

THE THERMAL ISOMERIZATION OF α -PINENE

A Thesis

Presented to the
Faculty of the Department of Chemistry
College of Arts and Sciences
University of Houston

In partial fulfillment
of the Requirements for the Degree
Master of Science

by
Patrick Yeager Howard

August 1970

545087

To my Parents,

Dr. and Mrs. Glenn T. Howard

ACKNOWLEDGMENT

The author would like to acknowledge Dr. M. Robert Willcott for his personal advice and financial support, the Robert A. Welch Foundation for its financial support and the NDEA Title IV Research Fellow program which donated finances for the great majority of the work contained herein.

Personal acknowledgements are too numerous to cover completely, but this paper would not have been submitted without the advice of Dr. Virgil H. Cargle and could not have been completed without the moral support and personal friendship of Mr. I. M. Rathburn, III.

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ABSTRACT

The kinetic and thermodynamic properties of the thermal isomerization of α -pinene have been examined. A stereospecifically deuterated α -pinene was synthesized and pyrolyzed. The positions of the label in the products were determined, and this information was used in formulating a mechanism for the pinene rearrangements. Arrhenius expressions for the thermal rearrangement of α -pinene to dipentene and allöcimene have been determined for rate data obtained from a stirred flow reactor. The new rates have been compared, in detail, to those determined in earlier studies and found to be similar, but not identical.

The pinene reaction is unimolecular and produces dipentene and allöcimene as primary products. It is not possible to construct a completely detailed mechanism from a review of all the available data. It has been found that the two primary products are not formed in two simultaneous independent reactions.

The report that pinene undergoes a thermal racemization has been disproved for temperatures less than 275°C.

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I.

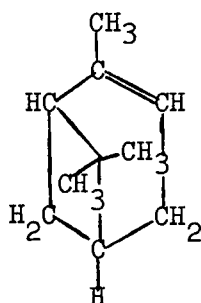
INTRODUCTION

INTRODUCTION

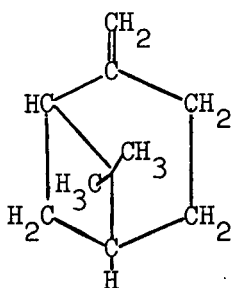
A. History of the Pinene Rearrangement

A review published in 1934¹ noted that pinene occupies a somewhat enviable position among the terpenes because its pyrolysis has been the most extensively studied (1). Assuming that the authors were correct, and a comprehensive review of terpene pyrolyses to that time indicates they were; it would seem most advantageous to discuss a few well-known facts about this extraordinary molecule.

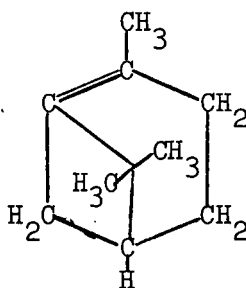
Pinene is a partially unsaturated, bicyclic terpene of empirical formula $C_{10}H_{16}$. It can assume any one of four geometrical forms, and each of these is capable of exhibiting some form of optical activity. The four isomers are shown below.



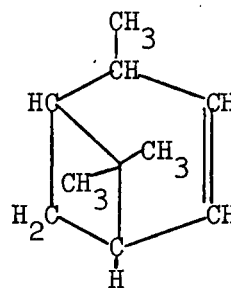
α -pinene



β -pinene



γ -pinene
unknown



δ -pinene
2-isomers

For centuries, a substance commonly referred to as turpentine has been used extensively by almost every advanced culture in the world and in an almost inconceivable variety of applications. It is an essential oil, found predominantly in trees of the spruce or pine variety. Records of its use extend from biblical times, in which it

is suspected that turpentine was rubbed on the skin and was purported to have certain medicinal properties, to the present, in which it is commonly used as a paint thinner and remover. This oil is almost always a predominant mixture of α -pinene complemented by a smaller percentage of β -pinene and other commonly occurring terpenes.

The fact that the thermal behavior of α -pinene has been so extensively studied might be attributed, then, to its natural abundance in turpentine. The average amount of α -pinene in turpentine ranges from 63% in Bordeaux (Pinus Maritima) turpentine, to 95% in Alpine (Pinus Halepensis) turpentine and constitutes about 71% of American (longleaf and spruce pine) turpentine. Additionally, α -pinene is almost always the more volatile (b.p. 156° at atmospheric pressure) constituent of turpentine and is, therefore, easily isolable by even the most rudimentary distillation methods.

A careful search of the literature reveals some 100 citations referring in one way or another to the pyrolysis of pinene. The earliest of these was performed by the noted Gay-Lussac and his assistant Lavi  re in 1841. It was found that pyrolysis of turpentine under extreme conditions gave certain less volatile and more volatile oils (2). This pyrolysis undoubtedly gave some thermal isomerization, but the main products in this experiment were due to decomposition rather than actual rearrangement of the pinene molecule. Gay-Lussac's work seems to be typical of much of the early experimentation, in which the pyrolysis of pinene (in the form of turpentine) was carried out under extreme conditions (turpentine was usually passed through red hot steel tubing

containing porcelain sticks)(3,4) and gave little or no thermal isomerization through rearrangement but yielded products from catalysis, cracking and decomposition, such as toluene, m-xylene, cumene, cymene, benzene, naphthalene, anthracene, methyl anthracene, phenanthrene and even some acetylene (5).

Actual reports of the rearrangement of α -pinene or turpentine under thermolytic conditions to give isomeric products make up only a small portion of the literature pertaining to the pyrolysis of pinene. Only these pertinent examples will be discussed throughout this paper.

Marcellin Berthelot, a French chemist, published an article pertaining to the action of heat on turpentine in 1853, which arrived at some remarkable conclusions concerning the rearrangement of α -pinene under thermolytic conditions (6). Citing work done by Regnault, in which turpentine changed to a liquid boiling around 300° when the starting material was boiled under many atmospheres of pressure and work done by Bouchardat, who found that by superheating turpentine, he could produce a change in its density, its odor and its ability to rotate light; Berthelot postulated that these observations appeared to be due to an isomeric transformation of the hydrocarbon. He further theorized that, in this particular case, the transformation presented a remarkable character, because the material was modified internally and passed, in its totality, to a new state, which was a type completely different, chemically, from the first. Since he could find no precedent for a reaction of this type, Berthelot undertook the task of determining

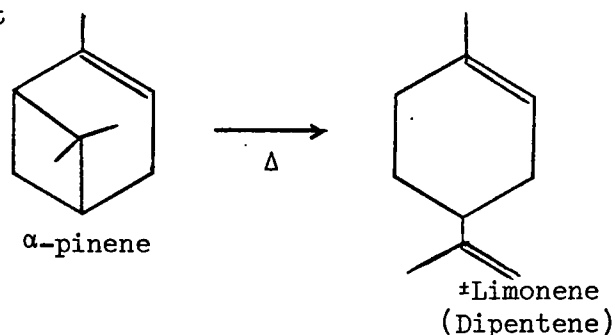
the exact temperature and heat intensity required for this transformation to successfully take place.

Berthelot's experiments were conducted in two ways. In the first, he refluxed samples of French, English and Swiss turpentine and looked at their optical rotations after times ranging from 1 to 60 hours. Since the rotations did not vary over any period of time, he concluded that no change in the turpentine resulted. A second series of experiments involved the heating of these same turpentines in sealed tubes at temperatures from 25 to 360° centigrade for times ranging from 1 to 60 hours. The results obtained from this set of experiments are fascinating indeed. At high temperatures and after several hours, all three turpentines had undergone changes in optical activity, density, boiling point and, to a certain extent, their chemical properties. Furthermore, he noticed that each of his oils required a different heating time and temperature before a change in the composition was noticeable. The most remarkable change was that of English turpentine, in which its optical rotation went from + to - after heating at 360° for 60 hours. Berthelot went even further with his work and found that he could separate a product boiling at 176-178°C, which he called isoturpentine. This was almost certainly a mixture of dl-limonene, commonly referred to as dipentene, which was later identified as one of the major rearrangement products of α -pinene. Though the credit for the isolation and discovery of dipentene as a product in the α -pinene rearrangement was given to another person some 25 years later, it seems incontrovertibly clear that Berthelot's work not only led the way to its discovery, but may have

even been unjustly neglected as the first evidence of dipentene formation from the thermal isomerization of pinene.

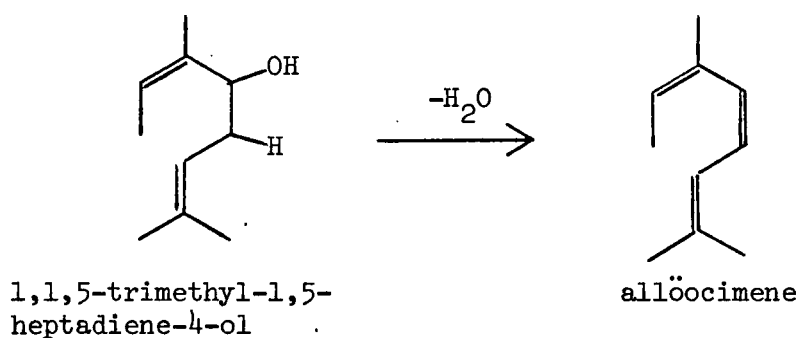
The next major contribution to the thermal isomerization of α -pinene came from a German chemist, O. Wallach (7), the "person" mentioned earlier, upon whom credit for the determination of dipentene as a product of the α -pinene rearrangement was bestowed. In obtaining his results, Wallach passed American turpentine through a steel tube heated from 250 to 270° and removed a fraction of the product which boiled from 175-185°. Through the careful use of halogenation and halohydrate techniques, he managed to arrive at an empirical formula of $C_{10}H_{16}$ for the hydrocarbon he had isolated. After redistillation of the product, its properties were compared with those known for dipentene and the molecule was thus identified. It is interesting to note that Mahood (8) duplicated Wallach's thermolysis in 1920 and found the same result.

By 1885, it was thus known that turpentine, a substance largely composed of α -pinene, could, on careful heating, rearrange to form a racemic mixture of limonene and some higher boiling materials. From a qualitative viewpoint, the story of α -pinene and its ability to undergo thermal isomerization seems to begin taking shape here, for it had been shown that

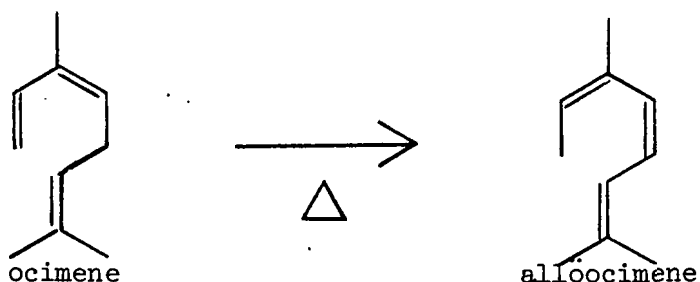


For the next 50 years, the qualitative examination of α -pinene and its rearrangement to isomeric products was neglected. To be sure, there were many instances in which the compound was altered catalytically, decomposed, and in general, subjected to the most violent chemical and pyrolytic techniques currently at hand; but no new isomeric products were identified until 1934.

In 1934, B. Arbusow performed a series of experiments in which he heated α -pinene to temperatures above 300° in the presence of a variety of catalysts, including copper, thorium and acetic acid (9). In a somewhat unobtrusive manner, he also decided to see what catalytic effect, if any, that glass might have on the thermolysis of pinene. After sealing α -pinene in a glass tube and heating it for several hours at 350° , he found unaltered α -pinene, Wallach's dipentene, and a third, higher boiling material (b.p. ≈ 193 - 195 @ 760 mm hg), having an extremely high refractive index. The refractive index was highly indicative of a $C_{10}H_{16}$ hydrocarbon known as allöocimene. From there, the identification was simple. Arbusow made allöocimene by dehydrating a previously prepared sample of 1,1,5-trimethyl-1,5-heptadiene-4-ol and compared its boiling point, refractive index and density with that of the product which he had isolated. In the final study, Arbusow found that ocimene

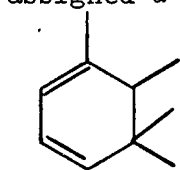
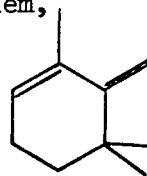


could be converted to allöocimene at the temperatures which he employed. This particular reaction, which will be discussed later in detail, has

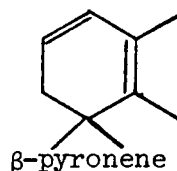


been referred to on occasion as being an intermediate step in the mechanism.

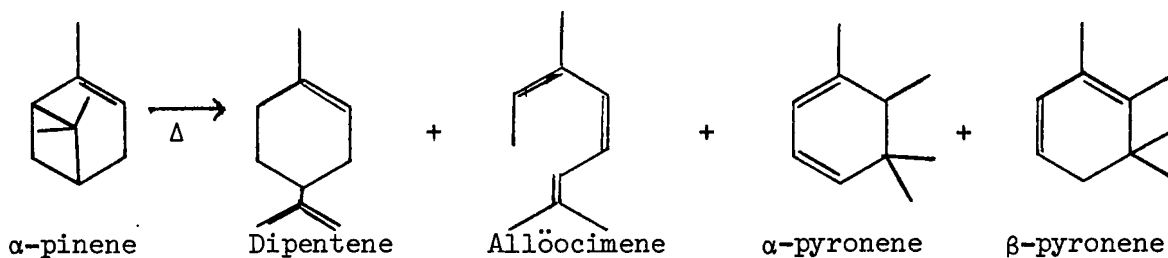
Only a very short time after Arbusow's allöocimene was shown to be a major product in the thermal isomerization of α -pinene, the package was neatly bound by the identification of two new isomers resulting from the pinene pyrolysis. These two constituents are scarcely worth mention and seem to offer no assistance in the elucidation of the pinene rearrangement but, nevertheless, can comprise up to 12% of the product mixture when the starting material is treated harshly enough. In 1935 Raymond Dulou and Georges Dupont used Raman spectroscopy to show the existence of two more isomeric structures in a mixture of pinene pyroly-
sate which had been treated in Arbusow's manner (350°C in sealed tubes and vapor phase) (10). They named the compounds pyronenes, for obvious reasons, and assigned α and β structures to them,

 α -pyronene β -pyronene

though it was later shown that β -pyronene actually has the structure



In summary, the isomeric rearrangement of pinene yields four major products. The concentrations of these vary with the thermal conditions which give rise to them. Generally, it is found that the formation of dipentene decreases with increasing temperature and that the formation of allöocimene and the pyronenes increases with increasing temperature (11). The most prominent products in the reaction mixture are always dipentene and allöocimene, with the pyronene concentration ranging from 0-5% at 250° for a short time in the vapor phase, to about 12% at 375° while flowing through a reactor at 250 g/hr (12).



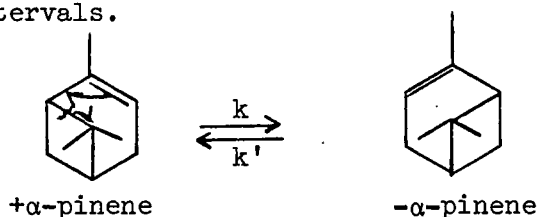
B. Kinetics of the Pinene Rearrangement

A comprehensive study of the rate of α -pinene rearrangement does not entail a great amount of reading. In short, α -pinene's rate of rearrangement at various temperatures has not been widely studied. Those studies which have been made were conducted in both the liquid

and vapor phases and will be discussed chronologically rather than by dependence upon what particular phase the authors chose to use for their experiments.

Only two unimolecular gas phase reactions had been recognized in 1927. Nitrogen pentoxide decomposed in the gas phase between 0-65° in a unimolecular fashion (13). The rate of thermal decomposition of sulfuryl chloride in the gas phase was presumably of the first order (14).

David F. Smith envisioned a third and more desirable reaction of this type - the vapor phase racemization of α -pinene (15). In a study proposed by G. N. Lewis, Smith postulated that optically active α -pinene should racemize in the vapor phase through the simple cleavage of one C-C bond and a corresponding rearrangement. Furthermore, Smith's model reaction would have equal forward and reverse rates and could be easily monitored by observing the optical activity of the mixture at various time intervals.



Since at every condition of equilibrium the concentrations of + and - pinene would have to be equal, Smith derived his method for determining the rate of pinene isomerization using the following considerations:

$$(1) K = k/k' = 1$$

Where K is the equilibrium constant and k and k' are the forward and reverse rates respectively.

$$(2) \frac{-dc}{dt} = kc - k'c' = k(c - c')$$

For the rate of decrease of concentration of $+\alpha$ -pinene where c and c' are the concentrations of $+$ and $-\alpha$ -pinene respectively at any time t .

$$(3) c' = c_0 - c + c'_0$$

If c_0 and c'_0 are the initial concentrations of $+\alpha$ -pinene and $-\alpha$ -pinene at any time t .

$$(4) \frac{-dc}{dt} = k(2c - c_0 - c'_0)$$

After substituting equation (3) into equation (2).

$$(5) \ln \frac{2c_1 - c_0 - c'_0}{2c_2 - c_0 - c'_0}$$

After noting that c_0 and c'_0 are constants for any given experiment and integrating equation (4) between the limits t_1 and t_2 .

$$(6) c_1 = c_0 - (c'_1 - c'_0)$$

At time t .

$$c_0 + c'_0 = c_1 + c'_1$$

$$(7) \ln \frac{c_1 - c'_1}{c_2 - c'_2} = 2k(t_2 - t_1)$$

After substituting equation (6) into equation (5).

$$(8) \ln \alpha_1 / \alpha_2 = 2k(t_2 - t_1)$$

Since the rotation at t_1 (α_1) is a measure of $c_1 - c'_1$ and the rotation at t_2 (α_2) is a measure of $c_2 - c'_2$.

Now, from the preceding derivation, it can be seen that equation (8) allows measurements of optical rotation at times t_1 and t_2 to produce the values of k .

Smith conducted his experiments under isothermal conditions in an oil bath and baths of constant boiling liquids. He sealed his samples under vacuum in glass tubes (this was apparently a first in the study of α -pinene thermolysis) and allowed them to sit for various lengths of time at temperatures ranging from 185 to 237°C. He also did ther-

molyses of α -pinene in different solvents, such as petrolatum, acetophenone and α -methyl naphthylene.

Smith's results showed an absence of wall catalysis in the vapor phase and comparable rates in both liquid and gas phase. Comparable rates were also obtained when concentrations were varied in the solvent solutions in either gas or liquid phase. These results indicated that the reaction was truly one of the first order. Heats of activation were calculated using T and the form of the Arrhenius equation,

$$Q = [RT_1T_2 \ln(k_{T_2}/k_{T_1})] / T$$

The best value obtained was 43.71 kcal.

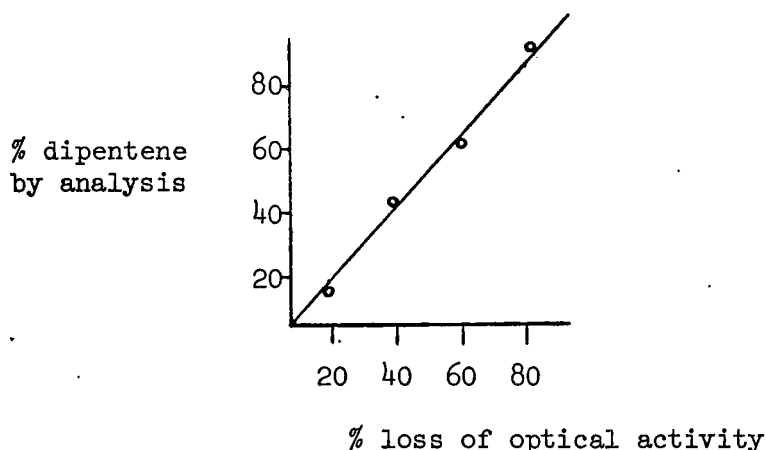
In summarizing his own work, Smith lays claim to the unprecedented discovery of a unimolecular racemization in the gas phase. He further states that the possibility of having formed isomeric products is negligible, hence the rates obtained were truly those for a simple racemization process. Table I gives Smith's values for the rate of α -pinene racemization at various temperatures.

From the amount of work which had been done concerning the thermal isomerization of α -pinene prior to 1927, it seems incomprehensible that Smith could have precluded the formation of isomeric products in his study. True, allöcimene had not yet been identified as a major rearrangement product, but the formation of dipentene, a racemic and optically inactive compound, from the pyrolysis of α -pinene had been known for years (6,7).

TABLE I
RATE OF α -PINENE RACEMIZATION AT VARIOUS TEMPERATURES

Temperature, 0°C	k value x 10 ⁵ min.
184.5	2.20
197.8	8.50
198.0	8.64
217.7	46.70
230.8	169.0
232.3	198.0
237.0	307.0

Using this fundamental knowledge of pinene behavior under thermolytic conditions, James Conant and G. H. Carlson, rather benignly, found Smith's work "inconclusive" (16). Two years after Smith's endeavor, Conant and Carlson postulated that he had not measured the rate of racemization of pinene but had, in fact, measured the rate of formation of dipentene from α -pinene. By heating α -pinene to $200 \pm 5^\circ$ in the vapor phase and plotting the percentage of dipentene present in the mixture versus the loss of optical activity in the mixture, they showed conclusively that their postulation was correct. Vacuum sealed tubes prepared in a fashion precisely analogous to that used by Smith were heated in order to obtain the points on their graph, which is shown below. The linearity of the points needs no explanation.



The year 1930 added two more significant contributions to the work done by Smith, Conant and Carlson. In a paper referring to attempts made at obtaining information concerning the 4 possible isomers of α -pinene, F. H. Thurber and C. H. Johnson found that the rate of decrease in optical activity differed in pinenes extracted from two different

oils (17). From these and other findings, they concluded that the rate of the reaction measured may be either the rate of racemization or the rate of rearrangement, depending upon which reaction is the slower. Shortly thereafter, Louis Kassel had a few important things to say pertaining to the thermal isomerization of α -pinene (18). Firstly, he was in agreement with the findings of Conant and Carlson and, therefore, called for an alteration in the rate values obtained by Smith. Since the reaction proposed by Smith was no longer feasible, his rate equation had to be altered by a factor of 2.

$$(9) \quad \ln \alpha_1 / \alpha_2 = 2k_1(t_2 - t_1) \quad \text{Smith's Equation}$$

$$(10) \quad \ln \alpha_1 / \alpha_2 = k_2(t_2 - t_1) \quad \text{Kassel's Equation}$$

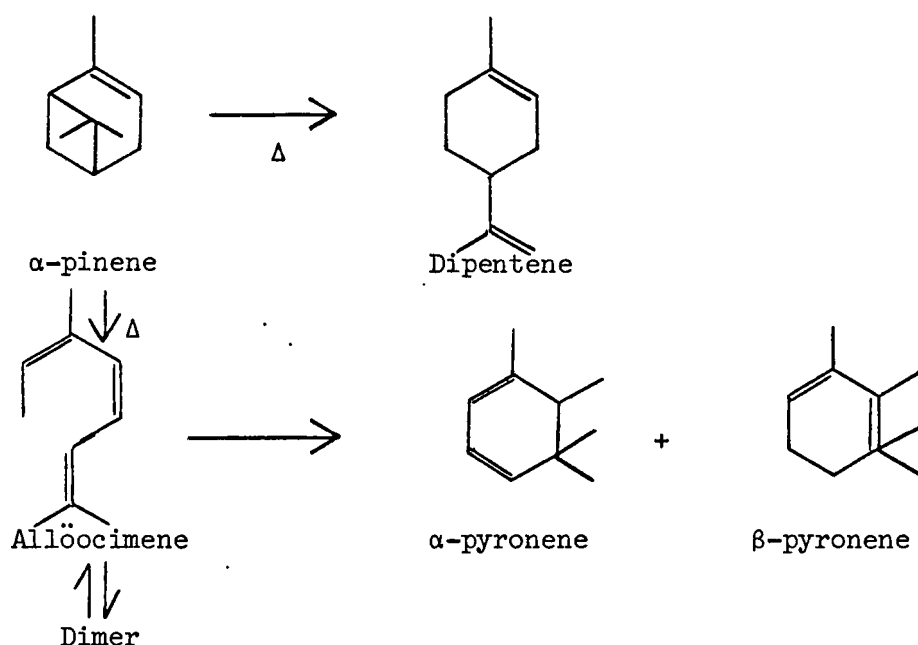
Kassel's logic in postulating his formula was that since the rates being measured were those of dipentene formation and not those of equal racemization rates, k_2 would be the overall rate of formation of dipentene and would be double the values obtained by Smith. In addition to his revision of Smith's data, Kassel stated his belief that the reaction could still be reasonably considered as occurring through a homogeneous unimolecular rearrangement. He further concluded that though the reaction no longer retained its theoretical simplicity, it was still the only known example of a presumably unimolecular rearrangement in the gas phase. Other reactions known to be first order in the gas phase were decomposition reactions.

This concludes a study of the work done toward determining the rate of the α -pinene rearrangement to dipentene, all of which was carried out before the formation of allöocimene and the pyronenes was recognized. Further rate studies and postulations came after the identification of these 3 isomers as products of the rearrangement.

Dupont and Dulou proposed a reaction sequence in which one step gave the α and β pyronenes while another step gave racemic limonene (10). According to them, allöocimene was formed simultaneously in a separate reaction. This was a qualitative treatment only and no actual reaction rates were measured. This type of study is included under the topic of "Kinetics," since no mechanism was proposed.

R. E. Fugitt and J. E. Hawkins published their first paper on the α -pinene rearrangement in 1945, and like those of Dupont and Dulou, their observations were of a qualitative nature (19). They heated vacuum-sealed tubes containing 94 ml. (80g) of α -pinene and made a quantitative determination of the products by distillation. Their findings agreed with those of earlier workers in that all four isomers were found in the product mixture from α -pinene thermolysis conducted at temperatures ranging from 190 to 285°C. Their significant conclusion was that dipentene and allöocimene are made in two separate side reactions and allöocimene goes on to form its dimer and the pyronenes.

Goldblatt and Savich confirmed these findings in the same year and found that they could be extended to the thermolysis of α -pinene in the liquid phase at much higher temperatures (11).



In 1947, Fuguitt and Hawkins furthered their work to give a quantitative interpretation of the rate constants involved in the pinene rearrangement. They used the same techniques employed in their 1945 study, even down to the sample sizes (94 ml) for pyrolysis. Their experiments were carried out by heating several samples for different lengths of time at 189.5° and following this with the heating of several more samples at 204.5°. Four rate constants were proposed for the rearrangement, with k' being the overall rate of isomerization of pinene, k_1 the rate of formation of dipentene, k_2 the rate of formation of allöocimene and k_3 the rate of racemization of α -pinene. Accordingly, the following formulas were used to determine the rate constants:

$$(11) k' = k_1 + k_2 = \frac{2.303}{t} \log \frac{a}{a-x}$$

Where a is the initial concentration of pinene and $a-x$ is the concentration at time t .

$$(12) k_3 = \frac{2.303}{t} \log \alpha_i / \alpha_t$$

Where α_i is the optical rotation of α -pinene prior to immersion in the heated bath, and α_t is the rotation at time t or after removal from the bath.

Table II shows the average rates obtained by Fuguitt and Hawkins in their study.

TABLE II
RATE CONSTANTS INVOLVED IN THE PINENE REARRANGEMENT

T°C	$k' \times \text{min}$	$k_1 \times \text{min}$	$k_2 \times \text{min}$	$k_3 \times \text{min}$
189.5	8.99×10^{-5}	5.96×10^{-5}	3.03×10^{-5}	9.3×10^{-6}
204.5	35.9×10^{-5}	22.9×10^{-5}	13.0×10^{-5}	4.2×10^{-5}

From this work, the authors concluded that the rate of racemization does not depend on the initial optical rotation of pinene. Furthermore, dipentene and allöocimene are alleged to be produced by simultaneous first order mechanisms. Finally, after calculating the energies of activation from the Arrhenius equation, Fuguitt and Hawkins claimed that the racemization of pinene requires the greatest energy of acti-

vation, and the thermal isomerization of α -pinene to dipentene requires the least energy of activation.

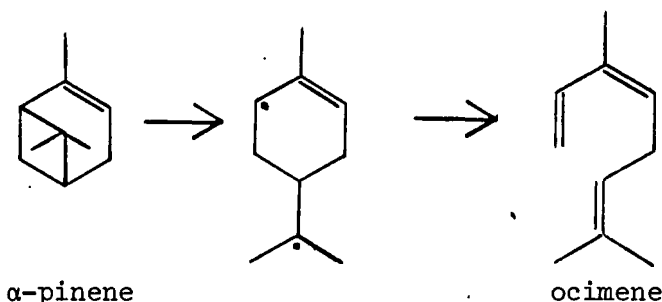
Currently, the work of Fuguitt and Hawkins seems to be the "last word," so to speak, concerning rate constants involved in the pinene rearrangement. More recent articles have referred to the mechanisms involved in attaining products, but quantitative accounts of rate studies are not prevalent in the literature.

C. Mechanism of the Pinene Rearrangement

It is often difficult to speak of mechanisms per se, without involving the inherent necessity of rate discussion. The actual attempts at postulating a mechanism for the pinene rearrangement have been few, and many of the papers mentioned earlier, which dealt with reaction sequences and rate studies, seemed to vigorously avoid mechanistic discussions. Ostensibly, the pinene rearrangement lends itself more readily to time trials than to photo finishes. Much of this stems, doubtlessly, from the precedents established in rate studies as opposed to those established for mechanistic exposition. Rate studies can be made according to long established paths of operation, which are of a general nature; while a detailed description of the mechanism involved in an elusive, unimolecular rearrangement such as that of pinene must be put together piece by piece from tidbits of knowledge gained in the mechanistic elucidation of similar rearrangements.

Perhaps the earliest mention of a mechanism for the pinene rearrangement occurred in 1935. In their book, The Aliphatic Free Radicals,

F. O. and K. K. Rice hinted that the most facile mode of rupture in the α -pinene molecule would be one in which a biradical was formed from rupture at the α -position (21). Such a cleavage, say the Rices, would lead to the formation of an isomeric molecule called ocimene.



The trouble with their theory, the authors freely related, was that earlier work had not been able to detect this terpene in pyrolysate of α -pinene. It was further mentioned that in pyrolyses involving cyclic compounds of this nature, two things could occur: either the elimination of molecular hydrogen to form a C=C bond or the rupture of a C-C bond to produce a bivalent radical which could decompose or rearrange easily into other molecules. The fact that Arbusow had pyrolytically rearranged ocimene to allöcimene the previous year (9) was not cited in their work.

William Mosher made a small contribution to the pinene rearrangement when he found that upon treatment with acid, both α and β pinene (see page 1) gave essentially the same products (22). This is to be expected, since both pinenes should result in formation of the same carbonium ion on protonation. Pyrolytically, however, β -pinene gives almost exclusively a terpene product called myrcene, while α -pinene

gives completely different results. From these facts, Mosher concludes that the pyrolysis of either α or β -pinene does not include a carbonium ion mechanism. His work was publicized in 1947.

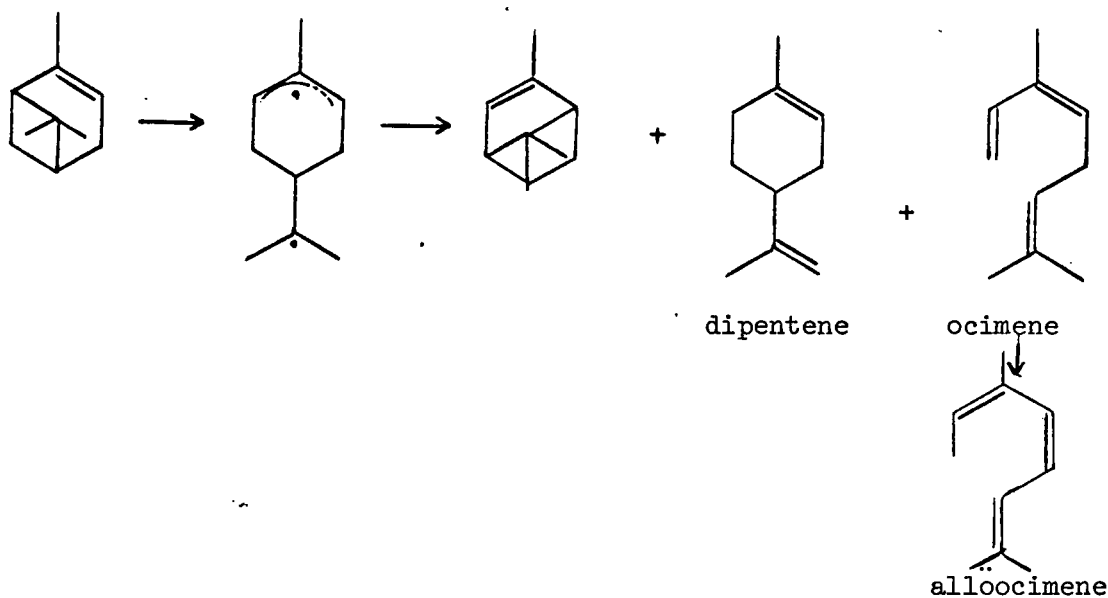
Three years later, Hunt and Hawkins (23) reacted α -pinene under conditions identical to those used by Fuguitt and Hawkins (2) in 1947, but modified the experiment by adding a proton donor (benzoic acid), an antioxidant (hydroquinone) and quinoline, a proton acceptor, to the pinene samples being thermolyzed. Using the rate formula from the Fuguitt and Hawkins paper, $k' = k_1 + k_2 = \frac{2.303}{t} \log \frac{a}{a-x}$, and employing the 204.5° temperature again, Hawkins and Hunt obtained the data in Table III. The obvious conclusion reached was that the presence of acid, base, or free radical inhibitor did nothing to alter the rate of the reaction. It also seems apparent then that the pyrolytic isomerization of α -pinene is not due to a carbonium ion, carbanion or free radical mechanism.

In spite of evidence refuting the possibility of a free radical mechanism, in 1951, R. L. Burwell published a paper which is still accepted in many circles as the elucidation of the mechanism for the pinene rearrangement (24). He suggests the formation of Rice's allylic biradical which can reclose to form racemic pinene, undergo a 1,5 hydrogen shift to produce dipentene and finally rearrange to form ocimene which subsequently rearranges to form allöocimene.

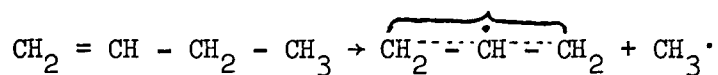
TABLE III

REACTION OF α -PINENE WITH THE ADDITION OF BENZOIC ACID,
HYDROQUINONE AND QUINOLINE

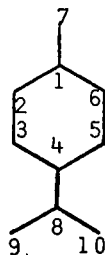
$k' \times \text{min}$	Substance added
3.3×10^{-4}	Nothing
3.4×10^{-4}	Quinoline
3.6×10^{-4}	Benzoic acid
3.4×10^{-4}	Hydroquinone



Burwell's argument considers the fact that even though the formation of isomers from α -pinene requires an activation energy of 41 kcal/mole (19) and the process:



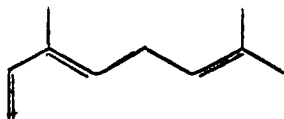
requires an activation energy of 62 kcal/mole (25), allowance for the strain in the cyclobutane ring of pinene lowers the latter figure to within the 41 kcal/mole range of the former. Also, considering the diagram below,



the 2-3 bond should not break as readily as the bond between carbons 2 and 8 because the latter forms a tertiary free radical and is, therefore, more stable.

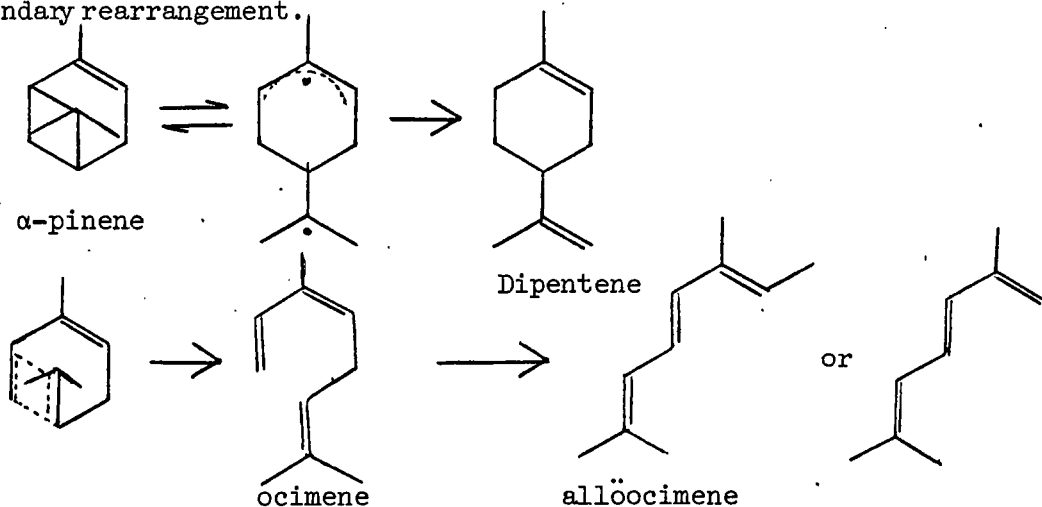
A few months following Burwell's article, Hunt and Hawkins released a publication supporting Burwell's mechanism by having shown that ocimene can indeed be formed from the thermolysis of α -pinene under carefully controlled conditions (26). It seemed apparent that in all previous experiments, the conditions had been too rigorous to allow any of the relatively unstable ocimene to remain in the pyrolysate. Arbusow (9) and Enklaar (27) were cited for having shown that ocimene rearranges to form allöcimene under thermolytic conditions. In their current work, Hawkins and Hunt had developed a method of allowing very short contact times for α -pinene at temperatures sufficient for rearrangement and obtained ocimene yields of 25% to 37%, depending upon the temperature at which rearrangement occurred. Of importance to the discussion of a mechanism for the pinene rearrangement is the fact that the authors assumed ocimene to be an intermediate in the rearrangement, which was not observed under ordinary pyrolytic conditions. The conditions at which pinene rearranges were apparently too high for ocimene to maintain its stability, and due to the rate of the reaction at these temperatures, ocimene would go quickly to allöcimene.

In 1962, Wolinsky, Chollar and Baird added some credence to Burwell's theory by showing that a 1,5 hydrogen transfer is involved in thermal isomerizations of 1,3 dienes in which a vinyl and alkyl group are cis to one another (28). Since α -ocimene is the ocimene allegedly produced in the α -pinene rearrangement, it easily falls into this category and a 1,5 hydrogen shift gives allöcimene.

 α -ocimene β -ocimene

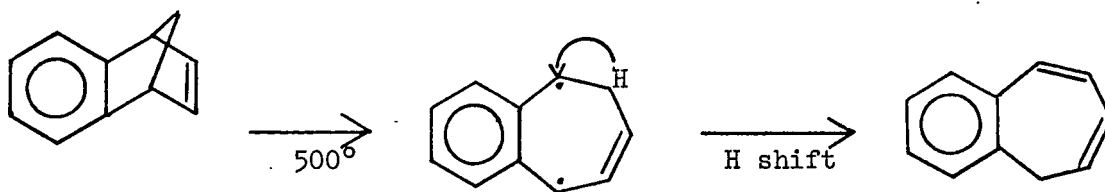
It has also been shown that at 400° α -ocimene is entirely transformed into a mixture of allöocimene and α and β pyronenes, while β -ocimene is stable at 450°C . It should be pointed out that though proof of a 1,5 hydrogen shift in thermal isomerization reactions enhances Burwell's theory, it can also give support to a mechanism entailing concerted thermal rearrangements for product formation.

Molecular Rearrangements, by Paul de Mayo, promulgates a slightly different mechanism for the pinene rearrangement (29). This version incorporates the advantages of both a concerted and biradical mechanism for the formation of pinene rearrangement products. In de Mayo's version, dipentene formation and racemic pinene formation purportedly arise from the formation of a biradical, while allöocimene stems from the concerted rearrangement of α -pinene to form ocimene which undergoes a secondary rearrangement.



A fairly recent summary of work done concerning the α -pinene rearrangement stated that all results point to Burwell's biradical mechanism, but concerted electronic reorganization cannot be ruled out (30).

The wide acceptance of Burwell's theory led other chemists to propose similar biradical mechanisms. Among these proposals was that of Cristol and Capel which stated that benzonorbornadiene undergoes the formation of a biradical intermediate which gives rise to product through a hydrogen shift (31).

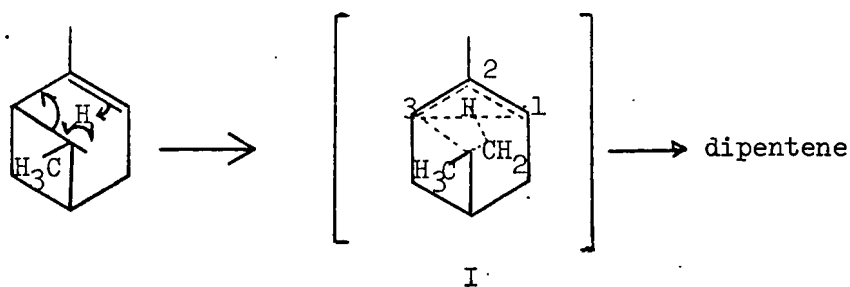


Their entire proposal was based on Burwell's theory.

Up to this time, the incompatibility of Burwell's theory with the findings of Hunt and Hawkins concerning the lack of rate diminution when rearrangement took place in the presence of a free radical inhibitor had not been questioned.

The most recent publication pertaining to this lack of agreement was made by Bochwic and Kapuscinski (32). They speculated that free radical catalysts should enhance the rate of the reaction, while free radical inhibitors should lower the product yields, if Burwell's mechanism was, indeed, the correct one. Their experiments showed that free radical catalysts (benzoyl peroxide, tert-butyl peroxide and azodiiso-

butyric nitrile) did not enhance the reaction, while free radical inhibitors (hydroquinone, diphenylamine, tetraphosphorous trisulfide and pyridine) did not slow the reaction down appreciably. Neither the catalysts nor the inhibitors appeared to affect the yield of dipentene from the thermal isomerization of α -pinene at 198° after 14 hours of heating. The authors further conclude that since the net gain in energy when dipentene is formed is 8.3 kcal/mole, and the energy of activation for this reaction is 36.1 kcal/mole, a biradical mechanism is improbable because such a small net gain in energy could not lead to the difference between 62 kcal/mole for the allylic radical formation from 1-butene as compared to the 36.1 kcal/mole activation energy required for pinene rearrangement. From these and considerations found in earlier literature, Bochwic and Kapuscinski propose a polycentered reaction for the rearrangement.



The first step in the reaction involves formation of the polycentered transition state (I) which can subsequently be transformed in two alternative ways. The first leads to + limonene, and the second leads to - limonene, thus giving rise to dipentene because neither direction is favored. If the hydrogen of carbon 9 goes to carbon 1

in the transition state, one limonene isomer is formed, while if the same hydrogen goes to carbon 3 in the transition state, its racemate is formed.

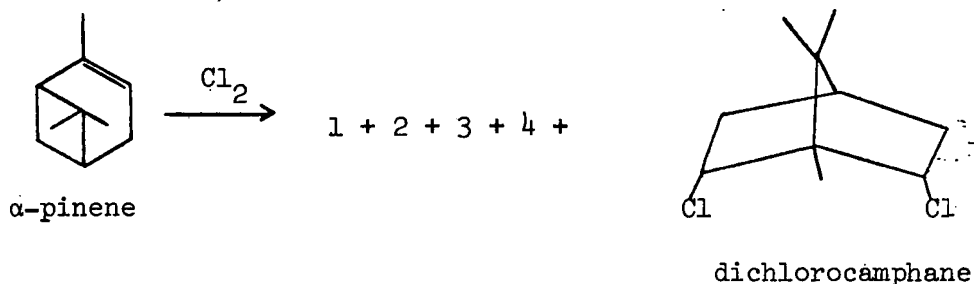
This discussion of mechanistic studies involving the rearrangement of α -pinene seems to at least partially discount the theory of a biradical mechanism, but, paralleling this, is the formidability of a polycentered transition state involving a heretofore unrecognized species. The work done up to this time seems, at best, to have many discrepancies and can, therefore, only be referred to as inconclusive. The biradical approach is effective for the explanation of the observed products, but seems to have been discounted in the experiments with free radical catalysts and inhibitors. The polycentered transition state, involving extremely complex bond-making and bond-breaking processes having at least a dual nature also seems unlikely and provides no mechanism for allöocimene formation.

II.
RESULTS

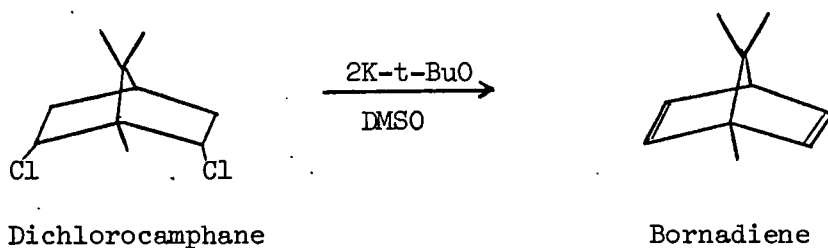
RESULTS

A. Chloropinene

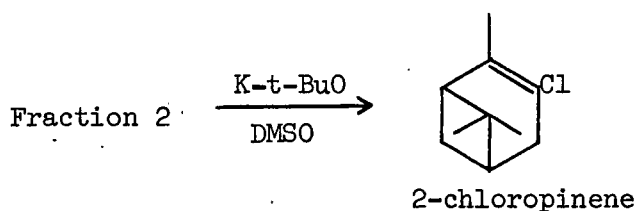
Dichlorocamphane was synthesized by chlorination of α -pinene. Distillation of the reaction mixture gave five fractions, the fifth and highest boiling of which was later identified as dichlorocamphane. At first, however, the second fraction was assumed to be the dichlorocamphane because it distilled in larger quantities at constant temperature.



Since fraction 2 was assumed to be dichlorocamphane, and the synthesis of bornadiene from this compound was the ultimate reason for its synthesis, this fraction, rather than the fifth, was initially to be used as the precursor for bornadiene. For these reasons, fraction 2 was treated with potassium tert-butoxide in dimethyl sulfoxide and the product constituents were extracted from the mixture.



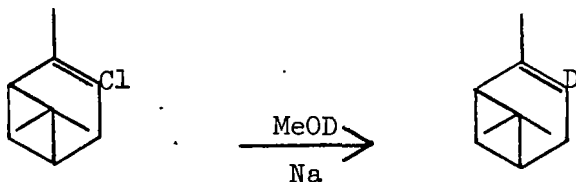
Analysis of the reaction products on a gas chromatograph showed no volatile hydrocarbons to indicate the presence of bornadiene, but when compared with a chromatogram of the starting material, showed a new peak having a retention time similar to that of α -pinene. Furthermore, bornadiene is a solid and no solid was found in the reaction mixture. The compound which gave rise to the new peak was isolated and its NMR spectrum was obtained. The NMR showed absorptions similar to those of α -pinene, but a proton in the olefin region was not apparent. When the sample was prepared neat, IR bands at 880 and 760 cm^{-1} showed chlorine in the molecule. Subsequent reduction of the product from fraction 2 by using sodium in methanol produced α -pinene. From this, it was concluded that treatment of fraction 2 from the dichlorocamphane synthesis with potassium tert-butoxide in dimethyl sulfoxide had produced 2-chloropinene.



B. Deuteropinene

The availability of chloropinene led the way to the synthesis of deuteropinene. Initially, a 10% solution of chloropinene in methanol was treated with a freshly prepared sodium dispersion. Products were analyzed on a gas chromatograph and a peak having the same retention time as α -pinene was observed. A sample of this peak was collected

and used to obtain an NMR spectrum which was compared with another spectrum for pure α -pinene and found to be identical. Synthetic conditions were varied until optimum yields of pinene could be obtained from chloropinene. Using these conditions, chloropinene was treated with deuterated methanol in a sodium reduction and produced deuteropinene. The deuteropinene was identified by an NMR spectrum which showed a complete lack of absorption in the olefin region while other peaks were essentially identical to those given by α -pinene.



Following the synthesis of deuteropinene, a mixture of pure pinene in pentane was thermolyzed in the vapor phase at 275° for 10 minutes to give about 50% conversion of pinene to products. The pyrolysate from this experiment contained α -pinene, dl-limonene and allöcimene. These compounds were identified by first isolating samples of each from the pyrolysate through gas chromatography and then comparing their individual NMR spectra with those for the known molecules.

A sample of deuteropinene was next pyrolyzed under identical conditions and NMR spectra were made of the pinene-d before and after pyrolysis. The two spectra were identical and neither showed any significant absorption in the olefin region. The experiment was repeated using approximately twice the original exposure time at the same temperature. Again, NMR spectra of D- α -pinene were made before and after pyrolysis,

and a spectrum of dipentene (or limonene) obtained from this pinene-d pyrolysate was also taken. The deuteropinene taken from pyrolysate again showed no significant absorption in the olefin region. The spectrum of dipentene, however, did show significant absorption in the olefin region. No comparisons of NMR spectra were made between pure allöocimene and that obtained through pyrolysis of D- α -pinene.

C. Pyrolysis of α -Pinene in a Flow Stirred Reactor

Samples of α -pinene were passed through a heated flow system at four different temperatures. At each temperature, the flow rate was varied over a wide range, and at all four temperatures rearrangement of α -pinene to dipentene and allöocimene occurred. Nitrogen gas was used to carry vapor samples of α -pinene through a carefully controlled heated reactor at the various flow rates.

Samples of pyrolyzed α -pinene were tested for optical activity at each temperature and their rotations compared with that of the pinene used before pyrolysis. The table below gives the observed results, where α_i is the rotation before pyrolysis and α_F the rotation after pyrolysis. It should be noted that those values for α_F obtained at temperatures above 272.3 show some racemization, while α_F values obtained at 247.3 and 272.3°C deviate from each other only negligibly. The lack of racemization at lower temperatures is contiguous with the lack of deuterium scrambling observed under similar conditions.

Rates of formation of dipentene and allöocimene from 1- α -pinene were obtained in the usual manner for flow systems (see Experimental).

TABLE IV

OPTICAL ACTIVITY AND ROTATIONS OF SAMPLES BEFORE AND AFTER PYROLYSIS

Temperature	% of unreacted α -pinene in pyrolysate	Flow rate in ml/sec	α_i	α_F
247.3	70.0	.121	48.90	48.98
272.3	53.5	.223	48.90	47.35
282.3	35.8	.200	48.90	38.88
, 306.2	4.5	.085	48.90	8.90

Similarly, rates for the total rearrangement of 1- α -pinene were obtained. These rate constants, determined at 247.3, 272.3, and 282.3° centigrade, were all found to fit the Arrhenius equation in the following form:

$$k = Ae^{-E_a/RT}$$

and

$$k_D = (9.6 \times 10^{10})e^{-\frac{34,700 \text{ cal/mole}}{RT}} \quad \text{for the formation of dipentene}$$

$$k_A = (9.3 \times 10^{12})e^{-\frac{39,800 \text{ cal/mole}}{RT}} \quad \text{for the formation of allöocimene}$$

and

$$k_T = (9.9 \times 10^{13})e^{-\frac{41,600 \text{ cal/mole}}{RT}} \quad \text{for the overall rate of pinene rearrangement}$$

III.

DISCUSSION

DISCUSSION

The chemistry of pinene, which is the subject of this thesis, can be conveniently discussed in three parts. The first section will be concerned with the comparison of the reactions of 1- α -pinene and deuterio- α -pinene. After the qualitative aspects of the reactions have been discussed, the kinetics derived in this work will be compared with all reported kinetics and the extent of agreement will be pointed out. Finally, in the third section, a mechanism for the rearrangement will be presented and discussed in light of the known chemistry of α -pinene.

Throughout this discussion, the necessity for referring to earlier work is indispensable but may introduce some confusion. The main points to be made, however, are contained in the following material, and it would be well to point them out now, prior to their reiteration in the remainder of this section.

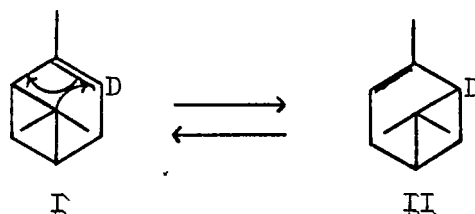
The purported racemization of α -pinene has been discounted for temperature below 275°C. This has been shown through deuterium scrambling techniques as well as through high precision, optical rotation studies. The data obtained in the low temperature deuterium scrambling experiment is well supported by the observations made in the optical rotation studies. The suspected production of limonene in its racemic form from the pyrolysis of α -pinene has been proven factual by the same deuterium scrambling techniques mentioned earlier, as well as by high resolution optical activity determinations. Activation energies obtained for the formation of individual isomers as well

as for total isomerization compare favorably with earlier work. But, as will be shown, all of these values are significantly below the predicted energies for rearrangement of α -pinene.

A. Thermolysis of α -pinene and α -pinene-2-d

Rate studies of the pinene rearrangement were not attempted using deuterated α -pinene as the starting material. Therefore, a discussion of internal agreement between the results obtained in the thermolysis of deuterated pinene and those acquired by thermolysis of 1- α -pinene must compare racemization (1- α -pinene) with deuterium label scramble (α -pinene-d). The optical activity of 1- α -pinene after pyrolysis and label scrambling in deuterio-pinene compared under similar conditions.

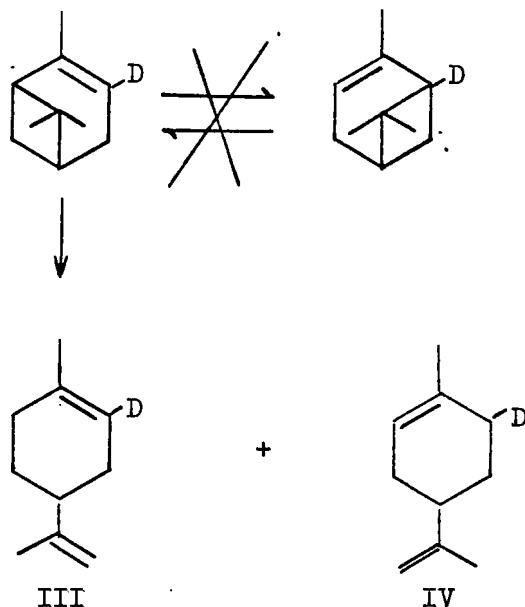
Several significant facts arise from the thermolysis of α -pinene-d. When the compound was heated for ten minutes at 275°C, the recovered pinene-d showed no absorption in the olefin region of the NMR spectrum, thus ruling out the reaction shown below.



Arguments pertaining to this rearrangement are based entirely on the fact that deuterons show no absorption in the proton NMR region. Hence, the NMR of the starting material (I) showed no detectable

absorption in the olefin region, indicating at least 98% isotopic purity for the α -pinene labeled with a deuteron at the olefin position. Compound II, on the other hand, would give an absorption corresponding to 1H in the olefin region but would show no resonance for the bridgehead proton. Between these two extremes lies the possibility of a 50:50 mixture of I and II, which would result if complete racemization of the starting material had occurred. From these considerations, it is clear that if the starting material (I), which shows no absorption due to a proton at the olefin position, had been racemized on thermolysis, an absorption having at least a measurable intensity would have appeared in the olefin region. The consequence of this statement is particularly important when the work of earlier chemists, which showed high degrees of racemization at much lower temperatures than those employed here (though the exposure times were quite lengthy) is considered. The fact that no olefin absorption was observed in α -pinene-d taken from the pyrolysate seems to show conclusively that no racemization occurred under the conditions employed for this pyrolysis of α -pinene-d.

The results obtained from a second thermolysis of α -pinene-d in which the exposure time was lengthened to 20 minutes were even more enlightening. In this case, dipentene was removed from the pyrolysate along with unreacted deuterio-pinene. The pinene-d again showed no absorption in the olefin region. An NMR spectrum of dipentene, however, did show significant absorption in the olefin region.



The ultimate results of the second thermolysis of deuterio-pinene show conclusively that one of the products formed when α -pinene is heated is, as has been noted, dipentene and not limonene. From the same considerations used to discuss the first thermolysis of α -pinene-d it is evident that the appearance of one-half a proton signal in the olefin region accompanied by an absorption in what had formerly been the bridgehead position in the NMR spectrum of the product indicates that an equal amount of compound IV is mixed with compound III, and the product is, indeed, dipentene and not a single optical isomer of limonene.

The results obtained from the pyrolysis of l- α -pinene in a stirred flow reactor were in perfect accord with those obtained from the thermolysis of deuterated α -pinene. Polarimetric investigations showed essentially no change in the optical activity of recovered l- α -pinene after thermolysis at 247.3 and 272.3°C when compared with its optical activity before pyrolysis at either temperature. A

*The fact that optically pure III or IV is called limonene, when the deuterium is replaced by a proton, has been mentioned before. Similarly, it has been noted that dipentene is the name given to a racemic mixture of the optically active limonenes.

measurement of the optical activity of dipentene collected from a 272.3° portion of pyrolysate showed a high degree of racemization (90%) and added further support to the results obtained when dipentene was removed from the pyrolysate of pinene-d and studied.

Briefly, but conclusively, a summary of the results obtained from the thermolyses of optically active α -pinene and deuterated α -pinene shows that the two pyrolyses give analogous results and that under the conditions at which these experiments were conducted, α -pinene does not itself racemize but can rearrange to a racemic mixture of limonenes.

B. Kinetics of the Reaction

The literature gives only three cases where rate constants involved in the pinene rearrangement have been calculated at various temperatures. The most recent of these (2) involved rate determinations at only two temperatures. This work, which was performed by Fuguitt and Hawkins in 1947, was used to draw graphs (which were, naturally, straight lines) in order to determine frequency factors and activation energies. Before this work, the rates of pinene isomerization over a range of three temperatures had been calculated for what another author fervently believed to be two different isomers of d- α -pinene (17). This belief was apparently so strong that he arrived at two sets of rate constants for each temperature, each constant differing by a factor of 4 from the other, and each allegedly from a different kind of d- α -pinene. Since it was impossible, even after the most careful scrutinization of his article, to determine which set of rate constants

applied to the thermal isomerization of α -pinene being discussed here, his results were ignored. The second set of rate constants employed herein were those obtained by Smith (15) for the rate of racemization of α -pinene, and they were used only after correction by Kassel's (18) factor of two. It was further assumed that Smith's constants had to be those for the total rearrangement of α -pinene, rather than those for racemization or dipentene formation, since allöocimene, a product which Smith was not aware of at the time of his publication, also exhibits no optical activity. Smith's rate constants were all determined by measuring the loss of optical activity of α -pinene after various lengths of time at different temperatures.

The bulk of our work in this area consisted of using the rates found from the pyrolysis of 1- α -pinene in the stirred-flow reactor to determine the pre-exponential or frequency factor, A, and the energy of activation, E_a , for use in the Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}}$$

This equation was then used to calculate the rates which should have been observed at the temperatures used by earlier workers. In addition, the reverse process was carried out and rates found by the early workers were used to determine energies of activation and A factors from their data, and these, in turn, were used to calculate rate constants for the temperatures used in the stirred-flow reactor pyrolyses. Following these calculations, comparisons of all results were made.

When the kinetic data obtained from the pyrolyses of 1- α -pinene in the stirred-flow reactor was used to calculate the rates which should have been observed by Fuguitt and Hawkins, the workers who made the most recent set of rate determinations at only two temperatures, the results deviated rather markedly in some areas. Using the A factors and activation energies obtained from our results to calculate rates expected at the temperatures used by Fuguitt and Hawkins, it was found that dipentene should have been formed four times faster under their conditions; allöocimene should have been formed three times as fast, and the over-all reaction should have occurred about one and a half times as quickly (see Experimental).

Similar parameters obtained from Fuguitt and Hawkins' data were used to calculate expected rates at our temperatures, and it was found that their predictions showed rates of about 1/2 of those which were observed in the laboratory for the three cases described above at three different temperatures (see Experimental).

Energies of activation obtained from the flow system data and the data of Fuguitt and Hawkins were next compared, and it was found that dipentene required 3.5 more kilocalories per mole in their studies, allöocimene required 1.6 more kilocalories per mole according to their data, and the over-all reaction required 2.3 kcal/mole less in their studies than in those made using the flow system. Note that Fuguitt and Hawkins show a greater energy of activation for the formation of allöocimene than for the entire reaction itself. Such an observation could only be possible if dipentene and allöocimene were being formed

in two simultaneous but completely independent reactions. Their evidence seems to preclude any relationship between the formation of dipentene and the formation of allöocimene from the thermolysis of α -pinene. The energies of activation obtained from the flow system show dipentene to have a lower energy of activation than the over-all reaction (see Experimental). This evidence may point to an interdependence or intermediate in the formation of the two major products.

Frequency factors and activation energies from our data were used to predict rates at three temperatures used by Smith, and the results showed our predicted values for the total reaction rate to be about twice those observed by Smith (see Experimental).

Insertion of the above factors obtained from Smith's data into the Arrhenius equation predicted rates of total product formation at our temperatures to be about a half of those which were actually obtained from the flow system (see Experimental).

When Smith's energy of activation was compared to the energy of activation for the total pinene rearrangement obtained in the lab, it was found that his was the greater by about 1.2 kcal/mole.

The rate comparisons made in this study are significant in that those rates obtained from the flow system are greater in every case than those found by the earlier workers. The discrepancy between our results and those obtained by Fugitt and Hawkins can largely be discounted due to the fact that their work was done entirely in the liquid phase, and the temperatures at which their work was done were time averages rather than actual constant temperatures, since they did

not have the degree of temperature control which can be obtained today. This second argument can be extended to the work done by Smith, in which his temperatures were obtained from an oil bath and from solutions of refluxing liquids, even though his pyrolyses were carried out in the vapor phase. When these facts are taken into consideration, the results obtained from the flow system agree quite favorably with the earlier work. Since the type of temperature control exercised in the flow-system pyrolyses was accurate to within .01 degrees, and the very nature of the system itself subjects it more readily to rate studies, it seems most plausible that the rates and energies of activation obtained from this system are highly reliable, particularly when compared to those obtained by less accurate methods in the earlier work.

The values obtained for the various energies of activation through the use of the flow system also seem to compare quite favorably with the early work. In both the laboratory work and in the work of Fuguitt and Hawkins, dipentene had the lowest energy of activation, even though that determined in the laboratory was by far the lower of the two. The two energies of activation for the formation of allöcimene also compared favorably in that they differed by only 1.5 kcal. When all three energies of activation for the total rearrangement of α -pinene are compared, the value found by Fuguitt and Hawkins appears to be a bit low, but the energy of activation determined from the flow system differs from that calculated using Smith's data by only a kilocalorie.

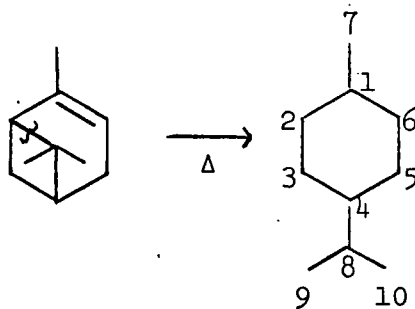
Finally, the series of experiments performed for this paper indicate that the reaction is one of the first order, since the concentrations of products at the same temperature and flow rate do not change when the vapor pressure of the starting material is varied by heating α -pinene (20-60°C) prior to introducing it into the heated reactor. This too shows strong agreement with the postulations of Smith as well as with those of Fuguitt and Hawkins.

With all kinetic aspects being considered, it appears that the rates of product formation and resultant energies of activation obtained from the data produced by the stirred-flow reactor are quite in keeping with information obtained earlier in these areas and may even be slightly improved.

C. Mechanism of the Reaction

Though the work performed for this paper can not fully elucidate the mechanism for a reaction which is, as will be shown, of a highly complex nature, it is believed that a significant contribution can be made toward explaining the ultimate process involved in the formation of products from the thermolysis of α -pinene.

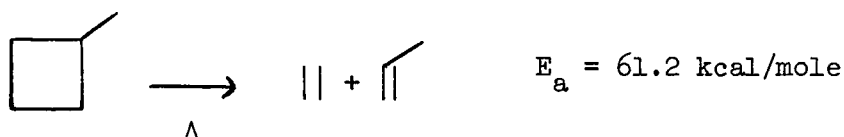
The most important step to be considered in the pinene rearrangement is the cleavage of the carbon-carbon bond between positions 2 and 8, regardless of the manner in which this cleavage is attained, and perhaps the best approach to a discussion of this step is a description



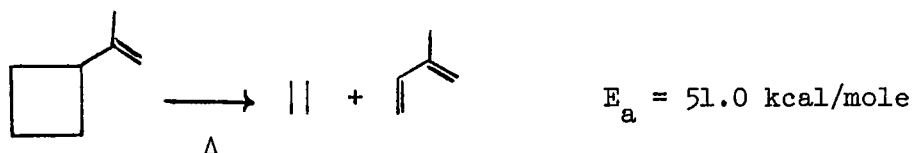
of activation energies required for such a cleavage. In cyclobutane, an activation energy of 62.5 kcal/mole is required to form 2 moles of ethylene (33).



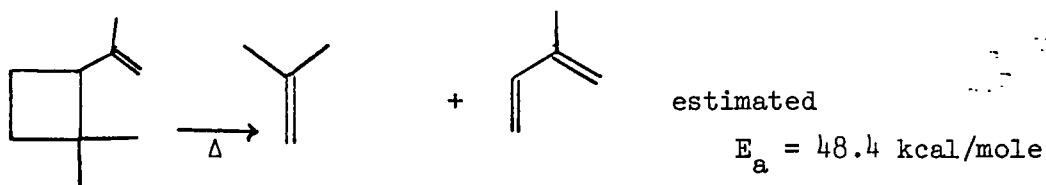
This energy is lowered by about 1.3 kcal/mole when one methyl group is found on the ring (34).



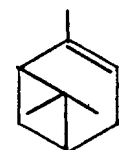
If the cyclobutane ring is substituted with an isopropenyl group, the energy of activation is lowered even further (35).



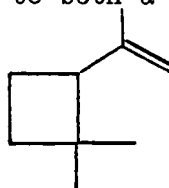
If an allowance of 1.3 kcal/mole for each methyl group is made, then 1-isopropenyl-2,2-dimethyl cyclobutane would be expected to require $51.0 - 2.6 = 48.4$ kcal/mole for cleavage.



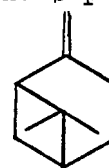
This compound is clearly analogous to both α -pinene and β -pinene.



α -pinene

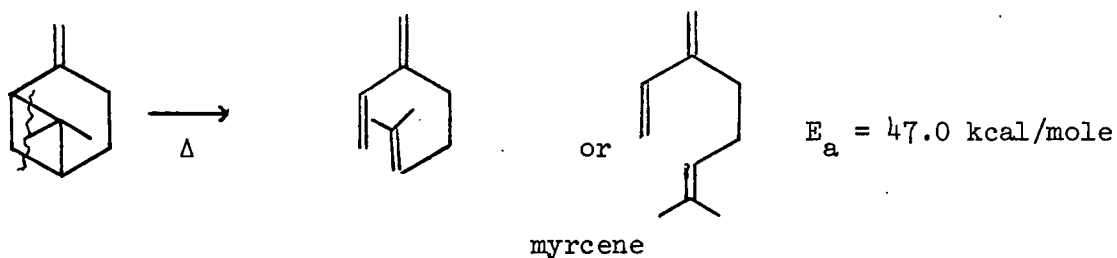


1-isopropenyl-
2,2-dimethyl
cyclobutane



β -pinene

It is reasonable to expect that the energy of activation in breaking these cyclobutane rings stems almost entirely from cleavage of the first bond (between the 2 and 8 carbons), while the second bond breaks quite readily. The energy of activation for the formation of myrcene from β -pinene has been found to be 47.0 kcal/mole (15), and agrees remarkably well with the predicted value of 48.4 kcal/mole.



If the rate determining step in the rearrangement of α -pinene requires breakage of the C-C bond between the 2 and 8 positions, then a similar activation energy should be seen, regardless of whether the next step is reformation of racemic pinene (15), formation of dipentene (24) or

formation of ocimene (20). Since the flow system showed no racemization of pinene at lower temperatures, the first possibility can be ruled out. The formation of ocimene under the conditions used in the flow system is suspected but the compound was not found in any pyrolysate samples, so the discussion may now be limited to the case of dipentene formation, for which energies of activation have been determined.

Standard manipulations of the data obtained by Fuguitt and Hawkins gave an energy of activation of 38.2 kcal/mole for the formation of dipentene from α -pinene. Identical treatment of data obtained from the flow reactor showed an energy of 34.7 kcal/mole required to form dipentene. Neither of these figures even approaches the predicted 48.4 kcal/mole. Energies of activation for the total rearrangement of α -pinene are only slightly better when compared to the theoretical 48.4 kcal/mole activation energy. The data of Fuguitt and Hawkins determines a value of 39.3 kcal/mole for the overall reaction; Smith's data yields 42.8 kcal/mole when treated similarly, and the flow reactor gives a value of 41.6 kcal/mole for the energy necessary to cleave the C-C bond between positions 2 and 8.

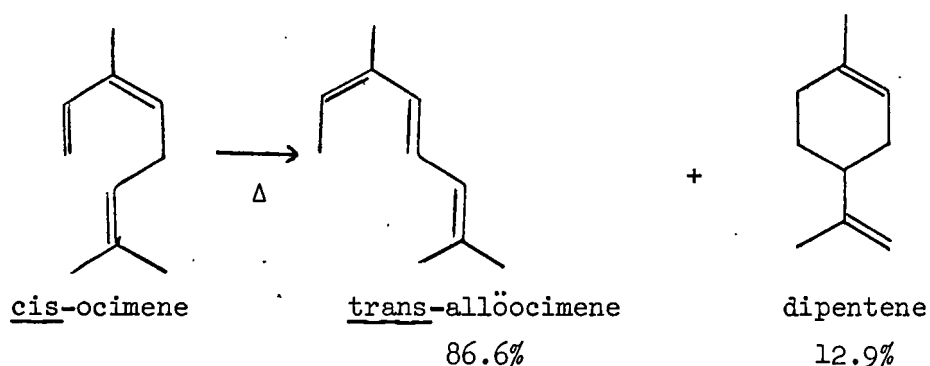
Certainly other considerations might be made with respect to α -pinene in order to further lower the predicted activation energy for cleavage of the C-C bond between the 2 and 8 positions, but one would find it difficult to produce legitimate thermodynamic principles to explain the extraordinarily low amount of energy required for the formation of dipentene.

From our results, it is apparent that more is involved in the mechanism for the rearrangement of α -pinene than a cleavage of the bond between carbons 2 and 8 in the first step followed by simple reactions leading to product formation.

Regarding the work done by Bochwic and Kapuscinski (32), in which a poly centered intermediate is formed, the first step requires cleavage of the 2-8 carbon to carbon bond and is not so unconventional as the entire mechanism would make it seem; but the complicated and unprecedented intermediate formed from such a cleavage can serve to rule this type of mechanism invalid.

The formation of a diradical transition state can not be ruled out due to earlier experiments involving the addition of free-radical catalysts and inhibitors. If a diradical is formed in the first step of the pinene rearrangement it may have a very short lifetime. Since the rearrangement involves a molecule which can undergo rapid internal rearrangement, it is quite possible that free-radical catalysts and inhibitors would have difficulty in intercepting the diradical and would, therefore, show no effect on the rate of the pinene rearrangement.

Among other possibilities for the mechanism occurring in the pinene rearrangement is the formation of ocimene in a first step, even though the preceding discussion seems to have ruled this out. A pyrolysis of cis-ocimene gave trans allöocimene as the major product and only a small portion of dipentene at the same conditions used for one pyrolysis of α -pinene in which a large amount of dipentene was produced along with about half as much allöocimene.



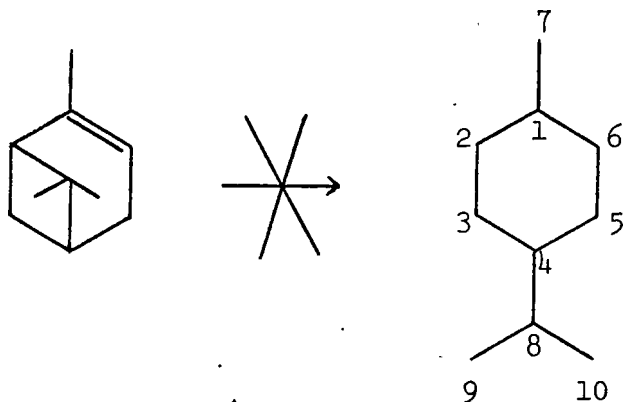
This experiment rules out the possibility of ocimene being formed as the sole intermediate in the first step, since pyrolysis of ocimene under conditions at which α -pinene gave large amounts of dipentene should also have given considerable amounts of the compound.

Another vital question concerning the α -pinene rearrangement has been that of the reaction sequence. Almost all early workers believed that dipentene and allöocimene were being formed by two simultaneous but completely independent paths (10,11,19,20). If these postulations were correct, then the ratio of dipentene concentration to allöocimene concentration would be expected to remain constant at a given temperature.

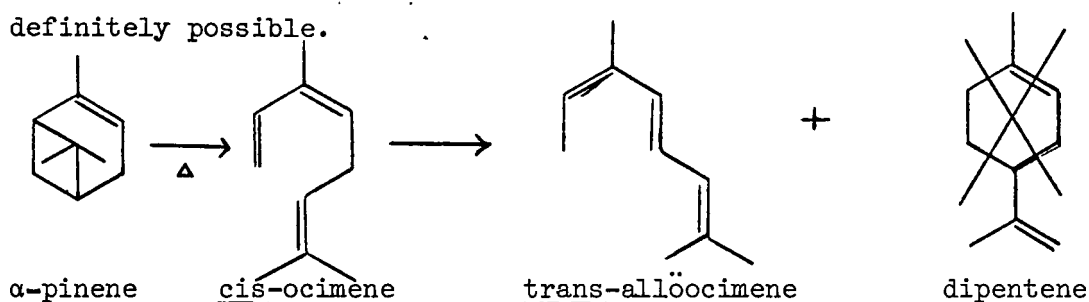
In an effort to answer this question, ratios of dipentene to allöocimene concentration were obtained for different flow rates at the same temperature for three different temperatures using the flow system. It would be expected that if all α -pinene had not reacted at any flow rate for a given temperature, then the ratio of dipentene concentration to allöocimene concentration would remain constant regardless of the flow rate, if the two compounds were being formed simultaneously by two different paths at a particular temperature. When ratios were

calculated from the flow system data obtained at 247.3°C, it was found that at a low flow rate of .045 ml/sec., the ratio of dipentene to allöocimene in the pyrolysate was 2.9, while at a high flow rate, .125 ml/sec., the same ratio was only 2.0. Similarly, the ratio of dipentene to allöocimene at a flow rate of .069 ml/sec. when the temperature of the flow system had been raised to 272.3°C was 2.2, while a flow rate of .222 ml/sec. at the same temperature gave a ratio of only 1.6 for the same two products. Finally, when the temperature of the flow system was raised to 282.3°C, samples analyzed at flow rates of .125 ml/sec. and .217 ml/sec. gave ratios of 2.5 and 1.5 respectively for the concentration of dipentene to that of allöocimene. These results preclude the possibility of product formation by two simultaneous but independent paths, unless the solubility of one of the components in the capturing solvent was flow-rate dependent.

In conclusion, it can be said that though no concrete mechanism for the rearrangement of α -pinene has been uncovered, certain aspects of the rearrangement have been examined and ruled out. In the first case, postulations dealing with simple cleavage of a carbon to carbon bond in the first step between positions 2 and 8 have been disproven.



Along with this, the possibility of ocimene being formed as an intermediate for the formation of both products has also been precluded, though the formation of one product, allöocimene, seems to be definitely possible.



These studies have also shown that lower temperatures reveal no racemization of α -pinene, and it would seem that in whatever mechanistic path is taken in the first step, either this step occurs too quickly or too irreversibly to allow a back reaction to form the racemate of α -pinene, or an intermediate or transition state is undergone in which no molecular symmetry is involved. It seems further evident that the formation of dipentene and allöocimene from the pyrolysis of α -pinene involves a single reaction or two reactions which show some dependence on one another rather than two simultaneous but completely independent paths.

IV.

EXPERIMENTAL

EXPERIMENTAL

A. Preparation of Chloropinene

Thirty ml. of fraction 2 (see Results) were placed in a 300 ml. three-necked reaction flask outfitted with a reflux condensor at one neck, a mechanical stirrer in the center neck and a pressure-compensated dropping funnel in the third. A solution of 14 g. of potassium tert-butoxide in 120 ml. of dimethyl sulfoxide was then added to the funnel with the stopcock remaining closed. The mechanical stirrer was next started and the butoxide solution was added to the flask in a drop-wise fashion over a period of about thirty minutes. The mixture was allowed to react with stirring for an additional hour following addition of the potassium tert-butoxide solution. The reaction mixture was then extracted three times with 30 ml. of n-pentane and the pentane mixtures were combined. The combined mixtures were then allowed to stand over magnesium sulfate for 12 hours in order to remove water. The pentane was then separated from the magnesium sulfate by filtration. Pentane was removed by distillation at atmospheric pressure and the residue was then evacuated to a pressure of 12 mm of mercury. The main portion of chloropinene was removed at 59-61°C under a pressure of 12 mm.

B. Preparation of Deuteropinene

A sodium dispersion was prepared by heating sodium metal in a test tube filled with xylene until the metal became molten; this was

followed by capping the tube and shaking it vigorously to give many tiny spheres of sodium metal.

A solution of 1 ml of chloropinene in 10 ml of deuterated methanol (CH_3OD) was introduced into a 50 ml two-necked reaction flask. One neck was fitted with a condensor, the other neck was fitted with a glass stopper after a magnetic stirring bar had been placed in the flask. Sodium from the freshly prepared dispersion was then added through the capped neck after removing the stopper, which was replaced immediately after the sodium addition. The sodium was added with stirring at such a rate as to allow sufficient reaction without letting the reaction become too vigorous. Sodium was added continually until all visible reaction had ceased. Excess sodium in the reaction mixture was then destroyed by the careful addition of D_2O until no further reaction was observed. The mixture was next extracted three times with 1/4 its volume of n-pentane and the pentane mixture was then allowed to sit over-night on magnesium sulfate. Magnesium sulfate was removed from the mixture by filtration and the deuteropinene was separated from the reaction mixture by collection from a gas chromatograph containing a 3/8 inch 40 ft. column filled with chromosorb-W coated with carbowax and maintained at 135°C . Deuteropinene was obtained in about 70% yield. The deuterated pinene was identified by its NMR spectrum which showed no absorption in the olefin region at 5.2 δ , while normal α -pinene showed considerable adsorption in this region. Other peaks in the deuteropinene spectrum were almost identical to those of α -pinene and it was obvious that deuterio-pinene had been made.

C. The Pyrolysis of Deuterated Pinene

Deuterated pinene was pyrolyzed by placing prepared samples into a large cylindrically shaped pyrex oven having an inner diameter of 5 cm and a length of approximately 40 cm. The pyrex tube was wrapped in chromel wire and covered with asbestos and the temperature was regulated by a rheostat connected to the chromel wire. Samples to be pyrolyzed were placed in the oven and the ends of the cylinder were then plugged with glass wool. Oven temperatures were measured through a thermocouple placed in the center of the oven cylinder, and the time used for pyrolysis was carefully noted.

Samples for pyrolysis were prepared by freezing solutions of 30 μ l of deuterated pinene in 30 μ l of pentane inside of 15 cm pyrex tubes having a 10 mm diameter and evacuating the tubes repeatedly to remove all air. The tubes were then sealed under vacuum and used for the ensuing pyrolysis.

The first pyrolysis of deuterated pinene was carried out by placing a sample prepared in the described manner into the oven at 275°C and allowing it to stand for 10 minutes before removal. Upon removal, the sample tube was allowed to cool and one end was then placed into a dry ice-acetone bath in order to liquefy the vaporous products. The tube was then opened and all pyrolysate was removed and injected into a gas chromatograph maintained at 135°C and containing a 40 ft. column having a 3/8 inch inner diameter and filled with chromosorb-W coated with carbowax. Unreacted deuterio-pinene was collected from this injection and was used to obtain an NMR spectrum (see Results) for comparison with the spectrum of starting material.

The second pyrolysis of deuterio-pinene was carried out in a manner exactly analogous to the above procedure, but the exposure time was lengthened to 20 minutes. The sample tube was then opened as before, and its contents were injected into the same gas chromatograph. From this injection, both unreacted deuterio-pinene and dipentene product were collected, and their NMR spectra were obtained (see Results).

D. The Stirred-Flow Reactor

Schematic diagrams of the entire flow system and of the actual reactor itself are seen in Figures 1 and 2. Figure 1 shows how the nitrogen (1) goes through a 30 pound regulator (2) followed by a 1 pound regulator (3), through a drying tube (4) and into a bath of sulfuric acid (5). The acid is used to keep a constant pressure head and further dry the nitrogen. The gas then passed through potassium hydroxide (6), a drying tube (7), and finally to a needle valve (8) which is used to control the flow. The water manometer (9) is used to monitor the flow rate so that sudden or drastic changes can be noted. After this, the nitrogen goes through another drying tube (10), the sample vaporizer (11), which can be temperature-controlled by passing heated water through it, and after picking up starting material, enters the oven (12). When the carrier gas leaves the oven, it passes the sample through a coil-heated length of pyrex tubing (13) in order to prevent condensation and into a removable collection vessel (14) which can be immersed in a dry ice-acetone bath. The bubble gas flow meter (15) is used for measuring the flow rate at a given setting of the needle

valve (8) and difference in water height (9). The two variable transformers (16) control the heat of the oven (12) and the outlet tube (13) respectively.

Figure 2 gives a more intricate picture of the oven itself. The starting material is carried into a pyrex two-necked flask (A) by the carrier gas. This cut-away view shows how the flask is imbedded in an aluminum cylinder (B) with a smaller aluminum cylinder (C) which fits snugly atop the flask within the larger cylinder. Enough heat is supplied through a variable transformer connected to four 200 watt cartridge heaters (D) at the base of the aluminum block to maintain a temperature about 40° below the desired temperature. The final temperature is obtained by a length of asbestos-covered chromel wire coiled around the entire cylinder (E) and connected to a Bayley linear temperature controller which is capable of maintaining a constant temperature within ± 0.1 degrees centigrade by responding to a thermistor inserted at F. The temperature of the system is measured by a chromel-alumel thermocouple placed in a small hole at position G in the diagram and connected to a Leeds and Northrup model 8686 potentiometer. A removable handle (H) is shown on top of the inner aluminum cylinder and is used to remove the cylinder when the system is to be cleaned.

E. The Flow System Pyrolysis of 1- α -Pinene

Thermolyses of 1- α -pinene were carried out at three different temperatures. Before beginning a set of thermolyses at a given

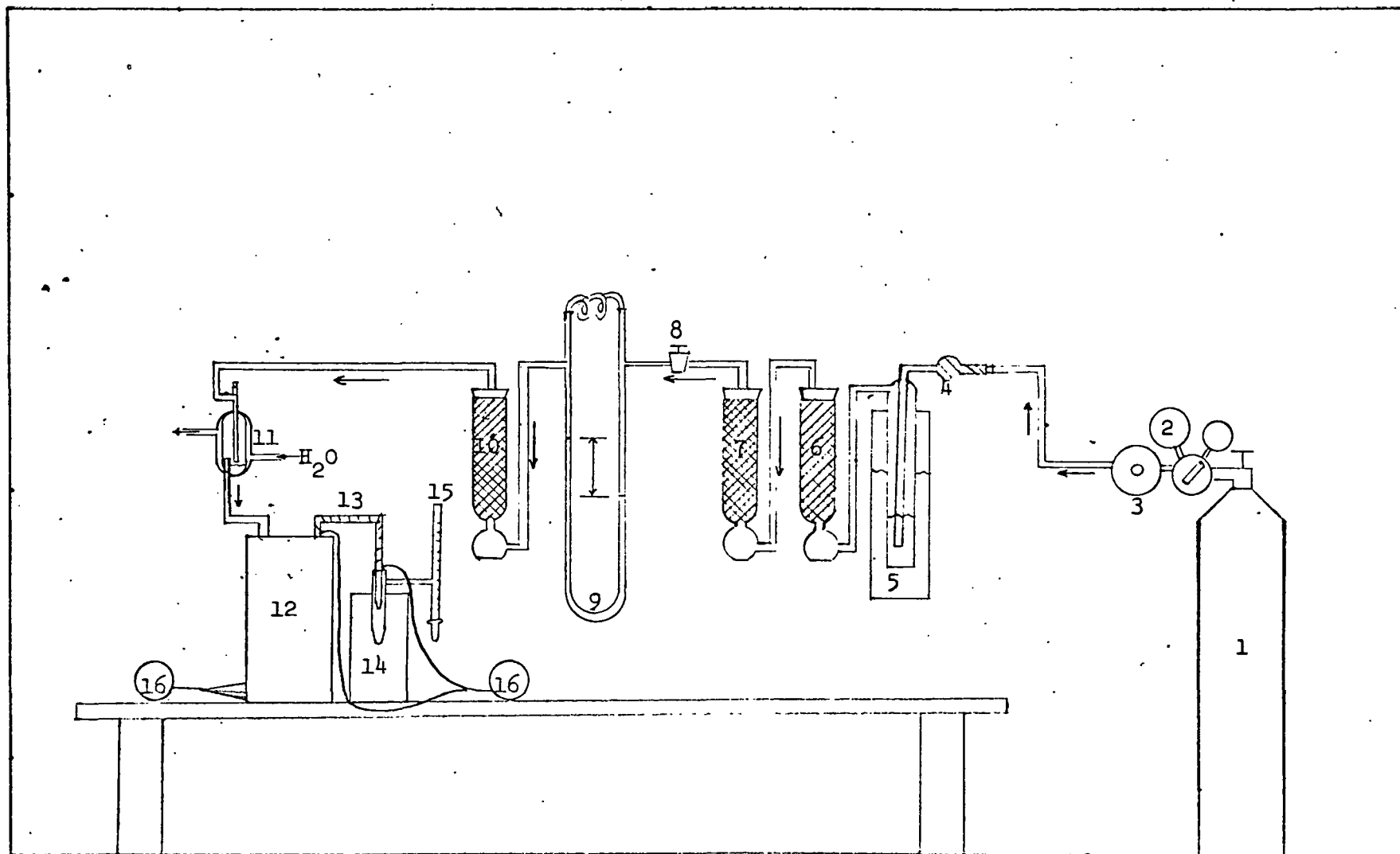


FIGURE 1. THE FLOW SYSTEM

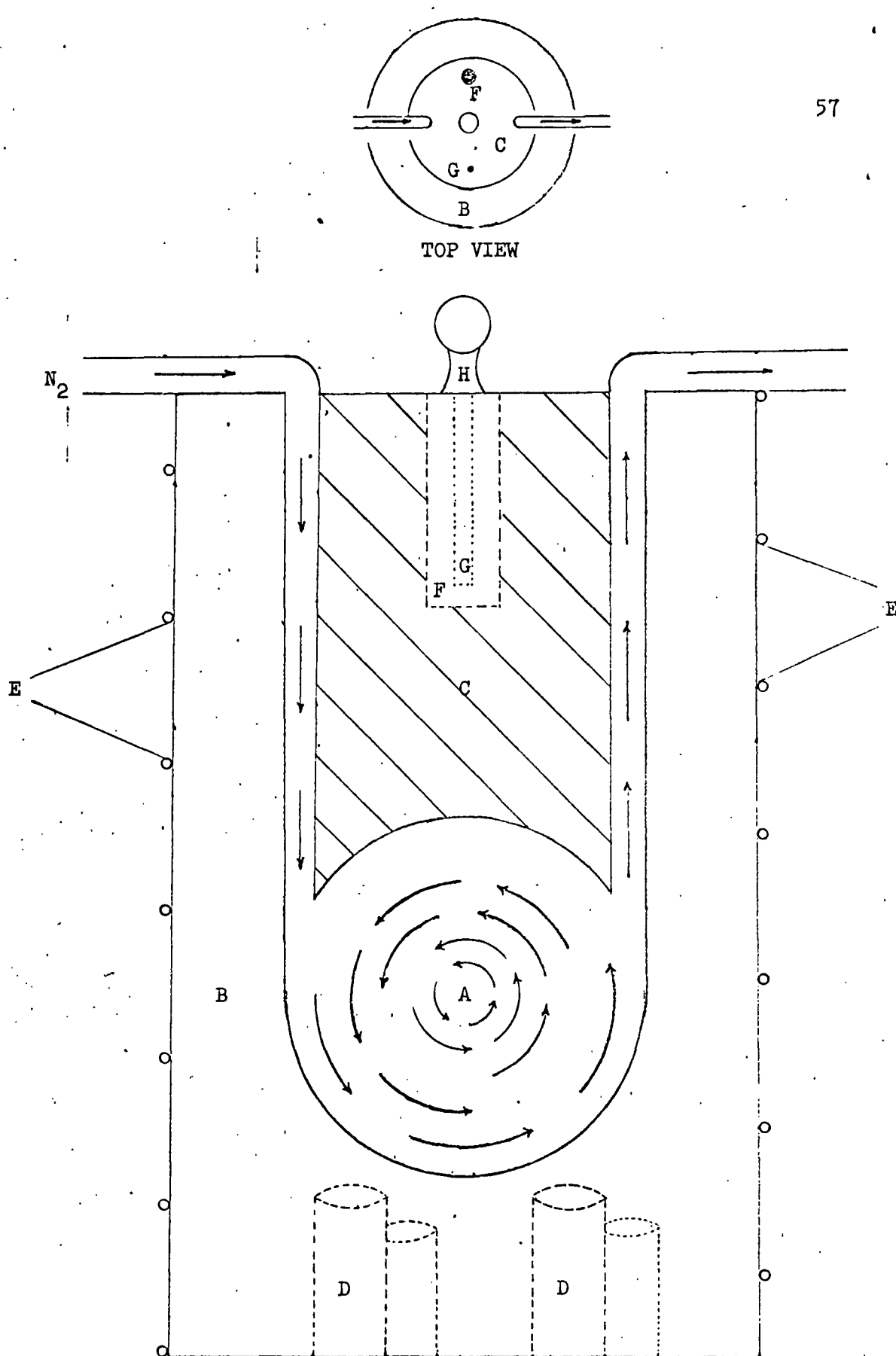


FIGURE 2. THE REACTOR

temperature, the cartridge heaters and the linear temperature controller were adjusted until the vicinity of the desired temperature was attained. Following these manipulations, several hours were allowed for equilibrium to be reached. When no change in temperature was observed over this period, it was assumed that the system was at equilibrium. Once equilibrium had been reached, the temperature regulating instruments were left untouched until a new temperature was desired.

Having arrived at the desired temperature, different flow rates were produced and pyrolysate from each of these was obtained in the collection tube. In a typical pyrolysis, the needle valve was adjusted until the preferred flow rate was measured by the bubble gas flow meter. The flow rate was then tested numerous times over a period of several hours to insure consistency. After the flow rate was obtained, a 250-500 μl sample of 1- α -pinene was introduced into the vaporizer. The pyrolysate from this starting material was collected until a volume of 30-60 μl could be observed in the collection tube. During this time, the flow rate was measured and recorded hourly. After collection was complete, the pyrolysate was removed and analyzed, and the flow rate was altered to a new value and tested for consistency. Once the new flow rate was constant over a certain time length, a new collection tube was attached and pyrolysate was collected as before. This process was repeated until samples had been collected and analyzed at all desired flow rates for a given temperature. The temperature was then changed as before and a new set of samples would be collected at various flow rates.

Using the method described above, 6 samples of pyrolysate were collected and analyzed at 247.3°C, 6 more were treated similarly at 272.3°C and 11 samples were analyzed at 282.3°C.

F. Analysis of Pyrolysis Products

Composition of pyrolysate was determined by examining samples collected at particular flow rates for a given temperature. A typical sample analysis was carried out by removing the pyrolysate obtained at a certain flow rate and temperature and injecting two μ l of it into a gas chromatograph. The chromatograph, which is an Aerograph Hy-Fi model 600, contained a 500 foot capillary column (.02 inch inner diameter) coated with a substrate of SF-96 (General Electric's silicon rubber coating) and was connected to a Leeds and Northrup Speedomax-W recorder. The recorder was connected in series to an Infotronics model CRS-10HB digital readout integrator. The entire analytical system was constructed so that peaks appearing on the recorder chart were simultaneously integrated and numbers corresponding to their relative areas were printed out and totaled by the integrator. The products giving rise to each peak were also known and it was simple to determine relative compositions from the peak integrals and total composition integrals. For each sample, 10 injections were made and integrals of the areas for α -pinene, dipentene and allöcimene were recorded along with the total integral for each injection. The product ratios obtained from these injections were calculated and averaged for use in determining rate constants.

G. Calculation of Rate Constants

In stirred flow reactors, the equation below has been found to be valid for unimolecular vapor phase reactions.

$$(1) \quad U[X] = k V[Y]$$

when [X] is the concentration of product after thermolysis, [Y] is the concentration of starting material after thermolysis, U is the flow rate in ml/sec, V is the volume of the reactor in ml, and k is the rate constant for the formation of X from Y in sec^{-1} .

Rearrangement of equation (1) gives:

$$\frac{U}{V} = k \frac{[Y]}{[X]},$$

hence a graphic plot of U/V versus $[Y]/[X]$ should have a slope k, equivalent to the rate of formation of X from Y. If 1- α -pinene is the starting material remaining after pyrolysis, [P], then rate constants should be determinable from graphs of

$$\frac{U}{V} \text{ vs. } \frac{[P]}{[D]}$$

for the formation of dipentene when [D] is the concentration of dipentene,

$$\frac{U}{V} \text{ vs. } \frac{[P]}{[A]}$$

for the formation of allöocimene,

and

$$\frac{U}{V} \text{ vs. } \frac{[P]}{[T-P]}$$

for the overall rate of reaction when [T-P] is the concentration of all products taken together except 1- α -pinene remaining in the mixture

The volume of the reactor in this case was 203.988 ml and the flow rates varied from sample to sample. The ratios involved were the best averages of ten analytical determinations per sample of pyrolysate. Tables V, VI, and VII include the data obtained in the flow system experiments. All flow rates were corrected by a factor of T/RT , where T is the temperature of the reactor in degrees Kelvin and RT is room temperature in degrees Kelvin.

Figures 3, 4, and 5 on the following pages show sample graphs used to obtain the various rate constants at 272.3°C from the data in Table VI. The rates obtained at all three temperatures, along with their calculated values from substitution of A factors and energies of activation (see next section) obtained from our data are shown in Table VIII.

H. Calculation of Activation Energies

Energies of activation were obtained from the laboratory results by taking the slope of a graph of $-\log k$ vs. $1/T$ in the standard Arrhenius plot, stemming from the form of the equation shown below.

$$(3) \quad -\log k = E_a \left(\frac{1}{2.303R} \right) \left(\frac{1}{T} \right) - \log A$$

The slope of such a plot would be

$$(4) \quad S = E_a \left(\frac{1}{2.303R} \right)$$

hence

$$(5) \quad E_a = (2.303R)S$$

TABLE V

DATA OBTAINED AT 247.3°C

Sample No.	U/V x 10 ⁴ sec	[P]/[D]	[P]/[A]	[P]/[T-P]
1	6.0	2.753	5.675	1.652
2	11.8	5.028	10.212	3.587
3	6.1	3.282	8.953	2.082
4	10.8	4.498	8.611	2.467
5	7.4	3.446	8.274	2.213
6	4.0	-	-	-

TABLE VI

DATA OBTAINED AT 272.3°C

Sample No.	$U/V \times 10^4 \text{ sec}$	$[P]/[D]$	$[P]/[A]$	$[P]/[T-P]$
7	6.2	.793	1.725	.4521
8	9.7	1.098	2.011	.6227
9	13.6	1.309	2.16	.7575
10	16.8	1.740	3.001	1.043
11	7.9	.902	1.705	.5290
12	20.1	1.923	2.99	1.106

TABLE VII
DATA OBTAINED AT 282.3°C

Sample No.	$U/V \times 10^4$ sec	[P]/[D]	[P]/[A]	[P]/[T-P]
13	6.1	.4291	1.047	.2576
14	21.8	1.010	1.521	.5624
15	9.8	.5748	1.178	.3535
16	16.5	.8773	1.448	.4940
17	18.4	.9920	1.580	.5625
18	12.1	.6265	1.198	.3658
19	8.4	.4919	.8815	.2788
20	16.5	.8978	1.359	.4924
21	20.0	1.033	1.548	.5644
22	4.0	.3111	.6868	.1882
23	11.3	.5942	1.508	.3772

FIGURE 3

Series 7-12 $T = 272.3$ $U/V \times 10^4$ sec vs. $[P]/[D]$

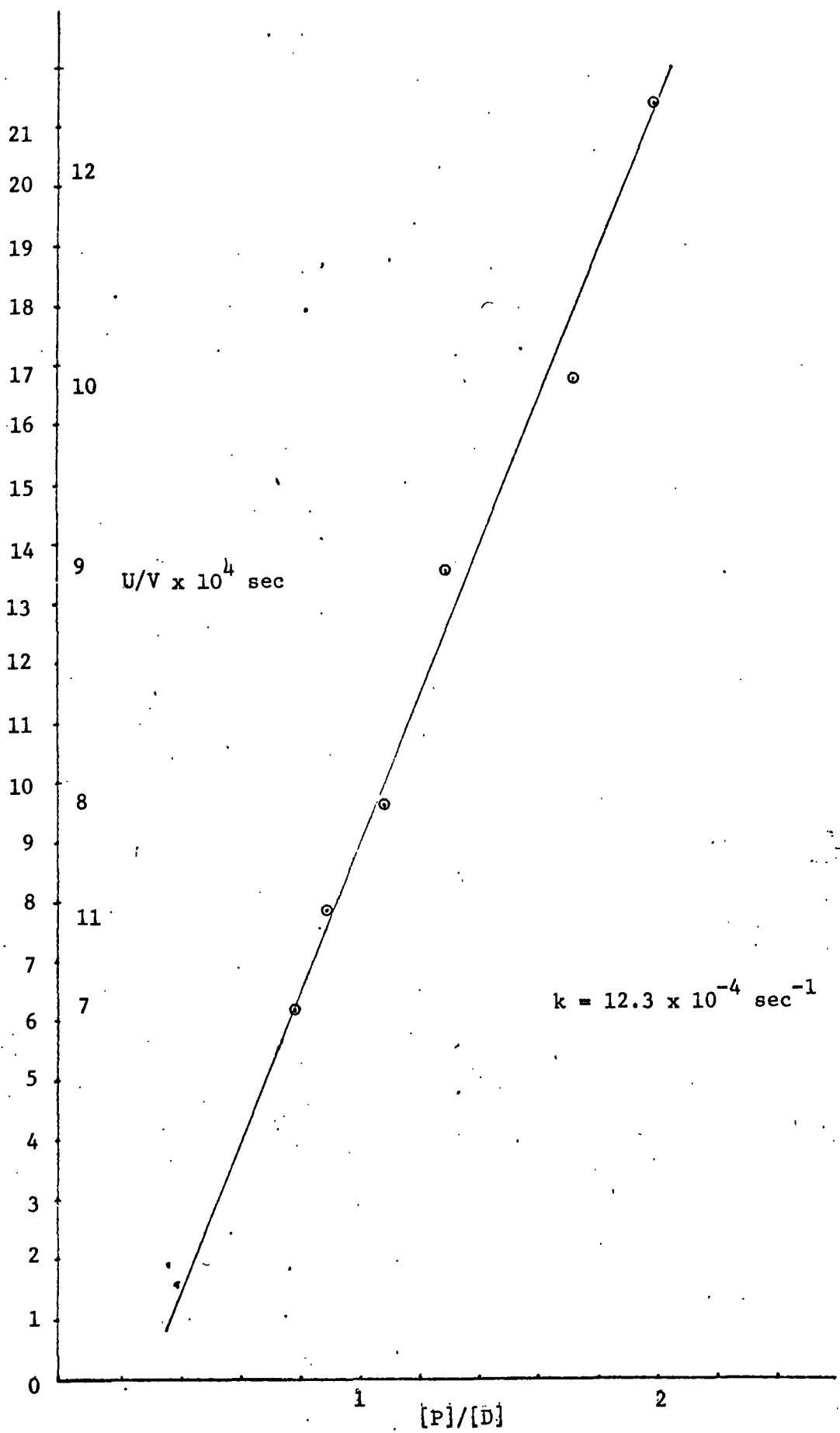


FIGURE 4

Series 7-12 $T = 272.3$ $U/V \times 10^4$ sec vs. $[P]/[A]$

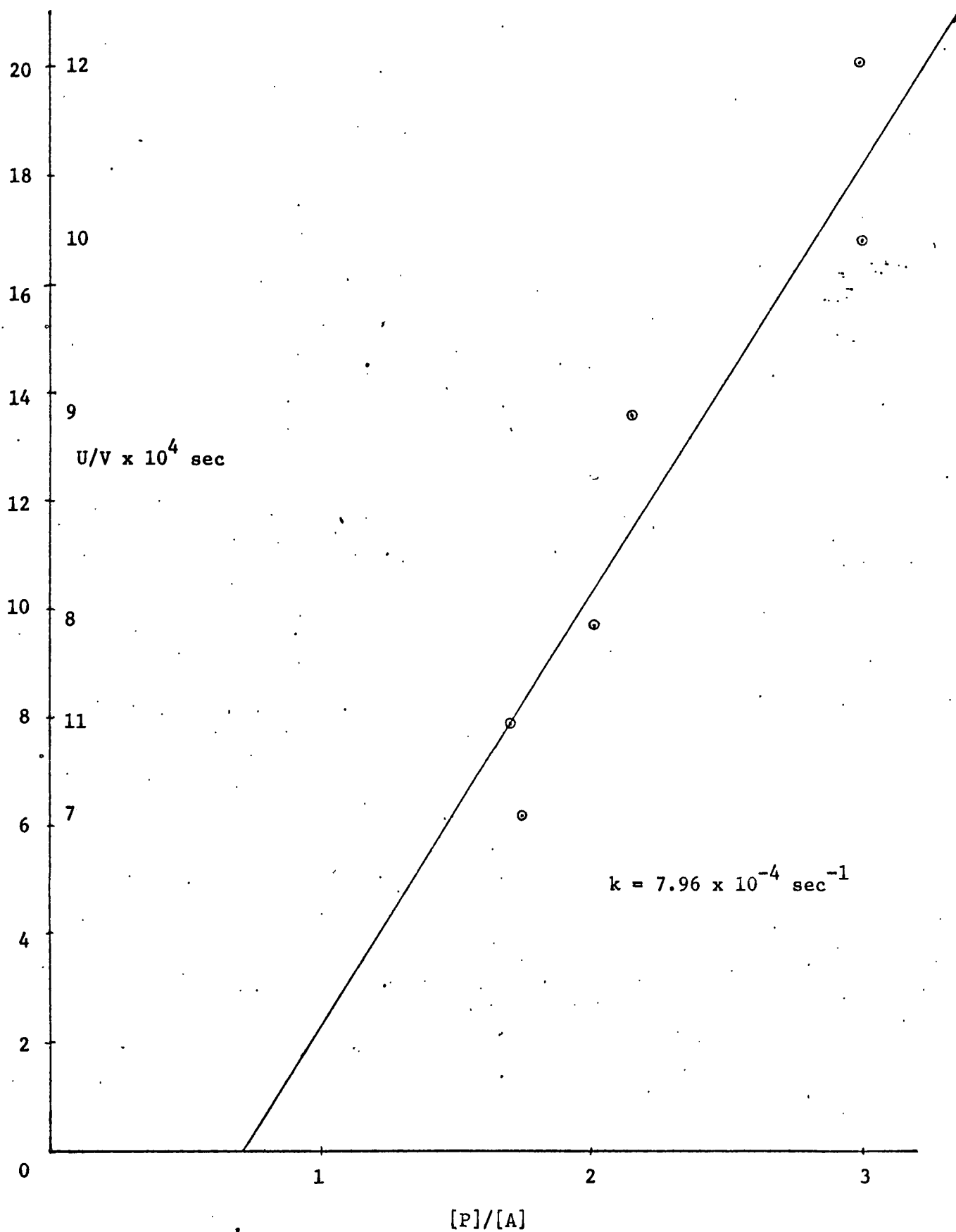


FIGURE 5

Series 7-12 $T = 272.3$ U/V vs. $[P]/[T-P]$

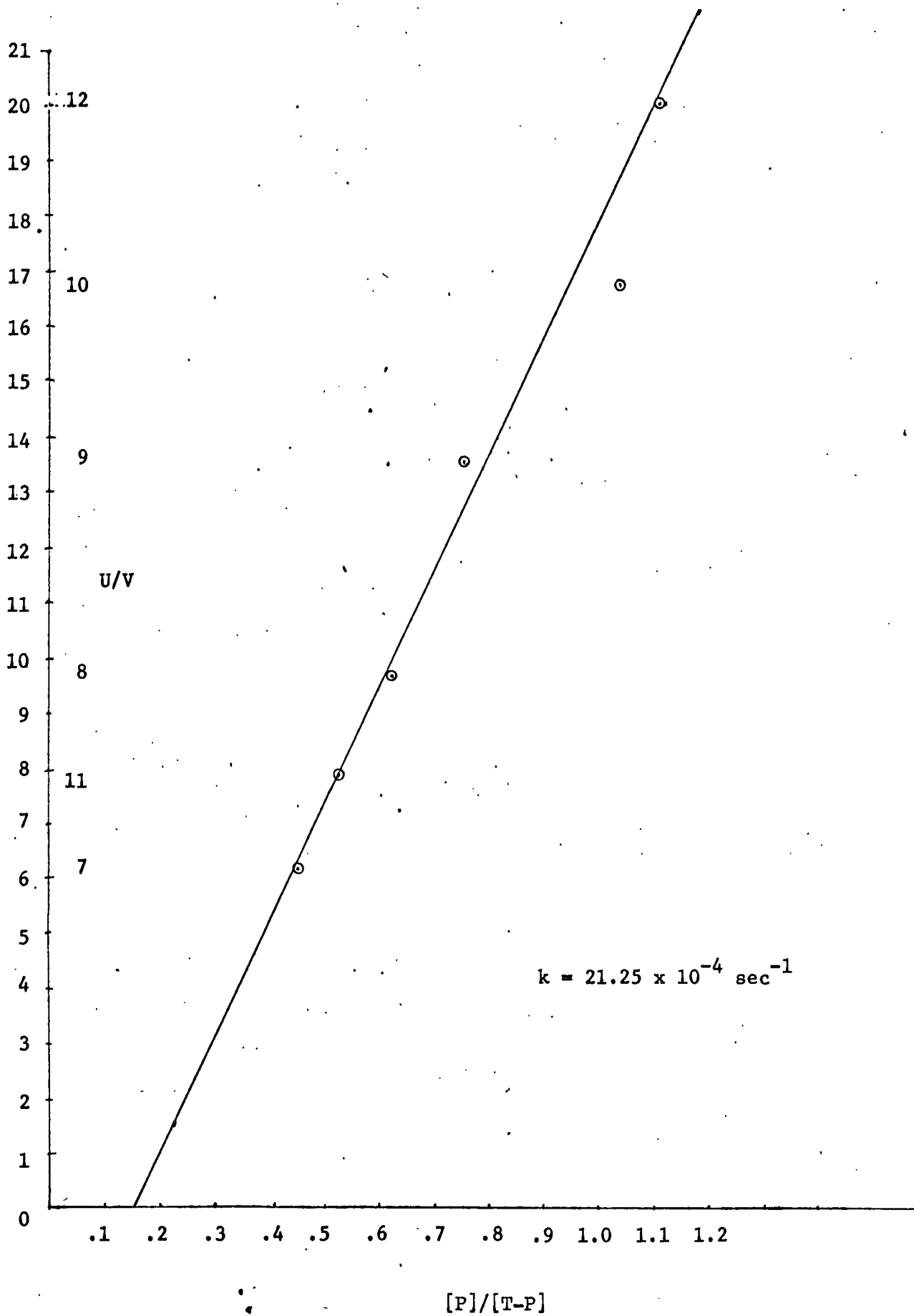


TABLE VIII
RATES OBTAINED AT THREE TEMPERATURES

	Temp°C	$k_D \times 10^4 \text{ sec}$	$k_A \times 10^4 \text{ sec}$	$k_T \times 10^4 \text{ sec}$
Observed	247.3	2.8	2.2	3.5
Calculated		2.7	1.8	3.3
Observed	272.3	12.3	8.0	21.3
Calculated		13.1	11.2	22.7
Observed	282.3	22.7	25.0	43.5
Calculated		22.9	21.4	44.4

and rearrangement of equation (3) now gives a method for determining the A factor for a given E, since,

$$(6) \quad \log A = \frac{E_a}{2.3RT} + \log k,$$

and T and log k can be picked from the graph. This procedure was used to determine A factors and energies of activation for the formation of dipentene, allöocimene and total product. The results shown in Table IX were obtained from our data and Figure 6 shows a typical plot from which these factors were obtained for the over-all reaction.

Smith's rates, and those of Fuguitt and Hawkins were treated identically, and results of these calculations are shown in Tables X and XI.

Using the data in Tables IX, X, and XI, rate constants for our temperatures were calculated from the formula

$$k = Ae^{\frac{-E_a}{RT}}.$$

The constants obtained from the factors in Table IX were considered to be our own results after correction. Table XII gives a comparison of the rates obtained from the three sets of parameters.

The final comparison of rate constants was carried out by using our factors from Table IX to calculate rate constants at the temperatures used by Smith and Fuguitt and Hawkins. The rates calculated in this manner are compared with the observed values in Table XIII.

TABLE IX
A FACTORS AND ENERGIES OF ACTIVATION FOR DIPENTENE,
ALLÖOCIMENE AND TOTAL PRODUCT

	E_a x mole/kcal	log A	A
k_D	34.7	10.98	9.6×10^{10}
k_A	39.8	12.97	9.3×10^{12}
k_T	41.6	13.99	9.9×10^{13}

FIGURE 6

$-\log k_T$ vs. $1/T \times 10^3$

$$\text{Slope} = 9.091 = \frac{E_a}{2.303(R)}$$

$$E_a = 4.576 (9.091) = 41.600 \text{ kcal/mole}$$

$$\text{Log } A = (S)(1/T) + \text{Log } k = (9.091)(1.792) - (2.300)$$

$$\text{Log } A = 13.991$$

$$A = 9.895 \times 10^{13}$$

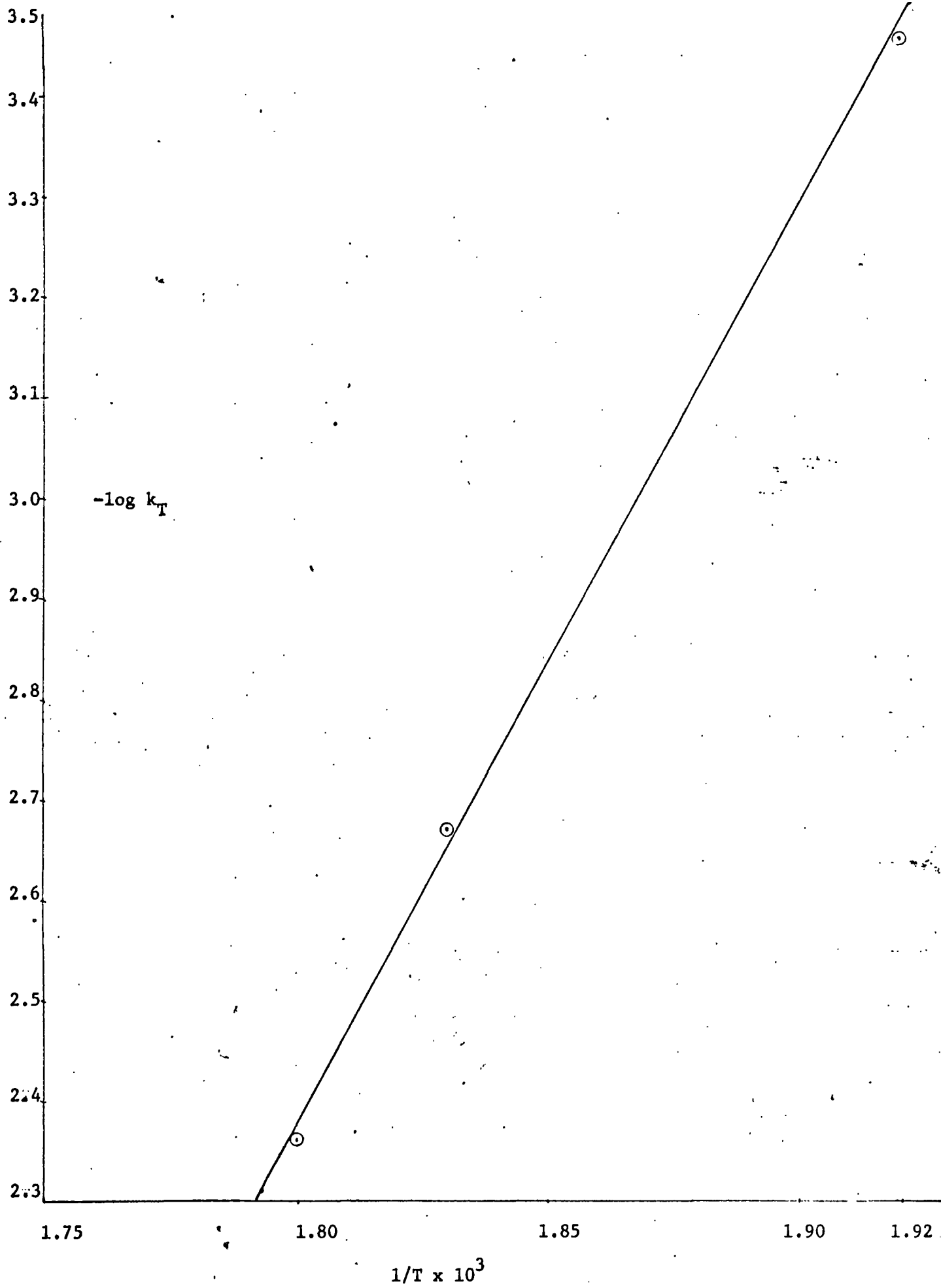


TABLE X
SMITH'S WORK

	E_a x mole/kcal	log A	A
k_D	42.8	14.23	1.7×10^{14}

TABLE XI

FUGITT AND HAWKINS' WORK

	E_a x mole/kcal	log A	A
k_D	38.2	12.05	1.12×10^{12}
k_A	41.4	13.24	1.7×10^{13}
k_T	39.3	12.72	5.3×10^{12}

TABLE XII

COMPARISON OF RATES OBTAINED

Table No.	Temp.	$k_D \times 10^4 \text{ sec}$	$k_A \times 10^4 \text{ sec}$	$k_T \times 10^4 \text{ sec}$
IX	247.3	2.7	1.8	3.3
	272.3	13.1	11.2	22.7
	282.3	22.9	21.4	44.4
X	247.3	-	-	1.9
	272.3	-	-	13.4
	282.3	-	-	25.5
XI	247.3	.97	.90	1.7
	272.3	5.7	4.9	10.1
	282.3	10.5	9.4	19.1

TABLE XIII

COMPARISON OF RATE CONSTANTS

Temp°C			$k_D \times 10^4 \text{ sec}$	$k_A \times 10^4 \text{ sec}$	$k_T \times 10^4 \text{ sec}$
Fuguitt and Hawkins	189.5	observed	.010	.005	.015
		calculated	.042	.015	.023
	204.5	observed	.038	.022	.060
		calculated	.138	.061	.097
	184.5	observed	-	-	.007
		calculated	-	-	.015
Smith	217.9	observed	-	-	.172
		calculated	-	-	.348
	232.3	observed	-	-	.660
		calculated	-	-	1.22

I. Determination of the Racemization of 1- α -Pinene and Dipentene

The optical activity of 1- α -pinene was determined by weighing 11.7 mg into a 1 ml volumetric flask, diluting this to the mark with absolute ethanol, and observing the optical rotation produced through the use of a Perkin-Elmer model 141 digital readout polarimeter. The absolute rotation was calculated from this reading and found to be 48.90°. Samples of 1- α -pinene obtained from pyrolysate at 247.3, 272.3, 282.3, and 306.2°C were treated in a similar manner and gave absolute rotations of 48.98, 47.35, 38.88 and 8.90° respectively (see page 32).

An 8.5 mg sample of dipentene obtained from pyrolysate at 272.3°C was weighed into a 1 ml volumetric flask and was then diluted to the mark with absolute ethanol. This sample was placed in the Perkin-Elmer polarimeter and subsequent calculations from this reading showed an absolute rotation of 4.35°. Optically pure limonene has an absolute rotation well above 100°, so the product was obviously racemic.

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