Kinetics of the Gallium Chloride Catalyzed Methylation of Benzene in Excess Methyl Chloride[1,2]

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Abstract: The kinetics of the reaction of methyl chloride with benzene and hexadeuteriobenzene, using methyl chloride as the solvent and gallium chloride as the catalyst, were determined at $-35.6°$, utilizing gas chromatography to follow the reaction. The reactions occur at the same rate and are first order in the aromatic and second order in gallium chloride. Product xylene isomerization was observed. The third-order rate constant decreases markedly with increasing reaction time from its zero-time value of 1.6×10^{-4} l.^{2} mol^{-2} min^{-1}. Disproportionation and catalytic inhibition due to σ-complex formation are suggested as causes of this effect. Data analysis eliminates disproportionation as its sole cause. Reaction mechanisms are proposed for alkylation in methyl chloride and 1,2,4-trichlorobenzene.

In an earlier paper[4] we reported that the aluminum bromide catalyzed reaction between alkyl bromides and aromatics followed third-order kinetics in 1,2,4-trichlorobenzene (1). A similar reaction in excess

$$\frac{d[HBr]}{dt} = k_3[AlBr_3]_0[RBr][ArH] \qquad (1)$$

benzene or toluene, catalyzed by gallium bromide,[5,6] obeyed the rate expression 2. At this time we proposed

$$\frac{d[HBr]}{dt} = k_2[GaBr_3]_0{}^2 \qquad (2)$$

the difference in the catalyst rate order dependence observed here to be due to the greater catalytic strength of aluminum bromide. It seemed reasonable to assume that the coordinating powers of this catalyst were strong enough to effect transfer of the alkyl group from the 1:1 addition compound $RBr{:}AlBr_3$ to the aromatic, whereas the weaker Lewis acid gallium bromide required the assistance of a second molecule of addition compound to bring about this transfer.

This proposal was tested by a study of the kinetics of the gallium bromide catalyzed alkylation reaction in 1,2,4-trichlorobenzene.[7] We found this reaction to be first order in gallium bromide, alkyl halide, and aromatic; consequently the change in catalyst rate order must be due to some as yet unexplained solvent effect. Nor do we know which of the solvents, if any, is causing the reaction to occur "normally." It seemed worthwhile, therefore, to make another kinetic study with a different catalyst and solvent, with the hope that an answer to these questions would be forthcoming.

Recently, Choi and Willard[8] found that under similar conditions, the rate constants for the Br^{82} exchange between methyl bromide and gallium bromide in 1,2,4-trichlorobenzene are about 20 times and 200 times greater than the respective rate constants for the gallium bromide catalyzed methylation of toluene and benzene with methyl bromide in the same solvent.[7] Conceivably if the polarized form of the alkyl halide–catalyst addition compound necessary for alkylation was such that exchange would also take place, the rate of exchange would provide an upper limit to the rate of alkylation. It was decided to test the relative rates of exchange and alkylation again under identical conditions, but with a different catalyst and solvent. The results of this comparison are given in a following paper.[9]

For this investigation gallium chloride was chosen as the catalyst and methyl chloride as the alkyl halide and the solvent. Unlike solutions of higher alkyl halides which undergo isomerization and dehydrohalogenation in the presence of gallium chloride,[10] the gallium chloride–methyl chloride system is stable for long periods of time.[11] In addition, since methyl groups on aromatics show relatively little tendency to isomerize and/or disproportionate in the presence of Friedel–Crafts catalysts at low temperatures,[12,13] the complicating effects of these side reactions were minimized.

Results

In some preliminary investigations Roth[14] found that both the gallium chloride catalyzed methylation and exchange reactions in excess methyl chloride proceeded at a slow but measurable rate at $-35.6°$, provided fairly high gallium chloride concentrations were used.

The alkylation reactions proved difficult to follow kinetically. We attempted to follow them by observing the rate of production of hydrogen chloride in the gas phase.[6] However the results obtained in this manner were not reproducible. We did achieve success by running the reaction for known time intervals,

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[1] The Catalytic Halides. XXXI. Directive Effects in Aromatic Substitution. LIX.

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

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[4] H. Jungk, C. R. Smoot, and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 2185 (1956).

[5] C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6245, 6249 (1956).

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

[7] S. U. Choi and H. C. Brown, *ibid.*, **85**, 2596 (1963).

[8] S. U. Choi and J. E. Willard, *ibid.*, **87**, 3072 (1965).

[9] F. P. DeHaan, H. C. Brown, D. C. Conway, and M. G. Gibby, *ibid.*, **91**, 4854 (1969).

[10] R. Wong and H. C. Brown, *J. Inorg. Nucl. Chem.*, **1**, 402 (1955).

[11] H. C. Brown, L. P. Eddy, and R. Wong, *J. Am. Chem Soc.*, **75**, 6275 (1953).

[12] H. C. Brown, and H. Jungk, *ibid.*, **77**, 5579 (1955).

[13] H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

[14] E. A. Roth, Ph.D. thesis, Purdue University, 1961.

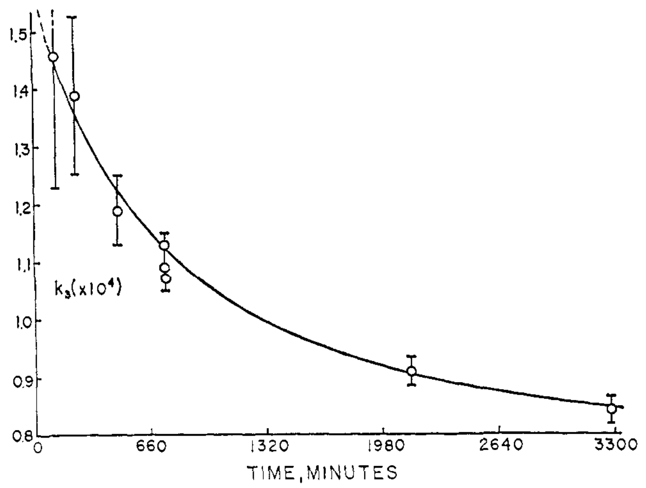

Figure 1. Change in the third-order rate constant with time for the gallium chloride (initial concentration, 1 *M*) catalyzed methylation of benzene (initial concentration, 1 *M*) in methyl chloride at −35.6°.

quenching them, and then analyzing them by means of gas chromatography.

Because of the increased reactivity of the reaction products[15] and the presence of a large excess of methylating agent, these reactions led to the formation of a large number of product polymethylbenzenes in widely varying amounts. Therefore, to permit easier interpretation of the chromatograms, we quenched the reactions after approximately 10% primary alkylation (alkylation of the products proceeded to the extent of 5–15% of the primary alkylation).

A number of reactions were analyzed to determine the rate order with respect to benzene and gallium chloride (Tables I and II). The initial benzene concentration and the per cent composition of the aromatics at the end of the reaction are given in Table III.

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

Run no.	Initial concn, *M* C_6H_6	$GaCl_3$	Reaction time, min	Rate constants × 10^4 $k_0{}^a$	$k_1{}^b$	$k_2{}^c$
1	0.623	1.25	536	1.30	2.22	3.79
2	0.796	1.33	434	1.94	2.57	3.41
3	1.12	1.33	434	2.70	2.58	2.41

[a] $k_0 = [(C_6H_6)_i - (C_6H_6)_f]/t$ mol l.$^{-1}$ min^{-1}. [b] $k_1 = (2.303/t) \log [(C_6H_6)_i/(C_6H_6)_f]$ min^{-1}. [c] $k_2 = (1/t)[(1/(C_6H_6)_f) - (1/(C_6H_6)_i)]$ l. mol^{-1} min^{-1}.

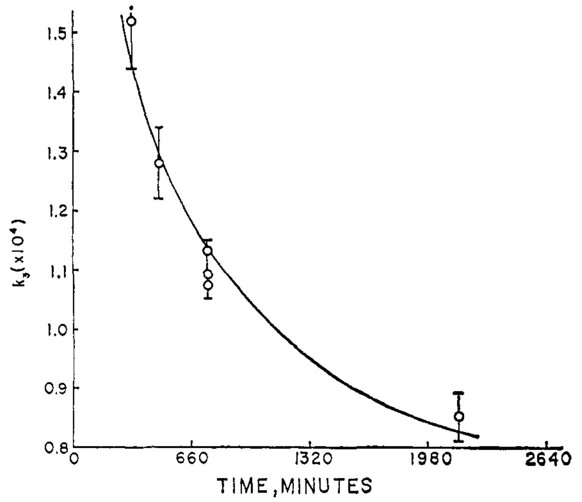

Figure 2. Change in the third-order rate constant with time for the gallium chloride (variable initial concentration) catalyzed methylation of benzene (initial concentration, 1 *M*) in methyl chloride at 35.6° (runs 7–14).

From Table I we see that the reaction is first order in benzene. However these first-order rate constants vary with the initial gallium chloride concentrations. In order to determine the reaction order with respect to the catalyst, higher order rate constants were calculated by dividing the values of k_1 by successive powers of the initial gallium chloride concentration. Runs 7–13, Table II, show that no simple order with respect to the catalyst produces an unvarying rate constant. Although the fourth-order rate constants show the most constancy we have other evidence for believing this reaction is third order, that is

$$\frac{-\mathrm{d}[C_6H_6]}{\mathrm{d}t} = k_3[GaCl_3]_0{}^2[C_6H_6] \tag{3}$$

In order to determine a more accurate value for the rate constant of the benzene reaction we ran a series of reactions having approximately 1 *M* initial gallium chloride and benzene concentrations for widely varying reaction times. The results of these runs, numbered 14–18, are given in Tables II and III and are plotted along with earlier runs of similar reactant concentrations (numbered 9–11) in Figure 1. Of significance is the marked decrease in the value of the third-order rate constant, k_3, with time. As Figure 2 illustrates,

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

Run no.	Initial concn, *M* C_6H_6	$GaCl_3$	Reaction time, min	Rate constants × 10^4 $k_2{}^a$	$k_3{}^b$	$k_4{}^c$
1	0.623	1.25	536		1.42	
2	0.796	1.33	434		1.45	
3	1.12	1.33	434		1.44	
4	0.627^d	1.27	480		1.51	
5	0.695^d	1.31	418		1.52	
6	1.11^d	1.26	480		1.48	
7	1.03	1.58	333	2.40	1.52	0.96
8	1.00	1.26	480	1.61	1.28	1.02
9	1.00	1.01	750.5	1.07	1.07	1.06
10	1.00	1.01	750	1.14	1.13	1.12
11	1.02	1.01	751	1.10	1.09	1.08
12	1.01	0.754	2160	0.642	0.85	1.13
13	1.01	0.502	6927	0.312	0.622	1.24
14	1.04	1.05	120		1.46	
15	0.963	1.04	240		1.39	
16	1.02	1.01	480		1.19	
17	0.995	1.00	2150		0.91	
18	0.996	1.01	3280		0.84	

[a] $k_2 = k_1/[GaCl_2]_0$ 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}. [d] Hexadeuteriobenzene.

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(15) (a) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1950); D. A. McCaulay, B. H. Shoemaker, and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950). (b) A. Streitwieser and L. Reif, *J. Am. Chem. Soc.*, **86**, 1988 (1964), have suggested that toluene disproportionation requires either traces of an alkene or the formation of the benzyl cation. Presumably this is true for the polymethylbenzenes as well. If this is the case the relative σ-complex stability would be unimportant.

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

Run no.	Benzene	Toluene	*p*-Xylene	*m*-Xylene	*o*-Xylene	1,2,4-Trimethyl-benzene	1,2,3-Trimethyl-benzene
1	88.7	7.33	1.42[b]		1.64	0.93	
2	89.6	6.82	1.29[b]		1.45	0.82	
3	89.7	7.10	1.26[b]		1.40	0.52	
4	89.1	7.22[c]	1.35[b]		1.86	0.50	
5	89.7	6.91[c]	1.35[b]		1.50	0.55	
6	89.4	7.46[c]	1.19[b]		1.49	0.50	
7	88.1	8.32	1.38[b]		1.71	0.44	
8	90.7	6.50	0.98[b]		1.32	0.50	
9	92.2	5.50	0.76[b]		1.01	0.56	
10	91.7	5.72	0.80[b]		1.04	0.72	
11	92.0	5.62	0.76[b]		1.03	0.64	
12	90.5	6.02	1.03[b]		1.17	1.31	
13	90.0	6.00	1.03[b]		0.90	2.03	
14	98.1	1.9					
15	96.5	3.04	0.14		0.26		
16	94.3	4.69	0.29	0.12	0.54		
17	82.2	7.85	1.12	1.46	3.09	3.00	1.2
18	75.5	8.69	1.32	2.28	4.32	5.47	2.4

[a] These values include thermal conductivity corrections, and are the average of two to four chromatograms. [b] *p*-Xylene plus *m*-xylene. First gas chromatography column used, 6 ft TCP on Chromosorb, did not separate these two components. [c] Hexadeuteriobenzene.

the value of k_3 for reactions 7–13 in which the gallium chloride concentration is varied shows a similar decline with time. Therefore we conclude that rate law 3 is being obeyed.

Discussion

Previous alkylation studies[4–7] implied that the aromatic was involved in the rate-determining step, but because the kinetics were determined by the production of hydrogen halides this was never conclusively proven. Consequently the possibility of the difference in the rates of alkylation of benzene and toluene being due to a solvent effect could never be entirely ruled out. Since we were able to show the reaction to be definitely first order in benzene this possibility is eliminated.

By using a 15 ft 5% diisodecylphthalate–5% bentone 34 column for gas chromatography analysis of runs 14–18, we were able to achieve almost complete resolution of the three xylene peaks. Our analysis indicated that even though the *p*- plus *m*-xylene to *o*-xylene ratio remained the same as that of the earlier runs, the percentages of *p*- and *m*-xylenes changed from 31% and 13% in run 16, to 17% and 29% in run 18. Under these conditions, *m*-xylene is some 3.5 times more reactive toward alkylation than either *o*- or *p*-xylene;[16] an increase in the relative percentage of *m*-xylene with time indicates concomitant isomerization is occuring.

This appears surprising in light of the fact that no measurable change in the isomer distributions was noticed for the gallium bromide catalyzed alkylation of toluene with methyl or ethyl bromide in excess toluene at 25°,[17] some 60° above our reaction temperature. However these reactions were run at a catalyst concentration of 0.02 *M*, 25 times more dilute than our lowest gallium chloride concentration. Others have reported extensive and rapid isomerization at around 0°[12,18,19] with catalyst concentrations greater than or equal to ours. Furthermore, Olah and coworkers have suggested that since the intermediate σ complex postulated for alkylation is identical with that postulated for isomerization, alkylation exclusive of isomerization may be impossible.[20,21] Their results indicate a minimization of concomitant isomerization during alkylation through the use of sufficiently basic solvents like nitromethane, in which σ complexes are not formed.

This apparently is not the case in methyl chloride, since Roth found experimental evidence supporting the existence of σ complexes in this solvent.[14] When various amounts of hydrogen chloride were added to gallium chloride and toluene dissolved in methyl chloride at −78.5°,[22] the resulting phase diagram indicated a slightly stable complex having the composition $C_6H_5CH_3 \cdot HCl \cdot Ga_2Cl_6$ to be existing in solution.

To our knowledge, the −35.6° of this study is *by far the lowest temperature reported for xylene* isomerization. It appears, however, that this side reaction is to be expected even at this temperature when high concentrations of an active Friedel–Crafts catalyst are present along with hydrogen halide[23] in solvents of low basicity.

The marked decrease with time of the third-order rate constants, Figures 1 and 2, could be taken as evidence of a concomitant disproportionation reaction. The possibility of disproportionation leads to a reasonable explanation of the shape of the curves in Figures 1 and 2. During the early stages of reaction, when a considerable portion of the catalyst would be present as the toluene σ complex $C_6H_6CH_3^+Ga_2Cl_7^-$, disproportionation would increase the benzene concentration, which would lower the calculated value of k_3 for benzene alkylation. As the alkylation reaction proceeds, one would expect xylene disproportionation to toluene, not benzene, to become increasingly important because of the increased stability of the xylene σ com-

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(16) F. P. DeHaan, H. C. Brown, and J. C. Hill, *J. Am. Chem. Soc.*, **91**, 4850 (1969).

(17) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

(18) H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955).

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

(20) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962).

(21) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, N. A. Overchuck, *ibid.*, **86**, 1046 (1964).

(22) Below −50°, the gallium chloride catalyzed methylation of toluene in methyl chloride is negligible.

(23) G. Baddeley, G. Holt, and D. Voss, *J. Chem. Soc.*, 100 (1952).

plexes relative to that of toluene.[15] Thus the apparent rate of decrease of the benzene alkylation constant, k_3, slows with time.

It must be stated immediately that the weight of previous experimental evidence makes disproportionation at −35.6° appear unlikely. Baddeley and coworkers[23] report "the absence of any considerable disproportionation" in homogenous mixtures of *p*-xylene, aluminum bromide, and hydrogen bromide after a day at room temperature. McCaulay and Lien[19,24] state that at temperatures below 80°, the xylenes are inert to $HF–BF_3$-catalyzed disproportionation. We have found less than 0.1% *m*-xylene is formed from a mixture having the mole ratio $6C_6H_5CH_3 \cdot HBr \cdot Al_2Br_6$ after 8 days at 0°.[13]

Catalytic inhibition, due to σ complex formation, appears to be a reasonable alternative explanation for the decrease of k_3 with time. When 1 mol of methyl bromide was added to a $6C_6H_5CH_3 \cdot HBr \cdot Al_2Br_6$ mixture, no methylation of toluene was observed in a reaction time of 3 min at 25°. Yet a $6C_6H_5CH_3 \cdot CH_3Br \cdot Al_2Br_6$ mixture underwent complete alkylation in less than 30 sec at 0°.[18] Aluminum bromide catalyzed alkylations with methyl and ethyl bromide in 1,2,4-trichlorobenzene became extremely slow after a short reaction period even though considerable alkyl halide and benzene remained.[4] Significantly, a similar inordinate decrease in reaction rate was observed at low temperatures (−45 to −78°) for the gallium bromide catalyzed isopropylation of toluene in excess toluene[6] but was not reported for the analogous methylation, ethylation, and *n*-propylation reactions at temperatures above 15°.[5] Roberts[25] has found the extent of aluminum chloride catalyzed rearrangement of *n*-propyl side chains to decrease in the series *n*-propylbenzene, *p*-*n*-propyltoluene, and 1,3-dimethyl-4-*n*-propylbenzene. He attributed this to the fact that the catalyst would be progressively less active due to complex formation with aromatics of increasing Lewis basicity.

Since σ complexes are stable at low temperatures in methyl chloride,[14] reaction inhibition due to their formation seems reasonable. If this occurred, the slowing of the rate of decrease of k_3 with time would not seem to jibe with the expectation that the amount of σ complex formation involving the more basic polymethylbenzenes would increase with time. However, this would result in a marked increase in the polarity of the medium, particularly at high reactant concentrations, which would increase the alkylation rate.

At this point it is impossible to choose between disproportionation and catalytic inhibition as the cause of the change in the rate constant with time. We can say however that *disproportionation alone cannot explain the extent of the decrease of the rate constant with time.* If we assume, in runs 9–18, that *all* of the xylene and trialkylated products resulted from disproportionation of toluene and correct the final benzene concentration by that amount, the resulting rate constants are still less than 1.6×10^{-4} $l.^{-2}$ mol^{-2} min^{-1}, the extrapolated value for $k_{3,\text{benzene}}$ at zero time (Figure 1).

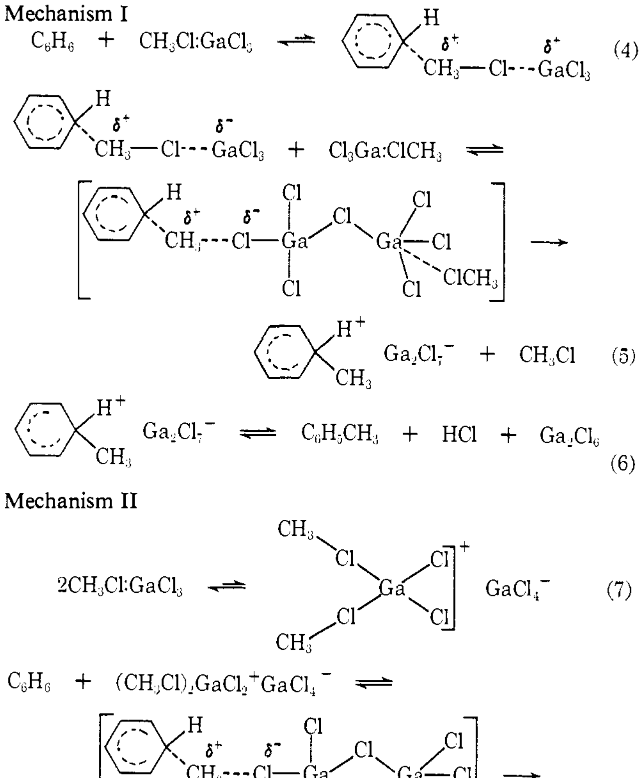
In runs 7–13, even though the percentages of benzene, toluene, and xylene remain constant, that of pseudocumene rises from 0.44 to 2.0%. This may be taken as evidence of *p*- to *m*-xylene isomerization rather than disproportionation, in that *m*-xylene is considerably more reactive toward alkylation than *o*-xylene and yields pseudocumene as its major product.[16]

Treating the data as a set of first-order series and parallel reactions, in a manner similar to that of Allen and Yats,[26] is not valid in that both isomerization and disproportionation in excess alkyl halide, unlike alkylation, are not pseudo-first-order reactions but depend upon hydrogen halide concentration as well as that of the aromatic.[12,23,15b]

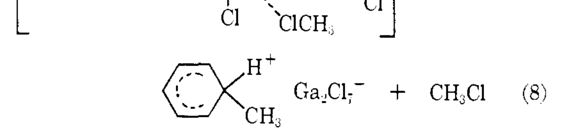
On balance, catalytic inhibition due to σ-complex formation appears the more plausible explanation. However, further study will be necessary to fully clarify the time dependence of k_3.

Two mechanisms, both consistent with the rate law 3, can be proposed for the gallium chloride catalyzed methylation of benzene in methyl chloride at −35.6°.

Mechanism I



Mechanism II



With either step 5 or 8 rate determining, the appropriate kinetic expression would be

$$\frac{-d[C_6H_6]}{dt} = k_3[CH_3Cl:GaCl_3]^2[C_6H_6] \qquad (9)$$

Vapor pressure measurements have shown the $CH_3Cl:GaCl_3$ complex to be the species existing in excess methyl chloride at −78.5, −64, and −50°.[11] Since

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(24) A. P. Lien and D. A. McCaulay, *J. Am. Chem. Soc.*, **75**, 2407 (1953); D. A. McCaulay, M. C. Hoff, N. Stein, A. S. Couper, and A. P. Lien, *ibid.*, **79**, 5808 (1957).

(25) R. M. Roberts and J. E. Douglass, *J. Org. Chem.*, **28**, 1225 (1963); R. M. Roberts, E. K. Baylis, and G. J. Fonken, *J. Am. Chem. Soc.*, **85**, 3454 (1963); R. M. Roberts, A. A. Khalaf, and J. E. Douglass, *J. Org. Chem.*, **29**, 1511 (1964).

(26) R. H. Allen, T. Alfrey, Jr., and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 42 (1959); R. H. Allen and L. D. Yats, *ibid.*, **83**, 2799 (1961).

the similar 1:1 addition compounds $CH_3Br:GaBr_3$ and $C_2H_5Cl:GaCl_3$ have been shown to be the solute species in methyl bromide and ethyl chloride at −36°[10,27] it is quite probable that gallium chloride also exists as the 1:1 species in methyl chloride solutions at −35.6°, the temperature of the alkylation studies. Moreover, it appears reasonable to assume, on the basis of the evidence, that at low temperatures large excesses of methyl chloride will convert essentially all the gallium chloride to the 1:1 addition compound.

For example we have found the rate of alkylation of benzene and toluene *at room temperature* to be independent of alkyl bromide concentration when $[C_2H_5Br]/[Ga_2Br_6] \geq 14$ and under circumstances such that the ethyl bromide does not compete with any Lewis base of comparable strength for complexation with the catalyst.[5]

Thus, since the methyl chloride:gallium chloride (dimer) ratio varied from 20:1 to 70:1 in this study, we can assume almost all of the catalyst to be present as the $CH_3Cl:GaCl_3$ complex.[28]

Under alkylation conditions at low temperatures the possibility of aromatic–catalyst interaction must also be considered. To test the effect of the aromatic, we dissolved known amounts of toluene and gallium chloride in methyl chloride (below alkylation temperature).[14] The vapor pressure lowering which we observed agreed within experimental error with the predicted lowering based on the complete formation of the $CH_3Cl:GaCl_3$ complex. The solution did turn a slight yellow, probably because of the presence of small amounts of an oriented π complex (4) similar to those formed between toluene, ethyl fluoride, and boron trifluoride at low temperatures.[29]

Korshak and Lebedev[30] first proposed the ion-pair dimer species (7) to explain the dipole moment, uv, and conductivity data of solutions of aluminum halides in alkyl halides. They concluded that the main complex species in solution was this dimeric ion pair. However, the vapor pressure lowering studies discussed previously, although they do not disprove the existence of minor amounts of this species, do prove that it is not the main complex species in solution. However this mechanism does not require more than a minor amount of dimer species.

Support for the ion-pair dimer intermediate comes from the electrolysis experiments of Wertyporoch,[31] Fairbrother,[32] and Van Dyke.[33] Although both their experimental results and their conclusions differ greatly, all three report a transport of aluminum to the cathode upon electrolysis of aluminum halide–alkyl halide systems. Wertyporoch found a similar amount of aluminum at the anode, which led him to suggest the species $Al(AlBr_4)_3$. Fairbrother and Van Dyke, however, proposed $C_2H_5AlBr_2^+$ and $AlBr_4^-$, and $AlBr_2^+$ and Br^-, respectively, as the current carrying species. Their disagreement may only be superficial, since it is possible, by assuming $CH_3BrAlBr_2^+$ and $AlBr_4^-$ carry an equal amount of current, to arrive at Van Dyke's experimental results.

Since the alkylation reaction under study is effected by isomerization (and possibly disproportionation as well) we propose, following Olah,[34] that the rate-determining step, either (5) or (8), involves a transition state which is in nature a σ complex rather than an oriented π complex. The methylation of hexadeuteriobenzene proceeds at essentially the same rate as benzene (Table II); therefore the rate-determining step does not involve the breakdown of the σ complex.

The alkylation mechanisms proposed here are essentially the same as those proposed for the gallium bromide catalyzed methylation and ethylation of benzene and toluene in excess aromatic.[5] We pointed out at that time that addition complexes of dimeric aluminum bromide and gallium bromide seem to be more stable than the corresponding compounds of the monomeric halides.[35] Thus we conclude that the squared rate expression term in gallium bromide (in excess aromatic) and the squared term in gallium chloride (in excess methyl chloride) might arise from the need for an additional pull of a second gallium halide (GaX_3) molecule in order to transfer the alkyl group from the halogen atom to the aromatic.

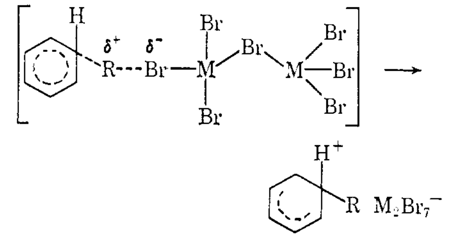
We wish to point out at this time that although catalytic first-order dependence was observed in 1,2,4-trichlorobenzene, *it does not necessarily follow* that one $AlBr_3$ or $GaBr_3$ molecule is sufficient for affecting alkylation in this solvent. The reaction kinetics do not permit a decision as to whether the catalyst term is $[MX_3]^1$ or $[M_2X_6]^1$. Therefore the rate law for alkylation in 1,2,4-trichlorobenzene (1) could also be written as

$$\frac{d[HBr]}{dt} = k_3[M_2Br_6]_0[RBr][ArH] \tag{10}$$

where M = Al or Ga. The mechanism shown in eq 11–13 (S = 1,2,4-trichlorobenzene) followed by a reaction similar to (6), with (13) determining, yields the

$$M_2Br_6 + S \rightleftharpoons S{:}M_2Br_6 \tag{11}$$

$$RBr + S{:}M_2Br_6 \rightleftharpoons RBr{:}M_2Br_6 + S \tag{12}$$



(13)

rate law (14) in substantial agreement with (10).

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[27] J. J. Byrne, Ph.D. thesis, Purdue University, 1958.

[28] This question is of particular importance in our analysis of the chlorine exchange data and is discussed at length in the following paper.

[29] R. Nakane, A. Natsubori, and O. Kurihara, *J. Am. Chem. Soc.*, **87**, 3597 (1965); R. Nakane, J. Oyama, and A. Natsubori, *J. Org. Chem.*, **33**, 275, (1968).

[30] V. V. Korshak and N. N. Lebedev, *J. Gen. Chem. USSR*, **18**, 1766 (1948); *Dokl. Akad. Nauk SSSR*, **57**, 263 (1947).

[31] A. Wohl and E. Wertyporoch, *Ber.*, **64B** 1357 (1931); E. Wertyporoch, *ibid.*, **64B**, 1369 (1931); E. Wertyporoch and T. Firla, *Z. Physik. Chem.*, **A162**, 398 (1932).

[32] F. Fairbrother and N. Scott, *J. Chem. Soc.*, 452 (1955).

[33] R. E. Van Dyke, *J. Am. Chem. Soc.*, **72**, 3619 (1950).

[34] 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); G. A. Olah and N. A. Overchuck, *ibid.*, **87**, 5786 (1965). Also G. A. Olah, Ed., "Freidel–Crafts and Related Reactions," Vol. I, Interscience Publishers, New York, N. Y., 1963, pp 853–935.

[35] See also S. U. Choi, W. C. Frith, and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 4128 (1966).

$$\frac{d[HBr]}{dt} = k_3[S:M_2Br_6]_0[RBr][ArH] \qquad (14)$$

Through freezing point lowering measurements at 17°, Choi[36] has found that aluminum bromide exists in 1,2,4-trichlorobenzene as the $S:Al_2Br_6$ complex (11). Thus it appears that the solvent effect in 1,2,4-trichlorobenzene is simply (12). In excess aromatic (at room temperatures) or methyl chloride as solvent, excess alkyl halide converts the 1:2 complex into the 1:1 complex (15). This results in a second-order catalytic dependence.

$$CH_3Cl + CH_3Cl:Ga_2Cl_6 \rightleftharpoons 2CH_3Cl:GaCl_3 \qquad (15)$$

Experimental Section

Apparatus. All experiments were carried out using a high vacuum apparatus and the usual vacuum line techniques. Reaction products were analyzed with Perkin-Elmer 154 and Research Specialties gas chromatographs.

Materials. Methyl chloride (Matheson, minimum purity 99.5%) was purified and handled in the manner described previously.[11] Gallium chloride was prepared by the direct reaction of the metal (Alcoa, 99.95% pure) with dry hydrogen chloride at 300°. The product, after several sublimations *in vacuo*, was sealed in break-tip ampoules. NBS and Matheson Coleman and Bell spectroquality benzene samples, each with purity greater than 99.9% by gc analysis, were introduced into the vacuum line over Drierite or calcium hydride and thoroughly degassed. Merck hexadeuteriobenzene, advertised as 99.5% isotopically pure, was introduced into the line over Drierite in a similar manner (previously gc analysis revealed 0.2% of an unknown impurity). Its ir spectrum was essentially free of C–H bonds. The reactions were quenched with Mallinckrodt anhydrous diethyl ether.

For calibration of the sensitivity of the thermal conductivity detector of the gas chromatograph for different products, we used MCB spectroquality benzene and *m*-xylene and Phillips pure grade toluene, *o*-xylene and *p*-xylene, each with purity 99.9% by gc analysis. The correction for both pseudocumene and hemimellitene was determined with Aldrich puriss. pseudocumene (purity 97.6% by gc). The mixtures were diluted with Phillips pure grade *n*-heptane.

Kinetic Procedure. The reaction mixtures were prepared in the following manner. A reaction flask consisting of a piece of constricted 8-mm glass tubing with a small bulb bottom was sealed to the vacuum line, evacuated, and cleaned by flaming. Known amounts of gallium chloride, methyl chloride, and benzene or hexadeuteriobenzene were condensed at −196° in the bulb using the usual vacuum line procedures. The flask was then sealed from the line at the constriction, the bottom portion being kept at liquid nitrogen temperatures at all times.

These reaction mixtures were conveniently stored under liquid nitrogen before and after reaction. Immediately prior to reaction the bottom of the reaction flask including the bulb was immersed in an acetone–Dry Ice bath (−78°). When the reaction mixture had liquified the flask was tapped lightly until all the contents had gone into solution. At this time the flask was completely submerged in an ethylene chloride slush bath for the required reaction time. When necessary the flask was quickly transferred to freshly made baths. The reaction was quenched by immersing the flask in liquid nitrogen. During the transfer the solutions were observed to be yellow orange in color, clear, and homogeneous.

When the time for analysis was convenient, the top of the flask was scratched with a file and opened. The flask was immediately transferred from the liquid nitrogen bath to an acetone–Dry Ice bath and 0.1–0.3 ml of precooled (−78°) ether was added with a syringe. The ether reacted with the gallium chloride providing a permanent quench for the reaction. The flask was kept at this temperature while small amounts of the solution were transferred into the gas chromatograph by means of a precooled (−78°) syringe.

A series of blanks were subjected to the same procedures. The results indicate both the amount of aromatic reacted and the amount of aromatic lost by these manipulations to be negligible.

Gc analysis gave results as follows: runs 1–13, 6-ft tri-*o*-tolyl phosphate (TCP) on Chromosorb column, column temperature 75°; runs 14–18, 15-ft 5% diisodecylphthalate–5% bentone 34 on 60–80 mesh Chromosorb W column, column temperature 75°. The latter column resolved all the aromatics. The TCP column did not separate *m*-xylene and *p*-xylene.

Thermal conductivity corrections were determined by analyzing known aromatic mixtures (in amounts very similar to reaction mixtures) under identical fractometer conditions. The various areas under the peaks were determined from the height of the peak times the width at half-height or half the base. Errors induced by assuming these peaks to be triangles appeared again in the analysis of similar reaction mixtures and consequently were canceled out. The same corrections were applied to the hexadeuteriobenzene reactions.

These procedures were tested in the following way. Typical aromatic mixtures were carefully weighed into stoppered flasks. Aliquots were then removed to the bulb of an opened reaction flask after which typical amounts of methyl chloride were condensed on them. These mixtures were subjected to the series of manipulations given above and then analyzed *via* gas chromatography. The per cent composition of these solutions as determined from the chromatographs agreed with the weight per cent composition within the experimental error of the thermal conductivity corrections (Table IV).

Table IV. Test of Experimental Technique through Analysis of Known Aromatic Mixtures

Method of determination	% composition of aromatics: Toluene	*p*-Xylene	*o*-Xylene	Pseudocumene	Hemimellitene
By weight	96.42	1.34	1.71	0.41	0.13
By area[a] (gc)	96.26	1.40	1.78	0.43	0.14
By weight	92.83	2.68	3.52	0.75	0.22
By area[a] (gc)	92.87	2.72	3.39	0.79	0.22
By weight	91.58	3.59	3.96	0.69	0.18
By area[a] (gc)	91.28	3.67	4.08	0.76	0.20

[a] After addition of methyl chloride followed by the complete experimental procedure. These values include thermal conductivity corrections, and are the average of two chromatograms.

Calculations. The volumes of methyl chloride, benzene, hexadeuteriobenzene, and gallium chloride present initially in a given solution were calculated from their number of moles and their densities at −36°. The density of methyl chloride at −36° was 1.025.[37] The density of gallium chloride was assumed to be equal to its value at 25°, 2.47. The density of benzene (and presumably hexadeuteriobenzene) was assumed to be equal to its value at 0°, 0.900.[38] The solution was assumed to be ideal,[39] *i.e.*, the total volume of the solution equaled the sum of the component volumes and remained constant during the reaction. Because of the small volumes of the reaction flasks the correction for the number of moles of methyl chloride in the vapor phase was typically only 0.2–0.3%.

The final concentration of benzene or hexadeuteriobenzene was calculated from the equation

$$[C_6H_6]_t = \frac{[C_6H_6]_i(\text{area,* benzene})}{(\text{area*, benzene} + \Sigma\ \text{area*, products})} \qquad (16)$$

where area* includes the thermal conductivity correction.

Error Analysis. The relative errors in the rate constant, $\Delta k_3/k_3$ were calculated from eq 17.[40] Because of the slowness of these reactions, the error in time measurement was considered negligible.

$$\left(\frac{\Delta k_3}{k_3}\right)^2 = \left(\frac{\Delta[C_6H_6]}{[C_6H_6]}\right)^2 + \left\{\left[\frac{(\Delta H^{\ddagger} + RT)}{RT}\right]\left(\frac{\Delta T}{T}\right)\right\}^2 \qquad (17)$$

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[36] S. U. Choi, Ph.D. thesis, Purdue University, 1957.

[37] K. S. Willson, W. O. Walker, W. R. Rinelli, and C. V. Mars, *Ind. Eng. Chem., News Ed.*, **21**, 1254 (1943).

[38] E. W. Washburn, Ed., "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928.

[39] D. G. Walker, *J. Phys. Chem.*, **64**, 939 (1960).

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

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.

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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).