The Polymerization and Aromatic Alkylation of Butene-1 with Calcined Ammonium Type Y Zeolite

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Infrared analyses and mass spectroscopic studies using 1-butene-4-^{13}C have been used to elucidate the mechanism of the reaction of 1-butene over calcined ammonium Y zeolite. It is concluded that olefin polymerization and benzene alkylation are independent of zeolite hydroxyl concentration and that isomerization to 2-butene precedes both reactions.

INTRODUCTION

The interaction between olefins and zeolites has been studied during recent years as part of a general investigation into the mechanism of zeolite catalysis. It is commonly accepted that the reactions of olefins over solid catalysts are proton catalyzed. However, it has been demonstrated that the protons need not necessarily be furnished by the catalyst since polymeric residues formed by olefin–catalyst interaction may also serve as catalytic sites (1). Infrared spectroscopic studies have indicated that olefins are adsorbed onto zeolites by hydrogen bonding. It has further been observed that as the extent of dehydroxylation of a deamminated ammonium Y zeolite increases, the fraction of chemisorbed olefin also increases (2).

Eberly has shown that 1-hexene adsorption on deamminated ammonium Y is accompanied by polymerization and aromatization (3). These reactions result in the formation of paraffins rich in isobutane. Shephard, Rooney, and Kemball, in a most elegant study, conclusively demonstrated that paraffins are formed by a hydrogen transfer mechanism and proposed a reaction scheme (4). Deuterium tracer work has shown that zeolitic hydrogen is in-

corporated into the coke polymer (3, 5). In addition, it has been suggested that zeolitic hydrogen is consumed in catalytic cracking reactions (6). It is reported that a proton-activated olefinic surface species is the reactive intermediate in benzene alkylation reactions over zeolites, but it is not evident that it is the same intermediate seen in the polymerization reactions (7).

The purpose of this study was to determine the role of the zeolite hydroxyl group in both alkylation and polymerization reactions and to elucidate the mechanism of benzene alkylation. In all cases the olefin used was 1-butene.

METHODS

Materials

1-Butene-4-^{13}C was obtained from Merck, Sharp, and Dohme of Canada, Ltd. and was 88% enriched. Nonlabeled butene was Matheson CP Grade and benzene was thiophene-free Reagent Grade. Both were used without further purification. Ammonium Y zeolite was prepared from Linde NaY Molecular Sieve by successive exchanges with aqueous NH$_4$Cl at reflux temperature. Analysis of the material is presented below:

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Al$_2$O$_3$	23.3 wt%	(NH$_4$)$_2$O/Al$_2$O$_2$	0.93
SiO$_2$	65.1 wt%	Na$_2$O/Al$_2$O$_3$	0.04
Na$_2$O	0.65 wt%	SiO$_2$/Al$_2$O$_3$	4.74
(NH$_4$)$_2$O	11.1 wt%		
C	0.20 wt%		

Procedure

Infrared studies were run using a Perkin-Elmer Model 225 grating spectrophotometer. A self-supporting wafer of 10–15 mg was placed in an infrared cell previously described by Angell and Shaffer (8). The zeolite was calcined in vacuum at 500 or 700°C depending on the extent of dehydroxylation desired. Twenty Torr (1 Torr = 133.3 N m^{-2}) of 1-butene was admitted into the cell at room temperature and allowed to equilibrate for 0.5 hr before evacuation. McBain adsorption measurements showed that 20 wt% of olefin remained on the zeolite after evacuation. In the alkylation studies 20 Torr of benzene was also added. Studies using labeled butene were conducted in the infrared cell with a larger pellet (250 mg) and the reaction product collected in a cold trap for subsequent analysis.

The percent of isotopic species formed in the reaction of benzene with 1-butene-4-^{13}C was determined on an A.E.I. MS 12 mass spectrometer integrated with a Hewlett Packard Model 5750 gas chromatograph. The gas chromatograph contained a 20-ft 20% W-98 on Gas Chrom Q column and the mass spectrometer was operated at 10.75 eV to minimize fragmentation. Unlike the typical analysis on a complex labeled product mixture, the sample was led directly into the mass spectrometer from the gas chromatograph. Four mass scans were taken over the single chromatographic peak studied. Isotopic fractionation in the column did not occur. Since the fragmentation pattern indicated that the leading edge of the chromatographic peak was isobutylbenzene while the remainder was sec-butylbenzene, a chromatographic analysis on the product was run separately using a MBMA SCOT capillary column.

Flow experiments were conducted in a microreactor to determine the effect of zeolite dehydroxylation on product distribution. A flow rate of 100 ml/min of 1% butene in helium at atmospheric pressure was used with a catalyst charge of 1 g. Samples were periodically analyzed by a Perkin-Elmer Model 880 gas chromatograph with a 12-ft squalane on Chromosorb plus 12-ft n-octane on Durapack column. This column separates all the C$_4$ hydrocarbons. After correction for detector response, the mole percent of products as a function of reaction time was found. A simple combustion procedure cannot be used for the determination of the H/C ratio of the coke since the dehydroxylation of the zeolite would give an anomalous hydrogen value. Thus an analytical procedure was developed similar to that described by Enterman and van Leuven (9). Basically the procedure consists of combusting the coked zeolite in an oxygen atmosphere and calculating the organic hydrogen from the oxygen pressure drop and the amount of CO$_2$ absorbed on Ascarite.

RESULTS

Infrared spectra of 1-butene adsorbed on deamminated ammonium exchanged Type Y zeolite at 0°C and at low coverage are shown in Fig. 1. The spectrum initiated at 1800 cm^{-1} to observe the species immediately formed shows a doublet at 1630 cm^{-1} and 1645 cm^{-1}, corresponding to the C=C stretching of 1-butene and cis-2-butene, respectively; this vibration is infrared inactive in trans-2-butene. This surface reaction has not been observed previously since radiant heating from the infrared beam causes polymerization. After a period of time the bands due to the unsaturated stretching frequencies disappear and are replaced by species having absorption bands at 2960, 2930, 2870, 1465, 1380, and 1365 cm^{-1}. These bands are characteristic of saturated C–H stretching and bending frequencies. Although the species have saturated characteristics they cannot, unlike an adsorbed paraffin, be physically desorbed at room temperature. Accompanying the formation of the saturated species is a decrease in the intensity of the OH stretching band at 3640 cm^{-1}.
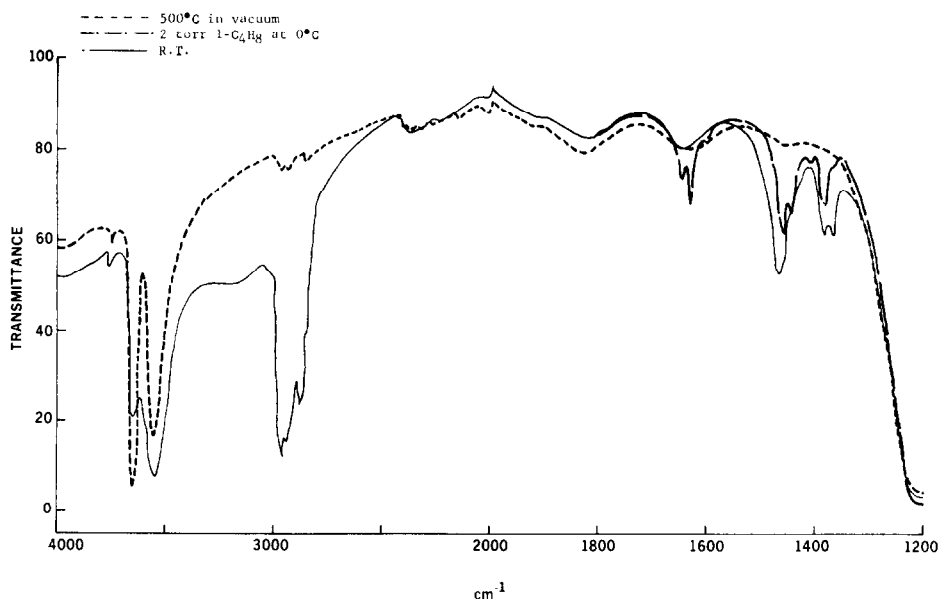
FIG. 1. Isomerization of 1-butene over deamminated ammonium exchanged Y.

The same surface species with the characteristic saturated C–H frequencies present on the deamminated zeolite are also observed with the dehydroxylated zeolite as shown in Fig. 2. At 300°C the bands in the 2900 cm⁻¹ region decrease in intensity and are replaced by a broad band at 1600 cm⁻¹ which has been attributed to highly unsaturated polymeric material (3). Identical results were obtained when the species in Fig. 1 were heated to 300°C. The diminution of the band in the 2900 cm⁻¹ region is accompanied by the evolution of saturated hydrocarbons. Gas chromatographic analyses of the evacuated product showed it to contain the same saturated hydrocarbons as obtained in the flow experiment.
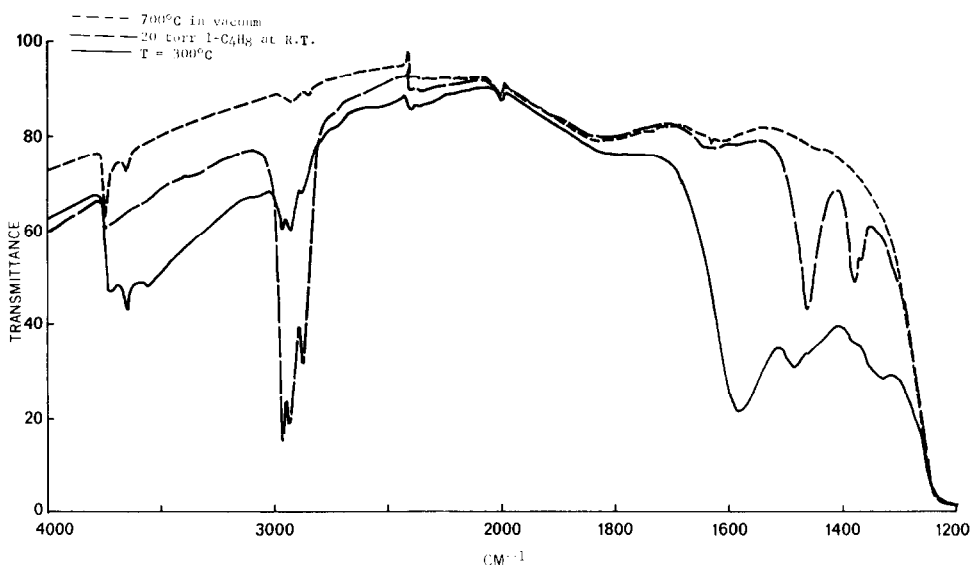

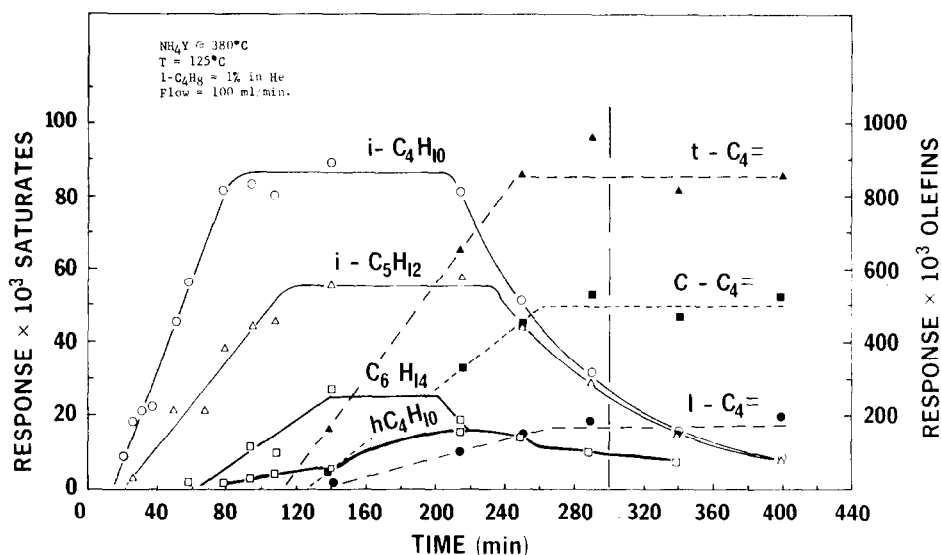FIG. 2. Reaction of 1-butene with dehydroxylated ammonium exchanged Y.

FIG. 3. Reaction products of 1-butene and deamminated ammonium exchanged Y.

The product distribution curve from a flow experiment over ammonium Y deamminated at 380°C (Fig. 3) was found to be the same as that from an ammonium Y dehydroxylated at 700°C. The total amount of saturated product formed at a particular reaction temperature was less for the dehydroxylated form than the deamminated form. The hexanes found were 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane. Table 1 presents an analysis of the products formed as a function both of zeolite calcination temperature and reaction temperature. This table shows the H/C ratio of the material remaining on the zeolite after reaction, the amount of butene converted to polymer (calculated from the percent carbon remaining on the zeolite) and the amount of butene con-

verted to saturated products (calculated by graphical integration of the product versus time curve). In all cases the butene flow was terminated before catalyst deactivation. The ratio of butene converted to saturated product to butene converted to polymer is plotted versus reaction temperature in Fig. 4.

The role of the surface species in catalysis was investigated by carrying out an alkylation reaction on the zeolite wafer in the infrared cell. The addition of benzene to the adsorbed olefin on deamminated ammonium Y at room temperature has no effect on the spectrum of the surface species as shown by Fig. 5. (After heating to 100°C a trace amount of sec-butylbenzene was formed, but the surface species predominated.) This experiment was repeated

TABLE 1
EFFECT OF REACTION TEMPERATURE ON PRODUCT DISTRIBUTION

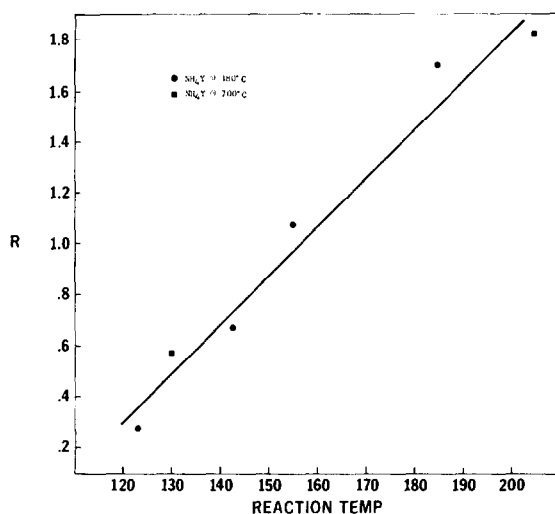|	Run					
	1	2	3	4	5	6
Zeolite calcination temp (°C)	700	700	380	380	380	380
Reaction temp (°C)	200	130	185	155	143	123
C_4H_8 converted to saturated product (ml)	43.2	11.7	64.8	42.2	34.8	13.0
C_4H_8 converted to coke (ml)	23.5	20.0	38.2	39.6	52.2	46.6
Ratio C_4H_8 as product/C_4H_8 as coke	1.84	0.58	1.70	1.07	0.67	0.28
H/C ratio of coke	1.29	1.70	1.27	1.63	1.64	1.77

Fig. 4. Ratio of saturated product carbon to polymeric carbon as function of temperature.

but the order of addition of the reactants was reversed as shown in Fig. 6. Upon 1-butene addition at room temperature *sec*-butylbenzene is immediately formed as is shown by the appearance of characteristic bands at 1615, 1380, and 1460 cm⁻¹. On evacuation at 300°C, the *sec*-butylbenzene is desorbed and the zeolite hydroxyl bands return to their original intensities. No polymeric residue could be seen via in-

frared. The alkylation reaction takes place with the same facility over dehydroxylated Y as is shown in Fig. 7. Analysis of the product mixture showed it to be 90% butylbenzenes with a ratio of *sec*-butyl to isobutyl of 70 to 30. Minor products were xylene, toluene, cumene, and dibutyl-benzenes.

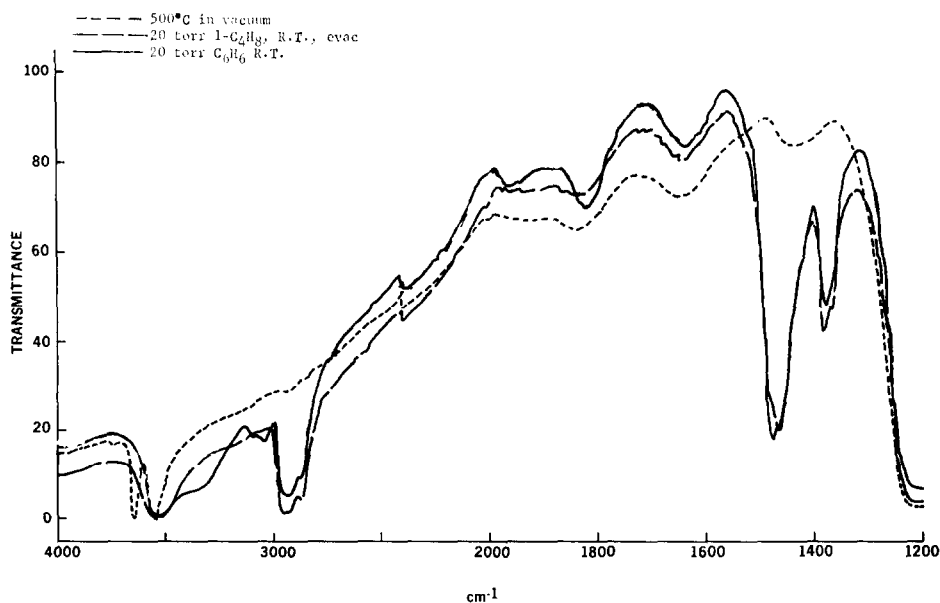The mechanism of this reaction was further investigated by using 88% 1-butene-

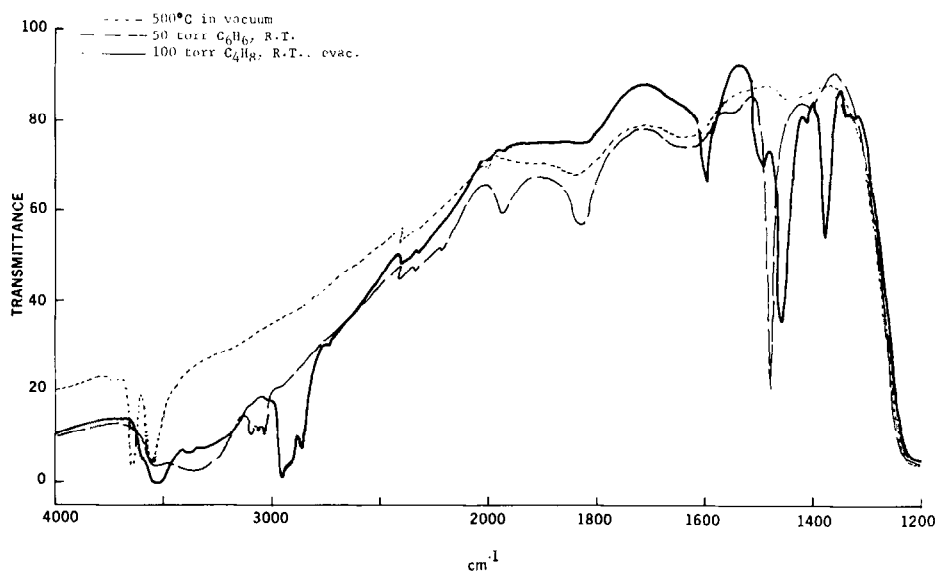Fig. 5. Inhibition of alkylation by polymerization on deamminated ammonium exchanged Y.

FIG. 6. Formation of *sec*-butylbenzene on deamminated ammonium exchanged Y.

4-^{13}C. Table 2 presents the labeling of the *sec*- and isobutylbenzene molecular ions and the fragments of principal interest. The loss of an ethyl group from *sec*-butylbenzene gives rise to an ion which is 50% labeled. Although the peak intensities for the loss of a methyl group from the two isomers were very weak and hence the

values obtained have a large degree of error, they indicate that the remaining ion is only 50% labeled. Upon losing a propyl group both ions are no longer labeled.

DISCUSSION

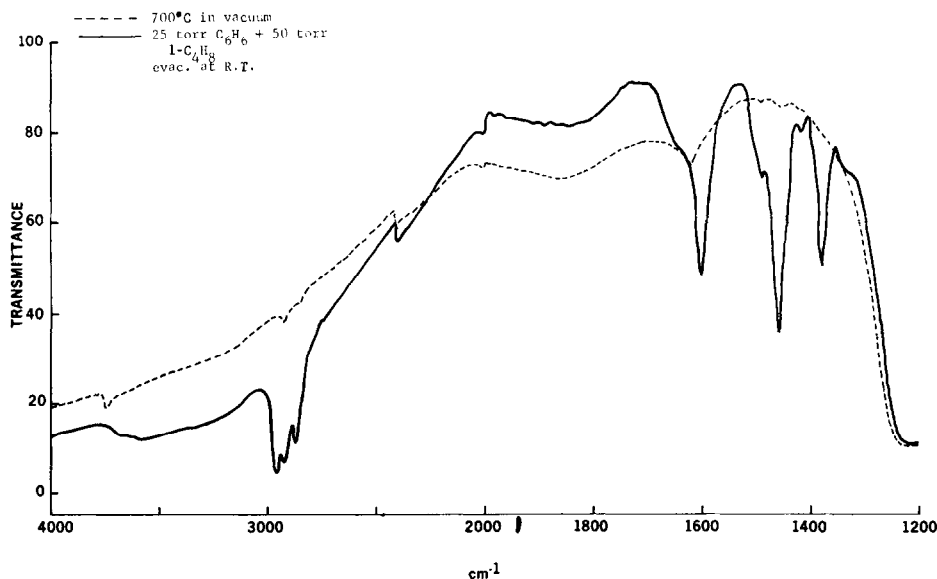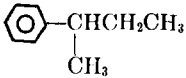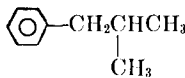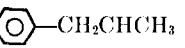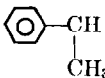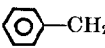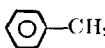The occurrence of surface species formed by the adsorption of olefins on deammi-

FIG. 7. Formation of *sec*-butylbenzene on dehydroxylated ammonium exchanged Y.

TABLE 2

Mass Spectroscopic Data of Sec- and Isobutylbenzenes

Sec-butylbenzene			Isobutylbenzene		
Ion	% of isotopic species		Ion	% of isotopic species	
	$^{13}C_0$	$^{13}C_1$		$^{13}C_0$	$^{13}C_1$
⬡—CHCH$_2$CH$_3$ / CH$_3$	11.3	88.7	⬡—CH$_2$CHCH$_3$ / CH$_3$	12.8	87.2
⬡—CHCH$_2$CH$_3$	49.0	51.0	⬡—CH$_2$CHCH$_3$	48.0	50.0
⬡—CH / CH$_3$	55.5	44.5	—	—	—
⬡—CH$_2$	100	0	⬡—CH$_2$	100	0

nated ammonium Y has been reported by several investigators. These species are characterized by the absence of unsaturated =CH and C=C stretching bands in the infrared spectrum and by the presence of saturated C—H bending and stretching bands. The formation of these species is not limited to deamminated ammonium Y since the identical species are observed when 1-butene is absorbed onto dehydroxylated Y. It is likely, therefore, that the species are attached to the zeolite at a dehydroxylated site, since these sites are also present in the deamminated ammonium exchanged material (10). (The term deamminated ammonium Y is preferable to the term hydrogen Y because the occurrence of dehydroxylation at low calcination temperatures prevents the formation of pure hydrogen Y.) The change in relative intensities of the doublet at 1365 and 1380 cm⁻¹ (ascribed to gem-dimethyl scissoring) would indicate that the surface complex is not a homogeneous material and that continuing reaction occurs at low temperatures (11). Figure 1 also shows that rapid isomerization of 1-butene to 2-butene precedes the formation of the saturated surface product. It is unlikely that isomerization occurs via these surface species since the latter cannot be desorbed at room temperature.

Table 1 and Fig. 4 show that the amount of saturated products formed are dependent only upon reaction temperature and not upon the extent of dehydroxylation of the zeolite. The fact that the H/C ratio is inversely proportional to temperature supports this contention. Hence at a higher temperature more hydrogen is eliminated which can saturate the branched chains of the polymer to produce additional paraffin. The equivalence of amount and composition of saturated product with respect to the polymer residue for both deamminated and dehydroxylated ammonium Y indicates that saturated product formation is independent of hydroxyl concentration. Thus it is unlikely that zeolitic hydrogen is consumed in the reaction. The products from both the deamminated and dehydroxylated materials in this study closely match those reported by Venuto, Hamilton, and Landis using ethylene on rare earth exchanged Y and Shephard, Rooney and Kemball using propylene on silica–alumina (4, 7). Since the nature of the saturated products appears to be independent of reactant olefin and the extent of catalyst hydroxylation, it is probable that the products are derived from the same surface intermediates. Figure 4 shows that below 100°C only polymerization and isomerization occur, but it is not clear if the polymer is the active site in the isomerization reaction. Although it has been shown that polymer formation is associated

with this reaction it is also evident that in some cases isomerization can occur in the absence of polymer if water is present (*12, 13*).

Figure 5 shows that the surface species formed by butene adsorption at room temperature is neither a reaction intermediate nor an active site in aromatic alkylation since it acts as an inhibitor. Complete conversion of benzene to *sec*-butylbenzene, as shown by the disappearance of the characteristic benzene frequencies, is achieved only when olefin addition follows that of the benzene (Fig. 6). Infrared spectra of aromatic compounds adsorbed on zeolites have shown a lowering in intensity in the aromatic C–H stretching region; this is also observed in this study (*14*). Also, hydrogen–deuterium exchange is observed between benzene and zeolites (*15*). Thus both the infrared and deuterium exchange results suggest that there is significant interaction between benzene and zeolites which may make the benzene more susceptible to alkylation by olefins.

Previous work by Venuto and co-workers has shown that a wide variety of aromatic alkylation reactions occur over zeolites, including the formation of *sec*-butylbenzene and isobutylbenzene from reacting 1-butene with benzene (*7, 16*). Although it was concluded from the above studies that alkylation is a proton-catalyzed reaction, alkylation has been shown to occur over a dehydroxylated ammonium Y (*17*). This latter conclusion is confirmed in Fig. 7 which shows that *sec*-butylbenzene is formed over a dehydroxylated

zeolite at room temperature. NMR studies of proton mobility in deamminated ammonium Y have shown that although significant mobility occurs near 300°C, it does not appear to occur at room temperature (*18, 19*). The fact that alkylation takes place rapidly at room temperature over dehydroxylated and deamminated material makes it unlikely that a few mobile protons are the catalytic species. Although the infrared technique is not sensitive to low hydroxyl concentration, one would expect the most reactive protons to be those earliest lost in dehydroxylation. Furthermore, it has been shown that the temperature of dehydroxylation is dependent only upon the extent of ammonium exchange and thus not upon the acidity of a few hydroxyl groups (*10*).

More insight into the alkylation mechanism is gained from the mass spectroscopic data given in Table 2. That the molecular ion data show the products to have the same degree of labeling as the starting butene proves the reaction is quantitatively bimolecular. The *sec*-butylbenzene fragment remaining upon losing a methyl or ethyl group is 50% labeled, hence isomerization to 2-butene precedes alkylation. If isomerization had not occurred prior to reaction, then the *sec*-butylbenzene fragments would have been 0% and 100% labeled upon losing the methyl and ethyl groups, respectively, since in both cases the bond β to the benzene ring is broken. This can be seen in Fig. 8 where equivalent methyl groups are indicated by an asterisk.
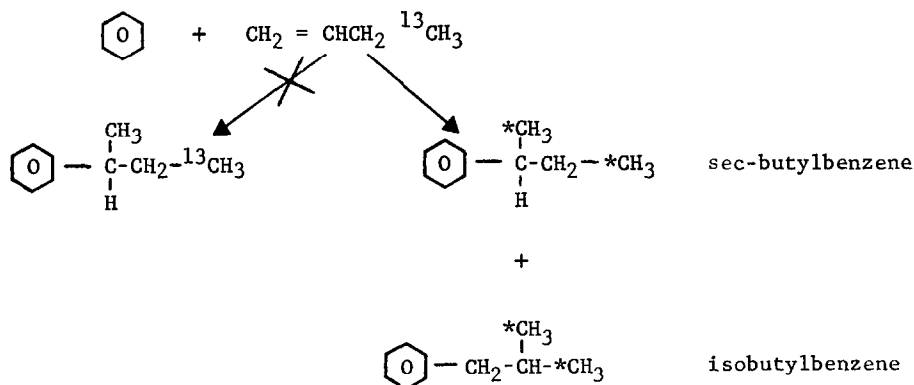
Although rearrangement in the beam of

FIGURE 8

a mass spectrometer is a known phenomenon, the results show this did not occur. Loss of an ethyl group is particularly facile from sec-butylbenzene and would not be expected to involve a rearrangement (20). Since the methyl groups on isobutylbenzene are equivalent, examination of this fragment does not yield any information.

Upon loss of a propyl group the isobutylbenzene and sec-butylbenzene fragments are not labeled. Thus not only do the 2 and 3 carbons of butene maintain their uniqueness in the alkylation reaction, but the rearrangement observed for t-butylbenzene in a mass spectrometer does not occur for iso- and sec-butylbenzene (22). These data show that isobutylbenzene is formed from the sec-butylbenzene via a methyl shift as has been previously reported with $AlCl_3$ (22). This then eliminates an isobutylene type intermediate, which would have resulted in 30% labeling on the α carbon. Thus it is evident that 2-butene or a π complex thereof is the reacting species. Previous investigators have studied the reaction of benzene with optically active secondary butyl methyl ether and BF_3 and shown that a sec-butyl carbonium ion was involved in the formation of racemic sec-butylbenzene (23).

It is possible that a common 2-butene–zeolite intermediate leads to both the room temperature surface species and the alkylation products. However, it was observed that even at low temperatures 2-butene immediately reacts to form the saturated surface species. That this did not occur in the alkylation reaction indicates either that the reacting butene intermediates are different in the two reactions or that presence of benzene prevents the same intermediate from polymerization. Unfortunately, the absence of competitive adsorption data between benzene and butene prevents a clear-cut choice between the two alternatives. In conclusion we may state that alkylation and condensation reactions over zeolites are independent of the zeolite hydroxyl concentration. Furthermore, although the saturated surface species formed by olefin adsorption at room temperature is not a

reaction intermediate in alkylation, the isomerization of 1-butene to 2-butene or a π complex thereof precedes both condensation and alkylation.

REFERENCES

1. HIRSCHLER, A. E., Amer. Chem. Soc. Meet., Chicago, Sept. 1970, Preprints Div. of Petrol. Chem. 15, No. 3, A97 (1970).
2. LIENGME, B. V., AND HALL, W. K., Trans. Faraday Soc. 62, 3229 (1966).
3. EBERLY, JR., P. E., J. Phys. Chem. 17, 1717 (1967).
4. SHEPHARD, F. E., ROONEY, J. J., AND KEMBALL, C., J. Catal. 1, 379 (1962).
5. CANT, N. E., AND HALL, W. K., J. Catal. 25, 161 (1972).
6. BOLTON, A. P., AND BUJALSKI, R. L., J. Catal. 23, 331 (1971).
7. VENUTO, P. B., HAMILTON, L. A., AND LANDIS, P. S., J. Catal. 5, 484 (1966).
8. ANGELL, C. L., AND SHAFFER, P. C., J. Phys. Chem. 69, 3463 (1965).
9. ENTERMAN, W., AND VAN LEUVEN, H. C. E., Anal. Chem. 44, 589 (1972).
10. BOLTON, A. P., AND LANEWALA, M. A., J. Catal. 18, 154 (1970).
11. JONES, R. N., AND SANDORF, C., "Chemical Applications of Spectroscopy" (Weissberger, Ed.), p. 337. Wiley (Interscience), New York, 1956.
12. OZAKI, A., AND KIMURA, K., J. Catal. 3, 395 (1964).
13. LOMBARDO, E. A., AND HALL, W. K., Prepr. 103, Int. Congr. Catal., 5th, 1972.
14. ANGELL, C. L., AND HOWELL, M. V., Surface Sci. 28, 279 (1968).
15. POPE, C. G., AND KEMBALL, C., Trans. Faraday Soc. 65, 619 (1969).
16. VENUTO, P. B., HAMILTON, L. A., LANDIS, P. S., AND WISE, J. J., J. Catal. 4, 81 (1966).
17. PICKERT, P. E., BOLTON, A. P., AND LANEWALA, M. A., Chem. Eng. Progr. 63, 50 (1967).
18. MESTDAGH, M. M., STONE, W. E., AND FRIPIAT, J. J., J. Phys. Chem. 76, 1220 (1972).
19. STEVENSON, R. L., J. Catal. 21, 113 (1971).
20. MEYERSON, S., Appl. Spectros. 9, 120 (1955).
21. RYLANDER, P. N., AND MEYERSON, S., Amer. Chem. Soc. 78, 5799 (1956).
22. PINES, H., AND ARRIGO, J. T., J. Amer. Chem. Soc. 80, 4369 (1958).
23. BURWELL, JR., R. L., ELKIN, L. M., AND SHIELDS, A. D., J. Amer. Chem. Soc. 74, 4570 (1952).