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.

Acknowledgment.—The author thanks Chevron Research Co. for permission to publish this work.

The Chlorination of Alkylbenzenes in Acetic Acid

R. J. DOLINSKI AND R. M. NOWAK

Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640

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-

---

(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).

TABLE I

RATE DATA FOR THE CHLORINATION OF ALKYLBENZENES IN ACETIC ACID (CONCENTRATIONS IN MOLE/LITER)

Alkylbenzene	Chlorine	Temp, °C	$k_2 \times 10^4$, l. (mol sec)	k_2(alkylbenzene)/k_2(benzene)
	Ethylbenzene			
0.0976	0.0982	25.0	4.33	
0.0997	0.0674	25.0	4.38	283
0.1188	0.0812	35.0	8.97	
0.0982	0.1021	35.0	8.92	220
	Cumene			
0.2158	0.2124	25.0	2.71	
0.1930	0.2002	25.0	2.68	175
0.2029	0.2003	35.0	6.00	
0.2011	0.3129	35.0	6.06	149
	t-Butylbenzene			
0.0993	0.1008	25.0	1.34	
0.1629	0.1123	25.0	1.40	88.9
0.2129	0.2113	35.0	3.21	
0.1839	0.1125	35.0	3.15	78.7

uene (**2**) have been measured previously,[4] and, other than the preliminary communication,[3] the only data available for ethylbenzene (**3**) is the time required to consume 15% of the chlorine from a solution of **3** in acetic acid.[5] At 25°, the mean value for the rate constant, k_2, was 4.35×10^{-4} l./(mol sec), giving a relative rate of k_2 (**3**)/k_2 (**1**) = 283; the literature value was 290. For cumene (**4**), the relative rate was found to be k_2 (**4**)/k_2 (**1**) = 175, in good agreement with the estimated value of 180.[2] The kinetics of chlorination of *t*-butylbenzene (**5**) were measured in an attempt to resolve the discrepancy between the two relative rates for **5** *vs.* **1** given in the literature.[6,7] The rate constant determined in this study [$k_2 = 1.37 \times 10^{-4}$ l./(mol sec)] is in agreement with that derived by Stock and Brown.[7]

Isomer Distributions and Partial Rate Factors.—An essential but experimentally difficult aspect of this investigation was the determination of the product isomer distribution. The *ortho* and *meta* + *para* values were obtained by vpc, but further resolution was not possible and the percentage of *meta* isomer was measured by infrared spectrophotometry. The data so obtained are given in Table II.

TABLE II

PRODUCT ISOMER DISTRIBUTIONS FOR THE CHLORINATIONS OF ALKYLBENZENES IN ACETIC ACID AT 25°

Alkylbenzene	Product, mol %		
	ortho	*meta*	*para*
Toluene	59.6	0.50	39.9
	59.8[a]	0.48	39.7
Ethylbenzene[b]	52.3	0.53	47.2
Cumene	41.0	0.96	58.0
t-Butylbenzene	23.5	1.95	74.5
	21.8[c]	2.1	76.1
	21.5[d]	2.29	76.2

[a] Data from ref 4. [b] The *ortho*/*para* ratio of the products from the chlorination of ethylbenzene has been reported in passing by H. C. Brown and A. H. Neyens, *J. Amer. Chem. Soc.*, **84**, 1655 (1962), where the *para* isomer was required as a reference compound for a structure determination problem. [c] Data from ref 6. [d] Data from ref 7.

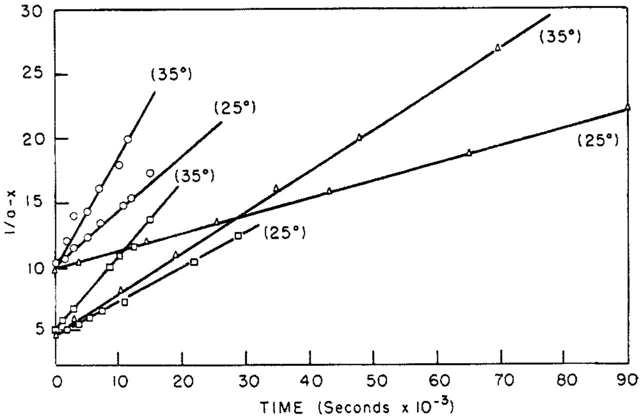

Figure 1.—Typical second-order rate plots for the chlorination of alkylbenzenes in acetic acid: ○—ethylbenzene; □—cumene; △—*t*-butylbenzene.

From these isomer distributions for the chlorinations of the alkylbenzenes and their reactivities relative to **1**, the partial rate factors for each position were calculated (Table III). In general, values for the alkylbenzenes used in this study are in reasonably good agreement with those estimated in the literature.[2] As anticipated, a trend of diminishing reactivity was observed relative to **1** through the series of alkylbenzenes, with methyl being more activating than *t*-butyl. A comparison of the positional partial rate factors (Figure 2) indicates a linear decrease in f_{ortho} as a function of the number of methyl groups substituted on the benzylic carbon. This decrease is most probably due to steric reasons and is virtually duplicated in the nitration of these compounds in acetic anhydride.[8] In the *para* position, however, there is essentially no difference in f_{para} in the chlorination reaction as one passes from methyl to ethyl. Only upon further substitution does a linear decrease in f_{para} become apparent. This is in contrast to the nitration data, where f_{para} parallels the inductive order; *i.e.*, ethyl is more activating than methyl. These nitration results are most probably due to a displacement of the transition state along the reaction coordinate because of the highly electrophilic character of the nitronium ion intermediate. Since the transition state is reached without a full perturbation of the π electrons, the inductive effects of the alkyl substituents become important for this reaction. The *meta* partial rate factor (f_{meta}) for the chlorination reaction remains

TABLE III

PARTIAL RATE FACTORS FOR THE CHLORINATION OF ALKYLBENZENES IN ACETIC ACID AT 25°

Alkylbenzene	Partial rate factors			Selectivity factor, S_f[a]
	f_{ortho}	f_{meta}	f_{para}	
Toluene[b]	617	4.95	820	2.219
Ethylbenzene	441	4.47	796	2.250
Cumene	213	5.02	606	2.082
t-Butylbenzene	62.7	5.2	403	1.890
	56.6[c]	6.0	401	

[a] The selectivity factor, S_f, is defined as log (f_{meta}/f_{para}) by H. C. Brown and C. R. Smooth, *J. Amer. Chem. Soc.*, **78**, 6255 (1956). [b] Data from ref 4. [c] Data from ref 7.

---

(4) H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, **79**, 5175 (1957).

(5) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

(6) G. A. Olah, S. J. Kuhn, and B. A. Hardie, *J. Amer. Chem. Soc.*, **86**, 1055 (1964).

(7) L. M. Stock and H. C. Brown, *ibid.*, **81**, 5615 (1959).

(8) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., Amsterdam, 1965, p 15.

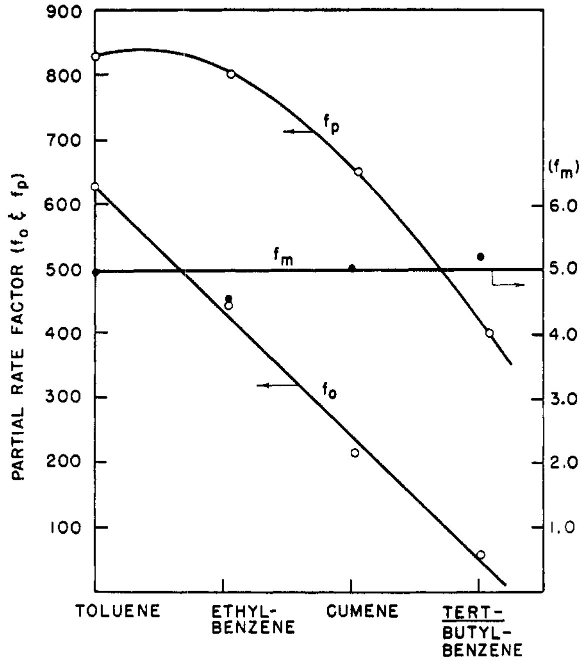

Figure 2.—Partial rate factors for the chlorination of alkylbenzenes in acetic acid.

essentially constant regardless of the alkyl substituent. This insensitivity is presumably due to the poor transmission of steric, inductive, and resonance effects to the *meta* position.

The partial rate factors were used to further confirm the validity of the selectivity relationship proposed by Brown and Nelson,[2] which relates the *para* partial rate factor and the product distribution. A plot of S_f *vs.* $\log f_{para}$ for 11 substitution reactions each of **3**, **4**, and **5**, including the values for the chlorinations from the present investigation, illustrates a linear relationship with a slope (b) = 1.31 and a zero intercept. A previous least-squares analysis[2] for 47 such reactions gave a slope of 1.31 and an intercept of 0.0071. The values of ρ from the Hammett relationship were calculated to be -9.9, -9.6, and -9.4 for the chlorination of **3**, **4**, and **5**, respectively, using the selectivity factors and Hammett substituent constants for electrophilic reactions. The estimated[2] value for ρ in these chlorination reactions is -10.0.

Activation Parameters.—The activation parameters[9] were calculated for the chlorination reactions from the rate constants obtained at the two temperatures and are shown in Table IV.

Table IV

Activation Parameters for the Chlorination of Alkylbenzenes in Acetic Acid at 298°K

Hydrocarbon	$E^{\ddagger}$, kcal/mol	$\Delta H_{298}^{\ddagger}$, kcal/mol	$\Delta F_{298}^{\ddagger}$, kcal/mol	$\Delta S_{298}^{\ddagger}$, eu
Benzene[a]	17.0	16.4	25.4	−30.0
Toluene[a]	13.6	13.0	21.9	−30.0
Ethylbenzene	13.1	12.5	19.8	−24.4
Cumene	14.5	13.9	22.2	−27.8
t-Butylbenzene	15.3	14.7	22.6	−26.5

[a] Data from L. M. Stock and A. Himoe, *J. Amer. Chem. Soc.*, **83**, 1937 (1961).

The activation energies are high, as anticipated for reactions of this type. The relatively high negative entropy of activation for these reactions suggests a rather crowded transition state, consistent with the currently accepted mechanism for molecular chlorination.

Conclusion

The data which are available in the literature and from the current investigation tend to support a mechanism for chlorinations in acetic acid involving the attack of molecular chlorine, probably solvated by acetic acid, on the substrate instead of the reaction of a chloronium ion followed by a rate-determining anionization of chlorine. Proton loss from this ionic intermediate has been established to be kinetically insignificant by the absence of a hydrogen isotope effect.[1]

The activation energy for these reactions is high because of the energy spent on chlorine–chlorine bond scission. The attacking chlorine molecules, therefore, tend to select nuclear positions which allow the attainment of the lowest possible energy levels in the transition state. Because of this, the molecular chlorinations are more sensitive to steric and electronic effects than are the more strongly electrophilic cations. Reactions involving cationic intermediates have lower activation energies, causing poorer selectivity and a more statistical distribution of isomers.[8]

Experimental Section

Materials.—Ethylbenzene (99.6%) and cumene (99.7%) were obtained from The Dow Chemical Company, and *t*-butylbenzene was obtained (99.0%) from Phillips Petroleum Company. Chlorine (99.5%) was obtained from the Matheson Company, and the acetic acid (99.7%), used as a solvent, was obtained from Fisher Scientific Company.

Kinetic Determinations.—Rate measurements were performed in black volumetric flasks immersed in a constant-temperature bath maintained at 25.0 or 35.0 ± 0.1° using the previously reported method.[4,7,10] A blank run without an alkylbenzene established that the reaction of solvent with chlorine in the dark and chlorine loss by evaporation were negligible. Second-order rate constants, calculated from seven to ten points per run, are summarized in Table I and Figure 1. Analyses of selected reaction mixtures revealed a maximum of 1% side-chain chloride compounds and therefore was neglected.

Isomer Distribution Determination.—The dried reaction product was subjected to vpc analysis at 150° on a 14 ft × 0.125 in. column packed with 5% E-4000 polyglycol (The Dow Chemical Company) on firebrick. The mole percentages of the *ortho* and *meta* + *para* isomers were determined from the corrected areas of the peaks, while analyses for the *meta* isomers were carried out using a previously reported[6] standard base-line technique on a Beckman IR-9 infrared spectrophotometer. For **2**, **3**, **4**, and **5**, the measurements of the *meta*-chloro isomers were carried out at 12.96, 12.90, 12.79, and 12.81 μ, respectively. The mean values of three trials for each alkylbenzene are given in Table II.

Selectivity and Partial Rate Factors.—These parameters were calculated using the method of Brown[2] and are given in Table III.

Activation Parameters.—Activation parameters were calculated by standard methods[9] using the mean rate constants measured at 25 and 35°. These data are illustrated in Table IV.

Registry No.—Acetic acid, 64-19-7; toluene, 108-88-3; ethylbenzene, 100-41-4; cumene, 98-82-8; *t*-butylbenzene, 98-06-6.

---

(9) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(10) L. M. Stock and A. Himoe, *J. Amer. Chem. Soc.*, **83**, 1937 (1961).