Values for $\Delta[C_6H_6]/[C_6H_6]$ were determined from a graphical representation of Benson's Table IV.8.[40] The analytical precision of the benzene analysis was typically 0.2 to 0.3%. Bath-temperature fluctuation was typically ±0.2°. A $\Delta H^{\ddagger}$ of 12 kcal/mol was assumed for this calculation.[5]

It is possible that the k_3 values, particularly at high catalyst concentrations are somewhat in error (too high) due to our method of calculating solution volumes. This effect probably explains the difference in the change of k_3 with time in Figures 1 and 2. It cannot account for the decrease of k_3 with time since Figure 1 is based upon reactions of similar concentrations.

Acknowledgment. We are indebted to the Atomic Energy Commission, National Science Foundation, and Research Corporation of America for their financial assistance. The assistance of E. A. Roth, W. D. Ellis, and J. C. Hill is gratefully acknowledged.

Kinetics of the Gallium Chloride Catalyzed Methylation of Toluene and the Xylenes in Excess Methyl Chloride. Partial Rate Factors for the Methylation Reaction[1,2]

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Abstract: Kinetic studies have been made of the gallium chloride catalyzed methylation of toluene and *m*-xylene in excess methyl chloride at −35.6°. These reactions were found to follow kinetics similar to that of the benzene reaction, the rate expression being $-d[ArH]/dt = k_3[GaCl_3]_0^2[ArH]$. Product xylene isomerization was observed in the toluene reaction. The rate constants decrease markedly with increasing reaction time from their zero-time values of $k_{3,\text{toluene}} = 7.9 \times 10^{-4}$ and $k_{3,m\text{-xylene}} = 6 \times 10^{-3}$ l.^{2} mol^{-2} min^{-1}. It is shown that disproportionation cannot be the sole cause of this effect. Catalytic inhibition due to σ-complex formation is also considered. Partial rate factors m_f 1.8, p_f 9.4, and o_f 8.3 are calculated from the extrapolated zero-time rate constants and isomer distribution of the benzene and toluene reactions. Zero-time rate constants and isomer distributions are predicted for the polymethylbenzenes, and are found to be in excellent agreement with those determined for the *m*-xylene reaction.

The gallium bromide catalyzed methylation,[5] ethylation,[5] and isopropylation[6] of toluene in excess toluene have been shown to obey the selectivity relationship.[7] Therefore it was of interest to see if methylation reactions in excess methyl chloride, under the influence of gallium chloride, would also obey these rules, particularly since Olah and coworkers[8] have reported alkylation reactions which do not.

We also wished to see if we could predict the rate constants in the methylation of the polymethylbenzenes by assuming the effect of the substituent constants to be additive. This proposal, which was considered originally by Scheffer and Condon,[9] has been tested in a number of substitution reactions, including mercuration,[10] chlorination,[11] bromination,[12] benzoylation,[13] and acetylation[14] of the polymethylbenzenes. With few exceptions the predicted and experimental rates of reaction of the polymethylbenzenes have been in good and sometimes very good agreement. A study of the methylation reaction in the presence of a large excess of methylating agent was of particular interest in that the problem becomes one of a series of consecutive reactions. In addition, the relatively large amounts of *meta* substitution[5,15] and the sensitivity of gas chromatographic analysis permit a further test of this proposal by a comparison of calculated and experimentally determined isomer distributions which was not feasible in many of the other reactions.

Our study of the gallium chloride catalyzed methylation of benzene in excess methyl chloride at −35.6°[15] revealed a surprisingly large amount of concomitant xylene isomerization and possibly disproportionation as well. In order to obtain more evidence on this point, we studied the methylation of toluene and *m*-xylene under identical reaction conditions.

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[1] The Catalytic Halides. XXXII. Directive Effects in Aromatic Substitution. LX.

[2] Based in part on a Ph.D. Thesis submitted by Franklin DeHaan, Purdue University, 1961.

[3] Graduate research assistant on contract AT(11-1)-170, Atomic Energy Commission (1958–1959); National Science Foundation Cooperative Fellow, Purdue University (1959–1961); address inquiries to Occidental College.

[4] Undergraduate research assistant (Occidental, 1962–1964), on a grant provided by the Research Corporation of America.

[5] (a) C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6245, 6249 (1956); (b) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

[6] S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

[7] H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953); H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300 (1955).

[8] G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962); G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuck, *ibid.*, **86**, 1046 (1964). Also G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. I, Interscience Publishers, New York, N. Y., 1963, pp 853–935.

[9] F. E. C. Scheffer and W. F. Brandsma, *Rec. Trav. Chim.*, **45**, 522 (1926); F. E. Condon, *J. Am. Chem. Soc.*, **70**, 1963 (1948).

[10] H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2310 (1955).

[11] H. C. Brown and L. M. Stock, *ibid.*, **79**, 5175 (1957).

[12] H. C. Brown and L. M. Stock, *ibid.*, **79**, 1421 (1957).

[13] H. C. Brown and G. Marino, *ibid.*, **81**, 3308 (1959); H. C. Brown, B. A. Bolto, and F. R. Jensen, *J. Org. Chem.*, **23**, 414 (1958).

[14] G. Marino and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 5929 (1959).

[15] F. P. DeHaan and H. C. Brown, *ibid.*, **91**, 4844 (1969).

Results and Discussion

The kinetic results of a series of gallium chloride catalyzed reactions between methyl chloride and toluene are given in Tables I–III. Table I shows the reaction to be first order in toluene. The first-order rate constants appear to decrease with increasing toluene concentration. Since methyl chloride and toluene have the dielectric constants 13.5 and 2.5, respectively, at −36°,[16] the expected decrease in the polarity of the medium with large increases in toluene concentration is likely a major factor.

As in the case of the benzene reaction,[15] no simple order with respect to the catalyst produces an unvarying rate constant (runs 7–12, Table II). The results of runs 13–17, plotted in Figure 1 along with runs 8 and 11, indicate that the reaction rate law is that indicated (1).

$$\frac{-\mathrm{d}[C_6H_5CH_3]}{\mathrm{d}t} = k_3[GaCl_3]_0^2[C_6H_5CH_3] \qquad (1)$$

However, the value of k_3 of the toluene reaction decreases markedly with time.

Table I. Reaction Order of Toluene in the Gallium Chloride Catalyzed Methylation of Toluene in Methyl Chloride at −35.6°

Run no.	Initial concn, M		Reaction time, min	Rate constants × 10^4		
	$C_6H_5CH_3$	$GaCl_3$		k_0[a]	k_1[b]	k_2[c]
1	0.378	1.51	45.0	0.93	2.7	7.3
2	0.734	1.48	45.0	1.4	1.9	2.8
3	1.08	1.45	45.0	1.8	1.8	1.7
4	1.41	1.44	45.0	2.0	1.5	1.1
5	1.74	1.41	45.0	2.4	1.5	0.84
6	2.60	1.35	45.0	3.3	1.4	0.51

[a] $k_0 = [(C_6H_5CH_3)_i - (C_6H_5CH_3)_f]/t$ mol l.$^{-1}$ min^{-1}. [b] $k_1 = (2.303/t)\log[(C_6H_5CH_3)_i/(C_6H_5CH_3)_f]$ min^{-1}. [c] $k_2 = (1/t)\cdot[(1/(C_6H_5CH_3)_f) - (1/(C_6H_5CH_3)_i)]$ l. mol^{-1} min^{-1}.

Table II. Rate Constants for the Gallium Chloride Catalyzed Methylation of Toluene in Methyl Chloride at −35.6°

Run no.	Initial concn, M		Reaction time, min	Rate constants × 10^4		
	$C_6H_5CH_3$	$GaCl_3$		k_2[a]	k_3[b]	k_4[c]
1	0.378	1.51	45.0		11.7	
2	0.734	1.48	45.0		8.7	
3	1.08	1.45	45.0		8.4	
4	1.41	1.44	45.0		7.0	
5	1.74	1.41	45.0		7.6	
6	2.60	1.35	45.0		7.4	
7	1.01	1.51	55.6	13.2	8.8	5.8
8	0.969	1.00	138.0	7.2	7.2	7.2
9	1.01	0.500	766	2.80	5.6	11.2
10	1.01	1.49	51.0		8.5	
11	0.971	1.01	140.0		7.3	
12	1.02	0.509	714		6.0	
13	0.979	1.00	11.2		7.3	
14	0.977	1.01	34.2		7.6	
15	1.01	1.00	69.5		7.7	
16	0.955	0.99	300		6.4	
17	0.974	1.00	510		5.4	

[a] $k_2 = k_1/(GaCl_3)_0$ l. mol^{-1} min^{-1}. [b] $k_3 = k_1/(GaCl_3)_0^2$ l.^{2} mol^{-2} min^{-1}. [c] $k_4 = k_1/(GaCl_3)_0^3$ l.^{3} mol^{-3} min^{-1}.

Unlike the benzene reaction, however, the change of $k_{3,\mathrm{toluene}}$ with time appears to be linear (Figure 1).

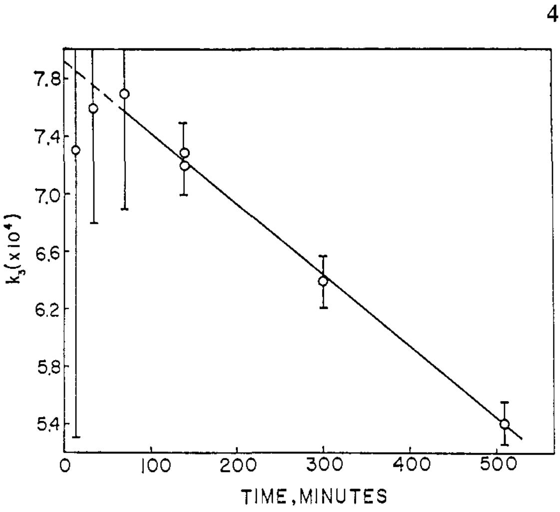

Figure 1. Change in the third-order rate constant with time for the gallium chloride (initial concentration, 1 M) catalyzed methylation of toluene (initial concentration, 1 M) in methyl chloride at −35.6°.

This difference might be due to concomitant disproportionation reactions; appreciable disproportionation of the xylenes rather than toluene during the latter stages of benzene alkylation could produce the change in $k_{3,\mathrm{benzene}}$ with time.[15] This would not occur in the toluene reaction if xylene disproportionation rather than trimethylbenzene disproportionation occurred. This fits the experimental data; no tetramethylbenzenes were observed.

The toluene used in reactions 12–17 contained approximately 0.5% benzene. Gas chromatographic analysis of the aromatics after reaction indicated a very small increase if any in the relative amounts of benzene to toluene, within that expected because of the higher reactivity of toluene. Furthermore, we found no evidence for toluene formation in the *m*-xylene alkylation reaction (see below). In either case this is weak evidence at best that disproportionation is not occurring. In the first place, in the presence of high concentration of catalyst and a large excess of methylating agent, one would not expect the concentrations of disproportionation-formed benzene or toluene to build rapidly. Secondly, xylene rather than toluene disproportionation, which appears more likely in the toluene alkylation reaction would not be expected to change the benzene concentration. As in the case of the benzene reaction,[15] the data do indicate that disproportionation alone cannot account for the extent of the decrease in $k_{3,\mathrm{toluene}}$ even when it is assumed that all the pseudocumene and hemimellitene resulted from disproportionation.

Catalytic inhibition, due to σ-complex formation, appears to be a reasonable alternative explanation for the decrease of k_3 with time.[15] However, if this is the case, it is difficult to rationalize the difference in the behavior of k_3 for the benzene and toluene reactions. It should be noted that because of the inherent uncertainty of rate constants determined for small percentages of reaction,[17] the possibility of curvature of the $k_{3,\mathrm{toluene}}$ line at small reaction times cannot be ruled out.

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(16) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951.

(17) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 86–94.

Table III. Per Cent Composition of Products[a] in the Gallium Chloride Catalyzed Methylation of Toluene in Methyl Chloride at −35.6°

Run no.	Toluene	*p*-Xylene	*b*	*m*-Xylene	*o*-Xylene	1,2,4-Trimethylbenzene	1,2,3-Trimethylbenzene
1	88.7		4.32		5.36	1.15	0.45
2	91.7		3.28		4.14	0.64	0.24
3	92.4		3.00		3.78	0.57	0.24
4	93.7		2.56		3.23	0.39	0.15
5	93.5		2.53		3.38	0.44	0.19
6	94.1		2.38		3.00	0.37	0.15
7	89.5		4.01		5.13	1.00	0.40
8	90.6		3.59		4.52	0.91	0.41
9	89.9		3.70		4.58	1.21	0.64
10	90.4	2.54		1.19	4.70	0.85	0.30
11	90.0	2.52		1.23	4.71	1.08	0.44
12	89.5	2.59		1.25	4.80	1.27	0.63
13	99.2	0.259		0.100	0.450		
14	97.3	0.85		0.35	1.54		
15	94.8	1.47		0.64	2.64	0.34	0.15
16	82.8	3.80		2.13	7.74	2.70	0.91
17	76.1	4.58		2.96	9.69	4.89	1.75

[a] These values include thermal conductivity corrections, and are the average of two to five chromatograms. [b] *p*-Xylene plus *m*-xylene.

Reactions 10–17 were analyzed with a diisodecylphthalate–bentone gc column which gave almost complete resolution of the xylenes. The xylene isomer distributions of runs with similar initial gallium chloride and toluene concentrations are shown in Figure 2.

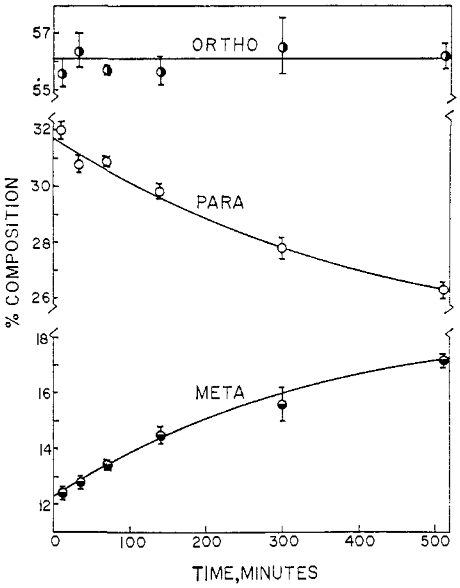

Figure 2. Change in the xylene isomer distribution with time for the gallium chloride (initial concentration, 1 *M*) catalyzed methylation of toluene (initial concentration, 1 *M*) in methyl chloride at −35.6°.

Since *m*-xylene is considerably more reactive toward alkylation than *p*-xylene (see below), the change in their relative amounts with time must be interpreted as evidence of *para* to *meta* isomerization. The *o*-xylene percentage does not change appreciably. In a benzene reaction in which *p*-xylene and *m*-xylene were 17 and 29%, respectively, the *o*-xylene value was 54% (run 18, previous paper[15]). This is consistent with the relative rates of isomerization of *p*-xylene as compared to *o*-xylene determined earlier: 4.53 at 25°,[18] 5 at 8°,[19] and 5.57[18] at 0°.

In order to check the selectivity relationship fit of the alkylation reaction, it is necessary to "subtract" out the side reactions (isomerization, perhaps disproportionation). The purely alkylation-produced values of the xylene isomer distribution, $k_{3,\mathrm{toluene}}$ and $k_{3,\mathrm{benzene}}$ can be estimated by extrapolating the respective curves to zero time. The values thus attained are 12.2% *m*-xylene, 31.7% *p*-xylene, 56.1% *o*-xylene, $k_{3,\mathrm{toluene}} = 7.9 \times 10^{-4}$ l.^{2} mol^{-2} min^{-1}. From Figure 1 of the previous paper,[15] we estimated $k_{3,\mathrm{benzene}}$ to be 1.6×10^{-4} l.^{2} mol^{-2} min^{-1}. From these values the partial rate factors were calculated to be $m_f = 1.8$, $p_f = 9.4$, $o_f = 8.3$ and the selectivity factor[5b] $S_f = 0.72$. Upon comparing these results with the usual log m_f or log p_f or log o_f *vs.* S_f plots,[5b] it appears that the fit is rather good for p_f and o_f and somewhat less satisfactory for m_f. The selectivity fit is about as good as expected, considering the curvature of the $k_{3,\mathrm{benzene}}$ line with time and the inherent uncertainty in both rate constants at short reaction times.

In addition, we used $k_{3,\mathrm{toluene}}$, $k_{3,\mathrm{benzene}}$, and the partial rate factors to predict isomer distributions and rate constants in the gallium chloride catalyzed methylation of the other methylbenzenes (Table IV). Note

Table IV. Predicted Isomer Distributions and Rate Constants for the Gallium Chloride Catalyzed Methylation of the Methylbenzenes in Methyl Chloride at −35.6°

	Methylation position, %[a]					
Compound	2	3	4	5	6	k_3[b]
p-Xylene	100					1.6
m-Xylene	30		68.5	1.5		6.1
o-Xylene		47	53			1.7
Mesitylene	100					52
Pseudocumene		43		48	9	7.8
Hemimellitene			90	10		8.3
Durene	100					12
Isodurene	100					63
Prehnitene	100					14
Pentamethyl	100					58

[a] Zero-time values. [b] $\times 10^3$ l.^{2} mol^{-2} min^{-1}. Zero-time values.

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(18) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, 77, 5579 (1955); see also Figure 1, H. C. Brown and H. Jungk, *ibid.*, 77, 5584 (1955).

(19) D. A. McCaulay and A. P. Lien, *ibid.*, 74, 6246 (1952).

Table V. Rate Constants for the Gallium Chloride Catalyzed Methylation of *m*-Xylene in Methyl Chloride at −35.6°

Run no.	Initial concn, *M* m-C_6H_4-$(CH_3)_2$	GaCl$_3$	Reaction time, min	Rate constants × 10^3 k_2[a]	k_3[b]	k_4[c]
1	0.74	1.50	7.20		5.9	
2	1.43	1.43	7.00		5.1	
3	2.28	1.37	7.00		4.9	
4	0.98	1.47	8.50	8.0	5.4	3.7
5	0.99	1.00	19.0	4.8	4.8	4.8
6	1.01	0.500	86.0	2.0	4.0	8.0

[a] $k_1/(GaCl_3)_0$ l. mol^{-1} min^{-1}. [b] $k_1/(GaCl_3)_0^2$ l.^{2} mol^{-2} min^{-1}. [c] $k_1/(GaCl_3)_0^3$ l.^{3} mol^{-3} min^{-1}.

Table VI. Per Cent Composition of Products[a] in the Gallium Chloride Catalyzed Methylation of *m*-Xylene in Methyl Chloride at −35.6°

Run no.	*m*-Xylene	1,3,5-Trimethylbenzene	1,2,4-Trimethylbenzene	1,2,3-Trimethylbenzene	1,2,4,5-Tetramethylbenzene	1,2,3,5-Tetramethylbenzene	1,2,3,4-Tetramethylbenzene
1	90.75	0.13	5.75	2.73	0.21	0.16	0.27
2	93.05	0.10	4.41	2.09	0.11	0.07	0.17
3	93.8	0.09	3.97	1.88	0.08	0.06	0.15
4	90.6	0.12	5.89	2.84	0.15	0.11	0.31
5	91.3	0.12	5.39	2.57	0.19	0.16	0.31
6	91.8	0.10	5.03	2.42	0.20	0.14	0.34

[a] These values include thermal conductivity corrections, and are the average of at least two chromatograms.

that both the isomer distributions and the rate constants are for zero-time, *i.e.*, pure alkylation values.

To test these predictions a study of the *m*-xylene reaction was undertaken. The rate constants and the per cent composition of the products are given in Tables V and VI. The reaction is seen to be first order in *m*-xylene, although again there is a significant decrease in the rate constant with increasing concentrations of aromatic. It is also interesting to note the decrease of the third-order rate constant with time for those reactions with essentially constant *m*-xylene concentration (Figure 3). The extrapolated rate constant, $k_{3,m\text{-xylene}} = 6 \times 10^{-3}$ l.^{2} mol^{-2} min^{-1}, is in excellent agreement with the predicted value (Table IV).

All six *m*-xylene reactions gave essentially the same trimethylbenzene isomer distribution, *i.e.*, hemimellitene 31.8%, pseudocumene 66.7%, and mesitylene 1.5%. In order to make comparisons with our predictions, it would have been proper to run reactions having 1 *M* gallium chloride and *m*-xylene concentrations for times less than 19 min. However, it seemed reasonable to assume that the rates of isomerization of the trimethylbenzenes would be comparable to that of the xylenes (Figure 2). Thus we conclude that in 19 min the expected hemimellitene → pseudocumene → mesitylene isomerization[20] would be very small, and therefore we may take the isomer distribution given as essentially the zero-time value. Again the agreement with the prediction (Table IV) is excellent.

The percentage of trimethyl products is about 6% in run 4, 7% in run 5, and 8% in run 6, even though the extent of apparent *m*-xylene reaction *decreases* in this series. The extent of this effect, assuming it to be due to disproportionation, is not enough to explain the decrease in k_3 for the three reactions. A similar trend is observed for the toluene reaction (runs 7–12). Significantly, the isomer distribution of the *primary* alkylation products does not change in either set of reactions. It is difficult to reconcile these results by either an isomerization or a disproportion mechanism.

In conclusion, it appears that the gallium chloride catalyzed methylation of benzene and the methyl aromatics obeys the selectivity relationship. However our results also provide support for Olah's contention that in weakly basic solvents alkylation exclusive of isomerization may be impossible.[8]

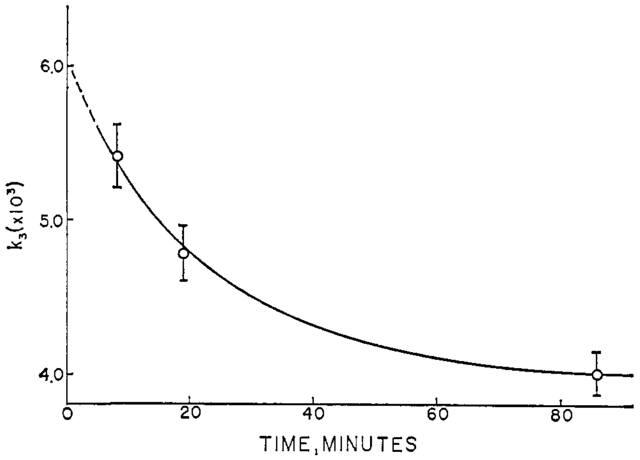

Figure 3. Change in the third-order rate constant with time for the gallium chloride catalyzed methylation of *m*-xylene (initial concentration, 1 *M*) in methyl chloride at −35.6°.

Experimental Section

The apparatus used for these reactions was described previously.[15]

Materials. The preparation and purification of methyl chloride and gallium chloride is described elsewhere.[15] A sample of Baker's reagent grade toluene, which had been previously purified by Roth,[21] was used in runs 1-9. He had distilled it through a column rated at 50 theoretical plates. Its subsequent freezing point depression indicated a purity of 99.7%. It was introduced into the vacuum line by distilling it away from powdered LiAlH$_4$ after which it was degassed in the usual manner. For runs 10–17 a Phillips pure grade sample of toluene (99.5% pure, impurity benzene, gc analysis) was introduced into the vacuum line over calcium hydride and thoroughly degassed. For the *m*-xylene reac-

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(20) Toluene and xylene (and presumably other methylbenzene) isomerizations occur through an intramolecular 1,2 shift of the methyl group. R. H. Allen and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 5289 (1959); H. Steinberg and F. L. J. Sixma, *Rec. Trav. Chim.*, **81**, 185 (1962). The relative rates and mechanism of tetramethylbenzene isomerization are discussed by M. Kilpatrick, J. A. S. Bett, and M. L. Kilpatrick, *J. Am. Chem. Soc.*, **85**, 1038 (1963).

(21) E. A. Roth, Ph.D. Thesis, Purdue University, 1961.

tions a sample of Phillips pure grade *m*-xylene [99% pure by cooling curve analysis, impurity *p*-xylene (gc)] was degassed and distilled into the line.

For thermal conductivity corrections (the polymethylbenzenes which are not listed here may be found in the previous paper[15]), mesitylene, hemimellitene, durene, and isodurene were available in the form of NBS samples. Prehnitene was procured from Delta Chemical Co. (greater than 99% pure, gc analysis).

Kinetic Procedures. A complete coverage of the kinetic techniques has been given previously.[15]

m-Xylene was measured out in the liquid phase in a calibrated capillary tube which was sealed on the vacuum line. Toluene was measured out as a gas.

Gas chromatographic analysis was performed on the following columns: toluene runs 10–17, 15 ft 5% diisodecylphthalate–5% bentone 34 on 60–80 mesh Chromosorb W, column temperature 95°; for toluene reactions 1–9 and *m*-xylene reactions, 6 ft TCP on Chromosorb, temperature 100 and 125°, respectively, for toluene and *m*-xylene reaction analysis. With the TCP column, *m*-xylene and *p*-xylene produced a single peak; durene and isodurene were only partially resolved.[22] Peak areas and thermal conductivity corrections were determined in the usual manner.[15]

Calculations. Reactant concentrations were calculated in the manner described previously.[15] Additional densities which were used: toluene, 0.917 at −36°;[23] *m*-xylene, 0.909 at −36°.[24]

Zero-time, *i.e.*, "pure," alkylation values of the rate constants and isomer distributions of the polymethylbenzenes were calculated following McGary, Okamoto, and Brown.[25] Thus

$$k_{m\text{-xylene}} = (o_t^2 + m_t^2 + 2o_tp_t)k_{\text{benzene}}/6 \tag{2}$$

$$\%\ \text{pseudocumene} = \frac{(2o_tp_t)100}{(o_t^2 + m_t^2 + 2o_tp_t)} \tag{3}$$

Error Analysis. Relative errors in the rate constants were calculated in the manner described in the previous paper.[15] The analytical precision of reactant toluene and *m*-xylene analysis varied from 0.2 to 0.4%. Bath temperature fluctuation was at worst ±0.2°.

Acknowledgment. We are indebted to the Atomic Energy Commission, National Science Foundation, and Research Corporation of America for their financial assistance. The assistance of E. A. Roth is gratefully acknowledged.

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[22] As a consequence of this, the durene and isodurene peak areas are subject to errors of the order of ±15%. However, because these components comprised less than 0.5% of the aromatics present, these errors had little effect on the calculated rate constants.

(23) E. W. Washburn, Ed., "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928.

(24) L. M. Heil, *Phys. Rev.*, 39, 666 (1932).

(25) C. W. McGary, Jr., Y. Okamoto, and H. C. Brown, *J. Am. Chem. Soc.*, 77, 3037 (1955).

Kinetics of the Chlorine-36 Exchange Reaction between Gallium Chloride and Methyl Chloride. The Dimethylchloronium Ion as a Possible Intermediate in the Exchange Reaction[1,2]

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Abstract: A kinetic study has been made of the chlorine-36 exchange reaction between gallium chloride and methyl chloride in excess methyl chloride. The reaction is second order in gallium chloride, with a second-order rate constant equal to $7.8 \pm 0.6 \times 10^{-4}$ l. mol^{-1} min^{-1}. From a comparison of the rate of chlorine exchange and methylation under identical conditions, it is concluded that the alkylation and exchange reactions cannot involve the same rate-determining intermediate. It is proposed that the mechanism for chlorine exchange involves the formation of the dimethylchloronium ion as an unstable intermediate. The applicability of this mechanism to other alkyl halide–metal exchange reactions is discussed. An equation is derived for homogeneous solution exchange reactions involving one volatile exchanging species.

Although many halogen exchange reactions between simple alkyl halides and Freidel–Crafts catalysts have been reported,[5] very little is known concerning the mechanism of this reaction under homogeneous conditions.

The first quantitative study under these conditions was performed by Brezhneva, *et al.*[6] They determined an activation energy of 11 ± 2 kcal/mol for the bromine-exchange reaction between ethyl bromide and aluminum bromide in carbon disulfide. The reaction appeared to them to be obviously bimolecular, and so the rate law was not determined.

In a more recent study, Sixma and coworkers[7] found the rate law for this reaction to be[8]

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(1) The Catalytic Halides. XXXIII.

(2) Based in part on a Ph.D. thesis submitted by Franklin P. DeHaan, Purdue University, 1961.

(3) Graduate research assistant on contract AT(11-1)-170, Atomic Energy Commission (1958–1959); National Science Foundation Cooperative Fellow, Purdue University (1959–1961); address inquiries to Occidental College.

(4) Undergraduate research assistant (Occidental College), 1968, on a grant provided by the Research Corporation of America.

(5) M. F. A. Dove and D. B. Sowerby in "Halogen Chemistry," Vol. I, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, Chapter 2.

(6) N. E. Brezhneva, S. Z. Roginskii, and A. I. Shilinskii, *Acta Physiochem. SSSR*, 7, 201 (1937).

(7) F. L. J. Sixma, H. Hendriks, and D. Holtzapffel, *Rec. Trav. Chim.*, 75, 127 (1956).

(8) Although the metal halide is written here as the monomer, it