Catalytic dealkylation of naphthenes and paraffins
by James F Ross

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of IMaster of Science in Chemical Engineering
Montana State University

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The activation energy for normal paraffins decreased regularly from about 48 k-cal/mol. for n-heptane to 40 k-cal/mol. for n-hexadecane.

The catalytic decomposition of normal paraffins wae estimated as proceeding about 750 times faster than the uncatalyzed thermal decomposition, under the conditions of this investigation.

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ABSTRACT

Several naphthenes and paraffins were passed over hydrogen fluoride activated alumina catalyst at temperatures of 500-550° C., liquid space velocities of 0.2/hr., and atmospheric pressure (640 mm. Hg.). Analysis of the gaseous and liquid reactor effluent showed that the sixteen compounds used (cyclohexane, methylcyclohexane, ethylcyclohexane, methylcyclopentane, n-hexane, n-heptane, n-octane, n-dodecane, n-hexadecane, neohexane, 2,2,4-trimethylpentane, 2,2,5-trimethylhexane, 2,3-dimethylbutane, 2,4-dimethylpentane, 3-methylpentane, and 3-methylheptane) all suffered fairly random carbon-carbon bond rupture. In every case, however, two of the main reaction products were a low boiling liquid, presumably the result of realkylation of dealkylated products, and propylene.

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INTRODUCTION

Dealkylation, as applied to hydrocarbons, may be defined as the rupture of specific carbon-carbon bonds in the molecule. Dealkylation can thus be distinquished from the more general term "cracking", which connotes a more general, random bond rupture.

Thermodynamically, almost every hydrocarbon is unstable with respect to its elements, carbon and hydrogen.(1) In general, also, larger hydrocarbons are more unstable than smaller homologues, (1) and these larger molecules will, under the accelerating influence of heat, be converted to smaller hydrocarbons, carbon, and hydrogen. Kinetically, it may be shown that, in general, hydrocarbons possess such a high energy of activation of decomposition that measurable rates for this reaction with simple molecules begin only at temperatures somewhat above 300° C.

Although the ordinary thermal decomposition of hydrocarbons has not been proved to proceed through a free radical mechanism, there is much evidence that the formation of free radicals is the first step in the decomposition of hydrocarbons at more elevated temperatures. Rice and coworkers (14) detected free radicals in high temperature hydrocarbon decomposition. Frey (3) was able to initiate butane decomposition at temperatures below the normal decomposition range by introducing methyl radicals. Rice and Dooley (12) found that lead mirrors were removed by the products of ethane dissociation at 850-950° C. Hobbs and Hinshelwood (8) demonstrated that nitric oxide inhibited the decomposition of ethane at 600° C.

On the basis of this and other evidence (18), it is reasonable to conclude that at low pressures, even at ordinary decomposition temperatures, hydrocarbons decompose to form free radicals.

Postulating a free radical mechanism, the first step in the thermal decomposition of a hydrocarbon becomes:

$$R{:}R' \longrightarrow R. + R.'$$

or

$$R{:}H \longrightarrow R. + H.$$

If the energy of activation of the reverse reactions:

$$R.\ \ R.' \longrightarrow R{:}R'$$

or

$$R.\ \ H. \longrightarrow R{:}H$$

is zero, or at least extremely small (as evidenced by the extremely short life of most organic free radicals), the energy of activation of the forward reaction becomes equal to the bond strength and it is possible to estimate the kinetic probability of the formation of a given radical from a comparison of experimentally determined bond energies.

Table I (18)

Bond Energies, k-cal.

Residue	R-H	$R-CH_3$	$R-C_2H_5$
CH_3	102	86	83
C_2H_5	97	83	80
$n-C_3H_7$	95	82	--
$iso-C_3H_7$	89	78	--
$n-C_4H_9$	94	81	--
Tert C_4H_9	86	76	--

Table I indicates greater ease of carbon-carbon rupture at a tertiary or quaternary carbon atom. Because of the higher energy involved, dehydrogenation to form an olefin of the same carbon skeleton should be a minor side reaction.

But bond energies alone will not allow prediction of products to be expected since the actual products obtained from thermal cracking are due to various secondary reactions. The free radicals formed may either decompose further or react with other molecules producing new reactive radicals. By considering various secondary reactions which would arise from a given free radical, a theory based on a free radical mechanism has been developed by Rice and Herzfeld (13) to account for many of the observed kinetic phenomena and products of thermal cracking.

Frey and Hepp (4) confirm the predictions deduced from Table I, having obtained the values for specific rate constants at 475° C. listed in Table II.

Table II

Thermal Decomposition Rate Constants

Substance	k
propane	1.5×10^{-3}
n-butane	4.8 x "
iso-butane	4.8 x "
n-pentane	5.7 x "
iso-pentane	6.5 x "
n-hexane	15. x "
iso-hexane	21. x "

Normal hydrocarbons above hexane possess a somewhat constant energy of activation for the decomposition reaction of 65 k-cal (C_6-C_{10}) to 60 k-cal (C_{10}-C_{32}) (15).

The extent to which a carbon skeleton is branched has a direct bearing on the stability of the compound. Good, Voge, and Greenfelder (6), studying the effect of chain branching, found that for similar conditions, the relative stability of the various hexanes was:

Neohexane $\rangle$ n-Hexane $\rangle$ 3-Methylpentane $\rangle$

2-Methylpentane $\rangle$ 2,3-Dimethylbutane

The products obtained from a thermal cracking reaction usually show that the higher normal paraffins cleave near the middle of the chain. Tilecheyev and Feigin (21) present the data recorded in Table III.

Table III

Fractions obtained from Thermal Cracking (21)

Hydrocarbon Cracked	Predominate Fractions of Decomposition Products
n-Decane	Gases, Pentanes, Pentenes
n-Dodecane	Gases, Pentanes, Pentenes, Heptanes, Heptenes, Octanes, Octenes
n-Hexadecane	Gases, Pentanes, Pentenes, Octanes, Octenes, Nonanes, Nonenes, 180-200° C.
Dotriacosane	Gases, Octanes, Octenes, Nonanes, Nonenes, C_{16} and C_{17} fractions

In these runs, hydrogen formation was almost negligible, ranging from 0.001 to 0.1%.

Naphthenes with long side chains behave similarly, the side chain resembling the corresponding paraffin. However, when the side chains are methyl or ethyl groups, the molecule becomes comparatively stable, and severe conditions are required to rupture the molecule (16). Quantitative data by Tilicheyev (20), listed in Table IV illustrate the relative stability of several naphthenes and the corresponding paraffins.

Table IV

Specific Rate Constants for Thermal Cracking of Naphthenes and Corresponding Paraffins at 500°C.

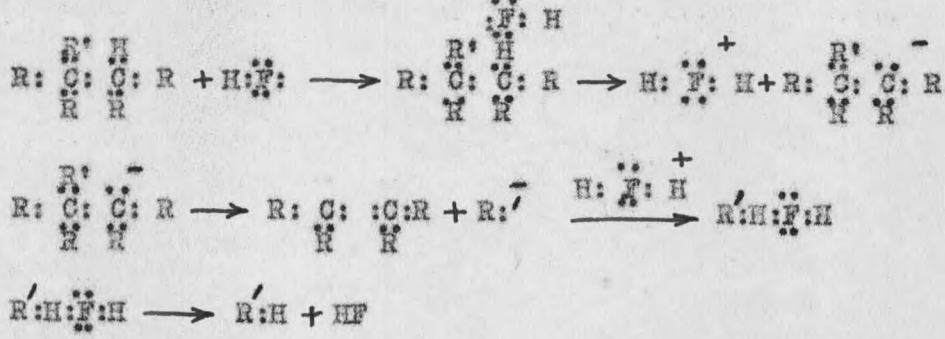
Hydrocarbon	k
Cyclopentane	0.12×10^{-4}
Cyclohexane	0.19 x "
Tetralin	3.2 x "
Decalin	3.7 x "
n-pentane	2.3 x "
n-hexane	10. x "
n-decane	74. x "

It is at once apparent that naphthenic rings possess a high degree of stability. In the presence of cracking catalysts, however, naphthenic rings become very unstable, the rate of decomposition being 10 to 20 times greater than that of the normal paraffin with the same number of carbon atoms (16).

Catalysts capable of accelerating hydrocarbon decomposition may be classified into three types: Friedel-Crafts, Intermediate, or Adsorption.

Friedel-Crafts catalysts such as $AlCl_3$, BF_3, HF, or H_2SO_4, are invariably nucleophilic reagents which initiate a reverse of Friedel-Crafts alkylation by forming a coordination complex with the hydrocarbon molecule. The mechanism of a paraffin dealkylation of this type begins with the catalyst coordinating with a hydrogen atom of

the hydrocarbon. The coordinated hydrogen leaves the paraffin, which causes an electron shift and ejection of a carbanion, which immediately unites with the proton previously ejected. The reaction is complete as the coordination complex separates into a lower paraffin and the catalyst (19).



Friedel-Crafts catalysts cause carbon-carbon cleavage to occur predominately at certain specific bonds. Under the influence of these catalysts, aromatics invariably split off side chains, yielding aromatic rings and olefins; paraffins usually split into isobutane or isopentane (where possible) and olefins (16). In paraffin dealkylation, the products to be obtained may sometimes be predicted on the basis of the electronic theory (11).

Intermediate catalysts behave much the same towards hydrocarbons as Friedel-Crafts catalysts, but are usually neither as active nor as specific. These catalysts, which are usually activated clays or metal oxides or sulfides, possess coordinate unsaturation which enables them to form a loose complex with hydrocarbons, but they do not catalyze other Friedel-Crafts reactions. Some of these intermediate catalysts,

such as Cr_2O_3 largely bring about terminal dehydrogenation to form an olefin of the same carbon skeleton, while others, such as the activated clays, mainly cause central carbon-carbon rupture (16).

Unlike Friedel-Crafts and Intermediate catalysts, which cause dealkylation by a mechanism totally different from thermal cracking, adsorption catalysts appear mainly to accelerate the thermal cracking reaction. Consequently, these catalysts bring about more random carbon-carbon rupture than the other types.

Adsorption, or surface active catalysts owe their catalytic activity both to a lowering of the activation energy and a large surface area. It may be shown (5) that for one square centimeter of surface:

$$\frac{k_c}{k_h} \cong 10^{-12} e^{\Delta E/RT}$$

where k_c is the specific rate constant for the heterogeneous, catalyzed reaction, k_h is the specific rate constant for the homogeneous, uncatalyzed reaction, and ΔE is the difference between the activation energies for the uncatalyzed and catalyzed reactions. It is immediately apparent that in order to be effective, a catalyst must possess a large surface, and must lower the energy of activation appreciably.

The lowering of the activation energy due to an adsorption catalyst can be related to the heats of adsorption (17). When the reactant molecule is adsorbed on a surface, heat is evolved, and the molecule assumes a lower energy state. But far less energy is required to activate the adsorbed molecule (17), since it may be shown (5) that the catalytic ac-

tivation energy equals the non-catalytic activation energy plus the energy of adsorption of the reactant minus the energy of adsorption of the activated molecule. Because the energy of adsorption of the activated molecule is greater than the energy of adsorption of the reactant, the reaction proceeds more easily.

It is possible to combine several types of catalysts into one by adsorbing a layer of hydrogen fluoride on activated alumina. Kindschy (9), Luke (10), and Herzel (7) have demonstrated the usefulness of this combination of catalysts in aromatic dealkylation, olefin isomerization and catalytic cracking respectively and it was thought that selective dealkylation of paraffins and naphthenes could be brought about by means of this catalyst.

The purpose of this thesis, therefore, is to evaluate hydrogen fluoride activated alumina as a dealkylation catalyst for naphthenes and paraffins.

EQUIPMENT, METHODS, AND MATERIALS

Equipment

The equipment used in this investigation consisted of the reactor assembly depicted in Figure 1, a precision rectification column, a low temperature fractionation gas analysis system, an Orsat gas analysis unit, and a refractometer.

The reactor was constructed from a 30 inch section of 2 inch schedule 80 steel pipe, both ends of which were closed with welded caps. In each cap, a hole was drilled axially and threaded to receive 3/4 inch pipe. On the upper end a 3/4 x 3/4 x 1/8 tee was screwed into the cap through a short nipple and connected the feed system to the reactor. The top of the tee was closed with a 3/4 inch plug. This arrangement permitted the catalyst to be inserted or changed through the top of the reactor.

Three thermowells, made from 1/8 inch steel pipe, were welded into the reactor eight inches apart, the lowest one six inches above the bottom of the reactor. The ends of the thermowells were placed in the axis of the reactor. When so placed, each thermowell was approximately halfway up each third of the catalyst bed.

Temperature measurements were made with iron-constantan thermocouples on a Leeds and Northrup potentiometer calibrated to read directly in degrees Centigrade.

The reactor was heated by two resistance windings, separated from the reactor and each other by layers of asbestos tape. The inner heater consisted of about 50 feet of B&S 20 gauge Nichrome wire (R = 35 ohms)

wound spirally from one end of the reactor to the other, then back again. The outer heater was composed of about 110 feet of the same wire (R = 75 ohms), wound in the same manner. The inner winding was connected to a 110 volt autotransformer, the outer to a 220 volt autotransformer. The reactor and heaters were insultated with a layer of asbestos tape, blocks of magnesite one inch thick, and an inch thick coating of asbestos mud.

The reactor was filled with a two inch layer of Berl saddles which acted as a catalyst support, followed by 900 ml. of 1/8 inch Harshaw Alumina pellets. The remaining space above the catalyst was filled with 1/2 inch steel ball bearings whose higher heat conductivity insured that the feed would approach the catalyst temperature before passing into the catalyst bed.

Feed was supplied to the reactor from a 1000 ml. graduated cyclinder by a Merkle-Korff type bellows pump. Saran tubing was used for the feed line to within six inches of the reactor. Copper tubing was used for the last six inches of line leading to thereactor because the temperature of part of this section of line sometimes exceeded the softening point of the Saran tubing. Copper tubing was not used throughout because the liquid remaining in the bellows of the pump after a run could only be removed by inverting the pump, and the flexibility of Saran tubing allowed the pump to be inverted easily.

Two water condensers cooled the reactor effluent. The first was made from three feet of 1/8 inch copper tubing encased in a lead pipe water jacket. The second condenser was a standard 20 inch bulb type

glass condenser. Gases passing through these condensers were conducted either to a gas sample bottle or to a three liter wet gas meter.

The precision rectification column was packed with 1/8 inch Fenske helices, and was calibrated at 30 perfect plates at total reflux. This column was 48 inches high. Reflux ratios were controlled through a Corad distilling head. Condenser temperatures were measured by a 0-200° C. glass thermometer graduated at intervals of 0.1° C. This thermometer was calibrated in condensing steam and melting ice.

A system was used for vacuum distillations composed of a Cenco Megavac pump joined through two surge tanks to the rectification column. Between the two tanks, a solenoid valve, activated through a mercury switch and an electronic relay, maintained the desired pressure in the second tank to within ± 1 mm Hg.

Refractive indices were read to five significant figures on a Valentine refractometer at $20.0 \pm 0.1°$ C.

Methods

Activation of Catalyst

The catalyst was activated by a method similar to that outlined by Berg et al (2). Drying the catalyst was accomplished by heating the reactor to 250-300° C. for at least two hours. Any water vapor remaining in the reactor was swept out by passing nitrogen through the reactor for one or two minutes. A calcium chloride drying tube was placed in the outlet line to prevent water vapor from entering the reactor while it cooled to room temperature.

The feed and condenser systems were disconnected from the reactor and a cylinder of anhydrous hydrogen fluoride connected to the top of the reactor by means of copper tubing. A kerosene bubbler and blowout line were substituted for the condenser system. Anhydrous hydrogen fluoride was passed through the reactor at room temperature for an hour, after which the reactor was heated to 400° C. and held at that temperature for two hours, while hydrogen fluoride was still passing through. After this, nitrogen was used to purge the catalyst of excess hydrogen fluoride.

During activation, alumium fluosilicate was formed from the silica impurity in the catalyst. Although most of this compound was carried down to the kerosene bubbler, enough usually remained in the fittings attached to the bottom of thereactor (which were not heated to the sublimation temperature of the fluosilicate) to necessitate their removal and unplugging.

Reaction Runs

The reactor was heated until the center thermocouple gave a reading approximately 5°C. above the desired temperature. Meanwhile, the density of the feed had been determined on a Westphal balance, and about 500 ml. of charge placed in the feed cylinder. Air was swept from the reactor by a 15 minute nitrogen purge. Following this, the feed pump was started and the gas meter set at a reading of zero. As the liquid feed reached the reactor, (the liquid level was visible through the Saran feed line) the liquid level in the feed cylinder, the reading of the gas meter, and the three thermocouple readings were recorded.

The feed level, gas volume, and temperatures were recorded at 15 minute intervals, so that the temperature could be averaged over nine points during the two hour runs.

If large volumes of gas were formed, some liquid was entrained in the gas stream. On the runs in which this occurred, the density of the effluent gas stream was determined by filling a 0.2082 liter evacuated flask with the effluent vapors. The flask was weighed to 0.1 mg. on an analytical balance to determine density. The weight of gas as determined by gas analysis was subtracted from the weight of gas and entrained liquid to yield the amount of entrained liquid. In making a material balance, the weight of entrained liquid was added to the weight of liquid reactor effluent.

After an hour on stream, the non-condensible vapor was allowed to displace 6-8 liters of water from a gas sample bottle. The volume of the vapor in the bottle was determined by weighing the water displaced. This volume was added on to the total volume recorded by the gas meter.

Runs were usually terminated after two hours on stream. Hydrocarbon vapors were removed from the reactor by a 15 minute nitrogen purge for light feeds, or 15 minute evacuation for heavy liquids. The liquid product was weighed to 0.1 gram and allowed to stand at -40°C. until rectified.

Burnoffs

As the hydrocarbons were dealkylated, small amounts of carbon were deposited on the catalyst, necessitating periodic burnoffs. These burnoffs were made immediately after each run while the reactor was still hot. Air was blown through the reactor until an Orsat analysis of the effluent gases showed an appreciable amount of oxygen. The temperature of the reactor bed was never allowed to reach 600°C. during these burnoffs, since the catalyst began to sinter above this temperature.

Rectification

Product rectification was started by flooding the column to wet the packing, then placing the column on total reflux for at least one hour. A dry ice trap connected to the column vent caught any hydrocarbons which boil below the minimum condenser temperature. After the column had reached equilibrium, the Corad head was set at a reflux ratio of 30:1, and the product withdrawn. The size of the samples drawn was determined by the rate of change of condenser temperature, so that samples ranged from 2 to 50 grams. If the condenser temperature reached 200°C. the column was cooled and distillation continued at reduced pressure.

Gas Analysis

Gas samples were analyzed in a low-temperature-fractionation-gas-analysis unit using liquid nitrogen as a coolant. The unit automatically recorded column head temperature as a function of volume of gas distilled, so that mol percentages of each component could be read almost directly. The breaks between all hydrocarbon gases boiling below isobutylene (methane through isobutane) were very sharp, but isobutylene, butenes and n-butane could not be distinguished accurately, and were reported as C_4H_8.

Additional notes

At first, several dry ice traps were placed between the reactor water condenser and the gas meter to retain C_3, C_4, and C_5 hydrocarbons. When the analysis of these light hydrocarbons was attempted in a vacuum jacketed packed column, no useful information could be obtained since the distillation curves had an almost constant slope, and losses always exceeded 10%.

Materials

All compounds used as charge stocks were purified to the specification listed below. Normally, this purification was accomplished by rectification alone, but in some cases where the presence of aromatics was suspected, rectification was preceded by an extraction with oleum.

Compound	Source	n_D^{20}	Boiling Point °C.	Pressure mm Hg.
Neohexane	Phillips, Tech Grade	1.3693	44.0	640
2,3-Dimethylbutane	Phillips, Tech Grade	1.3746	52.6-52.8	640
3-Methylpentane	Humphrey-Wilkinson	1.3769	59.0-58.4	640
n-Hexane	Phillips, Tech Grade	1.3749	62.7	640
2,4-Dimethylpentane	Phillips, Tech Grade	1.3810	74.4-74.5	630
n-Heptane	Phillips, Pure Grade	1.3879	92.1-92.3	640
2,2,4-Trimethylpentane	Phillips, Pure Grade	1.3907	92.9	640
3-Methylheptane	Phillips, Tech Grade	1.3990	111.2-112.0	640
2,2,5-Trimethylhexane	Phillips, Tech Grade	1.3992	115.5-115.7	630
n-Octane	Humphrey-Wilkinson	1.3983	119.1-119.5	640
n-Dodecane	Humphrey-Wilkinson	1.4217	145 -147	100
n-Hexadecane	Humphrey-Wilkinson	1.4340	162 -164	20
Methylcyclopentane	Phillips, Tech Grade	1.4102	66.1-66.5	640
Cyclohexane	Eimer & Amend, C.P. Grade	1.4260	75.3	640
Methylcyclohexane	Eastman-Kodak	1.4330	93.0-94.0	640
Ethylcyclohexane	Eastman-Kodak	1.4340	123-124	640

SAMPLE CALCULATIONS

The sample calculation of material balance and activation energy are based on run #4. The following data were obtained:

Volume of methylcyclohexane charged	365	ml.
Weight of methylcyclohexane charged	278	gms.
Weight of liquid product	149.5	gms.
Weight of gaseous product and entrained liquid	116.5	gms.
Mols of gaseous product	3.58	mols.
Time of run	2	hrs.
Average Reactor Temperature	554°	C.

An analysis of the liquid product shows that the liquid contained:

Liquid boiling below charge stock	11.5	weight per cent
Methylcyclohexane	67.0	
Heavier boiling compounds	21.5	

The gaseous product analyzed:

H_2	17.6 mol per cent	1.1 weight per cent
CH_4	20.5	10.7
C_2H_4	16.6	15.3
C_3H_6	25.4	35.0
C_4H_8	9.6	18.3
C_4H_{10}	10.3	19.6

Average molecular weight of gaseous product from gas analysis = 30.45

The weight of gas was therefore 30.45 x 3.58 = 109.0 gms.

The entrained liquid, 116.5 - 109.0 = 7.5 gms., must be added on to the weight of liquid product

Carbon and losses total, by difference = 278 - 116.5 - 149.5 = 12.0 gms.

These data yield the final material balance:

H_2	0.43 weight per cent
CH_4	4.20
C_2H_6	6.00
C_3H_8	13.72
C_4H_8	7.18
C_4H_{10}	7.69
Liquid boiling below charge stock	6.50
Methylcyclohexane	37.82
Heavier boiling residue	13.14
Carbon and Losses	4.32

The ultimate conversion is obtained by dividing the per pass composition by the per cent of methylcyclohexane converted, to yield:

H_2	0.7 weight per cent
CH_4	6.7
C_2H_6	9.6
C_3H_6	22.1
C_4H_8	11.5
C_4H_{10}	12.4

Liquid boiling below charge stock	10.5 weight per cent
Heavier boiling residue	19.5
Carbon and losses	7.0

Defining the liquid space velocity as the volume of liquid charged per volume of catalyst per hours,

$$LSV = \frac{365 \text{ ml. charged}}{2 \text{ hours}} \times \frac{1}{900 \text{ ml. of catalyst}} = 0.203 \text{ hr}^{-1}$$

If the specific rate constant is defined for a first order reaction:

$$k = 2.303 \log_{10} \left(\frac{100}{\text{Percent Unconverted}} \right) \frac{LSV}{3600 \text{ secs.}}$$

$$k = 2.303 \log \left(\frac{100}{57.82} \right) \frac{0.203}{3600}$$

$$= 5.48 \times 10^{-5} \text{ sec}^{-1} \text{ at } 554^\circ \text{ C.}$$

Run #3 shows that:

$$k = 2.86 \times 10^{-5} \text{ sec}^{-1} \text{ at } 493^\circ \text{ C.}$$

The intergrated Arrhenius equation

$$Ea = R \frac{T_1 T_2}{T_2 - T_1} \ln \left(\frac{K_1}{K_2} \right)$$

becomes: $$Ea = 4.575 \frac{(554 + 273)(493 + 273)}{(554-493)} \log \frac{5.48}{2.86}$$

$$= 15400 \text{ calories} = 15.4 \text{ k-cal/mol.}$$

The frequency factor, S, in the Arrhenius equation

$$k = S e^{-E/RT}$$

is calculated as

$$5.48 \times 10^{-5} = S e^{\frac{-15400}{1.987 (554 + 273)}}$$

$$S = 1.65 \times 10^{-3}$$

RESULTS AND DISCUSSION

Following the experimental work connected with this investigation, it was found that hydrogen fluoride activated alumina did not selectively dealkylate naphthenes and paraffins but rather caused fairly random bond rupture, giving preference, however, to the formation of propylene. In every run, the main reaction product was a mixture of gaseous olefins and paraffins containing propylene either as one of the main constituents or as the only gas present in significant amounts. Another product common to all runs, regardless of the nature of the charge stock, was a liquid with a lower boiling point than the original charge stock. Because of the analytical difficulties attached to the identification of these hydrocarbons boiling below the charge stock, no inquiry into their nature was made. These compounds may have been formed either as primary decomposition products, or as the result of secondary alkylation reactions. The latter mechanism is favored not only because hydrogen fluoride is known to be an efficient alkylation catalyst, but also because a residue with a higher boiling point than the original charge was produced, and the amount of methane and other light gases would rarely be equivalent to the amount of light liquid hydrocarbon formed.

Coke formation was slight, averaging less than two per cent of the material charged. In only a few cases did a combination of coke and losses exceed five per cent, and in no case did this combination reach ten per cent.

A direct correlation was found between the structure of a saturated hydrocarbon and the decomposition activation energy. As Figure 2 shows, normal paraffins require an activation energy of 40-45 k-cal/mol., while paraffins containing at least one tertiary carbon atom need only 18 k-cal. Cyclohexane derivitives are still easier to decompose, having an activation energy of 12 k-cal/mol,, while methylcyclopentane is somewhat more stable, since it requires an activation energy of 25 k-cal. Neohexane is only slightly less stable than normal paraffins, as demonstrated by an activation energy of 35 k-cal/mol. The stability of a given paraffin depends somewhat on its mass, since the decomposition activation energy decreases slightly with increasing chain length.

Naphthenes:

Four naphthenic compounds were used as charge stocks in this investigation: cyclohexane, methylcyclohexane, ethylcyclohexane, and methylcyclopentane. The three cyclohexanes were chosen to determine the effect of methyl and ethyl side chains on a naphthenic ring. Methyl cyclopentane was investigated to determine the difference in reactivity between five and six membered rings.

Cyclohexane differed from all other charge stocks in that it yielded large amounts of hydrogen. This hydrogen could have originated from two sources: formation of benzene and formation of butadiene. The higher refractive indices of the 70-75° C. liquid product cuts (Table XXII) indicates the presence of some aromatics, but since no separation of these cuts was attempted, the exact amount of benzene formed is unknown. Cyclohexane

is known, under certain conditions, to produce high yields of butadiene (16), but in this investigation, there was no evidence for or against the formation of butadiene. If any had been formed, the method of analysis used could not have distinguished it from C_4H_8. No methylcyclopentane was found in the reaction product, presumably because conditions were too severe for isomerization.

The distillation curves for the liquid products resulting from the dealkylation of naphthenes all showed that no materials boiling above the minimum condenser except the unconverted charge stock were present. A plot of condenser temperature versus per cent distilled rose almost vertically to the boiling point of the charge stock. The curve remained horizontal at the boiling temperature of the charge stock, then rose almost vdrtically again.

Methylcyclohexane yielded very little toluene and hydrogen, presumably because the presence of a tertiary carbon atom caused ring rupture before aromatization could occur. Methylcyclohexane decomposition produced no cyclohexene, and very little methane, indicating that the ring cleaves first to form an activated normal- or iso-olefin, which then undergoes further decomposition.

Ethylcyclohexane isomerizes aswell as decomposes. Thermodynamically, an equilibrium mixture of ethyl and dimethyl cyclohexanes includes only about fifteen per cent ethylcyclohexane at 527° C. (Table XXIII), so that the formation of dimethylcyclohexanes should be expected. The presence of 1,2- and 1,3-dimethylcyclohexanes in the reaction products could be demonstrated. The 118-127° C. distillation cuts from run

#5 (ethylcyclohexane) were found to possess high refractive indices, indicating the presence of aromatics. When the various cuts were treated with 20% oleum, 0.1 N NaOH, and water, the refractive indices dropped to constant values, and these refractive indices indicated that isomeric forms of ethyl and dimethyl cyclohexane were present (Tables XXII and XXIII).

In calculating the kinetic data for the ethyl cyclohexane runs, however, all isomers were considered as being pure ethylcyclohexane. No cyclohexane, cyclohexene, methylcyclohexane, or methylcyclohexene were formed, indicating that ring rupture predominated as the decomposition reaction. Isomerization is more probably a competing reaction than an initial step in decomposition.

Methylcyclopentane undergoes random ring rupture, as evidenced by the variety of gases formed. Neither cyclohexane nor cyclopentene were found in the reaction products, indicating that conditions were too severe for isomerization or demethylation. As with the cyclohexanes, methylcyclopentane undergoes ring rupture first, followed by decomposition. The higher energy of activation for methylcyclopentane demonstrates that a five membered ring is more stable than a six membered ring, a result that could have been predicted on the basis of bond strain.

Paraffins:

Twelve different paraffins were used as charge stocks. Five normal paraffins: hexane, heptane, octane, dodecane, and hexadecane, served to determine the effects of increased chain length. 2,3-Dimethylbutane

and 2,4-dimethylpentane were used in order to ascertain the effect of chain branching since these compounds contain two tertiary carbon atoms. Neohexane was run so that the effect of a quaternary carbon atom could be observed. 2,2,4-Trimethylpentane and 2,2,5-trimethylhexane served to show the effect of combining a quatenary and a tertiary carbon atom in the same molecule. 3-Methylpentane and 3-methylheptane were run in order to determine whether the kinetic effects were unique to certain tertiary carbon atoms, or whether they apply to all tertiary carbon atoms.

Normal hexane represents the sole case in this investigation where the decomposition activation energy is abnormal. In figure 2, all compounds except n-hexane plot on smooth curves. In an effort to discover where the anomaly lay, additional runs were made on n-hexane and n-heptane, but, as shown in figure 3, the data for each compound are consistant, so that significant errors in measurements or analysis are unlikely. Since all compounds were carffully purified before use, there would not be considerable quantities of isohexanes in the feed stock.

The other normal alkanes show that the decomposition activation energy falls off slowly with increased chain length. In the case of normal alkanes, data on the activation energy of the non-catalyzed, thermal decomposition reaction are available in the literature (18), so that the accelerating influence of the catalyst can be determined directly.

If the activation energy for the catalyzed reactions is 40 k-cal/mol. and is 64 k-cal/mol. for the non-catalyzed reaction, then the velocities

of the two reactions are in the ratio:

$$\frac{k_c}{k_h} = 10^{-13} \text{ (Area)} e^{E/rt}$$

If the effective catalytic area is 2.28×10^8 cm.^{2} (Table XXVI) then:

$$\frac{k_c}{k_h} = (2.28 \times 10^8)\ (10^{-12})\ e^{\frac{64000-40000}{RT}}$$

or

$$\frac{k_c}{k_h} = 750 \text{ at } 525^\circ \text{ C.}$$

Therefore, the catalyzed reaction is estimated to be about 750 times faster than the non-catalyzed reaction under the conditions of the investigation.

2,3-Dimethylbutane, 2,4-dimethylpentane, 2,2,4-trimethylpentane, 2,2,5-trimethylhexane, 3-methylpentane and 3-methylheptane all have activation energies near 18 k-cal/mol. showing that whenever a tertiary carbon atom is present in a paraffin, the same activation energy is required.

Neohexane, on the other hand, has an activation energy nearer to that of normal paraffins, indicating that a quaternary carbon atom has very little effect on the stability of a paraffin. Because 2,2,4-trimethylpentane and 2,2,5-trimethylhexane are just as unstable as other molecules containing a tertiary carbon atom, the neo structure apparently neither aids nor inhibits the decomposition of the molecule.

CATALYST

Properties of the catalyst determined during the course of this investigation are reported in Table XXIV. In order to determine the amount of available hydrogen fluoride on the catalyst, samples of catalyst were treated with distilled water. Every five minutes, the solutions were shaken vigorously. After an hours's leaching, the solutions were titrated with 0.1 N NaOH. This procedure was chosen because of the difficulty in analyzing for fluoride in the presence of alumina and because serious analytical errors would have developed if the pellets were allowed to leach long enough for all the HF to diffuse out of the pores of the catalyst beads. Since the hydrocarbons being dealkylated over the catalyst are not in contact with the catalyst for more than a minute or so, most of the hydrogen fluoride readily available to the hydrocarbon vapors should have been leached out after one hour.

According to this analysis, the catalyst bed contains roughly one fourth of a mol of readily available hydrogen fluoride. Every hydrocarbon molecule, then, has ample opportunity to coordinate with a hydrogen fluoride molecule and undergo dealkylation. From the small conversions obtained and from the magnitude of the Arrhenius frequency factor (Table XXI), it is apparent that paraffins and naphthenes cannot coordinate with hydrogen fluoride unless oriented correctly, that is, the catalyst is specific in its action. The variety of products obtained, however, can be explained by hypothesizing that the dealkylation products are more difficultly desorbed than the original molecules, and because

of their longer residence time on the catalyst surfaces, continue to degenerate until they become the easily desorbed light gases.

The temperature range chosen for this investigation was limited to 500-550° C. since no measurable reaction took place below 500°, and the catalyst began to sinter above 600° C. A liquid space velocity of 0.2/hr. was chosen to give conversion of between 10 and 50%.

None of the standard methods of calculating the surface area of the catalyst (Brunauer, Emmett, Teller, or Harkins-Jura) (22) is practicable with hydrogen fluoride activated alumina. During the activation, large amounts of silica are removed, so that the area of the activated catalyst might not be the same. The fluoride is held so tenaciously that sintering appears to be necessary to remove the hydrogen fluoride. The effective catalyst area was therefore calculated from the amount of fluoride on the catalyst, and the area of the HF molecule, assuming a monolayer of adsorbed fluoride, and closest packing of HF in the liquid state. The area so obtained is 2.54×10^5 cm^2 per milliliter (bulk volume) of catalyst.

Periodically, check runs were made on the catalyst to determine if its activity had fallen off. These check runs were made under the same conditions used by Kindschy (9), using the same charge stock, cumene. In every case, the yield of benzene formed from cumene was identical with the yield reported by Kindschy for a fully activated catalyst. No noticeable lessening of catalytic activity occurred even after more than sixty runs indicating that as long as the catalyst is held below its sintering point and carbon is burned off regularly, the catalyst retains full activity.

From the spread in the activation energy data, it may be concluded that the average deviation amounts to approximately 1 k-cal/mol. The corresponding frequency factors are presumably accurate to the appropriate power of 10.

The values of the decomposition reaction rate constant reported in the summary of this investigation were obtained by averaging the appropriate activation energies and the logarithms of the appropriate frequency factors.

SUMMARY

The results and conclusions derived from the experimental part of this investigation may be summarized as follows:

(1) Hydrogen fluoride activated alumina causes random carbon-carbon rupture in paraffins and naphthenes at low pressures and elevated temperatures, but does tend to form large amounts of propylene.

(2) Large amounts of hydrocarbons boiling below the charge stock are formed, probably as a result of secondary realkylation reactions.

(3) The kinetic data obtained with hydrogen fluoride activated alumina can be related to the structure of the paraffin or naphthene dealkylated.

(4) Average values for the decomposition rate constant defined in terms of liquid space velocity are:

Cyclohexane derivatives	$k = 2.6 \times 10^{-8} e^{-12500/RT}$
n-Paraffins	$k = 3.5 \times 10^{-16} e^{-41300/RT}$
Paraffins containing a tertiary carbon atom	$k = 3.0 \times 10^{-10} e^{-18300/RT}$
Neohexane	$k = 4.1 \times 10^{-15} e^{-35500/RT}$
Methylcyclopentane	$k = 1.7 \times 10^{-12} e^{-25000/RT}$

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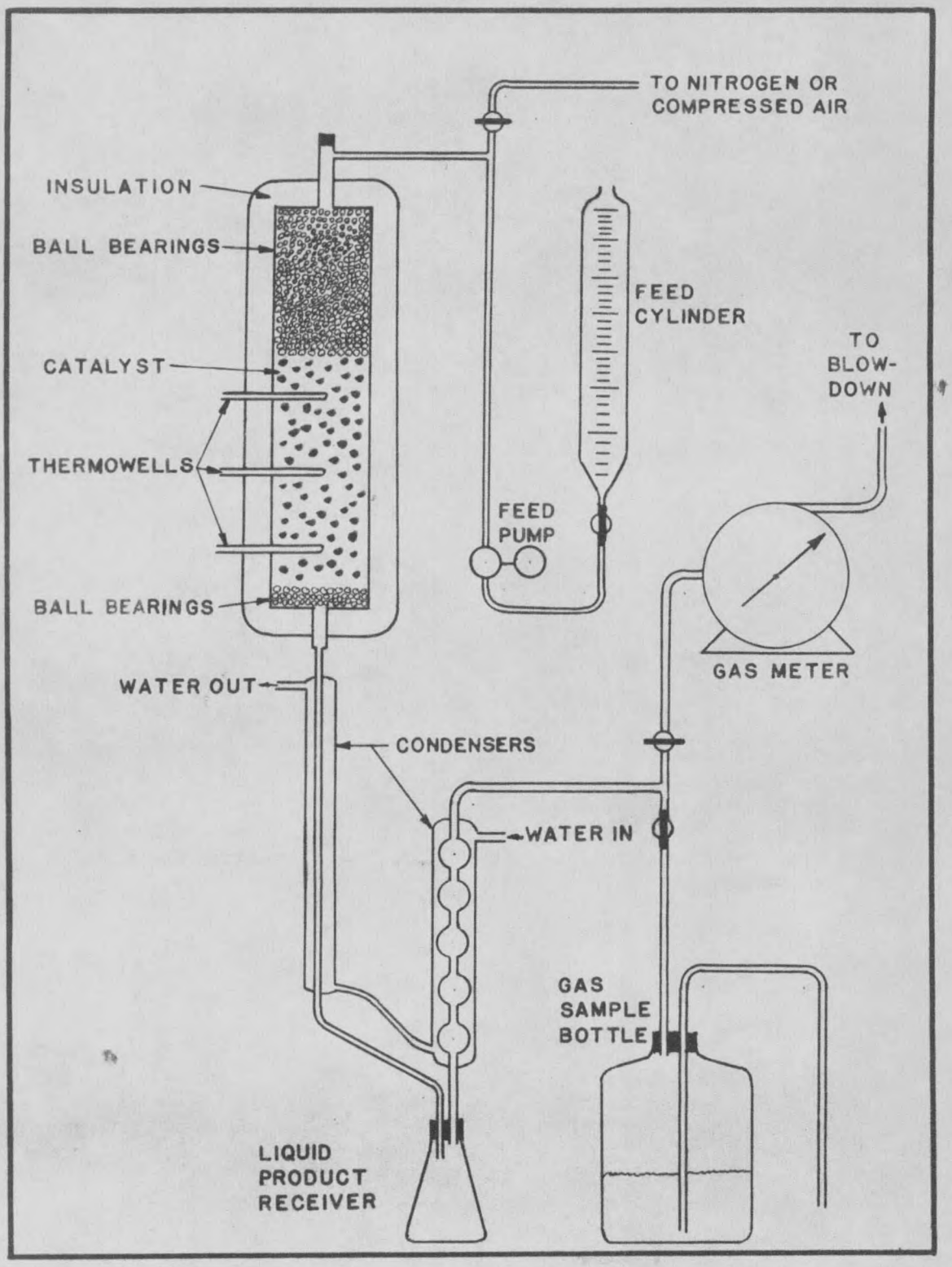

Figure 1

Diagram of Equipment

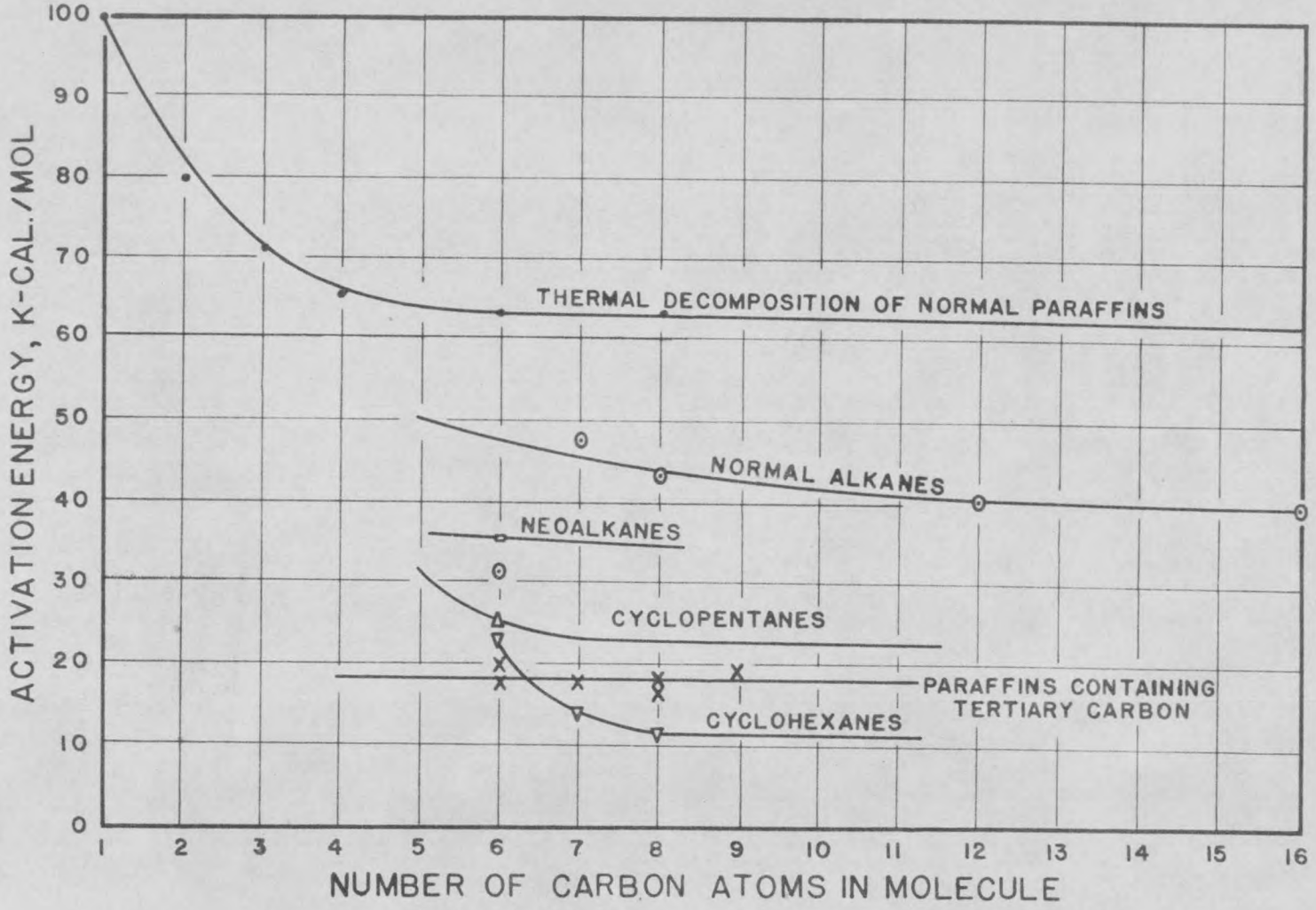

Figure 2 - Activation Energy Plots

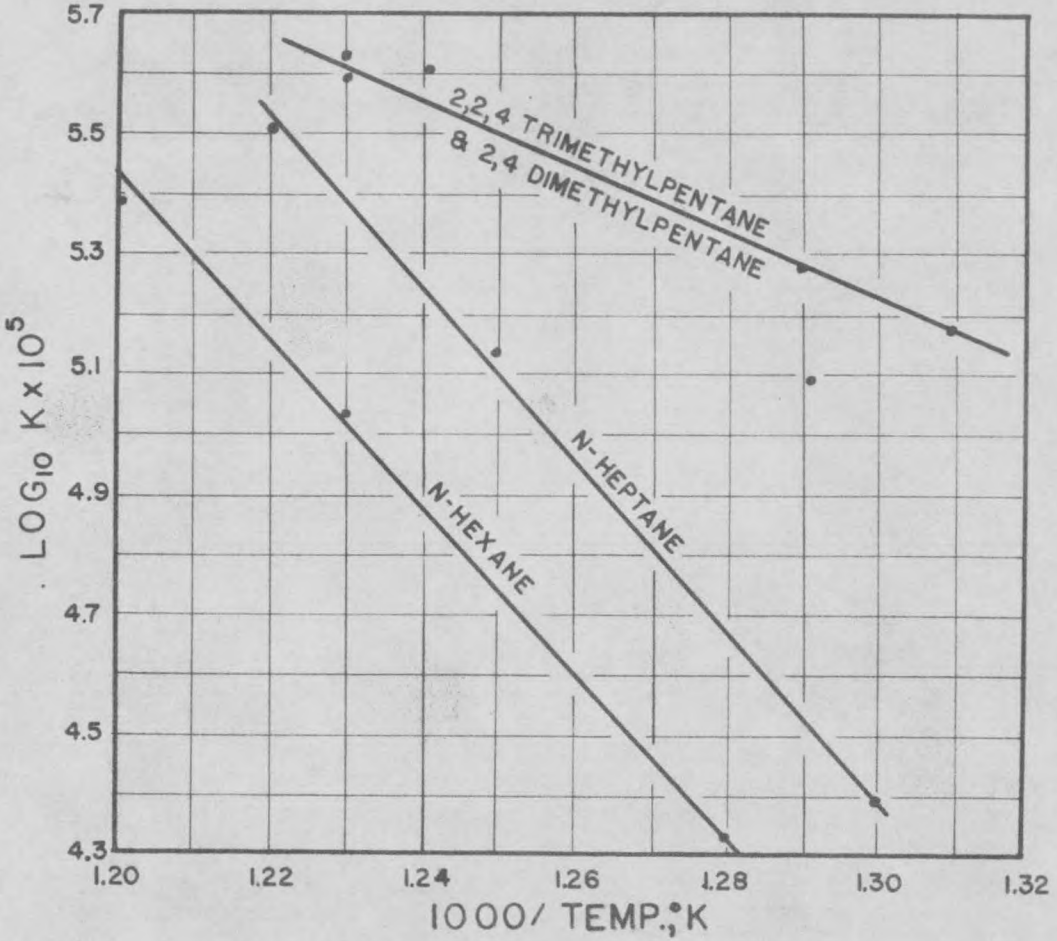

Figure 3 - Arrhenius Equation Plots

TABLE V

DEALKYLATION OF CYCLOHEXANE

Run Number		1	2
Gms. charge		305.5	294
Mols charged		3.64	3.50
Reactor Temp., °C.		518	545
Time of run, hrs.		2.0	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.219	0.211
Gas Produced, Lit.		22.4	44.4
	Mols	0.76	1.512
	Gms.	9.7	21.7
Gms. Liquid Produced		288.4	268.1
Gms. Coke & Losses		7.4	4.2
Gas	H_2	10.84	10.47
Analysis	CH_4	16.57	2.60
Weight	C_2H_4	13.50	6.80
Per Cent	C_2H_6	----	----
	C_3H_6	41.70	31.53
	C_3H_8	----	----
	C_4H_8	17.39	48.60
	C_4H_{10}	----	----
	C_5	----	----
Liq. Anal.	Low Boil Frac.*	8.0	6.9
Weight	Unconvent.	91.0	85.1
Per Cent	Residue	1.0	8.0

		Per Pass	Ultimate	Per Pass	Ultimate
Product	H_2	0.344	2.44	0.77	3.44
Analysis,	CH_4	0.526	3.73	0.19	0.85
Weight	C_2H_4	0.429	3.04	0.50	2.23
Per Cent	C_2H_6	-----	-----	----	----
	C_3H_6	1.324	9.39	2.33	10.40
	C_3H_8	-----	-----	----	----
	C_4H_8	0.552	3.91	3.59	16.05
	C_4H_{10}	-----	-----	----	----
	Low Boil Frac.*	7.55	53.55	6.29	28.06
	Unconvert.	85.90	----	77.60	----
	Residue	0.94	6.67	7.30	32.59
	Coke & Losses	2.42	17.16	1.43	6.38

*Condensible liquid boiling below charge stock

TABLE VI

DEALKYLATION OF METHYLCYCLOHEXANE

Run Number		3	4
Gms. charged		279.4	278
Mols charged		2.65	2.58
Reactor Temp., °C.		493	554
Time of run, hrs.		2.0	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.189	0.203
Gas Produced, Lit.		29.7	105.5
	Mols.	1.00	3.58
	Gms.	40.3	109.0
Gms. Liquid Produced		230.3	157.0
Gms. Coke & Losses		8.8	12.0
Gas Analysis Weight Per Cent	H_2	0.4	1.1
	CH_4	0.8	10.7
	C_2H_4	---	----
	C_2H_6	13.0	15.3
	C_3H_6	45.4	35.0
	C_3H_8	---	----
	C_4H_8	14.7	18.3
	C_4H_{10}	25.7	19.6
	C_5	---	----
Liq. Anal. Weight Per Cent	Low Boil. Frac.*	14.5	11.5
	Unconvert.	70.5	67.0
	Residue	15.0	21.5

		Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis, Weight Per Cent	H_2	0.06	0.1	0.43	0.7
	CH_4	0.12	0.3	4.20	6.7
	C_2H_4	----	---	----	---
	C_2H_6	1.87	4.5	6.00	9.6
	C_3H_6	6.53	15.6	13.72	22.1
	C_3H_8	----	---	----	---
	C_4H_8	2.12	5.1	7.18	11.5
	C_4H_{10}	3.70	8.9	7.69	12.4
	Low Boil. Frac.*	11.95	28.5	6.50	10.5
	Unconvert.	58.13	---	37.82	---
	Residue	12.37	29.5	12.14	19.5
	Coke & Losses	3.15	7.5	4.32	7.0

*Condensible liquid boiling below charge stock

TABLE VII

DEALKYLATION OF ETHYLCYCLOHEXANE

Run Number		5	6
Gms. charged		276.8	272.6
Mols. charged		2.81	2.78
Reactor Temp., °C.		502	546
Time of run, hrs.		2.0	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.209	0.192
Gas Produced, Lit.		55.4	107.6
Mols.		1.86	3.64
Gms.		59.7	125.2
Gms. Liquid Produced		215.2	139.8
Gms. Coke & Losses		1.9	7.6
Gas Analysis Weight Per Cent	H_2	1.9	8.2
	CH_4	0.7	0.9
	C_2H_4	12.0	17.1
	C_2H_6	---	28.8
	C_3H_6	39.3	26.3
	C_3H_8	2.3	1.5
	C_4H_8	6.3	4.6
	C_4H_{10}	19.7	18.6
	C_5	17.8	---
Liq. Anal. Weight Per Cent	Low Boil Frac.*	17.5	15.0
	Unconvert.	70.5	72.5
	Residue	12.0	12.5

		Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis, Weight Per Cent	H_2	0.41	0.91	1.01	1.61
	CH_4	0.15	0.33	0.41	0.65
	C_2H_4	2.60	5.74	7.86	12.52
	C_2H_6	----	----	13.24	21.11
	C_3H_6	8.50	18.80	12.10	19.31
	C_3H_8	0.50	1.10	0.69	1.10
	C_4H_8	1.36	3.00	2.12	3.38
	C_4H_{10}	4.26	9.43	8.55	13.61
	Low Boil Frac.*	17.45	38.58	7.69	12.24
	Unconvert.	58.78	----	37.20	----
	Residue	9.32	20.59	6.41	10.02
	Coke & Losses	0.69	1.52	2.79	4.45

*Condensible liquid boiling below charge stock

TABLE VIII

DEALKYLATION OF METHYLCYCLOPENTANE

Run Number		7	8
Gms. charged		306.0	269.0
Mols. charged		3.65	3.14
Reactor Temp., °C.		512	549
Time of run, hrs.		2.0	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.187	0.203
Gas Produced, Lit.		25.9	62.6
Mols.		0.887	2.13
Gms.		31.7	71.5
Gms. Liquid Produced		265.3	182.5
Gms. Coke & Losses		9.0	15.0
Gas Analysis Weight Per Cent	H_2	0.75	1.1
	CH_4	2.61	3.3
	C_2H_4	10.16	16.7
	C_2H_6	9.95	---
	C_3H_6	47.71	53.2
	C_3H_8	----	---
	C_4H_8	----	----
	C_4H_{10}	10.12	5.7
	C_5	18.71	20.0
Liq. Anal. Weight Per Cent	Low Boil Frac.*	8.0	6.5
	Unconvert.	86.0	84.5
	Residue	6.0	9.0

		Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis Weight Per Cent	H_2	0.08	0.3	0.29	0.7
	CH_4	0.27	1.1	0.85	2.0
	C_2H_4	1.05	4.1	4.45	10.3
	C_2H_6	1.03	4.0	----	---
	C_3H_6	4.94	19.4	14.16	33.2
	C_3H_8	----	---	----	---
	C_4H_8	----	---	---	---
	C_4H_{10}	1.05	4.1	1.52	3.6
	Low Boil Frac.*	8.87	34.9	9.73	22.8
	Unconvert.	74.56	----	57.32	---
	Residue	5.20	20.5	6.10	14.3
	Coke & Losses	2.95	11.6	5.58	13.1

*Condensible liquid boiling below charge stock

TABLE IX

DEALKYLATION PRODUCTS OF n-HEXANE

Run Number		9	10	11
Gms. charged		221.0	322.0	201.2
Mols charged		2.57	3.86	2.34
Reactor Temp., °C.		507	537	561
Time of run, hrs.		2.0	2.0	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.186	0.286	2.225
Gas Produced, Lit.		9.9	23.5	36.7
Mols.		0.338	0.830	1.26
Gms.		9.9	26.0	42.2
Gms. Liquid Produced		206.9	295.2	155.0
Gms. Coke & Losses		4.2	0.8	4.0
Gas Analysis Weight Per Cent	H_2	1.0		0.6
	CH_4	2.3	no	1.9
	C_2H_4	36.8		29.7
	C_2H_6	5.9	analy-	8.2
	C_3H_6	54.0		32.2
	C_3H_8	----	sis	----
	C_4H_8	----		----
	C_4H_{10}	----		27.4
	C_5	----		----
Liq. Anal. Low Boil Frac.*		2.5	8.4	3.3
Weight Per Cent Unconvert.		97.5	81.3	96.7
Residue		----	10.3	----

		Per Pass	Ultimate		Per Pass	Ultimate
Product Analysis, Weight Per Cent	H_2	0.05	0.6		0.12	0.5
	CH_4	0.10	1.1	no	0.40	1.6
	C_2H_4	1.65	18.9		6.24	24.5
	C_2H_6	0.26	3.0		1.72	6.7
	C_3H_6	2.42	27.8	analy-	6.76	26.4
	C_3H_8	-----	----		----	----
	C_4H_8	-----	----	sis	----	----
	C_4H_{10}	-----	----		5.76	22.5
	Low Boil Frac.*	2.34	26.8		2.54	10.0
	Unconvert.	91.28	----		74.47	----
	Residue	-----	----		----	----
	Coke & Losses	1.90	21.8		1.99	7.8

*Condensible liquid boiling below charge stock

TABLE X

DEALKYLATION OF n-HEPTANE

Run Number			12		13	14
Gms. charged			284.5		244.5	202.1
Mols charged			2.85		2.45	2.02
Reactor Temp., ^{o} C.			494		525	548
Time of run, hrs.			1.75		2.0	2.0
Liq. Sp. Vel., hr^{-1}			0.274		0.203	0.164
Gas Produced, Lit.			4.8		30.9	52.0
	Mols.		0.167		1.045	1.81
	Gms.		3.4		36.5	64.0
Gms. Liquid Produced			280.6		201.7	130.3
Gms. Coke & Losses			0.5		6.3	6.9
Gas	H_2		no		0.625	0.395
Analysis	CH_4				6.63	9.00
Weight	C_2H_4				12.00	18.11
Per Cent	C_2H_6		analy-		10.10	5.94
	C_3H_6				37.40	34.54
	C_3H_8				-----	-----
	C_4H_8		sis		14.90	16.83
	C_4H_{10}				-----	-----
	C_5				18.34	16.18
Liq. Anal.	Low Boil Frac.*		2.0		10.6	12.5
Weight	Unconvert.		97.0		87.6	77.5
Per Cent	Residue		1.0		1.8	10.0
			Per Pass	Ulti-mate	Per Pass	Ulti-mate
Product	H_2			0.056	0.26	0.12	0.24
Analysis,	CH_4			0.59	2.75	2.54	5.12
Weight	C_2H_4		no	1.07	4.96	5.74	11.56
Per Cent	C_2H_6			0.90	4.18	1.88	3.79
	C_3H_6			3.34	15.50	10.84	21.94
	C_3H_8		analy-	----	----	----	----
	C_4H_8			1.33	6.17	5.34	10.75
	C_4H_{10}			----	----	----	----
	Low Boil Frac.*		sis	11.13	51.70	13.35	26.64
	Unconvert.			78.44	----	50.27	----
	Residue			1.61	7.48	6.48	13.08
	Coke & Losses			1.54	7.15	3.42	6.89

*Condensible liquid boiling below charge stock

TABLE XI

DEALKYLATION OF n-OCTANE

Run Number		15	16
Gms. charged		234.0	231.0
Mols charged		2.05	2.02
Reactor Temp., °C.		501	538
Time of run, hrs.		2.0	2.0
Liq. Sp. Vel, $hr.^{-1}$		0.186	0.198
Gas Produced,	Lit.	29.3	71.4
	Mols.	0.998	2.43
	Gms.	40.5	93.7
Gms. Liquid Produced		188.4	127.7
Gms. Coke & Losses		5.0	9.6
Gas Analysis Weight Per Cent	H_2	0.28	0.17
	CH_4	2.47	2.00
	C_2H_4	11.51	22.23
	C_2H_6	1.04	5.88
	C_3H_6	43.12	22.79
	C_3H_8	-----	13.69
	C_4H_8	-----	12.82
	C_4H_{10}	33.92	8.50
	C_5	7.66	11.82
Liq. Anal. Weight Per Cent	Low Boil Frac.*	8.2	12.5
	Unconvert.	91.3	87.0
	Residue	0.5	0.5

		Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis, Weight Per Cent	H_2	0.05	0.19	0.07	0.13
	CH_4	0.43	1.62	0.81	1.56
	C_2H_4	2.00	7.55	9.02	17.38
	C_2H_6	0.18	0.68	2.38	4.58
	C_3H_6	7.48	28.21	9.24	17.80
	C_3H_8	----	----	5.55	10.69
	C_4H_8	----	----	5.20	10.02
	C_4H_{10}	5.89	22.21	3.49	6.72
	Low Boil Frac.*	7.95	30.04	11.70	22.54
	Unconvert.	73.49	----	48.09	----
	Residue	0.40	1.51	0.27	0.52
	Coke & Losses	2.14	8.09	4.16	8.01

*Condensible liquid boiling below charge stock

TABLE XII

DEALKYLATION OF n-DODECANE

Run Number		17	18
Gms. charge		130.0	252.0
Mols. charged		0.764	1.48
Reactor Temp., °C.		508	547
Time of run, Hrs.		2.0	2.0
Liq. Sp. Vel, $hr.^{-1}$		0.097	0.189
Gas Produced, Lit.		40.1	118.5
	Mols.	1.37	4.07
	Gms.	35.9	116.8
Gms. Liquid Produced		90.4	127.1
Gms. Coke & Losses		3.5	8.1
Gas Analysis Weight Per Cent	H_2	3.24	2.26
	CH_4	8.52	4.58
	C_2H_4	-----	11.97
	C_2H_6	6.04	2.11
	C_3H_6	-----	38.88
	C_3H_8	27.56	3.09
	C_4H_8	-----	9.52
	C_4H_{10}	27.93	10.53
	C_5	26.71	17.06
Liq. Anal. Weight Per Cent	Low Boil Frac.*	12.5	20.9
	Unconvert.	81.5	73.1
	Residue	6.0	6.0

		Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis, Weight Per Cent	H_2	0.90	2.08	1.05	1.66
	CH_4	2.35	5.44	2.12	3.36
	C_2H_4	----	----	5.55	8.79
	C_2H_6	1.67	3.86	0.98	1.55
	C_3H_6	----	----	18.02	28.54
	C_3H_8	7.62	17.63	1.43	2.27
	C_4H_8	-----	----	4.41	6.99
	C_4H_{10}	7.72	17.87	4.88	7.73
	Low Boil Frac.*	16.09	37.12	18.45	29.23
	Unconvert.	56.78	----	36.87	----
	Residue	4.18	9.67	3.03	4.80
	Coke & Losses	2.69	6.23	3.21	5.08

*Condensible liquid boiling below charge stock

TABLE XIII

DEALKYLATION OF n-HEXADECANE

Run Number		19	20
Gms. charged		369.0	391.0
Mols charged		1.63	1.73
Reactor Temp., °C.		484	546
Time of run, hrs.		2.25	2.0
Liq. Sp. Vel, $hr.^{-1}$		0.237	0.275
Gas Produced, Lit.		107.6	193.5
	Mols.	3.61	6.50
	Gms.	168.0	281.0
Gms. Liquid Produced		173.2	89.0
Gms. Coke & Losses		17.8	21.0
Gas	H_2	----	----
Analysis	CH_4	1.50	1.45
Weight	C_2H_4	5.99	8.82
Per Cent	C_2H_6	-----	-----
	C_3H_6	32.28	46.89
	C_3H_8	-----	-----
	C_4H_8	26.82	21.59
	C_4H_{10}	-----	-----
	C_5	33.41	21.25
Liq. Anal.	Low Boil Frac.*	21.9	26.2
Weight	Unconvert.	72.0	77.0
Per Cent	Residue	6.1	6.8

		Per Pass	Ultimate	Per Pass	Ultimate
Product	H_2	-----	-----	-----	-----
Analysis,	CH_4	0.68	1.03	1.04	1.26
Weight	C_2H_4	2.73	4.12	6.34	7.69
Per Cent	C_2H_6	----	----	----	----
	C_3H_6	14.70	22.20	33.70	40.86
	C_3H_8	----	----	----	----
	C_4H_8	12.21	18.44	15.52	18.82
	C_4H_{10}	-----	----	----	----
	Low Boil Frac.*	25.49	38.50	21.48	26.05
	Unconvert.	33.80	----	17.53	----
	Residue	2.86	4.32	1.55	1.88
	Coke & Losses	4.82	7.28	5.37	6.51

*Condensible Liquid boiling below charge stock

TABLE XIV

DEALKYLATION OF NEOHEXANE

Run Number		21	22
Gms. charged		255.5	178.5
Mols charged		2.97	2.08
Reactor Temp., °C.		500	552
Time of run, hrs.		2.0	2.0
Liq. Sp. Vel, $hr.^{-1}$		0.217	0.153
Gas Produced, Lit.		8.3	38.5
	Mols.	0.245	1.31
	Gms.	7.5	50.2
Gms. Liquid Produced		242.7	131.1
Gms. Coke & Losses		5.3	5.2
Gas	H_2	0.7	0.4
Analysis	CH_4	21.2	9.5
Weight	C_2H_4	10.3	14.9
Per Cent	C_2H_6	4.4	4.7
	C_3H_6	15.9	17.1
	C_3H_8	----	1.9
	C_4H_8	----	3.3
	C_4H_{10}	----	2.6
	C_5	47.5	45.6
Liq. Anal.	Low Boil Frac.*	1.9	6.6
Weight	Unconvert.	98.1	93.4
Per Cent	Residue	----	----

		Per Pass	Ultimate	Per Pass	Ultimate
Product	H_2	0.02	0.3	0.11	0.3
Analysis	CH_4	0.62	9.1	2.67	7.5
Weight	C_2H_4	0.30	4.4	4.20	11.8
Per Cent	C_2H_6	0.13	1.9	1.33	3.7
	C_3H_6	0.47	6.9	4.82	13.5
	C_3H_8	----	----	0.54	1.5
	C_4H_8	----	----	0.93	2.6
	C_4H_{10}	----	----	0.73	2.1
	Low Boil Frac.*	3.21	47.1	17.37	48.8
	Unconvert.	93.17	----	68.38	---
	Residue	----	----	----	---
	Coke & Losses	2.08	30.3	2.92	8.2

*Condensible liquid boiling below charge stock

TABLE XV

DEALKYLATION OF 2,2,4-TRIMETHYLPENTANE

Run Number		23	24
Gms. Charged		276.0	276.0
Mols charged		2.42	2.42
Reactor Temp., °C.		507	553
Time of run, hrs.		2.0	2.0
Liq. Sp. Vel, $hr.^{-1}$		0.223	0.223
Gas Produced, Lit.		23.1	64.0
	Mols.	0.78	2.18
	Gms.	31.8	75.7
Gms. Liquid Produced		237.1	191.2
Gms. Coke & Losses		7.1	9.1
Gas Analysis Weight Per Cent	H_2	0.2	0.4
	CH_4	5.1	13.7
	C_2H_4	7.8	3.6
	C_2H_6	----	8.2
	C_3H_6	42.0	29.0
	C_3H_8	----	----
	C_4H_8	5.0	5.5
	C_4H_{10}	28.4	25.5
	C_5	11.5	14.1
Liq. Anal. Weight Per Cent	Low Boil Frac.*	14.0	17.0
	Unconvert.	86.0	83.0
	Residue	----	----

		Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis Weight Per Cent	H_2	0.02	0.1	0.11	0.3
	CH_4	0.59	2.3	3.76	8.8
	C_2H_4	0.90	3.5	0.99	2.3
	C_2H_6	----	---	2.25	5.3
	C_3H_6	4.83	18.5	7.96	18.7
	C_3H_8	----	----	----	---
	C_4H_8	0.58	2.2	1.51	3.6
	C_4H_{10}	3.27	12.5	7.00	16.6
	Low Boil Fract.*	13.35	51.7	15.64	36.8
	Unconvert.	73.89	---	57.48	---
	Residue	----	---	----	---
	Coke & Losses	2.57	9.8	3.30	8.2

*Condensible liquid boiling below charge stock

TABLE XVI

DEALKYLATION OF 2,2,5-TRIMETHYLHEXANE

Run Number		25	26	27
Gms. charged		299.0	275.0	308.0
Mols charged		2.33	2.16	2.41
Reactor Temp., °C.		501	535	555
Time of run, hrs.		1.75	2.08	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.268	0.226	0.243
Gas Produced,	Lit.	16.3	67.8	86.4
	Mols.	0.561	2.28	2.90
	Gms.	21.4	83.7	102.8
Gms. Liquid Produced		264.6	175.5	186.8
Gms. Coke & Losses		13.0	15.8	18.4
Gas Analysis Weight Per Cent	H_2	0.655	0.378	
	CH_4	7.86	2.74	
	C_2H_4	16.86	11.08	no
	C_2H_6	-----	15.00	
	C_3H_6	27.10	33.66	analy-
	C_3H_8	----	-----	
	C_4H_8	28.50	37.14	sis
	C_4H_{10}	----	----	
	C_5	25.03	----	
Liq. Anal. Weight Per Cent	Low Boil Frac.*	10.9	15.7	18.1
	Unconvert.	87.4	81.6	78.0
	Residue	1.7	2.7	3.9

		Per Pass	Ultimate	Per Pass	Ultimate	
Product Analysis, Weight Per Cent	H_2	0.047	0.21	0.115	0.24	
	CH_4	0.56	2.48	0.835	1.75	
	C_2H_4	0.21	5.32	3.37	7.05	no
	C_2H_6	----	----	4.56	9.55	
	C_3H_6	1.94	8.55	10.24	21.45	analy-
	C_3H_8	----	----	----	----	
	C_4H_8	2.04	9.00	11.30	23.62	sis
	C_4H_{10}	----	----	----	----	
	Low Boil Frac.*	11.44	49.68	9.86	20.68	
	Unconvert.	77.33	----	52.50	----	
	Residue	1.51	6.66	1.70	3.56	
	Coke & Losses	4.35	18.20	5.75	12.03	

*Condensible liquid boiling below charge stock

TABLE XVII

DEALKYLATION OF 2,3-DIMETHYLBUTANE

Run Number		28	29
Gms. charged		317.0	204.6
Mols charged		3.68	1.70
Reactor Temp., °C.		513	568
Time of run, hrs.		2.0	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.226	0.180
Gas Produced, lit.		20.3	68.5
	Mols.	0.503	2.33
	Gms.	23.9	78.3
Gms. Liquid Produced		285.8	109.5
Gms. Coke & Losses		7.3	16.7
Gas Analysis Weight Per Cent	H_2	0.04	0.08
	CH_4	4.54	17.20
	C_2H_4	0.89	6.87
	C_2H_6	0.75	3.37
	C_3H_6	22.43	33.98
	C_3H_8	-----	-----
	C_4H_8	-----	-----
	C_4H_{10}	-----	-----
	C_5	71.35	38.50
Liq. Anal. Weight Per Cent	Low Boil Frac.*	15.7	19.0
	Unconvert.	84.3	81.0
	Residue	----	----

		Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis Weight Per Cent	H_2	0.003	0.012	0.03	0.05
	CH_4	0.343	1.43	6.59	11.65
	C_2H_4	0.067	0.28	2.63	4.64
	C_2H_6	0.057	0.24	1.28	2.26
	C_3H_6	1.69	4.05	13.00	22.95
	C_3H_8	-----	----	----	----
	C_4H_8	-----	----	----	----
	C_4H_{10}	-----	----	----	-----
	Low Boil. Frac.*	19.54	81.48	24.92	43.95
	Unconvert.	75.99	----	43.35	----
	Residue	-----	----	----	----
	Coke & Losses	2.30	9.60	8.20	14.50

*Condensible liquid boiling below charge stock

TABLE XVIII

DEALKYLATION OF 2,4-DIMETHYLPENTANE

Run Number		30	31	32
Gms. charged		178.7	234.5	204.3
Mols charged		1.79	2.35	2.04
Reactor Temp., °C.		493	516	557
Time of run, hrs.		2.0	2.0	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.251	0.195	0.226
Gas Produced, Lit.		20.2	14.4	62.4
Mols.		0.73	0.495	2.14
Gms.		22.4	18.9	65.5
Gms. Liquid Produced		154.2	308.0	119.8
Gms. Coke & Losses		2.1	7.6	19.0
Gas Analysis Weight Per Cent	H_2		0.82	1.25
	CH_4	no	2.06	15.75
	C_2H_4		8.10	5.30
	C_2H_6	analy-	3.06	5.00
	C_3H_6		47.51	31.90
	C_3H_8	sis	-----	-----
	C_4H_8		21.35	15.10
	C_4H_{10}		-----	-----
	C_5		17.10	25.40
Liq. Anal. Low Boil Frac.*		2.8	4.9	2.5
Weight Unconvert.		93.2	90.1	92.5
Per Cent Residue		4.0	5.0	5.0

			Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis Weight Per Cent	H_2		0.066	0.33	0.40	0.88
	CH_4	no	0.166	0.82	5.05	11.05
	C_2H_4		0.654	3.24	1.70	3.72
	C_2H_6	analy-	0.247	1.22	1.60	3.50
	C_3H_6		3.835	19.00	10.22	22.40
	C_3H_8	sis	-----	----	----	----
	C_4H_8		1.72	8.52	4.84	10.58
	C_4H_{10}		-----	----	----	----
	Low Boil. Frac.*		5.73	28.40	9.61	21.00
	Unconvert.		79.81	----	54.25	----
	Residue		4.43	21.95	2.94	6.40
	Coke & Losses		3.24	16.03	9.30	20.35

*Condensible liquid boiling below charge stock

TABLE XIX

DEALKYLATION OF 3-METHYLPENTANE

Run Number		33	34
Gms. charged		119.0	276.2
Mols charged		1.75	4.08
Reactor Temp., °C.		513	553
Time of run, hrs.		1.0	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.200	0.232
Gas Produced, Lit.		15.6	59.8
	Mols	0.530	2.035
	Gms.	15.3	62.2
Gms. Liquid Produced		93.8	190.1
Gms. Coke & Losses		9.9	23.9
Gas Analysis Weight Per Cent	H_2	0.21	0.14
	CH_4	3.31	3.38
	C_2H_4	18.25	17.20
	C_2H_6	10.40	8.00
	C_3H_6	26.72	26.80
	C_3H_8	-----	-----
	C_4H_8	-----	-----
	C_4H_{10}	-----	-----
	C_5	41.11	44.48
Liq. Anal. Weight Per Cent	Low Boil Frac.*	17.3	16.8
	Unconvert.	82.7	73.2
	Residue	----	10.0

		Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis, Weight Per Cent	H_2	0.027	0.063	0.03	0.06
	CH_4	0.426	1.22	0.73	1.49
	C_2H_4	2.35	6.75	3.70	7.56
	C_2H_6	1.34	3.85	1.72	3.52
	C_3H_6	3.44	9.88	5.77	11.80
	C_3H_8	----	----	----	----
	C_4H_8	----	----	----	----
	C_4H_{10}	----	----	----	----
	Low Boil Frac.*	18.92	54.35	21.29	43.50
	Unconvert.	65.17	----	51.10	----
	Residue	----	----	6.98	14.30
	Coke & Losses	8.32	23.89	8.67	17.75

*Condensible liquid boiling below charge stock

TABLE XX

DIALKYLATION OF 3-METHYLHEPTANE

Run Number		35	36
Gms. charged		386.3	207.0
Mols charged		3.38	1.81
Reactor Temp., °C.		508	538
Time of run, hrs.		2.0	2.0
Liq. Sp. Vel., $hr.^{-1}$		0.306	0.164
Gas Produced, Lit.		36.3	59.4
Mols.		1.218-	1.90
Gms.		40.3	61.8
Gms. Liquid Produced		336.6	129.5
Gms. Coke & Losses		9.4	15.9
Gas Analysis Weight Per Cent	H_2	0.68	0.83
	CH_4	1.37	12.28
	C_2H_4	13.65	7.28
	C_2H_6	2.84	6.30
	C_3H_6	37.41	30.95
	C_3H_8	-----	-----
	C_4H_8	10.83	13.16
	C_4H_{10}	22.55	16.20
	C_5	10.67	13.00
Liq. Anal. Weight Per Cent	Low Boil Frac.*	12.9	10.1
	Unconvert.	85.3	84.9
	Residue	1.8	5.0

		Per Pass	Ultimate	Per Pass	Ultimate
Product Analysis, Weight Per Cent	H_2	0.07	0.28	0.25	0.53
	CH_4	0.14	0.55	3.67	7.82
	C_2H_4	1.42	5.53	2.17	4.62
	C_2H_6	0.30	1.17	1.88	4.00
	C_3H_6	3.90	15.19	9.24	19.68
	C_3H_8	----	----	----	----
	C_4H_8	1.13	4.40	3.93	8.37
	C_4H_{10}	2.45	9.15	4.84	10.31
	Low Boil Frac.*	12.35	48.11	10.19	21.70
	Unconvert.	74.33	----	53.04	----
	Residue	1.56	6.08	3.13	6.64
	Coke & Losses	2.43	9.47	7.68	16.35

* Condensible liquid boiling below charge stock

TABLE XXI

KINETIC DATA FOR THE DEALKYLATION OF NAPHTHENES AND PARAFFINS

Compound	Run No.	Temperature °C.	Liquid Space Velocity hr^{-1}	Conversion Per Cent	Velocity Constant, k $sec.^{-1}$	Activation Energy, Ea k-cal/mol.	Frequency Factors
Cyclohexane	1	518	0.219	14.10	0.93×10^{-5}	22.7	1.01×10^{-11}
	2	545	0.211	22.40	1.49 "		
Methylcyclohexane	3	493	0.189	41.87	2.86 "	13.4	1.65×10^{-8}
	4	554	0.203	62.18	5.48 "		
Ethylcyclohexane	5	502	0.209	45.22	3.51 "	11.7	4.28×10^{-8}
	6	546	0.192	62.80	5.28 "		
Methylcyclopentane	7	512	0.187	25.44	1.54 "	25.0	1.72×10^{-12}
	8	549	0.203	42.68	3.15 "		
n-Hexane	9	507	0.186	8.72	0.48 "	31.2	8.45×10^{-13}
	10	537	0.286	24.40	1.11 "		
	11	561	0.235	25.53	1.84 "		
n-Heptane	12	494	0.274	5.00	0.40 "	47.8	9.17×10^{-17}
	13	525	0.203	21.56	1.38 "		
	14	548	0.164	49.73	3.23 "		
n-Octane	15	501	0.186	26.51	1.13 "	43.2	7.05×10^{-17}
	16	538	0.198	51.91	4.03 "		
n-Dodecane	17	508	0.097	43.22	1.53 "	40.2	8.80×10^{-16}
	18	547	0.189	63.13	5.24 "		
n-Hexadecane	19	484	0.237	66.20	7.14 "	39.9	2.20×10^{-16}
	20	546	0.275	82.47	13.31 "		

TABLE XXI (cont.)

KINETIC DATA FOR THE DEALKYLATION OF NAPHTHENES AND PARAFFINS

Compound	Run No.	Temperature °C.	Liquid Space Velocity hr^{-1}	Conversion Per Cent	Velocity Constant, k $sec.^{-1}$	Activation Energy, Ea k-cal/mol.	Frequency Factors
Neohexane	21	500	0.217	6.83	0.44×10^{-5}	35.5	4.07×10^{-15}
	22	552	0.153	35.62	1.88 "		
2,2,4-Trimethyl-pentane	23	507	0.223	26.11	1.88 "	16.7	1.30×10^{-10}
	24	553	0.223	42.52	3.42 "		
2,2,5-Trimethyl-hexane	25	501	0.268	22.67	1.92 "	19.1	6.66×10^{-10}
	26	535	0.226	47.80	4.09 "		
	27	555	0.243	47.32	4.31 "		
2,3-Dimethyl-butane	28	513	0.266	24.01	2.05 "	17.1	5.85×10^{-10}
	29	568	0.180	56.65	4.21 "		
2,4-Dimethyl-pentane	30	493	0.251	19.52	1.53 "	18.3	3.52×10^{-10}
	31	516	0.195	20.19	1.23 "		
	32	557	0.226	45.75	3.86 "		
3-Methylpentane	33	512	0.200	34.83	2.41 "	20.4	1.84×10^{-10}
	34	553	0.232	48.90	4.61 "		
3-Methylheptane	35	508	0.306	25.67	2.52 "	18.2	2.02×10^{-10}
	36	538	0.164	46.96	3.89 "		

TABLE XXII

REFRACTIVE INDICES OF SEVERAL CYCLOHEXANE AND ETHYL CYCLOHEXANE CUTS

Cyclohexane Cuts, Run #1

Refractive index of pure cyclohexane, n_D^{20} = 1.4262

Refractive index of pure benzene, n_D^{20} = 1.50110

Refractive indices of cuts boiling at 640 mm. Hg.

between: 70-71° C., n_D^{20} = 1.4310

71-72° C., n_D^{20} = 1.4316

72-73° C., n_D^{20} = 1.4506

73-74° C., n_D^{20} = 1.4411

74-75° C., n_D^{20} = 1.4285

Ethylcyclohexane Cuts, Run #5

Boiling Range 640 mm. Hg.	Refractive Index before wash	RI after 1 oleum wash	RI after 2 oleum washes	RI after 3 oleum washes
118.0-119.0	1.4359	1.4298	1.4297	------
119.0-120.0	1.4368	1.4315	1.4307	1.4304
120.0-121.0	1.4376	1.4312	1.4306	1.4306
121.0-122.0	1.4404	1.4318	1.4313	1.4312
122.0-123.0	1.4484	1.4366	1.4362	1.4362
123.0-124.0	1.4564	1.4434	1.4361	1.4361
124.0-125.0	1.4623	1.4335	1.4335	------
125.0-127.0	1.4678	1.4385	------	------

TABLE XXIII

EQUILIBRIUM OF DIMETHYL- AND ETHYL- CYCLOHEXANES
(Calculated at 800°K from Bureau of Standards Data)

Isomer	Boiling Point at 760 mm. Hg.	Refractive Index n^{20}	Equilibrium concentration at 800°K per cent
Ethyl Cyclohexane	131.78	1.43304	15.12
1,1-Dimethylcyclohexane	119.54	1.42895	6.56
cis 1,2- "	129.73	1.43596	5.78
trans 1,2- "	123.42	1.42695	13.98
cis 1,3- "	120.09	1.42494	24.51
trans 1,3- "	124.45	1.43085	13.98
cis 1,4- "	124.32	1.42966	6.97
trans 1,4- "	119.35	1.42090	13.10

TABLE XXIV

PROPERTIES OF THE CATALYST

Grams catalyst titrated:	4.287	4.312	2.153
Milliliters 0.1N NaOH needed:	11.8	12.0	5.9
Bulk density of catalyst	0.871 gms/ml.		
Mols HF/liter of catalyst	0.242		
Grams HF/liter of catalyst	4.85		
Average Area of HF molecule*	17.4×10^{-16} cm^2		
Area of catalyst/liter	2.53×10^{8} cm^2		
Catalyst in bed	0.900 liter		
Area of catalyst bed	2.28×10^{8} cm^2		

*Assuming closest packing of HF in liquid state (22).

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