

ISOTOPE EFFECTS AND THE QUESTION OF REACTION MECHANISMS:

A STUDY OF THE TSCHUGAEFF REACTION

by

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### ABSTRACT

Three simultaneous isotope effects have been determined for the Tschugaeff reaction, i.e., the thermal decomposition of an xanthate ester. The ratio of the rate constants,  $k_{32}/k_{34}$ , was found to be 1.009 for the thion sulphur atom and 1.002 for the thio-ether sulphur atom. The rate ratio,  $k_{12}/k_{13}$ , for the xanthate carbon atom was found to have a value of 1.000.

The findings of previous investigators of the Tschugaeff reaction had been consistent with either of two mechanisms. However, with the determination of the isotope effects referred to above, it has been possible to distinguish between the two possible mechanisms and to gain considerable information about the transition state of the Tschugaeff reaction.

The measured isotope effects have been discussed in terms of Bigeleisen's isotopic rate equation. In addition, it has been possible to carry out theoretical calculations for each reaction mechanism by assuming an appropriate potential function and in this manner make the interpretation of the measured isotope effects more quantitative.



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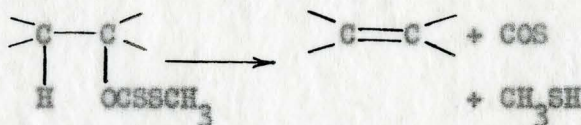
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## GENERAL INTRODUCTION

The thermal decomposition of the xanthate ester of an alcohol to give an alkene, carbonyl sulphide and a mercaptan is known as the Tschugaeff reaction. The methyl ester is usually employed in the synthetic applications of this reaction, e.g.,



There are many known methods of introducing an unsaturated linkage into an organic molecule, each associated with certain advantages and limitations. The majority of elimination reactions proceed via an ionic intermediate, and their most serious limitation is the occurrence of rearranged or impure products. The Tschugaeff reaction differs from these eliminations in that it exhibits a remarkable freedom from such side-reactions, and for this reason it has found wide application in the field of synthetic organic chemistry.

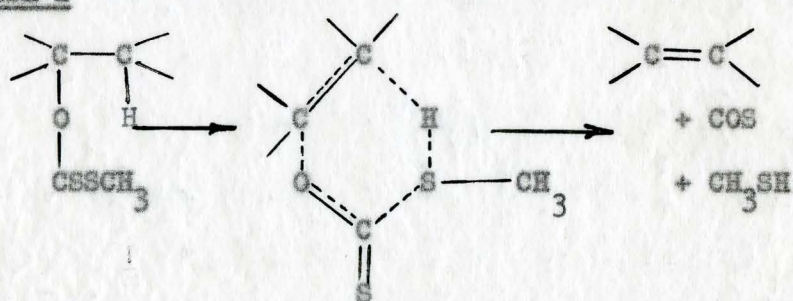
Stereochemical studies of elimination reactions have indicated that, in general, trans elements are lost in the formation of an unsaturated linkage. In recent years, however, a number of exceptions to this have been noted, among them the Tschugaeff reaction. It is necessary in the Tschugaeff reaction that a hydrogen be present on the carbon atom beta to the xanthate function and that this hydrogen possess a cis orientation with respect to the xanthate grouping.



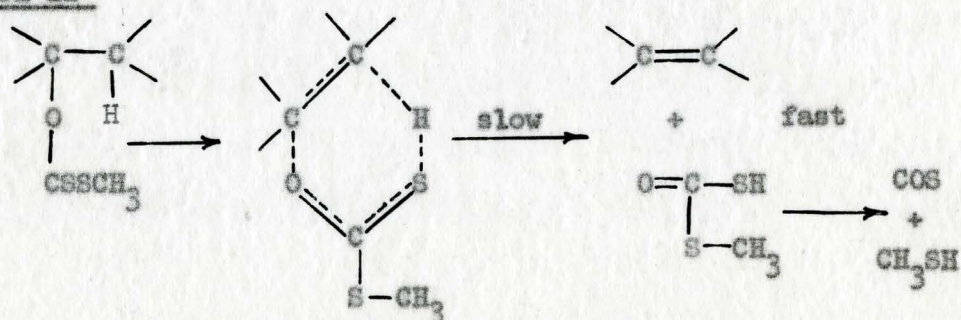
A cis elimination is to be expected in this case as the reaction is an intramolecular one; that is, one of the sulphur atoms of the xanthate grouping assumes the role played by the nucleophilic reagent in the usual type of elimination reaction by bonding with and abstracting a beta hydrogen atom. Since bonding between sulphur and hydrogen will undoubtedly involve the formation of a cyclic intermediate, a concept which has received further support from kinetic studies, the displaced groups must possess a cis orientation with respect to one another.

While it has been generally agreed that a cyclic transition state is indeed involved in this reaction, the exact formulation of the mechanism is still the subject of some dispute. The disagreement concerns the question as to which of the two sulphur atoms in the xanthate grouping undergoes bonding with the cis beta hydrogen atom in the rate-determining step. Two mechanisms have been proposed.

Mechanism I



Mechanism II





Mechanism I, in which the thio-ether sulphur atom is pictured as bonding with the hydrogen atom, has the reaction proceeding in a single step through an activated complex which leads directly to all three products. In Mechanism II the thion sulphur atom abstracts the hydrogen atom in the rate-determining step giving rise to a xanthic acid and an alkene. The xanthic acid, if formed, would be an unstable intermediate and would decompose in a rapid second step to carbonyl sulphide and methyl mercaptan.

Thus while classical methods such as steric and kinetic studies could and did lead to a general formulation of the reaction mechanism, they afforded no obvious method of differentiating between the two mechanisms pictured above. There is, however, a method of gaining an insight into the properties of the transition state. This method is dependent upon the measurement of isotope effects. The object of this thesis is to decide between the two proposed mechanisms by offering evidence obtained from such measurements.

Two isotopic species will exhibit a difference in their relative rates of reaction whenever their bonding energy undergoes a change in the step controlling the over-all reaction rate. Since the changes in bonding experienced by the thion and thio-ether sulphur atoms are very different in the two mechanisms, a knowledge of the isotopic fractionation incurred by these atoms will permit the assigning of definite roles to each in the rate-determining step. In addition, the mechanisms involve quite different bonding changes for the xanthate carbon atom, and, therefore, information regarding its isotopic fractionation should also prove helpful in distinguishing



between the two possibilities.

It is possible to make approximate predictions concerning the magnitude of the isotope effects to be expected for each mechanism. Compounds having a natural abundance of the isotopes were used in this study. Such compounds have the advantage over enriched materials in that the errors due to contamination are reduced to a minimum. Hence the predictions discussed below refer to  $S^{32}/S^{34}$  and  $C^{12}/C^{13}$  ratios.

#### Mechanism I

1. The carbon-sulphur double bond in this mechanism is not appreciably altered in the rate-determining step, with the result that the isotope effect for the thion sulphur atom should be very small.
2. Conversely, the thio-ether sulphur atom should exhibit a large isotope effect since the bond between it and the carbon atom is broken in the rate-determining step.
3. For the same reason the xanthate carbon atom should show a fairly large effect. Concurrent  $\pi$  bond formation between the carbon and oxygen atoms might tend to lower the effect from that expected for a simple bond cleavage process, nevertheless, the net effect should correspond closely to that observed in ordinary decarboxylation reactions, namely 2 to 3 percent for  $C^{12}/C^{13}$ .

#### Mechanism II

1. According to this mechanism the thion sulphur atom abstracts the hydrogen in the rate-determining step and consequently



the  $\pi$  bond between this sulphur atom and the carbon atom is broken. While the isotope effect resulting from  $\pi$  bond cleavage would not be expected to be as great as that from the breaking of a sigma bond, the effect should be appreciable, perhaps of the order of one percent.

2. The bonding between the thio-ether sulphur atom and the carbon atom undergoes no appreciable change in the rate-determining step of this mechanism, and therefore, only a very small effect, at the most a few tenths of a percent, is to be expected.
3. The xanthate carbon atom is unique in that it undergoes  $\pi$  bond formation and cleavage with the oxygen and thion sulphur atoms, respectively. Theory would predict that with the two processes occurring concurrently and to about the same extent in the transition state the isotope effect for the carbon atom should be very small or even zero.

As mentioned before, the products of the Tschugaeff reaction are an alkene, carbonyl sulphide and methyl mercaptan. The latter two products may be identified with the three atoms discussed above. The sulphur and carbon in carbonyl sulphide correspond to the thion sulphur and xanthate carbon atoms. The sulphur atom appearing in the methyl mercaptan is the thio-ether sulphur atom of the xanthate. Since the measurement of intermolecular isotope effects involves the determination of isotopic ratios in both the reactants and products, it has been necessary to develop a method which would permit the quantitative separation and recovery of all three of



the atoms whose isotopic ratios are to be determined. Included, therefore, in this thesis is a discussion of the method used for the quantitative separation of carbonyl sulphide and methyl mercaptan, and the quantitative conversion of the xanthate carbon and the two sulphur atoms to a form suitable for mass spectrometer analysis, namely sulphur dioxide and carbon dioxide.



### HISTORICAL INTRODUCTION

In 1899 a Russian chemist named Tschugaeff published a paper in the *Berichte der deutschen chemischen Gesellschaft*, in which he described a new method of obtaining olefins from the corresponding alcohols (1). The usual type of elimination reaction, in which the alcohol or alkyl halide is the reactant, invariably leads to rearranged products; but Tschugaeff found that by employing the xanthate ester of the alcohol in a pyrolytic decomposition, the formation of such products could be avoided. Thus the Tschugaeff reaction, as the method has come to be called, possesses a definite advantage over the common elimination processes of dehydration or dehydrohalogenation.

This advantage was clearly evident in Tschugaeff's original paper, wherein he described the conversion of S-methyl menthyl xanthate to menthene with very little loss in optical activity. In subsequent years, Tschugaeff published five more papers (2-6) dealing with applications of this new procedure in the field of terpene chemistry.

As Tschugaeff's original papers omitted many of the details related to both the manner in which the reaction was carried out, and the yields obtained, McAlpine (7) reinvestigated the decomposition of S-methyl menthyl xanthate and extended the reaction to the S-methyl ester of bornyl xanthate. She carried out the decompositions



in several ways, heating the ester alone or in various solvents and distilling the dry ester in a vacuum. In each case the products were a monoterpene, carbonyl sulphide and methyl mercaptan. In a subsequent paper (8) she compared the thermal stability of the methyl, isopropyl, benzyl and para-nitrobenzyl esters of menthyl and bornyl xanthates. She found that replacing the methyl group by an isopropyl group in either the menthyl or bornyl xanthate esters decreased the tendency towards decomposition. A decreased thermal stability was noted for the benzyl and para-nitrobenzyl esters, the latter ester showing the greatest tendency towards decomposition.

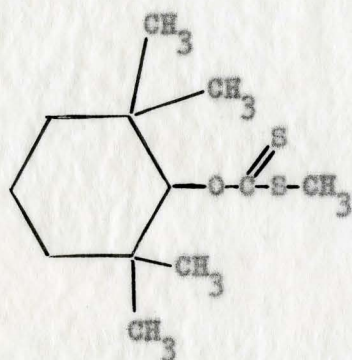
A curious discovery arose out of McAlpine's work. She noted that distillation of certain of the xanthates resulted in the formation of a substance identical with the original ester in composition, molecular weight, and physical properties including melting points alone or mixed, but differing in thermal stability. The new substance required a higher temperature for decomposition, but gave the same products as the original ester under otherwise similar conditions. These so called "stable" forms could also be formed in certain instances by heating solutions of the xanthates in various solvents. Menthyl methyl xanthate for example gave rise to its stable form when heated in an alcoholic or ethylene dibromide solution and, under certain conditions, by distillation in a vacuum. The bornyl ester formed its stable compound under all conditions of decomposition except in nitrobenzene solution at 200°C.

Substitution of an isopropyl group for methyl in menthyl methyl xanthate increased the tendency for the formation of the

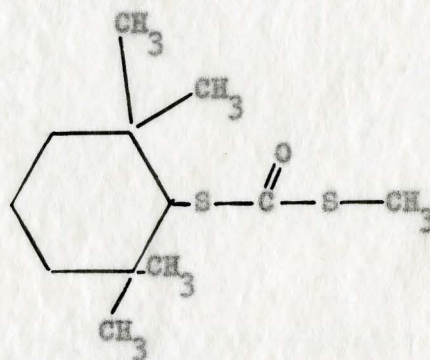


stable form and decreased the tendency for decomposition. Benzyl and para-nitrobenzyl groups, on the other hand, decreased the tendency for formation of the stable form, the para-nitrobenzyl group being most effective in this respect.

Laakso (25) while studying the thermal decomposition of xanthates having no replaceable beta hydrogen, also referred to the occurrence of "stable" forms. However, in the cases he investigated the stable form was shown to be an isomeric dithiolcarbonate which, while requiring a higher temperature for decomposition, was no longer an xanthate. For example, S-methyl-2,2,6,6-tetramethyl cyclohexyl xanthate (I) upon heating to 230°C. showed some decomposition, but the majority of the xanthate was isomerized to the dithiolcarbonate (II).



I



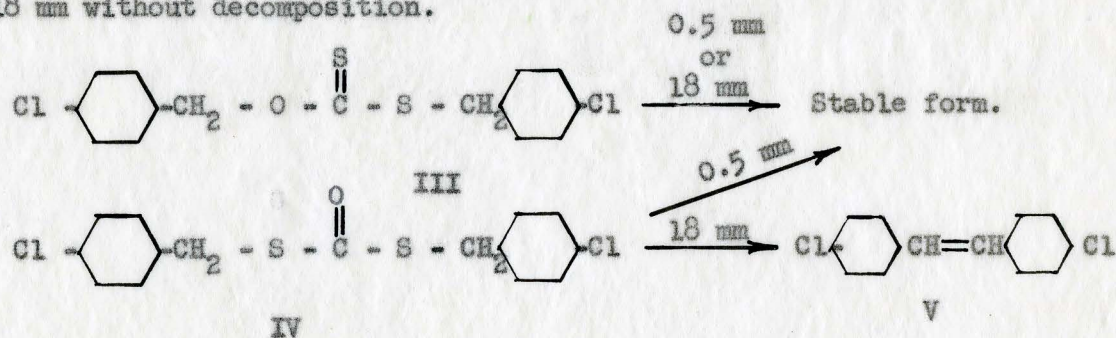
II

Compounds (I) and (II) have entirely different properties, both physical and chemical. Although this is indeed a conversion of an xanthate to a more stable compound, it is not analogous to McAlpine's work where the "stable" form apparently differed from the original xanthate only in its thermal properties.

Behavior similar to that observed by Laakso was noted by



Bulmer and Mann (24) while studying the thermal properties of isomeric xanthates and dithiolcarbonates. They found that O-para-chlorobenzyl S-para-chlorobenzyl xanthate (III) when distilled at either 0.5 or 18 mm isomerized to a stable form of the isomeric dithiolcarbonate. The dithiolcarbonate itself, S,S'-bis-para-chlorobenzyl dithiolcarbonate (IV), when heated at 18 mm decomposed affording 4,4'-dichlorostilbene (V) but when distilled at 0.5 mm it was converted to a stable form. The latter had the same composition, molecular weight and melting point as the parent dithiolcarbonate, but possessed a much greater thermal stability and could be distilled at 18 mm without decomposition.

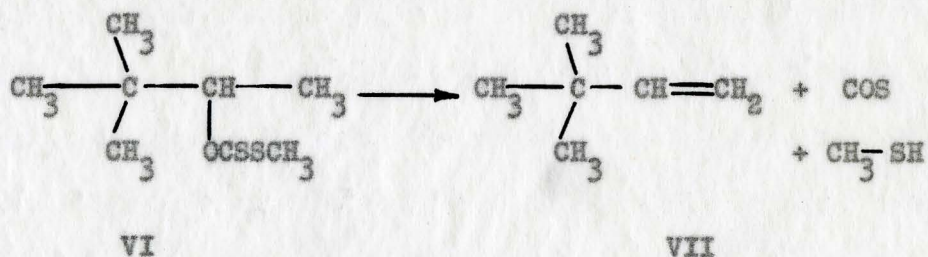


There are thus stable forms of both xanthates and dithiolcarbonates. The stable form of the xanthate is identical with the parent compound except in those instances where no replaceable beta-hydrogen exists, in which case the stable form is the isomeric dithiolcarbonate. No suitable explanation has been offered for these phenomena. Tarbell in a review of the chemistry of sulphur-containing compounds (23) suggests that the distillation leading to the formation of the stable compound may in effect be removing a

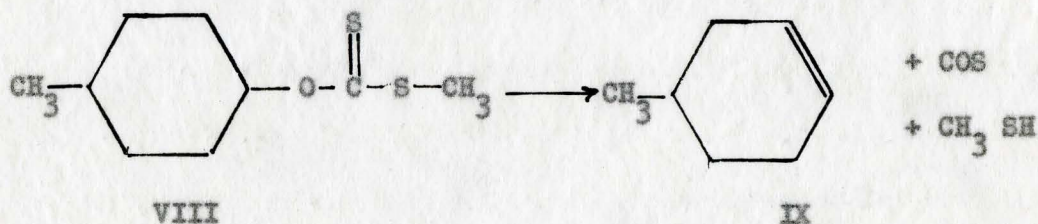


chain initiator in the form of an impurity. This seems unlikely in view of the fact that kinetic studies (20) have shown that the decomposition is first order and not a chain reaction. Further, repeated recrystallization of the xanthate in no way decreases the tendency towards the formation of the stable compound (24).

Applications of the Tschugaeff reaction to xanthates of varying structural types have appeared over the years and have established the versatility of the reaction. It was found to be a recommendable procedure when rearrangements were otherwise difficult to avoid. For example, Formin and Sochanski (9) prepared *t*-butyl-ethylene (VII) from the xanthate of pinacolyl alcohol (VI) without any accompanying formation of tetramethylethylene.



Namethin and Brussav (10) worked with various cyclohexanol derivatives, e.g., 4-methyl-cyclohexene (IX) was obtained from the pyrolysis of *S*-methyl-4-methylcyclohexyl xanthate (VIII).



The decomposition of xanthates derived from alcohols containing



no replaceable beta hydrogen was investigated by Nemethin and Kursanov (11, 12). The pyrolysis of S-methyl benzyl xanthate yielded a dimeric product, 1,2-diphenyl-ethylene, while the S-methyl xanthate of benzhydrol under similar conditions was reported to give tetraphenylethylene. Stevens and Richmond, however, on repeating the work (13) with the xanthate derived from benzhydrol, found that the product contained no tetraphenylethylene whatsoever, but consisted entirely of tetraphenylethane and diphenylethane.

In 1940 Huckel, Legutke and Tapp published a paper (14) that established the steric course of the Chugaev reaction. By carefully separating and noting the yields of the various products obtained from the thermal decomposition of the xanthates derived from ( )-menthol, S-neomenthol and several isomeric decalols, the surprising fact emerged that a cis-beta-hydrogen was preferentially removed. The result is in direct contrast to that observed in the more common elimination processes of dehydration and dehydrohalogenation where the reaction is not at all stereospecific or a beta-hydrogen, trans to the hydroxyl or halogen, is removed. Below is a list of the alcohols whose xanthates were submitted to thermal decomposition, together with the products obtained.

( )-Menthol	70% $\Delta^3$ -Menthene + 30% $\Delta^2$ -Menthene
S-Neomenthol	80% $\Delta^2$ -Menthene + 20% $\Delta^3$ -Menthene
<u>trans</u> - $\alpha$ -Decalol-(I)	80% <u>trans</u> $\Delta^{1,2}$ -Octalene + 20% $\Delta^{1,9}$ -Octalene
<u>trans</u> - $\alpha$ -Decalol-(II)	80% $\Delta^{1,9}$ -Octalene + 20% <u>trans</u> $\Delta^{1,2}$ -Octalene



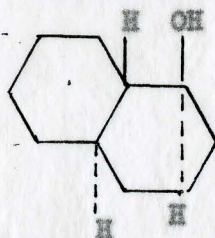
cis- $\alpha$ -Decalol-(I)

90% cis  $\Delta^{1,2}$ -Octalene +  
10%  $\Delta^{1,9}$ -Octalene

trans- $\beta$ -Decalol-(II)

80% trans  $\Delta^2$ -Octalene +  
20%  $\Delta^1$ -Octalene

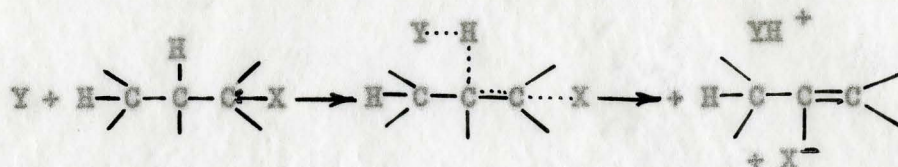
The Roman numerals following the name of the compound serve to differentiate further between the isomers. Thus the (I) placed after trans- $\alpha$ -decalol implies that the hydroxyl group bears a cis relationship with respect to the adjacent hydrogen attached to the carbon atom common to both rings, i.e.,



The Roman numerals (II) signify a trans relationship between the same two groups.

The particular hydrogen atom lost in an elimination reaction depends not only upon the steric relationship it bears with respect to the xanthate grouping, but also upon the nature of the electrical effects operative in the normal molecule and in the transition state (29). For certain types of elimination reactions (in particular the conversion of alkyl halides to alkenes) the polar effects can be summarized by means of an empirical rule proposed many years ago by Saytzeff (30) which states that the hydrogen atom lost will be from that carbon to which are attached the largest number of alkyl groups. The rule is capable of a theoretical interpretation when the electrical requirements of the transition state of a bimolecular elimination reaction are considered.





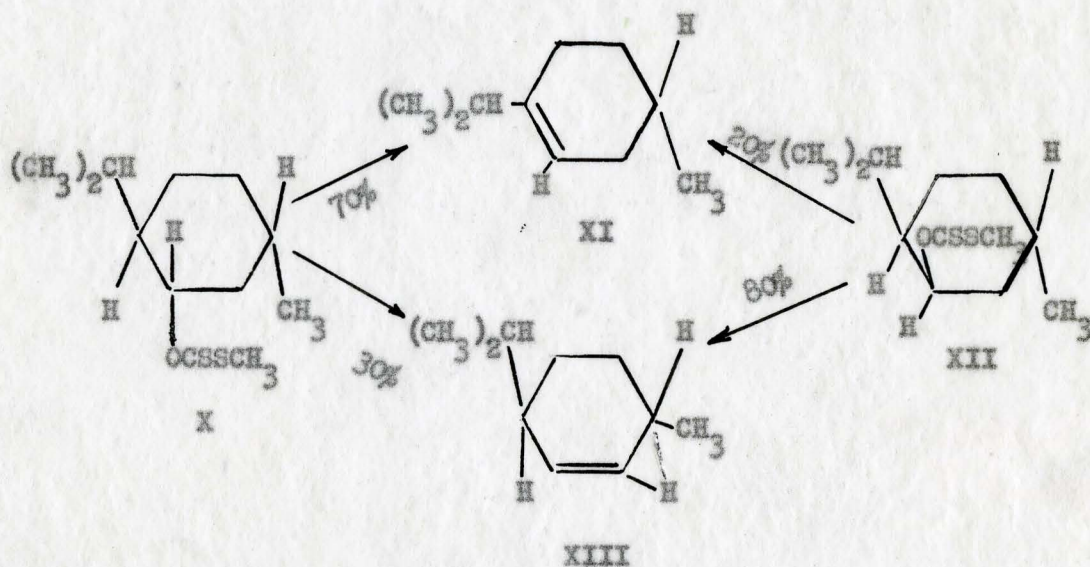
The departing group, denoted by X, is necessarily electrophilic in character, being initially either neutral or positively charged. The group represented by Y, which binds with and abstracts the proton in the rate determining step, is nucleophilic and is originally neutral or negatively charged. In the transition state a double bond is partly formed between the  $\alpha$  and  $\beta$  carbon atoms. A group which can contribute charge to this region of increasing electron density will stabilize the transition state and thereby reduce the energy of activation. Alkyl groups attached to either the  $\alpha$  or  $\beta$  carbon atoms possess this very ability and they exert it through the mechanism of hyperconjugation.

The electron pair associated with a carbon - hydrogen bond is so much less localized than the electrons in a carbon - carbon bond, that it may, somewhat like unshared electron pairs, undergo conjugation with an unsaturated center (31). This is hyperconjugation and when applied to the case at hand it means that the electron pairs of the gamma carbon-hydrogen bonds may conjugate with the double bond which is in the process of formation between the alpha and beta carbon atoms. Removing a hydrogen from a carbon atom to which the largest number of alkyl groups are attached will thereby give rise to the transition state of lowest energy.



The Tschugaeff reaction has been found to yield products in accordance with the Saytzeff rule as long as the steric requirement of cis orientation of eliminated groups could at the same time be accommodated. When the steric and electrical effects favoured the loss of two different hydrogen atoms, the steric effect was found to be over-riding. These facts may be illustrated by a consideration of Huckel's work.

S-Methyl-1-menthyl xanthate (X) represents a case where both effects, electrical and steric favour the loss of the same hydrogen atom.

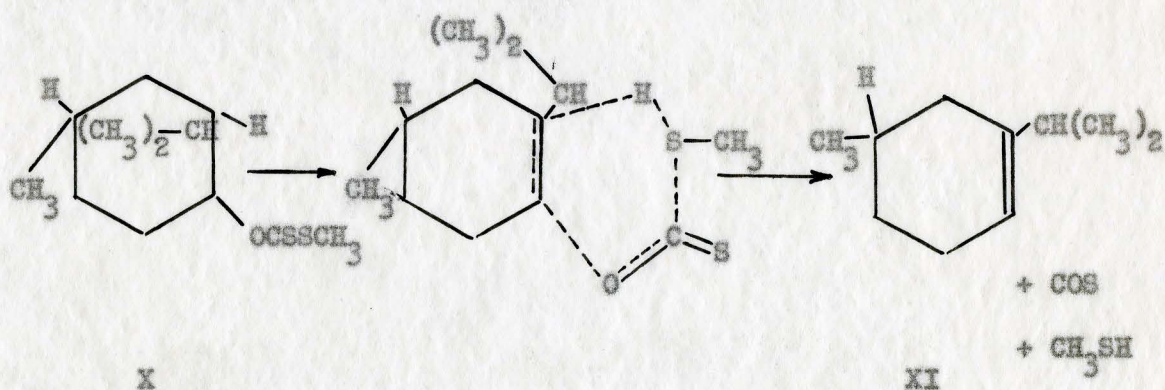


Compound (X) has a beta hydrogen that is not only tertiary but also possess a cis orientation with respect to the xanthate grouping. The predominating product in a pyrolysis of (I) is therefore  $\Delta^3$ -menthene (XI). d-neomenthyl xanthate (XII), on the other hand, illustrates a case where the steric and electrical effects operate in



opposition to one another. The hydrogen most favoured for elimination according to Saytzeff's rule is trans to the xanthate grouping. The result is a preponderant formation of  $\Delta^2$ -menthene (XIII), the product favoured for steric reasons. Huckel's results represented the first of a large body of work which has demonstrated that a cis-beta-hydrogen is preferentially eliminated in the Tschugaeff reaction.

Huckel felt that the Tschugaeff reaction represented an internal bimolecular elimination. With reference to the diagrams given earlier (page 14), this may be interpreted as meaning that in the Tschugaeff reaction the groups denoted by X and Y are both provided by the xanthate group. Thus the xanthate group is eliminated as is X while some atom in this group, Huckel envisaged the thio-ether sulphur atom, acting as the base Y abstracts the proton from the carbon atom. The result is the formation of a six-membered cyclic transition state.

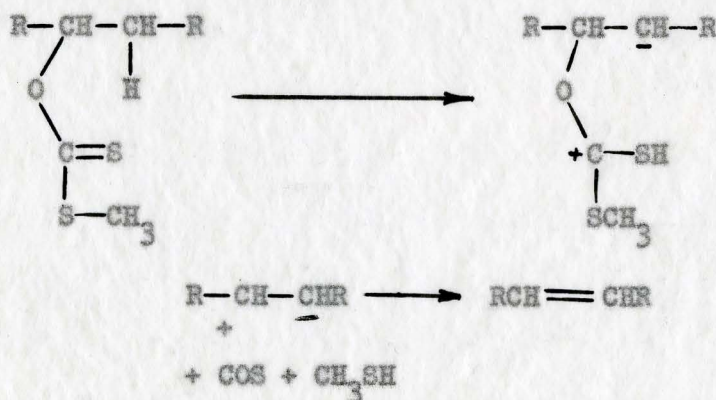


In proposing the cyclic transition state, Huckel accounted for the anomalous steric behavior of the Tschugaeff reaction since the formation of a six-membered ring requires that the xanthate group and the beta hydrogen atom possess a cis orientation with respect



to one another.

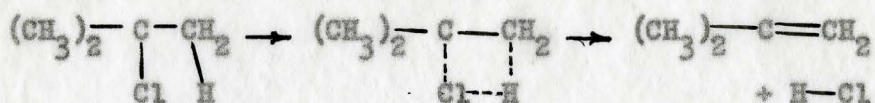
Almost simultaneous with the appearance of Huckel's work, was the publication of a paper by Stevens and Richmond (13) in which they, too, proposed a cyclic transition state for the Tschugaeff reaction. Their reasons for putting forth such a mechanism rested on an analogy drawn between this reaction and that of the eliminations undergone by quaternary ammonium salts. Both of these reactions show a remarkable freedom from rearrangements and to account for this effect the authors felt that a preliminary intermolecular hydrogen bonding with the beta-hydrogen atom followed by its complete removal were necessary steps in the reaction. The anionic species which were considered as entering into hydrogen bonding were the hydroxide ion in the case of the quaternary ammonium salts and the thion sulphur atom in the xanthates. This latter arrangement gives rise to a cyclic intermediate which is pictured below in the manner presented by Stevens and Richmond.



In 1949 it was pointed out by Barton (15), that cis rather



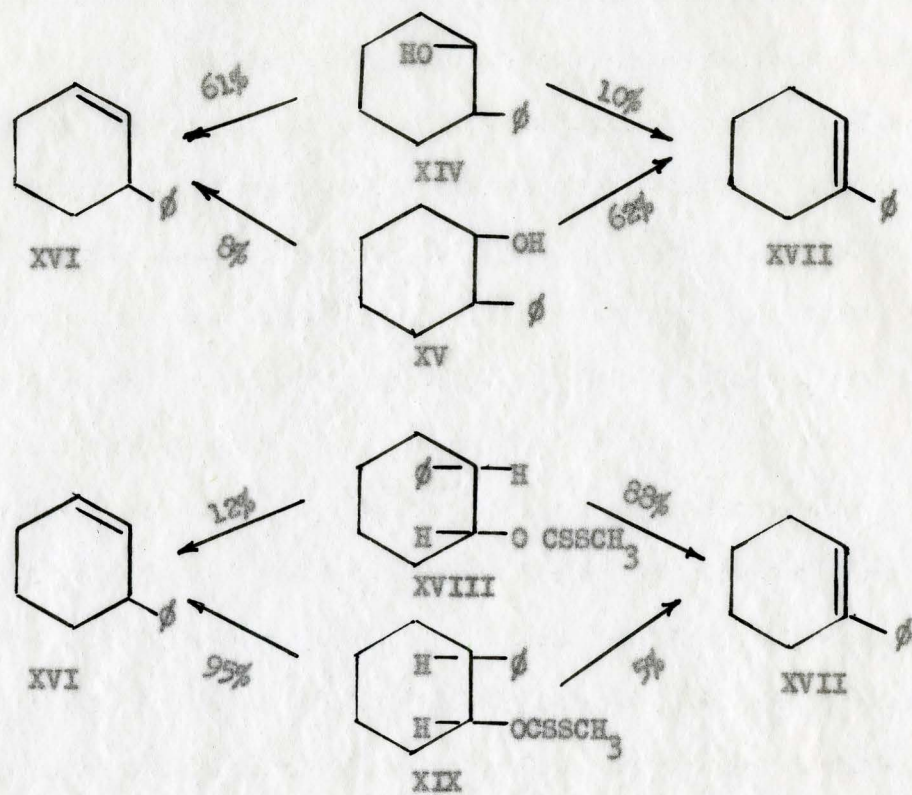
than trans elimination must be followed in certain homolytic, uni-molecular eliminations in the gas phase, since these reactions, like the Tschugaeff reaction, are postulated as having cyclic transition states. An example of such a reaction is the expulsion of hydrogen chloride from t-butyl chloride.



For such a four-membered ring to form, it is required that the eliminated groups possess a cis relationship with one another, thus leading to a cis elimination. Barton cites Huckel's mechanism for the Tschugaeff reaction, as another example of cis elimination.

Alexander and Mudrak (16) extended the stereochemical studies of the Tschugaeff reaction. Their first paper dealt with the products obtained from a pyrolysis of the xanthate ester of 2-phenyl cyclohexanol. Price and Karabinos (26) had already studied the stereochemistry of the products obtained from the dehydration of 2-phenyl cyclohexanol using a common dehydrating agent, phosphoric acid, and it was felt by Alexander and Mudrak that their work with the xanthate ester of this compound would permit a comparison of the stereochemistry of the products from the two reactions. The results of both methods are pictured schematically below.



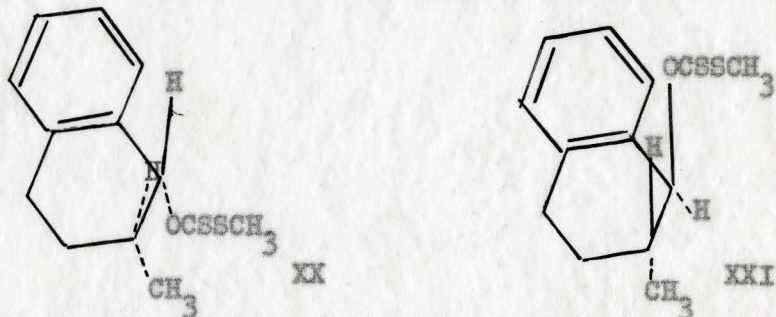


Dehydration of these two phenylcyclohexanols with phosphoric acid or anhydride gave chiefly 1-phenylcyclohexene (XVII) from the cis-isomer (XV) and 3-phenylcyclohexene (XVI) from the trans-isomer (XIV) another example of the well-known fact that elimination to form a multiple link, using the common methods of dehydration, takes place most readily when the elements lost are trans to each other (27). The results obtained from the pyrolyses of the isomeric xanthate esters of 2-phenylcyclohexanol are the very opposite to those just outlined for the treatment of the alcohols with phosphoric acid. The results clearly indicate that the xanthate decomposition decidedly favours an elimination of cis elements.

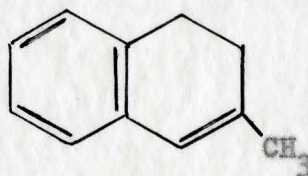


In all of the cases studied up until this time a hydrogen atom was attached to both beta carbon atoms and although the olefin formed by cis elimination was the preferred product some of the isomeric olefin, apparently arising from a trans elimination, was also obtained. The question arises as to whether elimination involves two different processes occurring at different rates, or whether the reaction involves the exclusive removal of the cis-beta-hydrogen, followed by rearrangement.

In an attempt to determine whether or not more than one mechanism is operative in the Tschugaeff reaction, Alexander and Mudrak (17) next studied the thermal decompositions of the xanthate esters of 2-methyl-1-tetralol, which have but one hydrogen beta to the xanthate linkage, and hence can give rise to but one product.



The trans form (XXI) was found to yield exclusively 2-methyl-3,4-dihydronaphthalene (XXII) as expected, while the cis form (XX) was thermally stable.

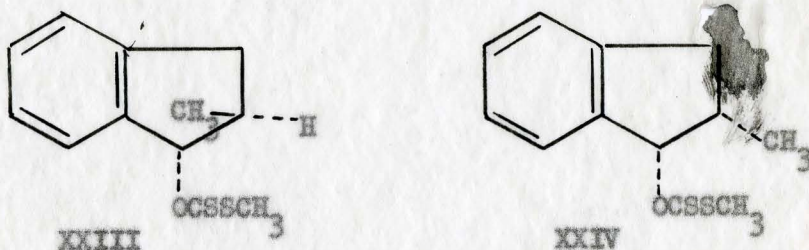


XXII

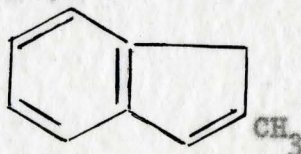
If a cis elimination is the only mechanism for the reaction, then



the difference in behavior of the cis and trans forms of the xanthate is very consistent with this view. Certainly with this information it was very tempting to conclude that the reaction did indeed proceed only by a cis elimination. There was, however, one point which did not allow the authors to draw this conclusion. It rested on the fact that while the trans form of the xanthate was a solid, the cis form was a liquid and had to be distilled in the course of its purification. There was a chance that this was an example of the "stable" form reported by McAlpine. Since the results of this study were therefore, not entirely conclusive, Alexander and Mudrak (18) searched for an alcohol which had but one hydrogen beta to the xanthate grouping and whose isomeric xanthate esters would be solids. The two isomeric xanthates of 2-methyl-1-indanol were found to have the desired properties.



The results of the thermal decomposition of these two isomeric xanthates indicated, that what seems to be a trans elimination, is possible. The trans form of the xanthate (XXIII) gave an 80% yield of 2-methyl-1-indene (XXV), but the cis form (XXIV) was by no means thermally stable, giving under all of the pyrolytic conditions employed the same 20% yield of (XXV).

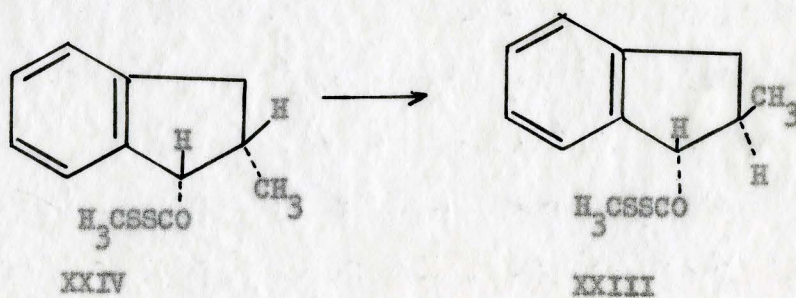


XXV



As the cis form of the xanthate has no beta-hydrogen possessing a cis orientation with respect to the xanthate grouping, it appears that another mechanism must be operative in this case.

The cis form of 2-methyl-1-indanol can be isomerized to the trans although the reverse of this is not true, and while the conditions under which the decompositions were carried out would seem to be capable of bringing about such a change in the case of the alcohol, no information was given concerning the convertibility of the cis form of the xanthate to the trans. The apparent trans elimination of the cis xanthate could, however, be explained on the basis of an isomerization. The first step would be the isomerization of the cis xanthate to the trans form, which then could proceed by a cis elimination.

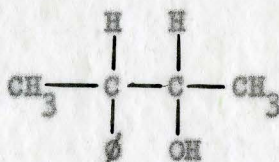


Xanthates possessing no beta-hydrogen atoms, it will be recalled, have a tendency to isomerize to the dithiolcarbonates. It is conceivable that compounds such as XXIV, possessing no cis-beta-hydrogen atom, could have this same tendency. If such an isomerization did occur in this case, with an inversion about the alpha-carbon atom, the resulting dithiolcarbonate would undergo an elimination with a loss of cis elements. This is another conceivable manner in which the apparent trans elimination could arise.



An entirely different mechanism might be involved. The possibility of a bimolecular reaction must not be overlooked. Such a mechanism seems probable with those compounds which have no beta-hydrogen atom.

An interesting application of the Tschugaeff reaction and its implied removal of a cis-beta-hydrogen atom was made by Cram (19) in his series of papers entitled "Studies in Stereochemistry." Cram was concerned with the Wagner Meerwein type rearrangements undergone by the tosylates of the four isomeric 3-phenyl-2-butanols (XXVI).

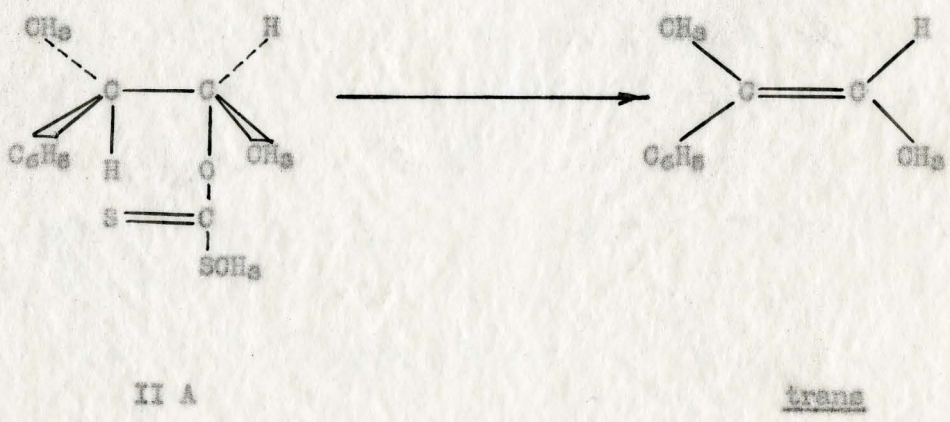
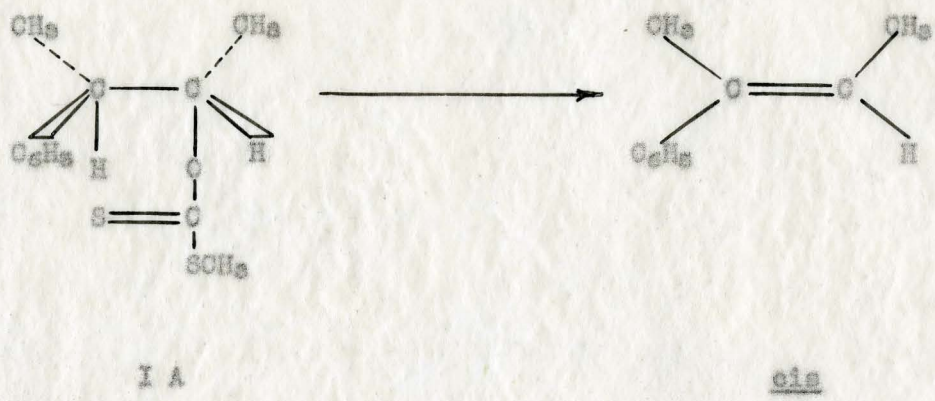


XXVI

He was able to assign relative configurations to the four stereoisomers as a result of the rearrangement studies. However, it was felt that a determination of the relative configurations by an independent method would be desirable and to this end he applied the Tschugaeff reaction. As an example of the manner in which he carried out this application, consider the decompositions of the xanthates of the isomeric 3-phenyl-2-butanols which in Cram's notation were labeled as IA and IIA. (See Diagram on Page 24)

Cram was able to identify the different 2-phenyl-2-butenes and this information, together with the now well-founded assumption that the Tschugaeff reaction involves a cis elimination, enabled him to assign relative configurations to the 3-phenyl-2-butanols. The configurations arrived at in this manner agreed with those ob-







tained from the rearrangement studies. Since both methods of obtaining the relative configurations led to identical results, this adds further proof to the fact that the Tschugaeff reaction does indeed involve the loss of cis elements.

The kinetic evidence of O'Connor and Nace (20, 21) provided further evidence that a cyclic transition state is involved in the Tschugaeff reaction. A thorough kinetic investigation was conducted on the thermal decompositions of the S-methyl xanthates of beta-cholestanol and cholesterol. Both reactions were found to be first order processes and with energies of activation of 34 and 33 kcal/mole respectively. Negative entropies of activation of approximately 5 e.u. were found in each case, showing that several degrees of freedom are restricted in the transition state and definitely implying a cyclic mechanism for the reaction.

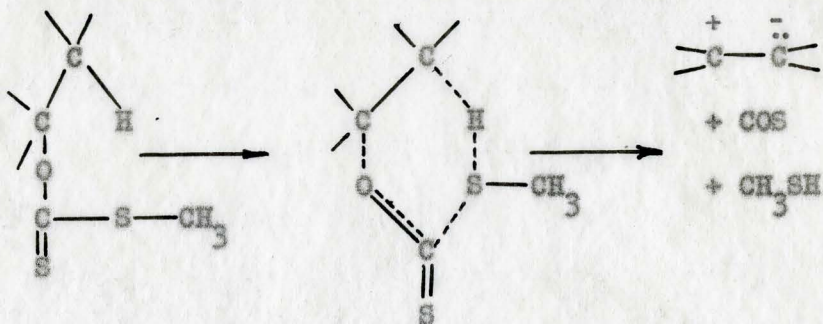
That a cyclic transition state is a valid concept for the Tschugaeff reaction could no longer be questioned with such abundant proof of both a steric and kinetic nature. However, two schools of thought arose as to the exact nature of this transition state. The first, originated by Huckel et al (14), favoured hydrogen bonding with the thio-ether sulphur atom, while Stevens and Richmond (13) maintained that this effect should be associated with the thion sulphur atom.

Huckel envisaged the thio-ether sulphur atom as abstracting the proton because, as mentioned above, he considered the  $\text{CH}_3\text{S}$  group as participating in a role similar to that played by the alcoholate ion in a regular bimolecular elimination reaction, e.g.,

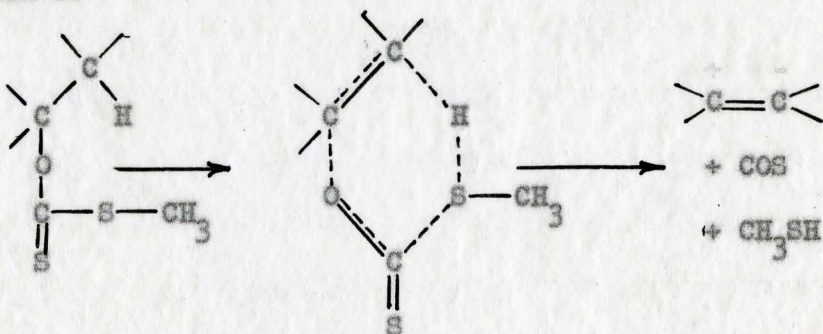




The exact formulation of Huckel's mechanism is shown below.



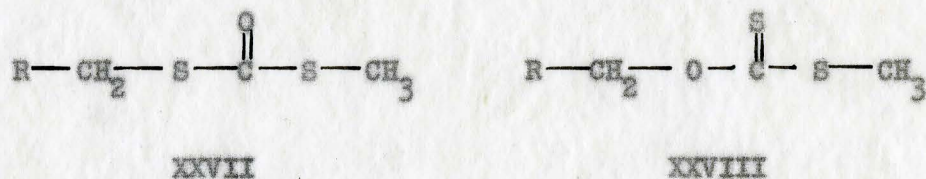
It is to be noted that while the mechanism is a concerted one, a polarized rather than the ground state form of the alkene results. The reversion of the polarized form of the alkene to the ground state of the molecule Huckel apparently considered to be a second and separate step. Barton (15), Ingold (22) and Bartlett (32) in citing this work also pictured the mechanism as being a concerted one and involving the thio-ether sulphur atom, but formulate it in such a manner as to produce the alkene directly. Their proposal is pictured below and henceforth it shall be referred to as Mechanism I.



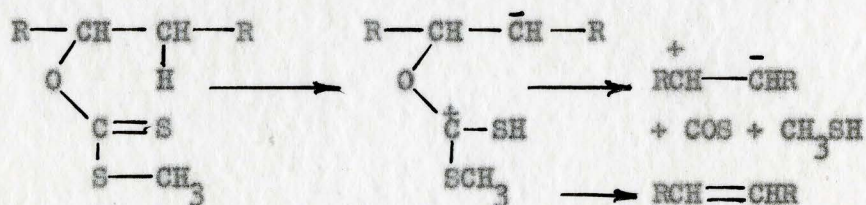


This same mechanism appeared in a paper by J. D. Roberts and C. W. Sauer (28).

Stevens and Richmond (13) favoured the thion sulphur atom for two reasons, the one being the greater overall chemical reactivity of the thio carbonyl group over that of the thio-ether group, and the other drawn from a comparison of the thermal stability of the xanthates with the dithiolcarbonates. It has been noted that dithiolcarbonates (at least those possessing no beta-hydrogen atoms), are more stable than the corresponding xanthates (24).

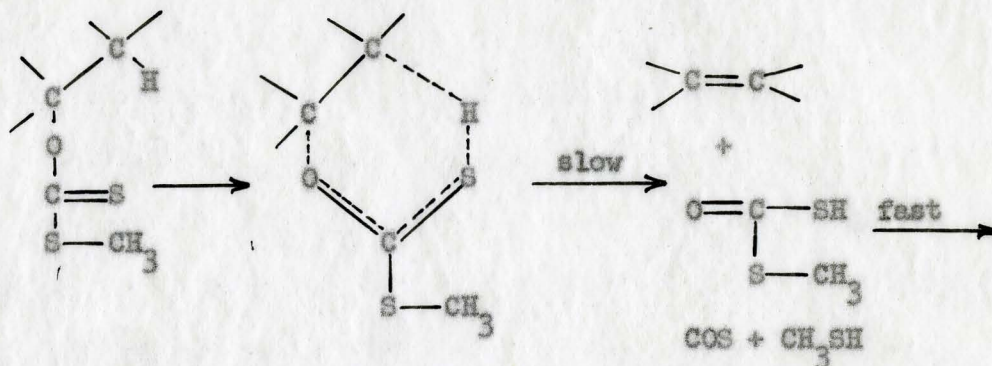


One of the major factors controlling the stability of the molecules pictured above is the bond strength of the C-O link in (XXVIII) and of the C-S link in (XXVII). It is known from bond energies and distances that the C-O bond is the stronger of the two. Hence if it were the thio-ether sulphur atom which bonded with the hydrogen, then the dithiolcarbonates should be the less stable of the two compounds, for the C-S link of (XXVII) is weaker than the corresponding C-O link of the xanthate. However, as the thermal stabilities are found to be the reverse of this prediction, they conclude that it cannot then be the thio-ether sulphur atom which abstracts the proton. The mechanism presented with their paper is pictured below.



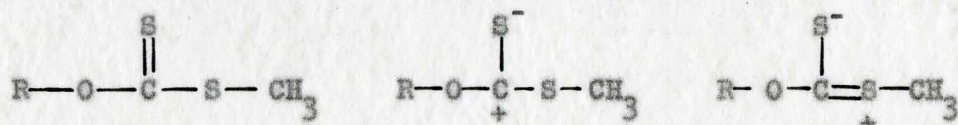


This mechanism, it is to be noted, is not of a concerted type. Cram (19) while agreeing with Stevens and Richmond on the choice of sulphur atom, pictured the mechanism as being concerted, producing the olefin in its ground state directly. The mechanism proposed by Cram is shown below and is designated as Mechanism II.



Mechanism II is a two-step process. The initial reaction involves the simultaneous formation of the alkene and a highly unstable xanthic acid intermediate which in the second step very rapidly decomposes into the remaining two products. Mechanism I on the other hand, involves but one potential energy barrier and leads to all three products directly. Thus the two mechanisms exhibit a fundamental difference not only in the functions assigned to the sulphur atoms but also in the manner which the activated complexes revert to products.

In support of Mechanism II Cram drew attention to the fact that the xanthate group may be considered as a resonance hybrid of the following structures.





Since in two of the above structures the thion sulphur atom possess a negative charge it would be expected that the proton affinity of this atom would be considerably enhanced over that of the thio-ether sulphur atom which is actually positively charged in one of the contributing structures. He further maintained that the ester group on the thio-ether sulphur atom would present steric problems not to be encountered with the thion sulphur atom.

Alexander et al (16) held essentially similar views although noting the fact that this represented a unique instance in which a departing group is not displaced by a rearward attack of an unshared electron pair. O'Connor and Nace (20) felt that reaction by such a mechanism would be very favourable as it would allow for a resonance stabilization of the transition state, as there are six  $\pi$  electrons available for distribution around a six-membered ring. Thus it is essentially a hybrid of starting material and products. The decomposition could then proceed by a further shifting of the atomic nuclei and a subsequent redistribution of the nonlocalized electrons, from which point on the process is energetically downhill.

In a second paper O'Connor and Nace (21) have reported effects of different substituents on the rate of pyrolysis of series of cholesteryl xanthates. The ester groups studied and their respective rates of thermal decomposition are shown below.

<u>Ester Grouping</u>	<u><math>k \cdot 10^4 \text{ min}^{-1}</math></u>
$\text{CH}_3 -$	143
$\text{CH}_3\text{CH}_2$	120



Benzyl -	214
<i>p</i> -Methoxy benzyl -	220
<i>p</i> -Chloro benzyl -	295
Diphenylmethane -	495
<i>p</i> -Nitro benzyl -	623
2,4-dinitrophenyl -	706
Triphenylmethyl -	1430

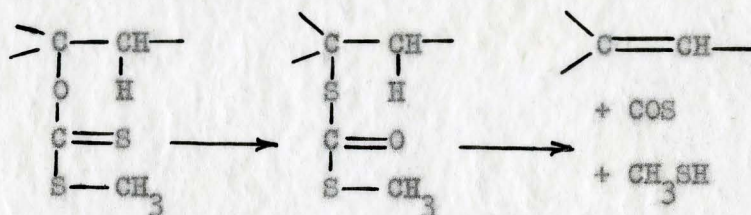
A Hammett plot of these velocity constants, with the exception of those for ethyl and methyl cholesteryl xanthates, gave a straight line with a slope of +0.87. From this data it is evident that the more electronegative the ester group, the more readily does decomposition occur. This behaviour might at first seem anomalous, for making the ester group more electronegative will decrease the nucleophilic character of the thion sulphur atom. The authors (21), however, noted that a unique driving force was possible in the xanthate ester decomposition. The initial products, according to Mechanism II, is a xanthic acid with a  $O=C-S$  linkage, as opposed to the  $-O-C=S$  linkage present in the xanthic ester. A transformation of the latter into the former compound results in a gain in energy, for the xanthic acid is the more stable of the two.

Thus it would appear that an electron deficiency about the central carbon atom lowers the activation energy for the formation of the cyclic transition state by facilitating partial bond making with respect to bond breaking in the linkage  $O-C-S$ . The more electronegative the ester group is, the greater is the tendency for bond making to have proceeded further than bond breaking at the trans-



ition state.

Tarbell and Harnish (23) have proposed a mechanism for the Tschugaeff reaction based on an initial isomerization of the xanthate ester to a dithiolcarbonate. This mechanism is not compatible with the existing facts, but is included for the sake of completeness. Tarbell reasoned that the xanthate ester, by availing itself of an initial isomerization to the dithiolcarbonate, would have available a keto oxygen to abstract the beta-hydrogen atom as opposed to either the thion or thio-ether sulphur atoms present in the xanthate ester.



The mechanism is not easily reconciled with the known steric results of the Tschugaeff reaction. In order that an overall cis elimination be observed, Tarbell must postulate a frontside displacement on the xanthate carbon atom by the thion sulphur in the isomerization step, or alternately, an isomerization with inversion followed by a trans elimination.

Bulmer and Mann (24) had demonstrated that dithiolcarbonates possessing no beta-hydrogen atoms were more stable than the corresponding xanthate esters, and very recently Saloami (see page 98 of the Discussion) has extended the validity of these relative stabilities to include those xanthate esters which do possess beta-hydrogen



atoms. Clearly, Tarbell's mechanism is not compatible with these relative stabilities.

Further evidence against this mechanism was provided by O'Connor and Nace (20) who examined the infrared absorption spectrum of a sample of cholesteryl-S-methyl xanthate decomposed to the extent of 30%. No bands were observed which could be assigned to the  $\text{-C=O}$  group as might be expected from a rearrangement of the xanthate ester to a dithiolcarbonate.



## ISOTOPE EFFECTS

The discovery of isotopes by Soddy in 1911 was not attended with any immediate theoretical or experimental interest. However, in 1930 a calculation was made predicting that water would be electrolyzed more rapidly than deuterium oxide, and in the same year the prediction was verified experimentally. Calculations such as these were forced to await the development of quantum mechanics, for according to classical mechanics, both the light and heavy isotopes should behave identically.

The reason classical mechanics fails to predict an isotopic separation is apparent from a consideration of the classical derivation of an isotopic exchange constant. The classical partition function may be expressed in the following form,

$$h^f Q = \frac{1}{s} \iiint \dots \iiint e^{-H(p,q)/kT} dp \dots dq, \quad (1)$$

where  $s$  is the symmetry number,  $h$  is Plank's constant,  $k$  is Boltzmann's constant, and  $H$  is the hamiltonian of the momenta  $p$  and the co-ordinates  $q$  of the constituent atoms. By the proper choice of co-ordinates the momenta of all three kinds of motion, translational, rotational, and vibrational may be expressed as squared terms of the type  $p^2/2m$ , and since these occur only in the kinetic energy, integration over the  $p$ 's leads to,

$$Q = \frac{1}{s} \prod_i \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} \times \iiint \dots \iiint e^{-\epsilon_p/kT} dq_1 \dots dq_k \quad (2)$$



The potential energies of the isotopic species being alike, the ratio of the partition functions for two isotopic species is thus reduced to a product of the ratio of the symmetry numbers and the isotopic mass ratio raised to the three-halves power, i.e.,

$$\frac{Q}{Q'} = \frac{s'}{s} \left(\frac{m}{m'}\right)^{3/2} \quad (3)$$

The ratio of the masses of the isotopes will cancel in any chemical equilibrium. Since the ratio of the symmetry numbers merely denotes the relative probabilities of forming symmetrical or unsymmetrical products, it will not, no matter what its value lead to any isotopic enrichment.

$$\text{That is, } K = \frac{Q_2}{Q_1} / \frac{Q_2'}{Q_1'} = \frac{s_2'/s_2}{s_1'/s_1} \left(\frac{m}{m'}\right)^{3/2} / \left(\frac{m}{m'}\right)^{3/2} = 1 \quad (4)$$

Similar calculation performed from a quantum mechanical standpoint do lead to an isotopic separation, for contained in this newer mechanics is the concept of zero point energy. The quantum translational partition function is the same as the classical one under all conditions, and the rotational partition function derived from quantum mechanics differs from the classical one only below room temperature, except in the case of hydrogen. Thus the separation factor is contained in the vibrational partition function, the one which involves the zero point energy term. The vibrational partition function in quantum mechanics is of the form

$$Q_{\text{vib}} = \prod_i \frac{e^{-u_i/2}}{1 - e^{-u_i}} \quad (5)$$



where

$$u_1 = \frac{h \nu_1}{kT} \quad (6)$$

where the product is taken over all of the vibrational frequencies

$\nu_1$ .

It is now convenient to define a function  $f$  such that

$$f = \frac{Q}{Q'} \prod_1 \left( \frac{m'_1}{m_1} \right)^{3/2} \quad (7)$$

The definition amounts to omitting the useless classical mass ratio  $(m/m')^{3/2}$  and is equivalent to calculating the ratio of the equilibrium constants for the dissociation of the two isotopic molecules into atoms, i.e.,

$$K'/K = \frac{Q'_{\text{atom}}}{Q_{\text{atom}}} / \frac{Q'_{\text{mol}}}{Q_{\text{mol}}} = \frac{Q_{\text{mol}}}{Q'_{\text{mol}}} \prod_1 \left( \frac{m'_1}{m_1} \right)^{3/2} \quad (8)$$

In classical mechanics the product

$$s/s' f \quad (9)$$

is unity, and such a result implies that there can be no separation of the isotopes. In quantum mechanics this same product assumes a value other than one and is of the form,

$$\frac{s}{s'} f = \prod_1 \frac{u_1}{u'_1} \frac{e^{-u_1/2} / (1 - e^{-u_1})}{e^{-u'_1/2} / (1 - e^{-u'_1})} \quad (10)$$

since  $f$  depends upon the vibrations only. The term  $u'_1$  may be replaced by  $u_1 + \Delta u_1$ , (and if the primed molecule is the lighter one)  $\Delta u_1$  is thus a positive quantity at all times. Equation (10) may now be rewritten as



$$\frac{s}{s'} f = \prod_1 \frac{u_1}{u_1 + \Delta u_1} e^{\Delta u_1/2} \frac{(1 - e^{-(u_1 + \Delta u_1)})}{(1 - e^{-u_1})} \quad (11)$$

The difference in the free energy of formation of two isotopic molecules from their respective gaseous atoms will then be given

by

$$\frac{\Delta F^\circ - \Delta F^{\circ'}}{RT} = \sum_1 \left[ -1/2 \Delta u_1 + \ln \left( 1 + \frac{\Delta u_1}{u_1} \right) + \ln \frac{(1 - e^{-u_1})}{(1 - e^{-(u_1 + \Delta u_1)})} + \ln \frac{s}{s'} \right] \quad (12)$$

Further if  $\Delta u_1$  is small which is true for all elements except hydrogen

$$\frac{s}{s'} f = 1 + \sum_1 \left( \frac{1}{2} - \frac{1}{u_1} + \frac{1}{e^{u_1} - 1} \right) \Delta u_1 \quad (13)$$

or

$$\frac{\Delta F^\circ - \Delta F^{\circ'}}{RT} = - \sum_1 \left( \frac{1}{2} + \frac{1}{e^{u_1} - 1} - \frac{1}{u_1} \right) \Delta u_1 + \ln \frac{s}{s'} \quad (14)$$

$(s/s')f$  will always be greater than 1, since  $\Delta u_1$  is positive. This implies that the heavy isotope is more stable in the molecule, while the lighter isotope favours the separated atoms.

The derivation presented above is due to Bigeleisen and Meyer (33), this particular one being given for reasons which will be apparent later in this section. Calculations of isotopic exchange constants using concepts similar to those presented above were performed by Urey in 1935 (34) for reactions involving elements of the first row of the periodic table. A typical calculation was concerned with the fractionation of the oxygen isotopes which occurred in the reaction represented by





The equilibrium exchange constant for this reaction was calculated to be 1.044 at zero degrees centigrade, which compares very favorably with the experimental value of 1.046.

Until recently it was generally assumed that while equilibrium exchange constants for isotopes other than those of hydrogen could be expected to differ significantly from unity, only the isotopes of hydrogen would exhibit measurable difference in their relative reaction rates in irreversible processes. However, this prevailing notion was shattered in 1948 when Calvin announced that he had obtained experimentally an 8% fractionation of the carbon isotopes  $\text{C}^{12}$  and  $\text{C}^{14}$  in the decarboxylation of malonic acid, which was labeled with  $\text{C}^{14}$  in one of the carboxyl positions (35). Interest was immediately aroused, if not some skepticism, and a concentrated effort was made to study such effects in many different laboratories. The results of these undertakings may be best studied by considering first the origins of isotope effects in unidirectional processes.

Two methods, permitting explicit calculations of isotope effects in unidirectional processes have been developed, the first by Eyring (36) and more recently one by Bigeleisen (37). The formulation due to the latter author is the more fundamental and a consideration of its derivation will show most clearly the origins of isotope effects in unidirectional reactions.

Bigeleisen limited his assumptions to those inherent in the transition state hypothesis. According to this hypothesis,



sometimes called the absolute rate theory, the reaction co-ordinate passes through a potential energy maximum. The reacting molecule, when at the top of the potential energy barrier and within a certain small but otherwise arbitrary distance  $\delta$  along the reaction co-ordinate, possesses a configuration somewhere between that of the eventual product molecule and the original reactant. This particular configuration is called the activated complex. It is considered as having but one unusual property, that of an instability to displacement in the direction of the reaction co-ordinate.

The other important assumption of the absolute rate theory is the validity of the application of thermodynamic concepts to the equilibrium that is assumed to exist between the activated complex and the reactant molecules, i.e.,



Since a number of the activated complexes are continuously disappearing over the potential energy barrier, a true equilibrium in a thermodynamic sense does not exist. The concentration of the activated complex  $C^{\ddagger}$  is calculated on the assumption that it is in equilibrium with both reactants and products. The result obtained is then applied to the case when products are absent, and it is assumed that their absence does not appreciably influence the forward reaction of reactants to products. The validity of this procedure has been discussed by Guggenheim and Fowler (47). For the reaction at equilibrium the mean velocity  $\bar{v}$  at which the complexes are moving to the right is calculable from kinetic theory and assumes the form,



$$\bar{v} = \frac{\int_0^{\infty} e^{-m^{\ddagger} x^2 / 2kT} dx}{\int_0^{\infty} e^{-m^{\ddagger} x^2 / 2kT} dx} = (2kT/\pi m^{\ddagger})^{1/2} \quad (a) \quad (16)$$

where  $m^{\ddagger}$  is the effective mass of the complex along the decomposition co-ordinate. The average time to move through the transition state to the right will then be

$$\delta/\bar{v} = (\pi m^{\ddagger} / 2kT)^{1/2} \quad (17)$$

and the rate of reaction in terms of the number of complexes moving to the right per unit volume per unit time will be

$$\text{rate} = (C^{\ddagger} / \delta) (kT/2\pi m^{\ddagger})^{1/2} \quad (18)$$

The rate of the reaction may also be expressed in the more familiar form as a function of the concentrations of the reacting species as

$$\text{rate} = k_r C_A^a C_B^b \quad (19)$$

and therefore the rate constant is equal to

$$k_r = \frac{1}{\delta} \frac{C^{\ddagger}}{C_A^a C_B^b} (kT/2\pi m^{\ddagger})^{1/2} \quad (20)$$

It is now possible, by using equation (20), to obtain a ratio for two isotopic rate constants, i.e.,

$$\frac{k_1}{k_2} = \frac{C_1^{\ddagger}}{C_2^{\ddagger}} \frac{C_{A_2}^{a_2}}{C_{A_1}^{a_1}} \left( \frac{m_2^{\ddagger}}{m_1^{\ddagger}} \right)^{1/2} \quad (21)$$

where the other reactants B etc., are monoisotopic.

Because of the very slight difference between the potential energy

(a) The double dagger will be used exclusively to denote quantities referring to the transition state.



surfaces of isotopic molecules,  $S_1 = S_2$ . It is significant to note that in unidirectional effects the ratio of the isotopic masses does not cancel as it did in the equilibrium exchange calculations, but rather it has an important bearing on the magnitude of the resultant isotope effect. The masses were incorporated by a consideration of the speeds at which the activated complexes traversed the energy barrier.

Since the ratio of the concentrations will be equal to the ratio of the probabilities of the two species, the relative concentrations in equation (21) may be replaced by the ratio of their respective partition functions.

$$\frac{k_1}{k_2} = \frac{Q_1^\ddagger}{Q_2^\ddagger} \frac{Q_{A2}}{Q_{A1}} \left(\frac{m_2}{m_1}\right)^{1/2} \quad (22)$$

As in the equilibrium exchange case, the ratio of the complete partition functions of the two isotopic molecules reduces to equation (10) which is simply a function of the vibrational energy levels of the two molecules. This serves to introduce the concept of zero point energy and equation (22) thus becomes

$$\frac{k_1}{k_2} = \frac{f}{f^\ddagger} \left(\frac{m_2}{m_1}\right)^{1/2} \quad (23)$$

When  $\Delta u_1$  is small as is the case for all the elements except hydrogen

$$\frac{k_1}{k_2} \frac{S_2 S_1^\ddagger}{S_1 S_2^\ddagger} = \frac{1}{2} \ln \frac{m_2}{m_1} + \sum_1^{3n-6} G(u_1) \Delta u_1 - \sum_1^{3n'-6} G(u_1^\ddagger) \Delta u_1^\ddagger \quad (24)$$

where  $G(u) = 1/2 - 1/u + \frac{1}{(e^u - 1)}$



or

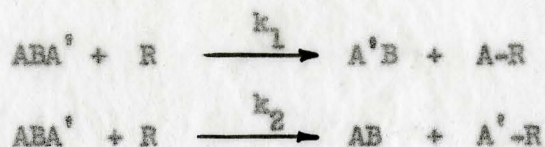
$$\frac{k_1}{k_2} = \frac{S_2^\ddagger}{S_1^\ddagger} \frac{S_1}{S_2} \left(\frac{m_2}{m_1}\right)^{1/2} \times \left[ 1 + \sum_1^{3n-6} G(u_1) \Delta u_1 - \sum_1^{3n^\ddagger-6} G(u^\ddagger) \Delta u^\ddagger \right] \quad (25)$$

If all of the molecules were in the lowest lying energy level the two summations in (25) would represent the difference in free energy divided by RT between the two isotopic species in both the reactants and activated complexes respectively, and this in turn could be explicitly expressed in terms of their respective zero point energies. However, at room temperature many of the higher energy levels are occupied, and the two summation terms provide a description of populations such as these. The spacing between the vibrational energy levels decreases as the temperature is raised, and at higher temperatures the levels will become so closely spaced that the vibrational partition function will assume the classical form. When this occurs, the difference in the activation energies of the two isotopic species disappears. Therefore, at room temperature, where levels other than the ground level are occupied, the difference in the activation energies between two isotopic reactions is always less than the difference of their zero point energies.

Isotopic fractionations may conveniently be classified into two groups, as inter-and intramolecular effects. Both types of effects will be discussed in turn making use of equation (25).

When a molecule such as ABA', where A and A' denote two groups which are identical except for the isotopic substitution of one of the atoms, undergoes some reaction with R, two slightly different reaction co-ordinates are possible, i.e.,





The relative rate of the two reactions  $k_1/k_2$ , is termed an intramolecular isotope effect.

A great simplification of equation (25) occurs when it is applied to intramolecular effects as a result of the equality of  $u_1$  and  $u_2$ . The two terms are equal in this case because an intramolecular effect compares the two alternate modes of decomposition of the same molecule  $\text{ABA}^{\dagger}$ . It is thus necessary to evaluate only  $\sum_1^{3n^{\dagger}-6} G(u_1^{\dagger}) \Delta u_1^{\dagger}$ , and for some very simple reactions this is in principle possible. However, for most reactions involving three or more atoms the problem of evaluating this sum is much too complex and in order to apply equation (25) a simplifying assumption is made. For all of the elements of the first row of the periodic table the summation  $\sum_1^{3n-6} G(u_1) \Delta u_1$  has a very small value, and since the activated complexes occupy even higher energy levels,  $\sum_1^{3n^{\dagger}-6} G(u_1^{\dagger}) \Delta u_1^{\dagger}$  will have an even smaller value. This latter summation may then be neglected to a first approximation. Thus for intramolecular isotope effects equation (25) reduces to

$$\frac{k_1}{k_L} = \frac{S_2^{\dagger}}{S_1^{\dagger}} \left( \frac{m_2}{m_1} \right)^{1/2}$$

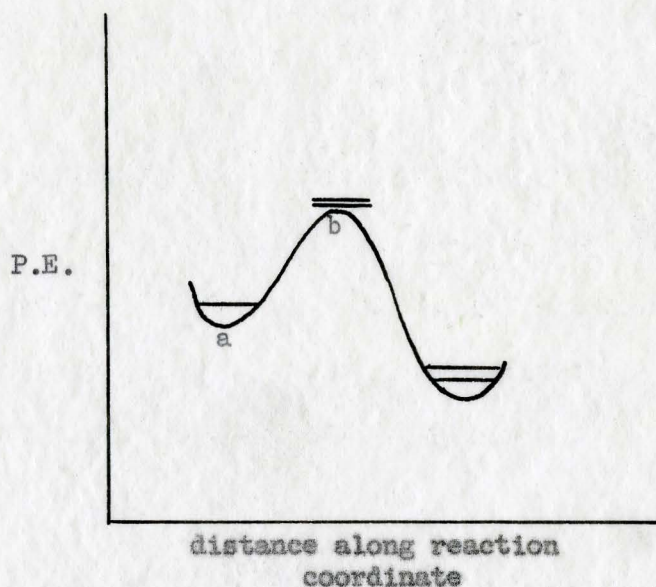
a ratio which is independent of the temperature.

A theorem due to Slater (38) has shown that in a reaction involving simple bond rupture the reduced masses may be calculated from the imaginary diatomic molecule composed of the atoms between



which the bond is broken in the rate determining step. The masses of any other atoms in the molecule are neglected.

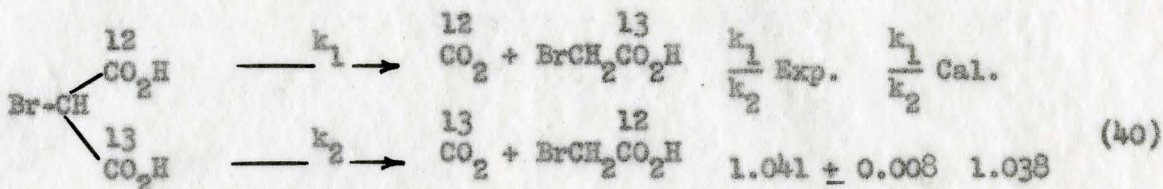
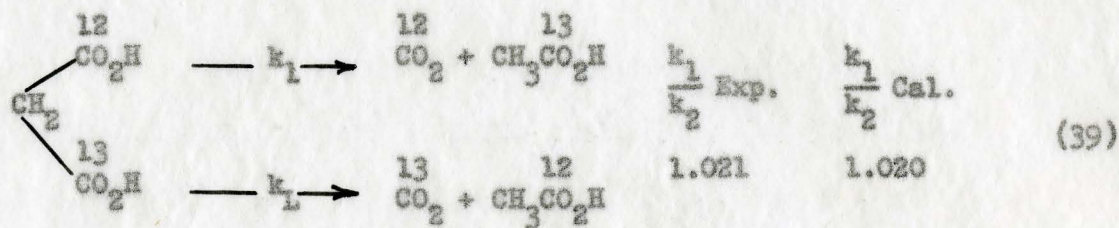
A potential energy diagram of the reaction co-ordinates representing intramolecular isotope effects has the appearance of the one shown below.



The reactants have a common potential energy well at a, but exhibit a very slight difference at b, the potential energy of the activated complex. Since in applying equation (25) we assumed that even the potential energy barriers are the same for the two isotopic molecules, the isotope effect will then be due solely to the difference in rate at which the two slightly different masses traverse this energy maximum.

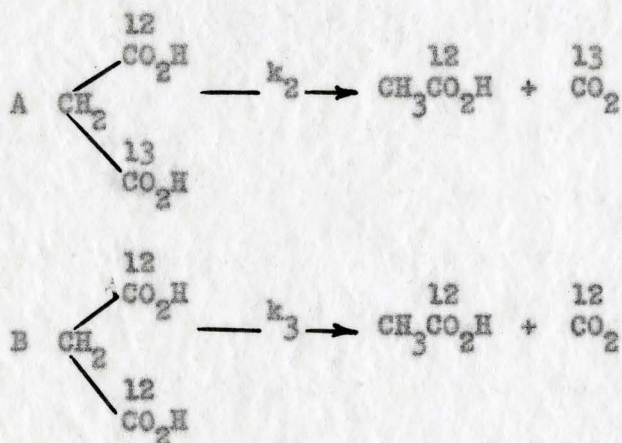
The agreement between the calculated and experimental results is very good, some examples being given below.





Intramolecular isotope effects are determined experimentally by comparing the isotopic ratio found in the product obtained after complete reaction with that found in the reactant.

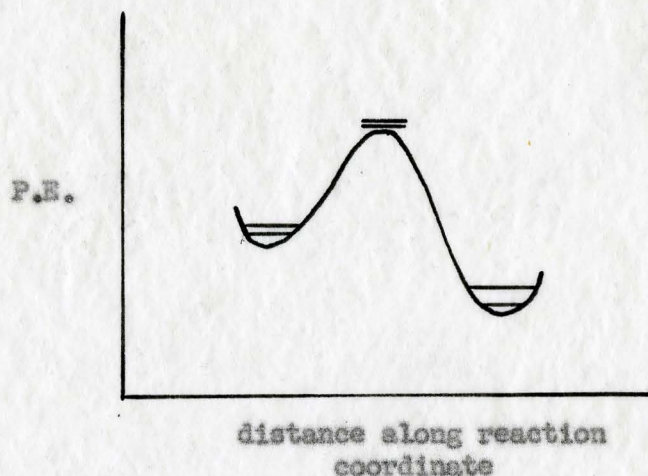
Isotopic fractionation in the decomposition of malonic acid may be considered in yet another way.



The ratio  $k_3/2k_2$  is called the intermolecular isotope effect. In consequence of the fact that molecule A can decompose in two different ways and B in but one, a 2 occurs in the denominator of the ratio in this particular case. Intermolecular isotope effects are encountered much more frequently than are intramolecular effects



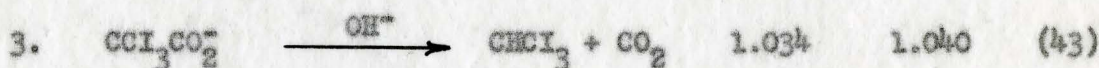
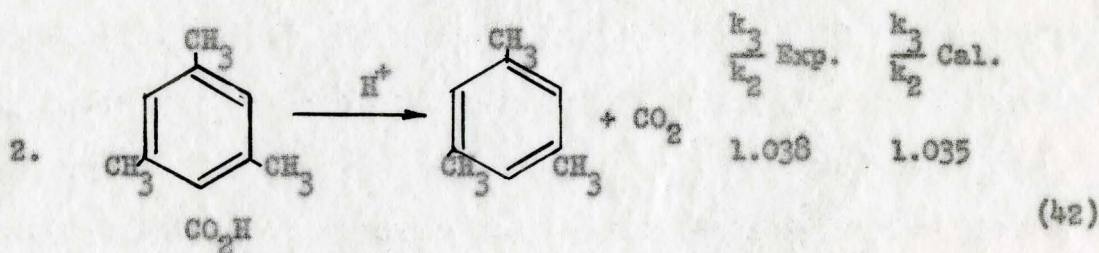
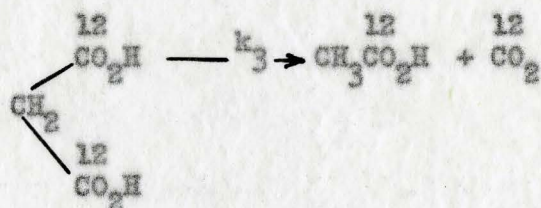
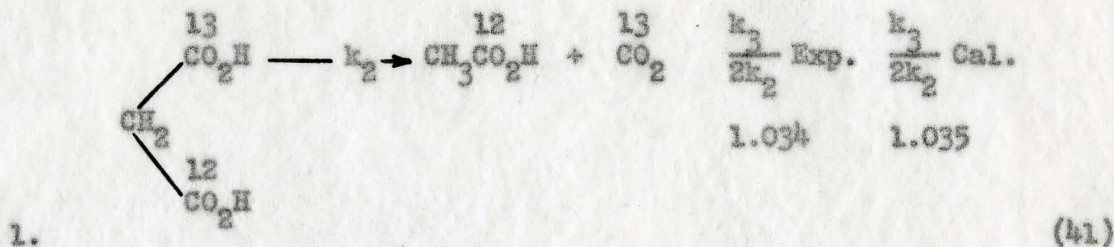
since the former effect refers to those cases where the isotopic substitution occurs in different molecules. Both the ground and activated states of the reactants will exhibit a difference in their thermodynamic properties for the two isotopic species, and a potential energy diagram plotted along the reaction co-ordinate will have the appearance of the one shown below.



For a calculation of intermolecular isotope effects all the terms of Bigeleisen's equation must be considered. Since the knowledge of the transition state is very limited, a model must be chosen on which to base the calculations. The simplest possible model and one which gives a result which represents an upper limit in regards to the magnitude of the effect, is to assume that the bond between the isotopic species and the other atoms is completely broken in the transition state, and further, that the frequencies of all bonds other than the one undergoing fission remain unchanged in going from the initial to the transition state. In other words, the reaction is considered as a simple dissociation of a diatomic



molecule into its constituent atoms. The summation  $\sum_1^{3n^*-6} G(u_i^\ddagger) \Delta u_i^*$  is thus zero, and all of the information necessary for a calculation is thus available. A comparison of calculated and experimental intermolecular isotope effects found for three different decarboxylation reactions is shown below.



Except in Example 2 the calculated values are all slightly higher than the experimental ones, as is to be expected when a model having  $\sum_1^{3n^*-6} G(u_i^\ddagger) \Delta u_i^* = 0$  for the transition state is assumed. Since the agreement between the two sets of values is close, it may be concluded that bond breaking has proceeded to a considerable extent



in the transition state for these particular reactions. It was assumed for the calculations that the bond was completely broken in the transition state.

Aside from such attempts at quantitative calculations of isotope effects, equation (25) is very useful in providing a qualitative idea of the direction and magnitude of intermolecular effects.

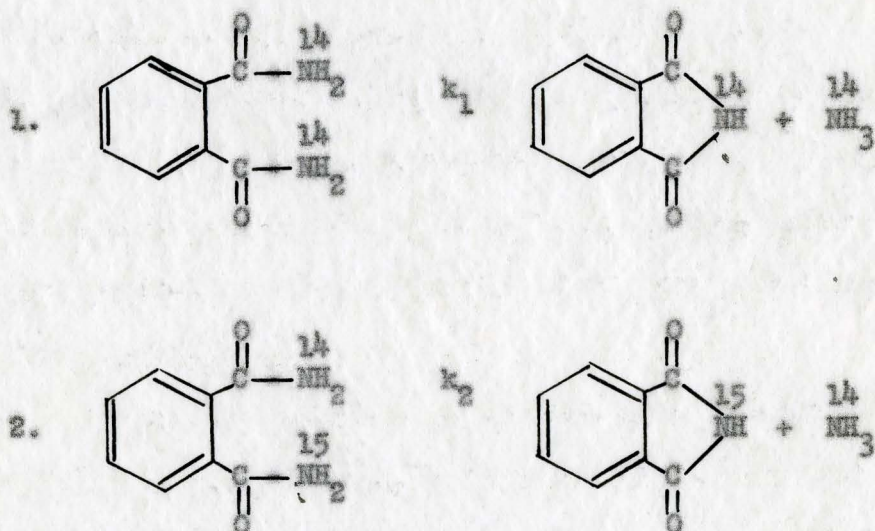
$$\frac{k_1}{k_2} = \frac{s_2^\ddagger}{s_1^\ddagger} \frac{s_1}{s_2} \left( \frac{m_2}{m_1} \right)^{1/2} \times \left[ 1 + \sum_i^{3n-6} G(u_i) \Delta u_i - \sum_i^{3n'-6} G(u_i^\ddagger) \Delta u_i^\ddagger \right] \quad (25)$$

For example, in a consideration of bond rupture reactions the energy term represented by the summation is greater for the reactants than for the activated complex; that is, the atoms are more tightly bound in the reactant molecule than in the transition state. The value of the square bracket term is thus greater than unity. The product of this term and the reduced mass determines the magnitude of the isotope effect, and since the former value is greater than unity, the reduced mass term represents an absolute lower limit for the particular isotope effect, and in all such cases reaction of the lighter isotopic molecule will be favoured. In bond formation reactions the reverse is true, for here the energy term is greater for the activated complex than for the reactants and the value of the square bracket is, therefore, less than one. This will have the effect of diminishing the reduced mass term and the overall isotope effect, and may, in fact, reverse the direction of the effect. Thus, in bond formation reactions the reduced mass term represents an upper



limit for an isotope effect favouring the lighter molecule, while in certain cases reaction of the heavier isotopic species may be favoured.

The condition that must be fulfilled if a reverse isotope effect is to be observed ( $k_1/k_2 < 1$ ), is that  $\sum_i^{3n^*-6} G(u_i^{\ddagger}) \Delta u_i^{\ddagger} > 1/2 \ln (m_2^{\ddagger}/m_1^{\ddagger})$  i.e.,  $f^{\ddagger} > (m_2^{\ddagger}/m_1^{\ddagger})^{1/2}$ . This condition holds only if the reaction is considered simply as a bond formation between two isolated atoms and that  $\sum_i^{3n-6} G(u) \Delta u = 0$ . A number of intermolecular isotope effects have been observed having values less than one, showing that such effects are indeed possible. For example, Stacey, Lindsay and Bourns (44) have investigated both the intra- and intermolecular nitrogen isotope effects in the deamination of phthalimide.

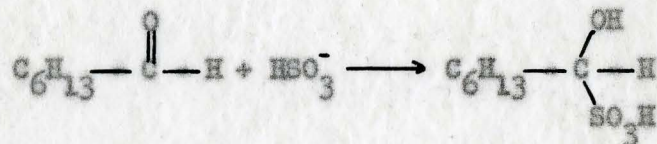


The value of  $k_1/2k_2$  was found to be 0.994 at 180°C. Both reactions involve the breaking of a  $C^{12}-N^{14}$  bond, but reaction 2 results in the formation of a  $C^{12}-N^{15}$  bond as compared with a  $C^{12}-N^{14}$  bond for reaction 1. It must be concluded then, that the activated complex



possessing the configuration wherein a  $C^{12}-N^{14}$  bond is ruptured and a  $C^{12}-N^{15}$  bond is forming has the lowest energy of activation.

A case where an approximate equality exists between the terms  $\sum_i^{3n-6} G(u_i) \Delta u_i^\ddagger$  and  $1/2 \ln (m_2^\ddagger/m_1^\ddagger)$  was found by Sheppard, Bader and Bourns (45) in a study of the relative rates of formation of  $C^{12}-S^{32}$  and  $C^{12}-S^{34}$  bonds in the bisulphite addition reaction of heptanal.



By proper experimental manipulations, the reverse reaction was reduced to a minimum and the isotope effect was obtained with reasonable accuracy by measuring the fractionation after varying short reaction periods and extrapolating to zero time. A value of  $1.000 \pm 0.001$  was found for  $k_L/k_H$ . An approximate calculation employing Bigeleisen's equation, with the factor  $\sum_i^{3n-6} G(u_i) \Delta u_i$  set equal to zero, and assuming that bond formation had proceed to virtual completion in the transition state, gave a result of 1.001 for the ratio  $k_L/k_H$ .

The general introduction to this thesis contains a statement to the effect that the use of isotope effects allows an insight into the properties of the transition state. That this is so is obvious from the above discussions and semi-quantitative calculations. Above all, isotope effects yield the ratio of the reduced masses along the reaction co-ordinate. This latter data is very important in determining which bonds are effectively altered



in the rate determining step.

The use of isotope effects in the elucidation of reaction mechanisms is by now an established practice, the literature containing many pertinent examples. One such example was provided recently by C.G. Swain (46) who began his paper with the following statement, "One of the most powerful and subtle methods for studying reaction mechanisms involves measuring the difference in chemical reactivity between two isotopes of the same element, i.e., the so-called "isotope effect"." The paper describes the effect of light and heavy water on the hydrolysis of alkyl halides and sulfonium salts.

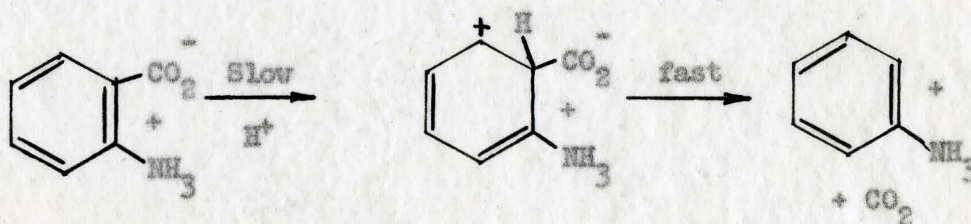
Methyl halides reacted at the same rate in both solvents, while t-butyl chloride hydrolyzed 40% faster in the light water than it did in the heavy water. The discrimination on the part of the latter compound shows that the formation of its activated complex is more heavily dependent upon electrophilic solvation. Since deuterium has a lower zero point energy than protium, light water will be more highly ionized (and more acidic) than heavy water, and the light water-water bonds will be more labile than those for heavy water. The disruption of the carbon-halogen bond and the water-water hydrogen bonds has proceeded much further in the activated complex of t-butyl chloride than in that of methyl chloride.

Identical rates of solvolysis were observed for t-butyl dimethyl sulfonium ion in both the light and heavy water. This result is to be expected, as the rate-determining step of the hydrolysis involves the splitting off of an uncharged dimethyl



sulfide group. This work illustrates a more subtle use of isotope effects. The solvating action of the water molecules is a secondary effect, still, the differing reactivity of the two isotopes provides useful information about the nature of the transition states.

Stevens, Pepper and Lounsbury (47) noted that the aqueous decarboxylation of anthranillic acid proceeded without any isotopic fractionation of the carbon isotopes. This effect can only be interpreted as meaning that the C-C bond rupture cannot be the limiting step in this particular reaction. The authors therefore considered a number of alternate mechanisms which would fit this rather surprising isotopic data, and the one they considered most plausible is pictured below.



This mechanism is consistent with the experimental result, as the decarboxylation step is not rate-determining.

In summary then, the atoms joined by any bond which is altered even slightly in the rate determining step of a reaction will undergo isotopic fractionation, the direction and magnitude of which provide useful information regarding the transition state.



## EXPERIMENTAL

The experimental work of this thesis is presented under the following main headings:

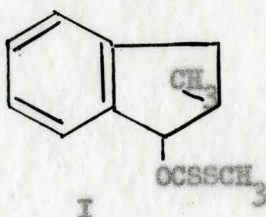
- (a) the synthesis of S-methyl-trans-2-methyl-1-indanyl xanthate,
- (b) the procedure for the quantitative separation of methyl mercaptan and carbonyl sulphide, and for the recovery of the thio-ether sulphur atom, the thion sulphur atom and the xanthate carbon atom in the form of solid compounds,
- (c) the experimental procedure employed in the partial and total decompositions of the xanthate ester,
- (d) the preparation of gaseous samples for mass spectrometer analysis,
- (e) mass spectrometry,
- (f) the calculation of isotope effects from mass spectrometer data.

### The Synthesis of S-Methyl-trans-2-methyl-1-indanyl Xanthate (I)

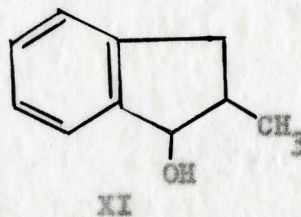
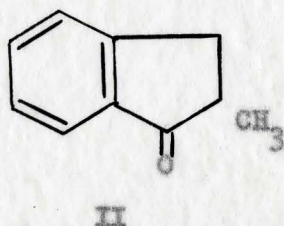
The compound employed in this investigation was S-methyl-trans-2-methyl-1-indanyl xanthate (I), the pyrolytic decomposition of which had been previously investigated by Alexander et al (18). This compound was chosen for the following reasons: it possesses but one hydrogen atom on a beta-carbon, the configuration is such



that cis elimination only can occur, it is a solid readily purified by recrystallization, and its decomposition proceeds with better than eighty percent yield of the gaseous products.



The synthetic work entailed the preparation of the ketone 2-methyl-1-indanone (II), which under proper conditions could be hydrogenated to yield only the trans form of the alcohol, 2-methyl-1-indanol (XI).

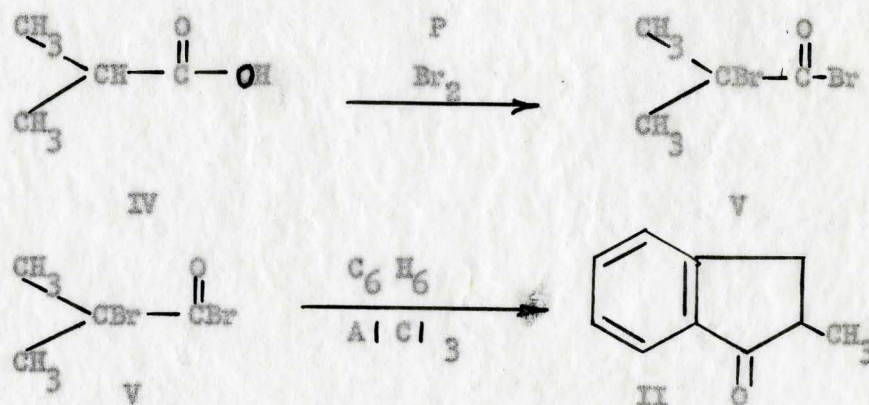


The carbon disulphide employed in the preparation of the xanthate methyl ester of trans-2-methyl-1-indanol contained carbon and sulphur of natural isotopic abundance.  $S^{34}$  is found in natural sulphur to the extent of 4.2 percent and differs from the more abundant isotope,  $S^{32}$ , by two mass units. It is, therefore, admirably suited for isotope effect studies. Measurement of the isotopic fractionation of  $S^{36}$  would necessitate the use of enriched material because of the low natural abundance of this isotope (0.016 percent).  $C^{13}$  occurs naturally to the extent of 0.7 percent and this is sufficient for mass spectrometric analysis.



## The Synthesis of 2-Methyl-1-indanone (II)

Two synthetic routes were employed for the preparation of this compound. The first, using isobutyric acid (IV) as the starting compound, was based on a method developed from existing procedures by Alexander and Madrak (18). It is shown schematically below.

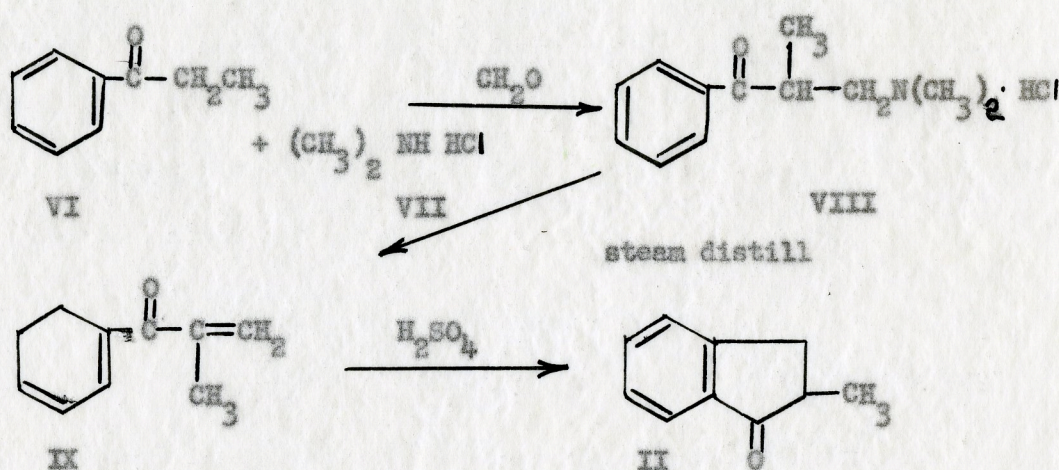


Treatment of isobutyric acid with red, amorphous phosphorous and liquid bromine resulted in the formation of alpha-bromo-isobutyryl-bromide (V). A Friedel Craft's condensation of (V) with benzene yielded the desired ketone (II). The detailed procedure for these steps is to be found in the paper by Alexander and Madrak (18). These directions were followed explicitly but for one modification. In working up the product of the Friedel Craft's condensation between compound (V) and benzene, Alexander omitted the alcoholic wash with potassium hydroxide which had been recommended in the original report on this reaction (48). It was found in the present investigation that the omission of the alkaline wash gave a product contaminated with what were presumably aliphatic bromide compounds. Such contaminants were found to be very detrimental in the subsequent hydro-



generation of the ketone.

The alternative route to 2-methyl-1-indanone, reported by Fuson and Burckhalter (49), employed as a first step a Mannich base reaction between propiophenone (VI) and dimethylamine hydrochloride (VII), giving beta-dimethylamino-alpha-methyl-propiophenone (VIII), which on steam distillation was converted to alpha-methylacrylophenone (IX). This latter compound, when poured into concentrated sulphuric acid, yielded the desired ketone (II).



The procedure reported by Fuson and Burckhalter was followed without modification. Of the two synthetic procedures, the latter method was found to give the purer product and the higher overall yield, namely 50 percent compared to 30 percent from isobutyric acid.

#### Hydrogenation of 2-Methyl-1-indanone (II)

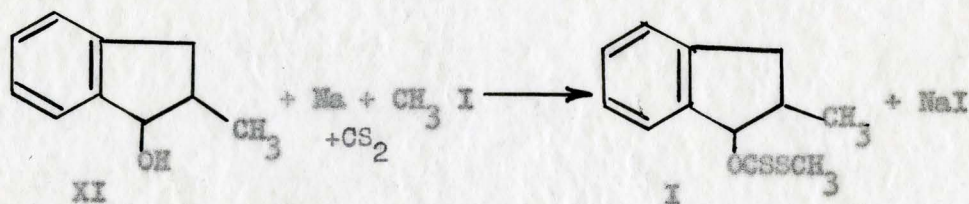
Alexander's work (18) had shown that the hydrogenation of 2-methyl-1-indanone (II) over copper-chromite catalyst was stereospecific, producing only the trans isomer of the alcohol 2-methyl-1-indanol (XI). The catalyst was prepared following the directions



given by Vogel (50). Hydrogenation of the ketone using the conditions reported by Alexander gave the trans alcohol (XI) in 44 to 63 percent yield.

Preparation of S-Methyl-trans-2-methyl-1-indanyl Xanthate (I)

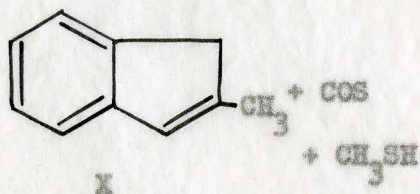
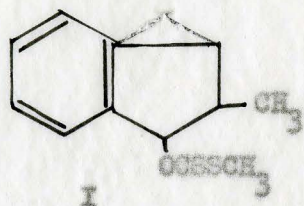
The procedure reported by Alexander was employed for the preparation of the xanthate methyl ester of 2-methyl-1-indanol (I). The synthesis involved the preparation of the sodium salt of 2-methyl-1-indanol and treatment of this product first with carbon disulphide and then with methyl iodide. Recrystallization of the crude xanthate from redistilled petroleum ether, b.p. 30 - 40°C, gave, in 48 percent yield, a white crystalline product with a m.p. of 60.0 to 60.2°C (corrected).



The Quantitative Separation of Carbonyl Sulphide and Methyl Mercaptan

Since it was necessary to measure the isotopic fractionation of the thion and thio-ether sulphur atoms and also of the xanthate carbon atom, it was necessary to develop a method for their quantitative separation and recovery. The products of the Tschugaeff reaction are an alkene, carbonyl sulphide, and a mercaptan. In this particular investigation, where S-methyl-trans-2-methyl-1-indanyl xanthate (I) was employed, the products were 2-methyl-1-indene (X), methyl mercaptan and carbonyl sulphide.





2-Methyl-1-indene is a high boiling compound and would under normal circumstances remain in the reaction flask.

The other two products, carbonyl sulphide and methyl mercaptan, are both gases at room temperature and may be rapidly removed from the reaction flask by using a stream of some inert gas. The three atoms whose isotopic fractionation is to be determined are contained in these gaseous products, the thio-ether sulphur atom in the methyl mercaptan and the thion sulphur and xanthate carbon atoms in the carbonyl sulphide. The quantitative separation of the two gaseous products was crucial, as no cross contamination of sulphur could be permitted.

After attempting several methods of separation, the one which ultimately proved successful was based on the fact that carbonyl sulphide is reportedly (51) unaffected by cold, fuming nitric acid, whereas methyl mercaptan is very rapidly oxidized to non-volatile methane sulfonic acid. After first establishing the quantitiveness of the capture of methyl mercaptan and the passage of carbonyl sulphide using pure samples of each compound taken separately, the ability of fuming nitric acid to effect a separation of synthetic mixtures of the two compounds was thoroughly investigated. In conjunction with this, procedures were developed for the conversion of



the two sulphur atoms and the xanthate carbon atom into solid compounds which, in the first instance, establish the effectiveness of the separation, and secondly, would be suitable for conversion into gaseous compounds for mass spectrometer analysis.

The methane sulfonic acid resulting from the action of the nitric acid on the mercaptan, was oxidized by the Carius technique to sulphate ion, and precipitated as barium sulphate. The carbonyl sulphide was collected in a liquid air trap in the presence of lead hydroxide and excess base. Subsequent warming of the trap converted the carbonyl sulphide into lead sulphide and lead carbonate. The latter was decomposed by the addition of acetic acid and the evolved carbon dioxide precipitated as barium carbonate. The thio-ether and thion sulphur atoms of the xanthate ester were thus recovered as barium sulphate and lead sulphide, respectively, while the barium carbonate contained the xanthate carbon.

Details of the preparation of methyl mercaptan and carbonyl sulphide, together with a description of the method of the separation procedure, and of the preparation of the solid samples are given in the following sections.

#### Preparation of the Methyl Mercaptan Samples

The methyl mercaptan was prepared from S-methyl thiouronium sulphate by allowing it to react with dilute sulphuric acid as described by Arndt (52). The product was purified by distillation in vacuo at the temperature of dry-ice. The product was condensed and stored in a receiver (labeled A in Diagram I) immersed in a



liquid air bath. When a sample of material was required, a weighed sample tube,  $T_1$ , was affixed to the line and the whole system was evacuated. The sample tube was then immersed in a liquid air bath and tube A in a dry-ice acetone slurry, and about one millimole of the mercaptan permitted to distill into  $T_1$ . Stopcock  $S_2$  was closed and the sample tube removed from the line and reweighed.

#### Preparation of Carbonyl Sulphide Samples

Carbonyl sulphide was prepared by the action of dilute sulphuric acid on ammonium thiocyanate (53). The train employed for the purification of the gas is illustrated in Diagram II. Flask A was cooled with a stream of water and charged with 400 cc of water and 290 cc of concentrated sulphuric acid. The whole of the apparatus was flushed for one hour with purified nitrogen gas before the generation of carbonyl sulphide was initiated by the addition of 50 cc of a saturated solution of ammonium thiocyanate. Trap B contained a fifteen percent solution of aniline in alcohol which served to remove the carbon disulphide formed as a by-product. Trap C contained a thirty-three percent solution of potassium hydroxide to remove the carbon dioxide. The carbonyl sulphide was finally dried by passing it through tube D, trap E and tube F containing calcium chloride, concentrated sulphuric acid and phosphorous pentoxide respectively, and was then condensed in a large narrow U-tube, G.

Tube G was attached to a vacuum line as shown in Diagram I, and evacuated while surrounded with a liquid air bath. A dry-ice acetone bath was then placed around trap G and stopcock  $S_1$  turned



several times to insure complete removal of carbon dioxide from the sample of gas. A small amount of carbonyl sulphide was also lost along with the carbon dioxide. A millimole sample of the gas was then transferred to a weighed sample tube,  $T_2$ , immersed in liquid air, by distillation from a dry-ice acetone bath. The tube was then removed from the line and reweighed.

#### Experimental Procedure Employed in the Separation

The apparatus employed in evaluating the method of separation, using synthetic mixtures of carbonyl sulphide and methyl mercaptan, is shown in Diagram III. The two sample tubes,  $T_1$  and  $T_2$ , containing the methyl mercaptan and carbonyl sulphide respectively, were arranged in series as shown. Trap A contained 2.5 ml. of fuming nitric acid and was immersed in an ice-water bath. Trap B was charged with 10 ml. of 1:5 carbonate free sodium hydroxide solution and 6 ml. of saturated lead acetate solution, also carbonate free. It was immersed in a liquid air bath. The air which entered trap B due to the cooling effect of the liquid air, passed through a soda-lime tube to prevent carbonate contamination.

A liquid air bath was placed around  $T_2$  and a dry-ice acetone slurry around  $T_1$ . Purified nitrogen gas was slowly admitted into  $T_2$  and then into  $T_1$ . The second stopcock on tube  $T_1$  was then slowly opened allowing the nitrogen gas to stream through the remainder of the apparatus. The liquid air bath was slowly lowered from around  $T_2$  and the carbonyl sulphide was flushed into trap B. The dry-ice acetone slurry was removed from the second sample tube one-half hour later.



When the apparatus had been flushed with nitrogen gas for a total time of two hours, stopcock  $S_1$  was turned so that trap B was sealed, at the same time allowing the nitrogen gas to exit through the other outlet of the stopcock.  $S_2$  was then closed and the trap removed from the line. While still well immersed in liquid air, the trap was connected to a water aspirator and evacuated. This served to prevent the build-up of excess pressures when the trap was removed from the cooling bath. After standing at room temperature for twenty-four hours, during which time the contents assumed a greyish colour due to the formation of lead sulphide and lead carbonate, air was readmitted through a soda-lime tube.

#### The Conversion of the Methane Sulfonic Acid to Barium Sulphate

The methyl mercaptan swept into trap A was immediately oxidized to methane sulfonic acid which is soluble in fuming nitric acid. To further oxidize the sulphur to sulphate ion the tube containing the nitric acid solution and the bubbler were removed from the bulb of trap A, both pieces wiped free from grease and placed in a large size carrius combustion tube together with another 0.6 ml. of fuming nitric acid. The combustion tube was carefully sealed and placed in a furnace maintained at 260 to 270°C for a period of twenty-four hours. This treatment oxidized all of the methanesulfonic acid to sulphate ion, carbon dioxide and water. After removal from the furnace, the tube was broken open and the liquid contents washed into a beaker. To this solution was added a



slightly more than equivalent amount of sodium chloride (that is, equivalent to the sulphate ion formed in the oxidation of the methyl mercaptan), and six ml. of concentrated hydrochloric acid. The resulting solution was evaporated to dryness on a steam plate. Three such evaporations were carried out, each with fresh additions of hydrochloric acid, to remove the nitrate ion from solution. The sulphate ion was precipitated as barium sulphate according to the procedure outlined by Kolthoff and Sandell (54). The precipitate was collected in a fritted glass crucible, and dried at 120°C for one hour. No methyl mercaptan was ever detected beyond trap A.

#### Isolation of Lead Sulphide and the Collection of Barium Carbonate

After the twenty-four hour hydrolysis period, trap B was connected to the apparatus employed for the collection of the carbon dioxide as shown in Diagram IV. Bulb D was filled with approximately thirty ml. of 1:4 acetic acid. The test tube part of trap C, containing three ml. of carbonate free base and twenty ml. of water, was not attached until the apparatus had been flushed for one hour with purified nitrogen gas.

When nitrogen gas was bubbling quite vigorously from the fritted tip of trap C, stopcock S<sub>5</sub> was opened allowing the dilute acetic acid to flow into the bulb of trap B. The contents of trap B were brought to a rapid boil and so maintained for one-half hour, following which the apparatus was flushed with nitrogen gas for another one-half hour. The bottom half of trap C was then rapidly removed from the line and its contents, together with the wash water



used to rinse the bubbler, were transferred to a flask. Two to three ml. of normal, carbonate free ammonium chloride solution was then added to the flask, followed by a slightly more than equivalent amount of carbonate free barium chloride solution. Air was removed from the flask using a water aspirator, the contents swirled, and then allowed to stand for fifteen minutes. Air was readmitted through a soda-lime tube and the precipitated barium carbonate collected on a fritted glass crucible, washed three times with hot, carbonate free water, dried at 120°C for one hour and then weighed. The procedure outlined above for the collection of the carbon dioxide is similar to that described by Calvin, Yankawich and Ried (55).

The precipitate of lead sulphide which remained in the bulb of trap B was collected on a sintered glass crucible, washed with hot water, dried for one hour at 100°C, and weighed. In the initial runs, employing only carbonyl sulphide, no sulphur in any form was ever detected in the fuming nitric acid of trap A.

In Table I are listed the percent recoveries of the three solid compounds that were obtained using the method of separation outlined above. The first six sets of results refer to the initial experiments which were performed using separate samples of methyl mercaptan and carbonyl sulphide. The remaining four rows of figures list the results obtained by applying the method to mixtures of the two gaseous compounds.



TABLE I

THE PERCENT RECOVERY OF PbS, BaCO<sub>3</sub> AND BaSO<sub>4</sub> FROM CH<sub>3</sub>SH AND COS

Number of milli- moles of COS	Number of milli- moles of CH <sub>3</sub> SH	% Recovery		
		PbS	BaCO <sub>3</sub>	BaSO <sub>4</sub>
	3.05			96.4
	1.64			103
	1.29			103
0.560		99.3		
0.710		99.0		
1.04		98.5		
1.72	1.26	101	102	98.0
1.47	1.54	96.7	101	103
0.780	1.00	98.0	113(a)	96.3
1.16	1.91	96.0	100	--(b)

(a) A leak developed in the apparatus used to collect the carbon dioxide.

(b) The combustion tube exploded while in the furnace.

#### The Thermal Decomposition of S-Methyl-trans-2-methyl-1-indanyl

##### Xanthate

The difference in the isotopic ratios of the reactant and product molecules is a function of the extent of reaction, the difference being a maximum initially and decreasing to zero after the reaction has proceeded to completion. The intermolecular isotope effect is therefore determined by intercomparison of the isotopic ratio in one of the products obtained after a few percent reaction (ideally zero percent reaction) with that of the reactant. To obtain the isotopic ratios of the reactant, a sample of the xanthate ester was completely decomposed. The isotopic ratios found in the products of such a complete decomposition would correspond to those



existing in the original xanthate ester. These ratios, together with the ones obtained from a partial decomposition of the xanthate ester, provide the necessary data for the calculation of the isotope effects occurring in the Tschugaeff reaction (see page 77)

#### Total Decompositions

The total decompositions were carried out in the manner described below, employing the apparatus shown in Diagram V. (Traps A and B in this diagram are the same traps similarly labeled in diagram III). On the day before the experiment was performed, the xanthate ester was repeatedly recrystallized until it exhibited a constant melting point. The material was stored overnight in a vacuum dessicator containing phosphorous pentoxide. A small portion of the xanthate ester, in the neighbourhood of one millimole, was accurately weighed and placed in the decomposition tube D. Before the traps A and B, charged as previously described, were attached to the line, tubes D and C were flushed for one hour with purified nitrogen gas. A dry-ice acetone bath was placed around trap C, an ice-water bath around trap A, and a liquid air bath around trap B. An oil bath, heated to a temperature of  $103^{\circ}\text{C}$ , was placed around tube D at such a height that the liquid level of the bath was slightly higher than that of the solid inside the tube D. The temperature of the bath was maintained at  $100\pm 2^{\circ}\text{C}$  by means of a small bunsen burner. Absolute temperature control was of no critical importance in the total decompositions. This action resulted in the rapid melting of the xanthate ester and in the



evolution of gaseous products. The methyl mercaptan condensed in the U-tube C, where it was visible as a clear colourless liquid. At no time did any of the 2-methyl-1-indene distill into tube C. One-half hour after the initial application of heat, the dry-ice acetone bath was slowly lowered from around trap C, and when a total of one and one-half hours had elapsed, the heating was discontinued. The nitrogen sweep was continued for one-half hour more, after which time traps A and B were removed from the line and their contents treated as previously described.

The work of Alexander and Mudrak (18) had indicated that the pyrolysis of S-methyl-trans-2-methyl-1-indanyl xanthate produced approximately eighty percent of the theoretical amount of gaseous products, a figure arrived at by measuring the volume of the evolved carbonyl sulphide and methyl mercaptan. Trial runs using the procedure outlined above gave results slightly higher than those reported by Alexander and Mudrak. Table II lists the results of three such runs. The percent yield of the methyl mercaptan is expressed in terms of the recovered barium sulphate and the carbonyl sulphide is similarly expressed in terms of the recovered lead sulphide and barium carbonate.

TABLE II

% YIELDS OF METHYL MERCAPTAN AND CARBONYL SULPHIDE OBTAINED FROM THERMAL DECOMPOSITIONS OF S-METHYL-trans-2-METHYL-1-INDANYL XANTHATE

Number of milli- moles of xanthate ester	% yield of PbS	% yield of BaCO <sub>3</sub>	% yield of BaSO <sub>4</sub>
1.01	85.6	91.4	83.5
1.15	85.5	89.4	91.6
0.974	86.2	88.5	92.4



## Partial Decompositions

Since the partial decompositions required only short heating periods, varying from two to three minutes, there was a possibility that some of the carbonyl sulphide and methyl mercaptan would remain dissolved in the unchanged reactant and the 2-methyl-1-indene. To circumvent this difficulty the partial decompositions were performed in an evacuated system, and the products collected in a liquid air trap, thus insuring the complete and rapid removal of the gaseous products from the melt. The total and partial decompositions were carried out on the same day.

The apparatus employed for the partial decompositions is shown in Diagram VI. A weighed amount of the xanthate ester, of the order of twenty millimoles, was placed in the bulb of flask E which was attached to a U-tube F, provided with two stopcocks. The other arm of the U-tube was connected to a high vacuum system. Stopcocks  $S_5$  and  $S_6$  were both opened and the system was evacuated to a pressure of  $10^{-5}$  mm of mercury or less. Tube F was then immersed in a liquid air bath, stopcock  $S_6$  was closed and an oil bath at  $70^\circ\text{C}$  was raised to cover the bulb of tube E.<sup>(a)</sup> The solid in tube E melted rapidly and the temperature was then raised to the desired value of  $80 \pm 1^\circ\text{C}$ . The reaction was allowed to proceed to only a small extent, usually 3 or 4% of completion. The time

---

(a) By first melting the xanthate ester at a temperature lower than that actually employed for the decompositions, it was possible to obtain a homogeneous reaction at the higher temperature while incurring only a minor amount of decomposition during the melting process.



necessary to attain this extent of reaction was of the order of two to three minutes. The contents of the bulb were allowed to cool after the removal of the oil bath. Stopcock  $S_5$  was then closed, the tube F detached from E and the vacuum line, and, while still immersed in liquid air, connected to traps A and B. (Tube F has thus replaced D and C in Diagram IV). With stopcocks  $S_5$  and  $S_6$  closed, a dry-ice acetone slurry was substituted for the liquid air bath. Stopcock  $S_5$  was then slowly opened to admit a stream of purified nitrogen gas. When the pressure within the tube had reached atmospheric, stopcock  $S_6$  was opened and the nitrogen gas allowed to flow through the remainder of the apparatus. Tube F was left immersed in the dry-ice acetone bath for one-half hour, after which time the slurry was removed and the nitrogen flush continued for another one and one-half hours. The line was then dismantled and the contents of traps A and B were treated as previously described.

#### The Preparation of Mass Spectrometer Samples

In the final stages of the procedure the three solid products, barium sulphate formed from the methyl mercaptan, and the lead sulphide and barium carbonate from the carbonyl sulphide, were converted to gaseous products suitable for mass spectrometer analysis. The lead sulphide was burned in a stream of oxygen gas to sulphur dioxide. The barium sulphate was converted to silver sulphide and this too burned in a stream of oxygen gas to sulphur dioxide. The barium carbonate was converted to carbon dioxide by



treatment with acid.

### The Preparation of Sulphur Dioxide from Lead Sulphide

Thode and his group have demonstrated that a heavy metal sulphide may be conveniently converted into sulphur dioxide by burning it in a stream of purified oxygen gas. The sulphur dioxide thus formed is purified and collected by means of the high vacuum system illustrated in Diagram VII. The essential features and operation of this line are as follows. A small stainless steel boat with an attached stainless steel wire containing approximately 50 mgm of the heavy metal sulphide was carefully pushed to the mid-point of the quartz tube Q. The remaining portion of the line had been previously evacuated to a pressure of  $10^{-6}$  mm. of mercury, as determined by the McLeod gauge.

The three-way stopcock,  $S_1$ , was turned so that the mercury diffusion pump was by-passed. Stopcock  $S_2$  was slowly opened thus evacuating the quartz tube Q. After the initial surge of air accompanying this operation had been eliminated by the mechanical pump M, stopcock  $S_1$  was turned to reintroduce the mercury diffusion pump H. The entire line was then evacuated until the McLeod gauge registered a pressure of less than  $10^{-5}$  mm of mercury, this operation requiring approximately ten minutes. As the line was pumped down, the entire system was thoroughly flamed with a hand torch.

When a high vacuum was again attained, stopcock  $S_2$  was closed and stopcock  $S_3$  was opened to arm a, thus connecting the tube Q with the two U-traps. Stopcocks  $S_4$  and  $S_5$  were closed to



the trap  $U_2$ . Stopcock  $S_2$  was then slowly opened to arm b, and purified oxygen gas <sup>(a)</sup> passed into the quartz tube and traps. When the pressure within this section of the apparatus had reached atmospheric, as indicated by manometer K, stopcock  $S_5$  was opened and the oxygen allowed to sweep through the tube and traps. The U-tubes were then immersed in liquid air baths and the full flame of a hand torch, burning gas only, was played on the central portion of the quartz tube Q. The sulphide sample glowed and the resulting sulphur dioxide was swept along with the stream of oxygen into the U-traps where it condensed. The tube Q was swept for three to four minutes after the sample ceased to flow. Stopcocks  $S_5$  and  $S_2$  were then closed and  $S_1$  turned so as to by-pass the mercury diffusion pump H. Stopcock  $S_4$  was opened very slowly to the U-traps and the system again evacuated. In this way all gases present in the combustion tube were passed through the cold U-traps thus insuring complete condensation of the sulphur dioxide. Stopcock  $S_1$  was then turned to readmit the mercury diffusion pump and the line was evacuated to a pressure of less than  $10^{-5}$  mm of mercury. Stopcocks  $S_4$  and  $S_3$  were turned to isolate the U-traps and the surrounding liquid air baths were removed. This operation freed the oxygen gas previously entrapped in the solid sulphur dioxide. The liquid air traps were then replaced around the U-tubes, and

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(a) The oxygen gas was purified by passage through three traps arranged in the following order: a fused glass bubbler immersed in concentrated sulphuric acid, a trap containing activated charcoal immersed in a dry-ice acetone slurry, and a large U-tube suspended in a dewar of liquid air.



after the sulphur dioxide had again solidified, stopcock  $S_4$  was opened, connecting the U-tubes with the manifold. This second condensation under a much reduced partial pressure of oxygen would entrap but a negligible amount of the gas in the sulphur dioxide. Stopcock  $S_4$  was then closed to the U-traps and the liquid air bath around  $U_2$  was replaced with a dewar containing a dry-ice acetone slurry. Stopcock  $S_4$  was turned so as to connect the U-traps with the sample line F. A liquid air bath was placed around the sample tube and the liquid air bath removed from around  $U_1$ . The sulphur dioxide rapidly distilled through  $U_2$  and condensed in the sample tube. The dry-ice acetone slurry around  $U_2$  served to retain any water vapour present in the U-traps. Even though the vapour pressure of sulphur dioxide is only a few mm. of mercury at the temperature of dry-ice, its distillation under these conditions was rapid and complete. To ensure complete transfer of the sulphur dioxide,  $U_2$  was allowed to attain room temperature with  $S_4$  closed, and then cooled again with a dry-ice acetone bath and stopcock  $S_4$  opened. No further condensation of gas was ever noted. When the sulphur dioxide had condensed in the sample tube, stopcock  $S_4$  was turned to connect the sample line with the manifold, and the sample tube was sealed from the line.

#### Reduction of the Barium Sulphate and Its Conversion to Sulphur Dioxide

The barium sulphate obtained from the oxidation of the methyl mercaptan was reduced to hydrogen sulphide and precipitated



as cadmium sulphide. The latter compound was converted into silver sulphide and this compound was burned to sulphur dioxide using the procedure described above. The reducing solution was prepared by adding 500 grams of hydriodic acid (50%) to a solution of 480 ml. of concentrated hydrochloric acid and 144 ml. of hypophosphorous acid. Boiling the solution for three-quarters of an hour served to remove any sulphur impurities from the reagents. The apparatus for the reduction is shown in Diagram VIII.

Approximately 150 mgm of barium sulphate was placed in flask A together with 125 ml. of the reducing solution. Trap B was filled with distilled water and trap C with 100 ml. of a solution prepared by adding 500 ml. of glacial acetic acid to a solution of 62.5 gm. of cadmium acetate dissolved in two liters of distilled water.

A stream of nitrogen gas was passed through the apparatus at a moderate rate. The contents of flask A were brought to a gentle boil by heating with the flame of a bunsen burner. The flame was of such a height that one-half hour elapsed before the onset of boiling. The contents of flask A were refluxed gently for a period of one-half hour, and then boiled vigorously for a similar period of time. The barium sulphate dissolved in the reducing solution and the evolved hydrogen sulphide was swept through the system to trap C where it was precipitated as cadmium sulphide.

At the end of the heating period, trap C and its bubbler were detached from the line and the cadmium sulphide was converted to silver sulphide by the addition of 25 ml. of 0.2 N silver nitrate



solution. The silver sulphide was filtered into a fritted glass crucible, washed with a small amount of dilute ammonium hydroxide solution to remove silver ions, and then with distilled water. The precipitate was dried for one hour at 110°C and a small sample of the precipitate converted to sulphur dioxide by burning it in a stream of oxygen as described above.

The quantitative nature of the above procedure was determined by converting a weighed amount of barium sulphate to cadmium sulphide. An excess of standard silver nitrate solution was added to the precipitate of cadmium sulphide, the excess silver nitrate solution removed by filtration, and then titrated with a standard solution of potassium thiocyanate. The amount of silver precipitated as silver sulphide could then be calculated, and the results indicated that the reduction of the barium sulphate had resulted in the collection of 98.4% of the theoretical amount of hydrogen sulphide.

#### Conversion of Barium Carbonate to Carbon Dioxide

The barium carbonate was converted to carbon dioxide using the high vacuum system shown in Diagram IX.

Approximately 60 mgm of barium carbonate was placed in bulb A and 10 ml. of concentrated sulphuric acid in bulb B. (a) The entire system was then evacuated to a pressure of less than  $10^{-5}$  mm of mercury. To ensure the complete removal of air from the sulphuric

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(a) The sulphuric acid had been previously heated to 160°C for one hour and stored in a desiccator over potassium hydroxide.



acid, it was frozen, by immersing B in a liquid air bath, and then thawed, this procedure being repeated three times in all. With a liquid air bath around trap C and stopcock  $S_2$  closed, flask B was very slowly inverted so as to permit the acid to flow into A. The evolved carbon dioxide condensed in trap C. Flask A was rotated from side to side to bring the acid in contact with all of the barium carbonate. A water bath, heated to  $60^\circ\text{C}$ , was then placed around A in order to insure the complete removal of the carbon dioxide gas from the acid solution. When the evolution of gas had ceased, stopcock  $S_1$  was closed and  $S_2$  was opened to the manifold for one-half minute permitting the removal of non-condensed gases. Stopcock  $S_2$  was closed and a dry-ice acetone slurry was substituted for the liquid air bath. Stopcocks  $S_3$  and  $S_4$  were then closed and stopcock  $S_6$  turned so as to connect the two U-traps with the sample line, and at the same time exclude the manifold. A liquid air bath was placed around the sample tube G. Stopcock  $S_2$  was then opened permitting the carbon dioxide to flow through a magnesium perchlorate drying tube D, and to condense in G. One minute was allowed for this distillation, after which time stopcock  $S_2$  was closed. To ensure complete transfer of the carbon dioxide to the sample tube, the U-tube C was permitted to come to room temperature then cooled again with a dry-ice acetone bath and stopcock  $S_2$  opened. One-half minute following this operation the sample tube was removed from the line.

A weighed sample of barium carbonate was decomposed employing the procedure described above, and the evolved carbon di-



oxide collected was in a weighed sample tube attached to the line. The amount of carbon dioxide collected was determined by reweighing the sample tube and was found to be 98.6% of the theoretical amount based on the original weight of the barium carbonate.

#### Mass Spectrometry

The relative abundances of the sulphur and carbon isotopes were measured using a 180 degree, directional focusing mass spectrometer of the Nier type equipped with an automatic recorder.

In the case of sulphur dioxide, the ion currents measured were due to the  $\text{SO}_2$  species. The  $\text{S}^{32}/\text{S}^{34}$  ratio may be calculated directly from the mass spectrometer ratio of 64 to 66, by making use of the corrections and data previously supplied by Thode (56). The corrections apply to the contribution made to the 66 peak by the species  $\text{S}^{32}\text{O}^{16}\text{O}^{18}$ . The contributions made by any molecule containing two or more heavy isotopes were neglected due to their exceedingly low frequency of occurrence.

The mass spectrometer mass ratio may be equated as follows,

$$\frac{64}{66} = \frac{\text{S}^{32}\text{O}^{16}\text{O}^{16}}{\text{S}^{34}\text{O}^{16}\text{O}^{16} + \text{S}^{32}\text{O}^{16}\text{O}^{18}}$$

Now the probability of occurrence of  $\text{S}^{34}\text{O}^{16}\text{O}^{16}$  as compared with that of  $\text{S}^{32}\text{O}^{16}\text{O}^{16}$  is given simply by the  $\text{S}^{34}/\text{S}^{32}$  ratio. However, since there are two molecules of oxygen in a molecule of sulphur dioxide, the probability of occurrence of the species  $\text{S}^{32}\text{O}^{16}\text{O}^{18}$  is twice the  $\text{O}^{18}/\text{O}^{16}$  ratio. Therefore, with the occurrence of all the species taken as relative to that of  $\text{S}^{32}\text{O}^{16}\text{O}^{16}$ , the 64/66 ratio may be re-expressed as follows,



$$\frac{64}{66} = \frac{1}{\frac{S^{34}}{S^{32}} + 2\frac{O^{18}}{O^{16}}}$$

Or,

$$\frac{S^{32}}{S^{34}} = \frac{1}{66/64 - 2\frac{O^{18}}{O^{16}}}$$

The  $O^{18}/O^{16}$  ratio has been previously determined by Thode (56) for tank oxygen and is 0.00208. The  $S^{32}/S^{34}$  ratios reported in this thesis are based on the same scale as that employed in all of Thode's papers. The value of the 64/66 mass ratio for the standard on this scale is 20.36 ( $S^{32}/S^{34} = 22.24$ ).

The procedure employed was to analyze the standard sample, the unknown, and then the standard again, all in the shortest possible time. When the  $S^{32}/S^{34}$  ratios determined for the standard sample differed by no more than 0.1%, the  $S^{32}/S^{34}$  ratio of the unknown was considered acceptable. Each 64/66 mass ratio was determined by averaging the values obtained for at least seven double spectrograms. All of the mass spectrometer ratios reported in this thesis have a precision of 0.1% or better.

The  $C^{12}/C^{13}$  ratios were determined by measuring the ion currents due to the  $CO_2$  species. The isotopic ratio may be calculated from the mass spectrometer mass ratio of 44/45, after applying a suitable correction for the contribution to the 45 peak by the species  $C^{12}O^{16}O^{17}$ . Thus, analogous to the expression for the 64/66 ratio, the 44/45 mass ratio may be equated as follows,

$$\frac{44}{45} = \frac{C^{12}O^{16}O^{16}}{C^{13}O^{16}O^{16} + C^{12}O^{16}O^{18}} = \frac{1}{\frac{C^{13}}{C^{12}} + 2\frac{O^{17}}{O^{16}}}$$



Therefore,

$$\frac{C^{12}}{C^{13}} = \frac{1}{\frac{45}{44} - 2 \frac{O^{17}}{O^{16}}}$$

The  $O^{17}/O^{16}$  ratio has also been determined by Thode (56) for tank oxygen and was found to be 0.00039. The same procedure was used to determine the  $C^{12}/C^{13}$  ratios as was used for the  $S^{32}/S^{34}$  ratios. The  $C^{12}/C^{13}$  ratios reported in this thesis are all relative to the value 93.37 assumed for the sample TD-9. This corresponds to a 44/45 ratio of 87.00 using the above value for the  $O^{17}/O^{16}$  ratio.

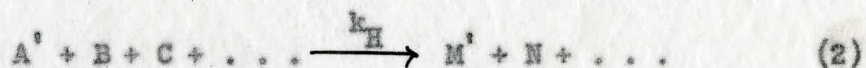
#### Calculation of Isotope Effects in Unidirectional Reactions

The isotope effect in a unidirectional reaction may be calculated from the following experimental data:

1. The isotopic ratio of the reactants.
2. The isotopic ratio of the products.
3. The percent reaction undergone by the reactants.

An equation employing this data has been derived by Stevens (57) in the manner illustrated below.

Consider any general unidirectional reaction,



where A represents the light and A' the heavy isotope. Let a, a', b, c, etc. be the initial concentrations of the reactants and x and x' be the amounts that have reacted in time t. Therefore, after the elapse of a period of time t, the concentrations of the various reacting species are (a-x), (a'-x'), (b-y), (c-z) etc.



The rates of the two isotopic reactions may then be expressed in terms of the above concentrations as

$$\frac{dx'}{dt} = k_L(a-x)(b-y)(c-z) \quad (3)$$

$$\frac{dx}{dt} = k_H(a'-x')(b-y)(c-z) \quad (4)$$

Therefore,

$$\frac{dx}{dt} / \frac{dx'}{dt} = \frac{k_L(a-x)(b-y)(c-z)}{k_H(a'-x')(b-y)(c-z)} \quad (5)$$

$$\text{or} \quad \frac{dx}{dt} / \frac{dx'}{dt} = \frac{k_L(a-x)}{k_H(a'-x')} \quad (6)$$

which upon integration yields,

$$\frac{k_L}{k_H} = \frac{\ln \frac{a}{a-x}}{\ln \frac{a'}{a'-x'}} \quad (7)$$

Equation (7) is true no matter what the overall order of the reaction may be, as long as it is of the first order with respect to A.

Now let  $a'/a$  equal  $s$ ,  $x'/x$  equal  $s'$  and  $a/s$  equal  $r$ . Then  $a'$  equals  $sa$  and  $x'$  equals  $s'x$  which equals  $rsx$ . If the reaction proceeds until  $x/a$  equals  $f$ , and if  $af$  is substituted for  $x$ ,  $sraf$  for  $x'$ , and  $sa$  for  $a'$ , equation (7) becomes

$$\frac{k_L}{k_H} = \frac{\ln \frac{a}{(a-af)}}{\ln \frac{sa}{(sa-sarf)}} = \frac{\ln \frac{1}{1-f}}{\ln \frac{1}{1-rf}} \quad (8)$$

$$\text{or} \quad \frac{k_L}{k_H} = \frac{\ln(1-f)}{\ln(1-rf)} \quad (9)$$

The  $S^{32}/S^{34}$  and  $C^{12}/C^{13}$  ratios obtained from mass spectrometer



measurements correspond to the quantities  $x/x'$  and  $a/a'$ . The  $r$  in equation (9) may therefore, be equated as follows in terms of the mass spectrometer ratios,

$$r = s'/s = \frac{x'}{x} / \frac{a'}{a} = \left( \frac{s_{32}}{s_{34}} \right)_{\text{react}} / \left( \frac{s_{32}}{s_{34}} \right)_{\text{products}}$$

While the factor  $f$  may be expressed in terms of the percent reaction as

$$f = \frac{x}{a} = \frac{\% \text{ reaction}}{100}$$

An example of such a calculation is given below for run number I, sulphide.

The available information is

$$\frac{a}{a'} = 22.20$$

$$\frac{x}{x'} = 22.38$$

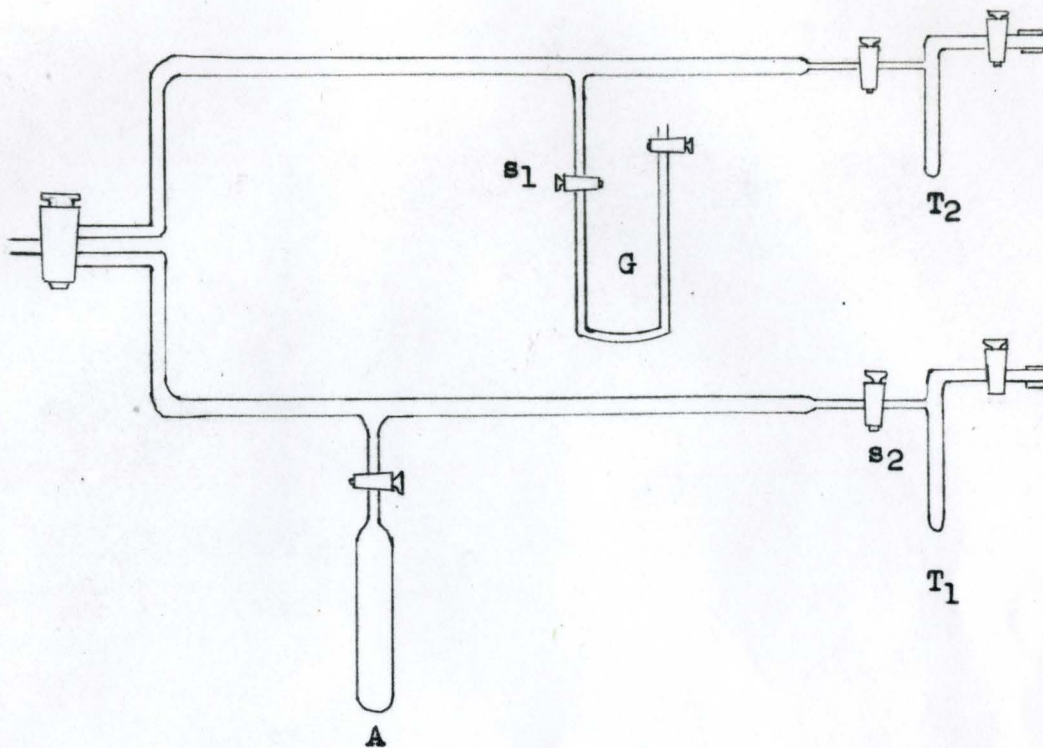
$$= 0.04$$

$$\frac{k_{32}}{k_{34}} = \frac{\ln(1 - 0.04)}{\ln(1 - \frac{22.20}{22.38} \times 0.04)}$$

$$\frac{k_{32}}{k_{34}} = 1.008$$

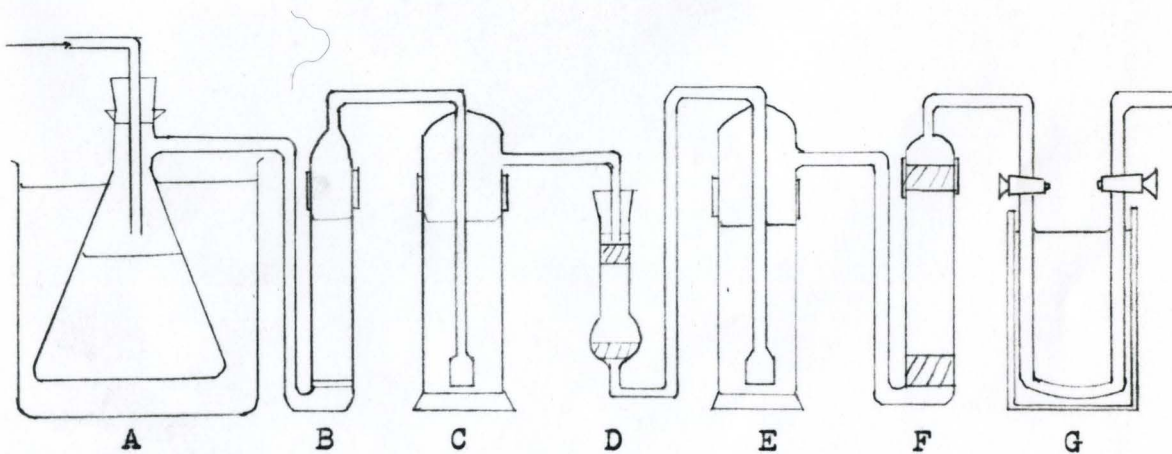


DIAGRAM I



Sampling Line for  $\text{CH}_3\text{SH}$  and  $\text{COS}$

DIAGRAM II



Preparation of  $\text{COS}$



DIAGRAM III

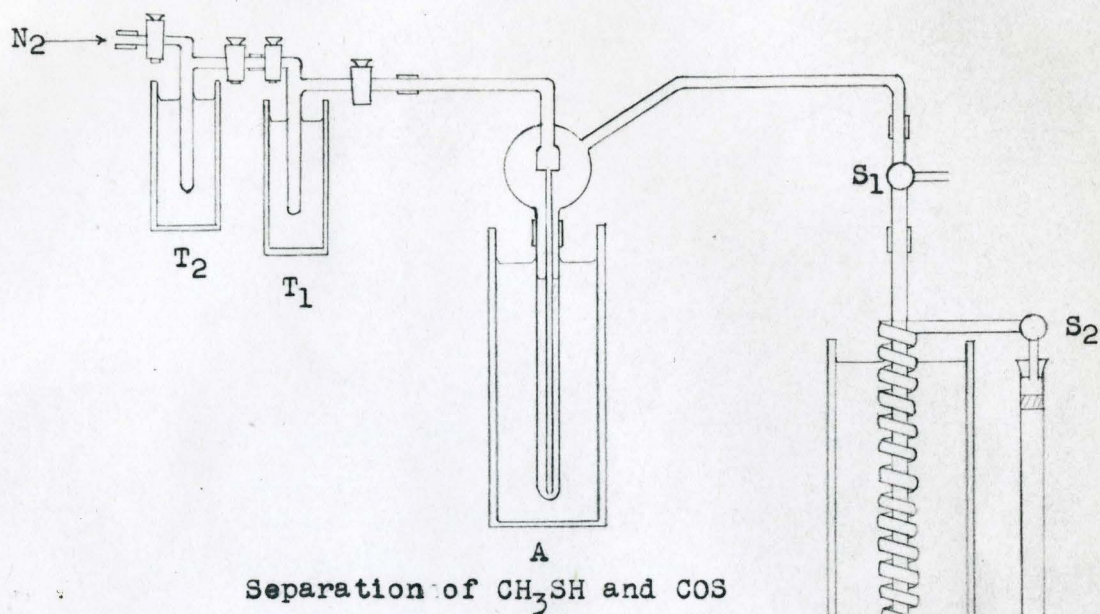


DIAGRAM IV

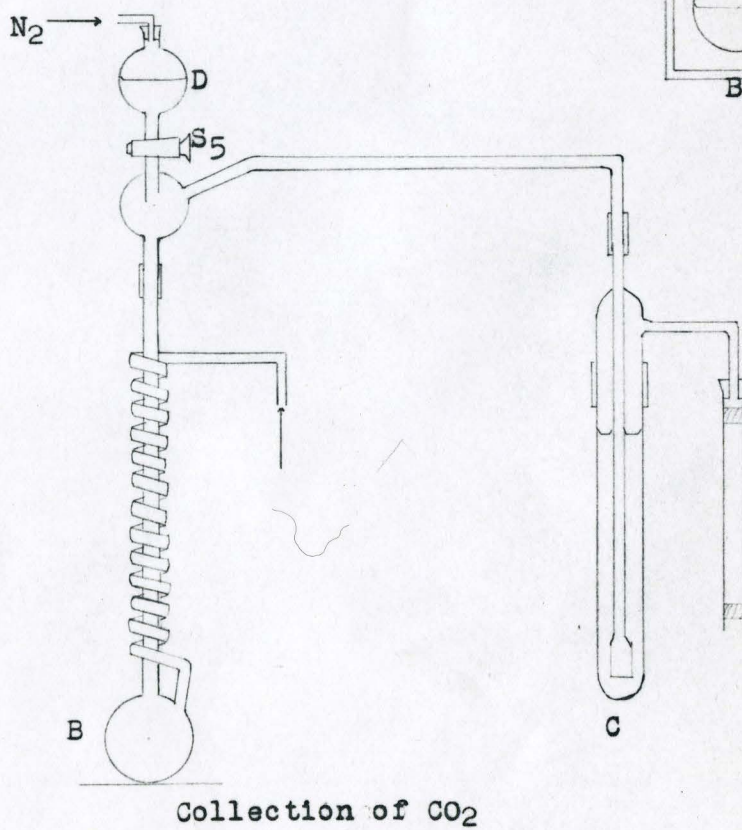
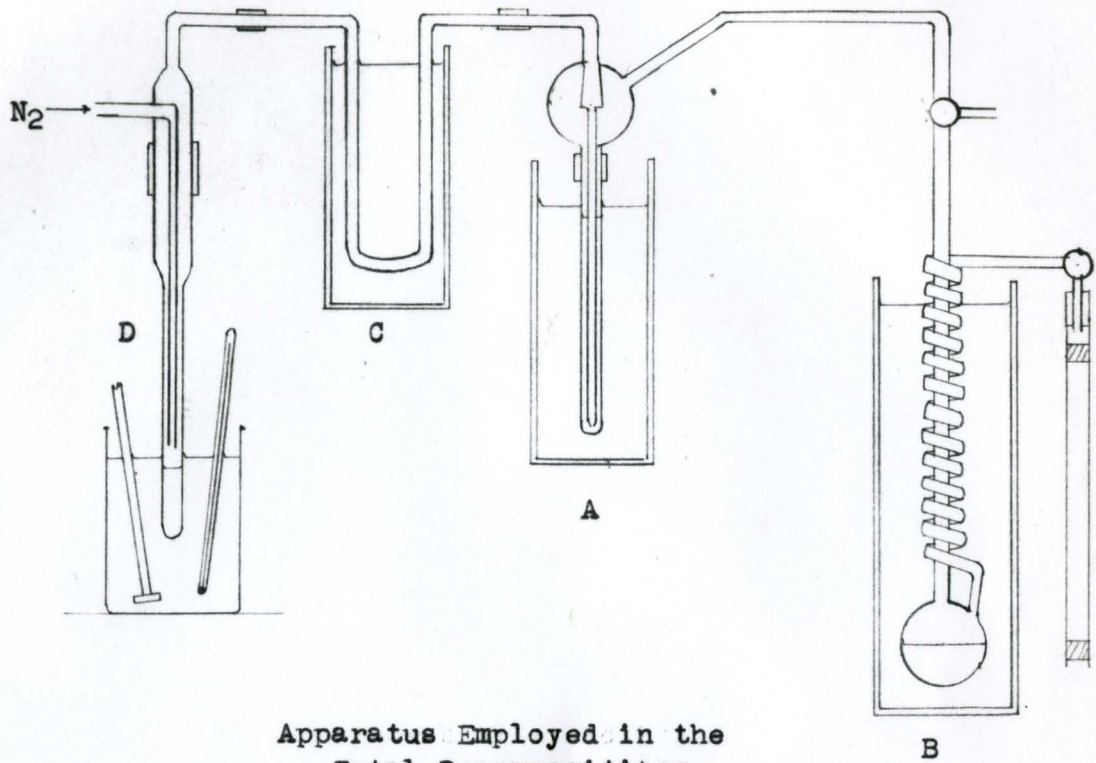


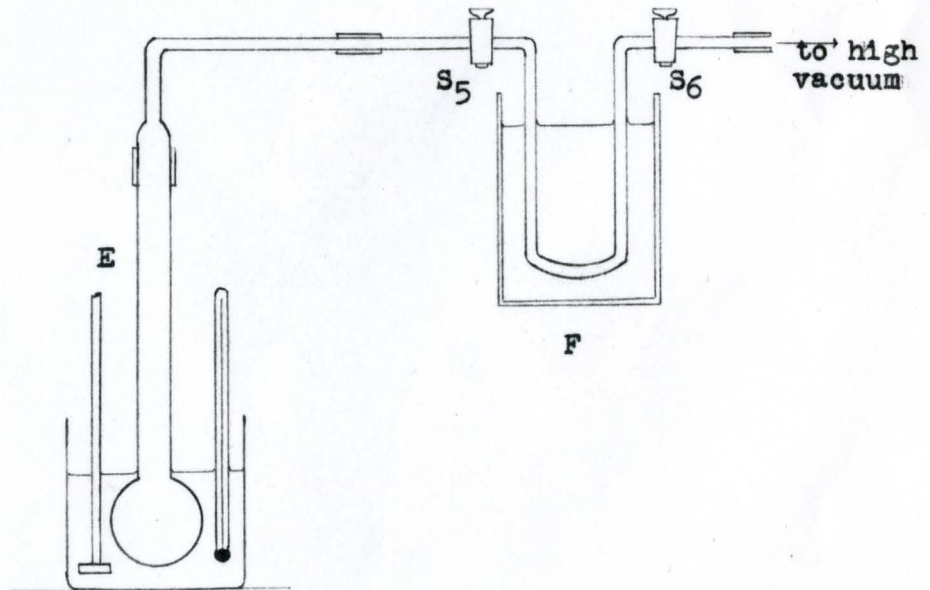


DIAGRAM V



Apparatus Employed in the  
Total Decompositions

DIAGRAM VI



Apparatus Employed in the  
Partial Decompositions



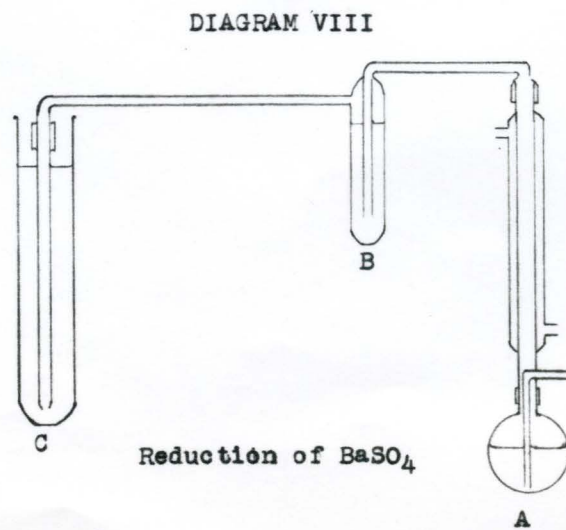
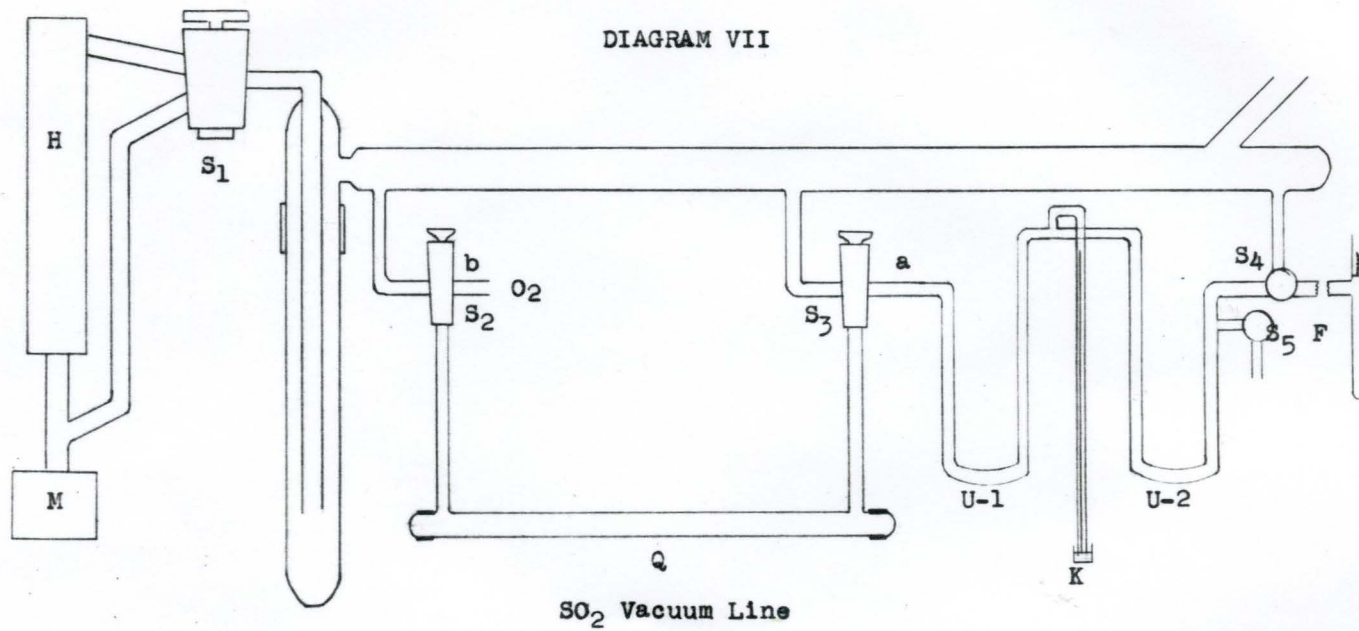
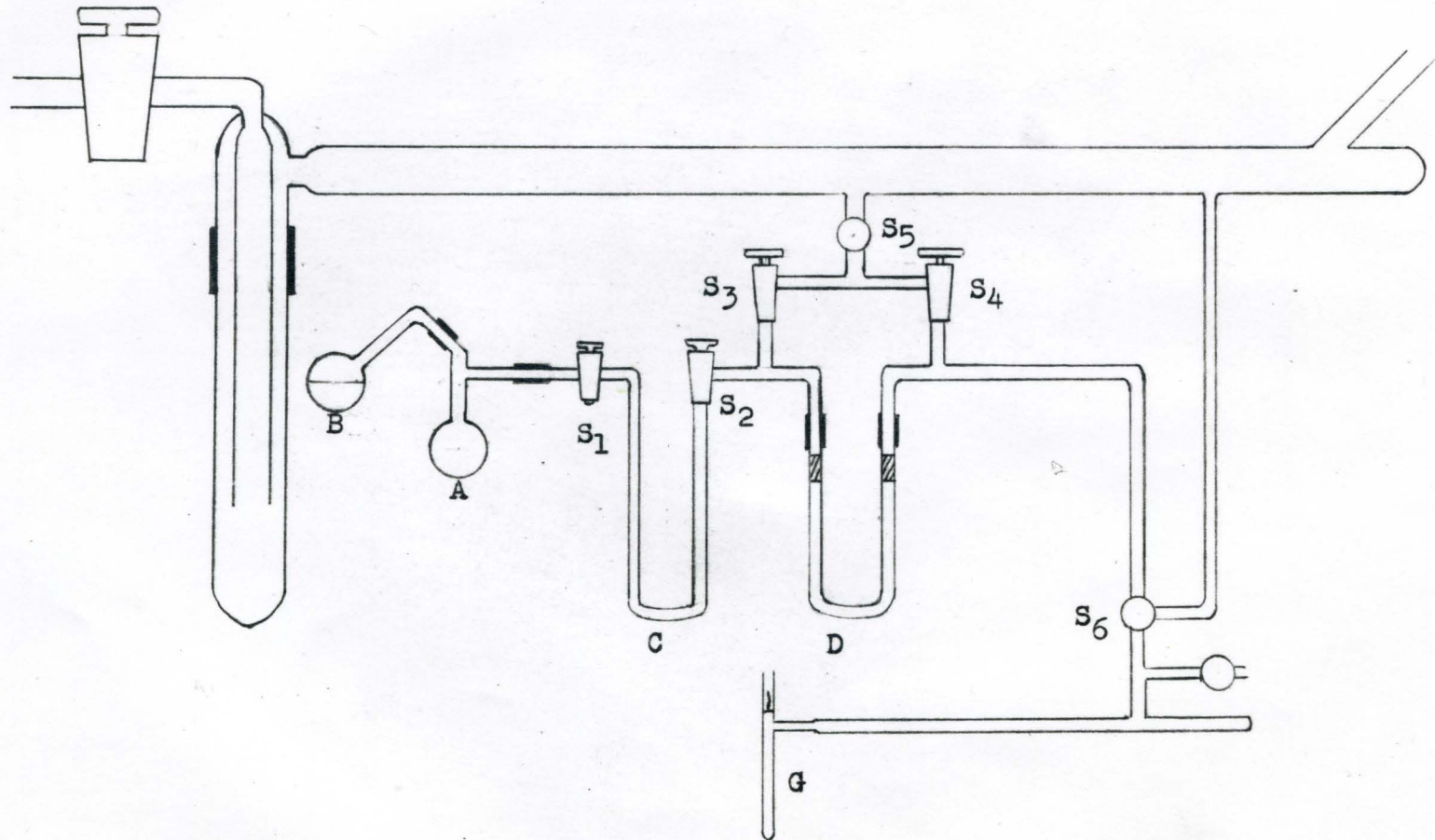




DIAGRAM IX



CO<sub>2</sub> Vacuum Line



## RESULTS AND DISCUSSION

### Experimental Results

In Table I are listed all of the experimental data related to the total and partial decompositions of S-methyl-trans-2-methyl-1-indanyl xanthate. The results for the total and partial decompositions (designated as TD and PD respectively), of one particular sample are grouped together.

Since the total decompositions proceeded only 80 - 85% to completion, a small difference will exist between the mass abundance ratios as determined from these values and the real isotopic ratios for the xanthate molecules. However, as the isotope effects encountered in the Tschugaeff reaction are small in themselves, the difference between the measured values determined in this manner and the real values will be very small. Furthermore, since interest was centered more on an intercomparison of the three isotope effects rather than on their absolute magnitudes, the small errors introduced by the above assumptions will be of little significance.

As the same sample of xanthate ester was not employed in all of the decompositions, the mass abundance ratios vary slightly. This, of course, has no effect on the resultant isotope effect.

The procedure for the decompositions was long and involved many operations. It was therefore difficult to avoid carbonate contamination. Carbonate contamination was made especially difficult



Table I

EXPERIMENTAL DATA FOR THE TOTAL AND PARTIAL DECOMPOSITIONS OF  
S-Methyl-trans-2-Methyl-1-Indanyl Xanthate

No.	Time of heating in min.	Temp. °C	Millimoles of Xanthate ester	% Yield of			Mass Spectrometer Abundance Ratios		
				PbS	BaSO <sub>4</sub>	BaCO <sub>3</sub>	Thion S atom S <sup>32</sup> /S <sup>34</sup>	Thio-ether S atom S <sup>32</sup> /S <sup>34</sup>	Xanthate C atom C <sup>12</sup> /C <sup>13</sup>
TD-I	90	100	1.15	81.0	77.6	84.2	22.20	22.28	93.63
PD-I	2	77	20.1	3.66	4.44	4.14	22.38	22.31	93.63
TD-II	90	100	1.36	83.5	83.3	82.6	22.18	22.27	93.72
PD-II	3	79	20.0	7.85	7.80	8.30	22.40	22.33	93.72
TD-III	90	100	1.12	88.0	-	83.0	22.20	-	-
PD-III	2.7	76	19.7	4.81	-	-	22.42	-	-
TD-IV	90	100	1.15	87.8	67.6	90.8	22.22	22.30	93.78
PD-IV	3.2	80	17.4	9.44	6.93	9.86	22.35	22.36	93.90
TD-V	90	100	1.13	86.7	86.7	93.4	22.23	22.31	94.25
PD-V	2.9	75	16.6	5.70	6.45	6.56	22.41	22.35	94.25
TD-VI	90	100	1.17	88.0	91.5	94.3	22.28	22.31	94.34
PD-VI	2.9	81	17.7	10.6	11.2	11.4	22.46	22.35	94.43



by the necessity of using a strongly basic solution (1:4 sodium hydroxide) for the hydrolysis of the carbonyl sulphide. However, as the carbon in the xanthate was of natural isotopic abundance, contamination due to the carbon dioxide present in the atmosphere would have but a slight effect on the resultant isotope effect.

The observed isotope effects as calculated from the mass spectrometer abundance ratios and the percent reaction using equation (9) are listed in Table II.

Table II  
ISOTOPE EFFECTS OBSERVED IN THE  
TSCHUGAEFF REACTION

No.	$k_{32}/k_{34}$ Thion S Atom	$k_{32}/k_{34}$ Thio-ether S Atom	$k_{12}/k_{13}$ Xanthate C Atom
D-I	1.0083	1.0014	1.0000
D-II	1.0103	1.0028	1.0000
D-III	1.0094	-	-
D-IV	1.0062	1.0028	1.0013
D-V	1.0083	1.0018	1.0000
D-VI	1.0085	1.0019	1.0010

The isotope effects have been averaged for all three atoms and the resultant effects listed in Table III. The precisions are expressed as standard deviation.



Table III

## AVERAGED VALUES OF THE OBSERVED ISOTOPE EFFECTS

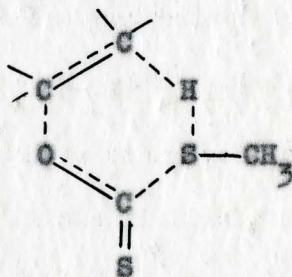
Atom	$k_L/k_H$	Value of $k_L/k_H$
Thion sulphur	$k_{32}/k_{34}$	$1.009 \pm 0.001$
Thio-ether sulphur	$k_{32}/k_{34}$	$1.002 \pm 0.001$
Xanthate carbon	$k_{12}/k_{13}$	$1.0000 \pm 0.0006$

## Predicted Isotope Effects for Mechanisms I and II

It was earlier demonstrated that Bigeleisen's expression, equation (25), may be used in a qualitative fashion to predict the magnitude and direction of isotope effects in unidirectional reactions. The isotope effects which were predicted as resulting from Mechanisms I and II and presented in the General Introduction are now to be examined more fully with the aid of equation (25). To add substance to these predictions an attempt has been made to calculate the isotope effects which could be expected to arise from each mechanism.

## Predicted Isotope Effects for Mechanism I

If Mechanism I were operative in the Tschugseff reaction the xanthate molecule would pass through the transition state shown below.





The xanthate carbon atom in this mechanism may be depicted as undergoing the following major bonding changes.



The first summation of equation (25) may be directly related to the difference in the free energies of formation of the isotopic molecules  $O-C^{12}-S$  and  $O-C^{13}-S$  from separated atoms. The second summation, for the transition state, may in a similar manner be related to the difference in the free energies of formation of the isotopic molecules  $O \cdots C^{12} \cdots S$  and  $O \cdots C^{13} \cdots S$  also from the separated atoms. The xanthate carbon atom is more strongly bound to oxygen and less strongly bound to sulphur in the transition state than it was in the ground state, and since carbon forms stronger bonds with oxygen than with sulphur, the summation term for the transition state will be of a magnitude comparable to that of the initial state, and may exceed it. The difference, however, will be small, and the overall result of the square bracket term in equation (25) is most likely to be a number slightly less than one. Since the effective mass term in this case will be given very closely by the ratio of the reduced masses of the molecules  $C^{12}-S^{32}$  and  $C^{13}-S^{32}$  raised to the one-half power, which has the value of three percent, the overall isotope effect for the xanthate carbon atom in Mechanism I should be of the order of two to three percent. The effect is somewhat lower in this case than that obtained from the rupture of an isolated carbon sulphur bond due to the bond formation between the carbon and oxygen atoms.



The major bonding changes undergone by the thio-ether sulphur atom in Mechanism I are illustrated by the models shown below.

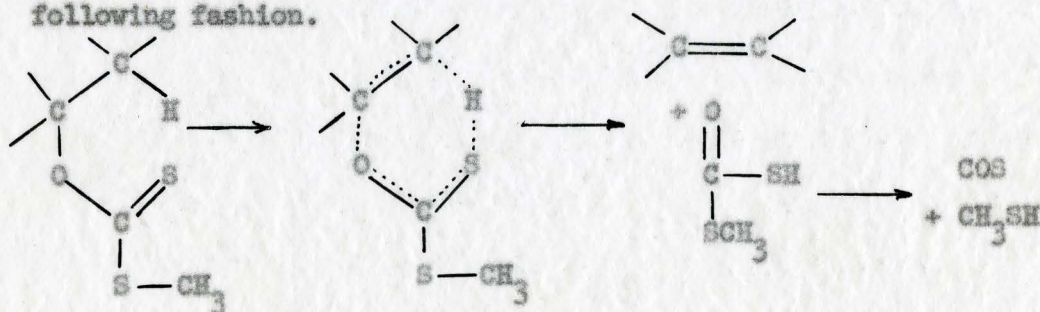


In this case, too, the isotope effect will not be very different from that observed for the rupture of an isolated carbon sulphur bond with the appropriate reduced mass term, which in this case has a value of 1.006. The difference of the two summations of equation (25) will be a positive quantity for while the  $G(u_1^\ddagger)$  term for the transition state is large,  $\Delta u_1^\ddagger$  is very small as it may be related to the ratio of the reduced masses of the molecules  $S^{32}-H$  and  $S^{34}-H$  which is a very small number. The product  $G(u_1^\ddagger)\Delta u_1^\ddagger$  will thus be a very small quantity. The product of the effective mass and square bracket terms will therefore fall in the range of one to two percent.

The bonding of the thion sulphur atom remains virtually unaltered if this mechanism is operative and the isotope effect for it should be zero or very small, a few tenths of a percent at most.

#### Predicted Isotope Effects for Mechanism II

Mechanism II, in which the thion sulphur atom abstracts the hydrogen atom in the rate determining steps, was formulated in the following fashion.





It is important to note that in this mechanism, the rate determining step does not result in the immediate and complete separation of the xanthate carbon atom and the thion sulphur atom, but merely in a lengthening of the bond between them. That is, the bond order decreases from two in the reactant state to one in the intermediate xanthic acid. The fact that the bonding between the two atoms is not completely severed in the rate determining step means that the ratio of the effective masses in equation (25) assumes a very small value. Exactly what the ratio of the effective masses reduces to in a case such as this is discussed in the section dealing with the theoretical calculations of isotope effects. It will suffice at this point to note that it is of the order of tenths of a percent. Because of this, the isotope effects for both the xanthate carbon and the thion sulphur atoms will be small for this mechanism.

In Mechanism II the xanthate carbon atom is essentially undergoing the changes in bonding depicted below.



In this case the first summation in equation (25) may be directly related to the difference in the free energies of formation of the molecules  $O-C^{12}=S$  and  $O-C^{13}=S$  from separated atoms. The second summation refers to a similar difference for the two isotopic molecules  $O \cdots C^{12} \cdots S$  and  $O \cdots C^{13} \cdots S$  from separated atoms. As carbon oxygen bonds are stronger than carbon sulphur bonds, the difference of the two summations in equation (25) is most likely to be a negative quantity. The overall result of the square bracket



term is therefore a number slightly less than unity. Since the reduced mass term in this case is small, the product of this term and the square bracket term will be unity or very close to it. The isotope effect for the xanthate carbon atom should be close to zero percent.

The thion sulphur atom in this mechanism may be depicted as undergoing the following changes in bonding.



The term appearing in the transition state summation due to the formation of the sulphur hydrogen bond will again be very small as the corresponding  $\Delta u_1^+$  is small. The difference of the two summations will therefore be a small positive number. The product of the square bracket term and the effective mass, the latter number being small in this case, will therefore be a number slightly greater than one. The isotope effect should not exceed one percent.

The bonding of the thio-ether sulphur atom is not appreciably altered in this mechanism and therefore the isotope effect will be very small or zero.

The qualitative predictions made above are summarized in Table IV.



Table IV

## PREDICTED ISOTOPE EFFECTS FOR THE TSCHUGAEFF REACTION

Mechanism I		$k_L/k_H$
Thion sulphur atom	$S^{32}/S^{34}$	1.000
Thio-ether sulphur atom	$S^{32}/S^{34}$	1.01 - 1.02
Xanthate carbon atom	$C^{12}/C^{13}$	1.02 - 1.03
Mechanism II		
Thion sulphur atom	$S^{32}/S^{34}$	1.01
Thio-ether sulphur atom	$S^{32}/S^{34}$	1.000
Xanthate carbon atom	$C^{12}/C^{13}$	1.000

## Theoretical Calculation of the Isotope Effects in the Tschugaeff Reaction

An attempt has been made to calculate the isotope effects that could be expected for the thio-ether sulphur and xanthate carbon atoms of Mechanism I and the thion sulphur and xanthate carbon atoms of Mechanism II. The calculations involved the determination of the normal frequencies and the shift in these frequencies due to isotopic substitution for simplified models which approximated the xanthate portion of the molecule. The isotope effects were then calculated from the frequencies and effective masses thus obtained by substitution of these values in Bigeleisen's expression, equation (25). No calculations were carried out for the thion sulphur atom of Mechanism I or the thio-ether sulphur atom of Mechanism II as they undergo but slight changes in bonding energy.



Even with the use of simplified models, the calculations are rather long and involved. Thus in order to preserve the continuity of this section, all of the work pertaining to the calculations has been placed in an appendix immediately following this section of the thesis and only the results of the calculations are given here. Furthermore, the interpretation of isotope effects entirely in the terms of the normal vibrational modes of a molecule and reduced masses, is of great interest in itself. For both these reasons then, an appendix has been added wherein this somewhat different, albeit equivalent, view of isotope effects is fully discussed.

Table V

PREDICTED ISOTOPE EFFECTS FOR THE TSCHUGAEFF REACTION  
 BASED ON THEORETICAL CALCULATIONS

Mechanism I	$k_1/k_H$	
Xanthate carbon atom	$C^{12}/C^{13}$	1.027
Thio-ether sulphur atom	$S^{32}/S^{34}$	1.013
Mechanism II		
Xanthate carbon atom	$C^{12}/C^{13}$	1.000
Thion sulphur atom	$S^{32}/S^{34}$	1.011

A Comparison of the Experimental and Predicted Isotope Effects and the Question of Mechanism

To facilitate the discussion which is to follow, the values listed in Tables III, IV, and V have been gathered and placed in one table for easy comparison.



The figures given under the heading "predicted" refer to the values obtained in a qualitative manner using Bigeleisen's equation, while the figures under the heading "calculated" represent the values for the isotope effects obtained, again with the aid of Bigeleisen's equation, in a more quantitative fashion.

Table VI

SUMMARY OF THE EXPERIMENTAL, PREDICTED AND CALCULATED ISOTOPE EFFECTS FOR THE TSCHUGAEFF REACTION

	$k_Y/k_H$ Experi- mental	$k_Y/k_H$ Mech. I		$k_Y/k_H$ Mech. II	
		Pred.	Cal.	Pred.	Cal.
Thio-ether S atom $S^{32}/S^{34}$	1.002	1.01-1.02	1.013	1.00	-
Xanthate C atom $C^{12}/C^{13}$	1.000	1.02-1.03	1.027	1.00	1.000
Thion S atom $S^{32}/S^{34}$	1.009	1.00	-	1.01	1.011

A comparison of the experimental results with those predicted for Mechanism I shows them to be incompatible. The absence of any isotope effect whatsoever for the xanthate carbon atom and a very small one for the thio-ether sulphur atom proves conclusively that the bond between them is not severed in the rate-determining step as is required by Mechanism I. Furthermore, Mechanism I allows for only a very small isotope effect for the thion sulphur atom, and can in no manner account for the nine-tenths of a percent actually measured.

The experimental results are, however, in excellent agreement with those predicted for Mechanism II. The zero percent isotope effect for the xanthate carbon atom illustrates conclusively



that neither of the carbon sulphur bonds are completely severed in the transition state. Partial  $\pi$  bond formation and breakage for the xanthate carbon atom does, however, account for a zero percent effect. The nine-tenths of a percent isotope effect for the thion sulphur atom is also accounted for by Mechanism II. Though this is a relatively small effect it does show that the bonding of this atom is altered significantly in the rate-determining step. This is compatible with the rupture of a  $\pi$  bond between the xanthate carbon atom and the thion sulphur atom.

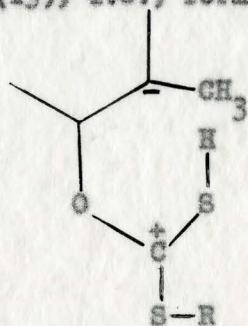
The two-tenths of a percent isotope effect observed for the thio-ether sulphur atom is explicable only if it is assumed to be undergoing no significant change in bond energy or type in the rate-determining step. This is indeed the case in Mechanism II.

From this comparison it is concluded that a mechanism is operative in the Tschugaeff reaction which follows the major steps that have been outlined in this thesis for Mechanism II. That is, the reaction proceeds via a two-step mechanism with the formation of an unstable xanthic acid intermediate. The initial step, wherein the thion sulphur atom bonds with the cis beta hydrogen atom leading to the intermediate xanthic acid, was pictured as being a concerted one. That the mechanism is indeed a concerted one is shown by the lack of an isotope effect for the xanthate carbon atom and is, perhaps, one of the most strikingly illustrated points that this study has brought to light. It will be recalled from the Historical Introduction that O'Connor and Nace (21), in order to account for the decreased thermal stability of xanthates with electronegative



ester groupings, had pictured the oxygen atom as forming a  $\pi$  bond with the xanthate carbon atom during the rate-determining step. The more electronegative the ester grouping, the larger the induced positive charge on the carbon atom and hence the greater the driving force due to the oxygen atom. Now, if this is indeed the case, it follows that the isotope effect for the xanthate carbon atom will be small or zero as both bond breaking and bond formation occur simultaneously. It further implies that all six bonds are undergoing changes at once. As the measured isotope effect for carbon was zero percent, this must then be the case.

Calculations for the xanthate carbon atom, for which the model and approximations were rather good, have shown that if the reaction is not concerted, but rather stepwise as pictured originally by Stevens and Richmond (13), i.e., forming the intermediate,



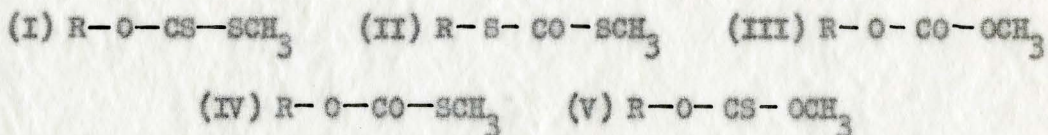
then the isotope effect for the xanthate carbon atom should be of the order of one percent. Since the publication of Stevens' paper in 1941 it has become increasingly clear that reactions do occur in a concerted rather than a stepwise fashion. Thus the above result is not surprising. Nonetheless it is evident that isotope effects do show most clearly the effect of driving force when it is operative. Further, it should be possible to relate the change



in an observed isotope effect with change in driving force. Thus for example, as the ester grouping in the xanthate ester is made more electronegative, the driving force should increase, with the result that the isotope effect observed for the xanthate carbon atom should drop to a value less than one.

During the writing of this thesis, a paper was presented at the Congress of the International Union of Pure and Applied Chemistry in Zurich by Salomaa (58) which also dealt with the problem of which of the two mechanisms is operative in the Tschugaeff reaction. The solution to the problem was sought in this case through classical means and gave a result which strongly indicated that the mechanism labeled in this thesis as II is indeed operative in the Tschugaeff reaction.

Salomaa had noted that the thermal decomposition of an xanthate ester (I) proceeded to give an unsaturated hydrocarbon while the corresponding dithiolcarbonate (II) did not react under these conditions.

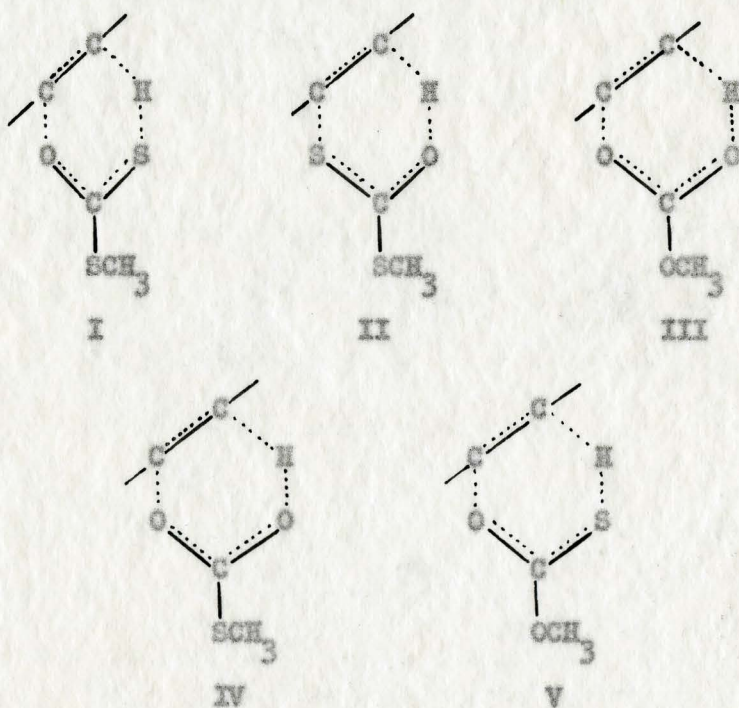


He, therefore, thought it of interest to study the thermal properties of compounds III to V which are respectively the carbonate ester, the thio ester and the thio carbonate ester. Esters of the types III, IV, and V were prepared for d-borneol, d,l-isoborneol and d- $\alpha$ -fenchol, and these esters then submitted to thermal treatment.



The esters of types III and IV remained unchanged upon distillation as did those of type II. The esters of type V, however, did decompose to yield an alkene, carbonyl sulphide and methanol corresponding to the three products obtained in the Tschugaeff reaction. Salomaa therefore concluded that since a thion sulphur atom must be present for decomposition to occur, the thion sulphur atom, rather than the thio-ether sulphur atom, must bond with the proton in the rate-determining step.

It is interesting to note that only in cases I and V is there a driving force of any significance. The transition states for the five esters are shown below.



In compounds of type II the xanthate carbon atom is more strongly bonded to the sulphur atom and less strongly bonded to the oxygen atom in the transition state than in the ground state. Such a process is energetically unfavourable and the free energy changes for



these bonding changes alone will be a positive quantity. In cases III and IV the net change in free energy will be very close to zero for the bonding changes about the xanthate carbon atom. Only in compounds of type I and V are the free energy changes, due to the prior bond formation to the xanthate carbon atom, of a favourable magnitude and sign, and, therefore, only in these cases is a driving force of the type previously described, operative.

The driving force due to the  $\pi$  bond formation of the oxygen atom must be of importance in this reaction for as earlier stated, Alexander and Mudrak (17) have pointed out that the Tschugaeff reaction represents a unique instance in which it appeared that an atom is displaced from a carbon atom without the backside approach of another. Rather, the reaction may be pictured as a displacement on the xanthate carbon atom brought about by the unshared pair of electrons on the oxygen atom. This prior bond formation is the leading step of the reaction and it results in a weakening of the alkyl - oxygen bond and in the displacement of the other electron pairs whose redistribution is involved in the transformation.



## APPENDIX

### THEORETICAL CALCULATIONS OF ISOTOPE EFFECTS

#### The Normal Modes of a Molecule

It is possible to interpret and predict isotope effects from a slightly different and at the same time more fundamental viewpoint than was done in the preceding section. Such an interpretation rests on a consideration of the so-called "normal vibrations" of the nuclear masses within a molecule. Furthermore, as the ratio of the partition functions of two isotopically substituted molecules may be reduced to a term which is a function of their vibrations only, (i.e., the  $u_i$  of equation 25), a calculation of the normal modes of the isotopic species is a requirement for any exact calculation of isotope effects.

An insight into what is meant by a normal vibration may be gained by a consideration of the ball and spring model depicted in Figure 1.

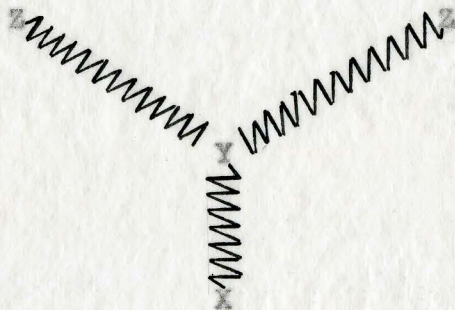


Figure 1



The restoring forces operating between Y and Z, and Y and X are strong, while weaker forces operate between the Z masses themselves, and between the Z's and the X. As a first consideration of this system assume that the  $YZ_2$  portion of the molecule is rigid. If X then undergoes displacement from its equilibrium position in a direction parallel to Z-Z, it will carry out a simple harmonic motion of frequency  $\nu_x$ . Similarly, if X is displaced in a direction perpendicular to the  $YZ_2$  plane, or in the direction of the XY spring, it will again undergo simple harmonic motions of frequencies  $\nu_z$  and  $\nu_y$ , respectively.

However, if X is displaced in any direction other than the above three the resulting motion is very complicated and is termed a Lissajous motion. Nonetheless, this motion, complicated as it is, may be resolved into three simple harmonic motions along the three coordinate axes. If now the assumption of the rigidity of  $YZ_2$  is dropped, any displacement of X will cause all of the particles to undergo Lissajous motions. It may be shown that all such complicated motions of the nuclei within the molecule, no matter how they arise, may be represented as a superposition of a number of normal vibrations. Each normal vibration is characterized by the fact that each particle carries out a simple harmonic motion and that all of the particles have the same frequency of oscillation and, in general, move in phase.

There are as many different normal or fundamental vibrations for a molecule as there are vibrational degrees of freedom. That is, to describe the motion of the N nuclei in a polyatomic molecule in



Cartesian coordinates,  $3N$  coordinates are necessary. There are, therefore,  $3N$  degrees of freedom. If interest is centered only on the vibrations that the nuclei undergo, then of the  $3N$  degrees of freedom, six are omitted. Three of the omitted degrees of freedom describe the translational motion of the molecule as a whole and the remaining three suffice to describe the rotation of the system relative to the mass center. If the molecule is linear, then two coordinates are sufficient to describe the orientation of the system in space. A non-linear molecule has, therefore,  $3N-6$  vibrational degrees of freedom and a similar number of normal modes, while a linear polyatomic molecule has  $3N-5$  such modes. The molecule  $XYZ_2$  has, therefore, six normal modes or normal vibrations and these are illustrated in Figure II.

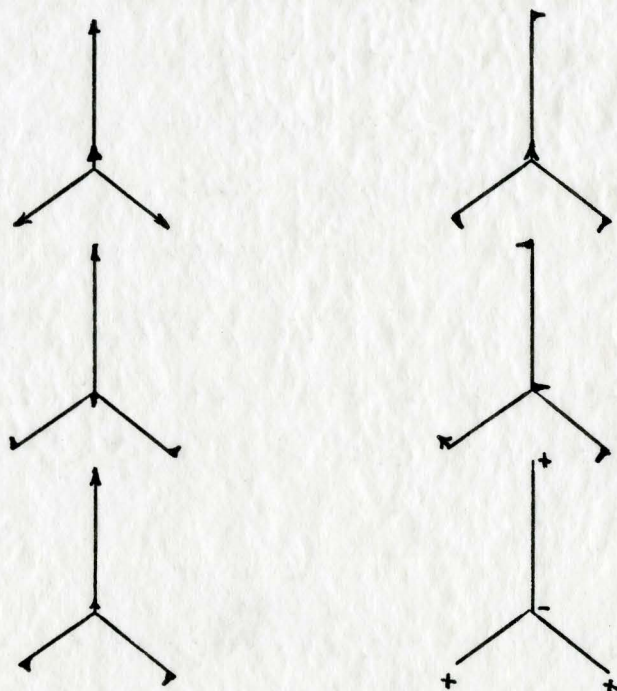


Figure II



Isotopic molecules have the same electronic structure and, therefore, the potential function under the influence of which the nuclei are moving is the same to a very high order of approximation. However, because of the difference in the masses, the vibrational levels and, therefore, the frequencies are different for the two species. In addition, the isotopic shift brought about in a certain frequency will be very small when the atom which is replaced by its isotope moves very little in that particular normal mode, whereas the shift will be relatively large when the atom in question has a large amplitude in that mode.

Since the isotope effect observed for a chemical reaction is dependent upon the magnitude of the isotopic shift in the frequency (i.e., the term  $\Delta u_1$ ), it follows immediately that the isotope effect will be great or small depending on whether or not the normal vibrations of the atom in question has a large amplitude in the direction of the bond that is ruptured or formed in the rate-determining step. The geometry of the molecule is, therefore, of importance in a consideration of isotope effects.

#### Determination of the Normal Modes

A diatomic molecule has but one normal mode and the frequency of this vibration may be determined from the expression

$$\nu_1 = \frac{1}{2\pi} \sqrt{\frac{k_1}{\mu}} \quad (1-A)$$

where  $k_1$  is the force constant of the molecule, and  $\mu$  is the reduced mass. The isotopic shift in the frequency is given simply by the inverse ratio of the reduced masses raised to the one-half



power.

$$\frac{\nu_1}{\nu_2} = \left( \frac{\mu_2}{\mu_1} \right)^{1/2} \quad (2-A)$$

For a more complex molecule relation (1-A) can no longer be used to determine the values of the normal modes, for the vibrations are now determined by all of the atomic masses and force constant of the molecule and can no longer be ascribed to the stretching of any one single bond. A new expression is required which takes into account this interdependence of the masses and force constants. The expression also takes into account the geometry of the molecule which has been stated as having an important bearing on the isotopic shift in the frequency. Since the molecule under consideration in this thesis is a complex one and non-linear, such an expression must be employed to determine the normal frequencies and the change in these frequencies due to isotopic substitution.

The normal vibrations of a molecule may be calculated from the roots of a determinantal equation which is arrived at by a consideration of small vibration in classical mechanics (59, 60).

The kinetic energy of a molecule is given by

$$2T = \sum_{\alpha=1}^N m_{\alpha} \left[ \left( \frac{d\Delta x_{\alpha}}{dt} \right)^2 + \left( \frac{d\Delta y_{\alpha}}{dt} \right)^2 + \left( \frac{d\Delta z_{\alpha}}{dt} \right)^2 \right] \quad (3-A)$$

where  $\Delta x_{\alpha}$ ,  $\Delta y_{\alpha}$ , etc. are the displacement coordinates of the mass  $m_{\alpha}$ . Equation (3-A) may be simplified by replacing the coordinates  $\Delta x_1, \dots, \Delta z_N$  by  $q_1 = \Delta x_1, q_2 = \Delta y, \dots, q_{3N} = \Delta z_N$ .



With this substitution equation (3-A) becomes

$$2T = \sum_{i=1}^{3N} m_i \dot{q}_i^2 \quad (4-A)$$

For small displacements, the potential energy  $V$  may be expressed as a power series in the displacement  $q_i$

$$2V = 2V_0 + 2 \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial q_i} \right) q_i + \sum_{i,j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right) q_i q_j + \text{higher terms} \quad (5-A)$$

By choosing the zero of the energy as that of the equilibrium configuration,  $V_0$  and  $(\partial V / \partial q_i)$  vanish identically, so that equation (5-A) becomes

$$2V = \sum_{i,j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right) q_i q_j \quad (6-A)$$

neglecting the higher order terms, i.e. assuming harmonic motion for the small displacements involved. A constant  $k_{ij}$  is now defined as

$$k_{ij} = \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right) \quad (7-A)$$

Equation (6-A) may now be rewritten as

$$2V = \sum_{i,j=1}^{3N} k_{ij} q_i q_j \quad (8-A)$$

Newton's equation of motion may be expressed in the form

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{q}_j} + \frac{\partial V}{\partial q_j} = 0 \quad j = 1, 2, \dots, 3N \quad (9-A)$$

Substitution of equations (4-A) and (8-A) into (9-A) gives



$$m_j \ddot{q}_j + \sum_{i=1}^{3N} k_{ij} q_i = 0 \quad j = 1, 2, \dots, 3N \quad (10-A)$$

Equation (10-A) is a set of  $3N$  simultaneous second-order linear differential equations, of which one possible solution is

$$q_i = A_i \cos (\lambda^{1/2} t + \epsilon) \quad (11-A)$$

where  $A_i$ ,  $\lambda$  and  $\epsilon$  are properly chosen constants. Substitution of this expression in equation (10-A) results in a set of algebraic equations:

$$\sum_{i=1}^{3N} (k_{ij} - \delta_{ij} m_j \lambda) A_i = 0 \quad j = 1, 2, \dots, 3N \quad (12-A)$$

where  $\delta_{ij}$  is the Kronecker delta symbol, i.e.,  $\delta_{ij} = 1$  for  $i = j$  and is zero otherwise.

Only for special values of  $\lambda$  does equation (12-A) have non-trivial solutions, and these values are those which satisfy the determinantal or secular equation.

$$\begin{vmatrix} k_{11} - m_1 \lambda & k_{12} \dots & k_{1,3N} \\ k_{21} & k_{22} - m_2 \lambda \dots & k_{2,3N} \\ \dots & \dots & \dots \\ k_{3N,1} & k_{3N,2} & k_{3N,3N} - m_{3N} \lambda \end{vmatrix} = 0 \quad (13-A)$$

In this equation,  $m_1 = m_2 = m_3 \neq m_4 = m_5 = m_6 \neq m_7 = \dots$ . The secular equation (13-A) consists of  $3N$  rows and columns, and consequently, upon expansion, it yields an algebraic equation in  $\lambda$  of the  $3N$ th degree. However, only  $3N-6$  of these roots possess non-zero values as six zero roots must be included in (13-A) to account for



the translation and rotation of the molecule. From the  $3N-6$  non-zero roots for  $\lambda$ , the values of a corresponding number of normal vibrations may be obtained since

$$\lambda_1 = 4\pi^2 \nu_1^2 \quad (14-A)$$

where  $\nu_1$  is the frequency of the  $i^{\text{th}}$  normal mode.

#### The Effective Mass Term in Absolute Rate Theory

Besides knowing the values of the normal modes, it is necessary to determine the value of the ratio of the effective masses before equation (25) may be solved for the value of  $k_L/k_H$ . In the section which dealt with isotope effects in general the effective mass was stated as being the mass of the activated complex along the coordinate of decomposition. Slater has shown (38) that in the case of a simple bond rupture, even in a complicated molecule, the effective mass term is given by the reduced mass of the hypothetical molecule made up of the two atoms between which the bond is broken. The ratio of the effective masses is in this case simply the ratio of the reduced masses for two such hypothetical molecules where one of them has been isotopically substituted.

The reduced mass ratio as it occurs in equation (25) is raised to the one-half power. According to equation (2-A), this ratio is equal to the ratio of the light to the heavy frequencies for the two molecules, i.e.,

$$\frac{\nu_1}{\nu_2} = \left( \frac{\mu_2}{\mu_1} \right)^{1/2} \quad (2-A)$$

The effective mass term in equation (24) is therefore a ratio of



two isotopic frequencies. It may also be shown from Slater's paper that each of these frequencies refers to that vibrational mode which is unstable to motion in the direction of the reaction coordinate. That is, it is no longer a vibrational motion but rather a type of translation when excited with the requisite amount of energy. Furthermore, the same paper demonstrates that the effective mass ratio of two isotopic species may always be equated to a ratio of the corresponding imaginary frequencies and this is true no matter how complicated the molecule or what manner of bonding change the molecule is undergoing. This follows because the potential terms are always the same for the two isotopic species.

The fact that the effective mass ratio may be related to a ratio of the imaginary frequencies can be demonstrated in a different fashion. Equation (25) as developed previously treated the crossing of the potential barrier as a translation, while the corresponding partition function was treated as a vibration. That is, the partition function for the activated complex was the complete partition function and referred to  $3N-6$  degrees of vibrational freedom.

Bigeleisen has shown (64) that his equation may alternately be derived by considering both the motion across the barrier and the corresponding partition function as a translation. This is done by treating the activated complex as a molecule possessing but  $3N-7$ , rather than  $3N-6$ , degrees of vibrational freedom. The remaining degree of freedom, the one corresponding to motion along the reaction coordinate, is treated as a translational motion. When this is done, the term  $m^\ddagger$  (which represents the mass of the activated complex along the reaction coordinate) appearing in equation (20)



of the original derivation

$$k = \frac{1}{\delta} \frac{C^\ddagger}{C_A^a C_B^b \dots} (kT/2\pi m^\ddagger)^{1/2} \quad (20)$$

cancel, giving equation (15-A).

$$k = \frac{kT}{h} \frac{Q^\ddagger}{Q_A Q_B \dots} \quad (15-A)^{(a)}$$

The term  $Q^\ddagger$  differs from  $Q^\ddagger$  in that it refers to but  $3N-7$  degrees of vibrational freedom. Equation (15-A) is, of course, the more familiar form of the absolute rate expression. Derivation of Bigeleisen's equation using expression (15-A) rather than (20) in an otherwise completely analogous fashion results in

$$k_1/k_2 = \left( \frac{\nu_{11}}{\nu_{21}} \right) f/f_N^\ddagger \quad (16-A)$$

and this is to be compared with the original expression

$$k_1/k_2 = \left( \frac{m_2^\ddagger}{m_1^\ddagger} \right)^{1/2} f/f^\ddagger \quad (23)$$

$\nu_{11}$  and  $\nu_{21}$  are the imaginary frequencies (or more correctly in this case, the accelerated translational motions) of the light and heavy isotopic complexes in the transition state. The term  $f_N^\ddagger$  is given by the expression

$$f_N^\ddagger = S_1^\ddagger/S_2^\ddagger \prod_i \frac{\nu_{2i}^\ddagger}{\nu_{1i}^\ddagger} e^{-\Delta u^\ddagger/2} \frac{(1-e^{-\mu_{1i}^\ddagger})}{(1-e^{-\mu_{2i}^\ddagger})} \quad (17-A)$$

---

(a) The concentration terms have been replaced by their respective partition functions.



Comparison of  $f^\ddagger$  and  $f_N^\ddagger$  shows them to differ by the factor,

$$\frac{\nu_{21}^\ddagger}{\nu_{11}^\ddagger} e^{-\Delta u^\ddagger/2} \frac{(1 - e^{-h\nu_{11}^\ddagger})}{(1 - e^{-h\nu_{21}^\ddagger})} \quad (18-A)$$

and equations (19-A) and (23) will thus differ by one over this factor. It can be shown, that upon expansion, equation (18-A) is equal to the Wigner tunnelling correction, and this correction is negligible for all reactions except possibly those involving hydrogen isotopes. Equations (23) and (16-A) are thus essentially equivalent.

Just as equation (23) was expanded into the more useful form of equation (25) so equation (16-A) may be thrown into a form corresponding to equation (25) which is valid for all cases where  $\Delta u_1$  is small.

$$\frac{k_1}{k_2} = \frac{S_2^\ddagger}{S_1^\ddagger} \cdot \frac{S_1}{S_2} \cdot \left( \frac{\nu_{11}}{\nu_{21}} \right) \left[ 1 + \sum^{3n-6} G(u_1) \Delta u_1 - \sum^{3n'-7} G(u_1^\ddagger) \Delta u_1 \right] \quad (19-A)$$

Equation (19-A) was employed for the calculations reported in this thesis. The mechanisms proposed for the Tschugaeff reaction involve simultaneous bond formation and bond breakage and hence the effective mass term could not be related to the reduced mass of a hypothetical diatomic molecule. Rather, the values for the two imaginary frequencies obtained from the secular equation (13-A) derived for an appropriate potential expression, were substituted directly into expression (19-A).



## The Calculation of Isotope Effects for Mechanisms I and II


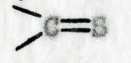



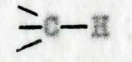
The calculations of the normal modes were performed in accordance with the valence force theory. This theory assumes that there is a strong restoring force in the line of every valence bond if the distance between the two atoms joined by this bond is changed. In addition there is a restoring force opposing a change in the angle between two valence bonds connecting one atom with two others. However, bending vibrations were neglected in the present calculations. The theory also neglects any anharmonicity terms and, therefore, expresses the potential energy in a quadratic form.

### Calculation of the Normal Modes of the Reactant Molecule

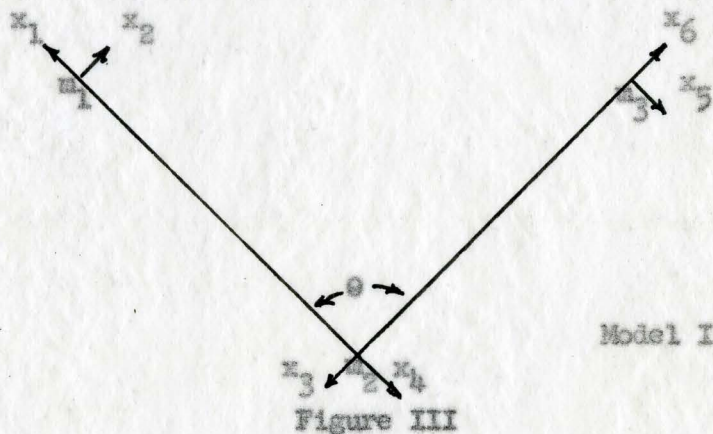
The force constant for a particular bond is almost an invariant quantity as long as the bond has a similar environment in the different molecules. Therefore the values of the force constants used in these calculations were chosen for bonds closely approximating those in the models used. Furthermore, isotope effects are more dependent upon the frequency shift than on the absolute value of the frequency, and it was to obtain good values for the former quantity that the calculations were primarily undertaken. Even so the values of the frequencies themselves will also be obtained to a very good approximation. The values employed for the force constants in the calculations to follow are tabulated below together with their literature sources.



Table I  
VALUES OF FORCE CONSTANTS USED IN CALCULATIONS

Bond	Stretching Force Constant $\times 10^{-5}$ dynes/cm.	Reference
	4.53	(61)
	7.50	(59)
	12.1	(59)
	2.23	(61)
	4.20	(62)
	4.97	(63)

The model employed in the calculations of the normal modes of the reactant molecule is shown in Figure III.



For both mechanisms, the mass  $m_2$  in the model referred to the xanthate carbon atom. Since this atom in the actual xanthate molecule is in the  $sp^2$  hybridized state, the angle  $\theta$  in the above model will be very close to  $120^\circ$ .



Two coordinate axes are sufficient to describe the motion of the nuclei in this system if out of the plane vibrations are neglected. The secular equation will, therefore, have  $2N$  roots. Of these roots three will be zero, two of which describe the resultant translational motion of the system along the  $x$  and  $y$  axes, and the third the rotation of the system as a whole. Since bending vibrations are neglected too, there will be altogether four zero roots. Omission of  $k_{\theta}$ , the bending force constant, is not a serious error. Bending force constants are generally less than the usual force constants by a factor of ten at least. Therefore, the frequency arising from bending motions of the molecule are much smaller than those due to a stretching of a bond. The isotopic shift of these frequencies will, therefore, be small as the magnitude of the shift is proportional to the magnitude of the frequency.

The potential function for Model I expressed in Cartesian displacement coordinates is

$$2V = k_{11} (x_1 + x_3 \cos \theta + x_4 \sin \theta)^2 + k_{22} (x_6 + x_3)^2 \quad (20-A)$$

The determinantal equation for this expression obtained from the coefficients of the displacements is

$$\begin{vmatrix} k_{11} - \lambda m_1 & 0 & k_{11} \cos \theta & k_{11} \sin \theta & 0 & 0 \\ 0 & -\lambda m_1 & 0 & 0 & 0 & 0 \\ k_{11} \cos \theta & 0 & k_{11} \cos^2 \theta + k_{22} & k_{11} \cos \theta \sin \theta & 0 & k_{22} \\ k_{11} \sin \theta & 0 & k_{11} \cos \theta \sin \theta & k_{11} \sin^2 \theta - \lambda m_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\lambda m_3 & 0 \\ 0 & 0 & k_{22} & 0 & 0 & k_{22} - \lambda m_3 \end{vmatrix} = 0 \quad (21-A)$$



which may also be written as

$$\begin{vmatrix} k_{11} - \lambda m_1 & m_1 \cos \theta & m_1 \sin \theta & 0 \\ k_{11} \cos \theta & -m_2 & 0 & k_{22} \\ k_{11} \sin \theta & 0 & -m_2 & 0 \\ 0 & m_3 & 0 & k_{22} - \lambda m_3 \end{vmatrix} \lambda^4 = 0 \quad (22-A)$$

after the four zero roots have been factored out. The value of this determinant is given by the quadratic expression

$$\begin{aligned} &^2(m_1 m_2^2 m_3) - (k_{11} m_2^2 m_3 + k_{22} m_1 m_2^2 + k_{11} m_1 m_2 m_3 + k_{22} m_1 m_2 m_3) \\ &+ k_1 k_2 (m_2^2 + m_2 m_3 + m_1 m_3 \sin^2 \theta + m_1 m_2) = 0 \end{aligned} \quad (23-A)$$

which may be solved for the two values of  $\lambda$ . From these two roots the frequencies corresponding to the two normal modes of the molecule may be calculated employing the expression

$$\lambda_i = 4\pi^2 \nu_i^2 \quad (12-A)$$

#### The Initial State of Mechanism I

Model I in this case refers to the enclosed portion of the xanthate molecule in Figure IV.

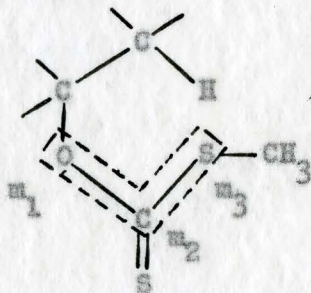


Figure IV



The normal frequencies of the model containing only the light isotopic species were first calculated and then the shifts in the frequencies due to isotopic substitution were determined by calculating the normal modes for the cases where carbon 12 was replaced by carbon 13 and sulphur 32 by sulphur 34. The frequencies obtained from these calculations are tabulated below, expressed in wave numbers, i.e.,  $\text{cm.}^{-1}$ .

	$\text{C}_{12}$	$\text{C}_{13}$	$\Delta\nu$		$\text{S}^{32}$	$\text{S}^{34}$	$\Delta\nu$
$\nu_1$	1090	1064	26	$\nu_1$	1090	1090	0
$\nu_2$	606	591	15	$\nu_2$	606	600	6

Isotopic substitution of the central atom brought about a large shift in both of the frequencies, while isotopic substitution, corresponding to the replacement of  $\text{S}^{32}$  by  $\text{S}^{34}$ , caused a shift in only one of the two normal modes. This illustrates the fact that when the amplitude of the vibration isotopically substituted is small in the direction of some particular normal mode, the isotopic shift is small, approaching zero.

#### The Initial State of Mechanism II

Model I in this case was used to calculate the normal modes of the combination of atoms indicated by the enclosed portion in Figure V.



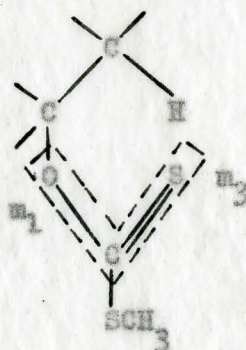


Figure V

The normal frequencies obtained from isotopic substitution of both the carbon and sulphur atoms are tabulated below, expressed in  $\text{cm.}^{-1}$ .

	$\text{C}^{12}$	$\text{C}^{13}$	$\Delta \nu'$		$\text{S}^{32}$	$\text{S}^{34}$	$\Delta \nu'$
$\nu_1'$	1317	1278	39	$\nu_1'$	1317	1311	6
$\nu_2'$	921	904	17	$\nu_2'$	921	916	5

Calculations for the Activated Complex and the Determination of the Effective Mass Term

In the development of equation (19-A) it was noted that the partition function for the activated complex referred to  $3N-7$  rather than  $3N-6$  vibrational degrees of freedom. The missing degree of freedom refers to that vibrational mode which is unstable to displacement in the direction of the reaction coordinate. That is, once energy of a certain critical value is carried to this mode, it no longer responds as a vibration but rather as a type of translation which leads to a separation of the molecule into two parts.

Therefore, to determine the normal modes of an activated complex it is necessary to include a term in the potential expression



such that one of the roots of this expression leads to an imaginary value for the frequency of this one particular normal mode. It was shown before that in the solution of such quadratic forms, when the roots are greater than zero they correspond to simple harmonic vibrations. The roots which were equal to zero corresponded to the translational and rotational modes of the molecule. In the same manner a solution to a quadratic equation when one of the roots is less than zero describes an accelerated translational mode, which is of course no longer a true frequency. The "frequency" calculated from such a negative root will be an imaginary number, (i.e.,

$$\nu_1 = \frac{1}{2\pi} |\lambda^{1/2} | \nu^{-1} |).$$

A potential function set up in this manner describes the portion of a potential surface outlined in Figure VI, i.e., the saddle point.

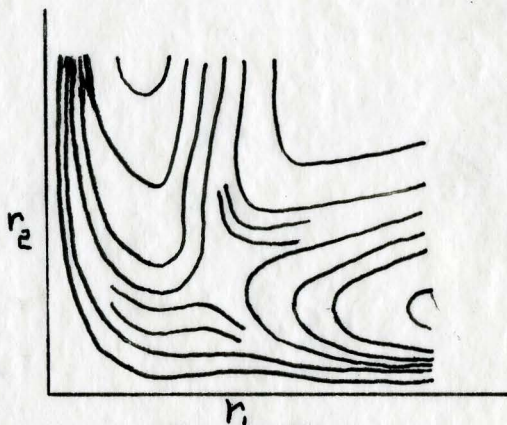


Figure VI

The accelerated translational mode may be interpreted as the movement of the products down the side of the potential energy barrier.

The model used in the calculations for the activated complex



was

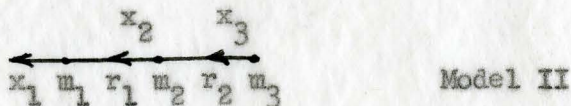


Figure VII

where as before the bending modes were omitted. The two remaining vibrational modes correspond to the motions illustrated in Figure VIII.

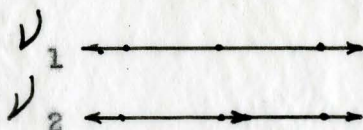


Figure VIII

$\nu_1$  does not correspond to a vibration which would lead to decomposition of the molecule. Frequency  $\nu_2$ , however, does describe a mode which would lead to rupture of a bond if this vibration were the critical one. The potential function must, therefore, give rise to a negative root which will determine the value of this imaginary frequency.

The potential expression for Model II is

$$2V = k_{11} r_1^2 + k_{22} r_2^2 + 2k_{12} r_1 r_2 \quad (24-A)$$

or

$$2V = k_{11}(x_1 - x_2)^2 + k_{22}(x_2 - x_3)^2 + 2k_{12}(x_1 - x_2)(x_2 - x_3) \quad (25-A)$$

where  $k_{12}$  is an interaction constant. To determine the conditions under which this will describe an unstable molecule, it is necessary to perform a linear transformation of the coordinates, such that

$$a = r_1 + r_2$$

$$b = r_2 - r_1$$



In terms of a potential energy diagram the new coordinates are seen to describe approximately the reaction coordinate.

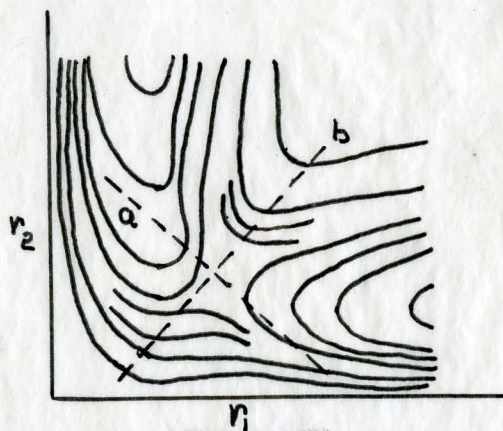


Figure IX

In terms of the new coordinates, the potential function assumes the form

$$4V = (k_{11} + k_{22} + 2k_{12})a^2 + (k_{11} + k_{22} - 2k_{12})b^2 + (2k_{22} - 2k_{11})2ab \quad (26-A)$$

If the molecule is to be unstable and decompose, then the curvature of the potential energy surface about the saddle point must be given by

$$\frac{\partial^2 V}{\partial a^2} > 0 \qquad \frac{\partial V}{\partial b^2} < 0$$

$$\therefore k_{11} + k_{22} > 2k_{12} \quad (27-A)$$

$$k_{11} + k_{22} < 2k_{12} \quad (28-A)$$

Thus it is necessary to give  $2k_{12}$  a value slightly greater than the sum of  $k_{11}$  and  $k_{22}$ , if the molecule is to be unstable in one degree of freedom. The difference  $2k_{12} - (k_{11} + k_{22})$  describes the curvature of the potential energy barrier. A large difference corresponds to a sharp barrier, while if the difference is small, the



saddle point is broader and flatter.

The determinantal equation for the potential energy expression for Model II is

$$\begin{vmatrix} k_{11} - \lambda m_1 & k_{12} - k_{11} & -k_{12} \\ k_{12} - k_{11} & k_{11} + k_{22} - 2k_{12} - \lambda m_2 & k_{12} - k_{22} \\ -k_{12} & k_{12} - k_{22} & k_{22} - \lambda m_3 \end{vmatrix} = 0 \quad (29-A)$$

After the extraction of the one zero root and simplifying transformations, equation (28-A) becomes

$$\begin{vmatrix} -m_1 \lambda & -m_2 & -m_3 \\ \alpha_1 & -(\alpha_1 + \alpha_2) - \lambda m_2 & \alpha_2 \\ -k_{12} & \alpha_2 & k_{22} - \lambda m_3 \end{vmatrix} \lambda = 0 \quad (30-A)$$

where  $\alpha_1 = -k_{11} + k_{12}$  and  $\alpha_2 = -k_{22} + k_{12}$

The roots are given by the following quadratic equation.

$$\begin{aligned} \lambda^2 (m_1 m_2 m_3) + \lambda m_1 m_3 (\alpha_1 + \alpha_2) + m_2 m_3 (\alpha_1 - k_{12}) - m_1 m_2 k_{22} - m_1 k_{22} (\alpha_1 + \alpha_2) \\ + m_2 (k_{12} \alpha_2 + k_{22} \alpha_1) + m_3 k_{12} (\alpha_1 + \alpha_2) \\ + m_1 \alpha_2^2 - m_3 \alpha_1 \alpha_2 = 0 \end{aligned} \quad (31-A)$$

The Transition State of Mechanism I

In this case Model II was used to calculate the normal modes of the system outlined in Figure X



Figure X



that is, the system wherein the carbon sulphur bond is broken and the sulphur hydrogen bond is formed. Now the bonds in the transition state are only partially broken and partially formed and, therefore, some intermediate value of the force constants must be chosen. Therefore, the values of the force constants for the carbon sulphur and sulphur hydrogen bonds listed in Table I were multiplied by a factor of two-thirds.

It was important to determine what effect the value of  $k_{12}$  would have on the values of the ratios of the imaginary frequencies  $\nu_{Li}/\nu_{Hi}$ . To do this three different values of  $k_{12}$  were chosen and the ratio of the imaginary frequencies was determined for isotopic substitution of  $C^{13}$ . The results of these calculations are listed in Table II.

Table II

$2k_{12} - (k_{11} + k_{22})$	$\nu_{Li}/\nu_{Hi}$
$0.51 \times 10^5$	1.038
$0.21 \times 10^5$	1.041
$0.11 \times 10^5$	1.041

The ratio of the frequencies, that is, the effective mass term, is seen to be rather insensitive to the value chosen for  $k_{12}$  as long as it is not too large. For small values of  $k_{12}$ , which are the most reasonable, the ratio appears to reach a limiting value. Such a result is to be desired, for while a reasonable guess at the value of  $k_{12}$  may be made, any attempt to assign an exact value to this term would be a most time consuming if not impossible task.



A value of 0.11 was chosen for the difference  $2k_{12} - (k_{11} + k_{22})$  in these calculations. The different values of  $k_{12}$  had but a very small effect on the value of the other frequency.

The values of the normal modes obtained for isotopic substitution of the xanthate carbon atom are tabulated below.

$\nu'$	$C^{12}$	$C^{13}$	$\Delta \nu'$
1	2229	2229	0
2	215 1	206 1	9

$$\frac{\nu'_L}{\nu'_H} = 1.041$$

The effective mass term is, therefore, 1.041, the value of the ratio of the imaginary frequencies. This is to be compared with a value of 1.03 which is the value calculated from the simple reduced mass relationship for the two hypothetical molecules  $C^{12} - S^{32}$  and  $C^{13} - S^{32}$ . The two answers are not meant to be the same, the comparison is merely made to show the reasonableness of the calculated value.

Mechanism I involves bond formation between the xanthate oxygen and carbon atoms and this has not been taken into account in the calculation of the imaginary frequencies for isotopic substitution of  $C^{13}$ . To have included the oxygen atom in the calculation would have complicated the calculations to a very large degree and far out of proportion to what would be gained. However, the effect due to this bond formation has been taken into account in a manner to be demonstrated later in the calculations. It involves, of course, an approximation, but it is a good and a necessary one.



Isotopic substitution in Model II of the atom corresponding to the thio-ether sulphur atom leads to the frequencies listed below.

	S <sup>32</sup>	S <sup>34</sup>	$\Delta \nu'$
$\nu'_1$	2229	2228	1
$\nu'_2$	215 1	213 1	2

The effective mass calculated from the two imaginary frequencies is 1.009. The value calculated from the reduced mass relationship for the hypothetical diatomic molecules C<sup>12</sup> - S<sup>32</sup> and C<sup>12</sup> - S<sup>34</sup> is 1.008.

#### The Transition States of Mechanism II

The carbon sulphur bond is not broken in the rate determining step of Mechanism II. It is not possible then to use Model II as it was employed for Mechanism I. The imaginary frequency in this case is represented by the resultant motions pictured in Figure XI.

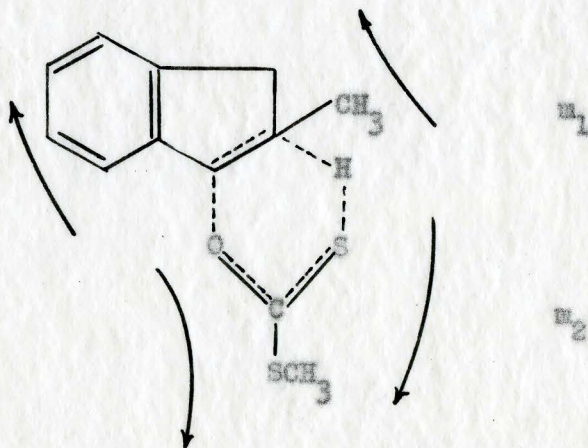


Figure XI

That is, the imaginary frequency is the one which leads to a separation of the xanthic acid from the rest of the molecule. To



attempt a direct calculation of this frequency would require the solving of an 18 by 18 determinant which is very difficult without access to a computer. One thing, however, is certain, the frequency shift of this mode due to isotopic substitution of either the xanthic carbon atom or the thion sulphur atom will be very small. Both of these atoms are one bond removed from the bonds that are ruptured in the rate determining step and neither atom would have a large amplitude in the direction of this particular mode.

The ratio of the imaginary frequencies will be related to some complicated ratio of the masses. Simply taking  $m_1$  and  $m_2$  as the masses of the two resulting molecules and  $m_2'$  as the isotopically substituted form of  $m_2$  gave reduced mass ratios to the one-half power of 1.004 for  $C^{12}/C^{13}$  and 1.003 for  $S^{32}/S^{34}$ .

Actually nothing more can be said about the effective mass terms in this case except that they will be of the order of a few tenths of a percent. For the sake of comparison, Model II was used to calculate the ratio of the imaginary frequencies for the boxed in system in Figure XII.

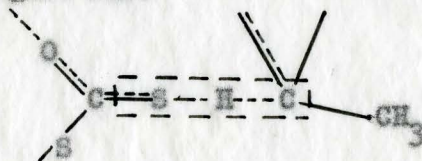


Figure XII

This calculation gave a value of 1.002 for the effective mass due to isotopic substitution of  $S^{34}$ . The values used were 1.003 for both  $C^{12}/C^{13}$  and  $S^{32}/S^{34}$ .

Model I was used to calculate the normal vibrations of the



transition state for the xanthate carbon atom and the thion sulphur atom. It will be recalled from the section on isotope effects that, in most of the calculations, the bonding changes were considered as complete in the activated complex and the same assumption was made in this case. The form of Model I was therefore,

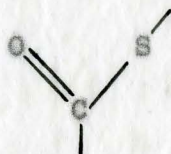


Figure XIII

The calculated values for the normal vibrations of the light and isotopically substituted species are listed below.

	C <sup>12</sup>	C <sup>13</sup>	$\Delta \nu'$		S <sup>32</sup>	S <sup>34</sup>	$\Delta \nu'$
$\nu'_1$	1745	1706	39	$\nu'_1$	1745	1745	0
$\nu'_2$	618	602	16	$\nu'_2$	618	612	6

#### The Isotope Effect for the Xanthate Carbon Atom of Mechanism I

The  $u_1$ 's of equation (19-A) are related to the frequencies by the expression

$$u_1 = \frac{h \nu'_1}{kT} \quad (32-A)$$

As before, let the primed  $u_1$  refer to the lighter of the two isotopes. Tabulated values of  $G(u_1)$  as a function of  $u_1$  are to be found in Bigeleisen's and Mayer's paper (33) on the calculation of equilibrium isotope effects.

The  $u_1$  values for the normal vibrations of the initial state



are therefore

$$\begin{aligned} u_1' &= 4.45 & u_2' &= 2.48 \\ u_1 &= 4.34 & u_2 &= 2.41 \\ \Delta u_1 &= 0.11 & \Delta u_2 &= 0.07 \end{aligned}$$

The values of the function  $G(u_1)$  are found from the tables referred to above for the corresponding value of  $u_1$ .

$$G(u_1) = 0.283 \quad G(u_2) = 0.184$$

The summation for the initial state is therefore

$$\sum_1 G(u_1) \Delta u_1 = 4.40 \times 10^{-2}$$

The effective mass term for the xanthate carbon atom is given by the ratio of the imaginary frequencies calculated from Model II.

$$\begin{aligned} \nu_L' &= 215 \text{ i} & \nu_H' &= 206 \text{ i} \\ \left( \frac{m_H}{m_L} \right)^{1/2} &= \frac{\nu_L}{\nu_H} & &= 1.041 \end{aligned}$$

The transition state summation must include a term for the bond formation between the xanthate carbon and oxygen atoms. This term was not given by either of the Models in this particular case but its frequency will be very close to that of the stretching frequency of a C=O double bond. This value was employed in the calculations.

$$\begin{aligned} u_1' &= 7.112 \\ u_1 &= 6.953 \\ \Delta u_1 &= 0.159 \\ \text{and } G(u) &= 0.357 \end{aligned}$$



The transition state summation is

$$\sum_1 G(u_1^\ddagger) \Delta u_1^\ddagger = 5.68 \times 10^{-2}$$

Therefore

$$\frac{k_L}{k_H} = 1.041 \left[ 1 + (4.40 - 5.68) \times 10^{-2} \right]$$

The ratio of the rate constants for the xanthate carbon atom is

$$\frac{k_L}{k_H} = 1.027$$

Isotope Effect for the Thio-Ether Sulphur Atom of Mechanism I

Data for the initial state:

$$\begin{aligned} u_1' &= 2.469 & u_2' &= u_2 \\ u_1 &= 2.446 & \Delta u &= 0 \\ \Delta u_1 &= 0.023 \\ G(u_1) &= 0.186 \end{aligned}$$

$$\therefore \sum_1 G(u_1) \Delta u_1 = 4.28 \times 10^{-3}$$

Data for the transition state: The values of the imaginary frequencies are

$$\nu_L = 215 \text{ i} \quad \nu_H = 213 \text{ i}$$

and therefore the effective mass term is

$$\frac{\nu_L}{\nu_H} = 1.009$$



The summation includes but one term

$$\begin{aligned} u_1^\ddagger &= 9.081 \\ u_1 &= 9.078 \\ \Delta u &= 0.0003 \\ G(u) &= 0.390 \end{aligned}$$

$$\therefore \sum_1 G(u_1^\ddagger) \Delta u_1^\ddagger = 1.17 \times 10^{-3}$$

The ratio of the rate constants is therefore

$$\frac{k_{\text{L}}}{k_{\text{H}}} = 1.009 \left[ 1 + (4.28 - 1.17) \times 10^{-3} \right]$$

From which the isotope effect for the thio-ether sulphur atom is calculated to be 1.013.

Isotope Effect for the Xanthate Carbon Atom in Mechanism II

Data for the initial state:

$$\begin{aligned} u_1' &= 5.364 & u_2' &= 3.751 \\ u_1 &= 5.208 & u_2 &= 3.683 \\ \Delta u_1 &= 0.156 & \Delta u_2 &= 0.068 \\ G(u_1) &= 0.313 & G(u_2) &= 0.254 \end{aligned}$$

$$\therefore \sum_1 G(u_1') \Delta u_1' = 6.61 \times 10^{-2}$$

Data for the transition state:

Effective mass term = 1.003

$$\begin{aligned} u_1^\ddagger &= 7.112 & u_2^\ddagger &= 2.520 \\ u_1 &= 6.953 & u_2 &= 2.454 \\ \Delta u_1 &= 0.159 & \Delta u_2 &= 0.066 \\ G(u_1^\ddagger) &= 0.357 & G(u_2^\ddagger) &= 0.186 \end{aligned}$$

$$\therefore \sum_i G(u_i^\ddagger) \Delta u_i^\ddagger = 6.91 \times 10^{-2}$$



$$\text{Therefore } k_V/k_H = 1.003 [1 + (6.61 - 6.91) \times 10^{-2}] = 1.000$$

The isotope effect for the xanthate carbon atom is therefore very close to zero per cent.

#### Isotope Effect for the Thion Sulphur Atom of Mechanism II

Data for the initial state:

$$\begin{array}{ll} u_1' = 3.751 & u_2' = 5.364 \\ u_1 = 3.732 & u_2 = 5.341 \\ \Delta u_1 = 0.019 & \Delta u_2 = 0.023 \\ G(u_1) = 0.256 & G(u_2) = 0.318 \end{array}$$

$$\sum_i G(u_i) \Delta u_i = 12.16 \times 10^{-3}$$

Data for the transition state:

$$\text{Effective mass term} = 1.003$$

$$\begin{array}{ll} u_1' = 2.52 & u_2' = 7.112 \\ u_1 = 2.50 & u_2 = 7.112 \\ \Delta u_1 = 0.02 & \Delta u_2 = 0.000 \\ \sum_i G(u_i) = 0.189 \end{array}$$

$$\sum_i G(u_i) \Delta u_i = 3.78 \times 10^{-2}$$



No term has been included in the transition state summation to account for the bond formation between the thion sulphur atom and the hydrogen atom. The corresponding value for this effect included in the calculation for the thio-ether sulphur atom, (as it was obtained directly from the use of Model II) was  $1.17 \times 10^{-3}$ . Although  $u_1^\ddagger$  itself was high for this term,  $\Delta u_1^\ddagger$  was very small, as is to be expected. The corresponding term in this case will be of the same order of magnitude and, therefore, affect the final result by only one or at the most two-tenths of a percent. Its omission does not result in a serious error.

The ratio of the rate constants is therefore,

$$\frac{k_L}{k_H} = 1.003 \left[ 1 + (12.16 - 3.78) \times 10^{-3} \right] = 1.011$$

and the isotope effect will be of the order of one percent.



Materials

Isobutyric Acid, Eastman Kodak white label.

Carbon Disulphide, Baker and Adamson, C.P. grade.

Bromine, British Drug House, Analar grade.

Methyl Iodide, Baker and Adamson, C.P. grade.

Propiophenone, Eastman Kodak white label.

Fuming Nitric Acid, British Drug House, Analar grade, sp. gr. 1.5.



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