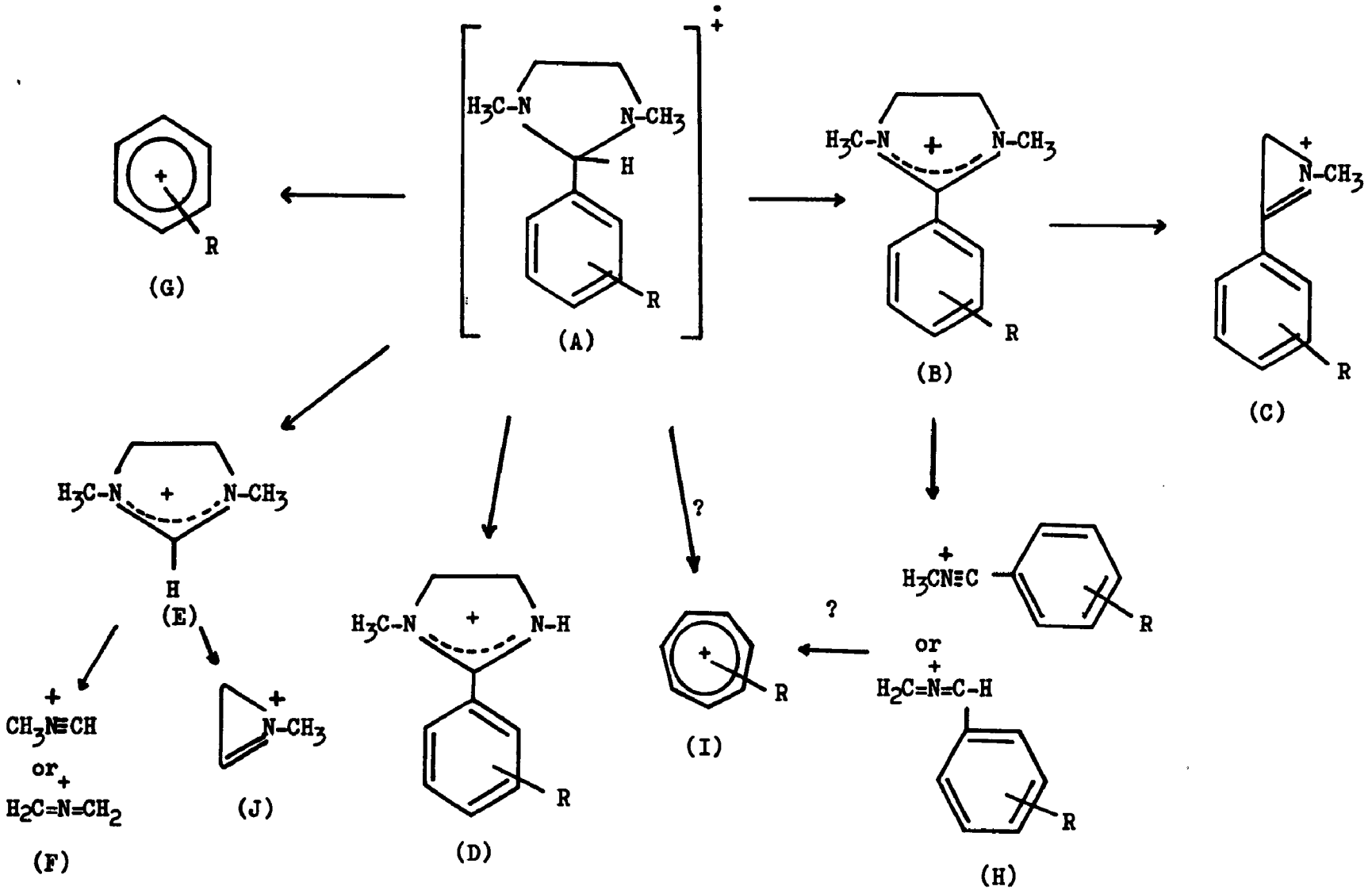


TABLE I Mass Spectral Correlations For The 2-Aryl-N,N Dimethyl-1,3-Imidazolidine Series According to Scheme IV

ION[1]	Aryl Substituent[2] H		pMe		pMeO		pCl[3]	
A	176	(8.01)	190	(13.8)	206	(18.0)	212 210	(3.34) (10.4)
B	175	(33.3)	189	(61.8)	205	(61.8)	211 209	(14.6) (41.5)
C	132	(45)	146	(47.0)	162	(72.4)	168 166	(4.23) (14.9)
D	161	(1.90)	175	(2.66)	191	(4.00)	197 195	(.84) (2.50)
E	99	(100)	99	(100)	99	(100)	99	(100)
F	42	(15.8)	42	(13.3)	42	(20)	42	(22)
G	77	(6.70)	91	(5.67)	107	(1.33)	113 111	(0.66) (2.60)
H	118	(7.28)	132	(14.4)	148	(12.8)	154 152	(3.31) (6.21)
I	91	(13.7)	105	(10.1)	121	(14.3)	127 125	(3.66) (10.6)
J	56	(4.13)	56	(3.32)	56	(5.04)	56	(7.15)

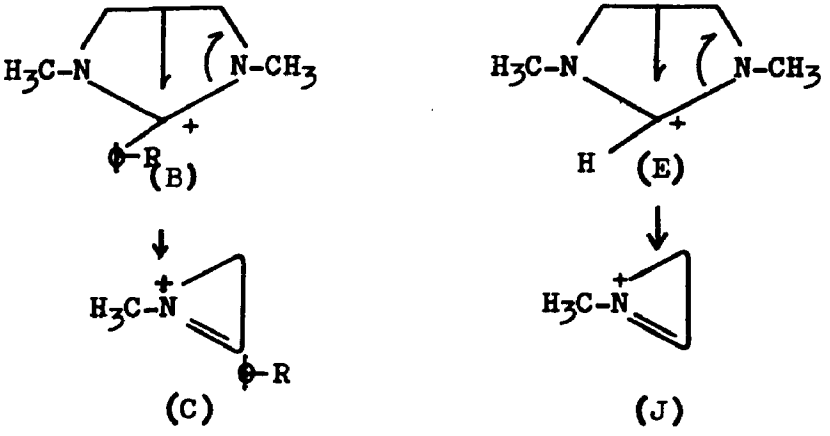
(1) According to Scheme IV

(2) M/e number (relative intensity in parenthases)

(3) 2 Isotopes of Chlorine

Scheme IV (derived from Table I) shows a likely pathway for the decomposition of the molecule.

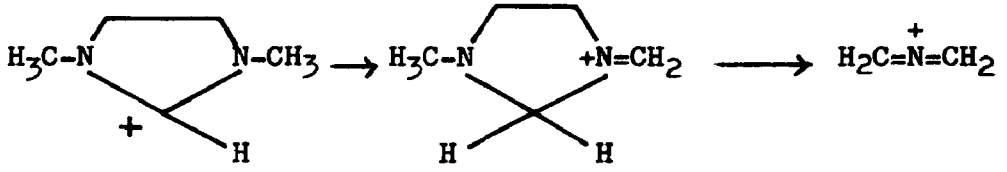
The formation of ion J from E is analogous to that of C from B. Ion C is formed in greater quantities than J. The larger quantities of ion C are probably due to the resonance stabilization of this ion with the phenyl ring. These ions are believed to arise from the following rearrangements of electrons:



The formation of ion G from the molecular ion is similar to that of ion E. The only difference is that the positive charge resides with the phenyl moiety and not the imidazolidine ring. In this series (see Table I, p. 20) there was an ion which corresponded to the loss of 15 mass units from the molecular ion. This ion is believed to be formed by the loss of a methyl group from a nitrogen atom in the imidazolidine ring, with a subsequent hydrogen imigration. In Scheme IV the hydrogen from the 2 position of the imidazolidine is the one shown to have migrated. It is possible for the hydrogen to have come from the remaining methyl group or some other part of the imidazolidine ring. Mass spectra of

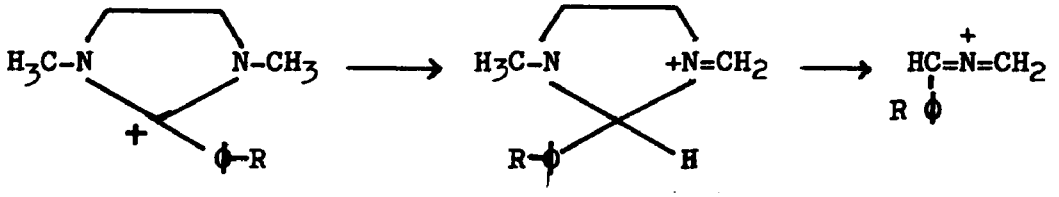
isotopically labeled compounds are necessary in order to establish exact hydrogen rearrangement if it occurs.

The formation of ion F from E is analogous to the formation of ion H from B in Scheme IV. Ion B has lost a hydrogen and ion E has lost aryl moiety from the 2 position of the imidazolidine. A possible pathway for the formation of F from E is illustrated below:



E F

In order for ion F to be formed, it is necessary for a hydrogen atom to migrate from the N-methyl group to the 2 position (imidazolidine ring) prior to the ion's formation. Analogously ion B may fragment to ion H via B'.



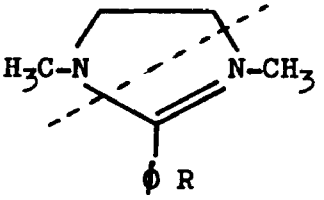
B B' H

It is possible in this reaction for ion B' to be the direct precursor of ion H. In this case the p-1 peak would correspond to the loss of a hydrogen from a methyl group instead of the benzylic carbon. It is believed that the main pathway for the formation of ion H is A → B → B' → H and not A → B' → H (according to Scheme IV).

There are alternative structures for ions F and H shown below:

H F

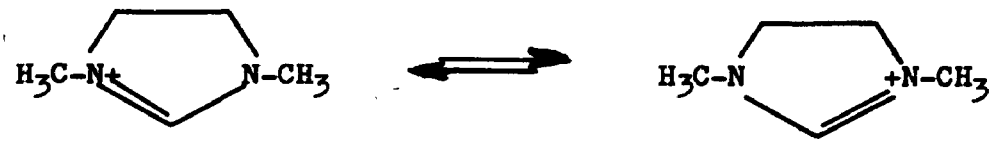
In the formation of these ions there would be no prior hydrogen migration. The ring would simply cleave as indicated:



A study of isotopically labeled compounds is also required here in order to determine which pathways are being used in the formation of ions F and H.

Meta-stable peaks were found in all the compounds used which correspond to the molecular ion producing the base peak (m/e 99). In two members of the series a metastable was found which indicated ion H going to a tropilium ion. No metastable peak was found for the transition of m/e 99 ⟶ M/e 42. This assignment was made because of the peak's appearance and its constant intensity in every spectrum.

Product stability is believed to be the driving force behind the M/e 99 peaks intensity. This ion is isoelectronic with a protonated amidine and the following resonance forms contribute to the ion's stability.

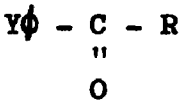


In the 1,3-dioxolane series a similar type of resonance would not be expected to stabilize the ion as effectively. This was seen experimentally by the greater variability in the intensity of the dioxolane ion in their spectra (see Table II, p. 28).

The aryl ring is much more important as a stabilizing influence in the dioxolane system than in the imidazolidine series. These factors will be discussed in greater detail in the next section.

C. Substituent Effects in Unimolecular Ion Decomposition

Correlation of data by linear free energy relationships as observed in mass spectra has been recently applied to the study of mechanisms in the gas phase.[94-103] The compounds studied in greatest detail are benzoyl compounds.



Where Y is the phenyl substituent and R is methyl, phenyl, hydroxyl and propyl.

Substituted bibenzyls and benzyl phenyl ethers also show kinetic effects of the Hammett $\sigma\sim\rho$ type. There are other systems which show little or no correlation.[104]

If a molecular ion M decomposes to a fragment ion A, the rate of change of concentration A in the ion source is given by Equation 16, where the second term on the right includes the terms for all decomposition modes of A, and the third term includes terms for real or apparent loss of A because of instrumental parameters:[101]

Equation 16

$$\frac{\delta (A)}{\delta T} = k_1 [M] - \Sigma k_2[A] - \Sigma k_{inst}[A]$$

Using the steady state approximation

$\frac{dA}{dT} = 0$ Equation 17 is obtained:

Equation 17

$$\frac{[A]}{[M]} = \frac{k_1}{\Sigma k_2 + \Sigma k_{inst}}$$

Correlations can be made between ions if common ion A is formed with the same energy distribution when it is formed from different molecular ions. Then the sum of the term on the right in Equation 17 is not dependent on the mode of formation of A.[101] If [A]/[M] is defined as Z then Equation 18 follows:

Equation 18

$$\frac{Z}{Z_o} = \frac{A/M}{A/M_o} = \frac{k_1}{k_1^o}$$

If there is a free energy relationship in formation of A from M due to substituent Y, and some other A' from M' then Equations 19 and 20 should be obeyed.

Equation 19

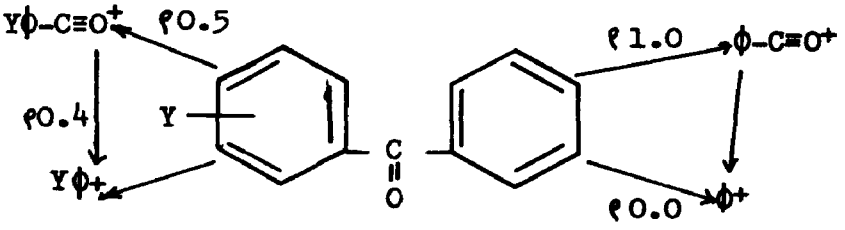
$$\log \frac{k_1^y}{k_1^o} = c \log \frac{k_1'^y}{k_o'}$$

Equation 20

$$\log \frac{Z}{Z_o} = c \log \frac{Z'}{Z'_o}$$

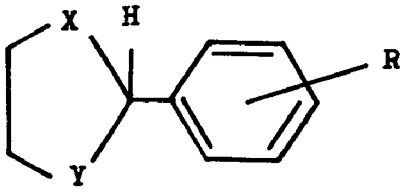
Using Equation 20 McLafferty was able to show that acetyl and benzoyl ions derived from substituted acetophenones and benzophenones respectively are formed with similar energy distributions.

The kinetic approach to benzophenone decomposition enabled McLafferty to determine the magnitude of the substituent effect through the Hammett equation, on all major decomposition pathways.



D. Results and Discussion of Substituent Affects in Unimolecular Decomposition

Compounds of the type:



(where X and Y are hetero atoms such as oxygen, sulfur and nitrogen) present some interesting prospects for the study of charge stabilization on the benzylic carbon in the gas phase as seen by the mass spectra, and for the relationships of mechanisms between heteroatomic series.

It has been reported[86] that 2-substitued 1,3-dioxolanes and 1,3-dithiolanes have as major fragments the ring with a residue in the 2 position. The spectra of 2-aryl-1,3-dioxolanes contain some differences from their 2-alkyl and 2-spiro analogues. The molecular ion in 2-aryl-1,3-dioxolanes is readily discernable although it is not in 2-alkyl and 2-spiro-1,3-dioxolanes. In 2-alkyl-1,3-dioxolanes the alkyl residue leaves in preference to the hydrogen atom.[90] The relative amount of aryl versus hydrogen lost from the 2 position was found to be dependent on the aryl substituent. The major fragments in the decomposition of 2-aryl-1,3-dioxolanes are shown in Scheme V.

TABLE II **Mass Spectral Correlations for the 2-Aryl-1,3-Dioxolanes According to Scheme V**

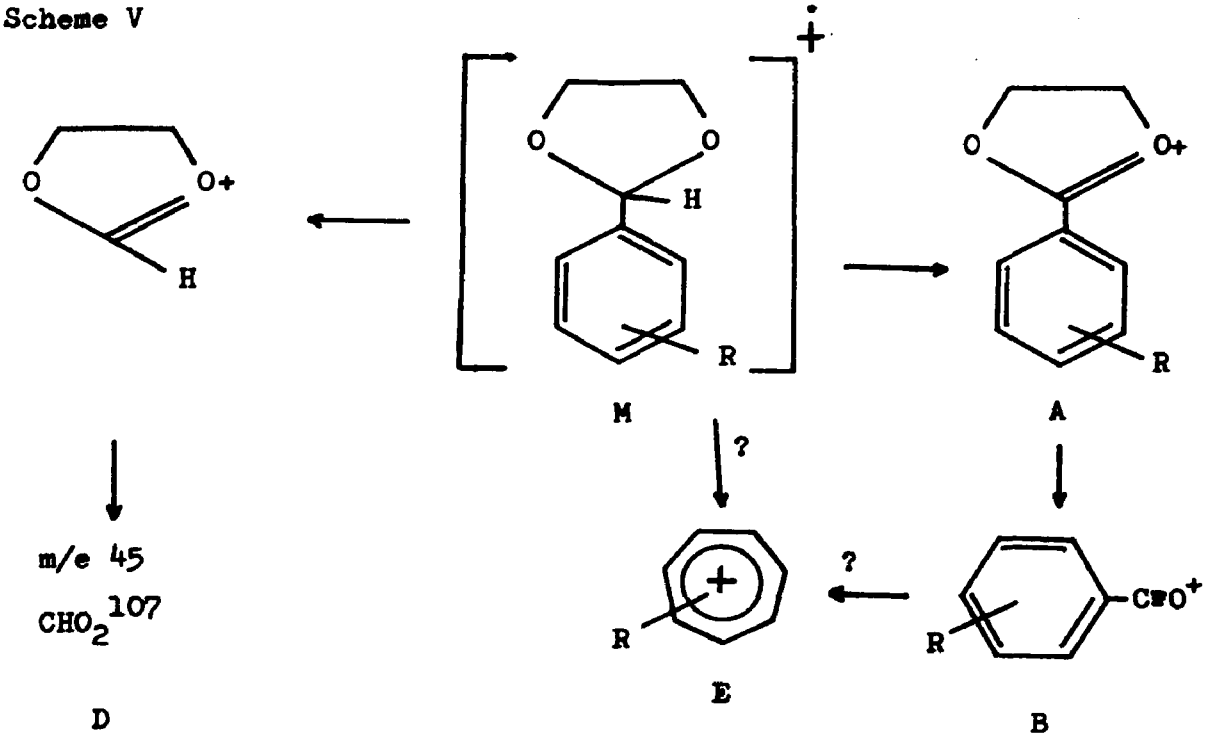
Aryl Substituents(1)

Ion	H	p-CH_3O	p-Cl	p-CH_3	m-NO_2	p-NO_2
M	36	41	59(2)	19	9.5	22
A	100	100	132(2)	68.5	53.5	78.5
B	45	76	63(2)	100	22	25
C	41.5	19	45.5	24	100	100
D	21	13	17.5	14.5	36	38
E	22	4	15.6(2)	13	11	3.5

(1) Relative Intensities

(2) Total for both isotopes

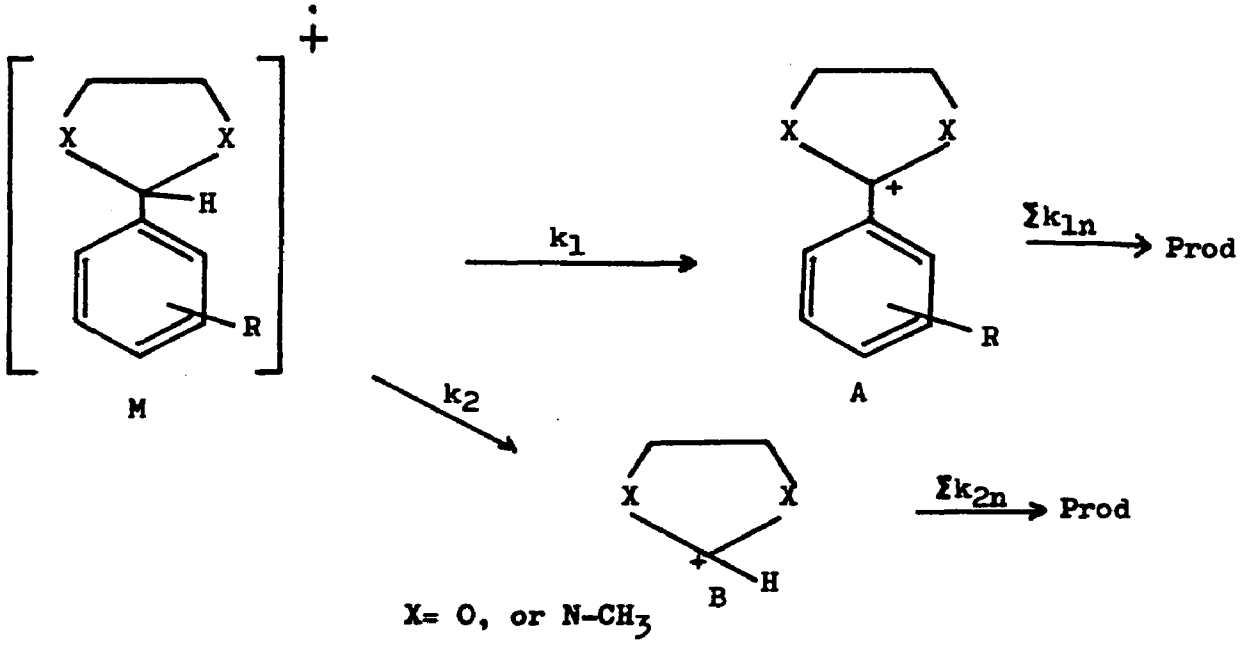
Scheme V



In all cases studied either ion A or C was the base peak of the spectrum, except for 2-(p-methyl phenyl)-1,3-dioxolane where ion C was the base peak. A meta stable peak was found at 27.8 (calc 27.7) which corresponds to m/e 73 → m/e 45 or ion C decomposing to D in every 2-aryl-1,3-dioxolane reported. In addition for all members of the series metastable peaks were found which correspond to the decomposition of A to B in Scheme V.

In the mass spectra of the dioxolanes and their heteroatomic analogues two major initial fragmentation processes are the loss of a benzylic hydrogen or the aryl moiety.

Scheme VI



If charge stabilization is important in the transition state for the loss of a hydrogen atom, then the relative amount lost should vary with phenyl substituents. And k_1/k_2 (in Scheme VI, p. 29) should correlate to some form of Hammett σ-ρ relationship.

The magnitude of the effect from series to series will depend on the heteroatoms attached to the benzylic carbon. As the heteroatoms become more effective in stabilizing charge on the benzylic carbon, the contribution to stabilization by the aryl moiety should become less. This effect should be reflected in the magnitude of rho values between the series tested.

The free energy relationships can be obtained from ion abundances and standard chemical kinetic arguments. Application of the steady state approximation to ions A and B in Scheme VI produces Equations 21 and 22:

$$(21) \quad k_1[M] = \Sigma k \text{ inst } [A] + \Sigma k_{1n} [A]$$

$$(22) \quad k_2[M] = \Sigma k \text{ inst } [B] + \Sigma k_{2n} [B]$$

Where the first term on the right is for losses of A and B due to the instrument, and the second term all decomposition paths of these ions (Scheme VI, p. 29).

The ratio of k_1/k_2 is given in Equation 23:

$$(23) \quad \frac{[A]}{[B]} = \frac{[\Sigma k \text{ inst} + \Sigma k_{2n}] k_1}{[\Sigma k \text{ inst} + \Sigma k_{1n}] k_2}$$

If B is formed with the same energy distribution from each molecular ion then the numerator of the coefficient on the right is not dependent on the mode of formation B.[94] Good correlations for fragments containing substituents can be obtained if $\Sigma k \text{ decomp} \sim 0$. Instrumental parameters are known not to vary greatly from compound to compound.[100] Under these simplifying conditions Equation 23 becomes Equation 24:

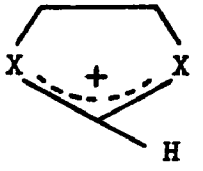
(24)
$$Z = \frac{[A]}{[B]} = \frac{k_1}{k_2}$$

where k's are composite rate constants in which decomposition path's k_n's are included.

If the magnitude of Z changes in a predictable way with different phenyl substituents, than the magnitude of this effect can be found from the Hammett relationship in Equation 25:

(25)
$$\log \frac{Z}{Z_o} = \sigma \rho$$

The 2-aryl-1,3-dioxolane and 2-aryl-N,N'dimethyl-1,3-imidazolidine show as major fragments the P-1 peak and the positively charged heteroatomic ring:



X = O, or N-CH_3

If the transition state leading to the formation of these ions is similar from one series to another then a free energy relationship as Equation 26 should be obeyed.

(26)
$$\log (Z/Z_o) = K \log (Z/Z_o)'$$

It is assumed here that the first terms of Equations (21) and (22) are negligible; and that the second terms arise from ions A and B (Scheme VI, p. 29) plus their assumed breakdown products. Equation (24) becomes:

$$Z = A/B = [E+A+B]/[C+D] = [B+C+H+I]/[E+F+J]$$

Scheme VI Scheme V Scheme IV

Z/Z_o refers to Scheme V, the dioxolane series.

$(Z/Z_o)'$ refers to Scheme IV, the imidazolidine series.

Z_o refers to unsubstituted compounds.

Z refers to substituted compounds.

FIGURE I: A Plot of Mass Spectra Peaks Z = [(E)+(A)+(B)] / [(C)+(D)] For 2-Aryl-1,3-Dioxolanes According to Scheme V

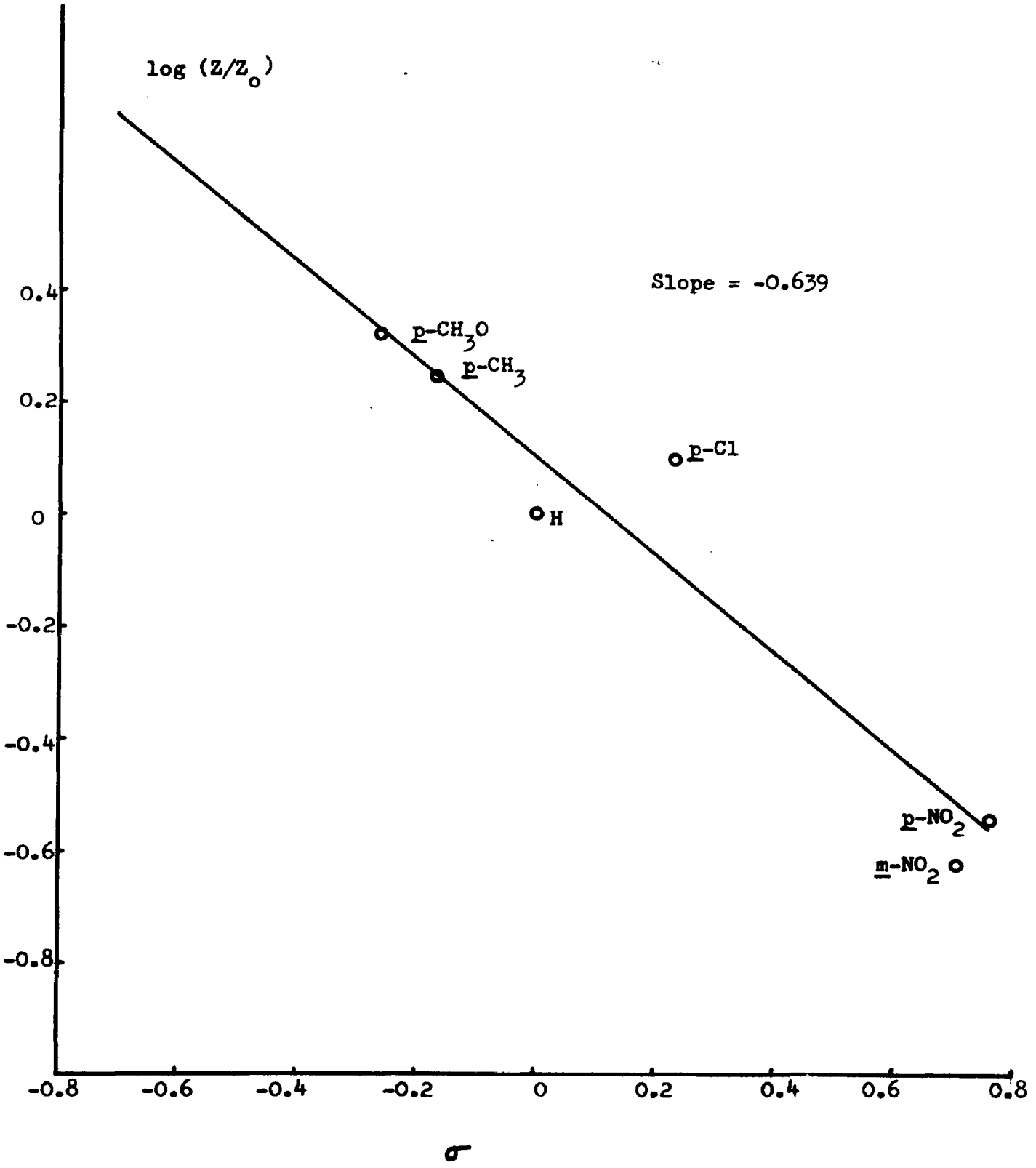


FIGURE II: A Plot of Mass Spectra Peaks of 2-Aryl-N,N' Dimethyl-1,3-Imidazolidines Where Z = [(B)+(C)+(H)+(I)] / [(E)+(F)+(J)] According to Scheme IV at 70ev

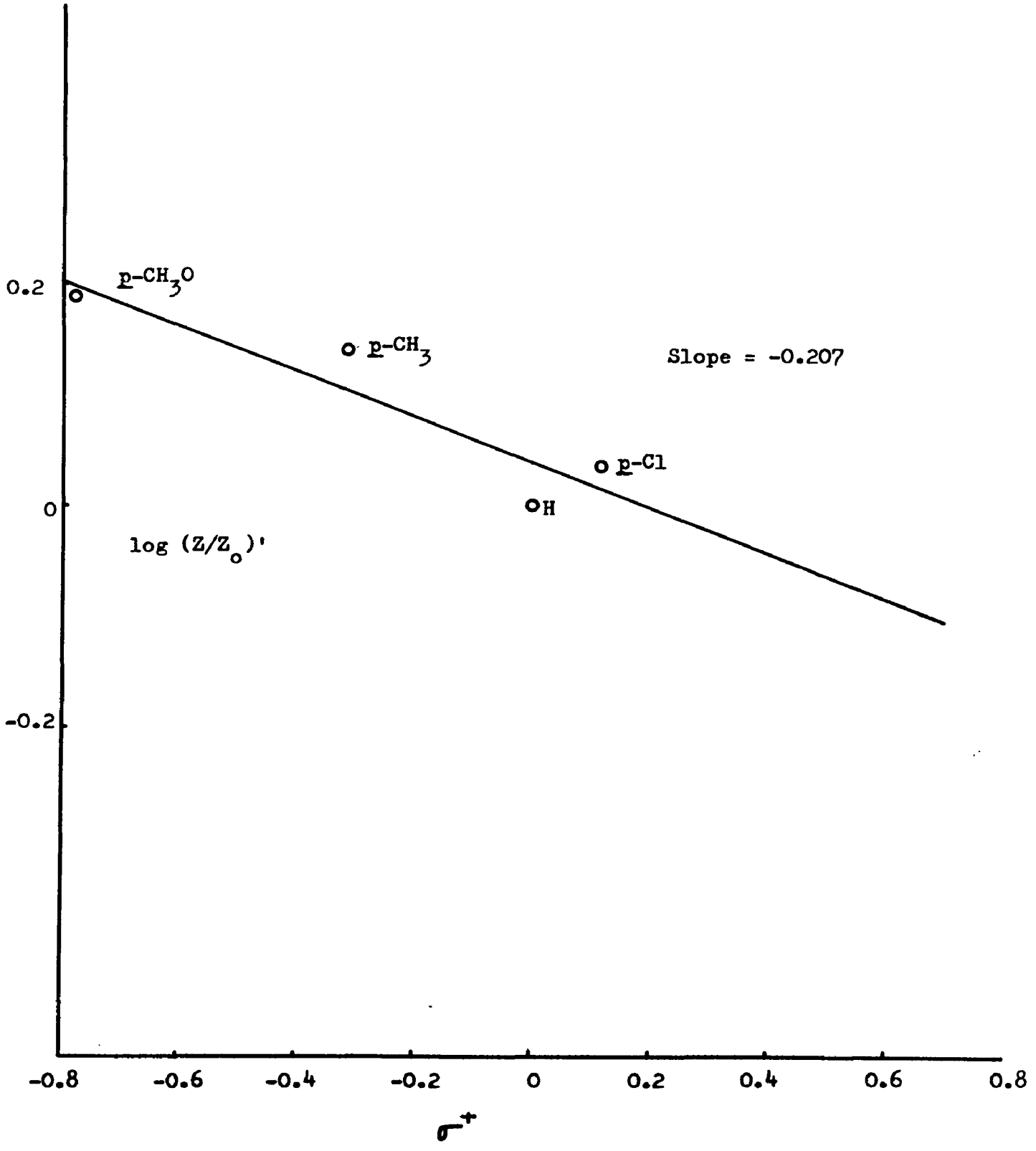


FIGURE III: Free Energy Plot of Imidazolidine Series vs Dioxolane Series

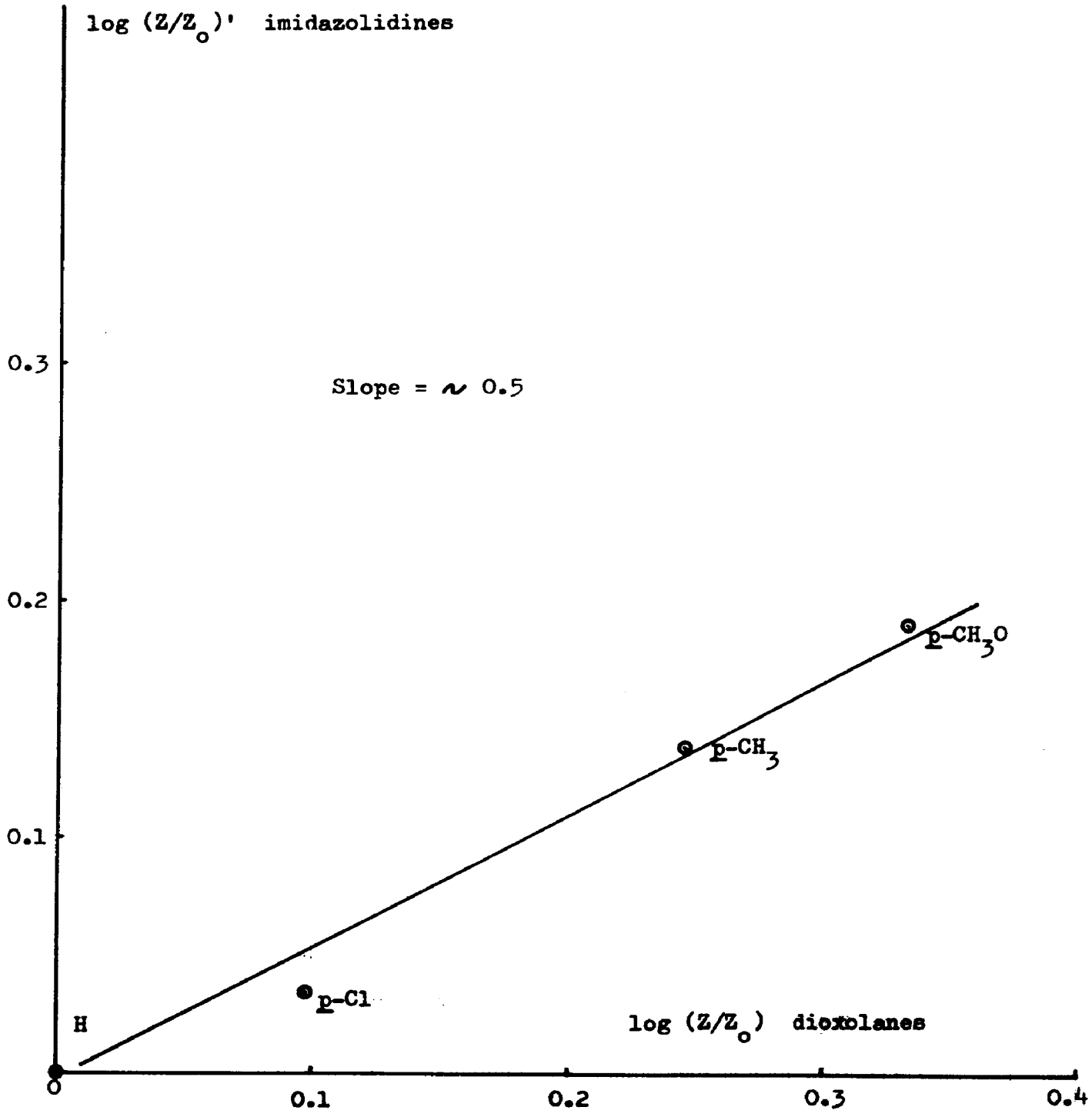
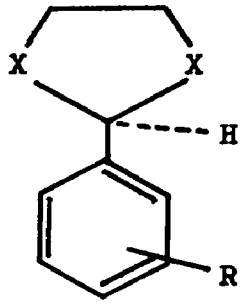


Figure I shows a plot of log (Z/Z_o), for the dioxolane series, versus σ in a Hammett plot. A ρ value of -0.871 (correlation coefficient -0.962) was obtained with only modest scatter. Figure II shows a similar plot of log (Z/Z_o) for the imidazoldine series versus σ^+ .[108] A ρ value of -0.207 (correlation coefficient -0.930) is obtained also with little scatter. Hammett plots of the dioxolane series versus σ^+ and the imidazolidine series versus σ produced figures with correlation coefficients of -0.940 and -0.825 respectively. Failure to include the secondary ions in calculations of ρ produced graphs with more scatter.

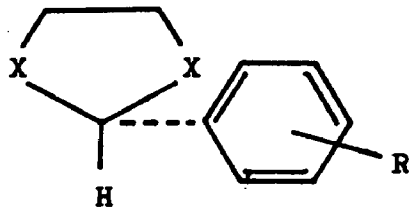
The negative slopes in Figures I and II indicate that the phenyl ring substituent affects k_1 more than k_2 in the two cases studied. This can be rationalized as follows:



X = O or N-CH_3

The transitions state resembles product more closely than the reacting ions,[109] which means that there will be high concentration of localized charge on the benzylic ion in the transition state. Electron donating groups on phenyl rings are known to stabilize positive charge and facilitate these reactions.

The substituent effect should be much less important in the transition state leading to products in reaction two (from Scheme VI, p. 29).



X = O, or N-CH_3

Bond-breaking is well underway so that the phenyl ring substituent is not as effective in charge stabilization as it is in the case of the hydrogen bond-breaking. In this reaction electron donating groups would still be expected to cause a rate enhancement.

The fact that the slope is negative shows that k_1 is affected more than k_2 as expected. If the phenyl ring substituent effect was more important in reaction 2 the Hammett plot would have a positive ρ value, since the direction of change is the same in k_1 and k_2. A slope of zero would indicate no substituent effect in k_1 and k_2 or one that was of the same magnitude for both.

The good correlation indicates that the phenyl rings are intact and that the geometry of the ring has not changed. The molecules also are not in electronically excited states. Compounds in electronically excited states generally produce poor Hammett correlations.[110] Figure III shows the relationship between the imidazolidines and the dioxolanes using Equation 26. The good correlation between these two series shows that the reaction profiles for both series of compounds is similar. The fact that the slope is less than 1 shows that there is a smaller amount of charge built up in the transition state, or that less participation to charge stabilization is needed by the aryl group in the imidazolidine series, and ρ in Figure I is greater than in Figure II. This would be

due to the greater ability of the nitrogen than the oxygen atom to donate its non-bonding pair of electrons to charge stabilization. This stabilization effect is in accord with the "New Bond Rule."[111]

The mass spectra of the oxathiolane and dithiolane series could not be correlated with the dioxolane and imidazolidine because of extensive fragmentation of the heteroatomic ring. The base peaks for these spectra were decomposition products of the heteroatomic rings, with the peaks that correspond to the heteroatomic ring being small. Pasto[140] has studied the mass spectra of the 1,3-oxathiolane ring and described the fragmentation reactions in detail.

III. Relative Reactivities using Free Radicals

A. Introduction

In the next two sections the free radical reactions of 2-aryl-1,3-dioxolanes, 2-aryl-1,3-dithiolanes, and 2-aryl-1,3-oxathiolanes with t-butoxy radicals and peroxy radicals will be discussed. The imidazolidine series was too reactive toward t-butoxy radicals under the conditions used to be studied quantitatively. This series will be treated in a qualitative manner, using the data from Appendix I.

In the previous section the imidazolidine series was compared to the dioxolane series, using mass spectrometry. It was found that the nitrogen atom was more effective than oxygen in stabilizing positive charge on the benzylic carbon. The dithiolane and oxathiolane series are not suitable for this type of study, due to extensive fragmentation of the heterocyclic ring.

In the following two sections, the ability of sulfur and oxygen to stabilize charge on the benzylic carbon will be compared to each other and to the aryl moiety. The mass spectral data will then be correlated to the free radical work through the dioxolane series, which is common for both.

The mass spectral and free radical reactions have in common some degree of positive charge on the benzylic carbon in the transition state. Because of this charge similarity in the transition state, it is felt that the comparison between these two systems is valid.

The kinetic schemes and major products for the oxathiolane and dithiolane series will be discussed in detail. The dioxolane kinetic scheme will also be compared to Huyser's.[80]

B. RESULTS

1. Relative Reactivities[146]

a. Alcohol: Acetone Ratios (Indirect Competition)

Table III (p. 41) presents data on the t-butyl alcohol to acetone ratios for substrates in this work and those from the literature which are pertinent. Di-t-butyl peroxide and di-t-butyl peroxyoxylate were the only sources of t-butoxy radicals sources used, and alcohol/acetone ratios were always measured by gas chromatography.

In the 2-aryl-1,3-dioxolane, 2-aryl-1,3-oxathiolane and 2-aryl-1,3-dithiolane series hydrogens are abstracted from the ethylene portion of the heterocyclic ring as well as the benzylic position. Dioxane, oxathiane and dithiane were used as model compounds in order to correct for hydrogen abstractions from the ethylene portion of the substrates. Each of these model compounds contains twice as many hydrogens as the ethylene portion of the substrate, and k_a/k_d values were statistically corrected.

In Appendix I t-butyl alcohol to acetone ratios were taken in the absence of solvent. The chain lengths for the 2-aryl-1,3-dithiolane and 2-aryl-N,N'-dimethyl-1,3-imidazolidine were not measurable because concentration changes were within experimental error. Chain lengths for 2-phenyl-1,3-dioxolane were less than 1.5 for the reaction in Table VI when values could be calculated.

Data in Appendix I shows that the t-butyl alcohol/acetone ratios for the imidazolidine series are very large. In most cases acetone could not be detected or was just within the limits of detectability (G.C. thermistor detectors).

TABLE III: t-ButylOH/Acetone Ratios of Benzylic Hydrogens For Various Substrates In Chlorobenzene Solvent[1]

Compound	0°C	55°C	101°C	115.25°C	128°C	140°C	kcal E_d-E_A	log A_a/A_d
$mNO_2\phi SS$[6]			23.0	12.7	6.51	4.39	13.4	-6.44
ϕSS	1420[2]		19.1	14.8	11.6	6.17	8.45	-3.60
pMeOϕSS			27.1		9.38		11.7	-5.40
pMeϕSS			20.7		9.88		8.09	-3.40
pClϕSS			23.7		11.03	10.0	7.12	-2.79
pMeOϕOO			23.3		14.6		5.17	-1.65
pMeϕOO			18.7		7.73	4.00	11.7	-5.54
$mNO_2\phi OO$			16.7	9.44	7.88	6.31	7.46	-3.16
pClϕOO			12.9	6.24	3.59		14.2	-7.16
ϕOO	3158[2]		11.07	7.24	3.40	2.87	11.4	-5.61
ϕSO	2426[2]		17.5	9.36	7.76	4.59	9.98	-4.59
mMeOϕSO			16.5	13.1	8.99		6.65	-2.65
pMeOϕSO				15.3				
pMeϕSO			16.6	15.2	11.2		3.27	-0.704
mClϕSO			15.0	11.3		5.34	8.29	-3.64
Dioxane	16.2[2]		2.07[2]	1.73	1.40[2]	1.26	4.09	-2.06
Dithiane	2.16[2]		1.17[2]	1.10	1.04[2]	1.00	1.23	-0.649
Oxathiane	2035[2]		4.95[2,3]	2.88[2,3]	1.82[2,3]	1.19[2,3]	12.0	-6.28
Benzaldehyde	15800[2]		21.7[2]	12.7	9.75	4.80	12.7	-5.97
Fluorene[4]	248[2]	20.7				2.20	8.04	-4.33
Toluene[4]	31.2		1.76	1.30	1.01	0.82	5.87	-3.68
Tetralin[4,5]	685						8.98	-4.91
Ethylbenzene[4,5]	146						7.93	-4.46
Allylbenzene[4]	187						8.90	-5.12

TABLE III (con't.)

1. E_d in Chlorobenzene 10.6 kcal

2. Calculated values

3. Taken from a least square slope of 5 points in this range

4. Taken from P. Wagner and C. Walling, J. Amer. Chem. Soc., 87, 5179 (1965)

5. Alpha Hydrogens

6. ΦSS, ΦNN, ΦOO and ΦSO are 2-phenyl-1,3-dithiolane, 1,3-N,N' dimethyl imidazolidine, 1,3-dioxolane and 1,3-oxathiolane respectively. The prefix is the phenyl substituent.

TABLE IV

Relative Reactivities by Direct Competition in Chlorobenzene using di-t-butyl Peroxide in a 6:1 substrate to peroxide ratio.[2]

Comp. A	Comp. B	k_a/k_b 115°C	k_a/k_b 128.5°C	E_b-E_a kcal	Log A_a/A_b
ΦOO[1]	ΦOO	1.00	1.00	0	0
ΦSO	ΦOO	1.601±0.464	1.907±0.420	-3.97	+2.43
ΦSS	ΦOO	1.681±0.487	2.049±0.451	-4.49	+2.75
p-ClΦOO	ΦOO	0.872±0.139	1.054±0.105	-4.30	+2.35
m-NO_2ΦOO	ΦOO	1.318±0.237	1.542±0.263	-3.56	+2.12
m-ClΦOO	ΦOO	1.093±0.153	1.024±0.083	+1.48	-0.794
p-NO_2ΦOO	ΦOO	2.880±3.2	2.454±1.301	+3.63	-1.58
m-CH_3ΦOO	ΦOO	0.923±0.143	1.054±0.105	-3.01	+1.66
p-MeOΦOO	ΦOO	0.837±0.134	0.778±0.078	+1.66	-1.01
p-MeΦOO	ΦOO	0.937±0.149	1.136±0.114	-4.37	+2.43
m-ClΦSO	ΦSO	0.805±0.081	0.731±0.132	+2.19	-1.32
p-MeΦSO	ΦSO	1.051±0.283	0.906±0.163	+3.37	-1.87
p-MeOΦSO	ΦSO	1.191±0.191	0.807±0.145	+8.83	-4.89
m-MeOΦSO	ΦSO	1.087±0.196	0.895±0.161	+4.41	-2.44
m-NO_2OSS	ΦSS	0.981±0.020	1.051±0.02	-1.56	+0.874
p-MeΦSS	ΦSS	1.237±0.532	0.862±0.448	+8.19	-4.51
p-MeOΦSS	ΦSS	1.034±0.445	0.639±0.332	+10.9	-6.12
p-ClΦSS	ΦSS	1.036±0.446	0.941±0.492	+2.18	-1.21
ΦOO	dioxane	22.5	11.6	---	---
ΦSO	oxathiane	25	25	---	---
ΦSS	dithiane	8.2	7.8	---	---

1. ΦSS, ΦNN, ΦOO and ΦSO are 2-phenyl-1,3-dithiolane, 1,3-N,N'-dimethyl imidazolidine, 1,3-dioxolane and 1,3-oxathiolane respectively. The prefix is the phenyl substituent.

2. All ratios determined by NMR except those between ΦOO:dioxane ΦSO:oxathiane and ΦSS:dithiane which were determined by gas chromatography.

b. Direct Competition Values

Table IV gives the relative reactivities of the benzylic H disappearance of 2-aryl-1,3-dioxolanes, 2-aryl-1,3-dithiolanes and 2-aryl-1,3-oxathiolanes as determined by NMR disappearance of the benzylic hydrogen. This method excludes the need for corrections due to ethylene hydrogen atom abstraction from the substrates.

In these runs the substrate concentration was kept at approximately 0.4 molar for each substrate and the di-t-butyl peroxide concentration was 1/6 the concentration of the total substrate concentrations. The reactions were run for approximately one half life of di-t-butyl peroxide. These conditions were chosen because they most closely simulate those used in measuring alcohol/acetone ratios, and comparisons between the two methods would have the greatest meaning.

The relative reactivity values for 2-phenyl-1,3-dioxolane vs. dioxane, 2-phenyl-1,3-dithiolane vs. dithiane, and 2-phenyl-1,3-oxathiolane vs. oxathiane were done directly between these compounds. The analysis for these competitions were done by gas chromatography and not NMR as in the previous cases.

The concentration changes during reaction for dithiane, oxathiane and dioxane were very small in the direct competition. Because of the small change in concentration the errors for these measurements are large (Table IV, p. 43). Oxathiane showed no change in concentration within experimental (±3%) error. Dioxane and dithiane were borderline cases just outside experimental error.

The chain lengths for the substrates in each of the three previously mentioned series was small. The 2-aryl-1,3-dioxolanes, 2-aryl-1,3-oxathiolane, and 2-aryl-1,3-dithiolanes had chain length in the region of the 0.9-2.1, 1.0-1.9, and 0.6-1.0, respectively.

TABLE V: Autoxidations of Substrate With AIBN[1] in Diphenyl Ether Solvent at 78°C

Compound	Substrate Conc. (Molar)	AIBN Conc. (Molar)	(Moles/Sec)x10^7	kx10^6	Chain Length d O_2 /d AIBN
ΦSO[2]	0.5017	0.0156	0.621	5.36	2.03
ΦSO	0.5017	0.0519	2.18	5.94	2.04
ΦSO	0.5017	0.0777	2.95	5.36	1.93
ΦSO	0.5017	0.156	6.21	5.63	1.53
ΦSO	0.1001	0.0519	1.63	9.91	0.998
ΦSO	0.2001	0.0519	1.34	5.76	1.24
ΦSO	0.4002	0.0519	1.74	5.27	1.33
ΦSO	0.8003	0.0519	1.97	4.24	1.79
ΦSO	1.003	0.0519	2.92	5.63	2.69
ΦSO	6.698	0.0519	8.82	6.56	10.3
ΦSO	1.003	0	0	----	----
ΦSS	0.5028	0.0156	0.915	8.27	2.22
ΦSS	0.5028	0.0518	2.30	6.25	2.13
ΦSS	0.5028	0.0777	3.39	6.15	2.28
ΦSS	0.5028	0.156	5.45	4.93	1.76
ΦSS	0.219	0.0519	1.72	6.85	1.64
ΦSS	0.337	0.0519	2.44	7.87	2.02
ΦSS	0.9877	0.0519	4.00	7.75	2.01
ΦSS	1.002	0.0519	2.43	4.67	2.14
ΦSS	3.29	0.0519	11.4	12.10	10.6
ΦSS	6.415	0.0519	8.00	6.10	7.95
ΦOO	5.980	0	0.656	----	----
ΦOO[3]	1.9 - 3.7	.01 - .04	10x10^{-5}		30[4]
mNO_2ΦSS	0.5004	0.0156	0	----	----
mNO_2ΦSS	0.5004	0.0519	0	----	----
mNO_2ΦSS	0.5004	0.0777	0	----	----
mNO_2ΦSS	0.5004	0.156	0	----	----
Dioxane	0.5007	0.0156	0	----	----
Dioxane	0.5007	0.156	0	----	----
Oxathiane	0.9792	0.0519	0	----	----

TABLE V (con't.)

1. AIBN = Azobisisobutrylnitrile

2. ϕSS, ϕNN, ϕOO and ϕSO are 2-phenyl-1,3-dithiolane, 1,3-N,N'-dimethyl imidazolidine, 1,3-dioxolane and 1,3-oxathiolane respectively. The prefix is the phenyl substituent.

3. See Reference 141

4. The chain length is based on AIBN and is not corrected for the self-initiating process, see p. 76.

2. Autoxidation

Table V lists the substrates that were autoxidized using azobisisobutrylnitrile (AIBN) as an initiator. The data shows that the autoxidation of 2-phenyl-1,3-dithiolane and 2-phenyl-1,3-oxathiolane have short chain lengths, which may be due to the development of inhibitors in the reaction. Attempts to determine the amount of peroxide formed iodometrically were unsuccessful. The starting material or hydrolysis products apparently reacted with iodine in aqueous acidified KI.[106]

The rates listed in Table V are initial rates of oxygen absorbed, and the orders of substrate and initiator were determined from initial rates and initial concentration. Occasionally there was a short induction time before reaction. In these instances the initial rate was taken as the rate immediately after the induction period. The chain lengths were calculated from the rate of AIBN decomposition (using an efficiency of 0.55[147]) and rate of O_2 absorption (corrected for N_2 evolution).

C. Discussion

1. Kinetics

a. Alcohol:Acetone Ratios (Indirect Competition)

When di-t-butyl peroxide is heated to suitable temperatures it decomposes unimolecularly forming two butoxy radicals. The butoxy radicals can then either abstract a hydrogen to form t-butyl alcohol or decompose to form acetone and methyl radicals. As long as these are the main reactions taking place measuring the t-butyl alcohol/acetone ratio can be used as a method for determining the relative reactivity of different types of hydrogens. (This will be known as the indirect method of determining reactivities).

The mechanism for the reaction between t-butoxy radicals and 2-phenyl-1,3-dioxolane using di-t-butyl peroxide as a radical source has been reported by Huyser.[80] A mechanism for this reaction is shown in Scheme VII (p. 49). It differs from Huyser's mechanism in the equilibrium step (Step 32). This step is used to explain the benzaldehyde/ethyl benzoate ratios and will be explained in greater detail below.

In reactions involving 2-aryl-1,3-dioxolanes, the aryl aldehydes and ethyl aryl esters were constantly found in this work as well as Huyser's.[80]

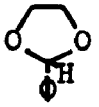
The expression for the t-butyl alcohol/acetone ratio for the 2-aryl-1,3-dioxolane series is:

$$39 \qquad \frac{\text{t-BuOH}}{\text{Acetone}} = \frac{\left[k_{29}(RH) + k_{30}(RH) + k_{35}(SH) + k_{36}(\phi CHO) + k_{37}(\phi COOEt)\right]}{k_d}$$

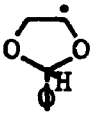
Scheme VII

27. $(\underline{t}\text{-BuO})_2 \longrightarrow 2\ \underline{t}\text{-BuO}\cdot$

28. $\underline{t}\text{-BuO}\cdot \longrightarrow \text{acetone} + CH_3\cdot$

29. $\underline{t}\text{-BuO}\cdot$ +  $\longrightarrow$ t-BuOH + 

I II

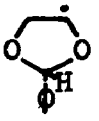
30. $\underline{t}\text{-BuO}\cdot$ +  $\longrightarrow$ t-BuOH + 

III

31. I + ($\cdot$S or $\cdot CH_3$) $\longrightarrow$ CH_4 or SH + II or III

32. II $\rightleftharpoons$ III

33.  $\xrightarrow{I}$ ϕCOOET + II or III

34.  $\xrightarrow{I}$ ϕCHO + CH_3CHO + II or III

35. $\underline{t}\text{-BuO}\cdot$ + SH $\longrightarrow$ $\underline{t}$-BuOH + S$\cdot$

36. $\underline{t}\text{-BuO}\cdot$ + ϕCHO $\longrightarrow$ $\phi\dot{C}$=O + t-BuOH

37. $\underline{t}\text{-BuO}\cdot$ + ϕCOOET $\longrightarrow$ $\phi COOC_2H_4\cdot$ + t-BuOH

38. Termination Steps

The steps listed above produce the following kinetic expressions:

Scheme VI

27. $k_{27}[\underline{t}\text{-BuO}\cdot]_2$

28. $k_{28}[\underline{t}\text{-BuO}\cdot] = k_d[\underline{t}\text{-BuO}\cdot]$

29. $k_{29}[\underline{t}\text{-BuO}\cdot][RH]$

30. $k_{30}[\underline{t}\text{-BuO}\cdot][RH^*]$

31. $k_{31}[I][S\cdot \text{ or } \cdot CH_3]$

32. $k_{32}[II] = k_{32}'[III]$ ------ $k' = \frac{[III]}{[II]}$

33. $k_{33}[II][RH]$

34. $k_{34}[III][RH]$

35. $k_{35}[\underline{t}\text{-BuO}\cdot][SH]$

36. $k_{36}[\underline{t}\text{-BuO}\cdot][\phi CHO]$

37. $k_{37}[\underline{t}\text{-BuO}\cdot][\phi COOC_2H_5]$

38. Termination

RH* = Ethylene hydrogen bond

RH = Benzylic hydrogen bond

SH = Solvent hydrogen bond

Note: k_d will be used in the future to designate hydrogen abstraction by t-butoxy radicals.

The solvent (SH) chlorobenzene was shown by Wagner and Walling[15] to have a k_a/k_d of 0.015 @ 40°C, and at higher temperatures this value increases showing that the energy of activation for abstraction of a chlorobenzene hydrogen is greater than the β scission of a t-butoxy radical.

At a temperature of 115°C the density of chlorobenzene is approximately 1.00,[137] which makes the chlorobenzene concentration slightly less than ~ 9 molar.

From data in Table VI (p. 54) and VII (p. 55) the k_a/k_d for chlorobenzene is estimated to be 0.038 @ 125°C which makes the chlorobenzene 1/450 as active per hydrogen as 2-phenyl-1,3-dioxolane. The concentration of chlorobenzene is essentially constant in these reactions, and therefore does not change the value of k_a/k_d of the substrate. The k_a/k_d value for chlorobenzene is obtained from the intercept of a plot of t-butyl alcohol/acetone vs. substrate concentration. Since the solvent hydrogens do not change the k_a/k_d value for the substrate hydrogens, there is a negligible error introduced by the solvent.

The k_a/k_d ratio of benzaldehyde is slightly greater than that of 2-phenyl-1,3-dioxolane (see Table III, p. 41). In Table VI (p. 54) the greatest benzaldehyde concentration for a 0.3053 Molar substrate concentration found was 0.0239M. If it is assumed that the average concentration of benzaldehyde is 1/2 the final concentration, the increase in the alcohol/acetone ratios will be a maximum of 6.0% of the total found and probably less in most cases. In the data presented this correction in Equation 39 (p. 48) was ignored.

The concentrations of ethyl benzoate are larger than those of benzaldehyde, but the k_a/k_d is ~ 0.1 times that of benzaldehyde.

The k_a/k_d values for ethyl benzoate varied from +1.00 to -1.00 in the 115° to 140°C range. Negative values for k_a/k_d are impossible in our kinetic scheme, because this means that the hydrogen abstraction rate would decrease as hydrogen donor increased in concentration. This indicates that there might be another reaction in competition with the simple abstraction reaction. Since the observed k_a/k_d and concentrations for ethyl benzoate in the temperature range studied are small no corrections are necessary in k_a/k_d for benzylic hydrogen abstraction.

The largest source of increase in the t-ButylOH/acetone ratio compared to the benzylic position alone comes from the abstraction of hydrogens from the dioxolane ring ($k_{30}[RH]$). This source of hydrogens accounts for approximately 18% of those being abstracted from 2-phenyl-1,3-dioxolane at 128°C.

The only correction made in the alcohol/acetone ratios was for the hydrogens in the heterocyclic ring. Dioxane, oxathiane and dithiane were used as model compounds for these corrections. The k_a/k_d for these compounds were statistically corrected for the extra hydrogens. The model compounds contain twice as many hydrogens as the corresponding dioxolane, oxathiolane and dithiolanes. There were no corrections made for hydrogen abstraction from methyl or methoxy substituents.

The alcohol/acetone ratios for the entire series of 2-aryl-1,3-dioxolanes now takes the form:

$$40. \quad \text{t-butyl alcohol/acetone} = \frac{k_{29}}{k_d}[RH] + \frac{k_{30}}{k_d}[RH]$$

according to Scheme VII (p.49).

In the reaction between t-butoxy radicals and 2-phenyl-1,3-dioxolane the existance of an equilibrium between the benzylic and ethylenic radical has been postulated to explain benzaldehyde/ethyl benzoate ratios (Scheme VII, Step 32). This was a step not originally included in Huyser's mechanism.[80]

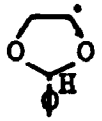
From Scheme VII:

$$33'.\quad d[\phi COOET]/dt = k_{33}[RH][II] = k'_{obs}[RH][(\underline{t}\text{-BuO})_2]^{1/2}$$

$$34'.\quad d[\phi CHO]/dt = k_{34}[RH][II] = k_{obs}[RH][(\underline{t}\text{-BuO})_2]^{1/2}$$

RH = 2-phenyl-1,3-dioxolane

II = 

III = 

assuming that radical concentration is at a steady state and termination is bimolecular.

TABLE VI: Reaction Between 2-Phenyl-1,3-dioxolane and di-t-Butyl Peroxide in Chlorobenzene With Different Substrate to Peroxide Ratios at 128°C.

Substrate[1] m/l	Substrate to Peroxide Ratio	% Peroxide and Product Accounted For	t-ButylOH m/l	Acetone m/l	ϕCHO m/l	ϕCOOET m/l	t-ButylOH / Acetone	ϕCHO / ϕCOOET
0.3053A	1.85:1	89.5	0.0792	0.0256	0.209	0.062	1.52	0.325
0.1527A	1.85:1	105	0.0352	0.0354	0.0092	0.029	0.994	0.317
0.0764A	1.85:1	119	0.0130	0.0196	0.0021	0.0069	0.645	0.304
0.3053A	5.55:1	103	0.268	0.0182	---	---	1.50	---
0.1527A	5.55:1	102	0.110	0.0116	---	---	1.00	---
0.0764A	5.55:1	100	0.0040	0.0072	---	---	0.566	---
0.3053A	18.5:1	89	0.0072	0.0044	0.0058	0.0196	1.67	0.296
0.1527A	18.5:1	77.5	0.00436	0.00404	---	0.0051	1.08	---
0.0764A	18.5:1	93.4	0.00170	0.00236	---	---	0.720	---
0.3053A	55.5:1	93.5	0.00228	0.00164	0.0044	0.0205	1.38	0.214
0.1527A	55.5:1	97.5	0.00106	0.00112	0.0014	0.0038	0.901	0.316
0.0764A	55.5:1	---	---	---	---	---	0.43	---
0.3053B	1.85:1	105	0.131	0.0952	0.0239	0.089	1.40	0.269
0.1527B	1.85:1	104	0.0504	0.0634	0.0128	0.0290	0.812	0.441
0.0764B	1.85:1	---	---	---	0.0035	0.0073	---	0.479
0.3053B	5.55:1	80.2	0.0418	0.0130	0.022	0.059	1.39	0.373
0.1527B	5.55:1	116	0.0208	0.0226	---	0.016	0.924	---
0.0764B	5.55:1	---	0.0078	0.00112	---	---	0.69	---
0.3053B	18.5:1	93.7	0.0130	0.0074	0.0094	0.0409	1.76	0.230
0.1527B	18.5:1	112	0.0056	0.0068	0.0022	0.0097	0.828	0.227
0.0764	18.5:1	112	0.00216	0.00392	---	0.0020	0.501	---
								Ave. 0.320 ±0.074[2]

1. A = 5 hour reaction time, B = 12 hour reaction time

2. Standard Deviation

TABLE VII: The Effect of Varying the Substrate:Peroxide Ratio and Time on k_a/k_d for 2-Phenyl-1,3-Dioxolane at 128°C in Chlorobenzene

Substrate/ Peroxide Ratio[1]	Time[2]	k_a/k_d	Intercept
1.85:1	A	4.4	0.36
	B	4.3	0.24
5.55:1	A	4.2	0.29
	B	3.5	0.46
18.5:1	A	4.8	0.42
	B	4.3	0.24
55.5:1	A	3.5	0.43
Average		4.1 $\pm$0.5[3]	0.35 $\pm$0.09[3]

1) Substrate concentrations were 0.1 - 0.3 molar in all cases.

2) A = 5 hour reaction time, B = 12 hour reaction time

3) Standard deviation

FIGURE IV: The Determination of k_{obs} in The Formation of Benzaldehyde in The Reaction of 2-Phenyl-1,3-Dioxolane With Di-t-Butyl Peroxide at 128°C

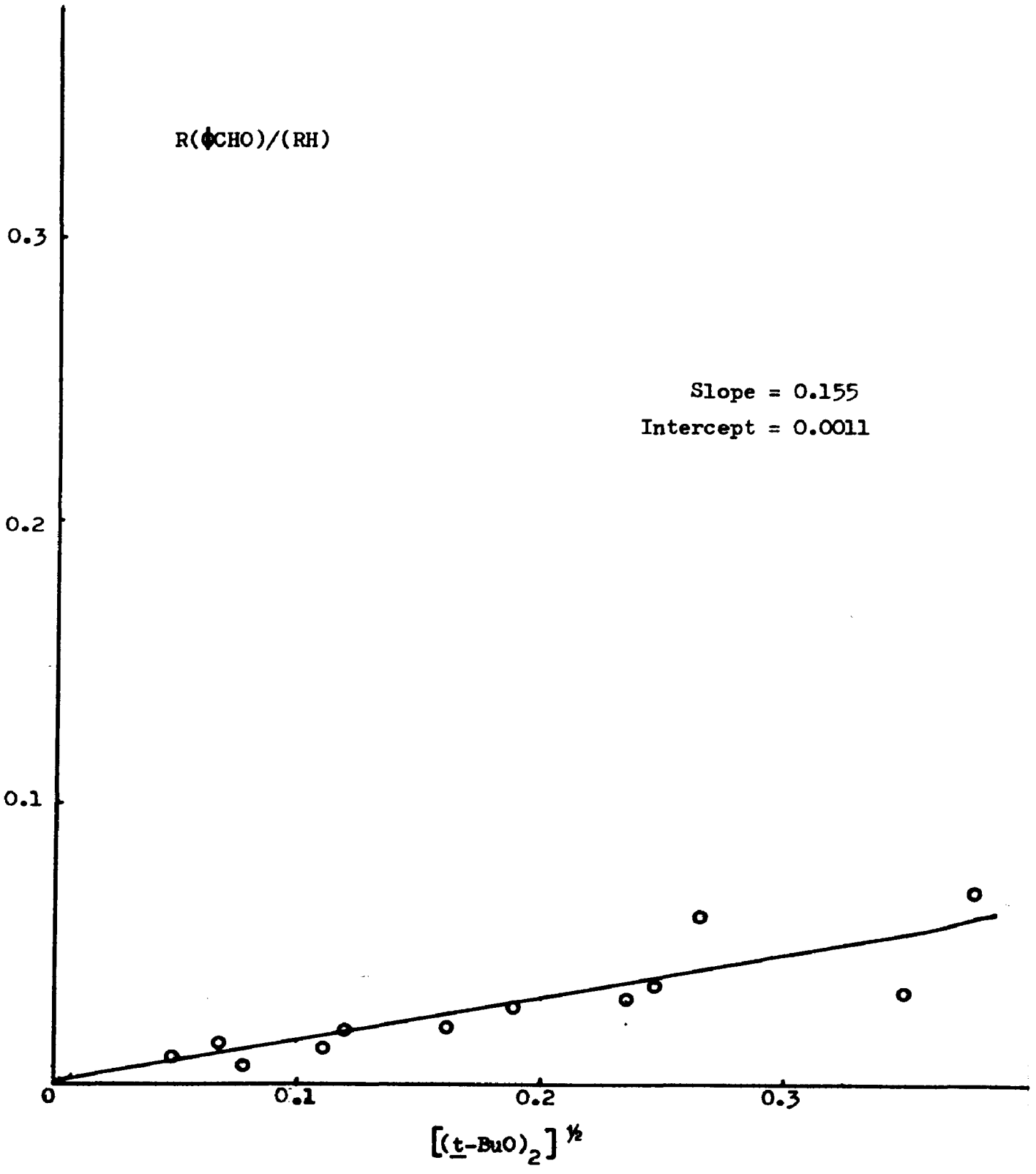


FIGURE V: The Determination of k_{obs} in The Formation of Ethyl Benzoate in The Reaction Between 2-Phenyl-1,3-Dioxolane With Di-t-Butyl Peroxide at 128°C

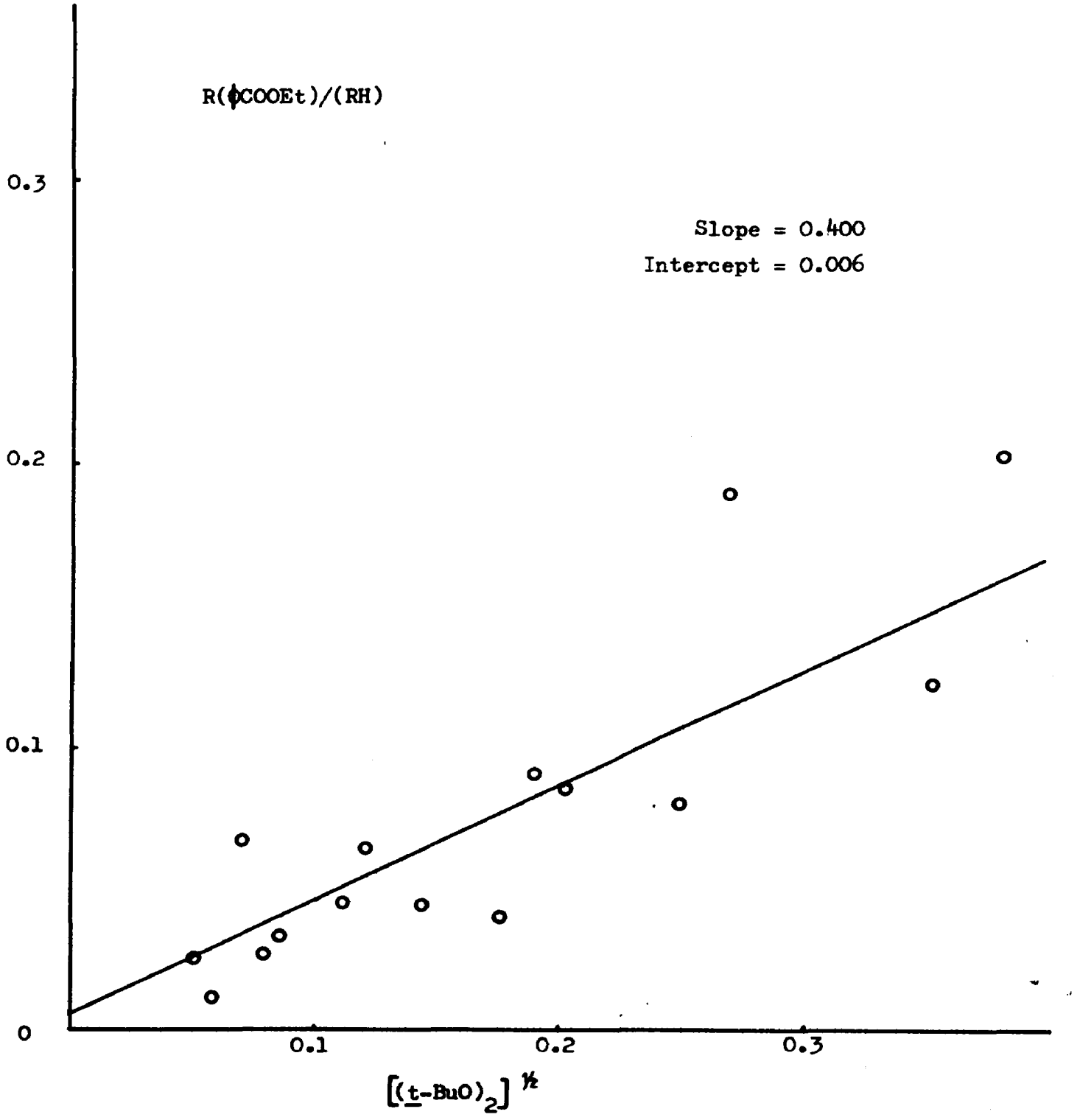


FIGURE VI: A Determination of The Order of Di-t-Butyl Peroxide in The Formation of Benzaldehyde In The Reaction of 2-Phenyl-1,3-Dioxolane With Di-t-Butyl Peroxide

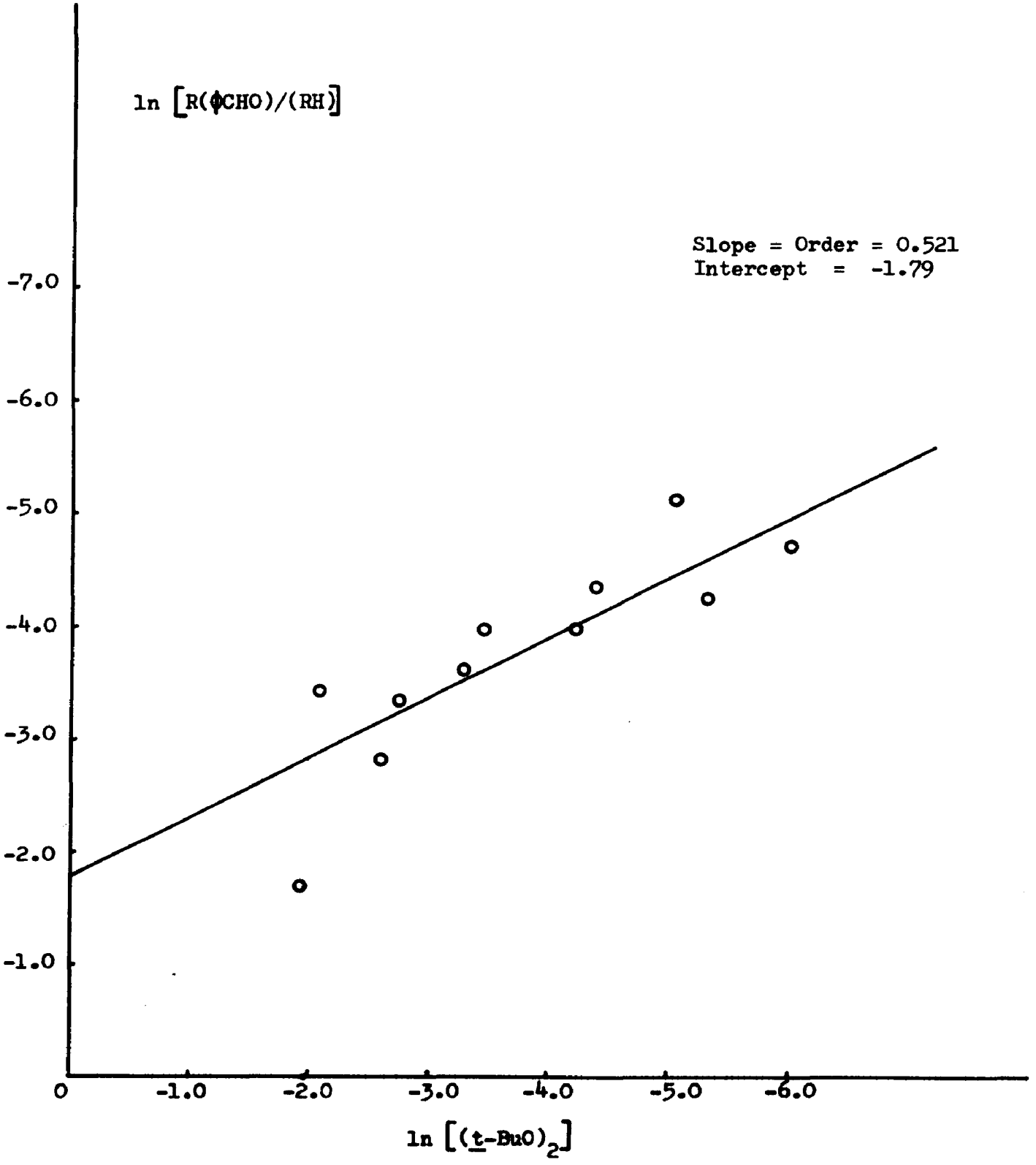
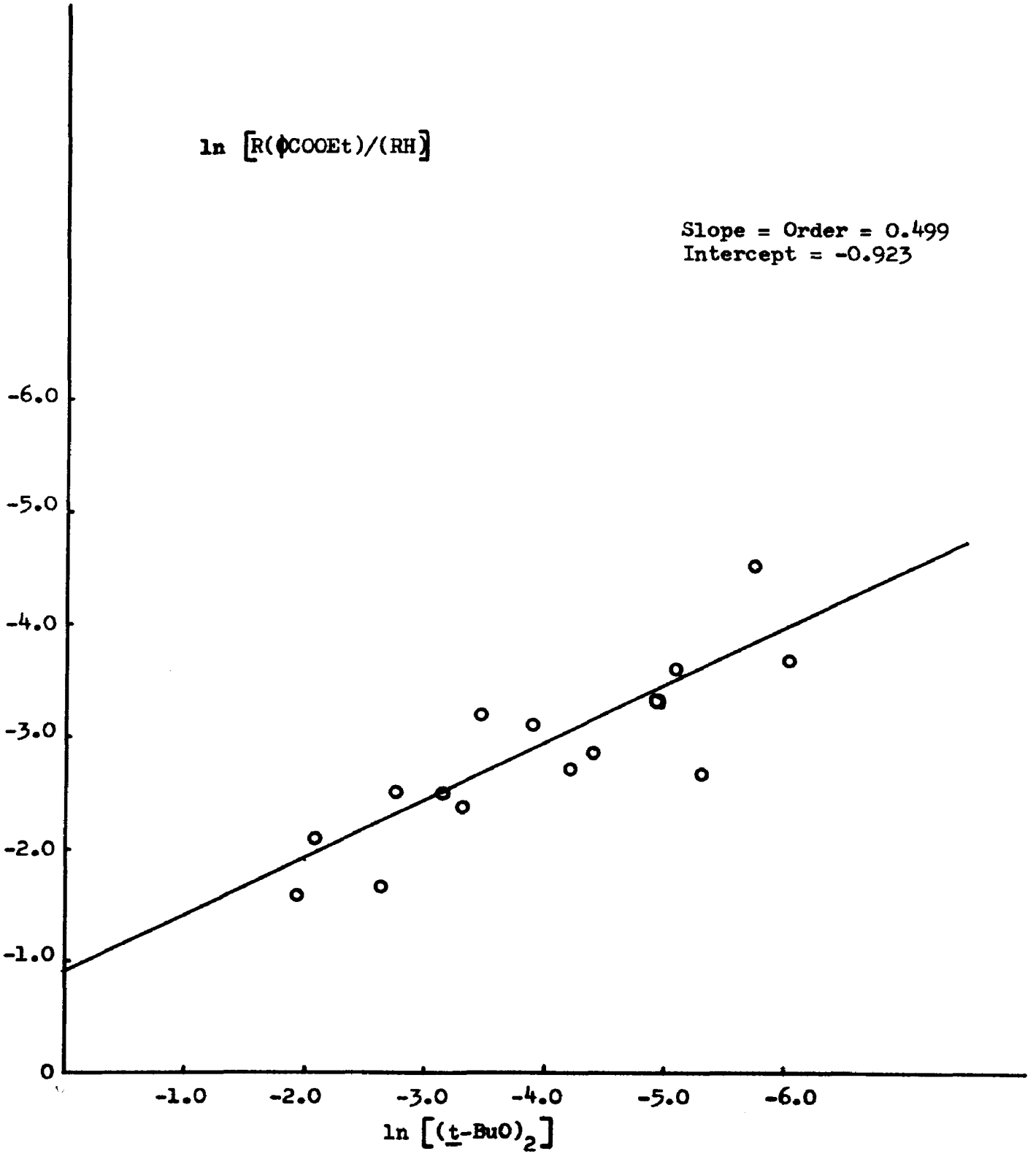


FIGURE VII: A Determination of the Order of Di-t-Butyl Peroxide in The Formation of Ethyl Benzoate In The Reaction of 2-Phenyl-1,3-Dioxolane With Di-t-Butyl Peroxide at 128°C



When the $\ln\left[(d[\text{ØCHO}]/dt)/[\text{RH}]_0\right]$ or corresponding ester function is plotted versus $\ln\left[(\underline{t}\text{-BuO})_{2\ ave.}\right]$ the slope should be ½ and the intercept the sum of the logs of the rate constants. Figures VII and VI produce slopes of 0.499 and 0.521 respectively by a least squares treatment, of the data of Table VI in reasonable agreement with 33' and 34'.

In Figures IV and V plots of $(d[\text{ØCHO}]/dt)/[\text{RH}]_0$ and $(d[\text{ØCOOET}]/dt)[\text{RH}]_0$ versus $(\underline{t}\text{-BuO})_{2\ ave.}^{\frac{1}{2}}$ respectively are shown. Dividing Equation 34' by 33' we obtain the following expression:

$$41.\quad \frac{[\text{benzaldehyde}]}{[\text{ethyl benzoate}]} = \frac{k_{34}{}^{II}}{k_{33}{}^{III}} = \frac{k_{34}}{k_{33}{}^{k'}}$$

The value benzaldehyde/ethyl benzoate ratio obtained from Figures IV (p.56) and V (p.57) is 0.388, which agrees with the value obtained from Table VI of 0.320 ± 0.074 obtained by a time independent method. This was done by dividing the benzaldehyde concentration by the ethyl benzoate concentration for each reaction in Table VI.

In Table VI (p.54) it can also be seen that the benzaldehyde/ethyl benzoate ratio is reasonably constant over the entire substrate-peroxide concentration range as would be expected from the above mechanism.

The benzaldehyde/ethyl benzoate ratios actually represent minimum values since the consumption of benzaldehyde and ethyl benzoate were not taken into account. Benzaldehyde, more reactive than ethyl benzoate, will be consumed at a greater rate making the true values higher. The k_a/k_d for benzaldehyde is about 10 times greater than ethyl benzoate's.

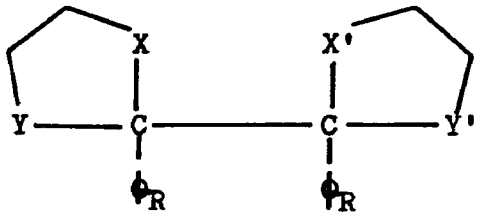
From the data in Table VI (p. 54) a maximum value of 0.21 is obtained using Huyser's mechanism.[80] The amount of benzaldehyde and ethyl benzoate formed according to Huyser's mechanism is proportionate to k_{30}[t-BuO·] [RH] and k_{29}[t-BuO·] [RH]respectively, if it is assumed that once the beta scission process starts in the 2-phenyl-1,3-dioxolane radical it proceeds uninterupted. This leads to the following expression:

42. $k_{30}/k_{29} = [\phi CHO]/[\phi COOET]$

If 1/2 the k_a/k_d value, 0.70, for dioxane (Table III, p. 41) is used to approximate the k_a/k_d for ethylene hydrogen abstraction and a value of 3.40 for the benzylic hydrogen's k_a/k_d, a value of 0.21 is obtained for the benzaldehyde/ethyl benzoate ratio at 128°C according to Huyser's[80] mechanism. This is a maximum possible value obtainable according to Huyser's scheme since it does not take the consumption of benzaldehyde and ethylbenzoate into account. It is lower than the value obtained from Table VI or Figures VI and VII which supports the equilibrium in Step 32, Scheme VII (p. 49). Reactions run with 2-phenyl-1,3-dioxolane deuterated in the two position would shed light on the equilibrium step.

The reaction between 2-phenyl-1,3-dioxolane and di-t-butyl peroxide was tested for the possibility of bimolecular side reactions involving di-t-butyl peroxide. The substrate to peroxide ratio was varied over a 30 fold range and reacted for 5 and 12 hours at 128°C. The results are tabulated in Table VII. The constancy of these values shows that there are no interfering reactions such as induced decomposition. Similar tests were made on the 2-phenyl-1,3-dithiolane series and identical results were obtained.

The kinetic schemes of the 2-aryl-1,3-oxathiolane and 2-aryl-1,3-dithiolane are much simpler. Ring opening reactions appear to be less prominent. Decomposition products similar to those of the dioxolane series were not found in the oxathiolane and dithiolane series. The only product found was the dimeric coupling product:



X = X' = Sulfur
Y = Y' = Sulfur or Oxygen
R = Ring Substituents

No other products were found, but if they are present their concentrations would be very small, and it has been assumed that no correction in measuring the relative reactivities by t-butyl alcohol to acetone ratio is necessary. The kinetic scheme for both these systems is undoubtedly the same, and is shown in Scheme VIII (p. 63) for 2-phenyl-1,3-oxathiolane.

Scheme VIII

27. $(\underline{t}\text{-BuO})_2 \longrightarrow 2\ \underline{t}\text{-BuO}\cdot$

43. $\underline{t}\text{-BuO}\cdot + RH \longrightarrow$  $+\ \underline{t}\text{-BuOH}$

IV

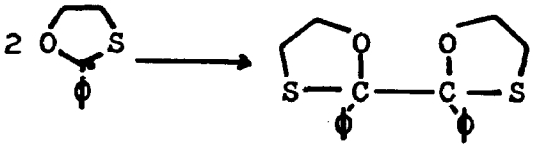
44. $\underline{t}\text{-BuO}\cdot \longrightarrow \text{Acetone} + \cdot CH_3$

45. $\underline{t}\text{-BuO}\cdot + SH \longrightarrow \underline{t}\text{-BuOH} + S\cdot$

46. $\underline{t}\text{-BuO}\cdot + RH \longrightarrow$  $+\ \underline{t}\text{-BuOH}$

47. 

48. $(\cdot CH_3 \text{ or } \cdot S) + RH \longrightarrow IV + (SH \text{ or } CH_4)$

49. 

The rate laws derived from Scheme VIII are:

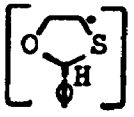
27. $k_{27}\ (\underline{t}\text{-BuO})_2$

43. $k_{43}(\underline{t}\text{-BuO}\cdot)(RH)$

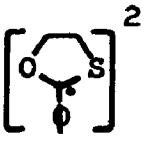
44. $k_d(\underline{t}\text{-BuO}\cdot)$

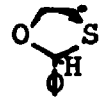
45. $k_{45}(\underline{t}\text{-BuO}\cdot)(SH)$

46. $k_{46}(\underline{t}\text{-BuO}\cdot)(RH)$

47. k_{47}  k' 

48. $k_{48}(RH)(\cdot S \text{ or } \cdot CH_3)$

49. k_{49} 

There is no evidence for Step 47 in this scheme. No coupling products containing a  radical were found. The expression for the t-butyl alcohol/acetone ratios in this scheme are:

$$50. \quad \frac{\text{t-butyl alcohol}}{\text{Acetone}} = \left[k_{43}\,[RH] + k_{45}\,[SH] + k_{46}\,[RH]\right]/k_d$$

where RH is either a 2-aryl-1,3-dithiolane or 2-aryl-1,3-oxathiolane substrate. The k_a/k_d ratios listed in Table III are all corrected for the abstraction of ethylene hydrogens, and no other corrections appear to be necessary.

The activation energies of hydrogen abstraction from dithiane, dioxane and oxathiane are 9.37, 6.51 and approximately 0 respectively. These values are consistent with sulfur's and oxygen's ability to stabilize radicals and activate carbons α to themselves. Hydrogens on carbon atoms α to an activating atom have enhanced reactivity while hydrogens on carbon atoms β to an activating atom have reduced reactivity.[112] Since the hydrogens are both α and β to activating atoms in dithiane and dioxane, the net activation is smaller than if they were just α to an activating group. Oxathiolane hydrogens are not α and β to the same heteroatom and the canceling effect cannot be as great, therefore this compound has hydrogens which are more reactive than dioxane or dithiane.

An example of this effect in the literature is the greater reactivity of tetrahydrofurans α hydrogens than dioxanes. They are about 3.2 times as reactive per hydrogen when reacted with t-butyl hypochlorite.[112]

These results indicate that the order of reactivity for the three series is $\phi SS > \phi SO > \phi OO$ at temperatures above 100°C. The temperatures

in Table III (p. 41) are however, above the isokinetic temperature for the three series (see isokinetic section, p. 95). At temperatures below the isokinetic temperature the reactivity becomes $\phi OO > \phi SO > \phi SS$. The reactivities of these compounds were extrapolated to $0^{\circ}C$ and compared to other compounds at that temperature. (See Table IX, p. 70).

The reactivities of 2-phenyl-1,3-dioxolane and 2-phenyl-1,3-oxathiolane are greater than any other benzylic hydrogen listed in Table IX (p. 70). This demonstrates oxygen's and sulfur's ability to activate benzylic hydrogens to abstraction by t-butoxy radical.

2. Direct Competition Values

A comparison of reactivities of direct versus indirect competitions is shown below in Table VIII. The relative reactivities of 2-phenyl-1,3-dioxolane, 2-phenyl-1,3-oxathiolane and 2-phenyl-1,3-dithiolane calculated by direct and indirect method agree within experimental error. The agreement is poor between compounds not containing benzylic hydrogens with those that do. A possible explanation for these discrepancies might be a reaction sequence shown in Scheme IX. The values for 2-phenyl-1,3-dithiolane and dithiane are not explained by Scheme IX (p. 67) since the ratio is less than unity.

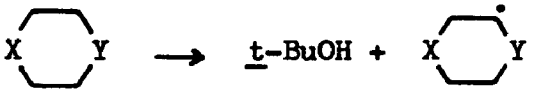
TABLE VIII: Direct and Indirect Reactivities of Substrates at 115.25°C in Chlorobenzene

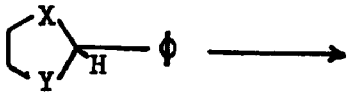
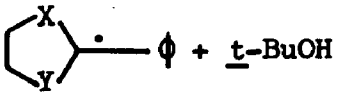
Substrate[1]		Reactivity (A/B)		Ratio
A	B	Direct[2]	Indirect[3]	Direct/Indirect
ϕSO	ϕOO	1.60±0.46	1.29	1.
ϕSS	ϕOO	1.68±0.49	2.04	1.
ϕOO	Dioxane	22.5	4.18	5.38
ϕSO	Oxathiane	25	3.25	7.80
ϕSS	Dithiane	8.20	13.8	0.594

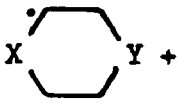
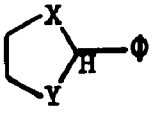
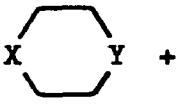
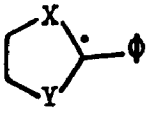
1. ϕSS, ϕOO, ϕSO are 2-phenyl-1,3-dithiolane, 2-phenyl-1,3-dioxolane and 2-phenyl-1,3-oxathiolane respectively.
2. Measured substrate disappearance using NMR (Table IV, p. 43)
3. Measured using alcohol/acetone ratios (Table III, p. 41)

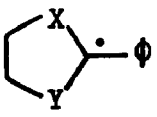
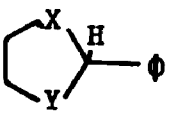
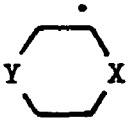
Scheme IX

27. $(\underline{t}\text{-BuO})_2 \longrightarrow 2\ \underline{t}\text{-BuO}\cdot$

51. $\underline{t}\text{-BuO}\cdot +$  $\longrightarrow \underline{t}\text{-BuOH} +$

52. $\underline{t}\text{-BuO}\cdot +$  $\longrightarrow$  $+ \underline{t}\text{-BuOH}$

53.  $+$  $\longrightarrow$  $+$ 

54.  $+$  $\longrightarrow$  $+$ 

55. Termination Steps

X = Oxygen
Y = Oxygen or Sulfur

Step 53 in Scheme IX would be thermodynamically favorable since the hydrogen bond strengths of dioxane, dithiane and oxathiane should be greater than the benzylic hydrogens to which they were compared.[113] This would explain the apparent great reactivity of the benzylic hydrogens when measured by direct competition. A possible indication of Step 53 (Scheme IX) might come from a study of deuterium isotope effects.

The main difference between direct and indirect competitions is in the nature of what is being measured. In indirect competition the measured alcohol/acetone ratios are a total of the alcohol/acetone ratios for each of the components of the system. If any of the components have active hydrogen that add significantly to the alcohol/acetone ratio, their contribution has to be accounted for. These measurements are usually

less sensitive to other radicals in the system, unless these competing radicals change the alcohol/acetone ratio.

Chlorine is an example of a radical which does interfere with alcohol/acetone ratios because of the HCl formed.[28] If t-butyl hypochlorite is used as a t-butoxy radical source, the following reaction occurs:

$$2\ t\text{-BuOCl} + 2HCl \longrightarrow 2\ t\text{-BuOH} + Cl_2$$

The Cl_2 which is formed regenerates HCl through the chlorine radical. C. Walling and P. Wagner[15] found that relative reactivities measured by indirect and direct competition do not always agree well. This discrepancy was subsequently shown to be due to Cl radical in their system.

In direct competition measurements the system is less sensitive to impurities than the measurement of alcohol/acetone ratios. This is true as long as the impurities do not produce interfering radicals, (radicals of comparable or greater reactivity than substrate radicals). In direct competition experiments the reactivity of the substrate to all the different types of radicals present is really being measured.

In Table IV (p. 43) there are activation parameters listed and they require some discussion. These values have very high uncertainty, often greater than 100%, even though the precision of the analysis was ±3%. This is due to the fact that the rate difference at the two temperatures measured do not change very much. The equation used to calculate the errors in E is:[114]

$$56.\quad (\Delta E/E)^2 = (T_2/T_1-T_2)^2(\Delta T_1/T_1)^2 + (T_1/T_1-T_2)^2$$
$$(\Delta T_2/T_2)^2 + \left[1/\ln(k_2/k_1)\right]^2 \left[(\Delta k_1/k_1)^2 + (\Delta k_2/k_2)^2\right]$$

The term that produces the high errors is $\left[1/\ln(k_2/k_1)\right]^2$. When k_2 and k_1 are close is value, the contribution to the error by this term becomes very large.

The activation parameters are nevertheless, useful in determining isokinetic temperatures. Isokinetic temperature plots are relatively insensitive to errors in activation parameters, since any error in E is compensated by a corresponding change in the log A term.[115] This effect will be discussed below.

Table IX (p. 70) correlates our data with values in the literature primarily from the work of Walling et. al. The relative reactivity data in Table IX for the compounds from this work were extrapolated from alcohol/acetone ratios since no direct competition experiments were done with any compounds that Walling and Mintz[112] used. The k_a/k_d of benzaldehyde, dithiane, and dioxane were calculated from two point activation energy plots at 115.25°C and 140°C.

The extrapolated reactivities of benzaldehyde and dioxane obtained from our data do not agree well in these two cases. The extrapolated values from this work are probably the values in error because they were calculated from two point activation curves, 115°C away from the extrapolated value. Dithianes' value in Table IX is also suspiciously low. A priori, the reactivity of dithianes' hydrogens would be expected to be in the vicinity of cyclohexane and dioxane.

TABLE IX: Direct and Indirect Relative Reactivities of Substrates Toward t-Butoxy Radical at 0°C Using Chlorobenzene or Benzene[5] Solvent

Compound	Relative Reactivity	
Benzaldehyde[3]	506[1]	(13)[6]
2-phenyl-1,3-dioxolane	101[1]	
2-phenyl-1,3-oxathiolane	77.8[1]	
Oxathiane	65.2[1]	
2,5-dimethyl tetrahydrofuran[2]	50.5	
2-phenyl-1,3-dithiolane	45.5	
Tetralin (α isomer)[2]	37.7[1]	
Cyclopentene[2]	36 [1]	
Propylene oxide[2]	33.6	
Trimethylene oxide[2]	33.5	
Dibenzyl ether[2]	30.3	
Tetrahydrofuran[2]	23.0	
Diethyl ether[2]	16.3	
Ethylene oxide[2]	13.1	
Tetrahydropyran[2]	10.8	
Diisopropyl ether[2]	10.6	
Cyclohexane[2]	8.04	
Fluorene	7.75[1]	
Dioxane[2]	6.66	
Dioxane	0.52[1,3]	
Toluene[4]	1.00	
Di-t-butyl ether[2]	0.311	
Styrene oxide[2]	0.235	
Isobutylene oxide[2]	0.204	
t-Butylbenzene[2]	0.170	
Dithiane[3]	0.069[1]	

1) Calculated from k_A/k_d ratios, source of t-butoxy radicals in this work is di-t-butyl peroxide.

2) After C. Walling and M. J. Mintz, J. Amer. Chem. Soc., 89, 1515 (1967) or P. Wagner and C. Walling, J. Amer. Chem. Soc., 87, 5179 (1965); Their source of radicals was t-butyl hypochlorite.

3) Questionable values these were calculated from 2 point activation energy curves at 115.25°C and 140°C.

4) All values were normalized to toluene. The k_A/k_d of toluene at 0°C is 31.2 (value taken from reference in footnote 2).

5) Solvent in this work always chlorobenzene, Walling and Mintz used chlorobenzene and benzene.

6) Reactivities per hydrogen using reference 2.

Values for k_a/k_d can be estimated from Walling's data if it is assumed that the relative reactivities at 0°C for benzaldehyde and dioxane should be equal to his values. A k_a/k_d value at 0°C can also be estimated for dithiane if it is assumed that reactivity per hydrogen for dithiane is intermediate between dioxane and cyclohexane. The relative reactivity of dithiane now becomes 5.55 according to Table IX.

Toluene has a k_a/k_d value of 31.2 which produces calculated k_a/k_d values at 0°C for dioxane, benzaldehyde and dithiane of 208, 2560 and 174 respectively. Activation parameters can be recalculated using the above values and data in Table I. These values become E_a-E_d 6.80 kcal, log A_a/A_d - 2.82; E_a-E_d 8.40 kcal, log A_a/A_d - 4.40 and E_a-E_d 8.64 kcal, log A_a/A_d - 4.48 for benzaldehyde, dioxane and dithiane respectively. Where E_a-E_d is E abstraction minus E decomposition and A_a/A_d is the ratio of P Z term in the Arrhenius equation. The other values in Table IX (p. 70) from this work were determined by extrapolating k_a/k_d to 0°C and dividing by 31.2 which is the k_a/k_d for toluene.

2. Autoxidations

The substrates 2-phenyl-1,3-dioxolane, 2-phenyl-1,3-dithiolane and 2-phenyl-1,3-oxathiolane were autoxidized in order to compare the reactivities of these substrates to peroxy as well as t-butoxy radicals. The autoxidation results are listed in Table V (p. 45). The autoxidation of 2-phenyl-1,3-dioxolane[141] produce results such that exponents X and Y could not be determined in the following equation:

$$57. \quad d[O_2]/dt = k_a(R_i/k_t)^X[RH]^Y$$

Where R_i equals rate of initiation, k_t equals k termination and RH equals substrate concentration.

FIGURE VIII: The Determination of the Order of AIBN in The Autoxidation of 2-Phenyl-1,3-Dithiolane

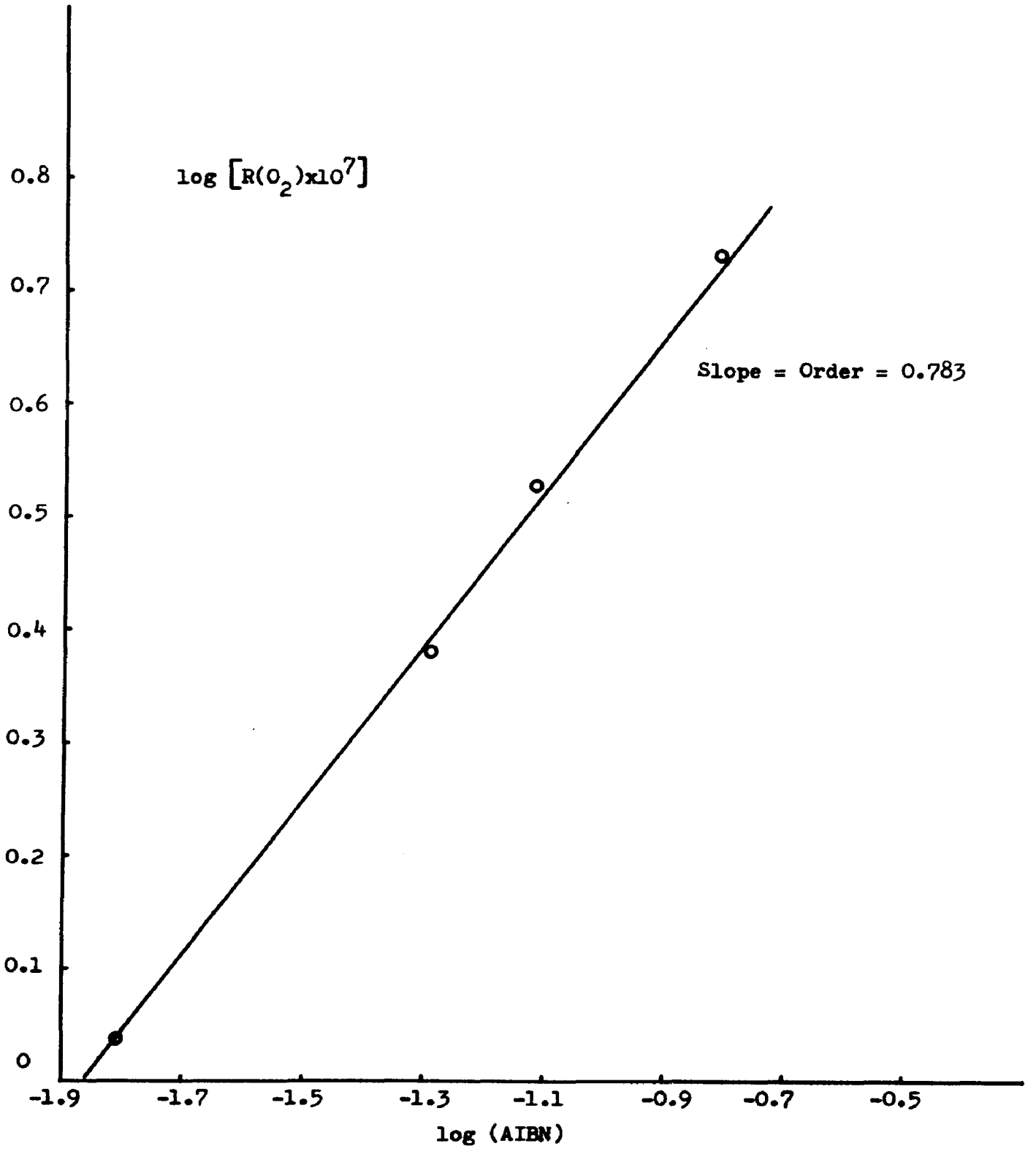


FIGURE IX: The Determination of the Order of 2-Phenyl-1,3-Dithiolane in The Autoxidation of 2-Phenyl-1,3-Dithiolane

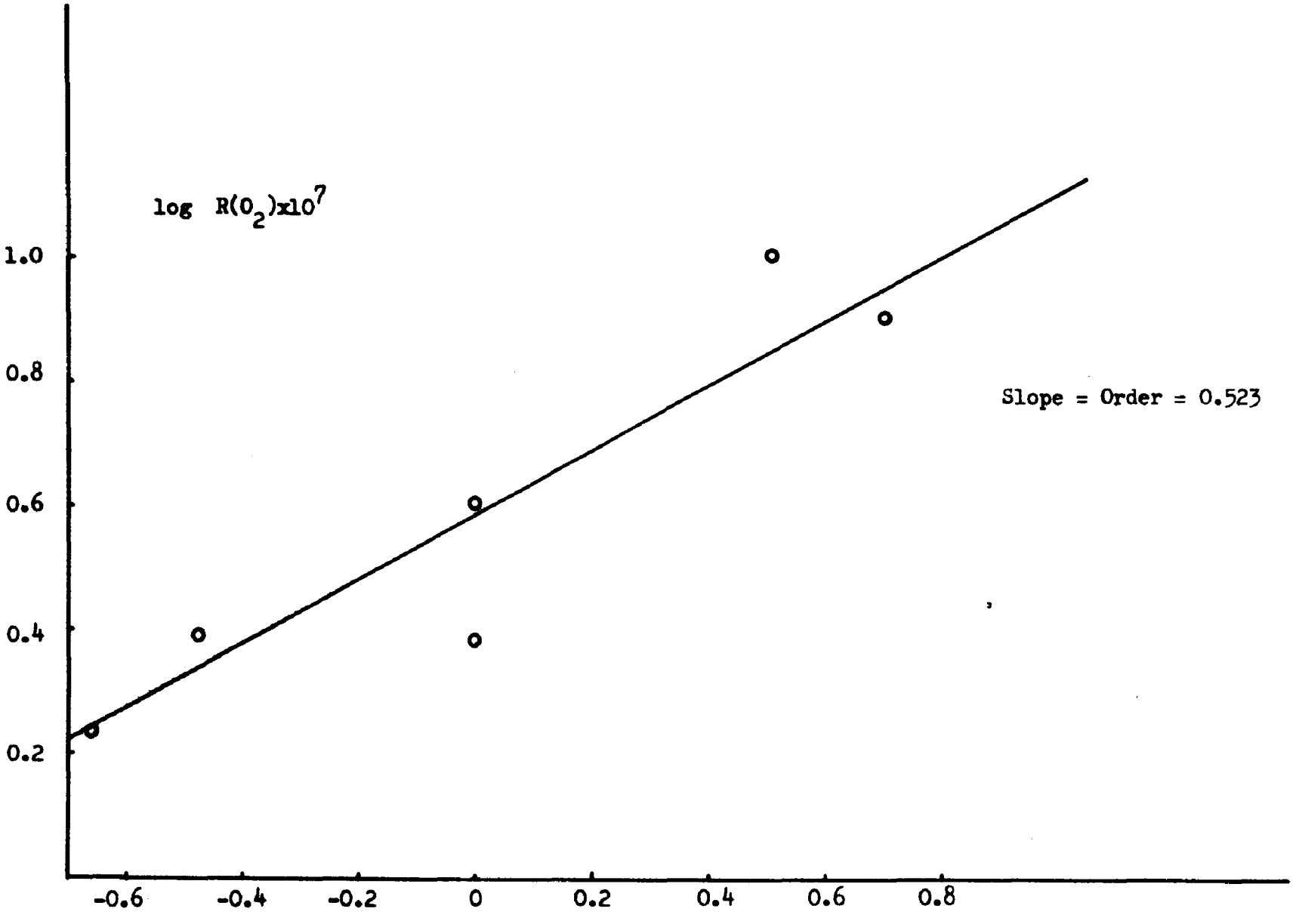


FIGURE X: The Determination of The Order of 2-Phenyl-1,3-Oxathiolane In The Autoxidation of 2-Phenyl-1,3-Oxathiolane

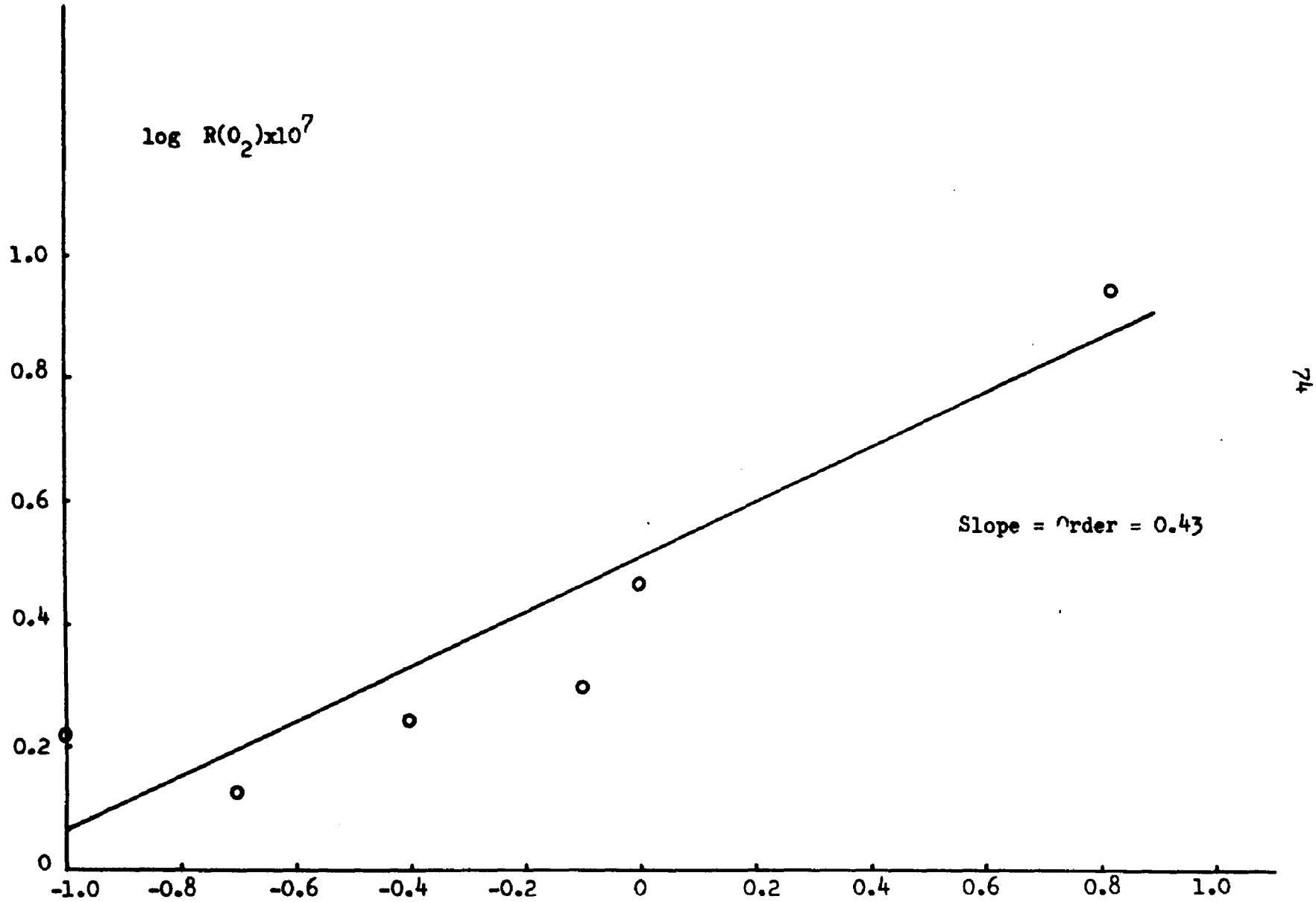
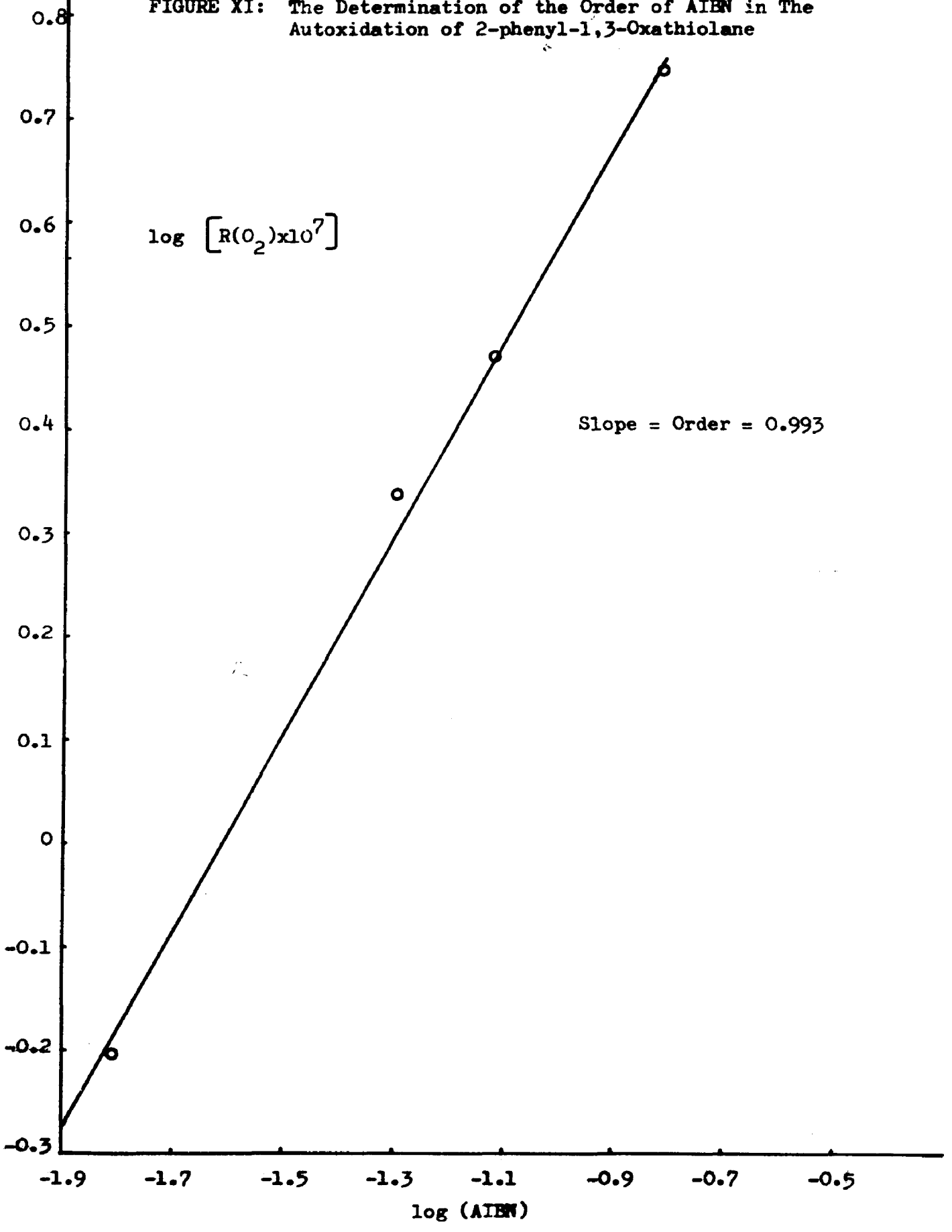


FIGURE XI: The Determination of the Order of AIBN in The Autoxidation of 2-phenyl-1,3-Oxathiolane



There was a self-initiating process which produced a rate of oxygen uptake which was comparable to reactions which contained AIBN. Attempts were made to determine whether impurities such as benzaldehyde and ethylene glycol were responsible, and results showed that they were not the cause.

The autoxidation of 2-phenyl-1,3-oxathiolane and 2-phenyl-1,3-dithiolane produce different results. The exponents X and Y usually have the values of 1/2 and 1 respectively for chain autoxidations. In the autoxidation of 2-phenyl-1,3-oxathiolane and 2-phenyl-1,3-dithiolane the values of X and Y are not what is expected for long chains.

Figures X and XIII show that these compounds are 1/2 order in substrate and first order in initiator and produces the following rate law:

58. $$d[O_2]/dt = k_{obs.}[AIBN][RH]^{1/2}$$

The chain lengths are also short with a usual value of approximately 2. These low values might be due to the formation of inhibitors during the course of the autoxidation. L. Bateman[142-144] has performed autoxidations on a variety of organic sulfides and found that after a small fraction of the substrate has reacted the reaction stops. It is possible that similar types of inhibtors are being produced in our reactions which shorten the chains.

An alternate reason for the short chains might be the diphenyl ether solvent. Ingold[116] has observed that some autoxidations were retarded by aromatic solvents which he attributes to phenol formation by the solvent. The complexing of radicals[117] and oxygen[118] with

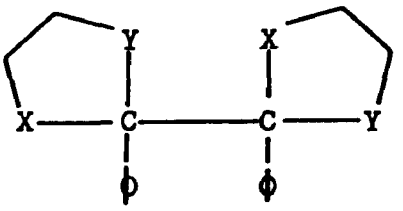
aromatic systems is also known. It is also known that poly-arylmethyl radicals persist in the presence of O_2 and retard autoxidation by trapping peroxy radicals to give non-radical products.[64] Radicals formed in these autoxidations might have similar properties.

In Table V it can be seen that 2-(m-NO_2phenyl)-1,3-dithiolane, dioxane and oxathiane do not autoxidize under these conditions. Dioxane and oxathiane were used as model compounds for the ethylene portion of the dioxolane and oxathiolane rings. Since dioxane and oxathiane do not autoxidize under these conditions it was assumed that only the benzylic hydrogen was reacting in these systems. It was also assumed that dithiane would produce results similar to dioxane and oxathiane and it was not subjected to autoxidation.

The sequence of reactivities of 2-phenyl-1,3-dioxalane, 2-phenyl-1,3-oxathiolane and 2-phenyl-1,3-dithiolane to autoxidation and t-butoxy radicals are the same at 78°C. The reactivities being 2-phenyl-1,3-dioxolane > 2-phenyl-1,3-oxathiolane > 2-phenyl-1,3-dithiolane. In Table III (p. 41) the reactivities of the above substrates toward t-butoxy radicals appears to be reversed. This reversal is due to the fact that the data in Table III was taken above the isokinetic temperature, which is 97°C (see isokinetic section, p. 95).

C. Determination of Dimer Structure

The only product found and isolated in the reaction of 2-aryl-1,3-dithiolane and 2-aryl-1,3-oxathiolane with di-t-butyl peroxide was the dimer which is connected through the two position of the heterocyclic ring.



X = Sulfur
Y = Sulfur, or Oxygen

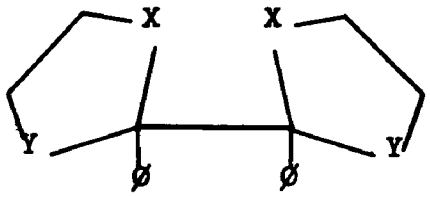
Gas chromatograms of reaction mixtures with, and without solvent failed to show any compounds, but the peroxide, decomposition products of the peroxide, and substrate. There are two small peaks which eluted from the column very quickly, and these were assumed to be methane and ethane. An NMR spectra of the original reaction mixtures failed to show any group of peaks which would correspond to an ethyl group and the possible existance of S-ethyl phenylthioate, O-ethylphenylthioate, or ethyl phenyldithioate.

In the reaction between 2-phenyl-1,3-oxathiolane and di-t-butyl peroxide (without a solvent) a white solid is isolated which when purified has a m.p. 214°C. This m.p. agrees well with the m.p. 212°C reported in the literature[119] for bis-2-phenyl-1,3-oxathiolane. However, no real proof of structure was given for the compound.

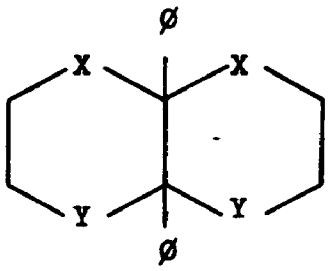
Spectral evidence will be presented to show that the structure of the compound is a bis-2-phenyl-1,3-oxathiolane. Coffen[120] studied the mass spectra of bis-dithiolanes and dithianes in detail and found that bis-1,3-dithiolanes have a strong peak at a mass 1/2 that of the parent peak, and this peak is missing in bis-dithiane structures. This is due to the symmetrical rupture of the 2,2' bond which leads to two fragments of equal mass.

Intense peaks were found at m/e 181 which corresponds to 1/2 molecular weight of the parent peak. An analogous peak (m/e 165) was

found in the mass spectra of the dimeric product isolated from the reaction between 2-phenyl-1,3-oxathiolane and di-t-butyl peroxide. In the mass spectra of the ØSS dimer a weak parent peak was observed, but none was observed for the ØSO dimer. Coffen[120] found weak parent peaks for the dimeric bis-1,3-dithiolanes used in his study, but no bis-1,3-oxathiolane spectra were run. The relationship in the mass spectra of the bis-2-phenyl-1,3-oxathiolane to fused oxathiane should be similar to the bis-2-phenyl-1,3-dithiolane to fused dithiane systems.



bis-2-phenyl-1,3-oxathiolane
or 1,3-dithiane

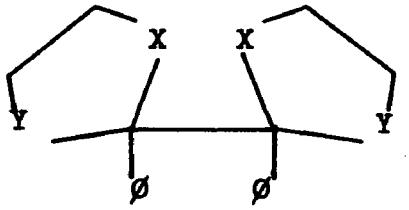


fused dithiane
or oxathiane ring

NMR spectra of the dimeric products ØSO and ØSS showed features which were similar to 2-phenyl-1,3-dithiolane and 2-phenyl-1,3-oxathiolane. The main difference being the absence of hydrogen at the two position of the oxathiolane ring. NMR spectra taken of pCH_3 ØSO and pCH_3 ØSS dimers again showed the same basic features as the substrate molecule minus the hydrogen in the two position of the heterocyclic rings.

Infrared spectra taken of the reaction product showed characteristic absorptions bands[145] of the 1,3-oxathiolane and 1,3-dithiolane rings.

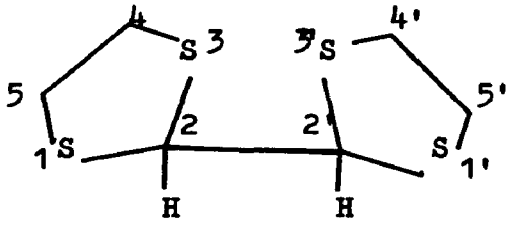
It was concluded from spectral evidence that the reaction product from 2-aryl-1,3-dithiolanes and 2-aryl-1,3-oxathiolanes were indeed the dimers shown below:



X = Oxygen
Y = Oxygen or Sulfur

Conformation of Dimeric Termination Product

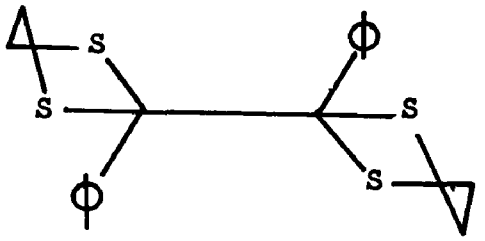
An x-ray crystallagraphic study has been performed on the following compound:



The main points of interest in Brahdis'[121] work are A) the shape of the heterocyclic ring and B) the positions of the rings with respect to one another.

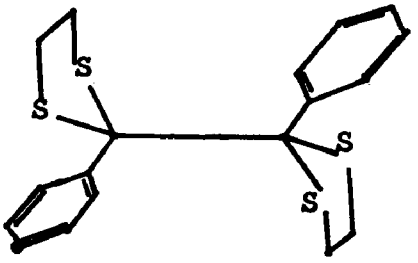
The shape of the dithiolane ring is best described by a plane containing $S_1C_2S_3$ which passes between C_4 and C_5 and two rings were pointed away from one another in the crystal. If we now substitute

phenyl rings for the hydrogen and keep the same basic picture, the following is obtained:



On the basis of NMR evidence taken in this laboratory it is felt that this is not the shape of the molecule when phenyl groups are attached, for the dithiolane or the oxathiolane. An NMR of the dimer shows a pattern which is almost identical with 2-phenyl-1,3-dithiolane or the 2-phenyl-1,3-oxathiolane minus the benzylic hydrogen absorption.

Models indicate that the ethylene hydrogen would be shielded by the phenyl ring and would be expected to move up field. This however is not the case, and it is felt that the heterocyclic rings are probably folded up and away from the phenyl ring as depicted below:



In this conformation the ethylene hydrogens of the heterocyclic ring would be away from the phenyl ring, and no shielding would occur.

Pasto[122] has studied NMR spectra of a variety of 2 substituted 1,3-oxathiolanes and suggests that the preferred conformation is an envelope with the oxygen at the flap. If a plane is now drawn through the OCS atoms, the ethylene group is to one side of the plane, which is in agreement with our model of the dimer. No attempt was made by Pasto to calculate dihedral angles in the ethylene segment because the authors felt that this method is too inaccurate.[122] Abrahams[123] however, did use the Karplus approximation to estimate the dihedral angle of the OCH_2CH_2O segment of 1,3-dioxolane and found it to be 38°.

5. Structure Reactivity Relationships

a. Substituent Effects

The importance of polar effects on reaction rates and equilibria can quite often be demonstrated by the Hammett equation: $\log k/k_0 = \sigma\rho$ where k and k_0 are the rate constants for the substituted and unsubstituted compound, and σ and ρ are the substituent and reaction parameters respectively.

The plots of $\log k/k_0$ for the 2-aryl-1,3-oxathiolane, 2-aryl-1,3-dithiolanes and 2-aryl-1,3-dioxolanes versus σ and σ^+(σ^+ is the substituent parameter where a positive charge is produced on or adjacent to the aromatic ring) show significant difference in the reaction with di-t-butyl peroxide except for the dioxolane series. Here the σ^+[108] values seem to produce a slightly better straight line. The NO_2 groups fall off the line most dramatically, but they are notorious for their misbehavior.[65,139]

FIGURE XII: A Hammet Plot of the 2-Aryl-1,3-Dithiolane Series at 128°C in Chlorobenzene Solvent Using t-Butyl Alcohol/Acetone Ratios

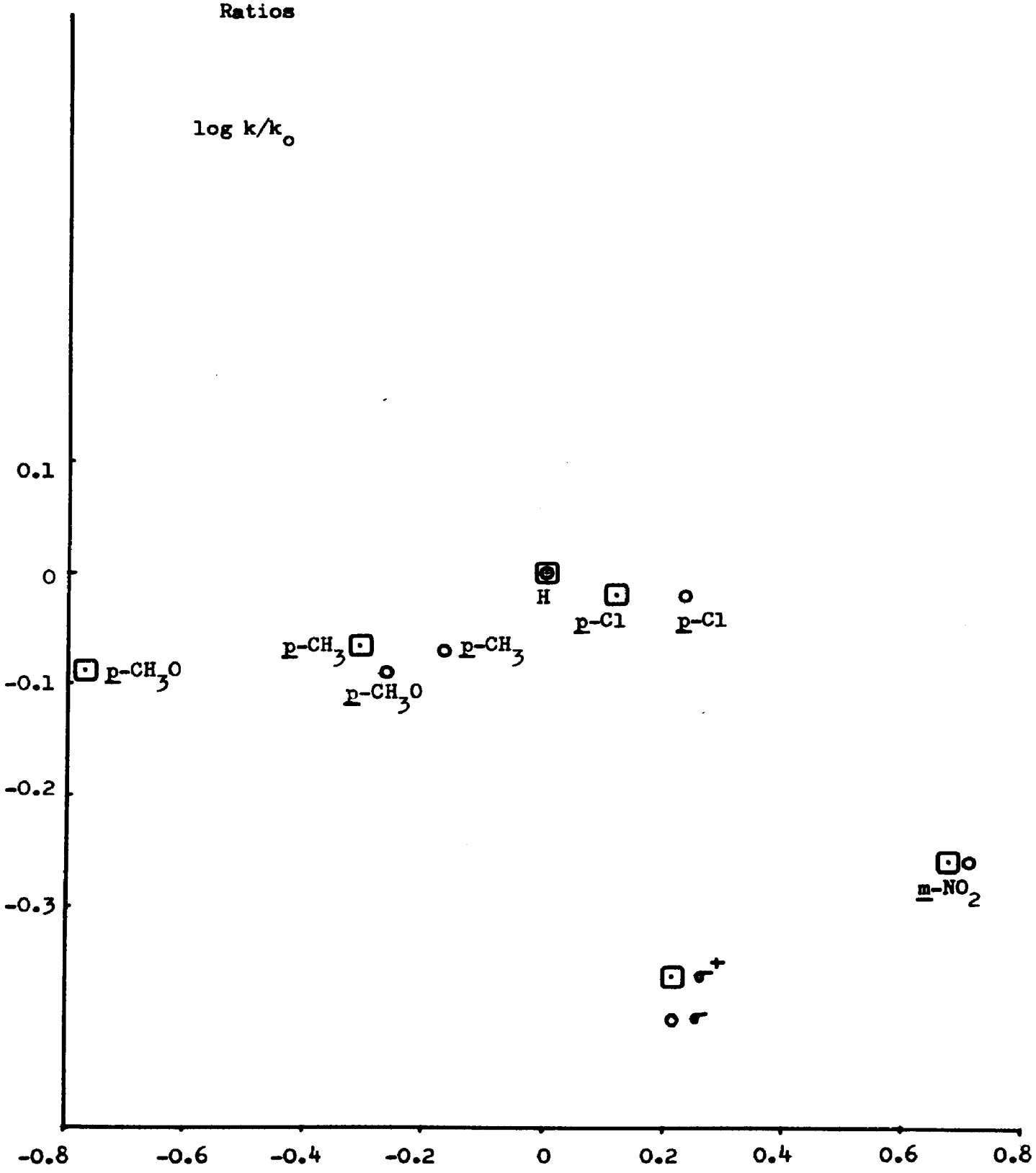


FIGURE XIII: A Hammet Plot of The 2-Aryl-1,3-Dioxolane Series at 128°C in Chlorobenzene Solvent Using t-Butyl Alcohol/Acetone Ratios

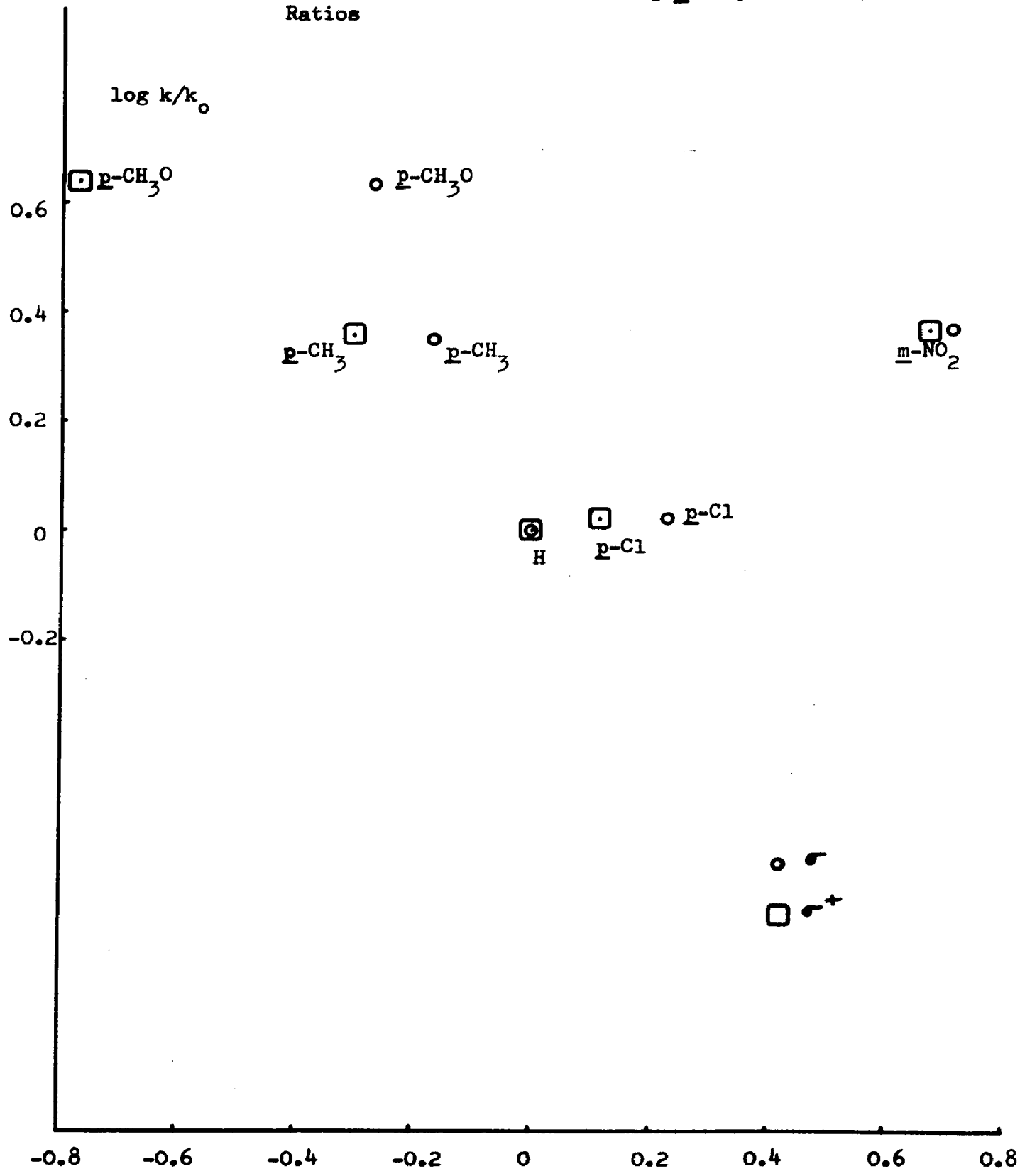
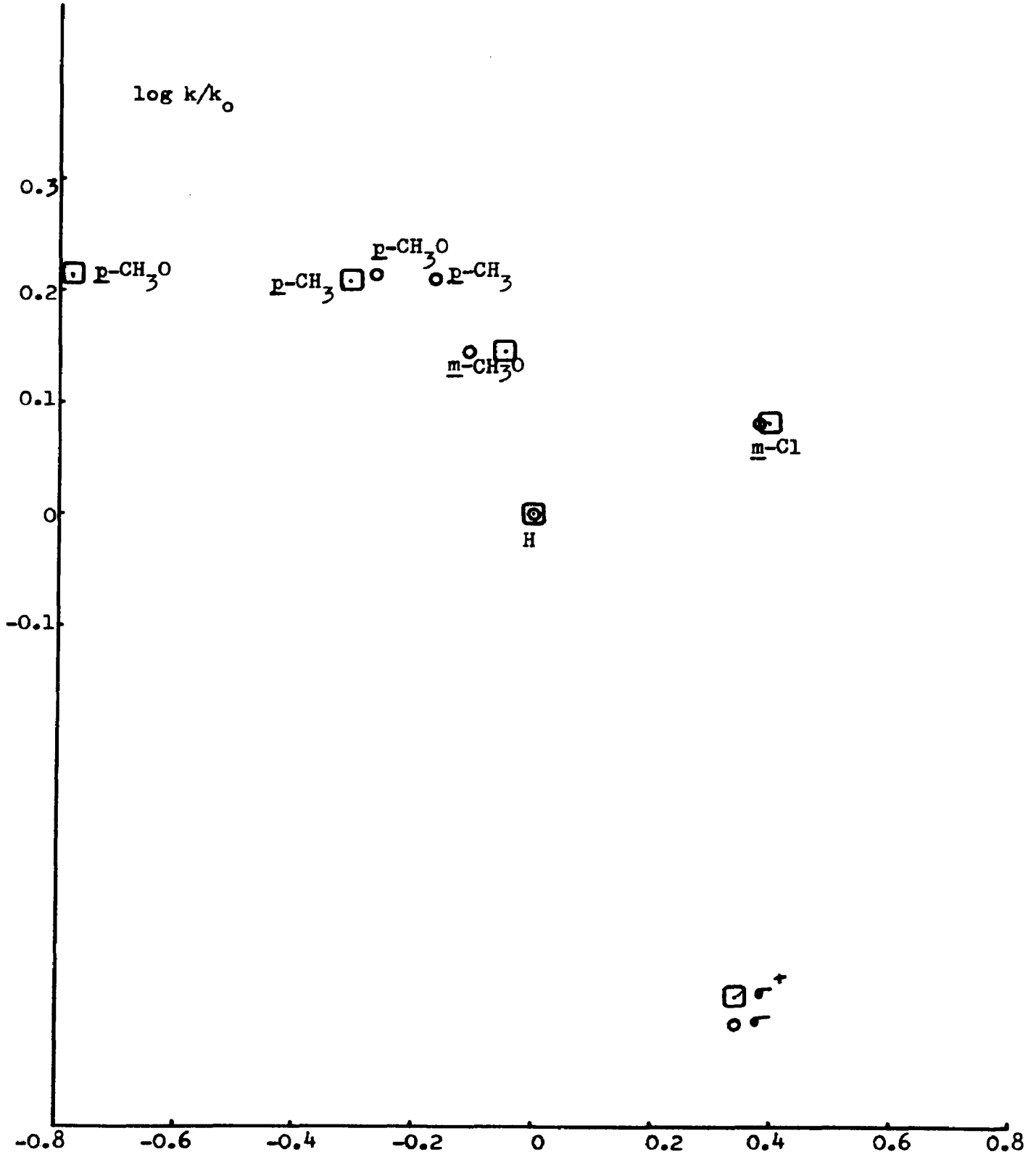


FIGURE XIV: A Hammet Plot of the 2-Aryl-1,3-Oxathiolane Series at 115.25°C in Chlorobenzene Solvent Using t-Butyl Alcohol/Acetone ratios



It is unfortunate that this work had to be done in a temperature range, which is near the isokinetic temperature. In addition, it is known that as the activity for hydrogen abstraction increases, the dependence on charge stabilization decreases. The relative reactivity of α-methoxy toluene had the greatest reactivity of a series of benzylic ethers toward bromine atoms and lowest ρ value ($\rho = 0$).[50] Therefore small ρ values were not unexpected in this work.

The relative reactivities of the compounds used in this work are high as seen in Table IX and their ρ values would probably be small even at temperatures further away from the isokinetic temperature. Since this work was performed in the vicinity of the isokinetic temperature, and because of the scatter of the points in Figures XVI, XVII and XVIII it is not possible to determine whether there is a polar dependence on the aryl moiety. Russell[60] has explained the insensitivity (to the substituent effect in oxidation reactions) of substituted benzyl phenyl ether to oxygen's non-bonding electrons participation in charge stabilization of the transition state.

FIGURE XV: Isokinetic Temperature Plots of Compounds Containing Various Types of Benzylic Hydrogens

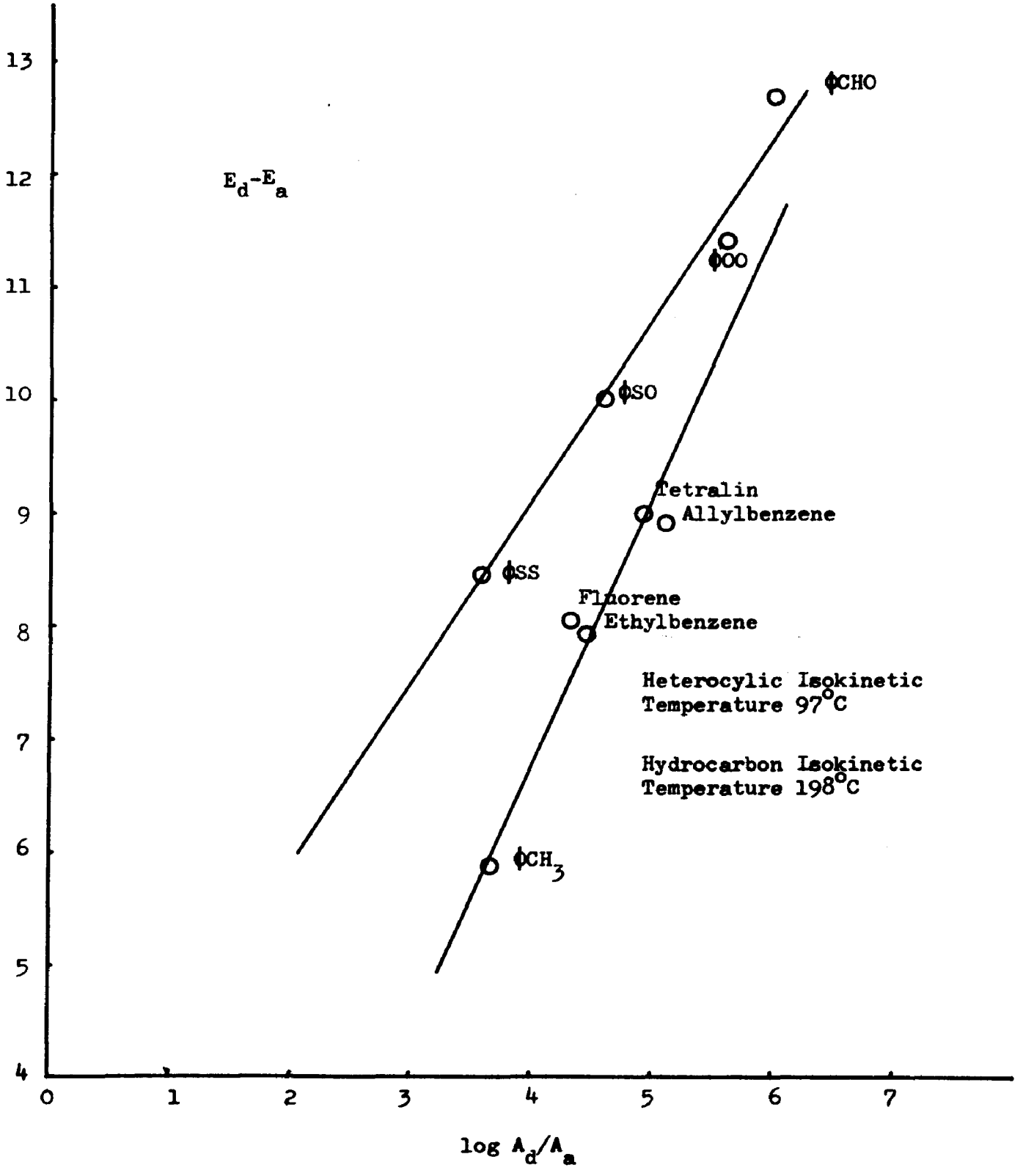


FIGURE XVI: An Isokinetic Temperature Plot of The 2-Aryl-1,3-Dioxolane Series Using t-Butyl Alcohol/Acetone Ratios

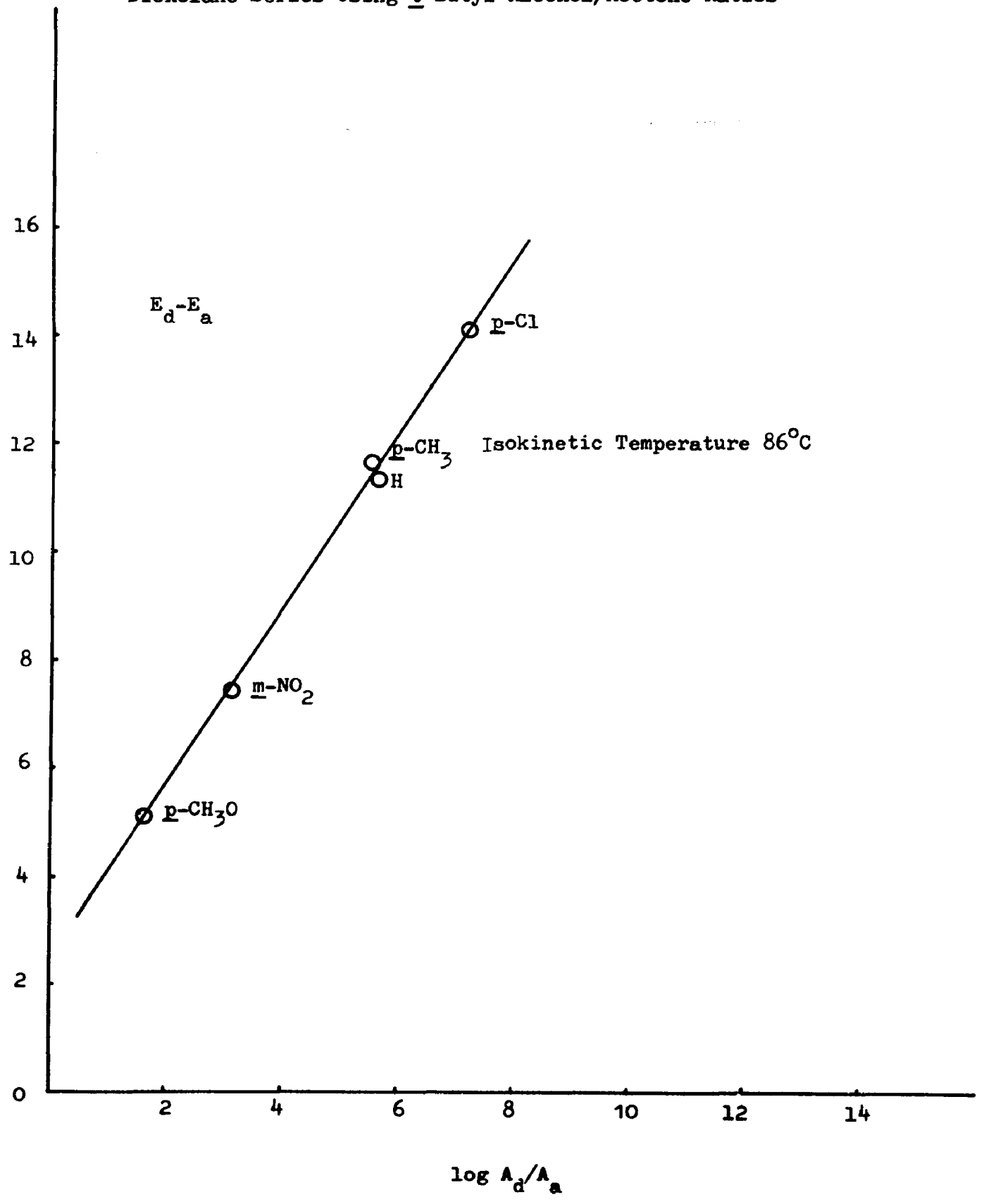


FIGURE XVII: An Isokinetic Temperature Plot of the 2-Aryl-1,3-Oxathiolane Series Using t-Butyl Alcohol/Acetone Ratios

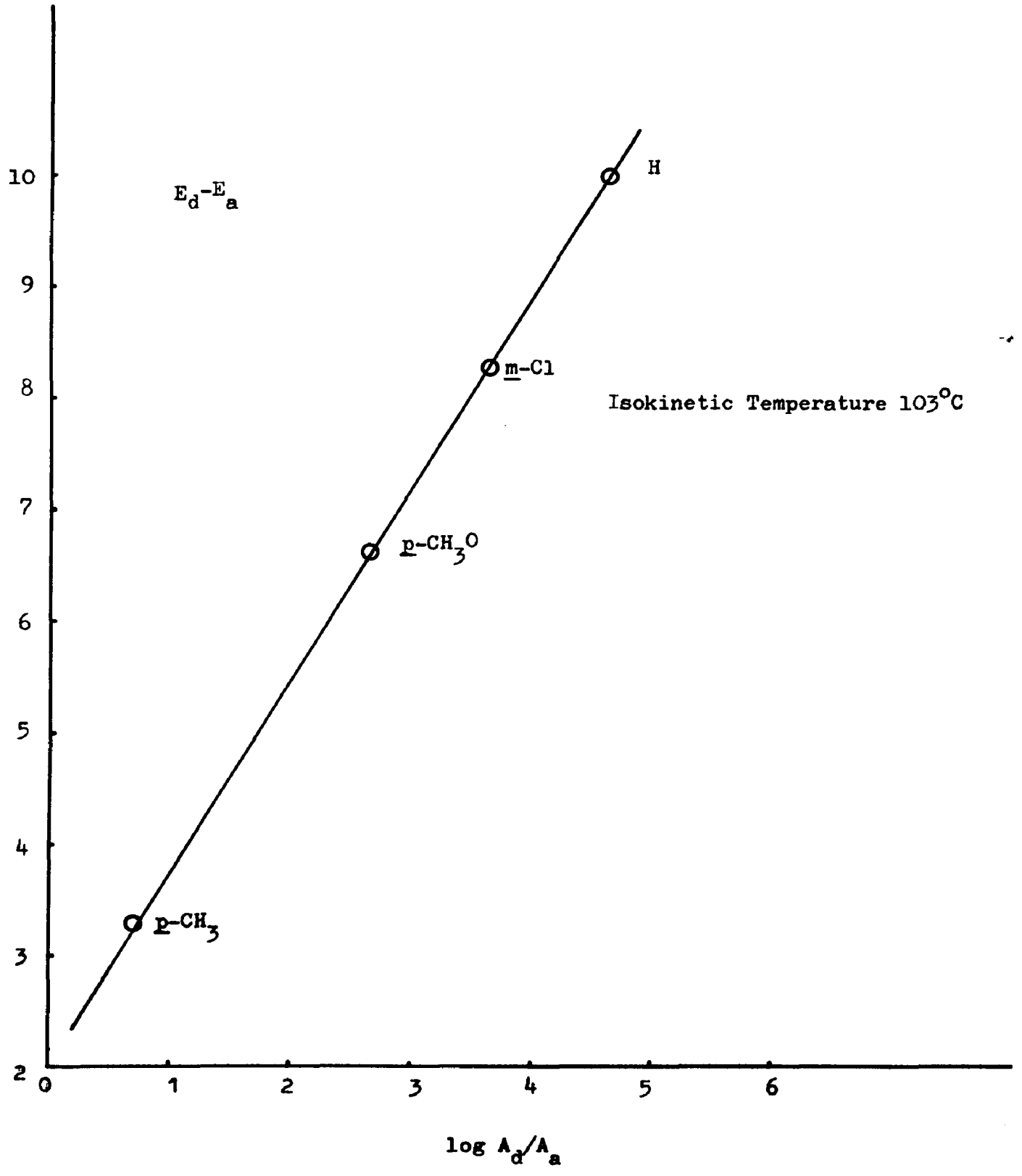


FIGURE XVIII: An Isokinetic Temperature Plot of the 2-Aryl-1,3-Dithiolane Series Using t-Butyl Alcohol/Acetone Ratios

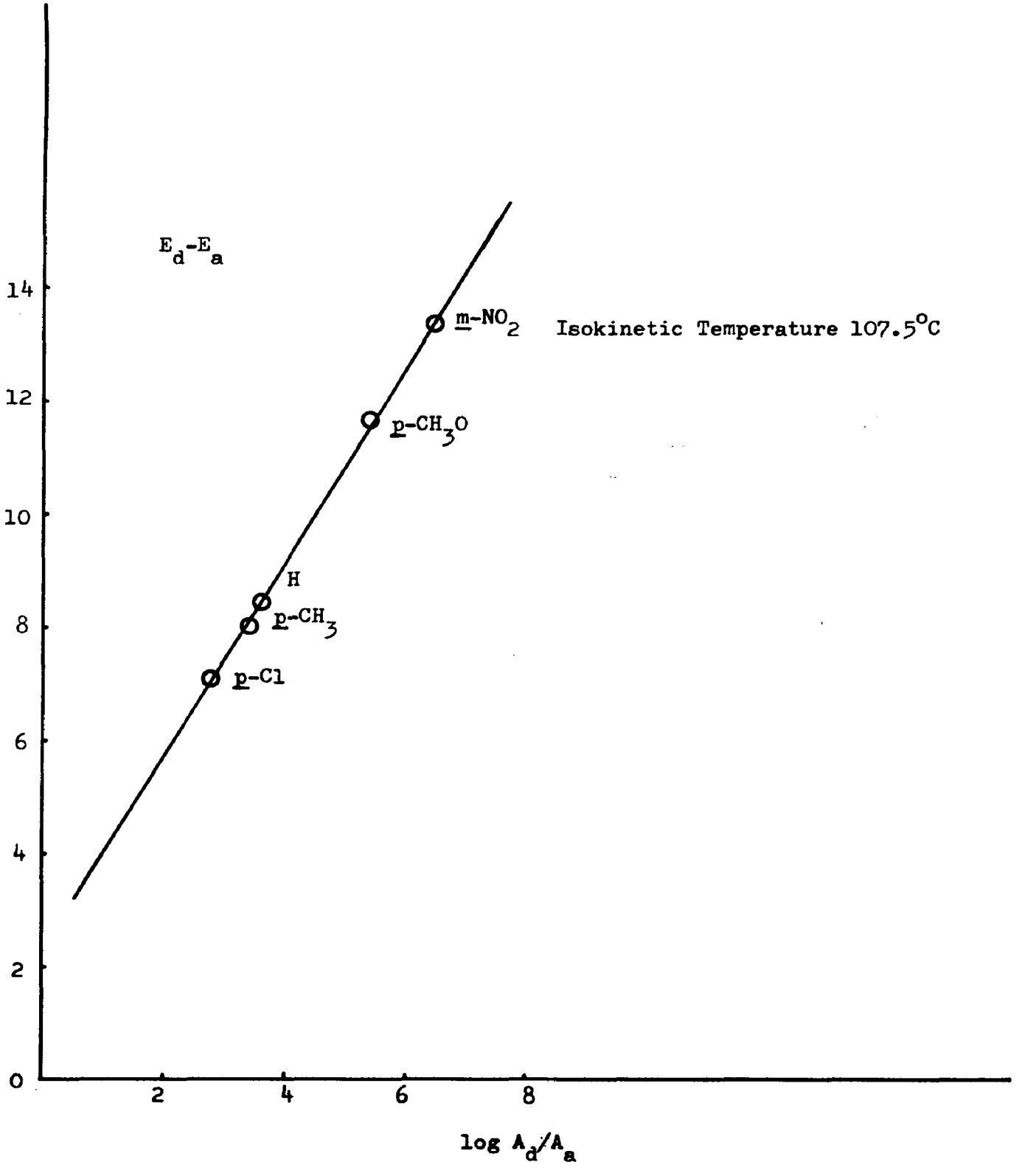


FIGURE XIX: An Isokinetic Temperature Plot of The Heterocyclic Analogues Using Direct Competition Data

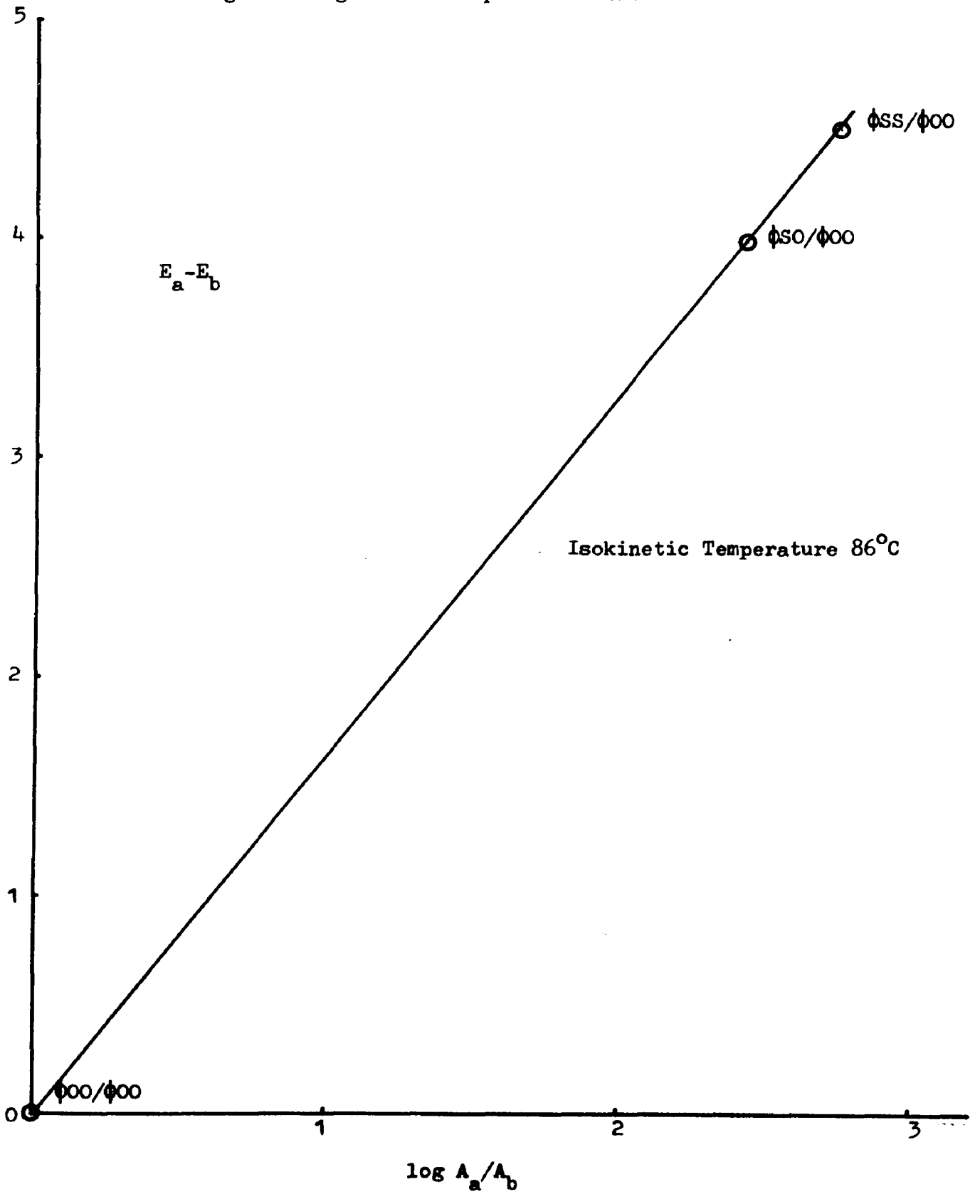


FIGURE XX: An Isokinetic Temperature Plot of The 2-Aryl-1,3-Oxathiolane Series Using Direct Competition Data

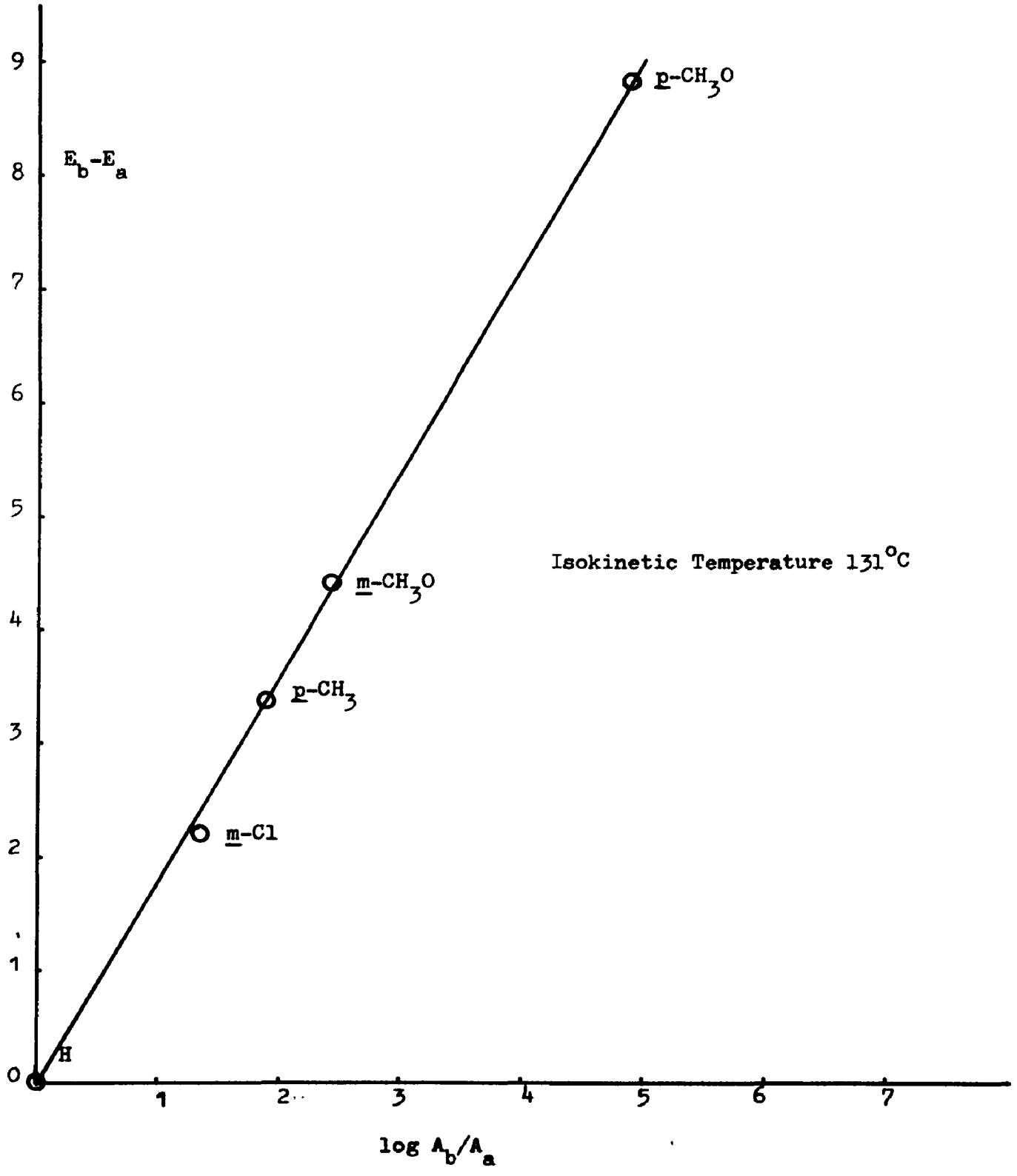


FIGURE XXI: An Isokinetic Temperature Plot of the 2-Aryl-1,3-Dioxolane Series Using Direct Competition Data

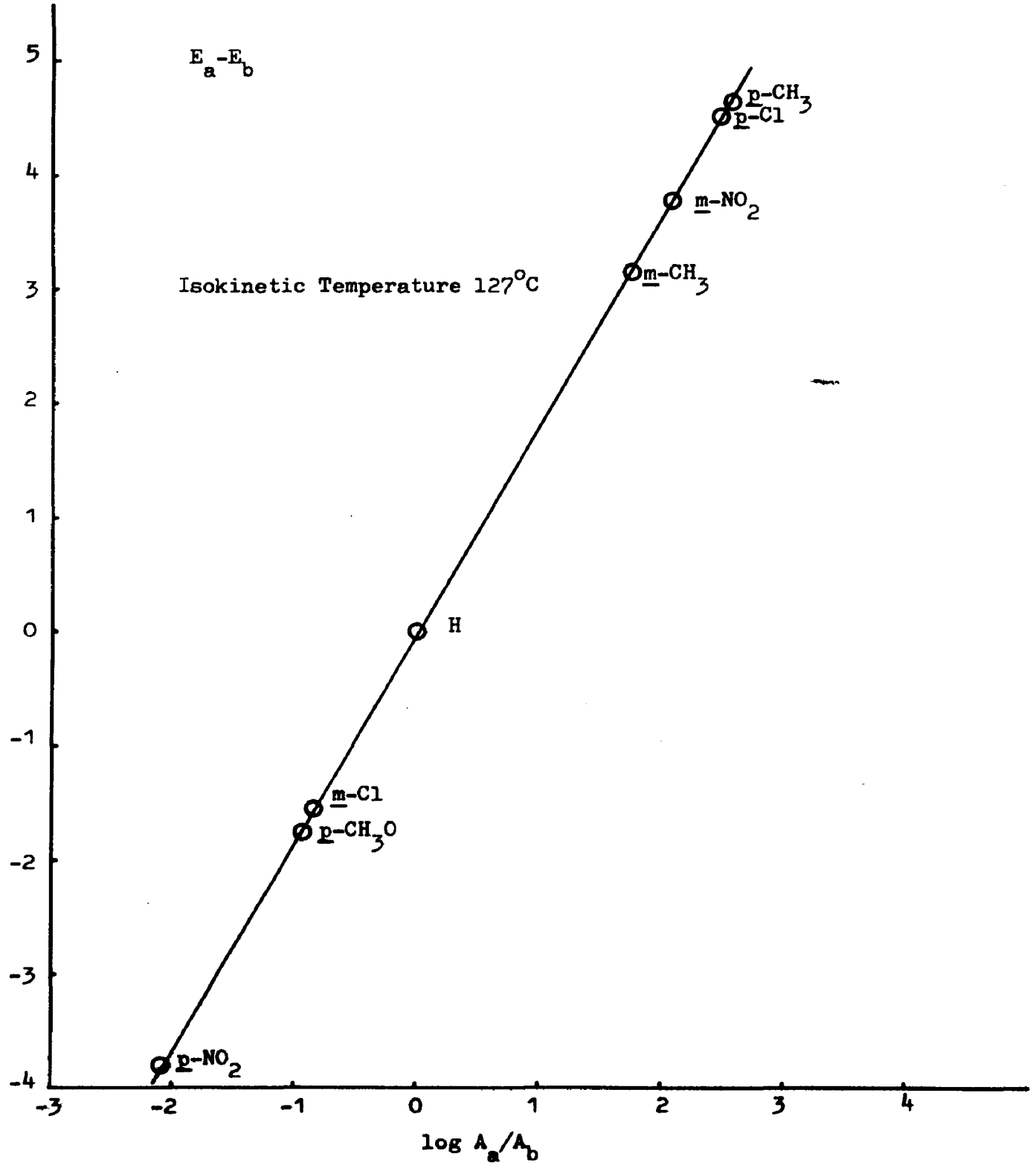
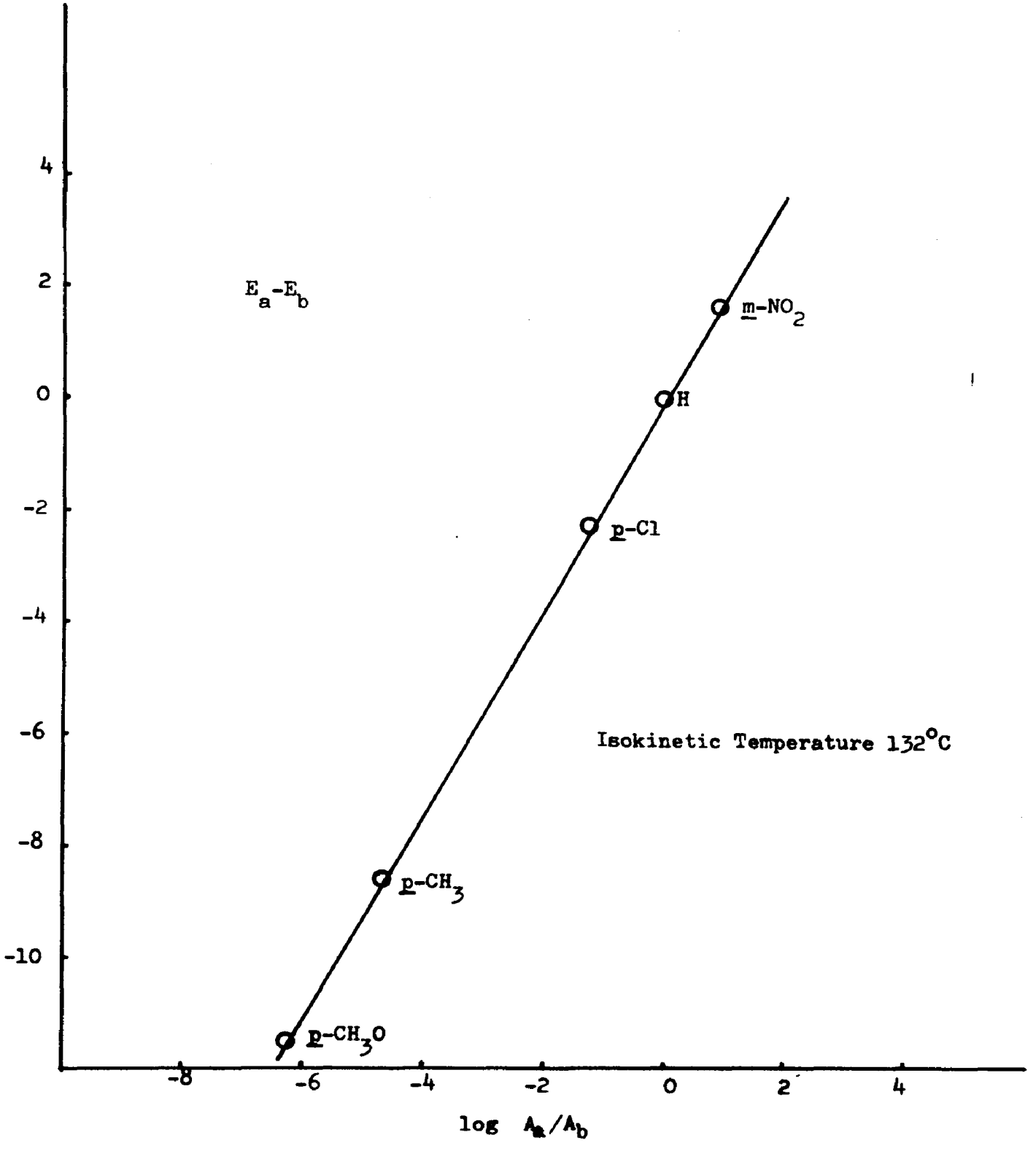


FIGURE XXII: An Isokinetic Temperature Plot of The 2-Aryl-1,3-Dithiolane Series Using Direct Competition Data



2. Isokinetic Temperature

Quite often changing a variable in a reactant or reaction mixture will cause one thermodynamic quantity to change as a function of another.[124] One such extrathermodynamic relationship is known as the isokinetic temperature.

59. $$\delta \Delta H = \beta \delta \Delta S$$

The quantity β is the isokinetic temperature and is the temperature at which the variable being studied has no effect on the rate of reaction. ΔS and ΔH are the entropy and enthalpy of activation, respectively. In the Arrhenius form the equation for the isokinetic temperature takes the following form:

60. $$(E_1 - E_2) = 2.303\ R\ \beta \log (PZ_1/PZ_2)$$

At times a change of substituent or medium operates by several distinct mechanisms. By changing the substituent we might change resonance, polarization or steric strain. The effect of these various interactions if additive, produce the following equations:

61. $$\delta_R \Delta F = \delta_1 \Delta F + \delta_2 \Delta F + \delta_3 \Delta F + - - - -$$

61a. $$\delta_R \Delta H = \delta_1 \Delta H + \delta_2 \Delta H + \delta_3 \Delta H + - - - -$$

61b. $$\delta_R \Delta S = \delta_1 \Delta S + \delta_2 \Delta S + \delta_3 \Delta S + - - - -$$

Where δ_R is the change in the interaction variable characteristic of the substituent, δ_1, δ_2, δ_3 - - - etc. are the contribution to the interaction variable by such things as resonance, polarization and steric strain which is caused by a substituent change.

The contribution from each of the interaction mechanisms produces a relationship which contains its own characteristic β value, and combining the above equations we obtain:

62. $$\delta_R \Delta H = \beta_1 \delta_1 \Delta S + \beta_2 \delta_2 \Delta S + - - - - - -$$

The corresponding equation in the Arrhenius form for two variables is the following:

63. $$\delta_R(E_1-E_2) = 2.303R\,\beta_1 \delta_1(PZ'_1/PZ_1) + 2.303R\,\beta_2 \delta_2(PZ'_2/PZ_2) + --$$

Often the double interaction mechanisms are difficult to separate into their respective parts so that they can be studied separately. Under these conditions the plots are produced by points which have scatter (unless both β_1 and β_2 are the same) the magnitude of which depends on the relative importance of the two interactions.

The relative magnitude of two different electronic effects upon this transition state stability of benzylic hydrogen abstraction by a butoxy radical have been determined. The two different electronic stabilizing moieties are the heterocyclic ring (e.g., 1,3-dioxolane, 1,3-oxathiolane and 1,3-dithiolane) and the aryl portion of the molecule.

Figures XIX and XXIII are isokinetic temperature plots in which one or more benzylic hydrogens of toluene were replaced by other atoms. In Figure XIX it is evident that all compounds containing oxygen or sulfur fall on one line and all substrates containing only carbons attached to the benzylic carbon lie on another line, with β's of 97°C and 198°C respectively. The main apparent difference between the two

slopes is that one contains 2 members of the oxygen family with oxygen in two different states of hybridization, and the other the carbon family with only carbon, in two different hybridized states. Conceivably each family in the periodic table might have its own representative isokinetic temperature in this reaction system.

For each heterocyclic system an isokinetic temperature was determined for the substituent effect in the phenyl ring (Figures XX, XXI, XXII, XXIV, XXV and XXVI using direct and indirect competition data. These values and those obtained in Figures XXIII and XIX represent effects due to heterocyclic ring stabilization, using indirect and direct competition data.

Isokinetic temperature plots are relatively insensitive to errors in activation parameters.[125] The errors tend to cause points to move along the line rather than perpendicular to it.

From the ρ values of the dioxolane series and imidazolidine series in the vapor phase as seen by the mass spectra (see mass spectra section) it can be seen that the aryl group is less important in charge stabilization in the imidazolidine than in the dioxolane series. In Appendix I it can also be seen that in the absence of solvent in the imidazolidine series produce only t-butyl alcohol in reactions with di-t-butyl peroxide which is further evidence for the enhanced reactivity of this series. Based on the above evidence it seems that the stabilization by heteroatoms for the four heterocyclic rings studied are N,N'-dimethyl imidazolidine > 1,3-dioxolane > 1,3-oxathiolane > 1,3-dithiolane.

F. Model For Transition State

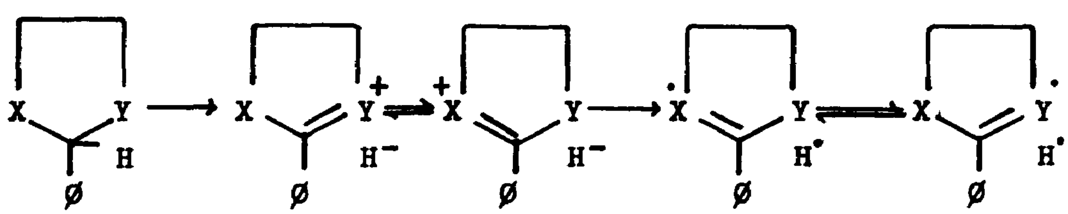
The results from the solution and gas phase (as seen by mass spectra) kinetics are consistent with the idea that there are polar contributions

to the transition state, and that they play important roles in determining reaction rates. The reactivities of the benzylic hydrogens of the four heterocyclic ring systems are determined by the heteroatoms ability to stabilize charge with its nonbonding electrons.

Oxygen's greater ability to stabilize charge compared to sulfur has been noted in the solvolysis of α-chloroethers and α-chlorosulfides.[126] The α-chloroethers solvolyze approximately 1,000 times faster than the α-chlorosulfides under Sn1 conditions, which is attributed to the greater effectiveness of 2p-2p π bonding as compared to 2p-3pπ bonding in sulfur.

Nitrogen nonbonding electrons are more available for resonsnce stabilization than oxygen's. This is seen in $\sigma_p - \sigma_m$ values which are a measure of the resonance effect, and it is found that the electron releasing effect fall in the order N > O > S. These facts are consistent with our results that the benzylic hydrogen reactivity is imidazolidine > dioxolane > oxathiolane > dithiolane.

The most important resonance structures in the transition state of the hydrogen abstraction probably has the following resonance structures for the heteroatoms, which is similar to one reported for alkyl ethers:[127]



X and Y = CH_3N ; S,S; S,O; O,O

IV. EXPERIMENTAL

A. Purification of Solvents and Reagents

1. Chlorobenzene

Fisher white label chlorobenzene was distilled through a two foot Vigereux column at atmospheric pressure - boiling range 132° - 133°C.

2. Mercaptoethanol and Ethanedithiol

The 2-mercaptoethanol (M370-1) and 1,3-ethanedithiol (E360) were obtained from Aldrich Chemical Company and used without further purification.

3. Ethylene Glycol

Ethylene Glycol was distilled before use - boiling point 197.5°C.

4. Arylaldehydes

The arylaldehydes used in making substrates were all reagent grade and used without further purification from freshly opened bottles. If the aldehydes were in opened bottles, they were purified by vacuum distillation.[128]

5. Ethyl Benzoate

Ethyl benzoate was obtained from Matheson Coleman and Bell and vacuum distilled before use - boiling point 41°C at .02 mm.

6. Di-t-butyl Peroxide

Di-t-butyl peroxide used was manufactured by Reichhold Chemicals and was free of t-butyl alcohol and acetone as shown by gas chromatographic analysis and used without further purification.

7. Acetone and t-Butyl Alcohol

Acetone and t-butyl alcohol used as gas chromatographic standards were dried over anhydrous potassium carbonate and distilled.

8. Dioxane

Dioxane was purified according to L. Fieser,[129] stored over lithium aluminum hydride and distilled before use.

9. Diphenyl Ether

The diphenyl ether (Matheson, Coleman and Bell) used as a gas chromatographic standard was found by gas chromatography to be free of interfering impurities and was not purified. All standards containing diphenyl ether came from the same bottle.

10. Toluene, Cycohexane and Isooctane

Toluene, cyclohexane and isooctane used as chromatographic standards were either spectrograde chemicals or purified by stardard techniques.[130]

11. p-dithiane

The p-dithiane (Aldrich white label t3360) was recrystallized from absolute ethanol and then sublimed in vacuum. The melting point was 110° - 111°C.

12. Thioxane

The 1,4 thioxane (Aldrich white label T3360) was distilled under vacuum from sodium hydroxide pellets, and the middle cut was taken each time - boiling point 66°C at $\sim$ 47mm. The distilled material was shown to be free of impurities by gas chromatograph using a carbowax 20M column.

13. Boron Trifluoride Etherate

Boron trifluoride etherate (Eastman Organic Chemicals) was used without purification.

14. Di-t-butylperoxyoxalate

Di-t-butylperoxyoxalate was prepared according to P. D. Bartlett.[131]

B. Preparation of Substrates

The substrates (2-aryl-1,3-dioxolanes, 2-aryl-1,3-oxathiolanes and 2-aryl-1,3-dithiolanes) were prepared by two basic procedures, 1 and 2 listed below. Only dithiolanes were made by procedure 1. When oxathiolane preparations were attempted by procedure 1, an amorphous white mass formed so this method was not used for this series of compounds and dioxolane synthesis was not attempted by method 1. All three families can be made by method 2.

Procedure 1.[132]

A mixture of 0.50 mole aryl aldehyde, 0.50 mole 1,3-ethanedithiol and 300 ml of glacial acetic acid was stirred rapidly with a teflon magnetic stirrer. A 5 ml solution of BF_3 etherate was added and an exothermic reaction started immediately. After two hours the reaction was cooled to room temperature and approximately 300 ml of methanol was added to the flask. Addition of a small piece of dry ice caused crystallization if the product was a solid. The product was filtered and washed with methanol. The product may be recrystallized from methanol.

Procedure 2.[133]

A mixture of 0.5 mole aryl aldehyde and glycol (or heteranolog) in 400 mls of benzene or toluene was refluxed with approximately 100 mg

of para-toluene sulfonic acid. The water was removed with a Dean Stark trap.

After cooling, the reaction mixture was washed with ~ 1 molar sodium hydroxide and dried with anhydrous potassium carbonate. After removal of the solvent, the product was distilled or recrystallized. Crude yields were nearly quantitative.

Dioxolanes and other easily air-oxidized materials can be conveniently stored in carius tubes under vacuum, after degassing by a standard freeze-thaw technique. Compounds stored cold in this manner remained peroxide free. Dioxolane air oxidizes altering an I.R. spectrum of freshly prepared acetal in less than one hour.[134]

TABLE X: Yields of 2-aryl-1,3-dithiolanes Prepared by Procedure 1.

Phenyl Substituant	% Yield
p-Cl	78
p-CH_3O	56.6
m-NO_2	72.3

C. Density, and Refractive Index

Density measurements were made in new water calibrated 1 ml volumetric flasks. Refractive index was measured on a Baush and Lomb refractometer, type 33-45-58, with prisms thermostated at 20°C.

D. Spectra

All I.R. spectra reported were taken on a Perkin-Elmer model 21. Absorption bands are reported in Appendix II are medium to strong in intensity and broad. Complete spectra were taken between 2 - 15.5μ(5000-645cm^{-1}) and characteristic absorptions where appropriate were noted at

expected wavelengths (phenyl, nitro etc.). The absence of carbonyl absorption at 5.6-6.0$_{\mu}$(1788-1667cm^{-1}) and gas chromatograms were used as an indication of sample purity.

N.M.R. spectra were taken with a Varian A60 operating at 60mc/sec. Chemical shifts are recorded on the δ scale relative to an internal tetramethylsilane referance. The sweep width used was 500 c.p.s.

Mass spectra were taken on A.E.I. MS9 double focusing instrument. Dr. John Wright of Harvard University was gracious enough to take the mass spectra for us.

E. Kinetics

1. Autoxidation

(a) Equipment

The autoxidations were performed in a jacketed flask which was wrapped with aluminum foil. An Eastern Industries Model D-6 pump was used to pump oil from a bath thermostated with a Yellowsprings Instrument temperature Controller Model 71 through the jacketed flask.[135]

The flask was connected to the oil bath regulated to $\pm$ 0.25°C by means of a five inch piece of glass tubing. Temperatures reported for the reactions were actually taken in the reaction flask. There was a reproducible 2.5°C temperature drop between the bath and reaction flask at 80°C.

(b) Procedure

A weighed (all weighings in this work were made on a Mettler H6T balance) amount of substrate, plus enough solvent to bring the volume to approximately 8 ml was put into a 10 ml volumetric flask, and hung in the thermostated bath for 10 minutes to come to equilibrium.

The flasks were then filled to the mark with solvent which was also heated in the thermostated bath. The entire contents of volumetric flask was then poured into the reaction vessel and allowed to drain for several minutes. It was found by reweighing the volumetric flask that greater than 99% delivery was achieved.

The reaction flask was then flushed with oxygen, stoppered and allowed to come to equilibrium for a few minutes. Then the azo bisisobutrylnitrile (AIBN) was charged into the reaction vessel by means of a powder funnel which was placed in thermometer joint. The thermometer was replaced and the clock started.

Before readings were taken, the height of mercury in the leveling bulb and buret were equalized, and the buret was tapped gently. When the buret reading was taken, a time reading was also taken.

The volume of oxygen that reacted was corrected to STP and for nitrogen evolution from the AIBN imitiator using the rate constants from Overberger's work.[136] The rates reported are initial rates of reactions. At times there was an induction period before the reaction proceeded. In these cases the initial rate is taken after the induction period.

2. t-Butyl Alcohol/Acetone Ratios

(a) Procedure for making tubes, volume correction, etc.

An amount of substrate which would produce approximately a 0.4M solution was weighed into a 10 ml volumetric flask, and then t-butyl peroxide was put into the volumetric so that its concentration was approximately 0.067M. The t-butyl peroxide was added in one of two ways either by weighing a sample directly into the volumetric flask or by pipeting in a 1 ml from a stock solution before it was brought to the

mark with solvent. The solvent used in all of these reactions was chlorobenzene.

The stock solution was diluted to produce a total of four different concentrations all with the same substrate to t-butyl peroxide ratio. In the reactions run without solvent, samples of substrate and t-butyl peroxide were weighed directly into carius tubes. A reaction mixture was put into a carius tube (8mm by 10mm by 200mm) and degassed a minimum of three times by the freeze-thaw technique.

The freeze-thaw technique is performed as follows: The carius tubes containing the reaction mixture are connected to a vacuum manifold which can obtain pressures $<$ 20 microns and is frozen in dry ice acetone baths or liquid nitrogen. Then the stopcocks to the vacuum manifold are opened and when all the air is pumped out they are closed. The reaction mixture is then allowed to thaw while still under vacuum, and the whole process is repeated at least two more times. After the final freeze-thaw cycle the tubes are sealed under vacuum.

The tubes were then immersed in a thermostated oil bath at the desired temperatures and allowed to react for approximately one half life. The time of reaction was found not to be critical. 2-phenyl-1,3-dioxolane produced the same k_a/k_d when reacted for five and twelve hours at 128°C.

When di-t-butylperoxyoxalate was used as a t-butoxy radical source, it was reacted for a time equal to 60 half lives. It was necessary to use essentially all the di-t-butylperoxyoxalate, because it was not stable to gas chromatographic conditions. The amounts of t-butylperoxide and di-t-butylperoxyoxalate were adjusted so that the same number of butoxy radicals was always produced.

Volume corrections were made by two methods. The first method consisted of placing a reaction mixture in a Mohr pipet which was graduated to the tip. The tip was sealed with epoxy glue, and the solutions were put in with a long hypodermic needle so that no air bubbles were trapped. A reading was taken at room temperature and then placed into a thermostated bath, allowed to come to equilibrium and a volume reading was again taken. Within experimental error, the volume expansion was the same for all the substrate solutions used at concentrations of approximately 0.4M at 128°C.

Volume expansion of solutions calculated from the following equation:[137]

Equation 64

$$d_T = \left[d_S + 10^{-3} \alpha\ (T - T_S) + 10^{-6} B(T-T_S)^2 + 10^{-9} \gamma\ (T-T_S)^3 \right] \pm \Delta$$

T = Temperature
T_S = 0°C
d_S, α, B, γ, and Δ are constants

(temperature range 0 - 70°C)

produces the same value within experimental error as our measured values at 128°C, even though the equation is being used above is recommended temperature.

This method of correcting for volume expansion was used to calculate the volume expansion for solutions in the range of 100°C to 140°C. For solutions above the boiling point of chlorobenzene (132°C) the equation was the only method available for determining volume changes. The error introduced by the equation is probably small. The equation produces values to six significant figures, and our data uses only three figures.

The equation's temperature range is probably greater than the suggested range value to three significant figures.

The mass balance for decomposition products of t-butyl peroxide and remaining peroxide was generally good, (better than 85% accounted for). Occasionally anomolous reactions occurred, e.g. more t-butyl peroxide decomposed than usual. In one instance all the t-butyl peroxide disappeared when approximately one half should have. Such anomolies seemed to be random occurances and at this time the reason for it is not known.

In the oxathiolane series there were two small closely spaced peaks with very short retention times compared to t-butyl peroxide and its decomposition products. It was assumed that these peaks were methane and ethane, which comes from methyl radical coupling and hydrogen abstraction. These reactions were under a noticable positive pressure when run without solvent.

(b) Description of gas chromatographic analysis used in alcohol/acetone ratio studies

i. General

The quantitative method used in determining concentrations of t-butyl peroxide, acetone, and a t-butyl alcohol was gas chromatography. The same liquid phase was used for all substrates, carbowax 20M. Table XI (p. 109) gives the relative retention times of substrates and decomposition products (in 2-aryl-1,3-dioxolane series) to internal standard. The approximate column temperatures used were 160°C, 200°C, and 225°C for the 2-aryl-1,3-N,N'-dimethyl imidazolidines, 1,3-dioxolane, and 1,3-dithiolanes respectively.

Gas chromatographs for substrates were performed on Aerographs A-90-P (T.C. detector), HyFi model 600D and F.M. 5750 with dual flame ionization detector.

Analysis of t-butyl peroxide acetone and t-butyl alcohol were performed with a variety of liquid phases. Table XI contains the relative retention times and conditions used for each liquid phase. All the t-butyl alcohol/acetone ratios data were taken with a Perkin Elmer 154D using thermistor or flame detector or an F & M 5750 (Hewlett Packard) dual flame ionization gas chromatograph.

Under the conditions listed in Table XII (p. 111) di-t-butyl peroxide is stable and does not decompose to acetone and t-butyl alcohol. The reproduceability of injections varied. At low reaction temperature and with low t-butyl peroxide concentrations, the amount of acetone that was produced was small. The gas chromatographs were operated at low attenuation and the acetone peaks were small, which makes the error in measuring this peak relatively high -- an estimated $\pm$ 10%. At higher temperatures and concentrations, the precision was usually better than $\pm$ 5%.

TABLE XI Relative Retention Times of Substrates and Products to Internal Standard with Carbowax 20M

Internal Standard	Substrate[1.]	Products A	Products B
ϕOϕ[2.]	p-MeOϕSS		
1	10.4		
ϕOϕ	p-Meϕ SS		
1	5.50		
ϕOϕ	ϕSS		
1	3.11		
ϕOϕ	p-Clϕ SS		
1	7.2		
ϕOϕ	ϕNN		
1	0.4		
ϕOϕ	p-MeOϕNN		
1	0.65		
ϕOϕ	p-Clϕ NN		
1	1		
Naphthalene	p-Clϕ NN		
1	2.60		
Glycol	p-Clϕ NN		
1	3.86		
ϕOϕ	ϕOO	ϕCO_2ET	ϕCHO
1	0.69	0.212	0.172
ϕOϕ	p-Clϕ OO	p-Clϕ CO_2ET	p-Clϕ CHO
1	1.50	0.65	0.45
Tetraethylene Glycol	p-Meϕ OO	p-CH_3ϕ CO_2ET	p-CH_3ϕ CHO
1	0.68	0.37	0.25
ϕCH_2OH	p-Meϕ OO	p-CH_3Oϕ CO_2ET	p-CH_3Oϕ CHO
1	4.22	2.22	1.71
ϕOϕ	p-Meϕ SO		
1	2.37		

1. ϕSS, ϕNN, ϕOO and ϕSO are 2-phenyl-1,3-dithiolane, 1,3-N,N'-dimethyl imidazolidine, 1,3-dioxolane and 1,3-oxathiolane respectively. The prefix is the phenyl substituent.

2. Diphenyl ether has retention times of 9 minutes at 160°C, 4 minutes at 200°C and 2 minutes at 225°C on a 5' x 1/4" 15% carbowax 20M (chrom W) with an approximate flow of 75ml per minute.

TABLE XII Relative Retention Times of t-Butyl Peroxide, Acetone, t-Butyl Alcohol and Internal Standards to t-butyl Peroxide

t-Butyl Peroxide	Acetone	t-Butyl Alcohol	Internal Standards A	B	C
1 [1.]	1.53	2.88	ϕCH_3 5.36		
1 [2.]	0.39	0.50	Cyclohexane 0.59	p-Dioxane 1.25	ϕCH_3 2.04
1 [3.]	1.15	1.36	Isooctane 0.74		
1 [4.]	1.43	1.90			

1. 2 Meter x 1/4" K column (Carbowax 1500) at 76°C and 10.1 lbs flow, t-butyl peroxide retention time -- 3 minutes.

2. 2 Meter x 1/4" A column (diisodecyl phthalate) at 92°C and 10.1 lbs flow, t-butyl peroxide retention time -- 7 minutes.

3. 11 1/2 x 1/8" carbowax 20M column (25% chrom P) at 94°C and 25 lbs flow, t-butyl peroxide retention time -- 2.4 minutes.

4. 2 Meter x 1/4" O (silicon grease) + 2 Meter x 1/4" R column (Ucon 550X) column in series at 76°C and 20 lbs flow, t-butyl peroxide retention time -- 7 minutes.

ii. Methods of Gas Chromatographic Standardization

The method used in determining the amount of substrate remaining in the t-butyl alcohol/acetone ratio study when no solvent was used was the direct weighing in of pure internal standard. Blanks were run (substrate with no peroxide) and found to be stable to the reaction temperatures. Samples of reaction mixture (in degassed carius tubes) were allowed to stand at room temperature for six weeks and no detectable reaction had occurred. It was therefore assumed that once reactions were quenched to room temperature, they are stable.

Equation 65 was used to find the substrate concentration.

Equation 65

$$\frac{\text{Peak Area Substrate}}{\text{Peak Area Standard}} = K \quad \frac{\text{Moles Substrate}}{\text{Moles Standard}}$$

K = Constant

The constant K was determined by gas chromatographing known quantities of substrate/standard. The peak area ratio/mole ratio is equal to the proportionality constant K.

In the determination of K, the mole ratio of substrate to standard was made approximately the same as in the actual determination of substrate. The same procedure was used in determining the t-butyl alcohol, acetone and remaining t-butyl peroxide concentrations in this series.

When the reactions were run in chlorobenzene solvent another method was used to determine the amount of substrate that remained. A stock solution of accurately weighed internal standard (diphenyl ether) was made in a volumetric flask using chlorobenzene as a solvent. The stock solution was kept in a volumetric flask with a greased glass stopper in

order to prevent solvent evaporation. Similar solutions were made for substrates and products to be analyzed at several concentrations.

Equal volumes of internal standard and substrate stock soltuions were pipetted into a test tube and mixed thoroughly before being gas chromatographed. A standard curve was then plotted of Peak area Sample/ Peak area Standard versus concentration of Sample. Good straight line plots were obtained for all the compounds analyzed by this method.

A calibration method which depended on constant volumetric delivery was also used. This method was used for determining the amounts of t-butyl peroxide, acetone and t-butyl alcohol with the Perkin Elmer 154D and thermistor detectors. The method was used because the concentrations of the solutions were so low that any further dilution due to internal standard had to be avoided. The volume of the injections used was between 30 and 80 μls. When t-butyl alcohol, acetone and t-butyl peroxide was analyzed, several injections were made before the chlorobenzene solvent reached the detector.

Stock solutions containing various concentrations of t-butyl peroxide, t-butyl alcohol, and acetone were taken up in accurately measured volumes in a 100μl Hamilton syringe and injected into the gas chromatograph. Great care was taken not to get air bubbles into the syringe. Air bubbles can be eliminated by drawing solution into the syringe slowly and expelling it very rapidly several times. Graphs of the amount actually delivered in moles was plotted against peak area or height and produced good straight lines, and reproducability of an injection was also very good.

Peak relationships were measured by disc integrator, Peak height x width at 1/2 height, and peak height. The method chosen for a particular

case was the one which gave the greatest reproducibility, and seemed most accurate.

If the base line was noisy, the disc integrator was not used, and peak height x width at 1/2 height was not usually used for peaks with a 1/2 height width of less than 4mm. When standard curves were drawn they were usually drawn for all the methods indicated above.

3. Direct Competition Experiments

All direct competition experiments were performed in carius tubes (200 mm x 10mm x 8mm) in vacuo. The reaction mixtures were degassed by the freeze-thaw procedure previously described. The solutions were made so that they contained $\sim$ 0.4M concentrations of each substrate and the t-butyl peroxide concentration was $\sim$ 1/6 of the total concentration of substrate.

Reactions were performed in a thermostated oil bath (described on page), for a reaction time equal to approximately 1 half life of t-butyl peroxide. One set of reaction tubes were reacted for two different times, five hours and 12 hours. There was no difference in relative reactivities due to time.

The analysis of the direct competition reactions was performed by N.M.R. (Varian A60) except for the reaction of 2-phenyl-1,3-dioxolane with 1,4-dioxane; 2-phenyl-,3-dithiolane with 1,4-dithiane; and 2-phenyl-1,3-oxathiolane with 1,4-oxathiane. The latter were done by gas chromatography.

The N.M.R. analysis was performed by pipetting 1 ml of reaction mixture into a test tube, and then 25 μl of 2-phenyl-1,3-oxathiolane; 2-phenyl-1,3-dioxolane; or 2-(p-chlorophenyl)-1,3-dioxolane was pipetted into the test tube with a 50 l Hamilton syringe. The 2-phenyl-1,3-

dioxolane, 2-phenyl-1,3-oxathiolane and 2-phenyl-1,3-dithiolane were reacted together. Identical procedures were performed on blanks which were carius tubes filled with unreacted reaction mixture stored at room temperature.

Only the areas of the benzylic hydrogens were measured in the analysis. This area was free of interfering peaks before and after reaction, areas were measured as peak heights and each sample was analyzed a minimum of three times.

The height ratio of substrate/standard was used as a function of concentration, and substituted into the Equation 66 and Equation 67 was obtained.

66

$$\frac{k_A}{k_B} = \frac{\log\left(\frac{(C_f)}{(C_i)_A}\right)}{\log\left(\frac{(C_f)_B}{(C_i)_B}\right)}$$

C_f = Final concentration

C_i = Initial concentration

67

$$\frac{k_A}{k_B} = \log\frac{\left(\frac{\text{P Substrate}_{(f)}}{\text{P Standard}}\right)_A}{\left(\frac{\text{P Substrate}_{(i)}}{\text{P Standard}}\right)_A} \Big/ \log\frac{\left(\frac{\text{P Substrate}_{(f)}}{\text{P Standard}}\right)_B}{\left(\frac{\text{P Substrate}_{(i)}}{\text{P Standard}}\right)_B}$$

P = Peak heights

This method agreed well with gas chromatographic analysis performed on identical samples. The agreement between the two methods was better than $\pm$ 3% in all cases tried.

F. Gas Chromatographic Modifications

1. Column Modifications For the Perkin Elmer 154D Using Thermal Conductivity Detectors.

In the gas chromatographic analysis of t-butyl peroxide, t-butyl alcohol and acetone, the chlorobenzene (solvent) has the longest retention item. Several injections are made before the chlorobenzene from the first injection reaches the detector. Then the chlorobenzene peaks elute taking as much time as the peaks of interest. This means 50% of the time is wasted waiting for solvent to elute.

Unfortunately, when the column-oven temperature is changed, the detector block temperature is automatically also changed, causing base-line drift with the thermal conductivity detector until thermal equilibrium is reestablished.

In order to reduce the dead time due to solvent elution, it was necessary to devise a method for heating the columns without changing the column-oven temperature.

It was found that this could be accomplished by making pyrex glass columns and wrapping them with heating wire. The columns are made of 4mm I.D., 6mm O.D. pyrex glass tubing bent into a simple "u" shape, with an overall length of 43 to 44 inches and packed with standard materials and plugged at the ends with glass wool. Such tubing fits the standard fittings of the instrument without leakage, even at maximum gas pressures.

Chromel wire was wrapped on the columns so that the loops were 1/2 inch apart. Columns may be used singly or in series.

In order to avoid base-line drift, the heat supplied externally to the columns should not be great enough to cause the oven temperature to rise. Each oven temperature has a maximum external power setting above which the oven temperature would rise if permitted to heat for long times. Actual column temperatures were measured by means of a thermocouple inserted in the end of the column.

Heating and cooling curves of the columns for any external power settings may be obtained. At an oven temperature of 77.5°C, the column temperature reached 95°C within seven minutes at the maximum permitted external power setting that did not raise the oven temperature. Cooling within the column itself to 77.5°C also occurred within seven minutes when the external power setting was turned off.

At an oven temperature of 103°C, the column temperature reached 130°C at the maximum allowable external power setting. Higher column temperatures could undoubtedly be obtained if insulating materials were used around the heating coil.

2. Modifications in the Perkin Elmer 154D Using Flame Detectors

Minor modifications were made in Perkin Elmer 154D column system so that the splitter could be eliminated and 1/8 inch columns used.

The adapter (flame detector) was placed in the thermal conductivity (T.C.) detector block in the packed-column-mode-position, (see Flame Ionization Accessory Kit Manual #154-0395 figure 4). A 5' by 1/4" piece of stainless steel tubing was placed in the remaining front hole of the T.C. detector block. The 1/8" column was then attached to this piece of

tubing with a 1/4" to 1/8" reducing union (Crawford Company). Another reducing union 1/8" to 1/16" was placed on the exit end of the column. The column was then connected to the flame detector block's 1/16" fitting closest to the rear of the instrument with a piece of 1/16" stainless steel tubing.

G. Products

1. The Reaction between 2-phenyl-1,3-dithiolane and di-t-butyl peroxide.

A carius tube was charged with 4.484gm (0.0222 mole) of 2-phenyl-1,3-dithiolane and 0.834gm (0.00572 mole) of di-t-butyl peroxide. The reactants were degassed by the freeze-thaw technique and sealed under vacuum. The carius tube was immersed in a 128°C oil bath for eleven hours and fifteen minutes.

After several days of standing at room temperature crystals started growing in the reaction mixture. The volatile products were distilled under vacuum at 100°C and collected in a liquid nitrogen trap. A great deal of gas was collected with the distillate (violent effervescence upon melting of distillate) which was presumed to be methane and ethane. The distillate was primarily t-butyl alcohol, acetone and unreacted peroxide with some 2-phenyl-1,3-dithiolane.

The pot residue was a mixture of an oil and crystals. The crystals were filtered and washed with n-hexane, weighed 0.675gm, and recrystallized from hot CCl_4/EtOH m.p. 185°-190°C; I.R. bands 10.0μ and 10.4μ (see Appendix II);[145] mass spec m/e 362, 302, 270 and 181.

2. The reaction between 2-phenyl-1,3-oxathiolane and di-t-butyl peroxide.

A carius tube was charged with 6.77gm (0.0405 mole) and 1.67gm (0.0114 mole) of di-t-butyl peroxide. This reaction was degassed and reacted at the same temperature for the same time as the previous reaction.

The volative products were distilled under vacuum at 100°C and the distillate was collected in a liquid nitrogen trap. The distillate was primarily t-butyl alcohol, acetone, and unreacted di-t-butyl peroxide (the distillate in this reaction also contained a great deal of gas which effervesced violently upon melting which was presumed to be methane and ethane).

The pot residue was a mixture of oil and crystals, which was filtered, washed with n-hexane and weighed 1.45 gm. The crystals were recrystallized from hot CCl_4/EtOH m.p. 211-213°C, I.R. bands 9.25μ, 9.35μ, 10.3μ and 10.8μ, (see Appendix II);[145] mass spec, no discernable parent peak, m/e 165, and 105.

V. SUMMARY

In this dissertation we have attempted to determine the relative importance of three different types of heteroatoms to the transition state stability of benzylic hydrogen abstraction. The stabilization by the heteroatoms fall in the order N $>$ O $>$ S, and seems to overshadow the importance of the aryl moiety.

APPENDIX I

t-butyl alcohol/acetone ratios for 2-aryl-1,3-dithiolane, 2-aryl-1,3-dioxolane, and 2-aryl-1,3-dimethyl-1,3-diazolidine in the absence of solvent

Compound	Run Number	Peroxide Substrate ratio	mmole substrate used	mmole peroxide used	mmole substrate remaining	chain length	t-BuOH/ acetone
2-(p-methoxyphenyl)-1,3-dithiolane	I.	39.1/1	1.830	.047	1.878	0	-
	II.	13.8/1	2.260	.164	2.363	0	.489
	III.	10.8/1	2.281	.211	2.357	0	.620
	Blank	-	.576	0	.613		av .555
2-(p-chlorophenyl)-1,3-dithiolane	I.	38/1	2.023	.053	1.949	0	-
	II.	25.9/1	2.51	.097	-	0	13.5
	III.	14.0/1	2.749	.234	2.824	0	22.0
	Blank	-	.812	0	.796		av 17.7
2-(phenyl)1,3-dithiolane	I.	60.1/1	3.305	.055	3.053		-
	II.	23.2/1	2.637	.114	2.618		2.30
	III.	9.11/1	2.191	.239	1.988		1.96
	Blank	-	1.555	0	1.594		av 2.13
2-(p-methylphenyl)1,3-dithiolane	I.	5.63/1	2.75	.488			6.246
	II.	2.92/1	2.70	.924			5.994
	III.	2.35/1	2.85	1.211			8.14
	Blank	-	1.055				av 6.79
2-(m-nitrophenyl)1,3-dithiolane	I.	5.26/1	2.65	.504			1.14
	II.	3.52/1	2.61	.743			1.07
	III.	2.56/1	2.24	1.07			1.45
	Blank	-	1.38	0			av 1.12

Compound	Run Number	Peroxide Substrate ratio	mmole substrate used	mmole peroxide used	mmole substrate remaining	chain length	t-BuOH/ acetone
2-phenyl-1,3-dimethyl-1,3-diazolidine	I.	35.0/1	2.380	.068	2.613		
	II.	14.9/1	2.227	.150	2.165		
	III.	11.1/1	2.376	.215	2.154		
	Blank	-	.988	0	1.051		
2-(p-methylphenyl)-1,3-dimethyl-1,3-diazolidine							
	I.	22.9/1	2.004	.090	1.986		
	II.	11.5/1	1.854	.161	1.746		
	III.	6.93/1	2.047	.296	1.787		
	Blank	-	1.547	0	1.779		
2-(p-methoxyphenyl)-1,3-dimethyl-1,3-diazolidine							
	I.	27.1/1	2.19	.0808	-		
	II.	13.4/1	1.85	.138	-		
	III.	7.60/1	2.19	.288	2.247		
	Blank		1.17	0	1.330		
2-(p-chlorophenyl)-1,3-dimethyl-1,3-diazolidine							
	I.	28.00/1	2.10	.075			
	II.	11.9/1	2.16	.182			
	III.	8.25/1	1.98	.240			
	Blank	-	1.36	0			
2-(phenyl)-1,3-dioxolane	I.	15.3/1	6.83	.446	2.304	5.08	12.61
	II.	12.0/1	6.92	.577	2.207	4.08	12.50
	III.	7.41/1	6.93	.935	1.343	2.99	11.56
	Blank	0	4.28	0	0	av	12.20
2-(p-chlorophenyl)-1,3-dioxolane	I.	16.9/1	6.37	.376	2.567	5.05	11.18
	II.	11.1/1	6.44	.582	2.002	3.80	11.53
	III.	7.26	6.16	.850	1.532	2.72	10.93
	Blank	-	2.95	0	2.95	0 av	11.23

Compound	Run Number	Peroxide Substrate ratio	mmole substrate used	mmole peroxide used	mmole substrate remaining	chain length	t-BuOH/ acetone
2-(p-methylphenyl)-1,3-dioxolane	I.	16.4/1	6.19	.378	1.641	6.02	9.14
	II.	11.8/1	6.15	.521	1.238	4.71	15.00
	III.	6.64/1	6.32	.953	.735	3.80	13.06
	Blank	-	3.98	0	4.14		av 12.40
2-(p-methoxyphenyl)-1,3-dioxolane	I.	13.04/1	5.93	.454			13.49
	II.	10.8/1	6.33	.587			8.38
	III.	7.24/1	6.26	.853			6.86
							9.57
2-(n-nitrophenyl)-1,3-dioxolane	I.	14.4/1	5.63	.396			5.518
	II.	9.27/1	5.93	.639			7.443
	III.	5.91/1	5.36	.907			5.52
							6.16

2-(chlorophenyl)-1,3-N,N'-dimethyl imidazolidine 70ev

m/e	%	m/e	%	m/e	%
212	3.34	102	1.37	59	0.89
211	14.6	101	0.81	58	5.19
210	10.4	100	7.58	57	6.29
209	41.5	99	100	56	7.15
207	1.05	98	0.65	55	4.16
197	0.84	97	1.65	54	1.87
195	2.50	91	2.74	53	1.39
169	2.39	90	1.94	52	1.74
168	14.9	89	4.63	51	3.45
167	7.09	86	0.81	50	3.13
166	4.23	85	5.32	49	0.76
155	0.81	84	3.23	46	0.65
154	3.31	83	2.42	45	17.9
153	1.77	82	1.65	44	7.68
152	6.21	81	3.74	43	22.5
151	2.34	80	1.40	42	22.0
140	0.73	79	1.97	41	6.61
139	0.92	78	6.37	40	1.42
138	1.13	77	3.77	39	5.16
137	1.45	76	1.56	38	1.19
133	0.81	75	4.61	37	0.65
132	4.52	74	1.44	36	1.08
131	3.63	73	1.21	32	6.71
130	0.82	72	1.21	31	4.77
128	0.53	71	0.85	30	2.94
127	3.66	70	1.58	29	4.61
126	1.29	69	1.73	28	37.9
125	10.6	68	0.89	27	5.48
120	0.81	67	2.77	26	2.10
119	0.97	66	1.02	18	6.00
118	0.85	65	1.44	17	14.4
117	1.81	64	0.65	15	12.9
116	1.26	63	2.52		
113	1.06	62	1.13		
112	1.50	61	0.82		
111	2.60	60	13.2		

2-(p-methoxyphenyl)-1,3-N,N'-dimethyl imidazolidine 70ev

m/e	%	m/e	%
207	2.04	99	100
206	18.0	97	1.88
205	61.8	92	1.73
203	1.27	91	4.94
192	0.53	90	1.98
191	4.00	89	1.43
190	1.53	79	2.18
177	0.82	78	5.27
176	0.82	77	6.43
175	0.57	76	1.45
164	1.69	70	1.16
163	12.8	69	1.02
162	72.4	67	0.92
161	1.90	66	0.92
151	0.47	65	3.22
150	3.84	64	2.04
149	2.65	63	2.55
148	12.8	58	6.43
147	2.70	57	3.98
136	1.33	56	5.04
135	2.57	55	1.92
134	1.84	54	1.18
133	2.96	53	1.04
132	3.41	52	2.00
131	1.18	51	4.49
122	2.45	50	2.92
121	14.3	44	4.80
120	1.33	43	2.86
119	1.63	42	20.0
118	1.22	41	4.53
117	1.22	40	1.53
108	0.71	39	4.49
107	1.33	38	1.27
106	1.57	32	6.73
105	2.61	30	2.96
104	1.84	28	51.0
103	1.63	18	9.89
100	6.94	15	7.96

2-(p-methylphenyl)-1,3-N,N'-dimethyl imidazolidine 13ev

m/e	%	m/e	%
191	2.37	100	6.53
190	20.2	99	100
189	50.9	98	0.70
175	1.77	92	0.35
161	2.46	91	0.30
147	5.30	58	0.53
146	17.2	57	0.54
134	1.26	44	0.40
133	1.702	43	0.37
132	3.95	42	0.49
120	0.72	41	0.30
119	0.53	28	0.49
118	0.53	27	0.47
117	0.67	26	0.46
106	0.39	18	1.58
105	0.44		

2-(p-methylphenyl)-1,3-N,N'-dimethyl imidazolidine 70ev

m/e	%	m/e	%
191	1.69	106	1.46
190	13.79	105	10.1
189	48.59	104	1.10
188	1.10	103	2.16
187	1.25	100	6.77
176	0.33	99	100
175	2.66	97	1.65
174	0.15	91	5.67
173	0.69	90	1.57
172	1.60	89	1.88
171	2.40	79	1.80
162	0.08	78	1.88
161	3.83	77	4.01
160	0.24	65	3.61
148	1.13	63	2.04
147	7.08	58	4.08
146	47.0	57	2.27
145	1.22	56	3.32
144	0.88	44	2.40
134	2.13	43	1.57
133	2.30	42	13.3
132	14.4	41	2.84
131	4.48	39	3.45
130	1.44	32	3.61
120	0.75	28	20.4
119	1.07	18	13.4
118	1.76	17	3.13
117	2.63	15	3.86
116	2.04		

2-phenyl-1,3-N,N'-dimethyl imidazolidine 70ev

m/e	%	m/e	%
177	0.86	77	6.70
176	8.01	65	3.33
175	33.3	63	2.14
173	0.92	59	0.31
161	1.90	58	5.20
159	0.61	57	2.45
133	6.48	56	4.13
132	45.0	52	1.56
119	1.22	51	4.92
118	7.28	50	4.92
117	4.28	44	2.72
105	0.35	43	1.83
104	1.28	42	15.8
103	1.77	41	3.21
100	6.88	39	3.55
99	100	32	2.14
97	1.53	30	2.45
92	1.50	28	17.125
91	13.7	27	3.85
90	1.68	26	1.47
89	2.17	18	1.53
78	3.36	15	5.96

2-(p-chlorophenyl)-1,3-N,N'-dimethyl imidazolidine 12ev

m/e	%	m/e	%
212	4.08	84	1.49
211	14.9	83	0.78
210	12.3	82	0.67
209	40.2	81	1.26
197	0.49	80	0.43
195	1.38	79	2.05
189	0.46	75	0.52
170	0.46	70	0.53
169	2.01	69	0.34
168	5.95	67	0.43
167	5.86	60	3.85
166	16.1	59	0.24
156	0.44	58	1.03
155	0.52	57	1.95
154	1.07	56	1.15
153	1.03	55	0.57
152	1.18	54	0.46
140	0.40	45	1.95
139	0.44	44	0.86
138	0.40	43	2.94
135	0.40	42	1.09
132	1.26	41	0.46
120	1.55	36	0.57
119	0.86	32	0.57
112	0.80	31	0.92
100	7.36	28	0.84
99	100	27	0.47
85	1.69	26	0.52

2-phenyl-1,3-N,N'-dimethyl imidazolidine 10ev

m/e	%
177	1.49
176	11.89
175	29.6
160	0.81
134	0.68
133	3.92
132	4.05
131	0.54
120	0.54
119	0.68
118	0.54
106	0.62
103	0.41
101	0.41
100	6.68
99	100
78	1.35

2-phenyl-1,3-oxathiolane 70ev

m/e	%	m/e	%
208	2.73	74	3.00
207	5.49	69	1.35
206	47.5	66	1.20
205	2.83	65	2.05
138	0.42	64	1.58
137	0.67	63	5.60
136	0.78	62	6.77
135	2.98	61	29.3
134	1.09	60	100
133	5.09	59	19.6
123	0.62	58	3.54
122	1.09	53	0.84
121	5.05	52	5.09
120	0.86	51	23.6
199	1.35	50	11.2
110	0.78	49	12.6
109	1.28	48	1.17
108	0.92	47	2.56
107	9.58	46	1.28
106	20.0	45	16.6
105	58.3	44	1.27
104	1.23	43	1.62
103	0.70	39	6.84
92	1.26	38	2.50
91	6.95	37	1.26
90	3.86	36	9.98
89	5.55	35	1.35
88	1.08	34	1.50
86	5.30	33	0.65
84	8.58	32	5.60
79	8.43	29	2.96
78	10.3	28	24.6
77	40.1	27	8.53
76	2.50	26	2.82
75	2.12	18	32.8

2-phenyl-1,3-dithiolane 70ev

m/e	%	m/e	%
184	1.31	74	6.47
183	1.69	73	2.81
182	10.6	63	5.44
156	0.86	62	2.14
155	1.46	61	1.59
154	6.10	60	1.22
153	9.66	59	1.29
150	0.94	53	1.69
149	2.16	52	22.51
135	1.50	51	32.83
132	1.03	50	23.1
123	1.13	49	9.66
122	3.66	48	1.50
121	11.1	47	3.53
119	3.47	45	4.41
117	2.81	44	3.19
107	1.05	43	3.02
106	14.3	42	1.22
105	11.6	41	2.25
99	2.25	39	16.9
92	1.88	38	6.04
91	4.82	37	4.60
90	0.94	36	1.13
86	3.38	35	1.78
85	2.06	32	7.71
84	5.40	29	2.06
83	2.78	28	29.4
79	6.75	27	6.19
78	100	26	4.60
77	31.7	18	3.66
76	5.91	17	9.04
75	2.81		

2-(m-nitrophenyl)-1,3-dioxolane 70ev

m/e	%	m/e	%
37	1.0	90	5.0
38	3.0	91	4.0
39	12.0	92	3.0
41	1.50	93	2.0
42	1.50	104	11.0
43	8.0	105	12.0
44	3.50	106	1.5
45	36.0	107	18.0
46	1.50	108	1.0
51	20.0	118	4.0
52	2.0	119	1.0
53	1.0	120	1.0
61	1.0	121	2.0
62	5.0	122	1.0
63	13.5	123	1.0
64	3.0	135	10.5
65	5.5	136	11.0
73	100	148	14.0
74	7.5	149	2.5
75	7.0	150	22.0
76	15.0	151	2.5
77	29.5	164	3.0
78	4.0	165	3.5
79	2.5	178	10.5
87	1.0	179	1.5
88	1.0	194	53.5
89	18.0	195	13.5
		196	2.0

2-(p-methoxyphenyl)-1,3-dioxolane 70ev

m/e	%	m/e	%
37	1.25	77	25.0
38	4.0	78	9.0
39	12.0	79	3.0
40	1.0	83	1.0
41	7.0	90	2.7
42	6.0	91	16.5
43	20.0	92	12
44	5.0	93	7.0
45	13.0	94	1.2
50	7.5	104	1.0
51	12.5	105	5.0
52	2.0	106	1.0
53	1.5	107	7.0
55	5.0	108	47
56	2.0	109	4.5
57	3.5	112	1.5
58	1.5	119	6.0
61	4.0	120	6.0
62	12.0	121	4.0
63	9.0	135	76.0
64	7.5	136	25.0
65	10.0	137	3.0
66	1.5	149	22.5
69	3.5	150	4.0
70	1.5	152	1.0
71	1.0	178	1.0
73	19.0	179	100
74	2.5	180	52
75	2.0	181	5.5
76	3.5		

2-(p-nitrophenyl)-1,3-dioxolane 70ev

m/e	%	m/e	%
37	1.5	89	21.5
38	4.5	90	11.5
39	15.5	91	12.0
41	2.5	92	5.5
42	2.0	93	3.0
43	12.5	103	1.5
44	4.0	104	17.0
45	38.0	105	9.5
46	1.50	106	3.0
50	23.0	107	22.5
51	27.0	108	1.5
52	3.0	118	13.0
53	1.50	119	2.0
61	1.50	120	3.50
62	7.50	121	2.0
63	19.5	123	2.0
64	4.0	135	3.0
65	5.0	136	3.5
66	1.5	148	26.5
71	1.5	149	3.50
73	100	150	25.0
74	10.0	151	2.50
75	10.5	164	3.0
76	17.5	165	2.0
77	48.5	178	18.0
78	8.0	179	2.0
86	1.50	194	78.5
87	2.0	195	28.0
88	2.0	196	3.0

2-phenyl-1,3-dioxolane 70ev

m/e	%	m/e	%
37	1.0	74	4.0
38	3.0	75	2.0
39	9.5	76	3.0
40	3.0	77	32.5
41	3.0	78	27.0
42	1.5	79	4.0
43	6.0	83	5.0
44	10.0	85	2.5
45	21.0	89	12.0
47	1.5	90	19.0
50	10.0	91	22.0
51	21.5	92	8.0
52	5.0	93	2.0
53	1.0	99	6.5
55	1.5	105	45.0
56	1.5	106	6.5
57	2.0	113	1.5
62	2.5	119	9.5
63	7.5	120	2.5
64	4.0	132	2.5
65	2.5	145	1.0
69	1.5	149	100
73	41.5	150	45.0
		151	5.0

2-(p-chlorophenyl)-1,3-dioxolane 70ev

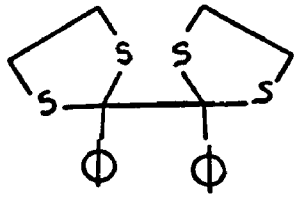
m/e	%	m/e	%
37	1.5	99	1.5
38	3.0	104	1.0
39	6.0	105	9.0
42	1.0	106	4.0
43	6.0	111	18.0
44	1.5	112	24.0
45	17.5	113	7.5
49	1.0	114	7.5
50	12.0	119	15.0
51	12.0	120	1.5
52	2.0	123	1.0
59	2.5	124	9.0
61	1.0	125	11.5
62	2.0	126	4.0
63	8.5	127	4.0
64	1.0	137	1.0
65	1.0	139	47.0
73	45.5	140	7.0
74	14	141	16.0
76	2.5	142	2.0
77	14.5	150	22.5
78	9.0	151	3.5
85	2.0	153	4.0
86	1.5	154	2.0
87	1.5	183	100
89	24.0	184	53.0
90	3.0	185	37.0
91	7.0	186	17.5
92	1.0	187	2.0

2-(p-methylphenyl)-1,3-dioxolane

m/e	%	m/e	%
37	1.5	78	7.5
38	4.5	79	1.5
39	23.0	86	1.0
40	2.5	87	1.0
41	5.0	89	7.0
42	2.0	90	5.0
43	8.0	91	77.5
44	3.0	92	28.0
45	14.5	93	3.0
50	9.0	102	17.0
51	15.0	103	7.5
52	4.0	104	9.0
53	2.0	105	13.0
59	1.5	106	1.5
60	1.0	118	1.5
61	2.5	119	100
62	7.0	120	52.5
63	20.0	121	5.0
64	4.0	133	2.5
65	20.5	134	1.0
66	2.5	149	25.0
73	24.0	150	2.5
74	2.5	162	1.0
75	2.0	163	68.5
76	1.5	164	26.0
77	10.0	165	3.5

180 300 120 200 60 100 0 CPS 0 CPS

SPECTRUM No.
DATE 3-18-71
FREQ. 60 MC NMR
NUCLEUS
SAMPLE



SOLVENT	$CDCl_3$
CONC.	
REFERENCE	
LOCK	
TEMP.	RT
R. F. LEVEL	S6
R. F. GAIN	3
A. F. LEVEL	
FIXED FREQ.	+10
VARI. FREQ.	
A. F. GAIN	2
RESPONSE	2
SWEEP	
WIDTH	9X 1 PPM
TIME	5 MIN
OFFSET	PPM

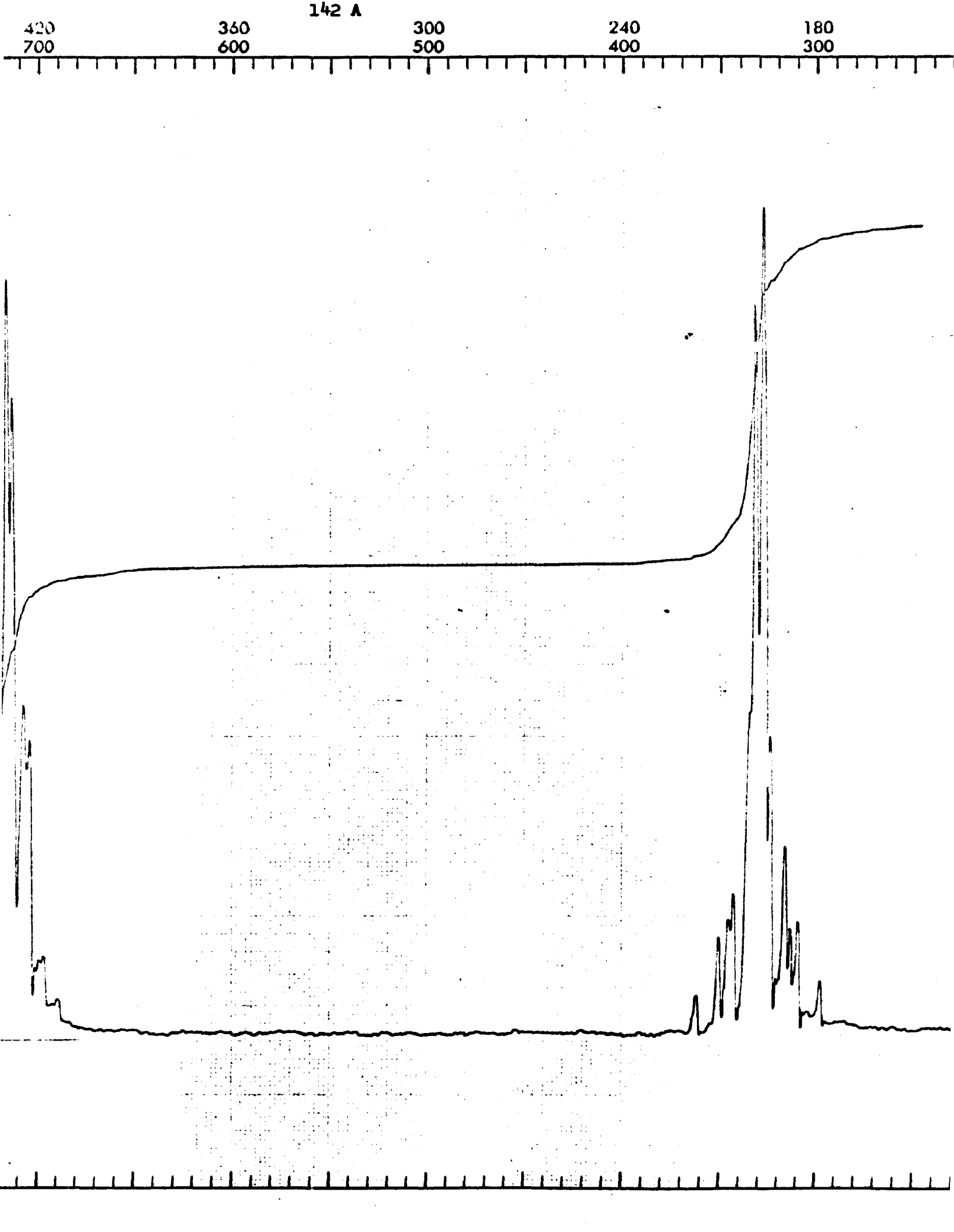
FREQ. FIELD/FREQ. X FIELD

OPERATOR

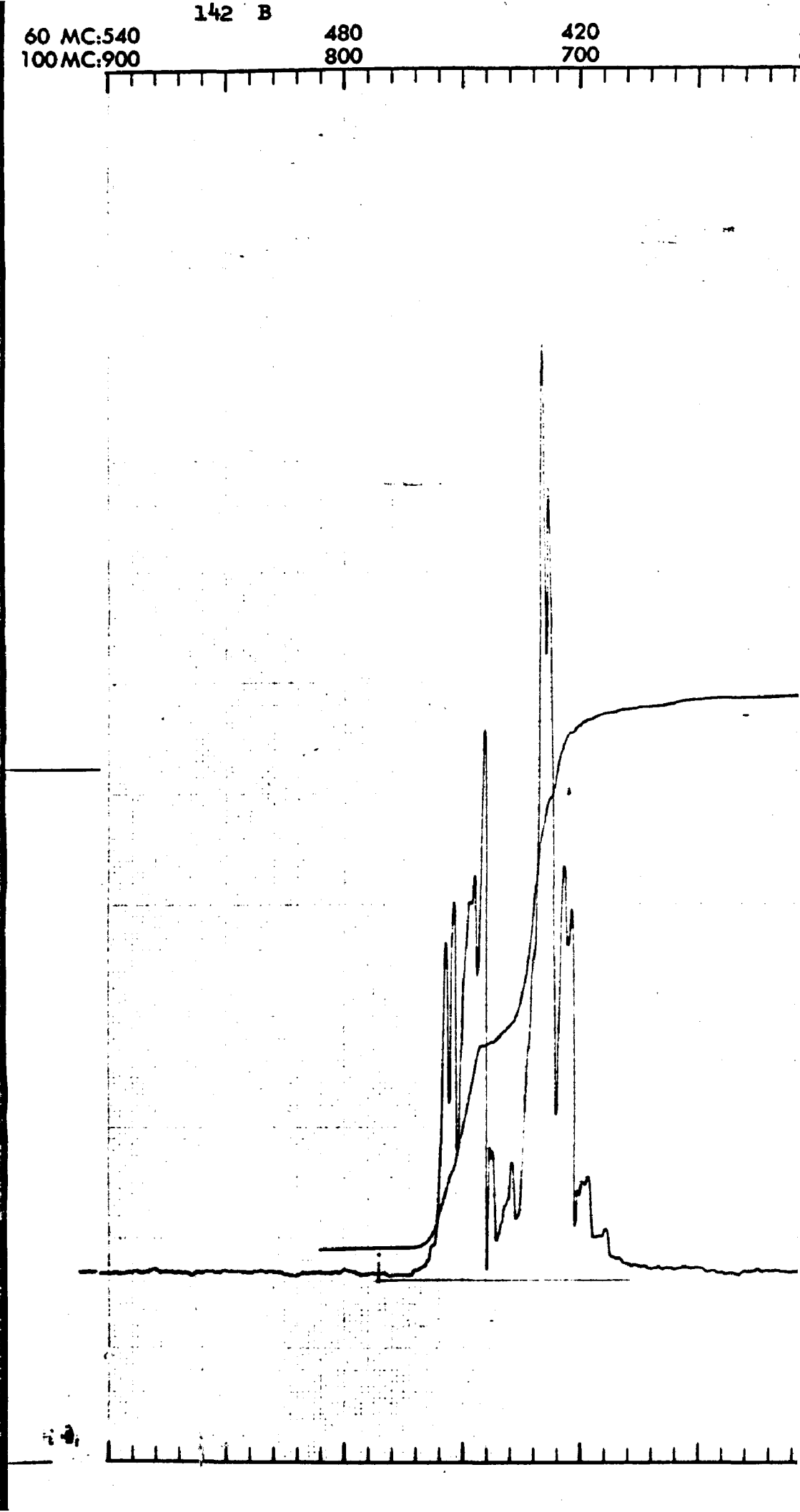
REMARKS:

142 A

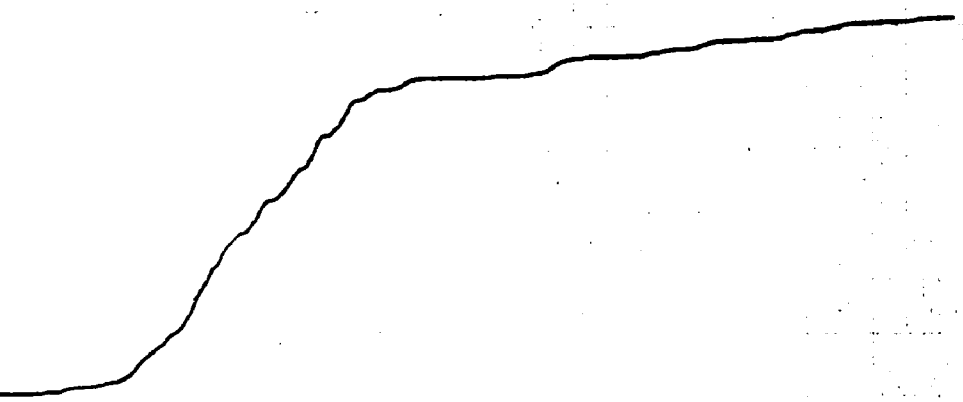
420 360 300 240 180
700 600 500 400 300

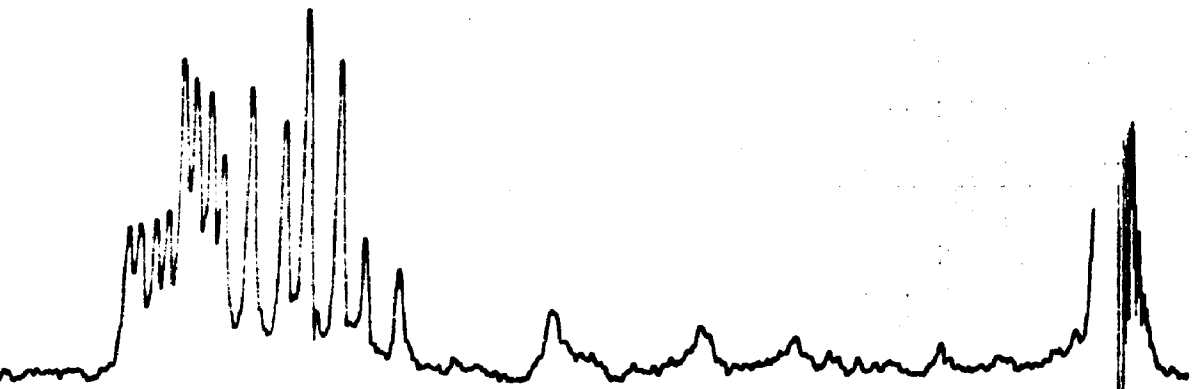


142 B



180 120 143 60 0 CPS
300 200 100 0 CPS





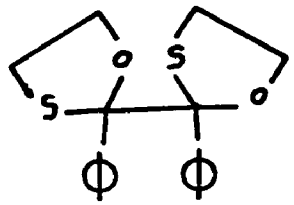
SPECTRUM No. _____

DATE 3-18-71

FREQ. 60 MC NMR

NUCLEUS _____

SAMPLE _____

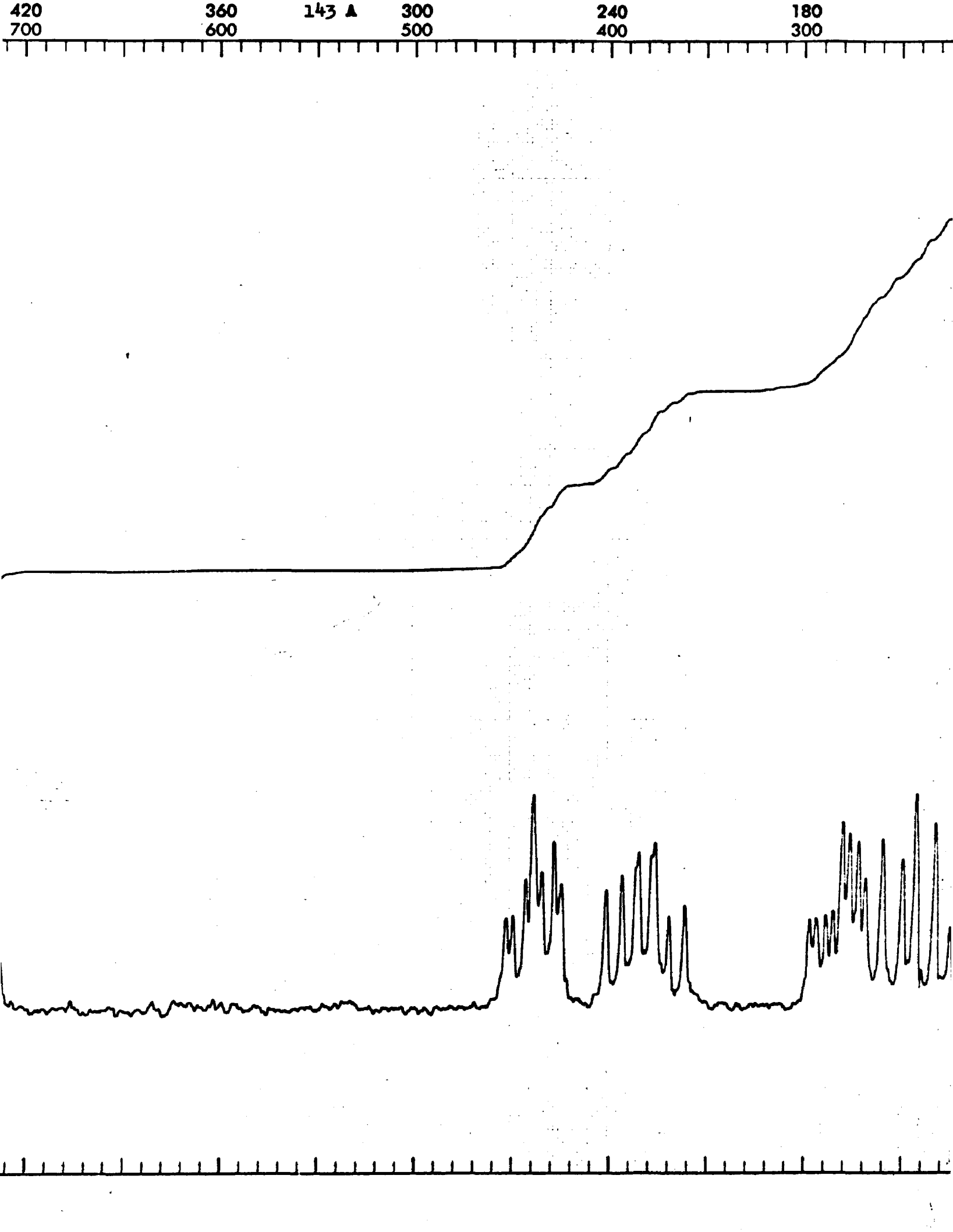


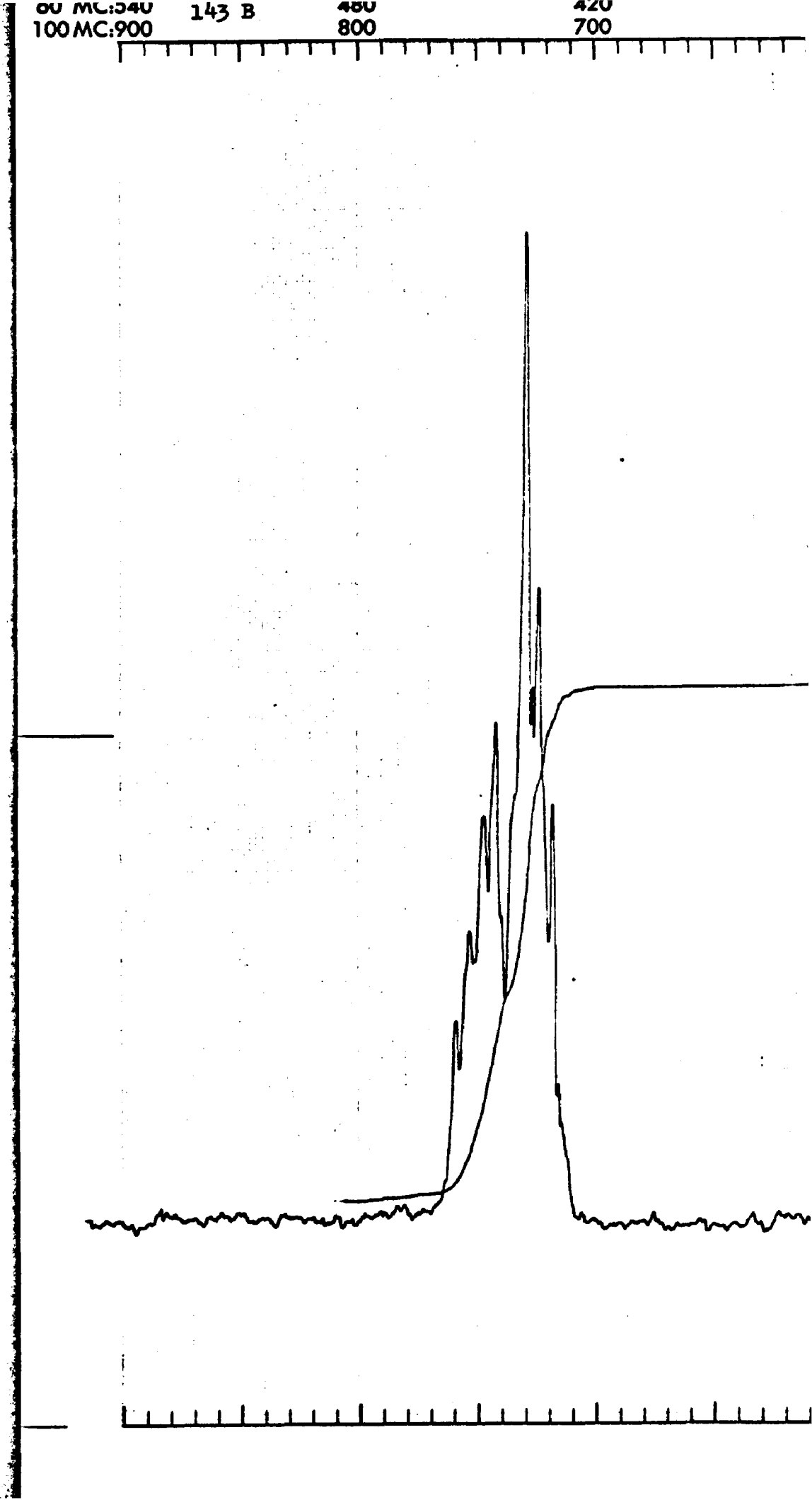
SOLVENT	$CDCl_3$
CONC.	
REFERENCE	
LOCK	
TEMP.	
R. F. LEVEL	54
R. F. GAIN	3
A. F. LEVEL	
FIXED FREQ.	4-10
VARI. FREQ.	6
A. F. GAIN	3
RESPONSE	
SWEEP	
WIDTH	9X PPM.
TIME	MIN.
OFFSET	PPM.

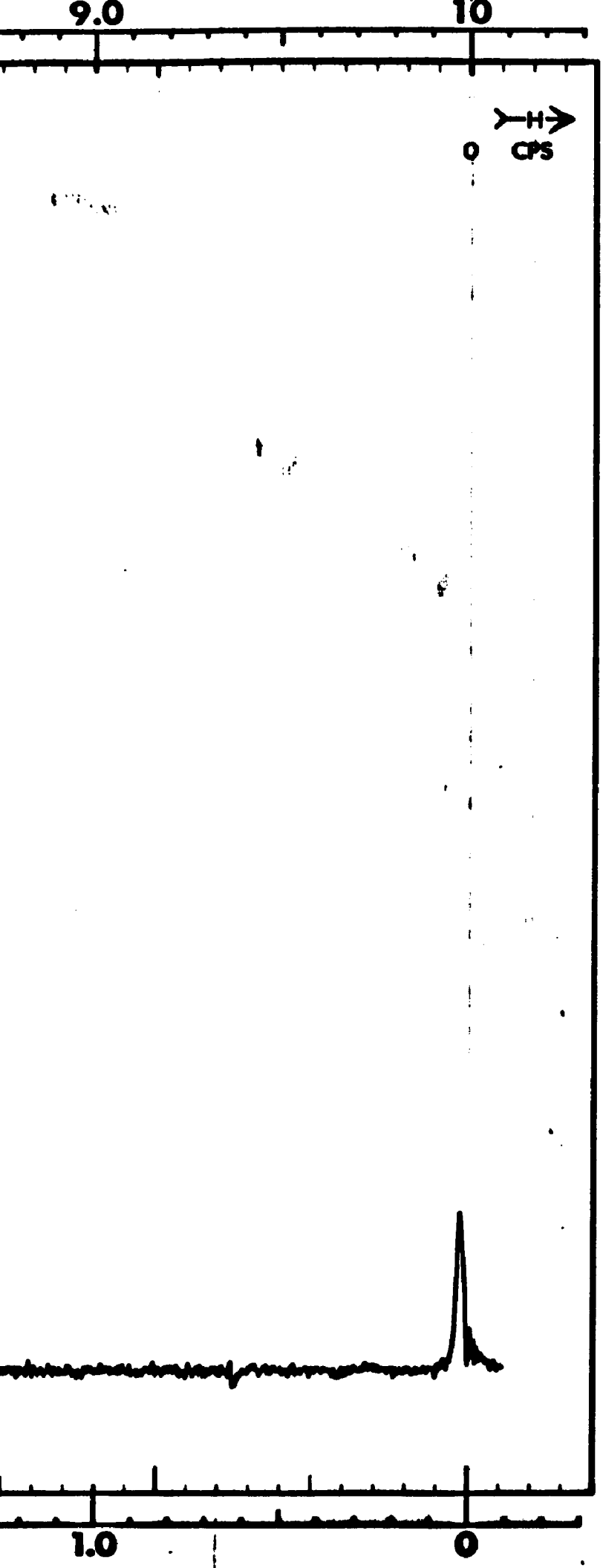
FREQ, FIELD/FREQ, _ FIELD_

OPERATOR _____

REMARKS:


420
700
360
600
143 A
300
500
240
400
180
300

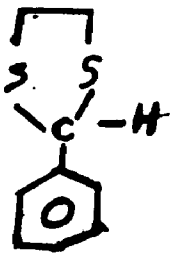

60 MC:540
100 MC:900
143 B
480
800
420
700



60 MC NMR
SPECTRUM NO.

OPERATOR: JVH DATE 4/8/67

SAMPLE:



	TMS				
SOLVENT	$CDCl_3$				
TEMPERATURE	37°C				°C
FILTER BANDWIDTH	4				cps
R.F. FIELD	0.025				mG
SWEEP TIME	500				sec
SWEEP WIDTH	500				cps
SWEEP OFFSET	0				cps
SPECTRUM AMP.	8.0				
INTEGRAL AMP.	2.0				

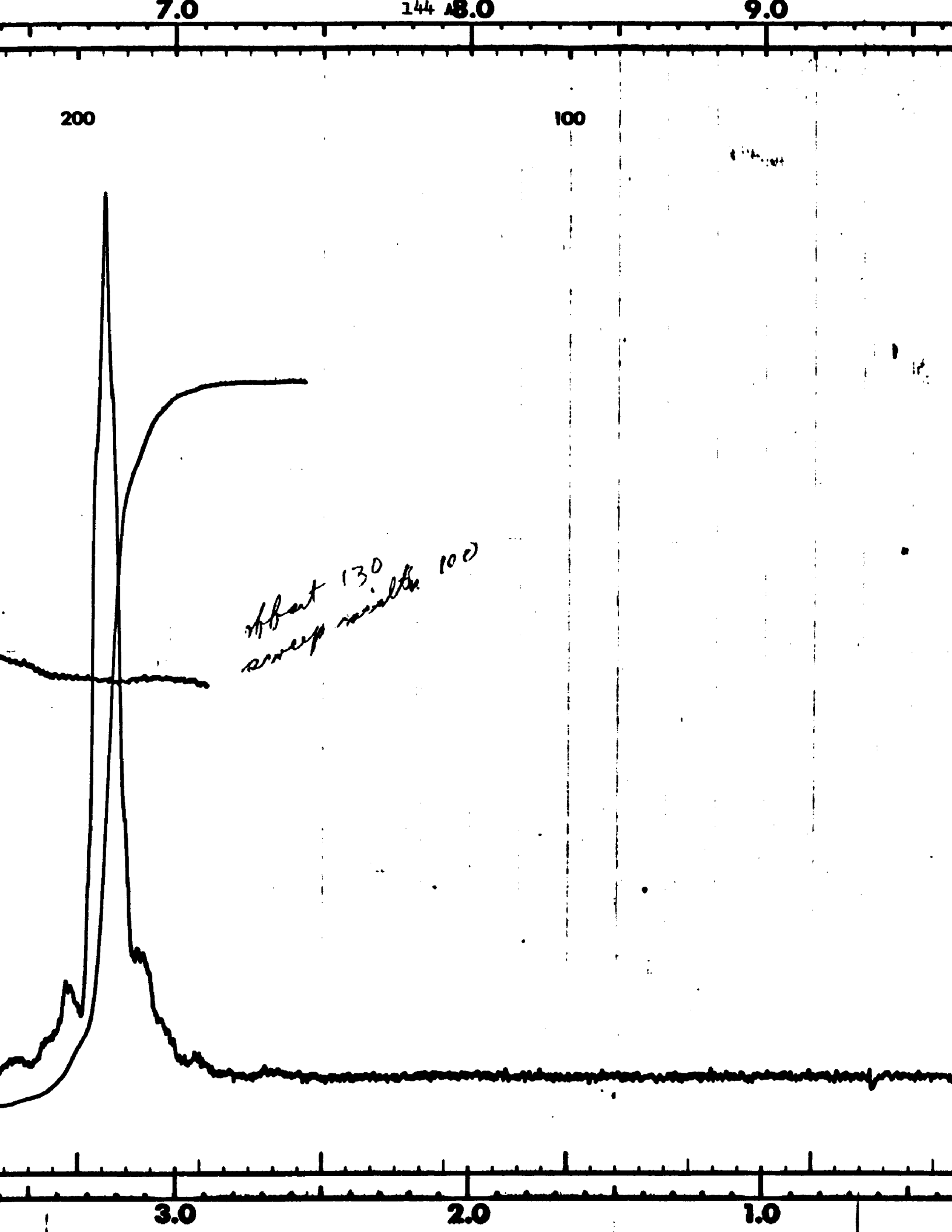
REMARKS:

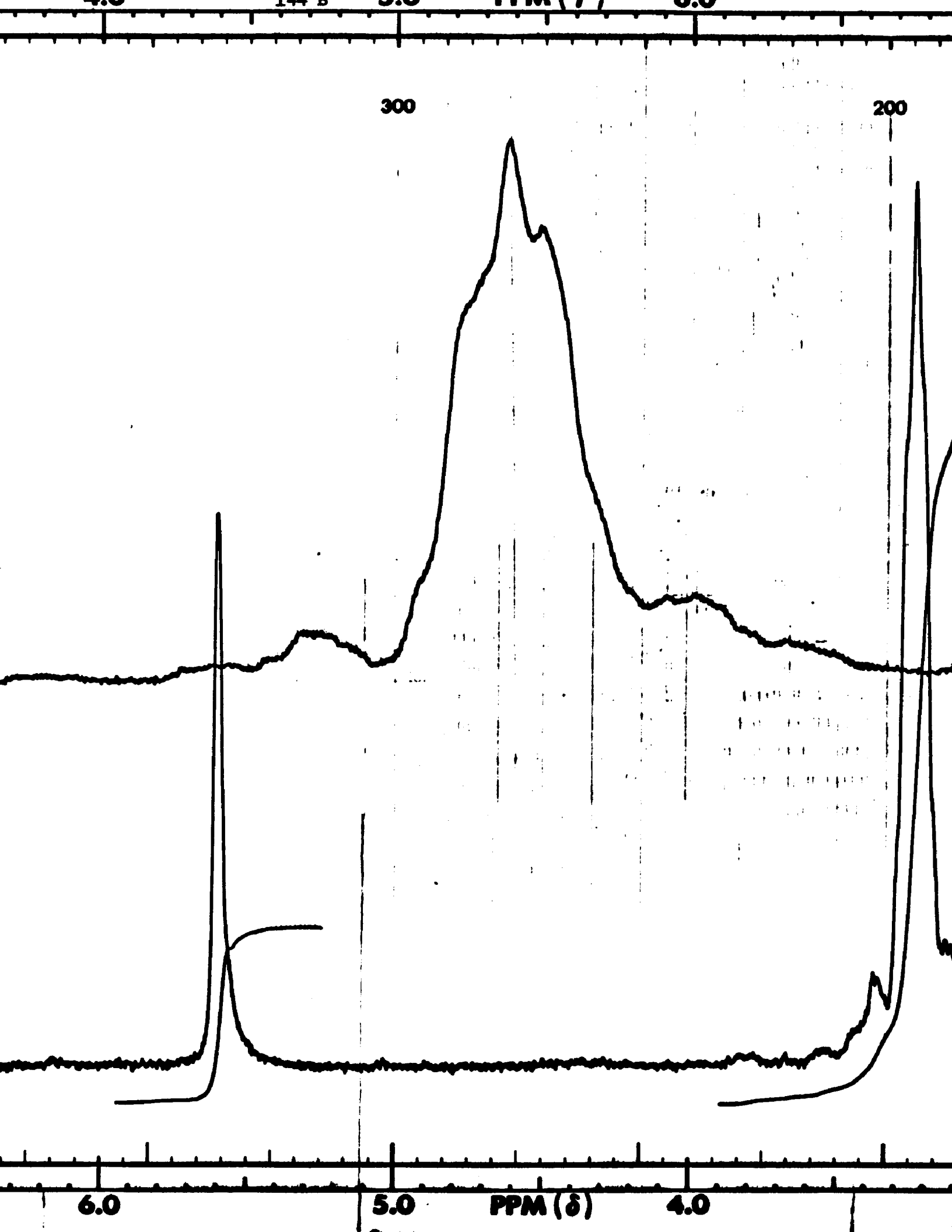
Internal TMS.

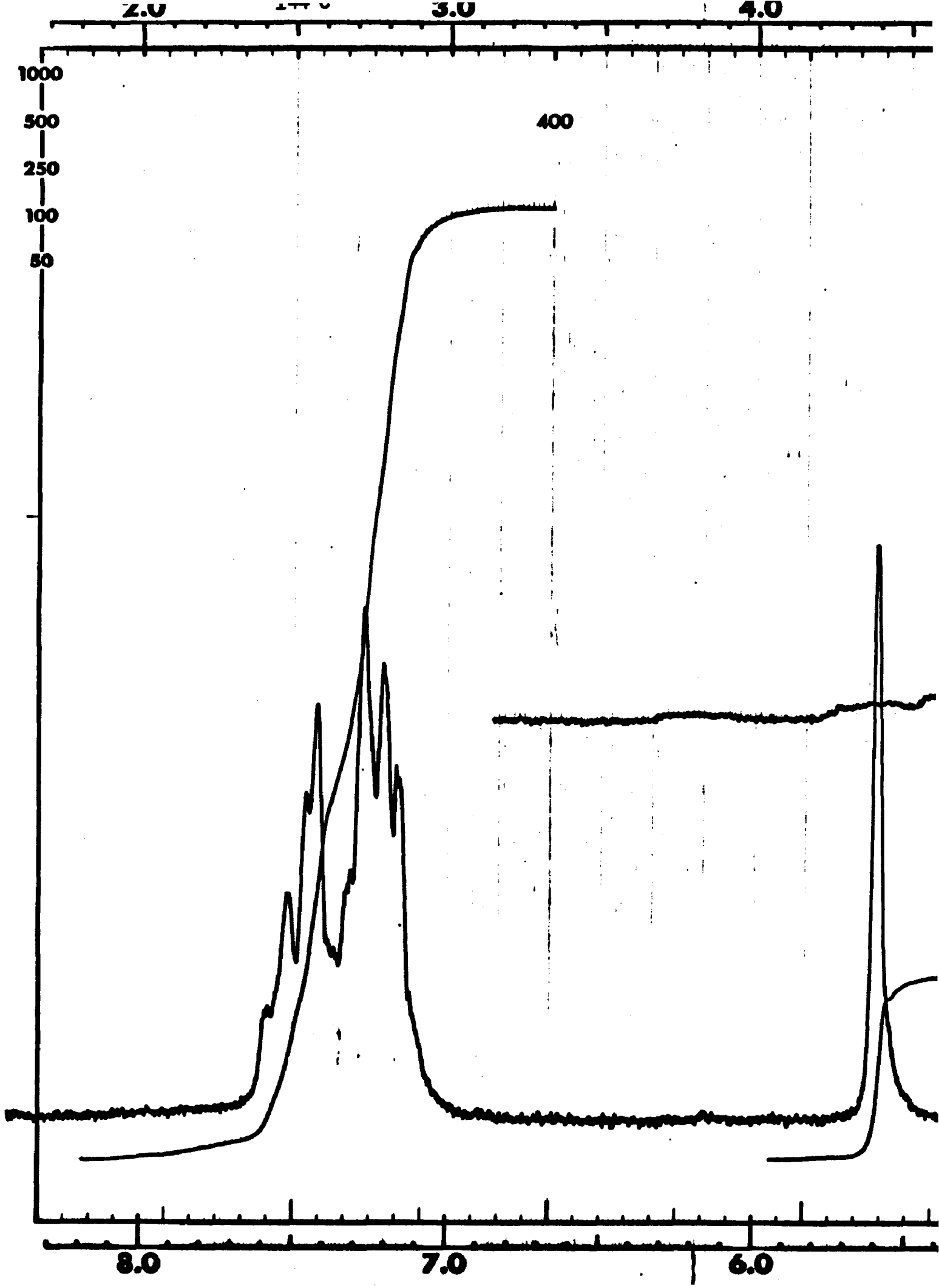
VARIAN associates

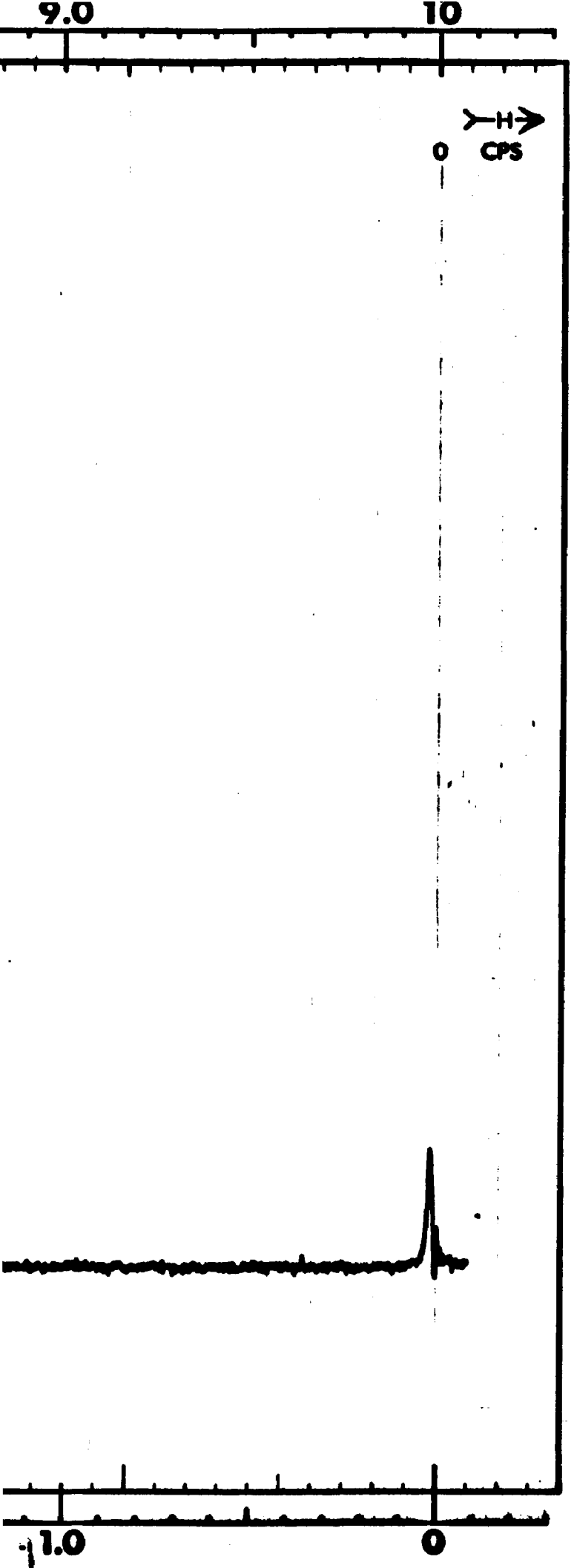
CHART S60-C

PRINTED IN U.S.A.


7.0
8.0
9.0
200
100
about 130
sweep width 100
3.0
2.0
1.0


300
200
6.0
5.0
PPM (δ)
4.0

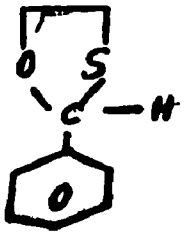

2.0
3.0
4.0
1000
500
250
100
50
400
8.0
7.0
6.0



60 MC NMR
SPECTRUM NO.

OPERATOR: VLH DATE 3/7/62

SAMPLE: 44W



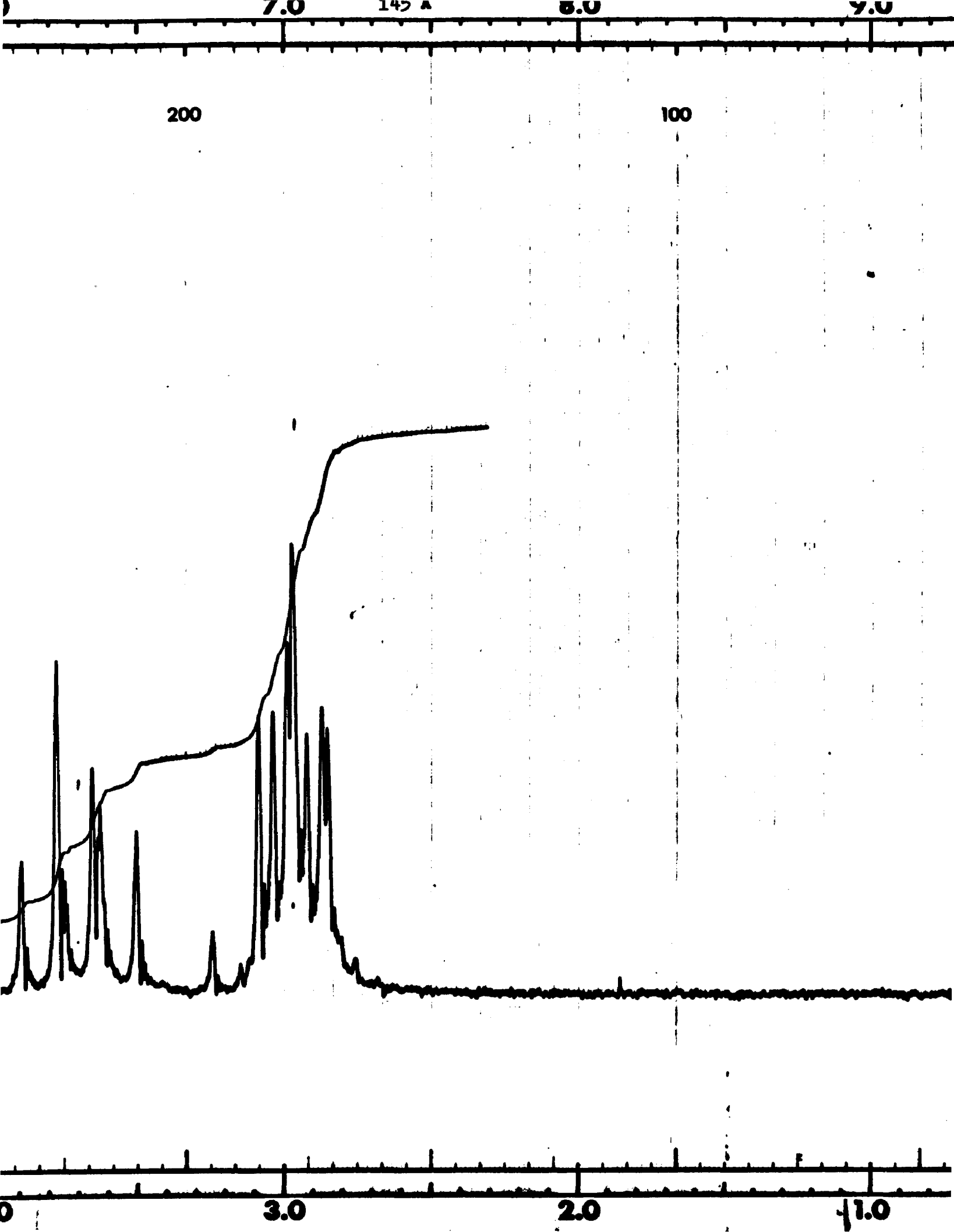
	TMS				
SOLVENT	$CDCl_3$				
TEMPERATURE	37°C				°C
FILTER BANDWIDTH	4				cps
R.F. FIELD	.025				mG
SWEEP TIME	500				sec
SWEEP WIDTH	500				cps
SWEEP OFFSET	0				cps
SPECTRUM AMP.	63				
INTEGRAL AMP.	16				

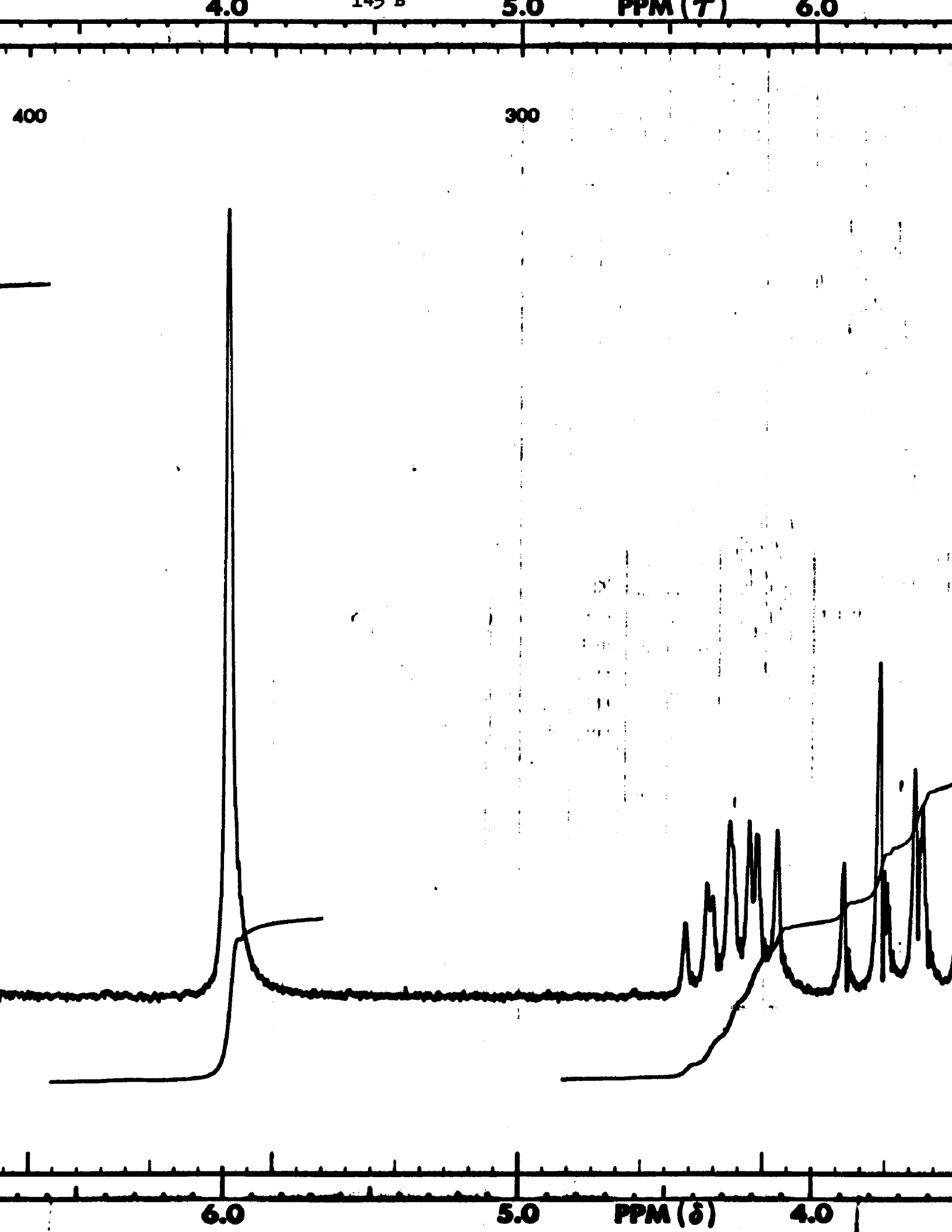
REMARKS:

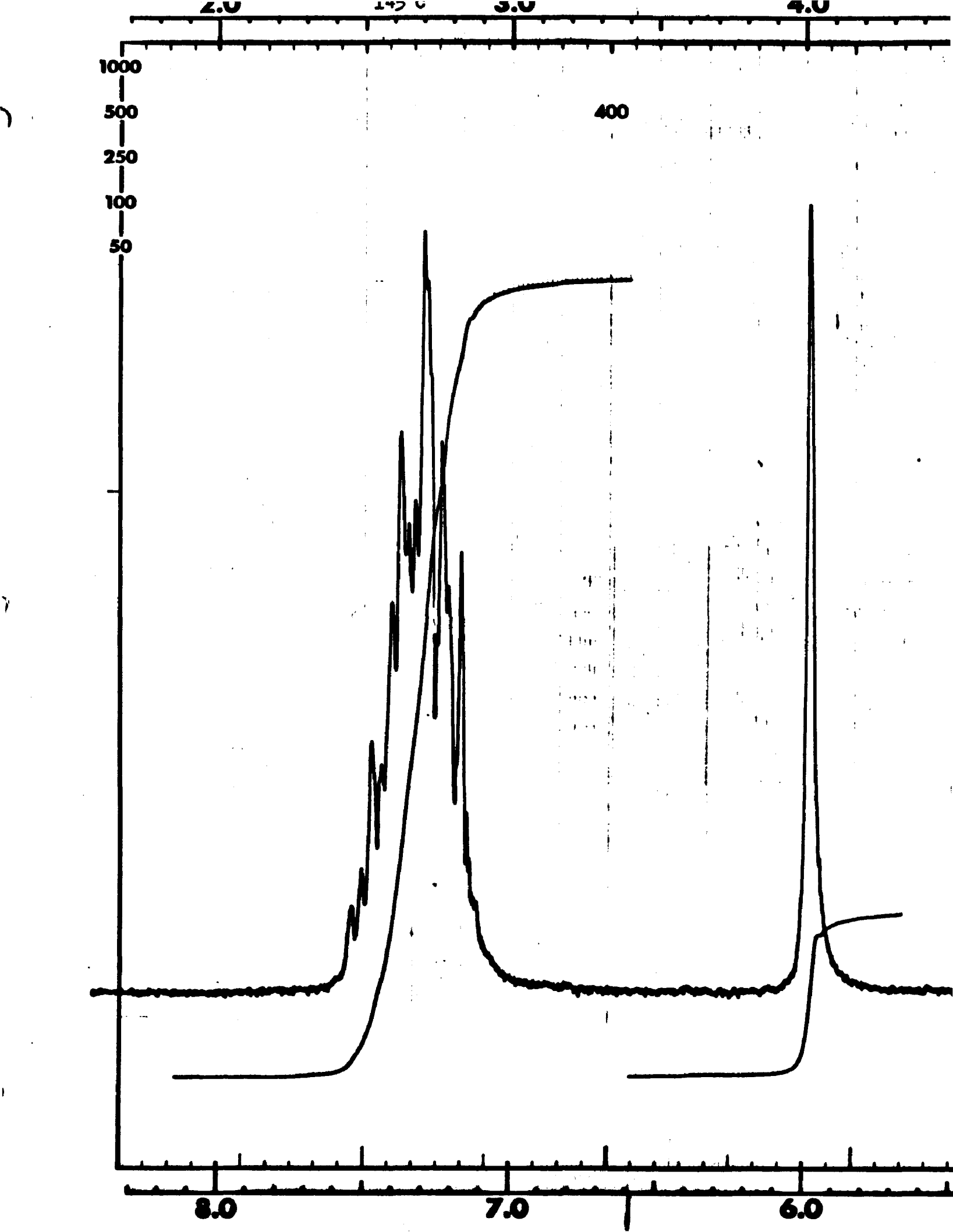
Internal TMS

Conc ~ 60%

Freshly distilled


7.0
145 A
6.0
9.0
200
100
3.0
2.0
1.0


4.0
5.0
PPM (τ)
6.0
400
300
6.0
5.0
PPM (δ)
4.0


2.0
145 c
3.0
4.0
1000
500
250
100
50
400
8.0
7.0
6.0

FOOTNOTES AND REFERENCES

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