

## Mechanism of Some Conversions over ZSM-5 Catalyst

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Various carbon-carbon bond formation reactions over ZSM-5 catalyst have been studied with the help of deuterium labeling. The reactions studied were: benzene methylation (benzene/methanol), benzene ethylation (benzene/ethanol and benzene/ethylene), and the conversion of propylene and of ethylene to higher molecular weight products, together with some ancillary exchange reactions. It is shown that, in the methylation of benzene, the methyl group remains intact throughout and does not undergo exchange with surface hydrogen or aryl hydrogen. All the carbon-carbon bond formation reactions are interpreted as Brönsted acid-catalyzed electrophilic alkylations. From these data it is suggested that the ZSM-5-catalyzed conversion of methanol to hydrocarbons involves electrophilic methylation of olefinic intermediates as the main propagation reaction for carbon-carbon bond formation.

The zeolite catalyst, ZSM-5, is able to effect a number of industrially significant conversions (1). The most important are the conversion of methanol to aromatic rich, gasoline-range hydrocarbons (2-7), and a variety of reactions which involve the substitution, migration, or removal of an alkyl group at a benzene ring (1).

ZSM-5 zeolite is most active in its protonated form (HZSM-5), and thus acid-catalyzed mechanisms are probable (4). However, it is not clear how acid-catalyzed mechanisms account for the conversion of methanol to higher hydrocarbons. Chang and Silvestri (3) suggest that methanol gives a carbene or carbenoid species ( $\sim\text{CH}_2\sim$ ), which is responsible for carbon-carbon bond formation. Derouane *et al.* (5), by contrast, suggest that methanol dehydrates via dimethyl ether to ethylene, which then gives higher hydrocarbons; they also suggest that methanol adds to olefins ( $\text{C}_n$ ) to give alkyl methyl ethers which dehydrate to higher olefins ( $\text{C}_{n+1}$ ).

Both suggestions imply that the C-H bonds of methanol are labile prior to, or at the point of, initial carbon-carbon bond formation. The complexity of the methanol reaction does not allow this point to be tested directly. Nevertheless, we have attempted to illuminate this point indirectly by using deuterium-labeling experiments which test the lability of various C-H bonds in some reactions which are relevant to methanol conversion, namely, the methylation of benzene to toluene, the ethylation of benzene to ethylbenzene, and the conversions of propylene and ethylene.

### EXPERIMENTAL AND RESULTS

#### *General*

The preparation, characterization, and pretreatment of the HZSM-5 catalyst (7), and microreactor operation, were as previously described (4). The catalyst, designated HZSM-5, was prepared in the hydrogen-exchanged form by decomposition of

the ammonium-exchanged form (4). Before each experiment, the catalyst (0.2 g) was pretreated in a flow of hydrogen overnight at 400°C. The reactor effluent was diluted by nitrogen (except when isotopic analysis of ethylene was desired) and analyzed by gas chromatography (6-m OV101 column; temperature-programmed mode).

Gaseous feeds were delivered to the reactor via flow-control needle valves, while liquid feeds were delivered by a motor-driven syringe to be vaporized by the preheater coil of the reactor.

Chemicals used were of C.P. grade. D<sub>2</sub>O, C<sub>6</sub>D<sub>6</sub>, and CD<sub>3</sub>OD were of 99.8, 99.6, and 99.4% isotopic purity in deuterium, respectively. In isotopic labeling experiments, the feeds (deuterated and undeuterated) were supplied to the reactor for about 30 min, so as to allow the H/D distribution on the catalyst to reach equilibrium before the isotopic distribution in the products was determined.

Mass spectra of the gas chromatographed products were obtained with a Ribber quadrupole mass spectrometer which directly accepted the gas chromatograph effluent. The mass spectrometer was operated at reduced electron energy (in the region of 20 eV) so as to simplify the fragmentation patterns. Distributions of the deuterioisomers were obtained by comparison with mass spectra of corresponding undeuterated material. In correcting for fragmentation due to the loss of H or D atoms, it was assumed that loss of H or D was on a random basis.

#### Toluene/Deuterobenzene

Toluene-*d*<sub>0</sub> ( $0.3 \times 10^{-4}$  mol min<sup>-1</sup>) and benzene-*d*<sub>6</sub> ( $1.4 \times 10^{-4}$  mol min<sup>-1</sup>) were fed (syringe feed) to the reactor together with nitrogen gas at a rate of 5 cm<sup>3</sup> min<sup>-1</sup>.

At a temperature of 310°C the only apparent reaction was deuterium exchange. Table 1 shows the distribution of deuterioisomers thus obtained. The table also lists the distributions expected (bearing in mind

TABLE 1  
Distribution of Deuterioisomers<sup>a</sup>

	Toluene			Benzene		
	Found	Calcd- (i)	Calcd- (ii)	Found	Calcd- (i)	Calcd- (ii)
<i>d</i> <sub>8</sub>	—	—	24	—	—	—
<i>d</i> <sub>7</sub>	—	—	37	—	—	—
<i>d</i> <sub>6</sub>	Very small	—	26	33	33	25
<i>d</i> <sub>5</sub>	44	41	10	42	41	39
<i>d</i> <sub>4</sub>	49	41	3	22	21	28
<i>d</i> <sub>3</sub>	7	14	—	3	5	8
<i>d</i> <sub>2</sub>	Very small	3	—	—	—	—
<i>d</i> <sub>1</sub>	—	—	—	—	—	—

<sup>a</sup> Expressed in mol%.

the relative proportions of the reactants) for (i) random scrambling of six deuterium atoms from benzene-*d*<sub>6</sub> and five hydrogen atoms from toluene-*d*<sub>0</sub> (i.e., assuming the toluene methyl group is inert), and (ii) random scrambling of six deuterium atoms from benzene-*d*<sub>6</sub> and eight hydrogen atoms from toluene-*d*<sub>0</sub> (i.e., assuming all hydrogen atoms in toluene to be equally available for exchange).

The distribution of products makes it clear that exchange was limited to the aryl hydrogens of toluene, and that exchange equilibrium was achieved.

Similar results were obtained at 206°C. At 396°C, the toluene peak at mass 98 was small but significant, indicating some deuterium entry into the methyl group of toluene.

#### Propylene/Deuterium Oxide

Propylene-*d*<sub>0</sub> (gas feed) was fed to the reactor at a rate of  $0.8 \times 10^{-4}$  mol min<sup>-1</sup>, together with deuterium oxide (syringe feed) at a rate of  $9 \times 10^{-4}$  mol min<sup>-1</sup> and nitrogen gas at 8 cm<sup>3</sup> min<sup>-1</sup>.

At a reactor temperature of 241°C the reactor effluent contained the following hydrocarbon components (mol%): C<sub>1</sub> + C<sub>2</sub>, ~2; C<sub>3</sub>, 21; C<sub>4</sub>, 46; C<sub>5+</sub>, 31. The mass

spectrum of the C<sub>3</sub> fraction indicated a mixture of isotopically labeled propylenes in the approximate proportions (mol%): propylene-*d*<sub>0</sub>, 50; propylene-*d*<sub>1</sub>, 33; propylene-*d*<sub>2</sub>, 17. Gas chromatography showed the C<sub>4</sub> hydrocarbons to consist almost entirely of a complex mixture of olefins, and this was confirmed from the mass spectrum, which was simplified for the purpose by omitting the deuterium oxide from the reactor feed.

#### *Ethylene/Deuterium Oxide*

Ethylene-*d*<sub>0</sub> was fed (gas feed) to the reactor at a rate of  $2 \times 10^{-4}$  mol min<sup>-1</sup>, together with deuterium oxide (syringe feed) at a rate of  $9 \times 10^{-4}$  mol min<sup>-1</sup> and nitrogen gas at 8 cm<sup>3</sup> min<sup>-1</sup>.

At a reactor temperature of 187–232°C the conversion of ethylene to other hydrocarbon products was <1 mol%, and the mass spectrum of the effluent ethylene showed no evidence for the presence of deuterioethylenes. At 252°C, 9 mol% of the ethylene was converted to C<sub>3</sub>–C<sub>5</sub> hydrocarbons, and at 282°C the conversion was 25 mol%. In all cases the effluent ethylene was deuterium free.

#### *Methanol/Deuteromethanol*

A flow of nitrogen gas, 5 cm<sup>3</sup> min<sup>-1</sup>, was saturated by passage through a mixture of CH<sub>3</sub>OH (56 mol%) and CD<sub>3</sub>OD (44 mol%) at 0°C. The total methanol feed rate calculated from vapor pressure data (8) was  $9 \times 10^{-6}$  mol min<sup>-1</sup>.

At 160°C, conversion of methanol to dimethyl ether was 90% complete, and at 207°C it was 100% complete. The mass spectrum of the dimethyl ether product was (mass/intensity, with the intensity at mass 46 normalized to 100): 45/200, 46/100, 47/106, 48/175, 49/150, 50/144, 51/0, 52/100. This leads to the composition of the dimethyl ether product (mol%): (CH<sub>3</sub>)<sub>2</sub>O, 30; (CH<sub>3</sub>)(CD<sub>3</sub>)O, 45; (CD<sub>3</sub>)<sub>2</sub>O, 25. The

absence of a peak at mass 51 showed that there could not have been a significant amount of (CHD<sub>2</sub>)(CD<sub>3</sub>)O. For comparison, the relative proportions of (CH<sub>3</sub>)<sub>2</sub>O, (CH<sub>3</sub>)(CD<sub>3</sub>)O, and (CD<sub>3</sub>)<sub>2</sub>O expected from a reactant containing CH<sub>3</sub>– and CD<sub>3</sub>– in a molar ratio of 5/4 would be (mol%): (CH<sub>3</sub>)<sub>2</sub>O, 31; (CH<sub>3</sub>)(CD<sub>3</sub>)O, 49; (CD<sub>3</sub>)<sub>2</sub>O, 20, assuming random pairing of methyl groups.

#### *Deuteromethanol/Benzene*

Benzene-*d*<sub>0</sub> was fed (syringe feed) to the reactor at a rate of  $1.8 \times 10^{-4}$  mol min<sup>-1</sup> together with a gaseous feed of nitrogen, 6 cm<sup>3</sup> min<sup>-1</sup>, saturated by passage through a mixture of CD<sub>3</sub>OD (25 mol%) and H<sub>2</sub>O (75 mol%) at 0°C. The feed rates calculated from vapor pressure data (8) were: methanol,  $1.5 \times 10^{-6}$  mol min<sup>-1</sup>; and water,  $0.3 \times 10^{-6}$  mol min<sup>-1</sup>.

At 207°C the reactor effluent contained 1.2 mol% toluene, 0.30 mol% dimethyl ether, and 98.5 mol% benzene: That is, 66 mol% of the reacted methanol yielded toluene. The dimethyl ether was entirely (CD<sub>3</sub>)<sub>2</sub>O, since the mass spectrum showed peaks at masses 52 and 50, corresponding to the parent and parent minus D, but no mass 51 peak. The toluene mass spectrum was (mass/intensity, with the intensity at mass 95 normalized to 100): 96/15, 95/100, 94/39, 93/19, 92/17, 91/7. From this it follows that the toluene product contained about 80 mol% toluene-*d*<sub>3</sub>, about 5 mol% toluene-*d*<sub>4</sub>, and about 15 mol% toluene-*d*<sub>0–2</sub> (largely toluene-*d*<sub>0</sub>).

A reaction was also carried out under the same conditions except that the methanol plus water mixture was made up using methanol-*d*<sub>0</sub> and methanol-*d*<sub>4</sub> in the molar ratio of 1/2. The mass spectrum of the toluene product was: 96/27, 95/100, 94/60, 93/28, 92/52, 91/27. This leads to the conclusion that the toluene product consisted of toluene-*d*<sub>3</sub> and toluene-*d*<sub>0</sub> in the approximate molar ratio of 2/1, with some toluene-

ene- $d_1$  ( $\sim 12$  mol%) but no large amounts of toluene- $d_1$  and toluene- $d_2$ .

#### *Ethanol/Deuterobenzene*

Benzene- $d_6$  was fed (syringe feed) to the reactor at a rate of  $1.8 \times 10^{-4}$  mol  $\text{min}^{-1}$  together with a gaseous feed of nitrogen, 8  $\text{cm}^3$   $\text{min}^{-1}$ , saturated by passage through a mixture of  $\text{C}_2\text{H}_5\text{OH}$  (23 mol%) and  $\text{D}_2\text{O}$  (77 mol%) at  $0^\circ\text{C}$ . The feed rates calculated from vapor pressure data (8) were: ethanol,  $2.8 \times 10^{-6}$  mol  $\text{min}^{-1}$ ; and water,  $1.8 \times 10^{-6}$  mol  $\text{min}^{-1}$ .

At  $197^\circ\text{C}$  the reactor effluent contained 2.1 mol% ethylbenzene, 14 mol% ethylene, and 84 mol% benzene: That is, 13 mol% of the reacted ethanol had been converted to ethylbenzene and 87 mol% to ethylene.

At  $247^\circ\text{C}$  the reactor effluent contained 2.1 mol% ethylbenzene and 11 mol% ethylene, indicating that 16 mol% of the reacted ethanol had been converted to ethylbenzene and 84 mol% had been converted to ethylene. The effluent benzene consisted of 67 mol% benzene- $d_6$  and 23 mol% benzene- $d_5$ , while the ethylbenzene was 67 mol% ethylbenzene- $d_5$  and 23 mol% ethylbenzene- $d_4$ . The main fragment peaks from the ethylbenzene were at masses 95 and 96, corresponding to (parent-15), that is, the loss of  $\text{CH}_3$ .

#### *Ethylene/Deuterobenzene*

Benzene- $d_6$  was fed (syringe feed) to the reactor at a rate of  $1.8 \times 10^{-4}$  mol  $\text{min}^{-1}$ , together with ethylene (gas feed) at  $0.8 \times 10^{-4}$  mol  $\text{min}^{-1}$ . Experiments were carried out with and without the addition of nitrogen diluent to the feed.

With the reactor at  $238^\circ\text{C}$  and with nitrogen diluent added at the rate of 7  $\text{cm}^3$   $\text{min}^{-1}$ , the reactor effluent contained (mol%): ethylene, 28; benzene, 72; ethylbenzene, 0.34; corresponding to 1.2 mol% conversion of ethylene to ethylbenzene.

In the absence of nitrogen, reaction at  $238^\circ\text{C}$  gave an effluent containing 2.6 mol% ethylbenzene, corresponding to 10 mol% conversion of ethylene. Reaction at  $276^\circ\text{C}$  in the absence of nitrogen gave an effluent containing 7.4 mol% ethylbenzene, corresponding to 22 mol% conversion of ethylene.

The effluent ethylene from reaction at  $276^\circ\text{C}$  in the absence of nitrogen was mainly ethylene- $d_0$  (75 mol%) together with some ethylene- $d_1$  (25 mol%). The effluent benzene was mainly benzene- $d_6$  (67 mol%) with some benzene- $d_5$  (33 mol%). The ethylbenzene consisted of ethylbenzene- $d_6$  (52 mol%) and ethylbenzene- $d_5$  (48 mol%). The main fragment peaks from the ethylbenzene were at masses 95 and 96, corresponding to (parent-16), that is, the loss of  $\text{CH}_2\text{D}$ .

## DISCUSSION

### *Brönsted Acidity*

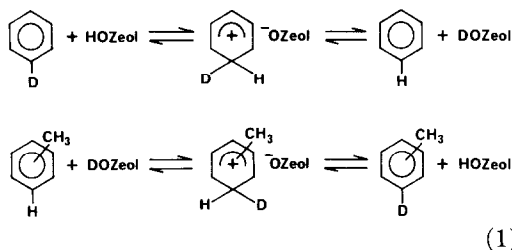
It is now clear that the catalytic activity of ZSM-5 resides in Brönsted acid sites. Our earlier results have shown (4) that only the hydrogen-exchanged form, HZSM-5, has high long-lived activity. The activity of the sodium-exchanged form, NaZSM-5, is low or very short-lived, depending on the reactant (4). It has also been shown that the activity of HZSM-5 is quenched by ammonia or other nitrogenous bases (4).

The activity of HZSM-5 for methanol conversion implies that the catalytic activity is not quenched by water which is a reaction product. Moreover, the present results show that the alkylation of benzene proceeds readily in the presence of water. These results make it clear that the active site is not of Lewis acid character.

### *Toluene/Deuterobenzene Exchange*

Exchange of the aryl hydrogens of toluene with the hydrogens of benzene is rapid at  $206^\circ\text{C}$ . The ease of this exchange and the absence of exchange of the methyl

hydrogens of toluene are fully consistent with reaction at Brönsted acid sites.

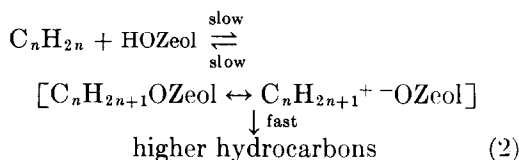


The results do not exclude the possibility of a Brönsted acid-catalyzed transfer of methyl between aromatic nuclei.

Under these circumstances, the surface is expected to be heavily deuterated by exchange with  $C_6D_6$  which is present in excess.

*Reactions of Propylene and of Ethylene.* When propylene- $d_0$  was reacted with excess  $D_2O$  at  $241^\circ C$ , the conversion to  $C_4$ ,  $C_5+$  hydrocarbons was  $\sim 70$  mol%, but the unconverted propylene was still 50% undeuterated. This relatively small amount of exchange in the unreacted olefin was even more evident with ethylene, where the reaction of ethylene- $d_0$  with excess  $D_2O$  at  $282^\circ C$  gave 25 mol% conversion to  $C_3$ - $C_5$  hydrocarbons, but the unconverted ethylene remained 100% undeuterated.

These results suggest that once protonation of the olefin occurs at a Brönsted site, further reaction leading to carbon-carbon bond formation is rapid compared with reconversion to the olefin.



We shall not enter into a detailed discussion of the nature of the bonding between the protonated olefin ( $C_nH_{2n+1}$ ) and the zeolite site (OZeol). The question of ionic vs polar covalent bonding exists for many of the species discussed in this paper, and the answer will doubtless depend upon the particular species involved. It may be

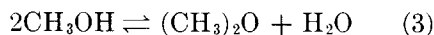
noted that ethylene, which would require the formation of a primary carbonium ion of very high energy, is much less reactive than propylene, from which a secondary carbonium ion is possible. The generation of higher hydrocarbons from olefins is discussed in a later section.

### Benzene Alkylation

The toluene produced at  $207^\circ C$  from deuteromethanol and benzene- $d_0$  was mainly toluene- $d_3$ , and a  $CH_3$ - and  $CD_3$ -methanol mixture gave toluene which was mainly a mixture of toluene- $d_0$  and toluene- $d_3$ . In both cases, addition of excess  $H_2O$  to the reactant ensured that the catalyst surface was predominantly in the H-exchanged form, the ratio  $H_{(s)}/D_{(s)}$  being 6-9 (assuming exchange equilibrium involving only -OH and -OD).

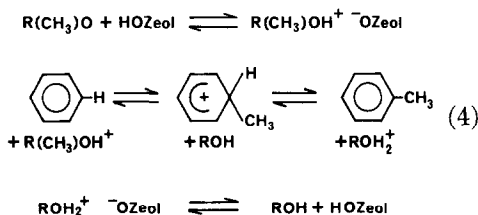
We conclude from the deuterium distribution in the toluene product that the latter was generated by a route which kept the methyl group intact (i.e., unexchanged). At no stage was there substantial exchange between the methyl group and surface hydrogen, between the methyl protons and aryl hydrogen, or between one methyl group and another.

Our results do not permit a definitive identification of the methylating agent. At the same temperature as used in the methanol/benzene reaction ( $207^\circ C$ ), but without benzene in the reactant feed, the conversion of methanol to dimethyl ether was  $\geq 98\%$ : This indicates that the equilibrium



was established, since  $K_p$  for reaction (3) at  $207^\circ C$  is  $5.6 \times 10^3$ . Although this is consistent with the proposal (3) that dimethyl ether is the active intermediate in the conversion of methanol (to aromatics), it is still conceivable that the equilibrium concentration of methanol is sufficiently high for the conversion to proceed directly from methanol rather than via dimethyl ether.

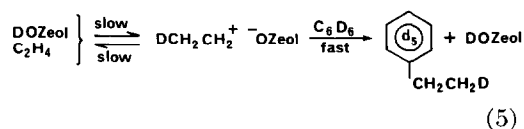
Bearing in mind the evidence which shows that in the methylation reaction the methyl group does not undergo hydrogen exchange, we may formulate this reaction as probably proceeding from R-O-CH<sub>3</sub> (R = H or CH<sub>3</sub>) via a reaction such as



Reaction between ethanol-*d*<sub>0</sub> and benzene-*d*<sub>6</sub> was carried out at 197–247°C. The presence of D<sub>2</sub>O ensured that the surface was predominantly in deuterium-exchanged form. The deuterium distribution in the ethylbenzene, considered in relation to the deuterium content of the benzene reactant, makes it clear that the ethyl group was undeuterated: No substantial exchange of hydrogen occurred involving this group and the surface or the benzene.

An ethylation mechanism may be postulated analogous to the methylation mechanism outlined in reaction (4). What is significant is that the ethyl substituent is largely undeuterated and so has not been formed via ethylene.

When ethylbenzene was formed by the reaction of ethylene-*d*<sub>0</sub> with benzene-*d*<sub>6</sub> (238–276°C), most of the ethylbenzene contained the ethyl group -CH<sub>2</sub>CH<sub>2</sub>D. In this case, the surface is expected to be heavily deuterated by exchange with C<sub>6</sub>D<sub>6</sub> which was present in excess (cf. previous discussion of the toluene-*d*<sub>0</sub>/benzene-*d*<sub>6</sub> exchange reaction). The occurrence of a mono-deutero ethyl substituent under these circumstances agrees with previous observations (9) for benzene alkylation over a deuterated rare earth-exchanged X-zeolite catalyst, and is consistent with the reaction scheme



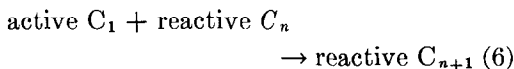
Ethylene is relatively unreactive in the alkylation of benzene. At 197–247°C the ethanol/benzene reaction yielded ethylene as the main product; only 13 to 16 mol% of the ethanol was converted to ethylbenzene. A higher reaction temperature was required for an increased extent of alkylation.

#### Hydrocarbon Synthesis over HZSM-5

It is useful at this stage to summarize the discussion. We have argued that the catalytic activity of HZSM-5 resides in the Brönsted acid sites, and we have demonstrated the isotopic redistribution of aryl hydrogens expected on this basis. We have shown that the alkylation of benzene by methanol, ethanol, and ethylene is as expected for a Brönsted acid-catalyzed alkylation mechanism. We have found that ethylene is comparatively unreactive, and that, in the reaction of methanol with benzene, there is no exchange involving the methyl hydrogens.

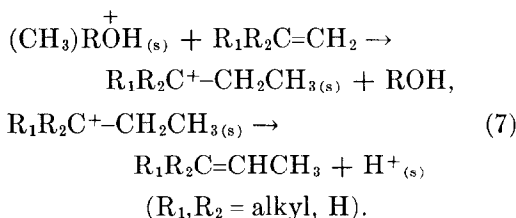
We thus infer, albeit on indirect evidence, that in the conversion of methanol to hydrocarbons over HZSM-5, the *initial* reaction step of the methanol does not involve a species which would lead to methyl group exchange, that is, it does not involve lability of the C-H bonds.

We have suggested previously (4) that hydrocarbon synthesis from a C<sub>1</sub> precursor over HZSM-5 proceeds by a process in which an activated C<sub>1</sub> species homologizes a suitably reactive C<sub>n</sub> species such as a C<sub>n</sub> olefin. That is, there is a general propagation mechanism of the type



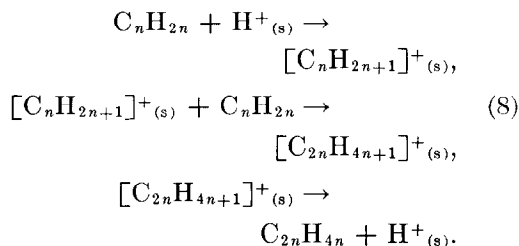
Clearly it is not suggested that, under the present circumstances, repetition of reaction (6) can lead to a very high molecular weight product, since the degree of polymerization is restricted by the channel size in the ZSM-5 catalyst, and by the conversion of C<sub>6+</sub> aliphatics to aromatics if the reaction temperature is high enough.

Nevertheless, our conclusions about the initial nonlability of C-H bonds in methanol (see above) infer that the  $C_1$  species in reaction (6) will not be a carbene, carbenoid, or oxymethylene species. Bearing in mind the Brönsted acid-catalyzed nature of the reaction, we propose for the active  $C_1$  species an entity of the type  $(CH_3)ROH^+$  ( $R = H$  or  $CH_3$ ). We propose that the reactive  $C_n$  species in reaction (6) is an olefin, which would be even more susceptible to electrophilic methylation than benzene. Thus, reaction (6) becomes



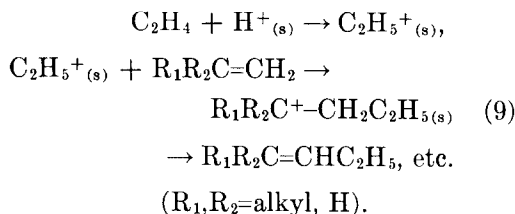
A direct test of mechanism (7) in the reaction between methanol and a simple olefin is not practicable because the result would be obscured by isomerization and further reactions of the olefins.

When the primary reactant is of carbon number greater than unity, the situation is rather different. A basic bond-forming reaction may be written (cf. (4)), starting with olefin reactant,  $C_nH_{2n}$  ( $n \geq 3$ ),



In the particular case of ethylene reactant, we have already noted that ethylene is of relatively low reactivity compared with methanol, and is unlikely to be an intermediate in methanol conversion. Ethylene is also of low reactivity compared with propylene. The reactivity of olefins toward

carbonium ion reagents generally increases with increasing degree of olefin substitution. Thus, even with ethylene as primary reactant, much of the basic reaction may occur preferentially between protonated ethylene and a higher olefin, for instance,

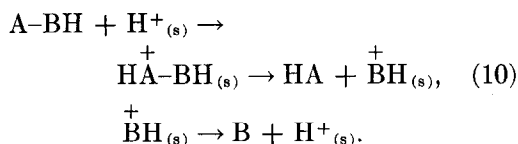


On this basis, one would not expect ethylene conversion to be an oligomerization to linear olefin (as suggested earlier (5)). Instead, we would expect the products from ethylene to resemble those from methanol or other reactants, with the aliphatic products being predominantly of branch-chain character.

Let us now consider the origin of the lower olefins which undergo carbon-carbon bond formation with reactants such as methanol. It is important to recognize that, in the formation of gasoline-type hydrocarbons from smaller precursors over HZSM-5, carbon-carbon bond rupture reactions must be occurring at the same time. We note, for instance, that propylene undergoes extensive conversion at 241°C (a temperature below that at which aromatic formation becomes of dominant importance), and that much of the product consists of  $C_4$  olefins. This must result from the occurrence of a complex sequence of carbon-carbon bond-forming and bond-breaking reactions.

Whenever a Brönsted acid-catalyzed carbon-carbon bond rupture occurs, one reactive species (a carbonium ion or an olefin which gives a carbonium ion on protonation) gives rise to two reactive species. Thus, an olefinic molecule, A-BH, in which part A contains the double bond, cleaves after protonation to an olefin AH and a carbonium ion  $BH^+$  which depro-

tonates to an olefin B:



Since the products of bond rupture are themselves precursors for further chain growth, it is clear that a range of reaction products with a continuous distribution of carbon number results, even when the primary reactant is a molecule such as propylene.

It is well appreciated (cf. (1-3) and particularly (4)) that the size of the channels in ZSM-5 in relation to the size of the guest molecules controls both the rate of molecular sorption and the size of molecules which can be synthesized therein. We therefore point out that the fate of a reactant or intermediate will depend not only on its intrinsic reactivity but also on its lifetime within the catalyst. Thus, if two reactants were of the same intrinsic reactivity but of different diffusivity in the catalyst channels, the overall result would be that the reactant of higher diffusivity would have the lower apparent reactivity. While we are at the moment not in a position to quantify further this concept, we note

that, in general, the rate of diffusion will decrease with increasing molecular size, and that this may, *in part*, contribute to the relatively low apparent reactivity of ethylene compared to higher olefins.

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