[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Rates of the Thermal Isomerization of α-Pinene and β-Pinene in the Liquid Phase[1]

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I

The rate of the thermal isomerization of α-pinene, (I) was first measured by Smith[3] in 1927. He concluded that he measured only a racemization process and found that the rate constants were approximately the same when the reaction was carried out in the gas phase, in the liquid phase or in solutions. Conant and Carlson[4] erroneously concluded that no racemization took place when α-pinene was heated. They attributed the decrease in optical activity of the substrate to the formation of dipentene which is optically inactive.

Kassel,[5] accepting the incorrect conclusions of Conant and Carlson, explained how the results of Smith should be corrected.

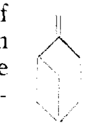
Thurber and Johnson[6] stated that racemization did take place and that another reaction was also present. However, they did not identify additional products nor determine their rates of formation.

Arbuzov,[7] Dupont and Dulou,[8] and Goldblatt and Palkin[9] studied the products of the continuous gas phase isomerization of α- and β-pinenes.

Savich and Goldblatt[10] investigated the continous liquid phase isomerization of α-pinene in which short contact times and high temperatures were used. They indicated that about the same proportions of the same products were formed as in the continuous gas phase isomerization at equal temperatures.

Fuguitt and Hawkins[11] in 1945 reported a study of the liquid phase reactions of α-pinene. They clarified the previous incomplete and contradictory[3,4,5,6] conclusions by showing that several processes took place simultaneously. These processes included racemization, isomerization to dipentene and isomerization to alloöcimene. The last compound, in turn, was shown to dimerize to a large extent and also to form small amounts of α- and β-pyronenes. The rates of the initial three simultaneous reactions were reported more recently.[12]

The present work was undertaken to obtain additional information concerning the thermal isomerization of α-pinene and to measure the previously unreported rate of the thermal isomerization of β-pinene.



II

Although Goldblatt and Palkin[9] found that the products of the thermal isomerization of β-pinene (II), are not identical with those of α-pinene when the reaction is carried out in the vapor phase, no information is available concerning the thermal isomerization of β-pinene in the liquid phase.

The carbonium ion theory, which is frequently used in explaining the rearrangements of terpenes,[13] involves a bimolecular reaction between the terpene and a proton. For this reason the study included the observation of the effect of the presence of a proton donor on the rate of the reaction. This was conveniently done by adding small amounts of benzoic acid. Also the effect of the addition of small amounts of hydroquinone which is both a proton donor and an antioxidant, and the effects of the addition of quinoline which is a proton acceptor, were observed. The measurement of the rates under these conditions should give valuable information which is useful in determining whether or not the process involves a proton or a peroxide. Additional experiments were conducted in which the pinenes were diluted with an equal volume of dipentene. This should give evidence of the presence or absence of chains or wall effects. It has been shown that dipentene is inert[11,14] under the conditions of these experiments.

It was found that the addition of small amounts of benzoic acid to β-pinene produced α-pinene which did not appear in the products of the other reactions. It is interesting to note that in small quantities (less than 1%) benzoic acid appears to promote a carbonium ion mechanism by converting β- to α-pinene but will not promote any further reactions of α-pinene. On the other hand it has been reported[15] that benzoic acid when present to the extent of 50% will cause α-pinene to form a variety of products. For this reason no further work using benzoic acid was conducted as it was desired to keep the reactions as simple as possible.

Purification of Materials.—Commercial d-α-pinene and l-β-pinene[16] were rectified in Lecky and Ewell columns

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(1) The material included in this paper is based upon a partial abstract of a dissertation presented to the Graduate Council of the University of Florida, by Harry G. Hunt, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1950.

(2) Naval Stores Division, The Glidden Company, Jacksonville, Florida.

(3) Smith, THIS JOURNAL, **49**, 43 (1927).

(4) Conant and Carlson, *ibid.*, **51**, 3464 (1929).

(5) Kassel, *ibid.*, **52**, 1935 (1930).

(6) Thurber and Johnson, *ibid.*, **52**, 786 (1930).

(7) Arbuzov, *J. Gen. Chem.*, **3**, 21 (1933); *Ber.*, **67B**, 563 (1934).

(8) Dupont and Dulou, *Compt. rend.*, **210**, 219 (1935).

(9) Goldblatt and Palkin, THIS JOURNAL, **63**, 3517 (1941).

(10) Savich and Goldblatt, *ibid.*, **67**, 2027 (1945).

(11) Fuguitt and Hawkins, *ibid.*, **47**, 242 (1945).

(12) Fuguitt and Hawkins, *ibid.*, **69**, 319 (1947).

(13) Mosher, *ibid.*, **69**, 2139 (1947).

(14) C. Harries, *Ber.*, **35**, 3256 (1902).

(15) (a) Austerweil, *Bull. soc. chim.*, **39**, 1643 (1926); (b) Bouchardat and J. Lafont, *Compt. rend.*, **113**, 551 (1891).

(16) Furnished through the courtesy of the Naval Stores Division, The Glidden Company, Jacksonville, Florida.

which exerted at least 60 plates on the mixture and which have been previously described.[17] The final product of α-pinene boiled within less than 0.1°, at 52° and 20 mm. pressure; its $n^{25}D$ 1.4631. The β-pinene was distilled at reflux ratios of at least 100 to 1. The final product boiled within 0.1°, at 60° and 20 mm. pressure; its $n^{25}D$ 1.4763-4. Previous work in this Laboratory showed that carefully purified β-pinene had an $n^{25}D$ 1.4768. Different refractometers were used but both were standardized against test pieces of glass. A sample of very carefully prepared β-pinene from a commercial laboratory[16] had an $n^{25}D$ 1.4764. At present the difference in the values of the refractive indices cannot be explained but is being investigated. It is believed that the discrepancy has no significance with relation to the work presented herein.

The dipentene was obtained by the pyrolysis of α-pinene, and was redistilled in a Lecky–Ewell column to a constant boiling point of 71° at 20 mm. Its $n^{25}D$ 1.4701. The hydroquinone, quinoline and benzoic acid samples were the best commercial grades obtainable. The quinoline was redistilled before use.

Apparatus and Procedure.—The apparatus and procedures were essentially those described previously.[11,12] Additional data covering the relation between the refractive indices and composition of mixtures containing β-pinene and limonene were determined and are listed in Table I.

TABLE I

REFRACTIVE INDICES OF MIXTURES OF β-PINENE AND LIMONENE

Wt. % β-pinene	$n^{25}D$ Obsd.	$n^{25}D$ Interp.
0.0	1.4706	....
40.4	1.4729	1.4729
61.5	1.4741	1.4741
100.0	1.4763	....

In the case of α-pinene the amounts of unconverted substrate, dipentene and the sum of the alloöcimene and polymer were determined. Other substances were not present in appreciable quantities.[12]

In the case of β-pinene the amounts of unconverted substrate, limonene and polymer were determined. Myrcene, which is the major product in the gas phase isomerization at about 400° as carried out by Goldblatt and Palkin,[9] was not present in significant quantities. The polymers found were those reported to form from myrcene.[14]

Results and Discussion

α-Pinene Reaction.—The calculations were based on the amount of α-pinene recovered and were made as previously reported.[12] The value of k' equals the sum of the constants for the simultaneous first order isomerizations to dipentene and alloöcimene.

$$k' = k_1 + k_2 = \frac{2.3}{t} \log \frac{100}{100\text{-}\%}$$

The results are shown in Table II.

The rate of disappearance of α-pinene followed the first order pattern whether the reacting mixture contained the basic quinoline or the acidic benzoic acid or hydroquinone or none of these substances. In every case the constant remained the same. This indicates that the thermal isomerization reactions do not involve a proton and that the carbonium ion mechanism is not applicable here. The anti-oxidant properties of hydroquinone would have caused a change in the rate if a peroxide mechanism, due to air contamination, played a significant part in the reaction. α-Pinene diluted with limonene (unreactive at this temperature) isomerized at the same rate as when not diluted, demonstrating that the existence of chains or wall effect was improbable.

TABLE II

ISOMERIZATION OF α-PINENE AT 204.5°

No.	Original concn. of α-pinene, %	Time, min.	First order $k' \times 10^4$
1	100	5090	3.2
2	100	5090	3.2
3	100	7875	3.3
4	100	7866	3.4
5	100	5060	3.5
6	100	5060	3.5
7	100	5030	3.0
8	100	4920	3.5
		Average	3.3
		Av. deviation, %	4.5
	Quinoline added		
9	99	3010	3.5
10	99	3010	3.4
11	99	6800	3.4
12	99	6800	3.3
		Average	3.4
		Av. deviation, %	3.6
	Benzoic acid added		
13	99	1400	4.0
14	99	3010	3.6
15	99	4970	3.7
16	99	6700	3.0
		Average	3.6
		Av. deviation, %	7.6
	Hydroquinone added		
17	99	1500	4.0
18	99	1500	3.6
19	99	6600	3.3
20	99	13700	3.4
21	99	13700	3.0
22	99	6800	3.2
23	99	6420	3.4
		Average	3.4
		Av. deviation, %	6.2
	Diluted with dipentene		
24	48.5	817	3.3
25	48.5	817	3.7
26	48.5	2200	3.0
27	48.5	2200	3.2
28	48.5	3600	3.1
29	48.5	3600	3.3
30	49.0	5400	3.3
31	49.0	5400	4.0
		Average	3.3
		Av. deviation, %	6.3

The value of k' obtained, checks satisfactorily the previously reported value of 3.6×10^{-4}

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[17] Stallcup, Fuguitt and Hawkins, *Ind. Eng. Chem.*, **14**, 503 (1942).

min.$^{-1}$ obtained by Fuguitt and Hawkins.[12] Smith[3] reported a value of 8.6×10^{-5} min.$^{-1}$ at 198°. Conant and Carlson[4] reported values between 4×10^{-5} and 23×10^{-5} min.$^{-1}$ at 200 ± 5°. Thurber and Johnson[6] reported the value of 4.3×10^{-5} min.$^{-1}$ at 185° and 74×10^{-5} min.$^{-1}$ at 218°. Kassel[5] recalculated Smith's value and reported 17×10^{-5} min.$^{-1}$ at 198°.

β-Pinene Reaction.—The first order isomerization constant k'', determined from the rate of disappearance of β-pinene is shown for 219.5° in Table III. Also shown are values of the same constant obtained when small amounts of a proton acceptor, quinoline, and a proton donor and antioxidant, hydroquinone, were added. These demonstrate that change in the available proton supply had no significance, and that change in the amount of peroxides from air contamination does not influence the reaction. Dilution with dipentene did not affect the reaction, so it is evident that the reaction is first order, and that there are no significant chain reactions or wall effects.

TABLE III

ISOMERIZATION OF β-PINENE AT 219.5°

No.	Original concn. of β-pinene, %	Time, min.	k_1/k_2	First order $k'' \times 10^4$
1	100	760		1.9
2	100	760		2.3
3	100	1500		2.2
4	100	1500		2.2
5	100	2900	0.45	2.1
6	100	2900	.44	2.1
7	100	5230	.46	2.1
8	100	5230	.39	1.9
		Average	.435	2.1
			Av. deviation, %	3.6
		Quinoline added		
9	99	750		3.1
10	99	1460		2.6
11	99	2900		2.4
12	99	4340		2.5
13	99	5780		2.5
			Average	2.6
			Av. deviation, %	6.9
		Hydroquinone added		
14	99	715		2.4
15	99	1430		2.6
16	99	2870		2.6
17	99	4310		2.3
18	99	5760		2.4
			Average	2.5
			Av. deviation, %	4.8
		Diluted with dipentene		
19	50	760		2.4
20	50	1500		2.5
21	50	2900		2.3
22	50	5230		2.0
			Average	2.3
			Av. deviation, %	6.5

Since at 150° myrcene is half converted to polymer in four hours[18], no appreciable amount of myrcene would be expected to accumulate in a reaction mixture held above 200°, the temperature at which it is necessary to isomerize β-pinene in a reasonable length of time. The amount of polymer formed was thus used as the measure of the amount of myrcene that had been formed and subsequently polymerized.

Included in Table III, No. 5 to 8, are values for the ratio of limonene to polymer in the column headed k_1/k_2. From k'' and this ratio, $k_1 = 0.64 \times 10^{-4}$ and $k_2 = 1.46 \times 10^{-4}$ at 219.5°. Similarly, Table IV shows the values of k'' and k_1/k_2 at 234.5°. When these data are used with one form of the Arrhenius equation, the activation energies are found to be approximately 50,000 and 47,000 cal./mole for the isomerization of β-pinene to limonene and myrcene, respectively. Using these values and the values of the rate constants expressed in reciprocal seconds, the values of log s are found to be 16.2 and 15.4 which are of the accepted order of magnitude for first order reactions.

TABLE IV

ISOMERIZATION OF β-PINENE AT 234.5°

No.	Original concn. of β-pinene, %	Time, min.	k_1/k_2	First order $k'' \times 10^4$
1	100	170		9.6
2	100	170		9.5
3	100	360		8.7
4	100	360		9.3
5	100	770	0.42	8.4
6	100	770	.49	9.2
7	100	1310	.48	8.8
8	100	1310	.49	8.6
		Average	.47	9.0
			Av. deviation, %	4.3

Summary

1. The rates of liquid phase isomerization of α- and β-pinene indicate first order reactions at about 200°. Dilution, or the addition of a mild base or acid, or an antioxidant, has no appreciable effect.

2. The reaction velocities were determined for the liquid phase isomerization of β-pinene at 219.5 and 234.5°.

3. Energies of activation for the formation of limonene and myrcene from β-pinene were determined.

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[18] Lebedev, *J. Russ. Phys. Soc.*, **45**, 1249 (1913).