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^{14}C Tracer Study of the Fate of Methylcyclohexane during Naphtha Conversion over Pt–Al_2O_3 Catalysts

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The ^{14}C distribution in the products show that methylcyclohexane is converted primarily to aromatics. The results suggest that dehydrogenation to toluene and demethylation to benzene occurs by a metal catalyzed pathway. Conversion of the aromatic (or naphthene) to paraffins occurs by a dual-functional metal-acid pathway.

INTRODUCTION

The reforming of naphtha is an important commercial process. However, direct evidence for the fate of individual naphtha components during reforming is lacking. The evidence for the fate of individual components has been obtained from kinetic analysis of the product distribution or the conversion of pure compounds (*1*). Emmett (*2*) has successfully used the technique of adding ^{14}C-labeled compounds to the charge in studying the fate of various intermediates in the cracking of paraffins over acidic catalysts. We have used this technique to follow the fate of a single naphthene, methylcyclohexane, during the conversion of a naphtha over a commercial acidic Pt–Al_2O_3 catalyst and a Pt on "nonacidic" alumina catalyst.

EXPERIMENTAL

Catalysts. A sample of Englehard's commercial RD-150 0.35% Pt catalyst was used for one run. For the other run, a "nonacidic" Pt–Al_2O_3 catalyst was prepared by impregnating alumina, obtained by precipitation from potassium aluminate, with chloroplatinic acid. The chlorine content of this catalyst was reduced to less than 0.05 wt% by reducing the catalyst at 500°C and then washing the catalyst two times with ammonium hydroxide. Results for dehydrocyclization studies using this catalyst have been reported previously (*3*).

Reaction conditions. A high pressure metal reactor was used for the runs. The liquid sample was collected under pressure in a liquid sampling vessel. Gaseous products were collected at atmospheric pressure after passing through a pressure reducing valve. Reaction conditions were: total pressure, 200 psig; LHSV, 1.0; a single pass reactor, H_2:hydrocarbon 9:1; and the preheater section of the reactor at 920°F. The fresh catalyst was reduced in flowing hydrogen at atmospheric pressure for 16 hr prior to beginning a run. The charge was a C_6–290°F Mid-Continent naphtha. Methyl [1-^{14}C]cyclohexane was obtained by diluting ring-labeled [1-^{14}C]toluene with unlabeled toluene and hydrogenating over a Pt catalyst at 3 atm pressure and 50°C in the liquid phase. The toluene, as received from the supplier, contained 3.95% ^{14}C impurity, which was identified as benzene by gc radioanalysis. The products were corrected for this activity by assuming that the benzene was hydrogenated to cyclohexane and then dehydrogenated to only benzene during the run. The charge contained 90 wt% naphtha and 10 wt% methylcyclohexane labeled with ^{14}C. After an initial "line-out" period of 1 hr, the liquid and gaseous products were collected during the next hour and subjected to analysis.

Product analysis and ^{14}C counting. The liquid products were separated using temperature programmed gc with a Carbowax

20M column; aromatics were completely separated from the paraffins and naphthenes, but naphthenes and paraffins were not separated from each other. The ^{14}C activity of the peaks, as they eluted from the chromatograph, was determined using a Nuclear-Chicago Gas Radiochromatographic System. A gas chromatogram and ^{14}C radiogram of the liquid products are shown in Fig. 1.

The gases were analyzed using a 3-ft silica gel column. The ^{14}C content of the C_2 and C_3 peaks was determined experimentally. To obtain the total ^{14}C activity of the C_1–C_5 gas fraction, it was assumed that all carbon fractions had the same specific activity. While the specific activity of the C_1, C_4, and C_5 fractions could not be exactly determined, they were determined accurately enough to show that this was a realistic assumption. The total C_1–C_5 gas fraction was obtained as the difference in weight of the charge and the liquid collected; mass spectroscopic analysis of the gas was used to obtain the carbon number distribution of the gaseous products.

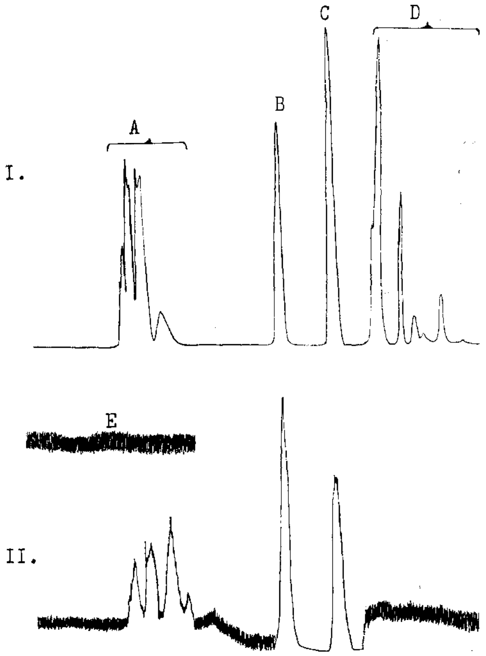


Fig. 1. Representative gas chromatogram and radiogram of the liquid products from naphtha conversion. (I) Gas chromatogram: peaks A, liquid paraffins and naphthenes; peak B, benzene; peak C (peak area reduced by 1/2 of other peaks), toluene; peaks D, C_8 and higher aromatics. (II) Radiogram of liquid products: time scale same as for gc in I (number refers to amount peak shown was reduced by attenuation); E (background), 1; naphthene and paraffin peaks, 1; benzene, 1/2; toluene, 1/20; C_8 and higher aromatics, 1.

Results and Discussion

The ^{14}C distribution for the two catalysts, corrected for the ^{14}C cyclohexane impurity, is shown in Table 1. In both runs, methylcyclohexane was not detected in the liquid fraction either by gc or by the ^{14}C radiogram. Thus, the naphthene underwent complete conversion over both catalysts, even though the total conversion of the paraffins in the naphtha was about 10% greater for the acidic catalyst. The predominate reaction for methylcyclohexane is dehydrogenation to toluene. The amount of demethylation to benzene is identical over both catalysts. However, the amount converted to gaseous hydrocarbons is about 10 times greater over the acidic catalyst, and the conversion to liquid paraffins nearly 3 times greater.

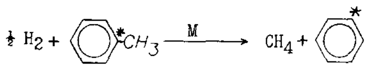
The results suggest that the demethylation occurs by the same process over both catalysts. Since the acidic function is less for the "nonacidic" catalyst, we believe the demethylation occurs exclusively, or

TABLE 1

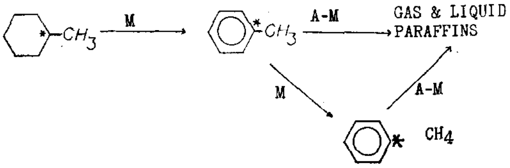
^{14}C Distribution in the Products from the Conversion of Naphtha Containing Methyl[1-^{14}C]Cyclohexane

Fraction	^{14}C distribution (% of total) Acidic $Pt-Al_2O_3$	Nonacidic $Pt-Al_2O_3$
C_1–C_5 gas	2.8	0.3
Liquid paraffins and naphthenes	6.1	2.3
Benzene	4.22	4.03
Toluene	86.8	93.4

nearly so, on the metal function. Since the ^{14}C in the C_1–C_5 gas is much less than that of benzene, the aromatic ring carbons can not become equivalent to the methyl group. This suggests the following reaction pathway for benzene formation (* represents ^{14}C; M = metal function):



The conversion to gaseous and liquid paraffins appears to arise from a dual functional metal-acid catalyzed reaction of the toluene. The lower conversion of ^{14}C to these products over the "nonacidic" catalyst is consistent with this mechanism. The catalyst containing 1% K is certainly less acidic than the commercial catalyst but, even though we label this catalyst "nonacidic," it still possesses some acidity. For example, it catalyzed the isomerization of cyclohexene to methylcyclopentene at 450°C and 1 atm at about 1/10 to 1/20th the rate of an "acidic" alumina from the hydrolysis of aluminum isopropoxide. Thus, our results for the conversion of methylcyclohexane over Pt–Al$_2$O$_3$ catalyst is consistent with the following mechanism (M = metal function; A = acid function):



Even over the acidic, commercial catalyst, the rate of dehydrogenation must be at least 9 times greater than the cracking reaction and is probably much greater than this.

This investigation has demonstrated that the addition of a ^{14}C-labeled hydrocarbon to a naphtha is a convenient and rapid method to follow the fate of a single component of a naphtha during reforming. Studies at lower conversions should enable one to obtain reliable kinetic data with a minimum of experimental effort.

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