Kinetics of the Halogen-exchange Reaction Between Alkyl Halides (RY) and Boron Trihalides (BX_3). Evidence for Formation of Adducts RY,BX_3

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A kinetic study has been made of the halogen-exchange reactions: $RY + BX_3 \longrightarrow RX + BX_2Y$ (R = Pr^n, Pr^i, Bu^n, Bu^s, or Me_3Si; Y = Cl or Br; X = Br or I), where X is heavier than Y, in cyclohexane or CCl_4 at 306·5 K by use of ^1H and ^{11}B n.m.r. spectroscopy. For all these reactions, the initial rate (r_0) depends on the initial concentrations of the reactants according to the relationship: $r_0 = k_3[RY]_0{}^2[BX_3]_0 + k_2[RY]_0[BX_3]_0$. In most of the systems studied, the reactions are simply third-order (k_2 negligible), but cases showing second-order (k_3 negligible) or mixed- (second- plus third-)order kinetics are also found. Reactions of Bu^tCl with BBr_3 or BI_3 are immeasurably fast, whereas those of Pr^nCl or Bu^nCl with BBr_3 are immeasurably slow under the conditions used. Only for reactions of isobutyl halides, which showed more complicated kinetic behaviour, was any isomerization of the alkyl groups detected (in these cases to t-butyl halide). The temperature-dependence of the rate of reaction of Pr^iCl with BBr_3 (in CCl_4) has also been studied. Possible mechanisms for the reactions are suggested, requiring initial adduct formation of type RY,BX_3.

RELATIVELY little is known about the donor properties of the halogen atom in alkyl halides. Complexes with Group IIIB trihalides have been implicated as intermediates in Friedel–Crafts alkylations [1-5] and kinetic and other evidence has been presented for the formation of unstable adducts RCl,AlX_3 (X = Cl or Br),[6] $EtBr,AlBr_3$,[7] and $RBr,GaBr_3$ (R = Me or Et).[8,9] Evidence for such interactions involving boron trihalides has been limited to low-temperature studies with BF_3,[10-12] and to interpretation of phase diagrams of $RCl–BCl_3$ systems.[13,14] In the latter investigations it was suggested that species '$EtCl(BCl_3)_2$' and '$(Pr^iCl)_3BCl_3$' were formed in the temperature range −100 to −150 °C, but such deductions are by no means unequivocal.

We sought vibrational spectroscopic evidence for interaction of the type $RY \cdots BX_3$, similar to that described [15,16] for $C_6H_6 \cdots BX_3$ systems. However, we found that the dominant feature was that of halogen-exchange which afforded compounds RX and $BX_{3-n}Y_n$ (n = 1, 2, or 3). Moreover, large variations in rate with changing R, X, and Y were apparent, and we undertook a kinetic study of these reactions in order to quantify these variations further. Very few data are available on the kinetics of substitution at 3-co-ordinate species such as boron trihalides, probably because such reactions are usually very fast, although several thermodynamic studies have been reported.[17] Further interest in these systems arises from the use of boron trihalides as halogenating agents.[18-20]

As we shall show, the present kinetic study affords strong evidence for formation of adducts of type RY,BX_3.

EXPERIMENTAL

The most convenient way of following the course of the the reactions studied was found to be by use of ^1H n.m.r. spectroscopy to measure the concentrations of the alkyl halides at suitable intervals. Measurements of ^{11}B n.m.r. spectra were also made on some systems. The procedures adopted have been described in detail,[21] and are given here in outline only.

Materials.—In view of the ease of hydrolysis of the boron trihalides and of the probable effect of hydroxylic compounds on the reaction rates, all reagents were carefully purified and stored under rigorously anhydrous conditions. Glassware was dried at 160 °C. Manipulations were carried out in an atmosphere of dry nitrogen.

Preparation of Solutions.—This was carried out by weighing the components directly into n.m.r. tubes which were then sealed with a flame and stored at −78 °C until used (less than 2 days). The volumes of the solutions (required to calculate the molar concentrations) were obtained from the known densities of the liquids or from pre-calibration of the n.m.r. tubes.

N.m.r. Spectra.—These were obtained with a Perkin-Elmer R10 spectrometer operating at 60 MHz (^1H) or 19·25 MHz (^{11}B). Spectra were recorded at the normal instrument temperature of $306·50 \pm 0·01$ K, or (^1H measurements only) at $333·0 \pm 0·5$ and $353·0 \pm 0·5$ K by use of the variable temperature probe.

Concentration Measurements.—The kinetics of the reactions studied were followed by noting the changes with

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time in the areas under suitable ^{1}H n.m.r. peaks arising from the alkyl halides present in the solutions. Where the signals due to the initial (RY) and product (RX) alkyl halides partially overlapped, careful calibration methods were used.[21] The areas were measured either by using a planimeter, or by cutting out and weighing the relevant peaks on the chart paper.

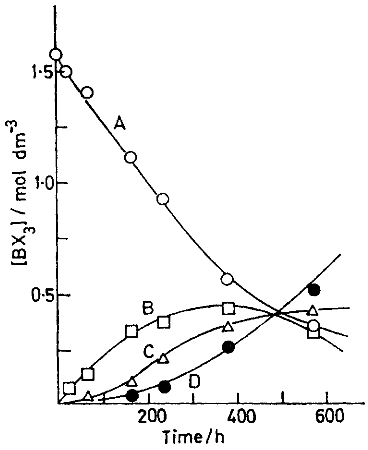

FIGURE 1 Variation in concentrations of boron trihalides with time during reaction of Bu^{n}Cl with BI$_3$ at 306·5 K; $[Bu^nCl]_0$ = 7·86 mol dm^{-3}; A, $[BI_3]$; B, $[BClI_2]$; C, $[BCl_2I]$; D, $[BCl_3]$

RESULTS

Figure 1 shows the variation of concentrations of halogenoboron species with reaction time, as obtained from ^{11}B n.m.r. measurements on a solution containing Bu^{n}Cl and BI$_3$. Other solutions on which similar measurements were made gave analogous results. These curves show that replacement of X in BX$_3$ by Y of RY follows the step-wise sequence (1). The situation is complicated by the occurrence of the well-known redistribution reactions[17,22]

$$BX_3 \xrightarrow{RY} BX_2Y \xrightarrow{RY} BXY_2 \xrightarrow{RY} BY_3 \qquad (1)$$

(2)—(4). A complete analysis of the kinetics of these

$$2BX_2Y \rightleftharpoons BX_3 + BXY_2 \qquad (2)$$

$$2BXY_2 \rightleftharpoons BX_2Y + BY_3 \qquad (3)$$

$$BX_2Y + BXY_2 \rightleftharpoons BX_3 + BY_3 \qquad (4)$$

systems is seemingly intractable. However, during the initial stages of the reaction the concentrations of the mixed halogenoboranes will be insignificant compared with that of BX$_3$, and it may be assumed that the scrambling reactions of the mixed species are insignificant. It thus becomes possible to describe the ***initial*** reaction rate in terms of the kinetics of the first exchange process (5).

$$RY + BX_3 \longrightarrow RX + BX_2Y \qquad (5)$$

These reactions were found to occur only when X was heavier than Y (*cf.* refs. 23 and 24), so that the reverse reaction may be considered as negligible.

Rate constants [a] at 306·5 K for the reactions RY + BX$_3$ ⟶ RX + BXY

	BX$_3$ = BBr$_3$			BX$_3$ = BI$_3$		
RY	Solvent	10^8k_2/mol^{-1} dm^3 s^{-1}	10^8k_3/mol^{-2} dm^6 s^{-1}	Solvent	10^8k_2/mol^{-1} dm^3 s^{-1}	10^8k_3/mol^{-2} dm^6 s^{-1}
Pr^{n}Cl	*b*	Slow [c]		C$_6$H$_{12}$	0	1·42 ± 0·23
Pr^{n}Br		*d*		C$_6$H$_{12}$	0	0·504 ± 0·042
Pr^{i}Cl	CCl$_4$ [e,f]	0	21·8 ± 1·4	C$_{61}$D$_2$ [e]	0	213 ± 13
	CH$_2$Cl$_2$	1290 ± 140 [g]	0			
Pr^{i}Br		*d*		C$_6$H$_{12}$	40 ± 8	0
Bu^{n}Cl	*b*	Slow [c]		C$_6$H$_{12}$	0	1·19 ± 0·09
Bu^{s}Cl		N.s.[h]		C$_6$H$_{12}$	0	818 ± 48
Bu^{t}Cl	CCl$_4$ [e]	Fast [i]		C$_6$D$_{12}$ [e]	Fast [j]	
Me$_3$SiCl	C$_6$H$_{12}$	35·8 ± 9·6	12·9 ± 4·8	C$_6$H$_{12}$	122 ± 8	0
Me$_3$SiBr		*d*		C$_6$H$_{12}$	417 ± 118	246 ± 58

[a] Errors quoted are standard deviations of slopes of best straight lines from plots of types shown in Figures 4 and 5 as appropriate. [b] No solvent used. [c] No reaction observed after *ca.* 2 months at 306·5 K. [d] The n.m.r. method is not applicable when Y = X. [e] N.m.r. signal of C$_6$H$_{12}$ obscures those of alkyl groups; BI$_3$ insufficiently soluble in CCl$_4$. [f] At 333 K: $k_2 = 0$, $10^8k_3 = 233 \pm 8$ mol^{-2} dm^6 s^{-1}; at 353 K: $k_2 = 0$, $10^8k^3 = 750 \pm 20$ mol^{-2} dm^6 s^{-1}. [g] Mean of 3 determinations. [h] N.s. = Not studied. [i] At 283 K, minimum value of initial rate of reaction (r_0) = $5{\cdot}77 \times 10^{-3}$ mol dm^{-3} s^{-1} when $[Bu^tCl]_0 = 1{\cdot}18$, $[BBr_3]_0 = 0{\cdot}751$ mol dm^{-3}; for Pr^{i}Cl and BBr$_3$ at similar initial concentrations at 306·5 K, r_0 = *ca.* $2{\cdot}5 \times 10^{-7}$ mol dm^{-3} s^{-1}. [j] Rate too large at 283 K to be measured by this method.

The System Pr^{i}Cl/BBr$_3$.—This reaction was studied in most detail and will serve as a general example of the methods used to treat the data obtained from the other systems. All experimental data are in ref. 21.

For each solution studied, the initial rate of reaction (r_0) was determined from the slope at zero time of a plot of [RY] as a function of time. The value of r_0 can be expressed as (6), where the suffixes refer to initial (' make-up ')

$$r_0 = k[Pr^iCl]_0^n[BBr_3]_0^m \qquad (6)$$

concentration values. By use of standard kinetic procedures, the value of $m = 1$ was shown by the linearity of a plot of r_0 against $[BBr_3]_0$ at various constant values of $[Pr^iCl]_0$ (Figure 2). On the other hand, with $[BBr_3]_0$ held constant, r_0 was found to be a distinctly non-linear function of $[Pr^iCl]_0$, but linear with respect to $[Pr^iCl]_0{}^2$ as shown in Figure 3. Hence the initial reaction between Pr^{i}Cl and BBr$_3$ may be described by the overall third-order kinetic equation (7). From plots of $r_0/[Pr^iCl]_0[BBr_3]_0$ against

$$r_0 = k_3[Pr^iCl]_0{}^2[BBr_3]_0 \qquad (7)$$

$[Pr^iCl]_0$ (Figure 4), values of k_3 at 306·5, 333, and 353 K were obtained by least-squares regression analysis as given in the Table.

Other Systems showing Third-order Kinetics.—By use of

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[22] M. F. Lappert, M. R. Litzow, J. B. Pedley, T. R. Spalding, and H. Nöth, *J. Chem. Soc.* (*A*), 1971, 383.

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analogous procedures to the above, third-order kinetics (second-order in $[RY]_0$, first-order in $[BX_3]_0$) were found for the initial reactions between BI_3 and the alkyl halides RCl (R = Pr^n, Pr^i, Bu^n, or Bu^s) and Pr^nBr. Values obtained for the rate constants k_3 from plots of $r_0/[RY]_0[BI_3]_0$ as functions of $[RY]_0$ are listed in the Table.

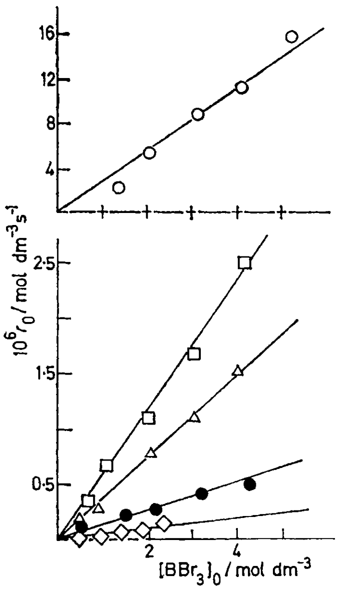

Figure 2 Plots of initial rate of reaction against initial concentration of BBr_3 in CCl_4 at 306·5 K for constant values of $[Pr^iCl]_0$ as follows: ○, 3·31; □, 1·67; △, 1·18; ●, 0·607; ◇, 0·348 mol dm^{-3}

Systems showing 'Mixed-order' Kinetics.—Application of statistical *F*- and *t*-tests [25] to the data obtained on the systems described as following third-order kinetics, showed that within experimental error the plots of type shown in Figure 4 pass through the origin.[21] However, for the initial reactions of Me_3SiCl with BBr_3, and of Me_3SiBr with BI_3, corresponding kinetic plots show intercepts which are significantly non-zero, and thus the kinetics follow the relationship (8). Previous reports that Me_3SiCl does not

$$r_0 = k_3[Me_3SiY]_0^2[BX_3]_0 + k_2[Me_3SiY]_0[BX_3]_0 \qquad (8)$$

react with BBr_3 under conditions of prolonged reflux [18,19] are inexplicable in the light of our results. Values for the third- and second-order rate constants obtained are shown in the Table.

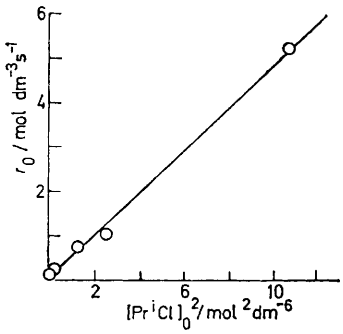

Figure 3 Variation of r_0 with $[Pr^iCl]_0^2$ for the reaction of Pr^iCl with BBr_3 in CCl_4 at 306·5 K with the value of $[BBr_3]_0$ held constant at 2·03 mol dm^{-3}

Systems showing Second-order Kinetics.—For the reactions of Pr^iBr or Me_3SiCl with BI_3, first-order dependence of the initial rate on the alkyl (or silyl) halide was found (Figure 5 and Table) showing that $r_0 = k_2[RY]_0[BI_3]_0$.

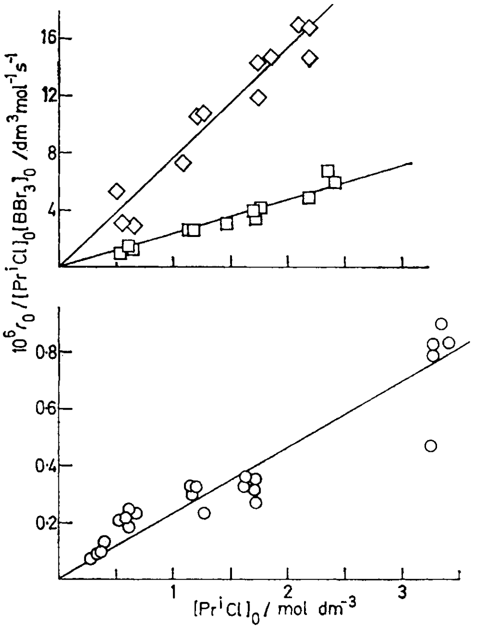

Figure 4 Plots of the overall third-order rate equation for the reaction of Pr^iCl with BBr_3 in CCl_4 at the following temperatures: ○, 306·5 K; □, 333 K; ◇, 353 K

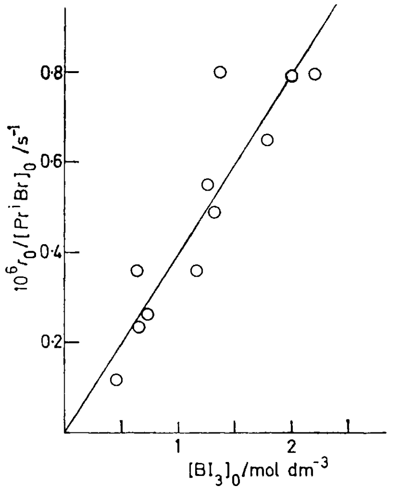

Figure 5 Second-order rate plot for reaction of Pr^iBr with BI_3 in C_6H_{12} at 306·5 K. A similar result was obtained for the reaction between Me_3SiCl and BI_3 in C_6H_{12} at 306·5 K

Rearrangement of Alkyl Groups.—In all the aforementioned systems, the alkyl halide (RX) produced in the reactions showed no rearrangement compared with the starting compound (RY). However, during reactions of Bu^iY with BI_3 (Y = Cl or Br) or BBr_3 (Y = Cl), small amounts of Bu^tI or Bu^tBr respectively were also formed. These re-

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[25] W. J. Youden, 'Statistical Methods for Chemists,' Wiley, New York, 1959.

actions were found not to conform to any simple kinetic behaviour, and clearly involve several competing mechanisms.

Other Systems.—No reaction could be detected between Pr^nCl or Bu^nCl and BBr_3 at 306·5 K even in the absence of solvent. In contrast, halogen-exchange between Bu^tCl and BBr_3 or BI_3 was immeasurably fast at this temperature (Table).

Temperature-dependence of Rate Constants.—The initial reaction between Pr^iCl and BBr_3 was found to follow the same third-order rate law at 333 and 353 K as at 306·5 K. The values of k_3 at these temperatures (Table) were used to determine the following values for kinetic parameters, from the good linear plots obtained of ln k_3 and ln (k_3/T) against $1/T$: $E^\ddagger = 70{\cdot}4$ kJ mol^{-1} (16·8 kcal mol^{-1}); $\Delta H^\ddagger = 66{\cdot}6$ kJ mol^{-1} (15·9 kcal mol^{-1}); and $\Delta S^\ddagger = -155$ J K^{-1} mol^{-1} ($-36{\cdot}9$ cal deg^{-1} mol^{-1}).

DISCUSSION

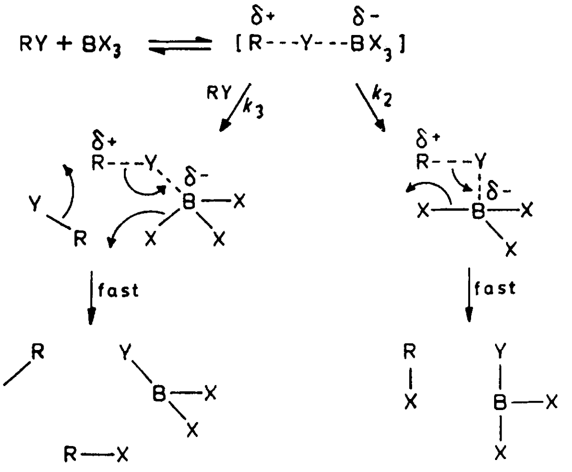
The kinetic results are summarised in the Table. In all the systems for which rate constants could be obtained, the initial rates may thus be fitted to the general equation (9). In most cases, pure third-order kinetics

$$r_0 = k_3[RY]_0^2[BX_3]_0 + k_2[RY]_0[BX_3]_0 \qquad (9)$$

are observed ($k_2 \longrightarrow 0$), but in two instances (Pr^iBr–BI_3 and Me_3SiCl–BI_3) the second-order term predominates ($k_3 \longrightarrow 0$), whereas in two further systems (Me_3SiCl–BBr_3 and Me_3SiBr–BI_3) both terms are significant.

In suggesting a mechanism (or mechanisms) consistent with these data, the following observations must also be considered: (i) the initial rate of reaction between Pr^iCl and BBr_3 is greater in CH_2Cl_2 than in CCl_4 solution by a factor of *ca.* 25; the kinetics are of the second order in CH_2Cl_2 but of third order in CCl_4 solution; (ii) Pr^nCl reacts 3 times more rapidly with BI_3 than does Pr^nBr; (iii) reaction of Pr^iCl with BI_3 is an order of magnitude faster than with BBr_3; (iv) with other factors being equal, the rate of reaction decreases with respect to alkyl groups as follows: $Bu^t \gg Bu^s > Pr^i > Bu^n \sim Pr^n$; (v) no isomerization of the alkyl groups was detected in these cases; and (vi) reaction of BBr_3 with Me_3CCl is very much faster than with Me_3SiCl.

The mechanism shown in the Scheme appears to be in accord with these criteria. The effect of the polar CH_2Cl_2 solvent is thus seen to be consistent with increased solvation of the $[R \cdots Y \cdots BX_3]$ complex, resulting in competition of CH_2Cl_2 with the second molecule of RY. The variations observed in the third-order rate constants with varying R, Y, and X can be rationalized at least in part by consideration of such factors as inductive effects of R, acceptor properties of BX_3, polarizability of C–Y bonds, *etc.* The value of $\Delta S^\ddagger$ for the Pr^iCl–BBr_3 reaction (-155 J K^{-1} mol^{-1}) is significantly more negative than is commonly observed (-80 to -125 J K^{-1} mol^{-1}) for bimolecular displacement reactions,[6] consistent with the third-order pathway suggested.



SCHEME

The second-order pathway is more likely to involve the 4-centre transition state shown in the Scheme than formation of an ion-pair $[R]^+[YBX_3]^-$ because (i) the solvent used is of low polarity; (ii) isomerization of the alkyl groups was not observed; (iii) the available evidence [26–28] is against the formation of siliconium ions in solution; and (iv) intermediates of this type have been frequently suggested in many redistribution reactions.[17,29–35]

Whatever the detailed mechanism of the first halogen-exchange reaction between RY and BX_3 (where X is heavier than Y), the occurrence of a third-order component to the rate can only reasonably be interpreted in terms of initial formation of an adduct RY,BX_3.

[2/930 *Received, 26th April,* 1972]

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