of a three-hour run and are typical of results obtained when using an alumina support.

Temp., °C.	% Pyridine	% Piperidine	% X
300	1.9	0	1.4
350	1.8	5	13
400	2.9	8	0
450	Trace	Trace	0

It is seen from the above results that the best yields of pyridine and piperidine are obtained on activated alumina at 400°.

Reaction of Dihydropyrane with Ammonia.—There was little or no reaction on chromium oxide–alumina catalyst at 350°. At 400° distillation of the products showed plateaux at 75, 91, 105 and 130°. By methods described in the experiments on tetrahydrofurfuryl alcohol, the latter three were found to have the same composition as previously found, *i. e.*, pyridine–water, azeotrope, piperidine, and the same unknown compound. The plateau at 75° which came over in two layers was found to be pentamethylene oxide (n^{20}D 1.4190 found, while for pentamethylene oxide it is 1.4200). This compound appears to have resulted from the hydrogenation of part of the dihydropyrane feed. The yields were 0.9 mole per cent. of pyridine, 8.9 mole per cent. of piperidine and 10 mole per cent. of pentamethylene oxide. There was a smaller loss of the initial feed as cracked gases or carbon on the catalyst than in the case of tetrahydrofurfuryl alcohol. The general similarity of this reaction to that between tetrahydrofurfuryl alcohol and ammonia makes it probable that both proceed by the same mechanism. In particular the existence of a plateau at 130° on the distillation of the reaction products of both reactions makes it likely that this unknown substance is readily derived from both tetrahydrofurfuryl alcohol and from dihydropyrane.

Reaction of Pentamethylene Oxide and Ammonia.—At 350° there was little reaction on activated alumina, the product being essentially unchanged pentamethylene oxide. At 400° there was some (10%) material boiling below 100° and a plateau at 106° corresponding to 16% yield of piperidine. These results agree with those reported by Yur'ev.[11] The yields for the condensation of pentamethylene oxide with ammonia were not much greater than those found with tetrahydrofurfuryl alcohol and dihydropyrane.

Summary

1. Free energy values were calculated on the basis of spectroscopic data for various methods of synthesis of pyridine.
2. Amylamine and diethylamine do not cyclicize to aromatic bases in the vapor phase over chromium oxide on alumina.
3. Furfuryl alcohol does not react with ammonia to give pyridine in the liquid phase at low temperature nor in the vapor phase over alumina or chromium oxide on alumina at high temperatures.
4. Tetrahydrofurfuryl alcohol reacts with ammonia in the vapor phase to give at 400° over alumina 3% pyridine and 8% piperidine. Higher boiling material and an unknown nitrogenous substance boiling at 130° are produced in considerable amounts.
5. Dihydropyrane and ammonia react over chromium oxide on alumina in the vapor phase at 400° to give 1% pyridine and 9% piperidine.
6. Pentamethylene oxide and ammonia react over alumina at 400° to give 16% piperidine and traces of pyridine.

(11) Yur'ev, Pervova and Sazonova, *J. Gen. Chem., U. S. S. R.*, **9**, 5904 (1939).

Princeton, N. J. Received July 14, 1944

[Contribution from the Department of Chemistry, Indiana University]

The Kinetics of the Hydrion Catalyzed Esterification of Some Substituted Benzoic Acids with Cyclohexanol[1]

By R. J. Hartman,[2] H. M. Hoogsteen[2] and J. A. Moede[3]

The type of esterification in which this investigation is concerned may be represented as

$$\mathrm{ROH} + \mathrm{R'COOH} + \mathrm{H}^+ \rightleftarrows \mathrm{R'COOR} + \mathrm{H_2O} + \mathrm{H}^+$$

where R is the cyclohexyl radical and R′ is a monosubstituted phenyl radical. Many qualitative studies have been carried out wherein attempts have been made to show the relationship between the nature and position of the substituent on the benzene ring and the rate of esterification.[4–12] Hammett[13] has expressed this relationship by the equation

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(1) This paper is constructed from a thesis presented by Harold Martin Hoogsteen to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry. Original manuscript received June 14, 1943.

(2) Present address: The Dow Chemical Company, Midland, Michigan.

(3) Present address: Radford Ordnance Works, Radford, Virginia.

(4) Goldschmidt, *Ber.*, **28**, 3224 (1895).

(5) Goldschmidt and Udley, *Z. physik. Chem.*, **60**, 728 (1907).

(6) Ingold and Ingold, *J. Chem. Soc.*, 756 (1932).

(7) Rolfe and Hinshelwood, *Trans. Faraday Soc.*, **30**, 935 (1934).

(8) Evans, Morgan and Watson, *J. Chem. Soc.*, 1168 (1935).

(9) Newling and Hinshelwood, *ibid.*, 1357 (1936).

(10) Fairclough and Hinshelwood, *ibid.*, 598 (1939).

(11) Datta, Day and Ingold, *ibid.*, 838 (1939).

(12) Hughes, Ingold and Masterman, *ibid.*, 840 (1939).

(13) Hammett, This Journal, **59**, 96 (1937).

$$\log k = \log k_0 + \rho\sigma$$

where k is the velocity constant of the reaction for the substituted organic acid reactant, k_0 that for the unsubstituted organic acid reactant, ρ a constant depending on the reaction medium and temperature and σ a substituent constant. This quantitative expression has been tested for many esterification reactions in methanol[14–19] and in ethanol.[16]

In order to determine the effect of an R group attached to an hydroxyl radical different in molecular structure and physical properties from methanol or ethanol on the hydrion catalyzed esterification velocity of a few substituted benzoic acids, Hartman, Storms and Gassmann[20] utilized cyclohexanol. This alcohol was chosen since it differs widely in physical properties and molecular structure from either methanol or ethanol, is a secondary rather than primary alcohol and possesses a higher boiling point than either methanol or ethanol, thus permitting reaction rate studies at higher temperatures where the tendency of any effects influencing bond energies should be more pronounced.

The effect of a drastic change in the R group of the alcohol on the esterification velocity can be expected to be constant for all acid reactants. Thus, any interpretation of such data will depend upon an attempt to correlate the relationship of such a constant factor to reaction rates in cyclohexanol with the parallel relationship to reaction rates in methanol or in ethanol. If the effect of the change in the R group of the alcohol is qualitatively negligible, it follows that the nature and position of the substituent of the acid is the predominating factor influencing the energy relationships of the molecule. On the other hand, if the change in the R group of the alcohol causes a significant difference, such might be indicative of a factor that could contribute to a better understanding of the complex mechanism involved in the reaction.

The reaction between the catalyst (hydrogen chloride) and the alcohol is known to complicate the interpretation of esterification kinetics studies. The reactions between hydrogen chloride and methyl, ethyl and propyl alcohols have been studied by Hinshelwood,[21] Kilpi[22] and Gassmann, Hochanadel and Hartman.[23] It was also found that below 80° in sealed tubes no appreciable reaction occurred between hydrogen chloride and cyclohexanol.[24] Some esterification work has been corrected by utilizing data obtained on the HCl–methanol reaction carried out in sealed tubes.[25] Although such corrections no doubt result in more exact kinetics data, the fact that the data used for correction were obtained from catalyst–alcohol reactions carried out in an isolated system in sealed tubes and the fact that during esterification this reaction is in the presence of the organic acid reactant and not in a sealed system, may mean that such corrections are not precisely applicable. In this investigation a procedure is followed whereby the determination of the change in catalyst concentration is followed under esterification conditions, thus enabling a more accurate correction.

The object of this investigation was to determine the velocity constants of hydrion catalyzed esterification reactions of a number of substituted benzoic acids with cyclohexanol employing a procedure enabling an exact correction for the reaction between the catalyst, hydrogen chloride, and the solvent, cyclohexanol. Since this correction was not made by Hartman, Storms and Gassmann,[20] the reactions reported by them were repeated according to the procedure followed in this study and the results included. The results thus obtained are then rationalized with the equation of Hammett[13] expressing the quantitative effect of substituent groups on reaction rate and that of Fairclough and Hinshelwood[10] indicating the differences of mechanisms between different reactants of the same reaction type.

Experimental

Materials.—C. P. cyclohexanol obtained from the Fine Chemicals Division of E. I. du Pont de Nemours and Company was dried according to the method of Bjerrum and Lund,[26] followed by refluxing over calcium oxide in the same manner employed by Danner and Hildebrand.[27] The fraction finally retained for use after distilling through a 60-cm. Vigreux column was found to possess a boiling point and refractive index in agreement with accepted values. The organic acids used were obtained either from the Eastman Kodak Company or from Dr. C. S. Marvel of the University of Illinois. After recrystallization and drying over phosphorus pentoxide, their melting points were found to be in agreement with accepted values. The hydrogen chloride used was generated by the action of sulfuric acid on sodium chloride. The gas was carefully dried by passing through a tube containing calcium chloride.

Procedure.—The anhydrous hydrogen chloride–cyclohexanol solution was prepared by passing dry hydrogen chloride into the cyclohexanol. The concentration was determined by titration with aqueous barium hydroxide and the solution diluted to the desired concentration. To 50-ml. portions of 0.1 N hydrogen chloride–cyclohexanol solution contained in 250-ml. glass-stoppered Erlenmeyer flasks, were added sufficient quantities of the organic acid reactants to yield a solution approximately 0.1 N with respect to the organic acid. It was sometimes found necessary to preheat the hydrogen chloride–cyclohexanol solution in order to dissolve the desired quantity of organic acid. The flasks were then immediately placed in constant temperature oil-baths maintained at 55.00, 65.000, ±0.05°

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(14) Kellas, *Z. physik. Chem.*, **24**, 220 (1897).

(15) Williamson and Hinshelwood, *Trans. Faraday Soc.*, **30**, 1145 (1934).

(16) Hinshelwood and Legard, *J. Chem. Soc.*, 1588 (1935).

(17) Hartman and Borders, This Journal, **59**, 2107 (1937).

(18) Smith, *ibid.*, **61**, 254 (1939).

(19) Hartman and Gassmann, *ibid.*, **62**, 1559 (1940).

(20) Hartman, Storms and Gassmann, *ibid.*, **61**, 2167 (1939).

(21) Hinshelwood, *J. Chem. Soc.*, 599 (1935).

(22) Kilpi, *Z. physik. Chem.*, **141A**, 424 (1929); **166A**, 285 (1933).

(23) Gassmann, Hochanadel and Hartman, This Journal, **65**, 988 (1943).

(24) Gassmann and Hartman, *ibid.*, **63**, 2139 (1941).

(25) Smith, *ibid.*, **62**, 1136 (1940).

(26) Bjerrum and Lund, *Ber.*, **64B**, 210 (1931).

(27) Danner and Hildebrand, This Journal, **44**, 2825 (1922).

and 75.00, 85.00 ± 0.08°. Using calibrated and corrected 5-ml. pipets, samples at the beginning and during the course of the reaction were withdrawn for analysis. Each sample was first titrated with aqueous barium hydroxide using phenolphthalein as indicator in order to determine the total acidity. They were each then titrated with silver nitrate solution according to the Mohr method, thus revealing the exact hydrogen chloride concentration. (In order to perform the Mohr titration after titrating with barium hydroxide, it was necessary to remove the barium ions from solution by adding sodium sulfate solution.) Since the hydrogen ion concentration resulting from the hydrogen chloride present is at all times, no doubt, equal to the chlorine ions present, it is possible to calculate precisely the concentration of the organic acid reactant present at any instant. Included in this study are also the organic acid reactants presented previously by Hartman, Storms and Gassmann.[20] These were repeated in this investigation for the purpose of obtaining more precise values for the velocity constants by correcting for the reaction occurring between the hydrion catalyst and the cyclohexanol.

The Goldschmidt equation[28] presupposes the change in c as the reaction progresses to be negligible. The fact that this value does change, though not greatly, is illustrated by the following figures for a typical esterification.

m-FLUOROBENZOIC ACID

Temp., 65°							
Time, min.	0	64,800	86,400	172,800	237,600	298.800	
$a - x$	0.1009	0.0738	0.0687	0.0462	0.0363	0.0291	
c	.1004	.0999	.0996	.0987	.0982	.0977	
$k \times 10^5$	. . .	5.06	4.72	5.05	4.93	4.87	Av. 4.93
Temp., 75°							
Time, min.	0	28,800	43,200	86,400	129,600	172,800	
$a - x$	0.1002	0.0745	0.0663	0.0451	0.0333	0.0269	
c	.1004	.0984	.0974	.0964	.0944	.0934	
$k \times 10^4$	. . .	1.10	1.05	1.08	1.04	.96	Av. 1.05

Calculations.—The velocity constants were calculated using the Goldschmidt equation[28]

$$k = \frac{(a + r) \ln \left(\dfrac{a}{a - x}\right) - x}{crt}$$

where k is the velocity constant expressed in g. moles/liter/sec., a the initial organic acid reactant concentration, r a constant compensating for the water formed during the progress of the reaction, x the quantity of organic acid esterified in t time and c the concentration of the hydrion catalyst. The values of r used in this investigation were calculated according to Williamson and Hinshelwood.[15] The value of c used for each determination of k was specific depending upon the analysis of the solution for chlorine ions. All velocity constants determined are for time periods wherein no less than 20% or no more than 80% esterification had occurred.

Temp., °C.	55	65	75	85
	0.60	0.30	0.25	0.20

Using the Arrhenius relation in its linear form the activation energies and the logarithm of the non-exponential factor were obtained by the method of least squares.

Results and Discussion

Table I includes the velocity constants for each of the esterification reactions at the four temperatures studied together with the corresponding values of the energy of activation and the values of the logarithm of the non-exponential factor PZ in the Arrhenius equation[8,29]

$$k = PZe^{-E/RT}$$

Owing to the fact that the data included herein take into consideration the reaction occurring between the hydrogen chloride catalyst present and the cyclohexanol by determining, as the reactions progress, the chlorine ion concentration, more nearly true estimates of the organic acid reactant present at any instant were made possible. It is not surprising, therefore, to note that the rate constant values obtained by Hartman, Storms and Gassmann[20] are not in exact agreement with those herein reported. In those instances where they obtained r values that increased with temperature it was necessary in this study to use r values that decrease as the temperature increases. It has been shown by Hinshelwood and Legard[16] and by Smith and Reichardt[30] that the value which r assumes is very sensitive to small variations in the rate constant and, therefore, only approximate values of r are necessary to produce good rate constant values. Since by definition $r = [ROH_2^+][H_2O]/[H_3O^+]$, a decrease of the value of r with increased temperature indicates that the ability of the alcohol to compete with the water for the proton decreases with an increase in temperature. It is possible, therefore, that water resulting from the reaction between the catalyst and solvent represents a complicating factor.

Assuming that the collision number, Z, remains constant for all the acids studied in this investigation or that the substituent does not alter the collision rate, any changes found in the value of log PZ must be attributed to changes in P. With the exception of *m*-toluic and *p*-methoxybenzoic acids, an inspection of Table I reveals that the introduction of a substituent group into the benzoic acid molecule decreases the values of

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(28) Goldschmidt, *Ber.*, **39**, 711 (1906).

(29) Nathan and Ingold, *J. Chem. Soc.*, 1168 (1935).

(30) Smith and Reichardt, THIS JOURNAL, **63**, 605 (1941).

TABLE I

VELOCITY CONSTANTS, ENERGIES OF ACTIVATION AND LOG PZ VALUES FOR HYDRION-CATALYZED ESTERIFICATION OF AROMATIC ACIDS WITH CYCLOHEXANOL

Acid	$k \times 10^5$ 55°	65°	75°	85°	Energy of activation,[a] E	Log of Arrhenius non-exponential factor[b] log PZ
Benzoic	1.56	4.26	9.08	19.70	19,500	8.229
o-Fluorobenzoic	2.35	5.45	11.10	22.60	17,500	7.047
m-Fluorobenzoic	2.21	4.93	10.30	23.40	18,200	7.480
p-Fluorobenzoic	1.48	4.43	8.37	15.30	17,900	7.145
o-Iodobenzoic	0.66	1.87	3.40	6.68	17,600	6.614
m-Iodobenzoic	3.16	7.11	14.30	27.00	16,700	6.612
o-Methoxybenzoic	5.23	12.60	25.30	56.10	18,200	7.876
m-Methoxybenzoic	1.91	5.04	10.00	23.90	19,300	8.145
p-Methoxybenzoic	0.72	1.96	3.50	10.70	20,200	8.328
o-Ethoxybenzoic	4.62	11.70	24.20	53.40	18,800	8.227
m-Ethoxybenzoic	1.89	5.50	11.20	22.00	18,900	7.898
p-Ethoxybenzoic	0.90	1.97	4.62	8.49	17,700	6.759
o-Toluic	.767	1.74	3.91	8.13	18,400	7.159
m-Toluic	1.73	4.13	11.46	21.38	20,000	8.576
p-Toluic	1.47	3.23	7.53	15.58	18,500	7.492
o-Nitrobenzoic	0.287	0.664	1.52	3.10	17,400	6.898
m-Nitrobenzoic	2.65	6.24	12.95	28.16	18,300	7.590
o-Bromobenzoic	0.995	2.26	5.10	10.94	18,700	7.444
m-Bromobenzoic	2.44	5.82	13.06	27.80	18,900	8.003
o-Chlorobenzoic	1.36	3.10	6.68	13.96	18,100	7.195
m-Chlorobenzoic	2.57	5.65	11.96	27.50	18,300	7.613
p-Chlorobenzoic	2.04	4.82	10.02	20.92	18,000	7.320

[a] $E = \dfrac{n(\Sigma \log k/T) - (\Sigma \log k)(\Sigma 1/T)}{n(\Sigma(1/T)^2) - (\Sigma/1T)^2} \times 2.303\,R$. [b] $\text{Log}\,PZ = \dfrac{(\Sigma \log k/T)\,(\Sigma 1/T) - (\Sigma \log k)(\Sigma(1/T)^2)}{(\Sigma 1/T)^2 - n(\Sigma(1/T)^2)}$.

TABLE II

COMPARISON AT 65° OF LOG k OBSERVED WITH LOG k CALCULATED USING THE RELATION, LOG $k = -4.371 + (0.422)\sigma$

Acid	$-$Log k obs.	$-$Log k calcd.	Difference
m-Fluorbenzoic	4.307	4.228	0.079
p-Fluorobenzoic	4.354	4.344	.010
m-Iodobenzoic	4.148	4.222	.074
m-Methoxybenzoic	4.298	4.322	.024
p-Methoxybenzoic	4.708	4.484	.224
m-Ethoxybenzoic	4.260	4.307	.047
p-Ethoxybenzoic	4.706	4.381	.325
m-Toluic	4.384	4.400	.016
p-Toluic	4.491	4.442	.049
m-Nitrobenzoic	4.205	4.071	.134
m-Bromobenzoic	4.235	4.206	.029
m-Chlorobenzoic	4.248	4.213	.025
p-Chlorobenzoic	4.317	4.275	.042
		Average	.082

both E and P. The fact that E and P changes are usually in the same direction has also been observed by Hinshelwood and Legard.[16]

From theoretical considerations Fairclough and Hinshelwood[10] have developed by a statistical method the following relationship between PZ and E

$$\log PZ = \mathrm{f}(E) + \text{constant}$$

It was found that this correlation is more precisely represented as

$$\mathrm{f}(E) = 1/\sqrt{E}$$

A graphical representation of the relationship between log PZ and $1/\sqrt{E}$ for the reactions included in this study is presented in Fig. 1. The approximate linear relation obtained indicates that the mechanism of the reaction is the same for these various reactions. Fairclough and Hinshelwood[10] have given a physical meaning to this phenomenon by assuming that a very highly activated molecule (large E) becomes so dislocated

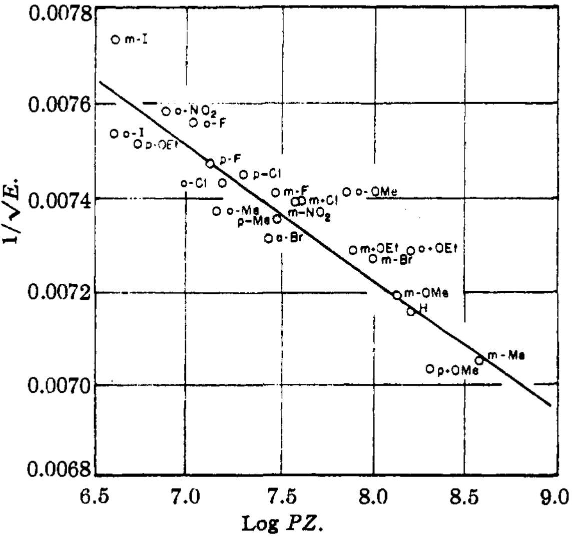

Fig. 1.—Relationship between log PZ and $1/\sqrt{E}$.

that a particular orientation is no longer necessary for reaction (large P).

Table II contains the observed rate constants at 65° for the meta and para acids studied together with the corresponding constants calculated by means of the Hammett equation. The value of ρ, 0.422, was obtained by the method of least squares and the values used for σ were those reported by Hammett.[13] The average difference between the observed rate constants and those calculated, namely, 0.082, compares favorably with the mean value of probable error in log k of 0.067 found by Hammett for a series of thirty-nine reactions. The higher mean value of probable error obtained for log k in this study is owing chiefly to the high differences obtained for *m*-nitro-, *p*-methoxy- and *p*-ethoxybenzoic acids. The differences of the *p*-methoxy and *p*-ethoxy acids may be related to the fact that they were the least soluble of those studied. It is interesting to note that Hartman and Gassmann[19] found high differences for *p*-methoxy-, *p*-ethoxy- and *p*-fluorobenzoic acids reacting with methanol. The results tabulated in Table II indicate that the Hammett equation might express approximately the effect of substituents on the esterification rate constant of benzoic acid with cyclohexanol.

Summary

1. Esterification rate constants of twenty-two substituted benzoic acids with cyclohexanol are determined taking into account the reaction between catalyst and solvent.

2. The experimental values of esterification rate constants for meta and para substituents are found to be in close agreement with those predicted by the Hammett equation.

3. For the esterification reactions studied it is observed that the energy of activation increases with the non-exponential factor of the Arrhenius relation and that the data obtained verify the Fairclough–Hinshelwood equation, log $PZ = 1/\sqrt{E}$ + constant.

MIDLAND, MICHIGAN RECEIVED JULY 26, 1944

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

Vapor-phase Thermal Isomerization of Pinane[1]

BY A. L. RUMMELSBURG

It has been shown[1a,2,3] that α-pinene forms the acyclic terpene *allo*-ocimene by controlled vapor-phase thermal isomerization. In addition, the acyclic terpene myrcene can be obtained by a similar isomerization of β-pinene.[3] The objective of the present work was to determine if a similar fission of the rings can occur by vapor-phase thermal isomerization of pinane (dihydropinene) to form dihydroacyclic terpenes.

Experimental

Pinane.—α-Pinene[4] was hydrogenated on a pilot plant scale using Raney nickel catalyst, a temperature of 120°, and hydrogen at a pressure of 75 lb./sq. in. to form pinane. Characteristics: $[\alpha]_D$ + 12°; n^{20}_D 1.4629; d^{20}_4 0.8566; b. p. 168–169° (760 mm.); bromine number 3.[5]

Apparatus.—Essential features of the isomerization apparatus were constructed from standard iron pipe (Fig. 1). The reaction tube had a free space of about 890 cc. The temperature within this tube was measured with a movable thermocouple. Liquid pinane was introduced through an attached glass flowmeter. During operation, the temperatures of three points (T_1, T_2 and T_3) within the reaction tube varied from 5 to 10° in the 500° range. This variation was in part caused by fluctuations in line voltage. The flash evaporator was kept at a temperature of about 285°. Preheating of the pinane from 285° to the reaction temperature was not employed, since this did not improve the ease of controlling the temperature within the reaction tube.[2]

Isomerization of Pinane.—The pinane was passed into the system at a liquid rate of 1550 cc. per hour. Thus, the contact time was about 5 sec. The maximum decrease in n^{20}_D and d^{20}_4 of the isomerization product with increasing temperature occurred within a temperature range of 495–515°. Above these temperatures, and up to about 550–580°, n^{20}_D and d^{20}_4 were somewhat greater, probably because of cyclization of acyclic hydrocarbons. The isomerization product obtained at 495–515° had the following characteristics: n^{20}_D 1.4500; d^{20}_4 0.8222; $[\alpha]_D$ +10°. A vacuum distillation indicated that terpene polymers were not present. In separate tests, similar results were obtained using a smaller all-glass pyrolysis system.

Fractional Distillation of Isomerized Pinane.—3900 g. of the product formed in the iron pyrolysis tube at 495–515° was distilled at 760 mm. pressure through a Fenske fractionating column having approximately 100 theoretical plates. The column was packed with small metal helices. The product was separated into 20–50 g. fractions. Pertinent physical characteristics of chosen fractions are plotted in Fig. 2. Fractions A, B, C and D are composites of smaller fractions; and their characteristics are described in Table I.

Catalytic Hydrogenation of Distillation Fractions.—In order to measure the unsaturation of specific fractions, 0.3000-g. samples were hydrogenated in duplicate at 25–30° in a small laboratory quantitative hydrogenation unit. The catalyst was 0.1000 g. of Adams platinum oxide. Glacial acetic acid was the solvent; and the hydrogen pressure was 760 mm. The quantity of hydrogen absorbed was corrected for blanks which were run simultaneously. The accuracy of this determination is about 1–2%. In order to obtain physical constants of suitable hydrogena-

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[1] Presented before the Division of Organic Chemistry at the 106th Meeting of the American Chemical Society, September, 1943, Pittsburgh, Pennsylvania. Original manuscript received October 8, 1943.

[1a] Arbuzov, *J. Gen. Chem.* (U. S. S. R.), **3**, 21 (1933); *Ber.*, **67B**, 563 (1934).

[2] Author, unpublished work in 1937.

[3] Goldblatt and Palkin, THIS JOURNAL, **63**, 3517 (1941).

[4] Hercules α-pinene 111, purity 95%. Characteristics: $[\alpha]_D$ +30°; n^{20}_D 1.4661; d^{20}_4 0.8602; b. p. 156–158° (760 mm.).

[5] The theoretical bromine number of α-pinene is 115. However, values greater than theoretical are actually obtained, apparently because of isomerization to monocyclic terpenes containing two double bonds during the determination.