est and many helpful suggestions offered during the course of this investigation.

Summary

1. Two samples of the GR-S copolymer of butadiene and styrene have been degraded by means of ozonolysis. A number of fragments have been isolated and identified so that an approximate idea of the structures of the copolymers has been obtained.

2. A series of butadiene copolymers has been treated with ozone in an attempt to determine the extent to which the butadiene has polymerized by 1,2-addition in contrast to 1,4-addition. Although the analytical procedure employed afforded only relative values, referred to as "ozonization numbers," the results indicate that the manner in which the butadiene molecule enters the growing copolymer chain is not greatly influenced by experimental conditions.

URBANA, ILLINOIS   RECEIVED JUNE 19, 1946

Rate of the Thermal Isomerization of α-Pinene in the Liquid Phase[1]

BY ROBERT E. FUGUITT[2] AND J. ERSKINE HAWKINS

In a previous article[3] the authors reported the results of their investigation of the reactions resulting from heating α-pinene in the liquid phase within the temperature range 189.5–285°. It was shown that dipentene (dl-limonene) and allo-ocimene are formed by simultaneous side reactions from the α-pinene and that the allo-ocimene in turn yields α-pyronene, β-pyronene and a dimer. It was observed that the optical rotations of the small amounts of unreacted α-pinene, which were sometimes recovered, had decreased markedly, thus indicating a partial racemization of the substrate. Formulas for all the compounds involved are given in the previous paper.[3] A full list of references is given in the earlier paper.[3]

Measurement of the rates of the individual reactions involved in this isomerization would determine whether the reactions are all of the expected first order or whether certain obscure effects complicate the process. In the present paper the measurements of the rates of racemization of α-pinene and its simultaneous isomerization to dipentene and allo-ocimene are reported. The data were obtained for the temperatures 189.5 and 204.5°. At these temperatures the reactions proceed slowly enough to permit the measurements to be made with a satisfactory degree of accuracy.

Experimental

Preparation and Purification of Reactants.—d-α-Pinene from wood turpentine and l-α-pinene from gum turpentine[4] were used in the investigation of the thermal isomerization reactions. For additional studies of the racemization of α-pinene, 300 g. of l-α-pinene of high optical rotation were obtained by refluxing pure l-β-pinene with 1% of

its weight of oxalic acid[5] for several hours and then distilling off the lower boiling product from the reaction mixture.

The spiral screen type of fractional distillation column, previously described,[6] was used to purify all of these materials. The products had the physical properties attributed to α-pinene of very high purity.[7] α-Pinene prepared from wood turpentine: b. p. (20 mm.) 52.3°; $\alpha^{25}D$ (2 dm.) +57.52° to +58.26°; $n^{25}D$ 1.4631–1.4632. α-Pinene prepared from gum turpentine: b. p. (20 mm.) 52.2°; $\alpha^{25}D$ (2 dm.) −6.49°; $n^{25}D$ 1.4631; d^{25}_4 0.8542. α-Pinene from β-pinene: b. p. (20 mm.) 52.3°; $\alpha^{25}D$ (2 dm.) −80.75; $n^{25}D$ 1.4631; d^{25}_4 0.8541.

Apparatus and Procedure.—Ninty-four cc. (80 g.) portions of freshly distilled α-pinene were sealed in tubes and heated in the constant temperature oil-bath, previously described,[3] to effect the isomerization. The temperatures at which the tubes were heated, 189.5 and 204.5°, were determined by means of a thermometer calibrated by the U. S. Bureau of Standards (reading directly to 0.1°). A Beckmann thermometer placed in the bath showed an average variation of ±0.03° and a maximum variation of ±0.04° at each temperature. It also indicated that the average temperature of the bath did not drift during the course of the heating of the tubes.

The volume of liquid in each sealed tube was so large that it was necessary to determine the time required for the liquid to come to the temperature of the bath. The rates of heating and cooling of the substrate were measured by means of a sealed tube containing the requisite amount of liquid and an enclosed thermometer. This was done by placing the tube in the oil-bath for different lengths of time and observing the temperature of the enclosed thermometer. The tube was allowed to cool to room temperature between each determination. Whenever the sealed tubes were placed in the bath for these tests and for all other experiments an additional 250-watt blade heater was turned on during the interval that the tube was being heated to temperature in order to counteract the cooling of the oil-bath by the cold tube. Five minutes after immersion the sealed tube containing 94 cc. (80 g.) of α-pinene was within 15° of the temperature of the oil-bath. However, the final temperature was not reached for another six or seven minutes. As an approximate correction, the time of heating of the α-pinene tubes was recorded as starting eight minutes after the tubes were immersed in the oil-bath. This correction is of no significance for tubes heated more than twelve hours.

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(1) The material included in this paper is based upon an abstract of a dissertation presented to the Graduate Council of the University of Florida in partial fullfilment for the degree of Doctor of Philosophy, May, 1943.

(2) Present address: Distillation Products, Inc., Rochester 13, New York.

(3) Fuguitt and Hawkins, THIS JOURNAL, 67, 242 (1945).

(4) Furnished through the courtesy of Southern Pine Chemical Company, Jacksonville, Florida.

(5) Bain, private communication.

(6) Stallcup, Fuguitt and Hawkins, Ind. Eng. Chem., Anal. Ed., 14, 503 (1942).

(7) Fuguitt, Stallcup and Hawkins, THIS JOURNAL, 64, 2978 (1942).

To determine the rate constants, duplicate tubes were heated for eight different periods of time, at each of the two temperatures employed. After the tubes had been heated for the desired length of time, they were opened and analyzed. Columns of 10 mm. (0.4 inch) inside diameter, four feet in length, with spiral screen packing, were used for the separation. Water at 4–12° was circulated through the column head condensers. All fractionations were made at constant pressure within the range of 10 to 20 mm. After the fractionation of each mixture the dimer of *allo*-ocimene remaining in the the kettle was weighed.

Quantitative Estimation of Components.—The use of refractive index data to analyze the composition of each fraction seemed practicable. With careful fractionation not more than two of the major components should be present in any major fraction.

Refractive index–composition data for known mixtures of α-pinene and dipentene and for *allo*-ocimene and dipentene were obtained and the relations were found to be practically linear (see Table I). The analyses were based on the straight line relation.

REFRACTIVE INDICES OF MIXTURES OF

α-Pinene and dipentene			*allo*-Ocimene and dipentene		
Wt.% dipentene	$n^{25}D$	Deviation from straight line, wt.%	Wt.% *allo*-ocimene	$n^{25}D$	Deviation from straight line, wt.%
00.0	1.4631	...	00.0	1.4702	...
19.4	1.4644	+1.1	14.3	1.4808	−0.6
29.2	1.4651	+1.0	24.9	1.4885	−0.8
53.6	1.4669	0.0	40.7	1.4999	−1.3
81.8	1.4689	+0.1	56.7	1.5112	−0.5
100.0	1.4702	...	71.1	1.5212	−0.5
			83.2	1.5299	−0.6
			100.00	1.5415	...

Since α- and β-pyronene have boiling points between those of α-pinene and dipentene, these substances are present in small amounts in the fractions collected between the boiling points referred to, and thus an uncertainty exists in calculating the percentages of the α-pinene and dipentene from refractive index data. However, the refractive indices of α- and β-pyronene are higher than that of α-pinene, and the average of their values is very close to that of dipentene. The quantity of material that boiled between pure α-pinene and pure dipentene amounted to only 2–9% of the total product so that the error introduced in analyzing this portion of the product would be greatly reduced when determining the amount of each component in the total product. The calculated percentage of α-pinene should be affected only slightly, and it is estimated that it can be determined within ±1%.

At the temperatures used the pyronenes increase in amount with the time of heating until, at the virtual completion of the isomerization of the α-pinene, they constitute about 3% of the reaction mixture.[8] Based on this final percentage an estimate of the concentration of the pyronenes in each reaction mixture was made, by assuming a linear increase in their concentration with respect to the amount of α-pinene reacted. By subtracting this correction from the percentage of dipentene, determined on the basis of refractive index, a more accurate value of the dipentene concentration is obtained.

In the fractionations of the reaction mixtures 1–1.5 g. of material usually was lost. When the column and head were not immediately rinsed out following a distillation a white gummy solid formed in small amounts in the column head and sidearm. *allo*-Ocimene forms such a compound when exposed to air and it is believed that most of the material unrecovered might be *allo*-ocimene. To investigate this loss of material and to determine the

(8) See ref. 3, Table I.

applicability of the combined distillation–refractive index method to the analysis of the components, four test mixtures containing known amounts of the four major components were fractioned in the analytical columns and the compositions of the resultant fractions were determined on the basis of refractive indices. For the complete distillation the average component losses were 0.05 g. of dimer, 0.2 g. of α-pinene, 0.2 g. of dipentene and 0.65 g. of *allo*-ocimene. To reduce the effect of this appreciable loss of *allo*-ocimene on the calculations a correction of 0.5 g. was added to the observed weight of *allo*-ocimene in each analysis.

Racemization of α-Pinene.—The optical rotations of the unisomerized, partially racemized, samples of α-pinene which were recovered from these reaction mixtures were observed. Racemization rate constants were calculated from these data.

To determine the effect of the initial optical activity of the α-pinene upon the observed racemization rate six mixtures of d-α-pinene (αD (2 dm.) +58.05) and l-α-pinene (αD (2 dm.) −80.75), were prepared which had optical rotations distributed relatively evenly over the range between the rotations of the two components. Duplicate 20-g. samples of each of the pure components and of their mixtures were heated in sealed tubes in the oil-bath at 204.5° for twenty-seven hours. The unreacted α-pinene was fractionated from each reaction mixture and the corresponding reaction rate constants calculated from the observed optical rotations.

Results and Discussion

The isomerization of α-pinene might be expected to produce the dipentene and *allo*-ocimene through simultaneous first order side reactions. This was determined by fitting the required data into the standard first order equations for such reactions and observing that the calculated reaction rate constants for several different degrees of completion at a specified temperature are constant within the limits of experimental error.

On the basis that dipentene and *allo*-ocimene are formed by first order reactions the rate of isomerization of the α-pinene, k', may be expressed by the equation

$$k' = k_1 + k_2 = \frac{2.303}{t} \log \frac{a}{a - x} \qquad (1)$$

where t is the length of time the α-pinene is heated at a given temperature, a is the initial concentration of the α-pinene, $a - x$ is the concentration of the α-pinene at time t, and k_1 and k_2 are the rates

ISOMERIZATION OF α-PINENE

Temperature = 189.5°

Tube no.	Time, min.	%, α-Pinene unreacted	k' × 10⁵ min.⁻¹	%, α- and β-pyronene	% Dipentene	% allo-ocimene	% Dimer	k_1/k_2
1	1230	88.4	10.03	0.4	7.5	1.6	2.2	1.79
2	1230	88.3	10.12	.4	7.1	3.0	1.3	(1.51)
3–4	3060	86.4	8.78	.7	15.6	4.5	2.8	1.95
5–6	4920	65.1	8.78	1.1	23.1	5.3	5.8	1.92
40–41	7800	50.4	8.80	1.5	32.9	6.0	9.3	1.97
7–8	10680	37.5	9.20	1.9	42.7	6.0	12.0	2.15
9–10	15030	25.9	9.02	2.2	49.1	5.9	17.0	1.96
11–12	22620	14.0	8.72	2.6	57.4	5.1	21.0	2.00
13–14	36420	4.5	8.57	2.9	63.1	3.8	25.7	1.95
		Av. k'	8.99 × 10⁻⁵			Av. k_1/k_2		1.97
		Av. dev.	0.33 × 10⁻⁵			Av. dev.		0.06
		%Av. dev.	3.7			%Av. dev.		3.0

of formation of the dipentene and *allo*-ocimene, respectively.

The ratio of the concentration of dipentene to that of *allo*-ocimene at any time would equal k_1/k_2 if no other complications were present. In this series of reactions the *allo*-ocimene simultaneously cyclizes to the pyronenes and dimerizes, so that the total amount of *allo*-ocimene that has been formed from the α-pinene at any time is equal to the sum of the *allo*-ocimene, dimer and the pyronenes present in the reaction mixture. Therefore, at any given time

$$k_1/k_2 = \frac{\text{(Dipentene)}}{(allo\text{-Ocimene}) + \text{(Dimer)} + (\alpha\text{- and }\beta\text{-pyronene)}} \quad (2)$$

TABLE III

ISOMERIZATION OF α-PINENE

Temperature = 204.5°

Tube no.	Time, min.	% α-Pinene unreacted	k' × 10³ min.$^{-1}$	% α- and β-pyronene	% Dipentene	% allo-Ocimen	% Dimer	k_1/k_2
15–16	440	85.9	34.7	0.4	8.2	4.1	0.6	1.81
17–18	825	74.3	36.1	.8	15.6	6.8	1.6	1.71
19–20	1200	65.1	35.9	1.0	21.5	7.7	3.4	1.83
21–22	1500	58.6	35.7	1.2	25.5	8.4	5.0	1.76
23–24	2040	48.1	35.9	1.6	31.9	8.5	8.2	1.75
25–26	3060	32.1	37.1	2.0	42.0	8.2	13.5	1.77
27–28	6060	11.2	36.2	2.7	54.7	6.9	21.9	1.74
29–30	16020	..		3.0	61.3	5.9	27.8	1.72
	Av. k'		35.9 × 10⁻³			Av. k_1/k_2		1.75
	Av. dev.		0.5 × 10⁻³			Av. dev.		0.02
	% Av. dev.		1.4			% Av. dev.		1.1

The values listed in the body of Tables II and III are the averages obtained from duplicate samples. The values for k_1/k_2 and the deviations indicated were obtained from the original data and not from the average values presented. These tables contain the analyses of the reaction mixtures obtained at 189.5 and 204.5°. The estimated corrections for the concentrations of the pyronenes are listed in column 5 of these tables. Tubes 40 and 41 contained *l*-α-pinene from gum turpentine. All other tubes contained *d*-α-pinene from wood turpentine.

Tables II and III also include the results obtained from equations (1) and (2). Column 4

TABLE IV

RACEMIZATION OF α-PINENE

Temperature = 189.5°

Tube no.	Time, min.	α_i (2 dm.), 25°	α_t (2 dm.), 25°	k_3 × 10⁶ min.$^{-1}$
1–2	1230	+58.14	+56.91	8.7
3–4	3060	+58.00	+54.77	9.4
5–6	4920	+57.77	+52.63	9.5
7–8	10680	+57.94	+47.39	9.4
9–10	15030	+58.01	+42.83	10.1
11–12	22620	+57.75	+35.94	10.6
13–14	36420	+58.13	+20.73	7.1
40–41	7800	− 6.49	− 5.91	(6.1)
			Av. k_3	9.3 × 10⁻⁶
			Av. dev.	0.9 × 10⁻⁶
			% Av. dev.	9.7

lists the values of k' calculated from equation (1) in which the concentrations of α-pinene are expressed by percentages, as determined by the analyses of the reaction mixtures. In column 9 are the values of k_1/k_2.

The constancy of the values of k' and k_1/k_2 calculated from these equations verifies the assumption that the two major products are formed by simultaneous first order side reactions. The rate constants k_1 and k_2, which are readily calculated from the averages of these values, are included in the summary in Table VII.

The decrease in optical rotation of the recovered unisomerized α-pinene was noted, without comment, in the data reported by Fuguitt and Hawkins.[8] The conclusion that the α-pinene racemizes when heated was discussed in a thesis[9] and by Savich and Goldblatt.[10]

The observed optical rotations of the middle fractions of α-pinene recovered from the reaction mixtures are listed in column 4 of Tables IV and V. These data are presented as the average of duplicate samples with the final values calculated from those from the individual tubes.

TABLE V

RACEMIZATION OF α-PINENE, TEMPERATURE, 204.5

Tube no.	Time, min.	α_i (2 dm.) 25°	α_t (2 dm.) 25°	k_3 × 10³ min.$^{-1}$
15–16	440	+58.00	+56.08	3.9
17–18	825	+58.00	+54.42	3.9
19–20	1200	+57.98	+52.46	4.2
21–22	1500	+57.92	+50.68	4.4
23–24	2040	+57.88	+48.62	4.3
25–26	3060	+58.12	+45.80	3.9
27–28	6060	+57.56	+32.70	4.7
			Av. k	4.2 × 10⁻⁵
			Av. dev.	0.27 × 10⁻⁵
			% Av. dev.	6.4

Column 5 of these tables contains the racemization rate constants calculated from equation (3)[11]

$$k_3 = \frac{2.303}{2t} \log \frac{\alpha_i}{\alpha_t} \quad (3)$$

where α_i is the initial optical rotation of the α-pinene and α_t is the optical rotation of the residual α-pinene after it has been heated at the specified temperature for a time t.

The deviation in the calculated racemization rate constants might be attributed partially to small amounts of unidentified compounds which either were present originally in the substrate or were formed during the reaction. Traces of such compounds could have an appreciable effect on the observed optical rotation of the recovered α-pinene without being present in sufficient quantities to be detected by the analytical methods employed.

The result for tubes 40 and 41, which contained *l*-α-pinene of low optical rotation, are given in

(9) Fuguitt, Thesis, University of Florida, May, 1943.

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

(11) Smith, *ibid.*, **49**, 43 (1927).

Table IV but were not considered in the determination of the average rate constant. The extreme deviation of this calculated rate constant from the average is undoubtedly due to the unavoidable errors in observing the optical rotations. These errors would be appreciable relative to the expected decrease in optical rotation for this substrate of low initial optical activity.

That the thermally produced decrease in optical rotation of the unreacted α-pinene is not a function of its initial optical activity is shown by the racemization rate constants obtained from the prepared sample c ntaining α-pinene of different optical rotations. These constants with corresponding data are contained in Table VI. The data are presented as the average values of duplicate determinations. The per cent. average deviation of all the constants was 5.6% and the average deviation of the individually calculated results was 0.24×10^5. The average rate constant was almost identical with that determined from the α-pinene samples recovered from the previously studied reaction mixtures which had been heated at the same temperature.

TABLE VI

RACEMIZATION OF α-PINENE OF DIFFERENT INITIAL OPTICAL ROTATIONS

Temperature, 204.5°; time heated, 1620 min.

Tube nos.	a_i (2 dm.), 25°	a_t (2 dm.), 25°	$k_i \times 10^5$, min.$^{-1}$
101–102	−80.75	−70.54	4.2
103–104	−60.75	−53.02	4.2
105–106	−45.54	−39.49	4.4
107–108	−31.40	−27.25	4.4
109–110	+10.80	+ 9.50	4.0
111	+21.95	+18.92	4.6
113–114	+38.70	+33.80	4.2
115–116	+58.05	+50.03	4.6
		Av. k	4.3×10^{-5}
		Av. dev.	0.24×10^{-5}
		% Av. dev.	5.6

The energies of activation for these reactions were calculated from the standard Arrhenius equation which relates the rate constants observed at two different temperatures. These are listed in Table VII. The values of log s, in equation (4), calculated at 189.5° are also included in the table.

$$\log s = \log k + E/2.303RT \qquad (4)$$

TABLE VII

SUMMARY OF RESULTS

Reaction	$k \times 10^5$ min.$^{-1}$ (189.5°)	(204.5°)	$E_{act.}$ cal./mole	log s (time in min.)
Racemization of α-pinene	0.93	4.2	44,150	15.8
α-Pinene → dipentene	5.96	22.9	37,000	13.3
α-Pinene → allo-ocimene	3.03	13.0	42,650	15.6

These values are of the order of magnitude which might be expected for such first order thermal reactions.

Summary

1. The reaction velocities at 189.5 and 204.5° and the energies of activation have been determined for the thermal racemization of α-pinene and the thermal isomerization of α-pinene to dipentene and allo-ocimene. These isomerization reactions were of the expected first order, indicating that there were no obscure complicating effects.

2. The observed rate of racemization evidences no dependence upon the initial optical rotation of the α-pinene.

3. The dipentene and allo-ocimene are produced from the α-pinene by simultaneous first order side reactions.

4. The racemization of α-pinene requires the greatest activation energy and the thermal isomerization of α-pinene to dipentene the least.

GAINESVILLE, FLORIDA RECEIVED JULY 15, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE]

Oxidation–Reduction Potentials of Thiol–Dithio Systems: Thiourea–Formamidine Disulfide

BY PAUL W. PREISLER AND LOUIS BERGER

Many attempts have been made to estimate the oxidation–reduction potentials of theoretically reversible systems of the type, 2 Thiol − 2H $\rightleftarrows$ Dithio (2RSH − 2H $\rightleftarrows$ RSSR). The methods used were[1] direct measurement of electrode potentials and[2] the action of oxidation–reduction potential indicators or other reactants of known potential upon the reductant or upon the oxidant.[3] Except possibly for the recent work by Ryklan and Schmidt[4] on such systems, the data of these investigations do not comply with criteria for freely reversible systems; nor do they approach the degree of accuracy readily

(1) J. C. Ghosh and S. C. Ganguli, Biochem. J., 28, 381 (1934); D. E. Green, ibid., 27, 678 (1933); J. C. Ghosh, S. N. Raychandhuri and S. C. Ganguli, J. Ind. Chem. Soc., 9, 43 (1932); J. W. Williams and E. M. Drissen, J. Biol. Chem., 87, 441 (1930); E. K. Fischer, ibid., 89, 753 (1930); L. Michaelis and L. B. Flexner, ibid., 79, 689 (1928); E. C. Kendall and D. F. Loween, Biochem. J., 22, 669 (1928); D. C. Harrison and J. H. Quastel, ibid., 22, 683 (1928); M. Dixon and H. E. Tunnicliffe, ibid., 21, 844 (1927); E. C. Kendall and F. F. Nord, J. Biol. Chem., 69, 295 (1926); M. Dixon and J. H. Quastel, J. Chem. Soc., 123, 2943 (1923).

(2) H. Borsook, E. L. Ellis and H. M. Huffman, J. Biol. Chem., 117, 281 (1937); J. S. Fruton and H. T. Clarke, ibid., 106, 667 (1934); E. C. Kendall and F. F. Nord, ibid., 69, 295 (1926).

(3) P. W. Preisler, ibid., 87, 767 (1930).

(4) L. R. Ryklan and C. L. A. Schmidt, Univ. Calif. Pub. Physiol., 8, 257 (1944).