the electrochemical reactions should be investigated in the presence of oxygen. Arylations with substituted phenyl radicals can be carried out since the diazonium cations are reduced at more positive potentials than those of any substituents.[9]

Registry No.—Benzenediazonium tetrafluoroborate, 369-57-3; benzene, 71-43-2; toluene, 108-88-3; anisole, 100-66-3; benzonitrile, 100-47-0; nitrobenzene, 98-95-3; bromobenzene, 108-86-1; naphthalene, 91-20-3.

Acid-Catalyzed Isomerization of Dialkylbenzenes

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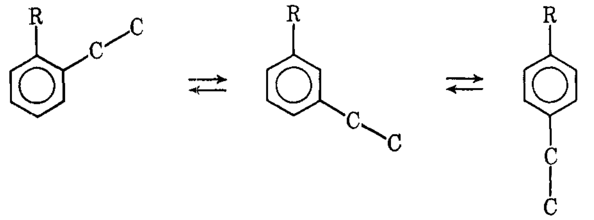
Isomerization and transalkylation are the principal reactions of 1-methyl-2-ethylbenzene over silica-alumina cracking catalyst and partially multivalent cation-exchanged, partially decationized Y-type faujasite molecular sieves. Isomerization proceeds by two different mechanisms. The first type consists of intramolecular 1,2 shifts. Transalkylated intermediates are involved in the second reaction. Xylenes and diethylbenzenes may be formed from methylethylbenzene by the same type of transalkylated intermediates. We suggest the name "alkyl exchange" for this reaction. The extent of intermolecular isomerization may be estimated from the level of alkyl exchange. The contribution of intermolecular isomerization decreases with increasing temperature. Above 300° isomerization primarily occurs by intramolecular 1,2 shifts. Below 200° isomerization *via* transalkylated intermediates predominates. At intermediate temperatures intermolecular and intramolecular processes contribute to over-all isomerization to a similar extent.

Two different mechanisms have been proposed for the acid-catalyzed isomerization of dialkylbenzenes. Carbonium ion involvement in both isomerization mechanisms is commonly assumed. According to Olah and his coworkers[1] and Matsumoto and Morita,[2] isomerization of dialkylbenzenes proceeds through a series of 1,2 shifts as shown below. On the other hand, Bolton and his coworkers[3] found that at 170° over partially decationized and partially cerium-exchanged Y-type faujasite isomerization proceeds *via* a transalkylation mechanism shown in Scheme I. This reaction has real merit only when easily abstractable α-hydrogen atoms are available.

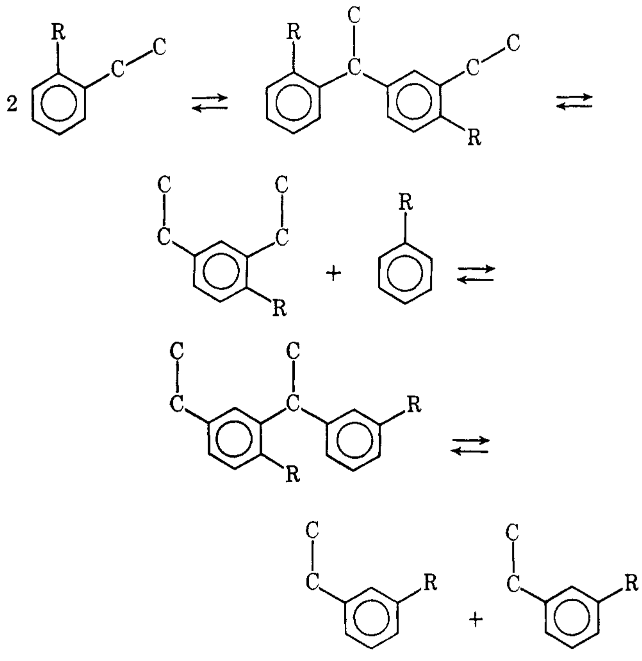


Simultaneous intramolecular and intermolecular processes were suggested by Allen and coworkers[4,5] and Ünseren and Wolf.[6] It is the intention of this work to resolve the apparent contradiction which involves the isomerization of dialkylbenzenes.

Experimental Section

1-Methyl-2-ethylbenzene was obtained from Columbia Organic Chemicals Co., Columbia, S. C. It was dried over sodium wire and purified chromatographically through activated silica gel under nitrogen. The purified material contained 99.77% 1-methyl-2-ethylbenzene, 0.15% 1-methyl-3- and -4-ethylbenzenes, and 0.08% xylenes and other hydrocarbons. The sulfur content was 0.3 ppm.

SCHEME I



The silica-alumina was a commercial cracking catalyst containing 10 wt % alumina, 90 wt % silica, and 0.1 wt % Na_2O. The B.E.T. surface area of the catalyst was 340 m^2/g. The catalyst was pretreated at 530° for 2 hr in helium and 1 hr in hydrogen before the experiments.

The calcium-ammonium Y-type faujasite was prepared the following way. Sodium Y-type faujasite (SK-40), prepared by the Linde Division of Union Carbide Corp., was first exchanged with $AgNO_3$. Silver was removed from the Ag sieve by NH_4SCN treatment. The ammonium Y-type sieve thus produced contained 6.75 wt % ammonium ions (Dumas N analysis). The sodium content was less than 0.01% (emission spectroscopy and neutron activation analyses). This ammonium sieve was treated with a solution of $Ca(NO_3)_2$, first at 100° for 3 hr, then at room temperature for 16 hr. Washed and dried at 100° *in vacuo*, the product Ca-NH_4^+ Y-sieve contained 1.47% ammonium ions (Dumas N analysis). The Ca/NH_4^+ equivalent ratio was 78:22. The catalyst was activated at 540° for 16 hr in dry hydrogen before the experiments.

The experiments were carried out in a continuous flow type reactor, consisting of a 50-cm-long, and 0.635-cm-o.d. stainless steel tube. The tube held 0.5 ml of catalyst. Experimental

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(1) G. A. Olah, M. W. Meyer, and N. A. Overchuk, *J. Org. Chem.*, **29**, 2313 (1964).

(2) H. Matsumoto and Y. Morita, *Kogyo Kagaku Zasshi*, **70**, 1674 (1967).

(3) A. P. Bolton, M. A. Lanewala, and P. E. Pickert, *J. Org. Chem.*, **33**, 1513, 3415 (1968).

(4) R. H. Allen, L. D. Yats, and D. S. Erley, *J. Amer. Chem. Soc.*, **82**, 4853 (1960).

(5) R. H. Allen, *ibid.*, **82**, 4856 (1960).

(6) E. Ünseren and A. P. Wolf, *J. Org. Chem.*, **27**, 1509 (1962).

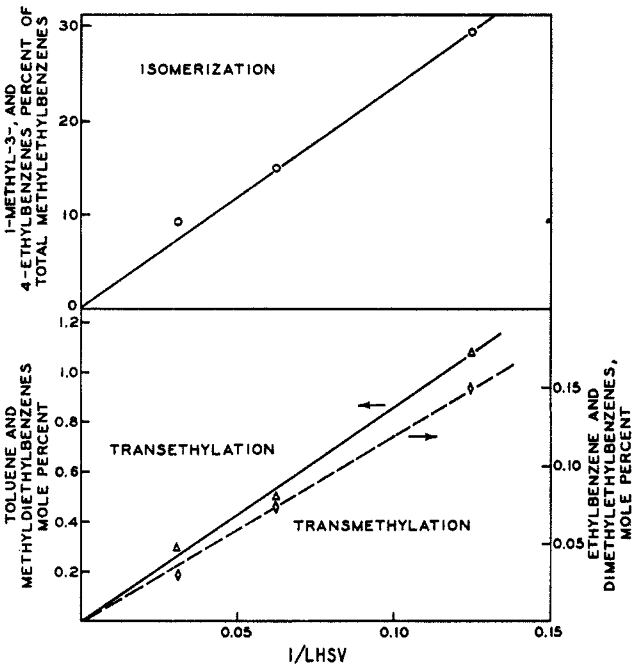


Figure 1.—Isomerization and transalkylation of 1-methyl-2-ethylbenzene over silica–alumina cracking catalyst at 400° at different space velocities.

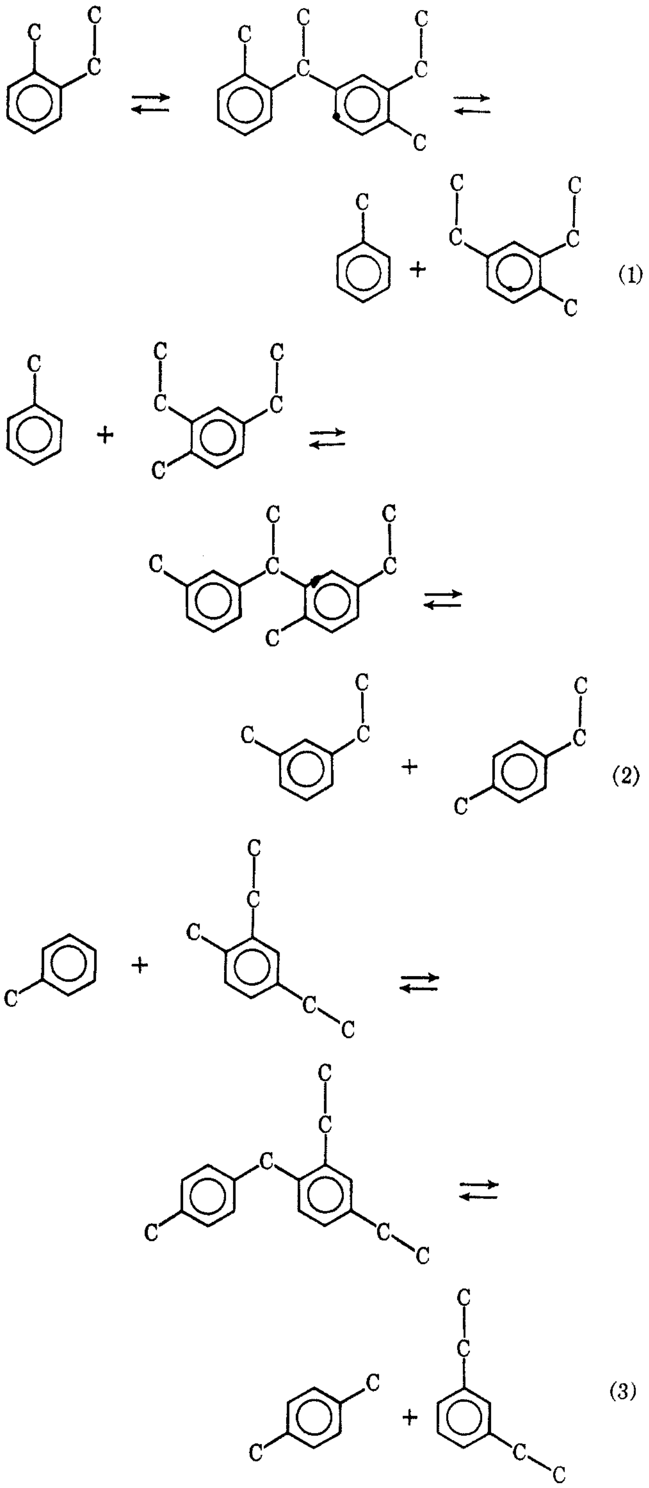
conditions were atmospheric pressure and hydrogen diluent with a hydrogen/methylethylbenzene mole ratio of 3:1. Reaction products were collected in an acetone–Dry Ice cooled condenser. Reaction periods were 65 min long. Catalysts were regenerated after each experiment at 480° with a 1:1 mixture of air and nitrogen. A 300-ft-long, 0.02-in.-i.d. capillary column was used for the gas chromatographic analyses of the liquid products. The column was packed with Ucon LB-550-X polypropylene glycol. The analytical procedure is described in detail by Baumann and Csicsery.[7] Detailed product analyses are shown in Table I.

Results

The primary reactions of 1-methyl-2-ethylbenzene over the silica–alumina and Ca–NH_4^+ Y-type faujasite catalysts are isomerization to 1-methyl-3- and -4-ethylbenzenes, and transalkylation. The amounts of 1-methyl-3- and -4-ethylbenzenes as per cents of total methylethylbenzenes present give the extent of isomerization in Table II. At equilibrium at 315 and 400°, 1-methyl-2-ethylbenzene constitutes 15.7 and 17.7% of the methylethylbenzene mixture. Conversion levels are far from equilibrium in our experiments.

Two types of transalkylation are possible. Transethylation gives toluene plus methyldiethylbenzenes. Ethylbenzene plus dimethylethylbenzenes are formed by transmethylation. In Table II transethylation is expressed as the sum of methyldiethylbenzenes plus an equivalent amount of toluene. Similarly, transmethylation is equal to the sum of dimethylethylbenzenes plus an equivalent amount of ethylbenzene. Toluene and ethylbenzene in excess of the amounts accounted for in transethylation or transmethylation are due to dealkylation. Xylenes, diethylbenzenes, trimethylbenzenes, and C_{12} alkylaromatics are probably produced in a combination of two or more steps of the above reactions.

Intramolecular isomerization of 1-methyl-2-ethylbenzene forms only 1-methyl-3- and -4-ethylbenzenes. Isomerization of methylethylbenzene proceeding through transethylated intermediates would produce some xylenes and diethylbenzenes also as shown in reactions 1–3.



Xylenes and diethylbenzenes may be similarly formed through transmethylated intermediates. Also, ethyl transfer from methyldiethylbenzene to ethylbenzene yields diethylbenzenes. Similarly, methyl transfer from dimethylethylbenzene to toluene gives xylenes. Some diethylbenzenes and xylenes might be formed by dealkylation of trialkylbenzenes.

In transalkylation, most 1,2,3- and 1,2,4-trialkylbenzenes may be formed from 1-methyl-2-ethylbenzene

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[7] S. M. Csicsery and F. Baumann, *J. Chromatog.*, **26**, 262 (1967).

Table I

1-Methyl-2-ethylbenzene Reaction Product Analyses

	Product composition, mol/100 mol of feed[a]								
	Silica–alumina cracking catalyst							Ca–NH$_4^+$ Y-type molecular sieve	
	204°	315°	371°	400°	427°	400°	400°	204°	315°
	Liquid hourly space velocity (LHSV), hr^{-1} = (ml of liquid feed/hr)/ml of catalyst								
Product	8	8	8	8	8	16	32	8	8
Benzene		0.01	0.02	0.01	0.03	0.01	0.01		
Toluene	0.20	0.40	0.64	0.76	1.25	0.50	0.28	1.87	2.80
Ethylbenzene	0.003	0.03	0.07	0.07	0.09	0.03	0.02	0.05	0.24
Xylenes		0.03	0.04	0.05	0.02	0.02	0.01		0.05
1-Methyl-2-ethylbenzene	99.35	94.80	78.00	69.50	45.20	84.40	90.30	95.20	86.30
1-Methyl-3- and -4-ethylbenzenes	0.24	4.33	18.65	28.96	52.66	14.75	9.21	0.96	7.60
Diethylbenzenes		0.001	0.005	0.006	0.01	0.002	0.001	0.02	0.06
Dimethylethylbenzenes	0.003	0.034	0.065	0.075	0.10	0.035	0.02	0.05	0.20
Methyldiethylbenzenes	0.20	0.36	0.48	0.54	0.594	0.25	0.15	1.85	2.75
Trimethylbenzenes			0.002	0.002	0.002				
C$_{12}$ alkylaromatics			0.03	0.02	0.04				

[a] Corrected for feed impurities.

Table II

Reactions of 1-Methyl-2-ethylbenzene over Different Catalysts[a]

	Silica–alumina cracking catalyst[b]							Ca–NH$_4^+$ Y-type molecular sieve[c]	
	204°	315°	371°	400°	427°	400°	400°	204°	315°
	LHSV								
	8	8	8	8	8	16	32	8	8
Isomerization									
1-Methyl-3- and -4-ethylbenzenes, % of total methylethylbenzenes	0.24	4.37	18.9	29.4	53.8	14.9	9.26	1.0	8.1
Transethylation									
Toluene and methyldiethylbenzenes, mol % of feed	0.40	0.72	0.96	1.08	1.19	0.50	0.30	3.70	5.5
Transmethylation									
Ethylbenzene and dimethylethylbenzenes, mol % of feed	0.01	0.07	0.13	0.15	0.20	0.07	0.04	0.10	0.40

[a] Reaction conditions: atmospheric total pressure and a H$_2$/feed mole ratio of 3/1. The experiments were 65 min long. [b] Commercial synthetic silica–alumina cracking catalyst, containing 10 wt % Al$_2$O$_3$, 90 wt % SiO$_2$, and 0.1 wt % Na$_2$O. Its B.E.T. N$_2$ adsorption surface area was 340 m^2/g; particle size = 100–200 mesh. [c] The catalyst contained 1.47 wt % ammonium ions and less than 0.01 wt % Na. The Ca/NH$_4$ equivalent ratio was 78:22; particle size = 60–100 mesh.

in a single alkyl transfer step. However, either isomerization of 1-methyl-2-ethylbenzene before alkyl transfer, or isomerization of one of the product trialkylbenzene isomers is required to form 1-methyl-3,4-diethylbenzene, 1-methyl-3,5-diethylbenzene, 1,2-dimethyl-4-ethylbenzene, and 1,3-dimethyl-5-ethylbenzene. The relative amounts of these four isomers are related to the extent of the isomerization of 1-methyl-2-ethylbenzene. They are produced in significant amounts only at high methylethylbenzene isomerization levels. At low isomerization conversion levels, 1-methyl-2,4-diethylbenzene and 1-methyl-2,5-diethylbenzene (all of them 1,2,4-trialkylbenzenes!) are the predominant products of transalkylation.[8]

Isomerization and transalkylation conversions increase linearly with increasing reciprocal space velocity (Figure 1 and Table II). Over the silica–alumina catalyst, isomerization and transethylation follow Arrhenius law between 204 and 427° (Figure 2). Logarithms of conversions plotted against reciprocal temperature yield straight lines. (An exception is the relatively high isomerization conversion at 204°. This deviation might be important. Its significance will be discussed later.)

Similar results are obtained over the Ca–NH$_4^+$ Y-type faujasite (Figure 3). This catalyst is similar to the Ce–NH$_4^+$ Y-type faujasite used in the diethylbenzene isomerization studies of Bolton and his coworkers.[3] Apparent activation energies are lower over the Ca–NH$_4^+$ sieve than over silica–alumina. Isomerization has significantly higher activation energy than transethylation over both the silica–alumina and the Ca–NH$_4^+$ sieve catalysts.

Discussion

Isomerization and transalkylation of polyalkylbenzenes proceed simultaneously over silica–alumina cracking catalyst and Ca–NH$_4^+$ Y-type faujasite. Isomerization may proceed through transalkylated intermediates. Evidence for a second, independent, intramolecular isomerization mechanism follows.

Isomerization observed in our experiments with both catalysts has significantly higher apparent activation energy than transethylation. This difference between the activation energy of transethylation and of the observed isomerization suggest that the two reactions proceed by different mechanisms with different reaction intermediates.

The isomerization of methylethylbenzene *via* transalkylated intermediates gives methylethylbenzene if both alkyl-transfer steps involve ethyl groups (reactions 1 and 2). Two methyl-transfer steps also yield isomerized methylethylbenzenes. An ethyl-transfer followed by a methyl-transfer step (reactions 1 and 3) produces diethylbenzenes and xylenes. The same products are obtained if ethyl transfer follows a methyl-transfer step. We suggest to call the reactions of

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[8] S. M. Csicsery, *J. Chem. Eng. Data*, **12**, 118 (1967).

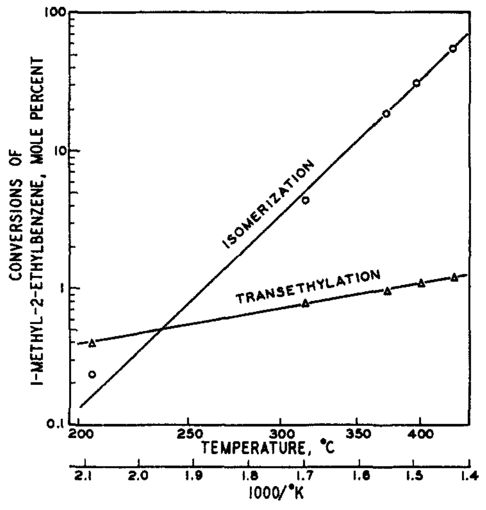

Figure 2.—Reactions of 1-methyl-2-ethylbenzene over silica–alumina cracking catalyst at atmospheric total pressure with a H_2/hydrocarbon mole ratio of 3:1 and at an LHSV of 8.

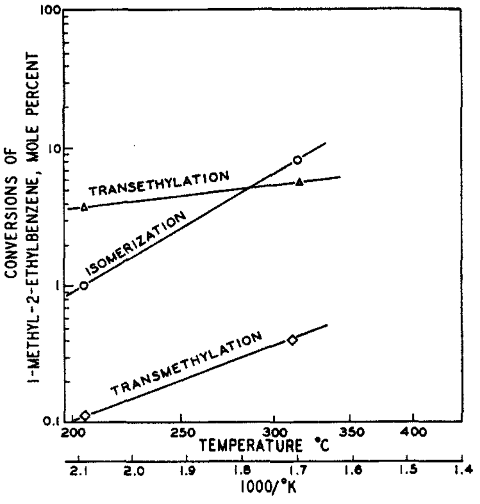

Figure 3.—Reactions of 1-methyl-2-ethylbenzene over calcium–ammonium Y-type faujasite at atmospheric total pressure with a H_2/hydrocarbon mole ratio of 3:1 and at an LHSV of 8.

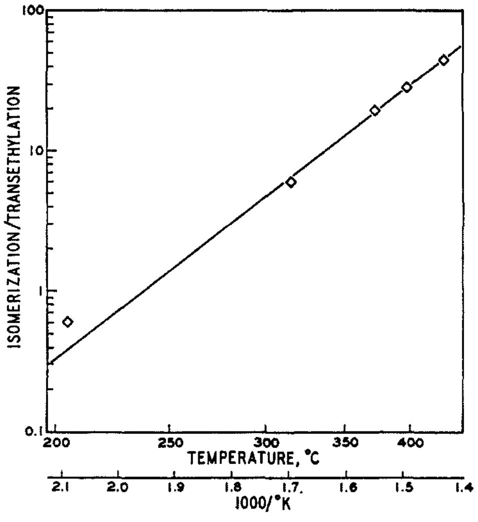

Figure 4.—Isomerization/transethylation ratio in the reaction of 1-methyl-2-ethylbenzene over silica–alumina cracking catalyst at atmospheric total pressure, at a H_2/hydrocarbon mole ratio of 3, and at an LHSV of 8.

methylethylbenzene giving diethylbenzenes and xylenes "alkyl exchange." Activation energies of these intermolecular processes are probably similar to that of transethylation. Over silica–alumina, ethyl transfer is about six to ten times faster than methyl transfer (Table II). Isomerization *via* transalkylated intermediates (a reaction consisting of two ethyl-transfer steps) is therefore most likely six to ten times more frequent than alkyl exchange (a reaction requiring one ethyl-transfer and one methyl-transfer step). Thus, the extent of intermolecular isomerization may be estimated from the amount of the products of "alkyl exchange," *i.e.*, xylenes and diethylbenzenes (Table III). Our estimates are possible maximum values because dealkylation of trialkylbenzenes also can yield xylenes and diethylbenzenes. At 400° over silica–alumina isomerization *via* transalkylated intermediates might amount to about 1% of the over-all isomerization (Table III). The apparent activation energy of isomerization *via* transalkylated intermediates is probably similar to that of transethylation. The contribution of this intermolecular process to total isomerization decreases with increasing temperature. At the higher temperatures, above approximately 300°, a different type of isomerization predominates. Stepwise, intramolecular 1,2 shifts are the most likely mechanism for this reaction. Its activation energy is substantially higher than that of the intermolecular process.

The isomerization conversion over silica–alumina at 204° is higher than expected from the correlations shown in Figures 2 and 4. At higher temperatures the contribution of the intermolecular process to over-all isomerization is negligible. Thus, the conversion *vs.* $1/T$ correlation (Figure 2) represents only the intramolecular isomerization reaction. At 204°, however, the rate of intramolecular isomerization is low, and most isomerization probably proceeds through transalkylated intermediates. This explains the deviation of the isomerization conversion at 204° from the value expected in Figures 2 and 4.

The contribution of the intermolecular process to over-all isomerization is higher over Ca–NH_4^+ Y-type sieve than over silica–alumina (Table III). At Bolton's conditions (170°, and using a catalyst similar to our Ca–NH_4^+ sieve) probably all but a trace of isomerization is intermolecular. However, at 315° >80% of the over-all isomerization proceeds by intramolecular 1,2 shifts over the Ca–NH_4^+ faujasite.

The isomerization/transethylation ratio increases with increasing temperature (Figure 4). At constant temperature the isomerization/transethylation ratio is nearly independent of the conversion level. For example, at 400°, total conversions at liquid hourly space velocities of 32, 16, and 8 are 9.7, 15.6, and 30.5 mole %, respectively. The corresponding isomerization/transethylation ratios are 31, 29, and 27. If isomerization involves transalkylated intermediates, the isomerization/transethylation ratio would increase with increasing conversion and contact time. (Here it actually decreases!) Thus, an intermolecular isomerization mechanism which proceeds through transalkylated intermediates cannot be a major contributor to over-all isomerization of 1-methyl-2-ethylbenzene around 400°. The correlation between the isomerization distributions of di- and trialkylbenzenes further substantiates this.[8]

TABLE III

ESTIMATED INTERMOLECULAR ISOMERIZATION CONVERSIONS IN THE REACTIONS OF 1-METHYL-2-ETHYLBENZENE OVER DIFFERENT CATALYSTS

	Silica–alumina cracking catalyst						Ca–NH$_4$$^+$ Y-type molecular sieve	
	315°	371°	400°	427°	400°	400°	204°	315°
	LSVH							
	8	8	8	8	8	32	8	8
Maximum intermolecular isomerization								
Mol/100 mol of feed[a]	0.32	0.33	0.40	0.18	0.16	0.08	0.74	1.51
% of total isomerization	7.4	1.8	1.4	0.34	1.1	0.9	77	20

[a] Estimated by multiplying the combined amounts of xylenes and diethylbenzenes with the ethyl transfer/methyl transfer ratio observed in the same experiment.

Conclusions

The silica–alumina cracking catalysts and the Ca–NH$_4$$^+$ Y-type faujasite catalyze the isomerization and transalkylation of polyalkylbenzenes. Isomerization might proceed by two different mechanisms: sequential intramolecular 1,2 shifts, or an intermolecular reaction involving transalkylated intermediates. This latter mechanism has real merit only when easily abstractable α-hydrogen atoms are available. Thus, it would not apply for tertiary butyl intermolecular group migrations. The intermolecular isomerization of methylethylbenzene is accompanied by "alkyl exchange," a reaction yielding xylenes and diethylbenzenes. The maximum extent of intermolecular isomerization may be estimated from the xylene and diethylbenzene produced. The contribution of intermolecular isomerization to total isomerization decreases with increasing temperature. Isomerization proceeding through 1,2 shifts has significantly higher activation energy than the isomerization process involving transalkylated intermediates. As a consequence, at higher temperatures (*i.e.*, above 300°) dialkylbenzenes isomerize primarily by 1,2 shifts. The intermolecular reaction involving transalkylated intermediates predominates at lower temperatures (*i.e.*, below 200°). At intermediate temperatures both processes contribute to over-all isomerization to a similar extent.

Registry No.—1-Methyl-2-ethylbenzene, 611-14-3.

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The Chlorination of Alkylbenzenes in Acetic Acid

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Received December 9, 1968

The chlorinations of toluene, ethylbenzene, cumene, and *t*-butylbenzene in glacial acetic acid are investigated at 25 and 35°. The reactions are found to obey over-all second-order kinetics, first-order in each of the reactants. As anticipated, a trend of diminishing reactivity relative to benzene is observed in the series toluene through *t*-butylbenzene. The isomer distributions of the products are measured by vpc and infrared spectrophotometric techniques, from which partial rate constants are derived. The *ortho* partial rate factors are a linear function of the α-methyl substituents on toluene, but the *para* factors do not follow this relationship. The activation parameters for each reaction are also calculated from the rate data obtained at the two temperatures.

A fruitful area of research has been the study of the chlorination of aromatic compounds, because of the utility of the products formed and because of the important kinetic and thermodynamic concepts derived from these reactions.[1] The majority of halogenations are catalyzed by Lewis acids, but another frequently used reaction condition involves molecular chlorination in a polar solvent. More specifically, the chlorinations of benzene and alkylbenzenes in glacial acetic acid and water–acetic acid solutions have been investigated extensively, usually by kinetic analysis of the reactions as well as by the determination of the isomer distributions of the chlorinated products.[2] In view of the interest in these reactions, it was surprising to note the paucity of accurate data for the chlorinations of ethylbenzene[3] and cumene in acetic acid and the discrepancy in reported results with *t*-butylbenzene. An investigation of the reactions between chlorine and the series of alkylbenzenes (ethylbenzene, cumene, and *t*-butylbenzene) was undertaken, including the direct measurement of the reaction rates, the isomer distributions of the products, and the activation parameters for the reactions.

Kinetic Analysis.—The rates of the reactions of chlorine with the alkylbenzenes in acetic acid were measured at 25 and 35° as described previously.[3] Light was excluded from the reaction vessels in order to minimize free-radical chlorination of the side chain or the solvent, and blank runs in the absence of the alkylbenzene indicated that the dark reaction of chlorine with solvent was negligible. The data for these rate determinations are summarized in Table I. The reactions all obey over-all second-order kinetics, first order each in substrate and chlorine. Typical plots of second-order reactions were obtained as shown in Figure 1. The kinetics of the chlorinations of benzene (1) and tol-

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(1) H. P. Braendlin and E. T. McBee in "Friedel–Crafts and Related Reactions," G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter XLVI.

(2) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, 35 (1963).

(3) R. J. Dolinski and R. M. Nowak, *J. Org. Chem.*, **32**, 2936 (1967).