



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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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 compound a used (cyclohexane, methylcyclohexane, ethylcyclo-hexane, methylcyclopentane, n-hexane, n-heptane, n-octane, n-dodecane, n-hexadecane, n-obexane, 3,3,4-trimethylpentane, 2,3,5-trimethylhexane, 2,3-dimethylbutane, 2,4-dimethylpentane, 3-methylpentane, and 3-methyl-heptane) all suffered fairly random carbon-carbon bond rupture. In every case, however, two of the main reaction products were a low boil ing liquid, presumably the result of realkylation of dealkylated pro-ducts, and propylene.

Decomposition activation energise were related to the structure of the molecule undergoing reaction. Normal alkanes required an activation energy of about 40 k-cal/mol. Paraffins possessing at least one tertiary carbon atom required only 18 k-cal/mol. while neohexane required 35 k-cal/mol. Alkyl cyclohexanes required an activation energy of 12 k-cal/mol. while methyloyolopentane needed 25 k-cal/mol.

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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A LITTLE PAPER



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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.

Decomposition activation energies were related to the structure of the molecule undergoing reaction. Normal alkanes required an activation energy of about 40 k-cal/mol. Paraffins possessing at least one tertiary carbon atom required only 18 k-cal/mol. while neohexane required 35 k-cal/mol. Alkyl cyclohexanes required an activation energy of 12 k-cal/mol. while methylcyclopentane needed 25 k-cal/mol.

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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 distinguished 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.



































































































































