Table VII. Variation of Specific Conductivity # $(ohm^{-1} cm^{-1})$ with Time for a Solution of p-Xylene in CF₃SO₃H (0.24 M) at 25.3 °C

3 5 10 15 25 35 45 110 120 ∞ $T, \min 0$ 10³ĸ $1.9 \ 2.2 \ 2.4 \ 3.0 \ 3.5 \ 4.2 \ 4.8 \ 5.0 \ 6.5 \ 6.7 \ 10.1$

which indicates that transalkylation reactions are not appreciable over the reaction period (usually ~ 2 h).

c. Conductivity Method. The appropriate volume of xylene was injected into 2.00 mL of CF₃CO₃H in a small test tube at 25 °C. After shaking, the conductivity of the solution was measured with an LKB-Producter AB Conductolyzer (LKB 5300 A)

equipped with a dip cell. The data for p-xylene appears in Table VII. The apparent second-order rate constant, k_2 , calculated from this data was 9.8×10^{-4} L mol⁻¹ s⁻¹, whereas that from the quenching method was 10.3×10^{-4} L mol⁻¹ s⁻¹.

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Registry No. CF₃SO₃D, 66178-41-4; SbF₅, 7783-70-2; HF, 7664-39-3; CF₃SO₃H, 1493-13-6; H₂, 1333-74-0; HBr, 10035-10-6; AlBr₃, 7727-15-3; o-xylene, 95-47-6; p-xylene, 106-42-3; m-xylene, 108-38-3; 1,3,5-trimethylbenzene, 108-67-8; 1,2,4-trimethylbenzene, 95-63-6; toluene, 108-88-3; sodium triflate, 2926-30-9.

Studies in Trifluoromethanesulfonic Acid. 3.1 Kinetics and Mechanism of **Transalkylation Reactions**

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Rates of disproportionation of ethylbenzene and *m*-diethylbenzene have been measured in the solvent trifluoromethanesulfonic acid (triflic acid). Ethylbenzene disproportionates very rapidly, whereas m-diethylbenzene reacts at a conveniently measurable rate. The reactions obey first-order kinetics over a wide range of concentration, and the results are interpreted as involving ethyl transfer to the triflate anion followed by alkylation via the ethyl triflate formed.

Introduction

Transalkylation reactions have long been known in aromatic chemistry and form the basis of important commercial synthetic processes. These reactions are very often accompanied by isomerization of the starting alkyl aromatic to a thermodynamically more stable isomer (e.g., *m*-xylene in the case of *o*- and *p*-xylenes). Transalkylation is usually carried out on an industrial scale, using mordenite or zeolite catalysts at high temperatures. Relatively little work has been done in homogeneous media and it is the purpose of this paper to report on the very facile transalkylations of ethylated benzenes in trifluoromethanesulfonic acid (triflic acid).

Results and Discussion

The mechanism of transalkylation has received a good deal of attention over the years. Early work by Heise and Töhl² on the disproportionation of *n*-propylbenzene in an AlCl₃-HCl medium at 100 °C showed that the reaction proceeded without rearrangement of the alkyl carbon chain. This work has been confirmed and extended by McCauley and Lien³ and others, using the same catalytic medium. An S_N2 type of mechanism was suggested to account for this observation.³ However, the relative rates of various alkylated aromatics varied over a very wide range (Me, 10^{-7} ; Et, 1; *i*-Pr, 10^2), which is at odds with the relatively small charge separation implicit on $S_N 2$ process. Brown and Smoot⁴ suggested a rapid equilibrium involving a "localized" π complex as an intermediate to account for these relative rates. This mechanism, however, implies that intramolecular isomerization should be much more rapid than transalkylation reactions, which is in conflict with experimental findings.⁵⁻⁷ Roberts and co-workers⁸ have shown that the observed scrambling of labeled carbon in the α and β positions for *n*-propylbenzene (*n*-Prbz) with AlCl₃ can be explained in terms of diphenylpropane intermediates. The carbenium ion, formed by dissociation of the n-Prbz-AlCl₃ complex, abstracts a hydride ion from a second *n*-Prbz and the resulting carbenium ion effects electrophilic substitution on a further substrate molecule.⁹

Streitwieser and Rief¹⁰ studied the kinetics of transalkylation of radiolabeled and optically labeled ethylbenzene in benzene with a galium tribromide-hydrogen bromide catalyst. Unfortunately, reproducibility in the system was poor. The conclusion reached was that a cation chain reaction occurred, probably catalyzed by the carbenium ion derived from HBr addition to styrene (a likely impurity in ethylbenzene). Moore and Wolf¹¹ have demonstrated from a study of disproportionation and isomerization reactions of ethylbenzene-1-¹⁴C in AlBr₂-HBr that para alkylation is dominant followed by an intramolecular 1,2 shift of an ethyl group to give the thermodynamically most stable isomer. Previous work suffered from problems of reproducibility caused by inhomogeneous reaction media. It is significant that very few attempts have been made to determine the order of the reaction components. Triflic acid, CF₃SO₃H, has the great advantage of providing a homogeneous medium of high acidity and is much more easily handled than the usual Friedel-Crafts catalytic mixtures.

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time, min	10°bz]	10²[Etbz]	$[Et_2bz]$	$[Et_3bz]^a$	$[Et_2bz]$ reacted	$[Etbz + Et_3bz]$	[Et ₃ bz] [bz]	
 0	0	0	0.200	0	0	0	·	-
10	0.17	1.60	0.163	0.019	0.037	0.035	11.1	
20	0.78	3.50	0.125	0.041	0.075	0.076	5.2	
30	0.92	4.70	0.079	0.065	0.121	0.112	7.1	
40	1.87	4.10	0.062	0.078	0.138	0.119	4.2	
60	3.64	2.80	0.048	0.094	0.152	0.122	2.6	
120	4.08	3.20	0.013	0.114	0.187	0.146	2.8	
2480	4.48	2.80	0.008	0.118	0.192	0.146	2.6	

^a Sum of 1,2,4 and 1,3,5 isomers.

Solutions of ethylbenzene (Etbz) in CF_3SO_3H at 25 °C rapidly disproportionate to give benzene and initially oand p-diethylbenzenes, which subsequently isomerize to the more stable meta derivative. The ratio of the ortho and para isomers at short reaction times is 1:3 in keeping with the electrophilic nature of the following reaction:

$$EtbzH^+ + Etbz \rightleftharpoons bz + o$$
 and p - Et_2bzH^+ (1)

At concentrations of 0.05 M, 83% reaction occurred in 2 min at 25 °C. Added sodium triflate slowed down the reaction, a 50% conversion being obtained for the same reaction time. The latter effect is probably due to a common ion effect that reduces the concentration of the protonated species. Isopropylbenzene reacts similarly to give 80% reaction in 2 min. Since the reactions of the monalkyl derivatives proved very rapid, attention was turned to the dialkylated series, in particular, to *m*-diethylbenzene (*m*-Et₂bz). Here problems of isomerization should be minimized since it is the thermodynamically most stable of the three isomers.

On quenching solutions of *m*-diethylbenzene in CF_3S -O₃H, it became evident that not only ethyl- and triethylbenzene were formed, but also some benzene. Thus the overall reaction scheme may be written as:

$$m$$
-Et₂bzH⁺ + m -Et₂bz \rightarrow Etbz + 1,2,4-Et₃Bz⁺H (2)

followed by a second disproportionation as depicted in reaction 1. Table I lists the changes of concentration of reactants and products with time. From reaction 1 and 2 it is clear that if process 1 is rapid and quantitative, then the ratio of $[Et_3bz]/[bz]$ should be 2.0 throughout the reaction. This is not found; the ratios in the early part of the reaction are very much higher although they approach the theoretical value in fully equilibrated solutions. The disproportionation of ethylbenzene is either slow or has an unfavorable equilibrium constant in the medium. This is somewhat surprising in view of the rapid disproportionation of ethylbenzene alone in CF_3SO_3H . However, Etbz is produced in reaction 2 in the presence of a large excess of Et_2bz in the initial stages of the reaction and this will drive equilibrium 1 over to the LHS. The data in Table II show that for Etbz alone, reaction 1 is rapid followed by the slower step. Added 1,3,5-Et₃bz does not alter the general pattern except that initial yields of Etbz are lower. This is probably the result of a small mass law effect since the 1,3,5 isomer is related to equilibria 1 and 2 via the less thermodynamically stable but kinetically more significant 1,2,4-triethylbenzene.

Returning to the disproportionation of Et_2bz itself, the fact that equilibrium 1 is mass law inhibited in the initial stages of the reaction means that the amount of Et_2bz that has reacted will be approximately equal to the sum of [Etbz] and [Et_3bz] formed in reaction 2. This can be seen to hold for about 40% reaction (Table I), which enables

Table II. Effect of Added Mesitylene and 1,3,5-Triethylbenzene on the Rates and Yields of Disproportionation of Ethylbenzene (0.2 M) at 25 °C in CF₃SO₃H

			0.2 M mesitylene		0.2 M 1,3,5- triethylbenzene	
time, min	R ^a	Рb	R	P	R	Р
5	1.77	78	1.93	79	0.89	64
10			2.37	86	1.06	68
15	2.37	86	2.12	84	0.96	65
30	3.4	87	3.72	88	0.95	65
60	2.89	85	4.57	91	0.71	58
120	2.20	81	5.42	90	0.49	49
2480	0.53	51	9.8	95		

^a R = [diethylbenzene], c/[ethylbenzene]. ^b P = percent reaction. ^c Combined yields of ortho, meta, and para isomers.

Table III. Values of First-Order Rate Constants (k_1, s^{-1}) for the Disproportionation of *m*-Diethylbenzene at Various Concentrations in CF₃SO₃H at 25.0 °C

[m-Et, bz]	0.01	0.02	0.04	0.10	0.20	0.50
10⁴k,	5.0	5.3	5.6	5.6	5.5	5.6

Table IV. Variation of First-Order Rate Constants (k_1, s^{-1}) with Temperature for the Disproportionation of *m*-Diethylbenzene in CF₃SO₃H

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^a From plots of ln [2 + 3R₂ + R₂R₃]. ^b From Et₂bz/ Et₃bz ratios. ^c From Et₂bz/Etbz ratios. ^d Arrhenius plot yielded $E_a = 15.8 \pm 0.5$ kcal mol⁻¹, $\Delta H^{\ddagger} = 15.2 \pm 0.5$ kcal mol⁻¹, and $\Delta S^{\ddagger} = 22 \pm 2$ cal K⁻¹ mol⁻¹.

simple first- or second-order kinetic expressions to be applied over this reaction range. The most striking feature of the results is the invariance of the first-order rate constants, k_1 , over a range of 0.01–0.5 M (Table III). (Streitwieser and Reif¹⁰ also found a first-order dependency on [Etbz] for transalkylations in the GaBr₃/HBr system.) The second-order constants varied considerably. The reaction thus seems to involve rate-determining release of an ethyl carbenium ion followed by rapid alkylation of another Et₂bz molecule.

The possibility that the ethyl cation transfers to the triflate anion first cannot be ruled out. Ethyl triflate itself alkylates aromatic derivatives relatively slowly, but the reaction is catalyzed by $AlCl_3$ and SbF_5 .¹² In the dis-

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Table V. Calculation of First-Order Rate Constants (k_1, s^{-1}) and Second-Order Rate Constants $(k_2, L \text{ mol}^{-1} s^{-1})$ for the Disproportionation of *m*-Diethylbenzene in CF₃SO₃H at 35 °C

T, min	R_1^{a}	R_{2}^{a}	R_3^{a}	x/a	$(R_2R_3)^b$	$10^{4}k_{1}^{c}$	$10^{3}k_{2}$
0		<u></u>			0.693		
1	22.2	0.045	0.906	0.080	0.777	13.9	7.2
3	8.33	0.120	0.745	0.184	0.896	11.3	6.3
4	5.05	0.198	0.775	0.272	1.011	13.2	7.8
5	4.08	0.245	0.702	0.315	1.072	12.6	7.7
10	1.72	0.580	0.508	0.504	1.395	11.7	8.5
20	0.46	2.16	0.329	0.782	2.218	12.7	15.0

^a $R_1 = [Et_2bz]/[Et_3bz], R_2 = R_1^{-1}, R_3 = [Etbz]/[Et_3bz].$ ^b Correlation coefficient 0.999, $k_1 = 12.6 \times 10^{-4} \text{ s}^{-1}$. ^c Average $k_1 = 12.6 \pm 1.0 \times 10^{-4} \text{ s}^{-1}$.

proportionation of Et_2bz , the rate of production of Et_3bz increased 2.6-fold when ethyl triflate was added to the reaction medium. This suggests that the latter could act as an intermediate alkylating species during the reaction. Support for this comes from the activation parameters for the reaction (Table IV). The most striking feature is the large negative value of ΔS^* (-22.4 cal K⁻¹ mol⁻¹), which is out of character with a simple dissocative mechanism but is consistent with bimolecular attack by triflate anion. Intimate ion pairing of the type postulated for methylated benzenes in CF₃SO₃H¹³ is unlikely to occur for the diethylbenzenes due to the much larger steric effects of the ethyl group and thus there should be sufficient concentrations of free triflate to effect ethyl transfer. On the other hand, there is no evidence at all of any accelerative effect of added CF₃SO₃⁻ either in the form of the sodium salt or of strongly basic aromatics (Table II). The interpretive difficulty lies in the compensatory effects of (a) a common ion effect on the equilibrium protonation of Et₂bz and (b) the possible first-order dependence of rate on $[CF_{3}SO_{3}^{-}].$

If the mechanism is a simple $S_N 1$ process, the ΔS^* values could be interpreted in terms of "freezing" the originally mobile proton H_A on going to the transition state. There would be, additionally, greater orientation of solvent dipoles around the relatively nondelocalized positive charge in the leaving group. Such arguments have also been used to explain the very comparable ΔS^* values for the isomerization of o- and p-xylenes to m-xylene in CF₃SO₃H,¹ a process that is unlikely to involve the triflate anion.

The carbenium ion, if formed, does not become free during the reaction since no skeletal rearrangements of *n*-alkyl groups have ever been observed. An intermediate, localized π complex has been suggested as depicted in reaction 3.^{14,15} This would lead to intramolecular alkyl



shifts being more rapid than transalkylation processes. In a very recent and elegant study using ¹³C labels,⁷ isotopic redistribution for ethyl benzene in $AlBr_3$ -HBr was found to be much slower than the disproportion reaction producing diethyl benzene and benzene. Therefore, we are forced to the conclusion that ethyl triflate is an intermediate in transalkylations in triflic acid.

Experimental Section

Triflic acid was purified as described previously.¹³ All alkylated benzenes were fractionated prior to use. Ethyl triflate was prepared by a standard literature method.¹⁶

Kinetic Technique. A known volume of CF₃SO₃H in a test tube with a ground glass joint was equilibrated in a thermostated bath at the desired temperature. An appropriate volume of m-diethylbenzene was injected into the acid and timing commenced. At suitable time intervals, 50 μ L of reaction solution was withdrawn and rapidly quenched alternately in mixtures of CCl_4 (1 mL)/H₂O (1 mL) and hexachlorobutadiene (1 mL)/H₂O (1 mL). The former quenching mixture allowed analysis of ethylbenzene, diethylbenzene, and triethylbenzenes, whereas the latter enabled the measurement of benzene concentrations. The halocarbon phase was pipetted out and dried with MgSO₄ and then analyzed by GLC, using a Perkin-Elmer F17 instrument [column: $15 \text{ m} \times 1/8 \text{ in.}, 5\%$ *n*-decylphthalate + 5% Bentone 34 on 80-100 mesh Chromosorb W]; 2-µL samples were injected at an injection temperature of 175 °C and a column temperature of 100 °C. Calibrations were obtained with use of standard solutions of the products and starting materials, and the relative proportionality factor relating concentrations to peak areas was evaluated. It was found more convenient to analyze data in terms of area ratios corrected for the different proportionality factors.

Analysis of Data. Method A. The ratio $Et_2bz/Et_3bz = R_1$ was obtained and substituted into

$$x/a = 2/(2+R_1)$$
(4)

from which the usual first-order plot was constructed. It is assumed in this method that the second step is unimportant during the first portion (ca. 40%) of the reaction. Data analyzed by this method appears in Table V. A similar approach can be made with $Et_2bz/Etbz$ ratios.

Method B. The effect of the slow second step is here taken into account in the calculation of Et_2bz :

$$Et_2bz \rightarrow Etbz + Et_3bz - (2x + y)x x x$$
$$Etbz \rightarrow Et_2bz + ybz$$

а

With use of the ratios $R_2 = [Et_3bz]/[Et_2bz]$ and $R_3 = [Etbz]/[Et_3bz]$ it can easily be readily shown that

$$[Et_2bz] = 2a(2 + 3R_2 + R_2R_3)^{-1}$$
(5)

and a plot of $\ln (2 + 3R_2 + R_2R_3)^{-1}$ vs. time would be linear with slope $-k_1$ if the reaction is first order in Et₂bz. Typical data appears in Table V. The agreement between the two methods is good. Within any one run, method A gives k_1 values accurate to $\pm 7\%$ and reproducibility between runs was $\pm 9\%$. Method B gave rather more accurate values ($\pm 5\%$ standard deviation).

Registry No. 1,3,5-Et₃bz, 102-25-0; 1,2,4-Et₃bzH⁺, 877-44-1; ethylbenzene, 100-41-4; *m*-diethylbenzene, 141-93-5; trifluoro-methanesulfonic acid, 1493-13-6; ethyl triflate, 425-75-2; triflate anion, 37181-39-8; sodium triflate, 2926-30-9; *p*-diethylbenzene, 105-05; benzene, 71-43-2; mesitylene, 108-67-8; *o*-diethylbenzene, 135-01-3.

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