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NOTE

An Attempt to Distinguish between CH_3-Type and CH_2-Type Species as Chain-Extending Intermediates in the Conversion of Methanol to Gasoline over the Catalyst H-ZSM-5

It has long been recognised that very reactive chain-building intermediates occur in the conversion of methanol to gasoline over the catalyst H-ZSM5, and the nature of these intermediates has frequently been discussed (1). The proposals as to the nature of these intermediates centre on the CH_3 type and the CH_2 type.

We have attempted to distinguish between these two possibilities by using the "benzene sequestration test" (2), in which benzene is added to the methanol feed and traps reactive intermediates as alkyl benzenes, which are then separated by gas–liquid chromatography, and provide evidence on the nature and fate of these early intermediates (3).

The above procedure was modified by using tri-deuteromethanol and unlabelelled benzene for the feed. Durene was the product chosen for analysis, and the distribution of H and D in the various methyl groups was determined by using $^{13}C\{^1H\}$-DEPT NMR spectroscopy.

In planning this study we were conscious of the chance that isotopic scrambling might occur during the gasoline synthesis but were encouraged to continue after reading a study (4) of a D_4 methanol/benzene conversion, the products of which were separated by mass spectrometry, and showed little isotopic scrambling and yielded D_3 toluene, more abundantly than other deuterated toluenes. This conversion was carried out at 207°C, a temperature at which the production of gasoline is slight.

A more recent paper by Novakova *et al.* (5) described conversion of a mixture of CD_3OH and CH_3OH over H-ZSM-5. The catalyst, which contained preadsorbed MeOH, was heated, and the gaseous products were determined using GC-MS. In the temperature range 22 to 247°C no deuterium exchange was detected and the principal products were CD_3 and CH_3 dimethoxy ethers. As the preadsorbed methanol concentration was increased, exchange of intact methyl groups was observed, giving rise to $(CH_3)_2O$, $(CD_3)_2O$, and CH_3OCD_3 in the ratio 1 : 1 : 2. In the temperature range 247 to 367°C at low preadsorbed methanol concentration the products observed were methane and formaldehyde. No H/D scrambling was observed under these conditions. When the concentration of preadsorbed methanol was increased, some H/D scrambling was detected and the principal products were lower alkanes and alkenes. Aromatic products were first seen at 300°C in modest yields, increasing considerably at about 370°C.

Our note therefore looks at a more typical MTG situation where the feed is passed over the catalyst under flow conditions at 300°C and moderate yields of aromatics are found. These yields were increased many fold when 10% benzene was added to the feed. The temperature of 300°C was chosen in the hope that under such mild conditions H/D scrambling would be minimal.

Our aim was to see whether the use of deuterium labelling in conjunction with the benzene sequestration method could provide mechanistic information on the early stages of the MTG reaction.

The conversion was carried out at 1 atm and 300°C over the H-ZSM-5 catalyst ("Conteka," Si/Al 15.5, 1 g). The feed contained CD_3OH (1.92 moles) and C_6H_6 (0.11 moles), giving a D/H ratio of 5.7/2.6, i.e., 2.2 in the whole mixture. The catalytic apparatus has been described previously (2) as has the procedure in which benzene (C_6H_6, AR grade) is added to the feed (CD_3OH, Aldrich, 99.5%D) as it enters the catalyst chamber. Due to the large excess of CD_3OH used a two phase product was obtained. This product was separated, the aqueous layer discarded, and the organic layer subjected to GLC separation on a semi-preparative scale. Only the durene fraction was collected.

^{13}C NMR spectra were recorded at 298 K on a Bruker AM-400 spectrometer operating at 100.614 MHz. The durene samples were dissolved in $CDCl_3$ and referenced internally to tetramethylsilane (TMS). Due to very low sample concentrations the interpulse delay was set to 0.1 s and around 23,000 transients were recorded for both the $^{13}C\{^1H\}$ and $^{13}C\{^1H\}$-DEPT spectra (64 K data points, sweep width 25 KHz). Assignment of the CH_mD_n groups was made using the DEPT spectra. Due to the complex CD couplings and associated intense crowding in the Me region (17.4–19.1 ppm) it was not possible to fully separate

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the individual signals and, as a result, we have used peak heights rather than integrals for the semiquantitative measurement of the nuclei associated with each signal.

Scanning electron microscope studies of the catalyst, after pelleting and easy crushing, showed particle sizes to lie in a restricted range from about 1–5 μm.

Methyl groups in the durene fraction showed deuterium abundance ratios as follows:

$$CH_3\ 1.0,\ CH_2D\ 5.0,\ CHD_2\ 7.5,\ CD_3\ 2.2.$$

It is at once clear that no single species, either of CD_3 or CD_2 type dominates the yield pattern and that distribution of D is more or less random in the durene methyl groups.

Furthermore, it is clear that the durene product contains more H in the methyl groups than would be expected from the relative abundances of H and D in the feed mixture, as Table 1 shows.

Clearly, a significant proportion of H has been added to the reaction mixture from some other source during conversion. Although the actual amount of H added has not been accurately determined, the results do demonstrate that the zeolite has donated protons in the course of the catalytic reaction. (see also Ref. 5).

A simple statistical treatment assuming complete random isotopic scrambling during conversion was carried out using a binomial probability distribution ($D/D + H = 0.57$ from the observed D/H ratio of 1.3) which demonstrated that the following ratios of deuterated isomers would be expected:

$$D_2/D_3\ 2.3,\ D_1/D_3\ 1.8,\ D_0/D_3\ 0.46.$$

Normalising so that the abundances total 100%, we have the projected group abundances as shown in Table 2.

Bearing in mind the difficulty of measuring precisely the yields of these species, these data establish satisfactorily that random distribution of isotopes has occurred, and that no particular isomer is present in excess.

Using the benzene sequestration method there exist three proton sources for scrambling the CD_3OH deuteriums: (i) the surface hydroxyls, (ii) the methanol hydroxyls, and (iii) the benzene protons. As we have seen above the results suggest that scrambling occurs with incorporation of protons from all three H sources, and we have established that deuterium scrambling in this reaction involves the zeolite hydroxyls. As any *CX*3-*R* (*X* = H, D, *R* = alkyl, aromatic) intermediates involved in the MTG reaction are rendered indistinguishable by such complete scrambling we conclude that the above method is unsuitable for temperatures over 300°C and at high feed loadings on the catalyst. Read in conjunction with the results of Anderson *et al.* (4) and Novakova *et al.* (5), our results place an upper limit (of around 250°C) on the temperature at which deuterium effects may be used to look at ambient pressure MTG reactions. Unfortunately, this is well below the temperature at which useful yields of gasoline are obtained.

TABLE 1

Relative Abundances of H and D Compounds in Conversion Products as Measured by NMR

	CH_3	CH_2D	CHD_2	CD_3	Totals
Relative abundance of groups	1	5	7.5	2.2	—
Relative abundance of D atoms	0	5	15	6.6	26.6
Relative abundance of H atoms	3	10	7.5	0	20.5

Note. D_{total}/H_{total}(obs) 26.6/20.5 = 1.3; D_{total}/H_{total} (starting material) = 2.2.

TABLE 2

Calculated and Observed Abundances of Deuterated Methyl Groups in Durene (%)

	CH_3	CH_2D	CHD_2	CD_3
Calculated	8.2	32.1	41.7	18.0
Observed	6.4	31.8	47.7	14.0

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Allan L. Odell
Jan M. Coddington†
Michael J. Liddell[1]

Department of Chemistry
University of Auckland
Private Bag 92019
Auckland, New Zealand

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† Deceased.

[1] To whom correspondence should be addressed.