screen and adding the required amount of solvent at room temperature to give a solution containing 20% solids. The flask containing the resin and solvent was placed on a shaking machine and agitated until the resin dissolved or until no more of the resin would go into solution.

All benzene solutions of zinc resinates reported in Table IV could be diluted with more than an equal volume of alcohol before the solution became cloudy.

CONCLUSIONS

A simple method of preparing fused zinc resinates has been developed by modifying rosin with an aldehyde and fusing this aldehyde-modified rosin with a reactive zinc compound. Zinc resinates prepared from aldehyde-modified rosins do not block and show good solubility in the common varnish solvents. Zinc resinates may be prepared from rosin derivatives which have acid numbers of less than 20.

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Rate of Isomerization of Cyclohexane

EFFECT OF ALUMINUM CHLORIDE AND HYDROGEN CHLORIDE

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ANY publications on hydrocarbon isomerization have dealt with the catalytic activity of aluminum chloride in conjunction with other substances, most frequently hydrogen chloride. It has been postulated by Powell and Reid (11) that the actual catalyst is the strong acid HAlCl₄, resulting from the association of the two catalyst components. However, all attempts to isolate HAlCl₄ as such have been unsuccessful (1, 16). Brown and Pearsall (1) have shown, on the other hand, that aluminum chloride and hydrogen chloride do interact stoichiometrically in the presence of a substance to which basic properties may be ascribed. Recent workers have found that, with carefully purified materials, aluminum chloride-hydrogen chloride does not catalyze the isomerization of either alkanes (9) or cycloalkanes (13) at moderate temperatures. However, these same workers have shown further (9, 10, 13, 17) that traces of other substances, such

as olefins, oxygen, or water, convert aluminum chloride or the aluminum chloridehydrogen chloride mixture into an active catalyst. Stevenson and Beeck (13) have postulated a partially heterogeneous catalysis with aluminum chloride in the presence of water. The nature of the catalyst in the presence of these added substances has remained obscure and the mutual effect of the components in the hydrogen chloride-aluminum chloride system has not been clearly established.

The principal purpose of the present work was to investigate the effect of aluminum chloride and hydrogen chloride concentrations on the rate of isomerization of hydrocarbons, using commercial reagents such as would be available in large scale industrial applications. Cyclohexane was chosen for investigation because of relative freedom from the side reactions normally encountered in isomerization of alkanes $(\mathcal{I}, \mathcal{I})$ and because of ease of analysis of the products.

During the investigation the equilibrium between cyclohexane and methylcyclopentane was determined at several temperatures and the effect of hydrogen pressure on reaction rate was investigated.

METHODS AND EQUIPMENT

Commercial reagents were used in all cases, and the experiments were carried out in a steel reaction vessel without special precautions to exclude traces of air or moisture.

> REAGENTS. Cyclohexane having a refractive index of 1.4262 at 20° C., from Dow Chemical Co., aluminum chloride from Hooker 'Electrochemical Co., and anhydrous hydrogen chloride from Harshaw Chemical Co. were used as obtained. To ensure uniformity of particle size as well as of composition, the aluminum chloride used in all runs was from the same batch.

> APPARATUS. The reactions were carried out in a 1550-ml. carbon-steel pressure reactor provided with a 1725-r.p.m. mechanical stirrer. The reactor was so jacketed that it could be quickly heated by steam or cooled by water. Auxiliary equipment was



Figure 1. Cyclohexane-Methylcyclopentane Equilibrium



provided for introducing measured quantities of hydrocarbon, hydrogen chloride, and hydrogen. Provision was made for withdrawal of the liquid hydrocarbon product from the settled aluminum chloride catalyst. This apparatus has been described in detail in a previous paper (10).

REACTION CONDITIONS. With the exception of the experiments to determine the composition of the equilibrium mixture and the effect of hydrogen pressure, all runs were carried out at 100° C. with 10 minutes reaction time and under an initial hvdrogen pressure of 600 pounds per square inch gage, measured at room temperature. Hydrogen was used, because it was found in preliminary runs that in its absence there was a tendency for the aluminum chloride to agglomerate; apparently as a result of this agglomeration and attendant change in particle size, reproducibility of conversion was poor. By the use of hydrogen, the aluminum chloride was recovered as a crystalline powder and reproducibility was good.

ANALYTICAL PROCEDURES. In the experiments carried out to determine the composition of the equilibrium mixture, 60-plate fractional distillation was employed for the analysis of the product. In all other experiments cited, refractive index of the product was used in calculating the conversion of cyclohexane to methylcyclopentane. This simplified technique was found to be accurate within 1% by actual comparison with fractionation data from a number of preliminary runs; these early runs demonstrated that no significant amounts of by-product were formed in the isomerization of cyclohexane at 100° C. under the reaction conditions employed in the present rate studies.

CALCULATION OF REACTION RATES. For calculation of the specific reaction rate, α , of the isomerization of cyclohexane to methylcyclopentane, the equation for a reversible first-order reaction was used

$$\alpha = \frac{X_{\bullet}}{at} \ln \frac{X_{\bullet}}{X_{\bullet} - X} \tag{1}$$

where, for the present study, a is the mole per cent cyclohexane in charge (100); t, the reaction time in hours; X, the mole per cent methylcyclopentane at time, t; and X_e , the mole per cent methylcyclopentane at equilibrium.

RESULTS AND DISCUSSION

Published data on the equilibrium concentration of cyclohexane and methylcyclopentane at temperatures above 80° C. are few and inconsistent. Since 100° C. was the most convenient temperature for the rate studies, the equilibrium distribution at this temperature was determined; measurements were also made at 160° and 167° C. to aid in defining the equilibrium curve at higher temperatures. To ensure the establishment of equilibrium, reaction times and catalyst concentrations were such as to provide overtreatment; this resulted in appreciable side reaction to give products boiling both below methylcyclopentane and above cyclohexane, as shown in Table I.

This type of overtreatment had been found (2) to have no significant effect on equilibrium distribution of alkanes; Stevenson and Morgan (14) have made the same observation specifically for cyclohexane-methylcyclopentane.

The equilibrium values thus obtained are plotted as a function of temperature in Figure 1, along with published values obtained with aluminum chloride catalyst systems (4, 8, 12, 14). The value at 100° C. agrees well with the general curve and is in excellent agreement with the reported value of Stevenson and Morgan (14). The fact that their work was conducted at atmospheric pressure and that the present work was carried out in the presence of a substantial hydrogen pressure indicates no significant influence of pressure on cyclohexane-methylcyclopentane equilibrium.

EFFECT OF HYDROGEN PRESSURE. In order to determine the effect of hydrogen pressure on reaction rate, a series of runs was carried out at initial hydrogen pressures of 0 to 1000 pounds per square inch gage, measured at room temperature. These experiments are summarized in Table II.

The results, plotted in Figure 2, show a definite decline in the isomerization rate of cyclohexane, probably as a linear function of hydrogen pressure over the range studied.

EFFECT OF CATALYST COMPOSITION. To determine the effect on reaction rate of changes in amounts of aluminum chloride and hydrogen chloride, a series of runs was carried out in which the amount of one component in the system was varied while that of the other was held constant. These experiments are summarized in Table III. In Run 11, in which cyclohexane was contacted with aluminum chloride in the absence of added hydrogen chloride, a small but positive conversion was obtained. Since pure aluminum chloride alone has no activity as an isomerization catalyst (13), the slight activity in Run 11 is attributed to traces of moisture or oxygen, inasmuch as no special precautions had been observed in this study to exclude these materials.

The data from Table III are plotted in Figure 3 to show the relationship between specific reaction rate, α , and the amount of the catalyst component in the system. With a constant hydrogen chloride concentration, the reaction rate increases with increasing amounts of aluminum chloride. Likewise, the reaction rate var-

Table I. Cyclohexane-M Equilibri	Iethylcyc um	LOPENTAN	E
Run No.	1	2	3
Temperature, ° C. Reaction time, minutes Hydrogen pressure, lb./sq. inch gage Cyclohexane, grams Aluminum chloride, grams Hydrogen chloride, grams	$ \begin{array}{r} 100 \\ 70 \\ 600 \\ 420.0 \\ 66.0 \\ 9.4 \end{array} $	$160 \\ 70 \\ 600 \\ 451.0 \\ 84.5 \\ 20.5$	$167 \\ 30 \\ 600 \\ 617 \\ 84.5 \\ 20.5$
Liquid products, volume % Boiling below methylcyclopentane Methylcyclopentane Cyclohexane Boiling above cyclohexane	3.6 33.3 62.9 0.2	21.0 17.2 16.1 45.7	$12.2 \\ 30.8 \\ 26.8 \\ 30.2$
Methylcyclopentane to cyclohexane fraction Mole % methylcyclopentane	on 33.8	50.8	52.6
cyclohexane	0.51	1.03	1.11

TABLE II. EFFECT OF HYDROGEN PRESSURE ON REACTION RATE

Char Tem Read	rge. Cyclohexane Aluminum ch Hydrogen chl perature. 100° C. ction time. 10 min	420 grams (5.0 loride 33 4 grams (0 oride 9.4 grams (0 outes	0 moles) 1.25 mole) 1.25 mole)
Run No.	Hydrogen, Lb./Sq. Inch Gage	$\operatorname{Conversion}_{\%}$	Reaction Rate, α
4 5 6 7	0 300 600 1000	27.6 26.9 23.4 21.6	3.22 3.02 2.29 2.00

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Effect of Catalyst Components on Figure 3. **Reaction Rate**

ies directly with the amount of hydrogen chloride when aluminum chloride is held constant. If the data are replotted to show α as a function of the square root of the amount of either of the catalyst components, the curved lines are converted essentially to straight lines.

The close similarity of the two curves, Figure 3, demonstrates the equivalence of hydrogen chloride and aluminum chloride in determining the activity of the catalyst.

SPHERE OF CATALYTIC ACTIVITY. It is significant that the relationships shown in Figure 3 hold, even when the amount of aluminum chloride exceeds many times its probable solubility in the hydrocarbon under the reaction conditions. Because the rate, therefore, depends primarily on the amount of aluminum chloride in the reactor and not on the amount dissolved, it follows that the reaction is catalyzed largely by undissolved aluminum chloride. From this it would appear that the rate-controlling reaction takes place on the surface of the catalyst.

NATURE OF CATALYTIC ACTION. As has been mentioned, Brown and Pearsall's work (1) showed that no interaction occurs between pure aluminum chloride and pure hydrogen chloride, but that in the presence of a basic substance-i.e., a proton acceptora complex is formed in which the aluminum chloride and hydrogen chloride are associated stoichiometrically. In the present

TABLE III.	EFFECT OF CATALYST COMPOSITION
yclohexane charg	e. 420 grams (5.0 moles)

Hydrogen pressure. 600 pounds per square inch gage (initial). Temperature. 100° C. Reaction time. 10 minutes

Variable Studied	Run No.	Catalyst Concn., Mole/Mole Cyclohexane		Con- version.	
		AlCl,	HCl	%	a
AlCla	8 9 6 10	$\begin{array}{c} 0.012 \\ 0.025 \\ 0.050 \\ 0.100 \end{array}$	0.050 0.050 0.050 0.050 0.050	10.2 17.9 23.4 29.3	$0.70 \\ 1.45 \\ 2.29 \\ 3.27$
HCl	11 12 6 13	$0.050 \\ 0.05$	0.000 0.025 0.050 0.100	$\begin{array}{r} 4.2 \\ 21.6 \\ 23.4 \\ 28.1 \end{array}$	0.26 1.97 2.29 3.38

experiments, however, no proton acceptor was added. The observed catalytic activity is attributable to the fact that the techniques and commercial reagents employed resulted in the presence in the reaction mixture of a proton acceptor, by virtue of traces of moisture, oxygen, or other contaminants. Under the controlled conditions of the experiments any variations in the amount of proton acceptor would be insufficient to affect the general trends observed. These trends appear to be well established and have not been evident in previous work using purified reagents.

On the basis of Brown and Pearsall's work with the aluminum chloride-hydrochloric acid system and as the result of analogous investigations on the hydrofluoric acid-boron trifluoride system (6, 7), it is postulated that the proton acceptor serves to force the following series of reactions to the right:

$$HCl + AlCl_{3} \stackrel{\longrightarrow}{\longrightarrow} [HAlCl_{4}] \stackrel{\longrightarrow}{\longrightarrow} H^{+}AlCl_{4}^{-}$$

It is further postulated that it is the resulting product—in the form of the ionized complex with the proton acceptor-which acts as the effective catalyst.

Catalytic action may be pictured as a simultaneous protonanion attack on the hydrocarbon molecule, in manner similar to the push-pull mechanism conceived by Swain (15) to explain displacement reactions of organic halides. Thus, when the electrophilic proton portion of the catalyst approaches a methylene group, it tends to attract the electrons around the carbon atom. At the same time the nucleophilic AlCl₄⁻ portion of another catalyst molecule approaches from the other side and attracts the hydrogen atom of the methylene group. The simultaneous attack effects an over-all electron displacement which results in the formation of an activated complex, with subsequent rearrangement of the hydrocarbon molecule.

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