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 ± 0.6 × 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 Friedel–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

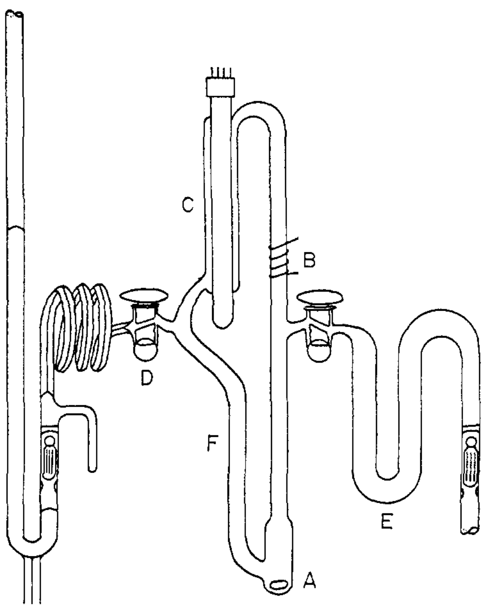

Figure 1. Apparatus for the exchange reactions.

$$\text{rate} = k_3[\text{AlBr}_3]^2[\text{C}_2\text{H}_5\text{Br}] \qquad (1)$$

Although a push-pull displacement mechanism seemed to them to be in accord with the data, no detailed reaction mechanism was suggested.

Bromine exchange reactions involving gallium bromide have been the subject of two studies by Choi and Willard and Kwun. They found that exchange with either methyl[9] or ethyl[10] bromide in either 1,2,4-trichlorobenzene or nitrobenzene follows the rate law

$$\text{rate} = k_3[\text{GaBr}_3]^2[\text{RBr}] \qquad (2)$$

They also report ethyl bromide exchange to be significantly faster than that involving methyl bromide. However, somewhat surprisingly, Polaczek and Halpern[11] have found iodine exchange between aluminum(III), gallium(III), and indium(III) iodide and alkyl iodides to *decrease* in the order Me > Et > *n*-propyl.

Thus far only Kwun and Choi have ventured to propose a mechanism for these reactions.[10] However there is evidence (see below) which suggests that their mechanism may not be satisfactory for their reaction in 1,2,4-trichlorobenzene or for Sixma's system.

In view of the contradictory results concerning the effect of the alkyl group and as well as the question of the mechanism, further study of these exchange reactions seemed in order. We were also very interested in the fact that, under similar conditions, the gallium bromide catalyzed exchange reaction[9,10] was faster than the corresponding alkylation reaction and involved a different catalytic rate-law dependence.[12] 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, therefore, to test the relative rates of exchange and alkylation again under identical conditions, but with a different catalyst and solvent. The results of the alkylation reaction are given in the preceeding papers.[13,14]

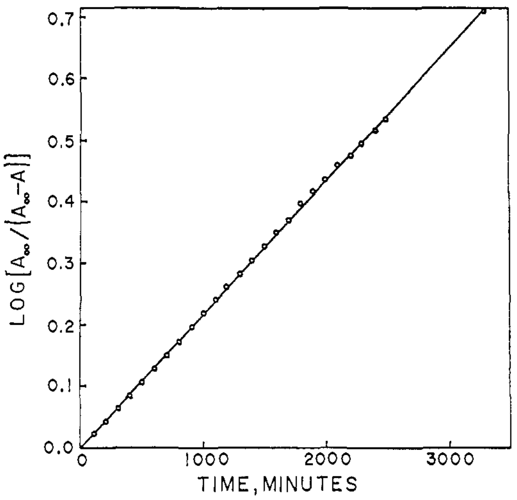

Figure 2. Fraction of chlorine exchanged as a function of time, run no. 1.

The choice of gallium chloride as catalyst and methyl chloride as alkyl halide and solvent was dictated mainly by their feasibility as alkylation agents. Moreover, the gallium chloride–methyl chloride system is stable for long periods of time,[15] and is therefore a good choice for a kinetic study of the exchange reaction.

Results

In some preliminary investigations Roth[16] found the rate of the gallium chloride catalyzed methylation of toluene in excess methyl chloride to be essentially negligible below −50°. However, both the methylation and exchange reactions proceeded at a slow but measurable rate at −36°, provided fairly high gallium chloride concentrations were used. It would have been preferable kinetically to run these reactions at much higher temperatures with lower catalyst concentrations, but the low boiling point of the solvent methyl chloride, −24°, constituted a severe experimental handicap for the high vacuum line technique required for these studies.

In a typical exchange run, known amounts of gallium chloride, containing small amounts of chlorine-36, and methyl chloride were condensed together at −196° in the bottom of the exchange reaction apparatus (Figure 1). After a short time at −78.5° to permit liquification of the methyl chloride, the solution was brought to reaction temperature and stirring commenced. Shortly thereafter the vapor pressure of methyl chloride reached its equilibrium value and then remained sensibly constant throughout the rest of the reaction. The methyl chloride vapors were continually circulated through the Geiger-Müller counter and then recondensed on the solution by means of a thermal pump B.[9] The increase in radioactivity of the methyl chloride vapor was determined periodically by noting the counts per given time interval; in each reaction the

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would have been equally proper to use the dimeric form Al_2Br_6, since kinetically one cannot distinguish between them.

(9) S. U. Choi and J. E. Willard, *J. Am. Chem. Soc.*, **87**, 3072 (1965).

(10) O. C. Kwun and S. U. Choi, *J. Phys. Chem.*, **72**, 3148 (1968).

(11) A. Polaczek and A. Halpern, *Nukleonika*, **8**, 667 (1963); *Nature*, **199**, 1286 (1963).

(12) S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 2596 (1963).

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

(14) F. P. DeHaan, H. C. Brown, and J. C. Hill, *ibid.*, **91**, 4850 (1969).

(15) H. C. Brown, L. P. Eddy, and R. Wong, *ibid.*, **75**, 6275 (1953).

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

activity rose smoothly and exponentially. Computer analysis of the data from the first 75% of reaction yielded good values of the count rate at infinite time and the rate of exchange.

The results of these exchange reactions are tabulated in Table I. A typical run is shown in Figure 2.

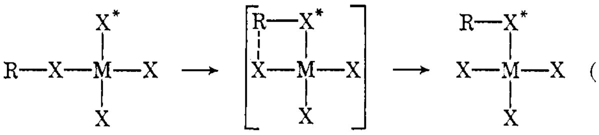
Table I. Rate Constants for the Chlorine-36 Exchange Reaction between Gallium Chloride and Methyl Chloride at −35.6°

Concn, *M*		Rate of exchange[a] × 10⁴ mol l.⁻¹ min⁻¹	Rate constant × 10⁴		
GaCl₃	CH₃Cl		k_1[b]	k_2[c]	k_3[d]
0.506	19.6	2.14	4.2	8.4 ± 0.2	16.5
1.00	18.9	7.9	7.9	7.9 ± 0.4	7.9
1.48	18.2	15.8	10.7	7.2 ± 0.3	4.9
			Av	7.8 ± 0.6	

[a] Calculated by means of a modified form of the quantitative exchange law, derived in the Appendix. [b] Rate/[$GaCl_3$] min^{-1}. [c] Rate/[$GaCl_3$]^2 l. mol^{-1} min^{-1}. [d] Rate/[$GaCl_3$]^3 l.^{2} mol^{-2} min^{-1}.

Discussion

A comparison of the relative rates of exchange and alkylation is of considerable interest. Since the rate of bromine exchange between gallium bromide and either methyl[9] or ethyl bromide[10] was considerably faster than the corresponding alkylation of either benzene or toluene,[12] there seemed to be the possibility that the rate of alkylation was limited by the rate of exchange. For example, one proposed mechanism of exchange[15] involved the nonionic intramolecular transfer of the alkyl group


(3)

If the center species of this equation was present as an unstable intermediate and if the corresponding alkylation reaction involved an attack by the aromatic on this species (or for that matter on an unstable ionic intermediate), the rate of exchange would provide an upper limit to the rate of alkylation.

A comparison of the gallium chloride catalyzed exchange and methylation reactions provides an answer to this question. It is apparent from Table II that the rate of methylation can exceed the rate of exchange. This is supported by the fact that alkylation reactions occurring at a greater velocity than the exchange reactions remain first order in the aromatic. Therefore the two reactions cannot proceed through the same rate-determining intermediate.

Table II. A Comparison of the Gallium Chloride Catalyzed Rates of Chlorine Exchange with Methyl Chloride and the Rates of Gallium Chloride Catalyzed Methyl Chloride Methylation of Aromatics

Reaction (at −35.6°)	Max rate obsd at 1 *M* GaCl₃ concn, mol l.⁻¹ min⁻¹
Chlorine-36 exchange	7.9 × 10⁻⁴
Methylation of benzene[b]	1.6 × 10⁻⁴ [a]
Methylation of toluene[c]	7.9 × 10⁻⁴ [a]
Methylation of *m*-xylene[c]	60 × 10⁻⁴ [a]

[a] Zero-time value for reactions 1 *M* in aromatic. [b] Reference 13. [c] Reference 14.

The available data on the enthalpies and entropies of activation of the gallium or aluminum halide–alkyl halide isotope exchange reactions[17] are summarized in Table III. On the basis of the similarities in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and the fact that the same rate law (4) appears to hold in each case, one is tempted to suggest that all of these reactions proceed through a common mechanism.

Table III. Enthalpies and Entropies of Activation of Gallium or Aluminum Halide–Alkyl Halide Isotope Exchange Reactions

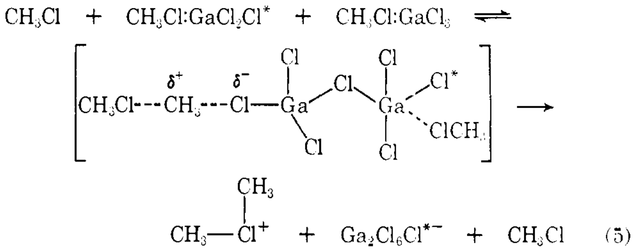
System	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)
$AlBr_3$–C_2H_5Br–CS_2[a]	11	−23
$GaBr_3$–CH_3Br–1,2,4-$C_6H_3Cl_3$[b]	13	−24
$GaBr_3$–C_2H_5Br–1,2,4-$C_6H_3Cl_3$[c]	8	−40
$GaBr_3$–CH_3Br–$C_6H_5NO_2$[b]	17[d]	−22[d]
$GaBr_3$–C_2H_5Br–$C_6H_5NO_2$[c]	12	−29

[a] Calculated *via* the McKay equation from the rate constants and temperatures reported in ref 7. [b] Calculated *via* the McKay equation from the rate constants and temperatures reported in ref 9 [c] Reference 10. [d] These values were miscalculated in ref 10.

$$\text{rate} = k_3[MX_3]^2[RX] \qquad (4)$$

The gallium chloride–methyl chloride exchange appears to be consistent with the other data. The reaction is second order in gallium chloride (Table I) and quite probably first order in methyl chloride.[18] Unfortunately this could not be established, since methyl chloride was also the solvent. However, almost all the past evidence[19] (which will be discussed shortly) indicates that this reaction is first order in methyl chloride. We suggest that this first-order dependence may be due to a rate-determining attack by methyl chloride on two 1:1 addition compounds or an ion-pair dimer[20] formed from them (Schemes I and II).

Scheme I



$$CH_3Cl + CH_3Cl{:}GaCl_2Cl^* + CH_3Cl{:}GaCl_3 \rightleftharpoons$$

$$CH_3\text{—}\overset{\overset{\displaystyle CH_3}{|}}{Cl^+} + Ga_2Cl_6Cl^{*-} + CH_3Cl \qquad (5)$$

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(17) In these papers no correction was made for the presence of an appreciable amount of radioactive alkyl halide in the gas phase (see Appendix). Thus the calculated rate constants and therefore $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are in error to some unknown extent.

(18) The enthalpy and entropy of activation of this reaction were not determined. However, the values for the ethyl chloride–gallium chloride exchange reaction are typical: $\Delta H^{\ddagger} = 10.6 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = -22 \pm 4$ eu; F. P. DeHaan, M. G. Gibby, and D. R. Aebersold, *J. Am. Chem. Soc.*, **91**, 4860 (1969).

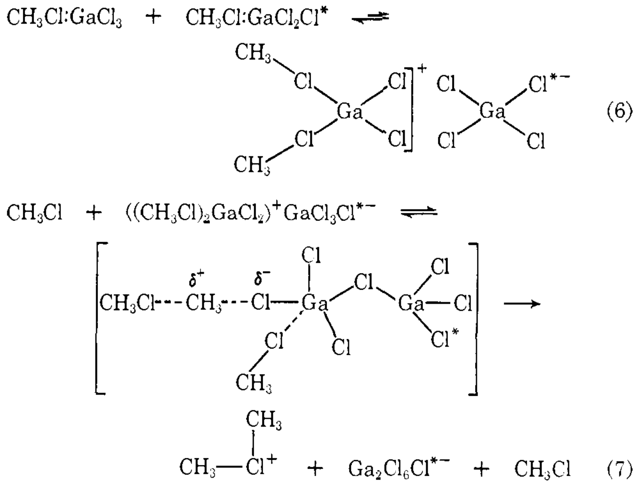
(19) The only exception, H. S. A. Dowes and E. C. Kooyman, *Rec. Trav. Chim.*, **83**, 276 (1964), mentions the unpublished work of M. J. Beers, thesis, Amsterdam, 1958, who found the rate law

$$R = k[AlBr_3]^2[n\text{-}PrBr]^{1/2}$$

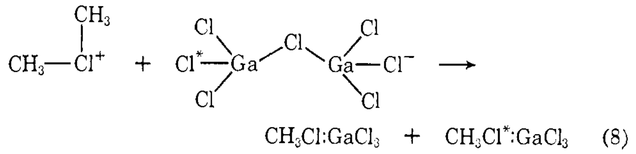
for the bromine exchange between aluminum bromide and *n*-propyl bromide.

(20) Evidence supporting the presence of small amounts of the ion-pair dimer (Scheme II) was given in an earlier paper.[13]

Scheme II



This slow step would be followed in either case by a series of rapid reactions in which the chlorine exchange actually occurs. This could take place through a recombination of the ions or a collapse of the ion pair $[(CH_3)_2Cl^+][Ga_2Cl_6Cl^{*-}]$, the only requirement for exchange being the rotation of the anion before recombination.



$$CH_3Cl + CH_3Cl^*:GaCl_3 \rightleftarrows CH_3Cl^* + CH_3Cl:GaCl_3 \quad (9)$$

Both Schemes I and II follow the kinetic expression

$$\text{rate} = k_3[CH_3Cl:GaCl_3]^2[CH_3Cl] \quad (10)$$

As discussed earlier,[13] it appears that large excesses of methyl chloride at low temperatures will completely convert gallium chloride to the 1:1 addition compound, $CH_3Cl:GaCl_3$.[21] Since the methyl chloride:gallium chloride (dimer) ratio in these reactions was varied from 24:1 to 40:1, it follows that the concentration of 1:1 compund *is independent of the concentration of methyl chloride*. Thus eq 10 can be reduced to the form

$$\text{rate} = k[GaCl_3]^2[CH_3Cl] \quad (11)$$

The deduction of a reaction mechanism from the rate law of metal halide–alkyl halide halogen exchange in other solvents requires a quantitative knowledge of the degree of solvent–metal halide complexation as well as that between alkyl halide and metal halide. Consider the aluminum bromide–ethyl bromide exchange reaction in carbon disulfide.[7] Boiling-point elevation experiments show aluminum bromide to exist as the dimer Al_2Br_6 in carbon disulfide;[22] the catalyst also has a zero dipole moment in this solvent.[23] Thus it appears there is little or no complexation between these species. Granting this, we still must know the solute concentrations of uncomplexed ethyl bromide, uncomplexed aluminum bromide (dimer), and of any of their addition compounds existing in solution at the temperature of the exchange reaction studies.

These may be estimated in the following manner. In their elegant microwave study of the aluminum bromide catalyzed isomerization of *n*-propyl bromide, Adema, Teunissen, and Tholen[24] determined the equilibrium constant for the reaction

$$2n\text{-}C_3H_7Br + Al_2Br_6 \rightleftarrows 2n\text{-}C_3H_7Br:AlBr_3 \quad (12)$$

in carbon disulfide at 24.0°, $K = 1.3$ l. mol^{-1}. Because experimental values are lacking, we assume the analogous reaction involving ethyl bromide to have a similar equilibrium constant at this temperature.

The enthalpy change for the ethyl bromide–aluminum bromide reaction is also unknown. However it should be *at least* as exothermic as ΔH for the reaction

$$2CH_3Br + Al_2Br_6 \rightleftarrows 2CH_3Br:AlBr_3 \quad (13)$$

which has a value of $\Delta H = -11.4$ kcal.[25]

Using these values for K and ΔH, and assuming ΔH to be constant over the temperature range, we calculate a value of $K = 66$ l. mol^{-1} for the reaction

$$2C_2H_5Br + Al_2Br_6 \rightleftarrows 2C_2H_5Br:AlBr_3 \quad (14)$$

in carbon disulfide at −26.3°, the temperature at which Sixma[7] performed the bulk of his bromine exchange studies.

By means of our estimated value of the equilibrium constant together with the concentrations of ethyl bromide and aluminum bromide reported by Sixma, we determined estimated concentrations of uncomplexed ethyl bromide and aluminum bromide (dimer), and of the $C_2H_5Br:AlBr_3$ addition compound. The most significant feature of these results is this: we found that within the ethyl bromide:aluminum bromide (dimer) range of 5:1 to 80:1 at which Sixma worked, essentially all of the aluminum bromide is tied up as the 1:1 complex and the concentration of this complex *is independent of excess alkyl halide*. For example, Sixma's runs numbered 7 and 3 had initial concentrations $[C_2H_5Br] = 0.244$, $[Al_2Br_6] = 0.048$ and $[C_2H_5Br] = 0.921$, $[Al_2Br_6] = 0.0465$, respectively. For these runs, our calculations yielded for run 7: $[C_2H_5Br] = 0.156$, $[Al_2Br_6] \simeq 0.005$, $[C_2H_5Br:AlBr_3] = 0.086$; and for run 3: $[C_2H_5Br] = 0.831$, $[Al_2Br_6] \simeq 0.0015$, $[C_2H_5Br:AlBr_3] = 0.090$. Thus we are left with the surprising fact that even though a fourfold increase in ethyl bromide leaves the concentration of the 1:1 complex virtually unchanged, the reaction remains *first order in ethyl bromide*. In fact we find Sixma's data can best be represented by the expression

$$\text{rate} = k[C_2H_5Br:AlBr_3]^2[C_2H_5Br] \quad (15)$$

A mechanism involving the diethylbromonium ion, similar to Scheme I or II, is consistant with the data.

Kwun and Choi proposed a different mechanism for bromine exchange between gallium bromide and alkyl

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[21] Although a careful phase study of the type used earlier[15] was not attempted for the gallium chloride–methyl chloride system at −35.6°, the vapor pressure above each of the exchange reactions was determined (Figure 1). In each case the extent of the vapor pressure lowering from that of pure methyl chloride at −35.6° definitely shows the existence of gallium chloride in solution to be predominantly that of the monomeric rather than dimeric form. Moreover, in view of the fact that "free," *i.e.*, uncomplexed monomeric gallium chloride does not exist in solution, this may be taken as evidence that the 1:1 addition compound $CH_3Cl:GaCl_3$ is the major solute species in excess methyl chloride at −35.6°.

[22] E. P. Kohler, *Am. Chem. J.*, 24, 385 (1900).

[23] H. Ulich and W. Nespital, *Z. Elektrochem.*, 37, 559 (1931).

[24] E. H. Adema, A. J. J. M. Teunissen, and M. J. J. Tholen, *Rec. Trav. Chim.*, 85, 377 (1966).

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

bromides in nitrobenzene and 1,2,4-trichlorobenzene,[10] eq 16–18 (S = solvent). In solvents like nitrobenzene,

$$RBr + S\text{–}GaBr_3 \rightleftharpoons R^{\delta+}Br^{\delta-}GaBr_3 + S \quad (16)$$

$$S\text{–}GaBr_3 + R^{\delta+}Br^{\delta-}GaBr_3 \xrightarrow{\text{slow}} R^+Ga_2Br_7^- + S \quad (17)$$

$$S + R^+Ga_2Br_7^- \rightleftharpoons RBr + S\text{–}Ga_2Br_6 \quad (18)$$

this seems to be a plausable alternative mechanism. Aluminum halides exist in nitrobenzene as the monomeric addition compounds $C_6H_5NO_2:AlX_3$.[22,26,27] These solutions conduct very weakly, indicating the addition compounds to be of the polarized rather than ion-pair type.[27] Plotnikov and Vaisberg[28] report a heat of solution of aluminum bromide in nitrobenzene of 24.5 kcal/mol, much higher than found with alkyl halides (*e.g.*, with ethyl bromide 0.95 kcal/mol[29]). Since methyl and ethyl bromide are much weaker bases than nitrobenzene, reaction 16 would lie far to the left. Two important conclusions follow: (1) the RBr:$GaBr_3$ complex is dependent upon the concentration of the alkyl bromide even if the alkyl bromide is in excess, and (2) the formation of a RBr:Ga_2Br_6 complex analogous to (6) may be inhibited entirely.

It may be that a weak nucleophile like an alkyl halide can affect alkyl group transfer only with the more polar 1:2 (or ion-pair) complex; thus (17) is a reasonable rate-determining step in nitrobenzene rather than a reaction like (5) or (7). However any meaningful further discussion of the mechanism must await an accurate determination of the solute species in this system and their concentrations.

Aluminum bromide exists in 1,2,4-trichlorobenzene as the 1,2,4-$C_6H_3Cl_3$:Al_2Br_6 complex.[26] Although the 1,2,4-trichlorobenzene–gallium bromide system was not studied, the data, Table IV, appear to rule out a 1,2,4-$C_6H_3Cl_3$:$GaBr_3$ complex. Therefore mechanisms 16–18 would not be applicable to the exchange reactions made thus far in this solvent. Again, definite conclusions concerning the mechanism of this reaction cannot be made until the solute species are identified and their concentrations determined.

Table IV. Solute Species Present in the Solutions of Aluminum and Gallium Bromides in Halobenzenes[a]

Solvent	Freezing pt, °C	$AlBr_3$	$GaBr_3$
Fluorobenzene	−42	1:2[b]	Uncomplexed dimer
Chlorobenzene	−45	1:2	Uncomplexed dimer
o-Dichlorobenzene	−17	1:2	
1,2,4-Trichlorobenzene	17	1:2	
Bromobenzene	−31	1:1[c]	1:2
Iodobenzene	−31		1:1

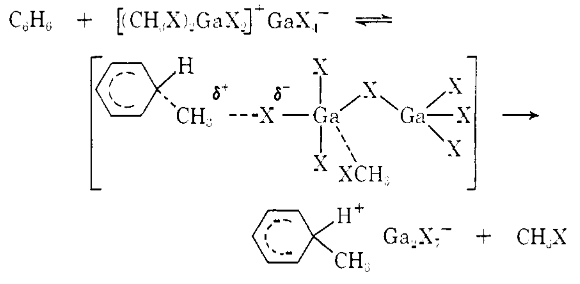
[a] Data taken from ref 26. [b] Halobenzene: M_2X_6. [c] Halobenzene: MX_3.

The mechanisms proposed, Schemes I and II, involve the dialkyl chloronium and bromonium ions $(CH_3)_2Cl^+$ and $(C_2H_5)_2Br^+$. Although they appear unusual, the tendency for onium salt formation among elements of periodic groups five, six, and seven is well known.[30] Cyclic and dialkylhalonium ions have been proposed as reaction intermediates.[31] Olah and coworkers[32] have now prepared a number of cyclic halonium (chlorine, bromine, iodine) ions which are stable in antimony pentafluoride–sulfur dioxide solution at −60°. Since species of the type we propose have just been prepared in solution[33] we feel their presence as unstable intermediates to be reasonable, especially since it explains the similarity between the rates of reaction (Table II) and the enthalpies and entropies of activation (Tables III and V) of the alkylation and exchange reactions. This can be easily seen by comparing the proposed rate-determining step of the exchange mechanism (7) with that proposed for the gallium halide catalyzed alkylation reactions in excess aromatic[34] and methyl chloride.[13]

Table V. Enthalpies and Entropies of Activation of Friedel–Crafts Alkylation Reactions

System	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)
$GaBr_3$–CH_3Br–C_6H_6[a]	12	−29
$GaBr_3$–C_2H_5Br–C_6H_6[a]	12	−23
$GaBr_3$–CH_3Br–$C_6H_5CH_3$[a]	12	−27
$GaBr_3$–C_2H_5Br–$C_6H_5CH_3$[a]	11	−22
$AlBr_3$–CH_3Br–C_6H_6–1,2,4-$C_6H_3Cl_3$[b]	15	−20
$AlBr_3$–C_2H_5Br–C_6H_6–1,2,4-$C_6H_3Cl_3$[b]	11	−25

[a] Reference 34. [b] H. Jungk, C. R. Smoot, and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 2185 (1956).



(19)

Experimental Section

Apparatus. All experiments were carried out using a high vacuum apparatus and the usual vacuum line techniques.

The exchange reaction system, patterned after the phase study system of Byrne,[35] is shown in Figure 1.

The exchange reaction solution was stirred with a Teflon-covered magnetic stirring bar A. By means of a thermal pump B similar to that of Choi and Willard,[9] the methyl chloride vapor was circulated continuously through an all glass GM tube C having a Pyrex window thickness of 30 mg/cm². A coiled capillary connected this system to a mercury monometer through stopcock D. Counting was accomplished by means of a scalar and an Ametron counter containing a print out mechanism and an adjustable repeat-cycle timer.

Materials. The purification and handling of methyl chloride (Matheson, 99.5% pure) was described previously.[15] Gallium chloride containing ^{36}Cl was prepared through the reaction between the metal (Alcoa, 99.95% pure) and diluted dry ^{36}HCl (Oak Ridge

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[26] S. U. Choi, Ph.D. Thesis, Purdue University, 1957.

[27] R. E. VanDyke and H. E. Crawford, *J. Am. Chem. Soc.*, 73, 2018 (1951).

[28] V. A. Plotnikov and R. G. Vaisberg, *Zap. Inst. Chim. Akad. Nauk SSSR*, 7, 71 (1940); *Chem. Abstr.*, 35, 2405 (1941).

[29] N. N. Lebedev, *J. Phys. Chem. USSR*, 22, 1505 (1948).

[30] H. G. Heal, *J. Chem. Educ.*, **35**, 192 (1958).

[31] For example see I. Roberts and G. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937); P. E. Peterson and F. J. Slama, *ibid.*, **90**, 6516 (1968); E. D. Cohen and C. N. Trumbore, *ibid.*, 87, 964 (1965).

[32] See G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968), and earlier papers.

[33] G. A. Olah and J. R. DeMember, *ibid.*, **91**, 2113 (1969).

[34] C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6245, 6249 (1956).

[35] J. J. Byrne, Ph.D. Thesis, Purdue University, 1958.

National Laboratories) gas at 300°. Purification methods were mentioned earlier.[13]

Kinetic Procedure. A known amount of radioactive gallium chloride was sublimed into the bottom of the apparatus (Figure 1) in a manner similar to that described by Choi and Willard.[9] The quantity of methyl chloride necessary for a predetermined solution concentration was then condensed on top of the gallium chloride at −196°. Reaction temperatures were maintained by means of 1,2-dichloroethane slush baths.[36]

Calculations. Determination of Reactant Concentrations. A first-order value of the solution volume was calculated in a manner described elsewhere.[13] The difference between this value and the apparent volume[37] of the exchange system is the volume occupied by the methyl chloride in the gas phase. The number of moles of methyl chloride vapor followed from this difference together with the average temperature and pressure above the solution. This value was subtracted from the total number of moles of methyl chloride to give more correct solution concentrations.

Curve Fitting. For our purpose the quantitative exchange law equation, as derived in the Appendix is

$$\ln [A_\infty/(A_\infty - A)] = k't \qquad (20)$$

where $k' = R[(1 + \alpha)a + nb]/nab$; R is the rate of exchange; α is the ratio of moles of methyl chloride in the gas phase to that in solution; a and b are the molar concentrations of methyl chloride and gallium chloride, respectively. A and A_∞ are the counts per minute values of gaseous methyl chloride at time t and $t = \infty$; n is the number of equivalent halide atoms per molecule of metal halide (taken here as 3). Because it was often impractical to obtain an experimental value of A_∞, an IBM 1620 computer was programmed to guess A_∞ in a systematic fashion until the standard deviation σ for the least-squares calculated k' was minimized.

Error Analysis. The total uncertainty in the rate constant was taken to be due to the uncertainty in the metal halide concentration, the reaction temperature fluctuation (typically ±0.25°), and the uncertainty in the curve-fitting process σ (in these reactions σ varied from 0.017 to 0.036). Errors in time measurement were negligible. Thus we have, assuming these factors to be independent[38]

$$\Delta k = k\{(p\Delta b/b)^2 + [(\Delta H^{\ddagger} + RT)/RT]^2(\Delta T/T)^2 + \sigma^2\}^{1/2} \qquad (21)$$

where p is the reaction rate order of the metal halide. The enthalpy of activation $\Delta H^{\ddagger}$ was assumed to be 13 kcal/mol (Table III).

Implicit in this method of following an exchange reaction is the assumption that the rate of passage of tagged methyl chloride from the solution into the counter is fast relative to the rate of exchange. This was tested in the following way. During the second exchange reaction the solution was cooled to −78.5°, thoroughly stirred, and brought back to reaction temperature. The count rate was unaffected by this procedure. This test was performed near the end of the reaction and consequently may not be too meaningful. However Choi[9] followed exchange reactions which were considerably faster in a similar apparatus; he found he could not affect the observed rate of exchange by changing either the rate of stirring or the volume of the system. Thus it appears safe to say that we were observing the true rate of exchange and not a rate of diffusion.

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Appendix

Derivation of a More General Quantitative Exchange Law Equation. For isotopic exchange reactions in a stable homogeneous phase

$$AX + BX^* \rightleftharpoons AX^* + BX \qquad (22)$$

the rate R at which X atoms exchange is given by the McKay equation[39]

$$R = \frac{ab}{(a + b)t} \ln \left(\frac{x_\infty}{x_\infty - x}\right) \qquad (23)$$

where $a = [AX] + [AX^*]$; $b = [BX] + [BX^*]$; x and x_∞ are the specific activities of the originally untagged species, AX, at time t and $t = \infty$, respectively.

Although it has been used, the McKay equation is either not applicable or an approximation under conditions such that one of the exchanging species exerts a vapor pressure above the reaction solution. Consider the case in which the originally untagged species AX is the volatile species. Let a, b, x, y signify the total *solution* concentrations of [AX] + [AX*], [BX] + [BX*], [AX*], and [BX*], respectively. The rate of increase (dx/dt) of AX* *in solution*, following Friedlander, Kennedy, and Miller,[40] is

$$\frac{dx}{dt} = R\frac{y}{b}\frac{(a - x)}{a} - R\frac{x}{a}\frac{(b - y)}{b} = R\left(\frac{y}{b} - \frac{x}{a}\right) \qquad (24)$$

Since the total number of radioactive atoms must be conserved[41] we have

$$(1 + \alpha)x + y = (1 + \alpha)x_\infty + y_\infty \qquad (25)$$

where α = (moles of gaseous AX)/(moles of AX in solution). We have assumed that the specific activity of the gas phase is at all times equal to that of AX in the liquid phase.

When equilibrium is reached, at $t = \infty$, $dx/dt = 0$ and (24) reduces to

$$y_\infty/b = x_\infty/a \qquad (26)$$

or in other words, the specific activity of BX equals that of AX *in solution* (and for that matter, of AX in the gas phase as well).

The elimination of y_∞ from (25) and then y from (24) yields

$$\frac{dx}{dt} = R\left[\frac{(1 + \alpha)a + b}{ab}\right](x_\infty - x) \qquad (27)$$

which upon integration gives

$$R = \frac{ab}{[(1 + \alpha)a + b]t} \ln \left(\frac{x_\infty}{x_\infty - x}\right) \qquad (28)$$

When allowance is made for molecules containing n equivalent X atoms, BX_n, we have

$$R = \frac{nab}{[(1 + \alpha)a + nb]t} \ln \left(\frac{x_\infty}{x_\infty - x}\right) \qquad (29)$$

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[36] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley & Sons, Inc., New York, N. Y., 1948.

[37] The apparent volume of the exchange system was determined by measuring the pressure of a known amount of carbon dioxide in this system when a low-temperature bath was in its usual position and the thermal pump was at its usual temperature.

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

[39] H. A. C. McKay, *Nature*, 142, 997 (1938).

[40] G. Friedlander, J. W. Kennedy, and J. M. Miller "Nuclear and Radiochemistry," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1964, pp 196–198.

[41] We assume the necessary corrections for radioactive decay have been made.