147. *Chlorine Exchange between Antimony Trichloride and Trimethylchlorosilane in Benzene and Hexane. Part II.* Kinetics and Mechanism of Exchange.*

By A. F. Reid and R. Mills.

Isotopic halogen exchange occurs between trimethylchlorosilane and, severally, hydrogen chloride and the chlorides of aluminium, antimony, and magnesium, and between the corresponding bromine compounds. The kinetics of the exchange between antimony trichloride and trimethylchlorosilane in hexane were initially of first order with respect to each reactant, and probably so in benzene also. The kinetics are complicated in hexane by formation of a species allowing more rapid exchange with increased time of contact of the reactants, and further complicated in benzene by the interaction of the solvent with antimony trichloride.

SILICON–HALOGEN compounds undergo a large number of halogen or " pseudo-halogen " replacement reactions. Numerous studies with silver salts have been reported,[1] and various other compounds such as ammonium fluoride [2] are effective. Of particular interest are the large number of replacements effected by the covalent metal halides, *e.g.*, reactions of antimony trifluoride [3] and trichloride [4] with trimethylchloro- and trimethylbromo-silane, aluminium iodide with silicon tetrafluoride,[5] aluminium halides with triorganofluorosilanes,[6] halides of antimony, aluminium, arsenic, and titanium with silicon cyanates and thiocyanates,[7] and magnesium bromide with trimethyliodosilane.[4] It would be worth discovering whether, when a particular halogen replacement occurs, the corresponding isotopic halogen exchange can also occur. The present work deals with the trimethylhalogenosilanes and the halides of aluminium, antimony, and magnesium, and the effect of hydrogen chloride. The last is the hydrolysis product of the other reactants; it exchanges chlorine atoms with silicon tetrachloride,[8] and was found to exchange with trimethylchlorosilane. Exchange was found between each of the metal halides and the corresponding halogenosilanes, but that exchange reactions involving ionic displacements (as for the exchange reactions of alkali halides with alkyl halides in various solvents) need not necessarily occur with halogenosilanes, is indicated by the fact that lithium bromide and calcium chloride, despite favourable solubility relations, do not effect halogen replacement with triethylfluorosilane, whereas aluminium iodide does.[6]

It is noteworthy that the covalent metal halides mentioned all contain central metal atoms with unoccupied valence orbitals, and that in each compound the metal atom can form further relatively stable bonds by co-ordination processes, as for example in aluminium halide dimers. A reaction process involving co-ordination of the halogen atom of the halogenosilane to the central metal atom has been shown to occur in the reaction of methylmagnesium halides with trimethylhalogenosilanes,[4] and it is feasible that a general pattern of mechanisms of this kind occurs. The consequent process, a concerted rearrangement of a four-centre transition state, provides compensation of bonds and charge, and thus allows of a low activation energy. Temporary formation of a quinquecovalent silicon

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* Part I, preceding paper.

[1] Macdiarmid, *Quart. Reviews*, 1956, **10**, 208; Eaborn, *J.*, 1950, 3077; Anderson, *J. Amer. Chem. Soc.*, 1950, **72**, 2761.

[2] Wilkins, *J.*, 1951, 2726.

[3] Wowski, *J. Amer. Chem. Soc.*, 1950, **72**, 919.

[4] Reid and Wilkins, *J.*, 1955, 4029.

[5] Schumb and Breck, *J. Amer. Chem. Soc.*, 1952, **74**, 1754.

[6] Eaborn, *J.*, 1953, 494.

[7] Anderson, *J. Amer. Chem. Soc.*, 1953, **75**, 1576.

[8] Klaus, Clusius, and Haurmarl, *Z. phys. Chem.*, 1942, **51**, *B*, 347; Herber, *J. Chem. Phys.*, 1957, **27**, 653.

species would be involved; these have often been discussed and their occurrence demonstrated.[9] The observations in the present study are consistent with such a mechanism.

The aluminium and antimony halides are of additional interest because of their catalytic action in a number of organosilicon reactions.[10] Antimony trichloride was chosen for initial study, with trimethylchlorosilane, because the former is readily prepared and purified, and in the vapour [11] and the solid [12] state has a monomeric structure with all chlorine atoms equivalent. Although there is considerable evidence for the persistence of an antimony trichloride–benzene complex in liquid benzene,[13] it appeared possible that a rapid turnover of bound and unbound antimony trichloride molecules might provide simple exchange kinetics. The concentration dependences of the exchange rates observed were not, however, direct functions of the reactant concentrations. The stability of antimony trichloride–aromatic compounds decreases markedly with withdrawal of electronic charge from the aromatic nucleus,[14] and since the trichloride appears to form adducts only with donor molecules, an aliphatic hydrocarbon should be unreactive towards it. Antimony trichloride has a limited (0·08M at 20°) solubility in n-hexane, a solvent with molecular weight and volatility similar to those of benzene, indicating that compound formation or a high degree of solvation is absent.

FIG. 1.

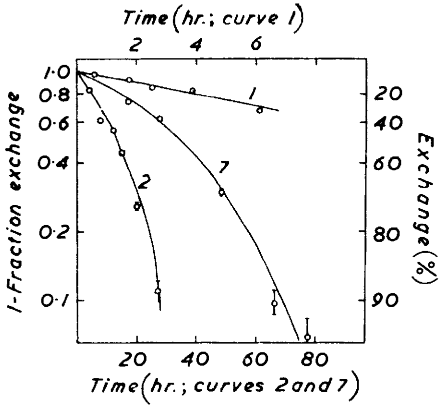

FIG. 2.

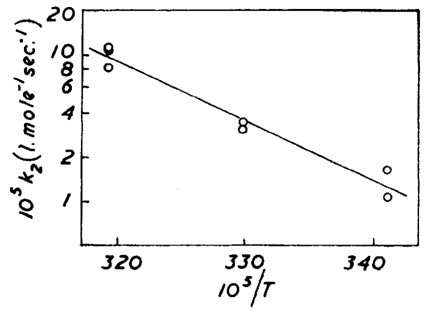

FIG. 1. *Exchange between* M_3SiCl *and* $SbCl_3$ *in hexane at* 40°.

	Me_3SiCl (M)	$SbCl_3$ (M)	$t_{\frac{1}{2}}$ (hr.)
Curve 1	0·35	0·057	11·5
,, 7	0·0193	0·0535	41
,, 2	0·406	0·00522	13·5

FIG. 2. *Temperature-dependence of bimolecular rate constants for exchange between* Me_3SiCl *and* $SbCl_3$ *in hexane.*

Other Exchange Systems.—In preliminary experiments, based on the techniques described in Part I, isotopic exchange was observed under anhydrous conditions in the following systems: HCl, $AlCl_3$, $SbCl_3$ with Me_3SiCl; $MgBr_2$, $AlBr_3$, $SbBr_3$ with Me_3SiBr. The magnesium bromide exchange was conducted in ether, and the others in benzene; hydrogen chloride also exchanged in the absence of solvent. The compounds were mainly

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[9] Stone and Seyferth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 112; Aylett, *ibid.*, 1956, **2**, 325; Eaborn, *J.*, 1955, 2047; Sommer and Bennett, *J. Amer. Chem. Soc.*, 1959, **81**, 251.

[10] Eaborn, *J.*, 1949, 2755; Chernyshev and Petrov, *Bull. Acad. Sci. U.S.S.R.*, 1953, 630; Sommer, Whitmore, *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 1976, 2108; 1954, **76**, 801; Yakubovich and Motsarev, *J. Gen. Chem. U.S.S.R.*, 1955, **25**, 1748.

[11] Kisliuk, *J. Chem. Phys.*, 1954, **22**, 86.

[12] Lindquist and Niggli, *J. Inorg. Nuclear Chem.*, 1956, **2**, 345.

[13] Daash, (a) *J. Chem. Phys.*, 1958, **28**, 1005; (b) personal communication.

[14] Shinomiya, *Bull. Chem. Soc. Japan*, 1940, **15**, 259.

separated by distillation, but magnesium bromide was separated from trimethylbromosilane in ether solution by precipitation with dioxan.[15] Of these systems, antimony trichloride–trimethylchlorosilane was chosen for detailed study for the reasons outlined in the introduction.

TABLE 1. *Exchange data for benzene solution.*

Expt. Set	Temp.	Concn. (M) Me_3SiCl	$SbCl_3$	$t_{\frac{1}{2}}$ (hr.)	10^5 " k_2 " (l. mole^{-1} sec.$^{-1}$)
1	40°	0·110	0·0214	2·0	164
2	25	0·112	0·0218	14·5	23
3	25	0·112	0·269	14·5	4·3
4	25	0·0395	0·0953	47·5	3·8
5	25	0·018	0·0158	1·0	890

Kinetics.—Exchange kinetics in benzene (see Table 1). At 25° the exchange curves were concave downwards, and at 40° concave upwards. Exchange rates were estimated from the initial slopes of the curves. Each fraction of exchange on the curves was obtained by a separate experiment.

The complicated concentration dependence at 25° indicates that increase of the antimony trichloride concentration slows the exchange reaction, presumably by compound formation with the solvent, but direct dilution of a particular reaction solution with further benzene (sets 3 and 4) decreases the initial rate as calculated for bimolecular kinetics.

Exchange kinetics in hexane (see Table 2). The exchange curves obtained by the direct mixing of the reactants in hexane, although near-linear initially, all showed downward curvature. Typical curves are in Fig. 1. However, if initial slopes are taken, the reaction obeys a second-order rate law with reasonable accuracy over the range of temperatures and concentrations used. This procedure appears justified by the consistency of the results, and by the facts that no irreversible chemical reaction was found to occur, and extraneous effects were apparently unimportant (see below).

TABLE 2. *Exchange kinetics in hexane.*

Temp.	Concn. (M) Me_3SiCl	$SbCl_3$	$t_{\frac{1}{2}}$ (hr.)	10^5k_2 (l. mole^{-1} sec.$^{-1}$)	Temp.	Concn. (M) Me_3SiCl	$SbCl_3$	$t_{\frac{1}{2}}$ (hr.)	10^5k_2 (l. mole^{-1} sec.$^{-1}$)
40°	0·35	0·057	11·5	9·7	30°	0·644	0·00484	28	3·2
	0·406	0·00522	13·5	10·2		0·0238	0·0495	120	2·8
	0·0198	0·0535	41	7·5	20	0·621	0·00504	62	1·5
	0·737	0·0357	8·0	8·7 *		0·376	0·0354	118	1·2
	0·0364	0·0747	3·5	63 †					

* In the presence of added benzene.

† Pre-equilibration of inactive $SbCl_3$ with Me_3SiCl before addition of $Sb^{36}Cl_3$; apparent k_2.

The plot of log k against $1/T$ was linear (Fig. 2) and the rate law for the initial exchange can be expressed as

$$R = 2{\cdot}2 \times 10^8 \{\exp - (18{,}600 \pm 1100)/\boldsymbol{R}T\}[Me_3SiCl][SbCl_3]/3$$

The calculated activation entropy was 18 ± 4 cal./degree.

Pre-equilibration of reactants in hexane solution. Addition of a small labelled amount of the compound already in excess ought to allow the observation of the exchange behaviour of the excess with any complex (assumed 1 : 1 for the design of this experiment) which had formed between the reactants. Antimony trichloride was used in excess; the exchange rate, assumed as bimolecular, on addition of a small amount of $Sb^{36}Cl_3$ to the solution pre-equilibrated for 36 hr., was 7 times as great as that calculated for direct mixing, and the (uncorrected) exchange curve was linear to more than 90% exchange. It is thus evident that on equilibration of the reactants a comparatively stable species is formed (dissociable

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[15] Dessey, *J. Amer. Chem. Soc.*, 1957, **79**, 3476.

by evaporation) which allows of more rapid exchange between added $Sb^{36}Cl_3$ and, presumably, bound trimethylchlorosilane, than occurs on direct mixing. The downward curvature of exchange curves after direct mixing must be due to an increased rate of exchange brought about by formation of this species.

Addition of benzene to hexane solutions. A hexane solution of antimony trichloride containing benzene thrice that required for formation of $2SbCl_3,C_6H_6$ was equilibrated at 40° for 17 hr. before mixing it with trimethylchlorosilane. The exchange curves and initial rate were indistinguishable from those obtained in the absence of benzene. Apparently, therefore, compound formation between antimony trichloride and benzene does not persist in hexane, or at least does not affect the exchange.

Subsidiary Studies.—A number of subsidiary experiments were made to determine if the complicated nature of the reaction data was due to extraneous effects. Light had no apparent effect on the exchange, and the presence of finite amounts of moisture (giving rise to hydrogen chloride by hydrolysis of the reactants) and antimony pentachloride, and of traces of chlorine, had measurable but not marked effects on the exchange rates. Fractional distillation of mixtures of antimony trichloride, trimethylchlorosilane, and benzene after prolonged refluxing gave practically quantitative recoveries, with no evidence of other compounds. Lack of reaction was further confirmed by the normal vapour pressure of a saturated solution (11 moles % at 20°) of antimony trichloride in trimethylchlorosilane, with no change of vapour pressure with time, by the recovery of up to 98% of hydrolysable chloride from the separated silane during exchange experiments, and by the recovery of practically pure antimony trichloride. Solutions of antimony trichloride in benzene or hexane were non-conducting, and this behaviour was not altered, over long periods, by the presence of trimethylchlorosilane in the solutions.

DISCUSSION

The bimolecular rate dependence of the direct exchange is in accord with the conductance data, and with the fact that no mechanism of reaction of an organosilicon compound has been substantiated which involves formation of silicon ions. Mechanisms covalent with respect to, or involving initial co-ordination of, antimony trichloride have been demonstrated for the exchange of antimony atoms between the tri- and penta-chlorides in carbon tetrachloride [16] and hydrochloric acid solution [17] (in the latter $SbCl_6^-$ and $SbCl_3$ are the postulated exchange species) and, for example, in the reaction of antimony trichloride with diazonium or hydrazine compounds.[18] The increased rate of exchange with time for direct mixing experiments, and the more rapid, constant rate after pre-equilibration, show that a comparatively stable species (dissociable by evaporation) is formed, which allows more rapid exchange between trimethylchlorosilane and antimony trichloride, and between the former presumably in the bound state and an added amount of the latter. Addition compounds of volatile substances do often have moderate dissociation pressures; for example, the crystalline addition compounds of antimony trichloride with benzene [13] and dioxan,[19] and the various adducts of silicon halides with amines. A comparatively stable compound $PhSiCl_3,SbCl_3$ has been isolated [20] (m. p. —30°); in it, addition almost certainly occurs between the $-SiCl_3$ group and antimony trichloride because of the de-activating effect of the former on the benzene nucleus.

The most obvious form of addition compound between the reactants is one in which the chlorine atom of the trimethylchlorosilane is co-ordinated to antimony on the opposite side to the pyramidally disposed chlorine atoms, and this is also a probable transition-state configuration for the direct exchange. A four-centre transition-state complex for

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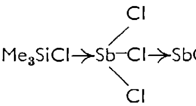
[16] Barker and Kahn, *ibid.*, 1956, **78**, 1317.
[17] Neumann and Brown, *ibid.*, 1956, **78**, 1843.
[18] Bruker, *J. Gen. Chem. U.S.S.R.*, 1948, **18**, 1297.
[19] Kelley and McCusker, *J. Amer. Chem. Soc.*, 1943, **65**, 1307.
[20] Yakubovich and Motsarev, *Doklady Akad. Nauk S.S.S.R.*, 1954, **99**, 1015.

the direct exchange would involve a tetrahedral disposition of the chlorine atoms about antimony, and penta-co-ordination to silicon,[9] both compatible with known structures or configurations of these elements. If we suppose that intramolecular rearrangement in an addition compound without subsequent separation of reactants is more rapid than direct exchange, it would then be necessary for there to be a rapid exchange of chlorine atoms between added antimony trichloride and that bound to trimethylchlorosilane. Rapid exchange has been observed [17] for the exchange of antimony atoms between $SbCl_6^-$ and $SbCl_3$, and by analogy with the transition state proposed for that exchange, the structure (I) would be consistent with the present experimental observations. Configurations similar to those of ref. 17 are suggested for the antimony atom exchange in carbon tetrachloride.[16]



(I)

The exchange in benzene was further complicated by interaction of, presumably, antimony trichloride with the solvent. Many crystalline stable antimony trichloride–aromatic compounds are known,[14] some of which persist strongly in the liquid phase.[21] Dissociation pressures show that $2SbCl_3,C_6H_6$ has an energy of formation of 12 kcal. mole^{-1},[13b] and infrared measurements show that it persists in liquid benzene,[13a] with, probably, a continued structure with two out-of-plane antimony atoms bridging two benzene molecules.[13b] The exchange curve at 40° showed that, approximately, after 80% exchange in 12 hr., the exchange rate had fallen to one-tenth of its initial value, and back-extrapolation of the slope at this time cuts the fractional exchange axis at 70% exchange. This indicates that 30% of antimony trichloride, at the concentration employed, exists as a compound with solvent, with a slow rate of turnover such that a substantial fraction of the compound is undissociated during 12 hr.

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[21] Naumova and Zhitkov, *J. Gen. Chem. U.S.S.R.*, 1949, **19**, 1429.