The Kinetics of Reactions of Chlorine, Bromine, Bromine Monochloride, Iodine Monochloride, and Iodine Monobromide with Phenyltrimethylsilane

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Halogens and interhalogens, XY, react with $PhSiMe_3$ in 98.5% aqueous acetic acid to give $(Me_3Si)_2O$, H^+, Y^-, and PhX (X = Y = Cl, Br; X = Br, Y = Cl; X = I, Y = Br or Cl). Kinetic measurements at 30.0 °C show that all reactions are first order in $PhSiMe_3$, reactions with BrCl and Cl_2 are first order in halogen, reactions with ICl and IBr are second order in halogen, and reactions with Br_2 involve both first- and second-order terms. Rate coefficients for all the reactions are reported. The kinetics of the reactions of Br_2, ICl, and IBr are complicated by formation of trihalide complexes between the halogen and halide ion product. The formation constants for these complexes have been measured, and a numerical integration method is described to calculate the rate coefficients for these halogenations from the experimental data.

SOME years ago one of us carried out a detailed study of the reaction between bromine and phenyltrimethylsilane [equation (1; X = Y = Br)] in solution in aqueous

$$XY + PhSiMe_3 \longrightarrow PhX + \tfrac{1}{2}(Me_3Si)_2O + H^+ + Y^- \quad (1)$$

acetic acid.[1,2] It was found that below a bromine concentration of *ca.* 0.005 mol dm^{-3} the reaction was first order in both bromine and silane [equation (2; X = Y = Br) with k_3 0] but that the overall order of reaction

$$d[\text{products}]/dt = k_2[XY][PhSiMe_3] + k_3[XY]^2[PhSiMe_3] \quad (2)$$

increased as the concentration of bromine increased due to a third-order reaction [k_3 term in equation (2; X = Y = Br)]. The reported second-order rate coefficients, k_2, were difficult to calculate [3] because of complex formation between the reactant bromine and bromide ion product [equation (3; X = Y = Br)] and no third-order rate

$$XY + Y^- \overset{K}{\rightleftharpoons} XY_2^- \quad (3)$$

coefficients, k_3, were evaluated. Chlorination of phenyltrimethylsilane [equation (1; X = Y = Cl)] was briefly studied and found to be overall a second-order reaction which was *ca.* 1.4 times faster than bromination.

Stock and Spector [4] studied the reaction of iodine monochloride with phenyltrimethylsilane in acetic acid [equation (1; X = I, Y = Cl)] and reported it to be first order in each reactant, with complex formation between ICl and Cl^- [equation (3)]. They calculated second-order rate coefficients, k_2, using an approximated, rather than the correct, integrated rate equation. We are unaware of any reports of reactions of other interhalogen compounds with arylsilanes.

We report here the relative reactivities of phenyltrimethylsilane with chlorine and bromine, and with the interhalogens bromine monochloride, iodine monochloride, and iodine monobromide. For each reaction the appropriate rate equation has been established, and relative reactivities are discussed in terms of the rate coefficients.

EXPERIMENTAL

Materials.—Phenyltrimethylsilane was purified by fractional distillation using a 60 cm annular Teflon spinning band column. The fraction boiling between 174.4 and 174.6 °C was collected and contained no impurities detectable by g.l.c. or n.m.r. analysis. AnalaR acetic acid was dehydrated by boiling with triacetyl borate,[5] and was then distilled. The appropriate volume of distilled water was added when making 98.5% aqueous acetic acid (acetic acid containing 1.5% wt. water) and the water content checked by measuring the f.p.[6]

AnalaR bromine, and fresh reagent grade iodine monochloride and iodine monobromide were used unpurified. Bromine monochloride was prepared by mixing equimolar solutions of bromine and chlorine in acetic acid. Chlorine from a cylinder was washed with water, passed through copper sulphate to remove hydrogen chloride, and dried over phosphorus pentaoxide. Potentiometric titration with silver nitrate of the halide ions derived from solutions of interhalogens by reduction with sodium sulphite showed that the two halogens in each case were present in a 1 : 1 molar ratio.

Kinetics.—Equal volumes of solutions of the reactants at the thermostat temperature (30.0 °C) were mixed. Samples were run into potassium iodide solution and the liberated iodine was titrated with sodium thiosulphate solution using a Radiometer Autotitrator TTT2 fitted with an Autoburette and recorder. A reaction vessel based on a gas syringe was used for chlorinations.[7] There was no air space above the solution and evaporation of chlorine into the usual space left after removal of a sample was prevented. Reaction vessels were covered with aluminium foil to keep out light.

Rate Coefficients.—For the reaction of a halogen or interhalogen with phenyltrimethylsilane (initial concentrations b_0 and a_0 respectively) the rate equation can be written as (4), where p and b are the concentrations of product and

$$dp/dt = k_2(a_0 - p)b + k_3(a_0 - p)b^2 \quad (4)$$

halogen present at time t. The reactions of chlorine and bromine monochloride with phenyltrimethylsilane are second order (*i.e.* k_3 is zero and $b = b_0 - p$) and rate coefficients were calculated using the usual integrated rate equations. For other halogenations (with bromine, iodine monochloride, and iodine monobromide) where the halogen XY can react with Y^- [equation (3)] the concentration of halogen, b, is given by equation (5) [3] where q is given by equation (6).*

$$b = [-q + \sqrt{q^2 - 4K(p - b_0)}]/2K \quad (5)$$

$$q = 2Kp + 1 - Kb_0 \quad (6)$$

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* The equations of Bradfield *et al.*[3] are given using an equilibrium constant $K = [Br_2][Br^-]/[Br_3^-]$ which is the inverse of K as generally defined and as used in this paper.

If the rate equation (4) includes only the first (k_2) term it can be integrated analytically to give a solution of the form $F(a_0,b_0,p,K) = k_2t$.[3] A plot of F against t should be linear with slope k_2. A computer program was used to calculate the least-squares slope of such plots.

For halogenations with bromine, iodine monochloride, and iodine monobromide the rate equation contains either only the k_3 term, or contains both k_2 and k_3 terms. Analytical integration is not possible for these and numerical integration was used. For the rate equation containing both k_2 and k_3 terms, values of k_2 and k_3 were guessed. Knowing the initial concentrations of the reactants, numerical integration using Gear's method [8] gave values of the concentration of products, p_t^{calc}, at various reaction times t making appropriate allowance for trihalide ion formation. These were compared with the experimentally measured concentrations, p_t^{exp} and the function $R = \sum_{t=0}^{=\infty} (p_t^{\text{calc}} - p_t^{\text{exp}})^2$ was calculated. Then new values of k_2 and k_3 were chosen and R recalculated. A minimisation procedure [9] was used to search for the values of k_2 and k_3 which give the smallest value of R, which were then the desired rate coefficients. This method was checked by setting $k_3 = 0$ and using the computer program to calculate the rate coefficient k_2 for a reaction where the value of k_2 could also be obtained using the integrated rate equation.[3] The two methods gave the same values for k_2. A similar method was used to calculate k_3 when only a k_3 term was present in the rate equation.

TABLE 1

Rate coefficients for the reaction of halogens and interhalogens, XY, with phenyltrimethylsilane in 98.5% aqueous acetic acid at 30.0 °C

XY	10^3 [XY] [a]/ mol dm^{-3}	10^5 [PhSiMe$_3$] [a]/ mol dm^{-3}	k_2/ dm^3 mol^{-1} s^{-1}	Mean k_2 [b]/ dm^3 mol^{-1} s^{-1}	k_3/ dm^6 mol^{-2} s^{-1}	Mean k_3 [b]/ dm^6 mol^{-2} s^{-1}	K [c]/ dm^3 mol^{-1}
Cl_2	2.87	2.86	0.0486	0.0487 (9)			
	8.55	8.50	0.0489				
Br_2	2.18	2.12	0.0345	0.0344 (9)			182
	87.2	200	0.0344 [d]		0.584	0.563 (4)	(340—360)
BrCl	3.13	8.16	2.34	2.32 (9)			
	10.8	12.0	2.38				
ICl	4.57	50			6.88	6.43 (10)	259
	34.4	32.5			6.00		(340—350)
	8.71	100			6.20		
IBr	14.1	20.0			0.52 [e]		523
	81.3	102			0.62 [e]	0.54 [e] (8)	(380)

[a] Representative runs given to show range of concentrations used. [b] Mean of all experiments, number of runs in parentheses. [c] Wavelength (nm) used to measure K shown in parentheses. [d] Fixed to calculate k_3 (see text). [e] Calculated from initial part of reaction.

Equilibrium Constants.—Values of K for the trihalide equilibria [equation (3)] were determined using the spectrophotometric method of Ketelaar *et al.*[10] A Unicam SP 500 spectrophotometer was used to measure absorbances at 30.0 °C of solutions containing XY and HY at wavelengths where the extinction coefficients of XY and XY_2^- are dissimilar. The wavelengths used are given in Table 1.

Product Analysis.—The appropriate reaction mixture (2 cm^3) (in 98.5% aqueous acetic acid) was shaken with tetrachloromethane (2 cm^3), and the acid neutralised with 2M-Na_2CO_3 solution. The organic layer was separated, dried (Na_2SO_4), and examined by g.l.c. using a 3.5 m column packed with 3% OV225 silicone on 100—120 mesh Gaschrom Q at 90 °C. Another portion of the tetrachloromethane solution was examined by 60 MHz n.m.r. spectroscopy.

RESULTS AND DISCUSSION

Reaction Products.—Chlorine and bromine react with phenyltrimethylsilane in 98.5% aqueous acetic acid to give chloro- or bromo-benzene and hexamethyldisiloxane. The interhalogens XY (XY = BrCl, ICl, and IBr) give hexamethyldisiloxane and PhX, but PhY is not found. Halogenations carried out in tetrachloromethane show that trimethylsilyl chloride or bromide, as appropriate, is formed first. Addition of deuterioacetic acid to trimethylsilyl chloride in tetrachloromethane does not give any trimethylsilyl acetate, but addition of a trace of water (D_2O) causes the rapid hydrolysis of trimethylsilyl chloride to hexamethyldisiloxane, probably *via* trimethylsilyl hydroxide as n.m.r. spectra show a trace of this compound. Analysis by g.l.c. and n.m.r. did not show any other aromatic or organosilicon products.

Reaction of Chlorine with Phenyltrimethylsilane.—Tables 1 and 2 give the values of k_2 found for this reaction. Rate measurements extended to 90% of reaction (over three half-lives) with no evidence of departure from second-order kinetics.

TABLE 2

Rate coefficients for the reactions of chlorine, iodine monochloride, and iodine monobromide with phenyltrimethylsilane in glacial acetic acid at 30.0 °C

Halogen	k_2/dm^3 mol^{-1} s^{-1}	k_3/dm^6 mol^{-2} s^{-1}	K/dm^3 mol^{-1}
Cl_2	0.020 [a]		
ICl		5.97 [b]	21.8
IBr		0.46 [c]	478

[a] [Cl_2] = 0.0258 mol dm^{-3}, [PhSiMe$_3$] = 0.0475 mol dm^{-3}. [b] Mean of 10 runs with similar concentration range to that in 98.5% aqueous acetic acid. [c] Mean of three runs with similar concentration range to that in 98.5% aqueous acetic acid, calculated from initial part of reaction.

Reaction of Bromine Monochloride with Phenyltrimethylsilane.—This reaction is also first order with respect to each reactant, and is much faster than the reaction of either bromine or chlorine; Table 1 gives the values of k_2 found. The higher reactivity of this polar molecule is not due to reaction by the very reactive electrophile Br^+, because although there may be a very low concentration of Br^+ in equilibrium with undissociated bromine monochloride at the start of reaction, chloride ions formed as product will effectively reduce the concentration of Br^+ to negligible amounts.

Bromine monochloride is extensively dissociated [equation (7)]. In tetrachloromethane K' is 0.145 (55%

$$2\,BrCl \overset{K'}{\rightleftharpoons} Br_2 + Cl_2 \qquad (7)$$

dissociation) [11] and White and Robertson [12] indicate that it is similarly dissociated in acetic acid. However we do not detect any chlorobenzene as a product as might be expected if free chlorine is present. This is in accord with the rate coefficients measured. The initial rates of formation of bromobenzene and chlorobenzene will be $(k_2^{BrCl}[BrCl] + k_2^{Br_2}[Br_2])[PhSiMe_3]$ and $k_2^{Cl_2}[Cl_2][PhSiMe_3]$ respectively, and the relative rate of formation of bromobenzene compared with chlorobenzene is given by equation (8). As k_2^{BrCl} is so much greater

$$d[PhBr]/d[PhCl] = (k_2^{BrCl}/K' + k_2^{Br_2})/k_2^{Cl_2} = 126 \qquad (8)$$

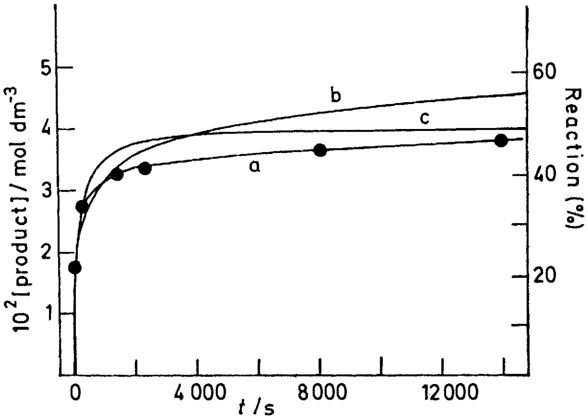
than $k_2^{Cl_2}$ only a tiny amount (1/126) of the product will be chlorobenzene.

Reaction of Bromine with Phenyltrimethylsilane.—We measured K for tribromide ion formation at 30.0 °C (Table 1) and our value in 98.5% aqueous acetic acid is the same (182 $dm^3\ mol^{-1}$) as that found earlier at 25 °C.[1]

At bromine concentrations below *ca.* 0.005 mol dm^{-3} bromination in 98.5% aqueous acetic acid is first order in each reagent,[1] and the k_2 values are given in Table 1. When the bromine concentration is above 0.005 mol dm^{-3}, calculated k_2 values increase as the bromine concentration increases suggesting that a higher order kinetic term in bromine is present. Data from kinetic runs at higher bromine concentrations have been used to calculate the value of k_3 (Table 1). Consistent values of k_3 were obtained by the numerical integration method if k_2 was set to the value found at low bromine concentrations. The contribution that the second-order term in bromine makes to the initial rate of bromination increases from 1.6% at $[Br_2]$ 0.001 mol dm^{-3} to 61.9% at $[Br_2]$ 0.1 mol dm^{-3}.

Reaction of Iodine Monochloride with Phenyltrimethylsilane.—The complex ion ICl_2^- formed during reaction is ineffective as an electrophile, and does not react with phenyltrimethylsilane. Its formation constant K falls from 259 in 98.5% aqueous acetic acid to 21.8 $dm^3\ mol^{-1}$ in glacial acetic acid. This is in accord with the reported decrease in K for the formation of Br_3^- as the water content of the solvent is reduced.[13] Study of the initial reaction rates, when formation of ICl_2^- can be neglected, over the range [ICl] 1—11 × 10^{-3} mol dm^{-3}, showed that in 98.5% aqueous acetic acid the orders of reaction with respect to iodine monochloride and phenyltrimethylsilane were 1.83 (2.00 in glacial acetic acid) and 0.86 respectively. Accordingly the kinetic data were analysed using the k_3 term of equation (2). Data to over 80% of reaction gave a good fit and the k_3 values found are shown in Tables 1 and 2.

In the previous study of this reaction in glacial acetic acid by Stock and Spector [4] initial rate measurements were not reported, and they concluded that the reaction is second order overall. Their conclusion is incorrect. In analysing their data they used a value of 250 $dm^3\ mol^{-1}$ for K. This value had been measured by Keefer and Andrews using acetic acid with m.p. 16.2 °C as the solvent.[14] This m.p. indicates that the acid contained 0.2% water.[6] The value of 250 $dm^3\ mol^{-1}$ is much higher than that of 21.8 $dm^3\ mol^{-1}$ which we found in glacial acetic acid. The data from the representative kinetic run reported by Stock and Spector fits the appropriate second-order rate equation quite well if the wrong value of K (250 $dm^3\ mol^{-1}$) is used (in agreement with their conclusion), but with the correct value of K (21.8 $dm^3\ mol^{-1}$) the fit is poor. Their data together with the correct value for K give a good fit to the third-order rate equation with k_3 5.18 $dm^6\ mol^{-2}\ s^{-1}$ (at 25 °C), and this accords well with our value of 6.43 $dm^6\ mol^{-2}\ s^{-1}$ at 30 °C.



Reaction of iodine monobromide (0.0813 mol dm^{-3}) with phenyltrimethylsilane (0.102 mol dm^{-3}) in 98.5% aqueous acetic acid at 30.0 °C: *a* and ●, experimental values; *b*, best fit using K 523 $dm^3\ mol^{-1}$; *c*, best fit with K 3 × 10^8 $dm^3\ mol^{-1}$

Reaction of Iodine Monobromide with Phenyltrimethylsilane.—The complex ion IBr_2^- formed during reaction is ineffective as an electrophile, and its formation constant K does not vary much with the water content of the solvent (Tables 1 and 2) in contrast to those for Br_3^- and ICl_2^-.

Initial rate measurements over the first 10% of reaction, when formation of IBr_2^- can be neglected, gave orders of reaction of 1.94 and 0.96 with respect to iodine monobromide and phenyltrimethylsilane respectively. Accordingly values of k_3 (Tables 1 and 2) were calculated from data over the early part of reaction by the numerical integration method using the k_3 term of equation (2). However if k_3 is calculated in a similar way using data taken over the whole reaction a lower value of k_3 is found (in 98.5% aqueous acetic acid 0.26 compared with 0.54 $dm^6\ mol^{-2}\ s^{-1}$) and the rate equation gives a poor fit to the data (see Figure).

The reaction does not go to completion as expected (see Figure) but stops after *ca.* 47% of the titratable interhalogen has been used up. Potentiometric titration of the remaining halogen and halide with silver nitrate (after reduction with sodium sulphite) shows a $Br^- : I^-$ ratio of two, consistent with formation of IBr_2^- ions. However, if K is *ca.* 500 $dm^3\ mol^{-1}$ as measured the reaction should go to completion. There is not an equilibrium between reactants and products. The final amount of reaction does not depend upon the initial concentrations of iodine monobromide and phenyltrimethylsilane and a mixture of the products, hexamethyldisiloxane, hydrogen bromide, and iodobenzene, does not react to give any iodine monobromide or phenyltrimethylsilane.

The analogous reaction of iodine monobromide with *p*-methoxyphenyltrimethylsilane also stops after *ca.* 50% reaction. As expected this reaction is much faster (k_3 *ca.* 40 $dm^6\ mol^{-2}\ s^{-1}$) than that of phenyltrimethylsilane, but we have not carried out a comprehensive range of kinetic studies since the kinetics are complicated by concurrent hydrolysis, catalysed by the acetic acid solvent, of *p*-methoxyphenyltrimethylsilane to anisole. Addition of hexamethyldisiloxane, iodobenzene, or a mixture of these two compounds did not alter either the initial reaction rate, or the final extent of reaction.

We can suggest two possible explanations for reaction stopping when only half the titratable interhalogen has been used up. If the formation constant of IBr_2^-, K, is very large IBr_2^- will not dissociate appreciably to give iodine monobromide and the reaction can be written as equation (9). This would result in reaction stopping

$$2IBr + PhSiMe_3 \longrightarrow PhI + \tfrac{1}{2}(Me_3Si)_2O + H^+ + IBr_2^- \qquad (9)$$

when half the titratable interhalogen has been used up. The computer program used for numerical integration was modified to give the ' best value' of K as well as k_3, and good fits to the data were obtained with k_3 0.50 $dm^6\ mol^{-2}\ s^{-1}$ and K very large in the range 4—40 × 10^7 $dm^3\ mol^{-1}$ (see Figure). This value of k_3 is quite close to that obtained using the measured value of K and data from the early part of the reaction (0.54 $dm^6\ mol^{-2}\ s^{-1}$). A large value for K conflicts with our measured value of *ca.* 500 $dm^3\ mol^{-1}$ and could indicate that the spectroscopic method we used for measuring K[10] is giving misleading results for IBr_2^-.

A second possible explanation is that iodine monobromide complexes strongly with a reaction product other than the bromide ion. However we have been unable to detect such a complex by studies of the u.v.–visible spectra in 98.5% aqueous acetic acid of iodine monobromide (either alone or mixed with hydrogen bromide) with hexamethyldisiloxane, iodobenzene, or a mixture of these two compounds.

Relative Reactivity of Halogens and Interhalogens.—Halogenation of phenyltrimethylsilane can proceed *via* a bimolecular (for chlorine, bromine, and bromine monochloride) or a termolecular (for bromine, iodine monochloride, and iodine monobromide) process. de la Mare[15] has suggested that the role of the second halogen molecule in a termolecular process may be to help remove a halide ion from a complex formed between the substrate and the first halogen molecule. The complexing ability of a halogen may be assessed by the value of K [equation (3)]. When K is small as for the Cl_3^- ion (in water K for Cl_3^- is only 1/100 of K for Br_3^-,[16] and a similar ratio probably applies in acetic acid) the third-order route is not found. The value of K for bromine monochloride forming a complex with chloride ions ($BrCl_2^-$) has not been measured.* We suggest that, as we did not observe any third-order pathway using bromine monochloride up to a concentration of 0.01 mol dm^{-3}, K for $BrCl_2^-$ must be less than that for Br_3^-. Scott[19] has calculated that the Lewis acidity of bromine monochloride is between that of iodine monochloride and iodine monobromide and greater than that of chlorine or bromine, but his calculations are based upon doubtful data for bromine monochloride.

The most reactive halogen by the third-order mechanism is iodine monochloride although this does not form such strong trihalide complexes as iodine monobromide. The greater polar character of iodine monochloride must be the dominant factor in deciding reactivity. Iodine monobromide and bromine appear equally reactive in third-order halogenation and reactivity must depend upon a balance between size (smaller bromine able to attack the silane more easily) and polarity and complexing ability.

In second-order halogenation the polar bromine monochloride is very much more reactive than bromine or chlorine. As its reaction products are so specific it could be a useful synthetic reagent for reactions where halogenation with bromine or chlorine takes place slowly. The relative reactivities of chlorine and bromine (comparing values of k_2) are almost exactly the same as reported earlier.[1,2]

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* The work of Pungor *et al.*[17] proposing a complex ion $BrCl_6^{5-}$ has been severely criticised by Appelman[18] and is probably unreliable.

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