

**146.** *Chlorine Exchange between Antimony Trichloride and Trimethylchlorosilane in Benzene and Hexane. Part I. Apparatus and Techniques.*

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An apparatus based on vacuum-techniques has been developed to study the exchange of chlorine between antimony trichloride and trimethylchlorosilane in benzene and hexane. The method of separation utilizes differential evaporation and is generally applicable to systems containing a volatile and an involatile reactant. Exchange at zero time and the effect of incomplete separation are discussed.

In this Part are described the techniques developed for a study of chlorine exchange between antimony trichloride and trimethylchlorosilane in hexane and benzene. The high susceptibility of both reactants to hydrolysis made vacuum-handling the most convenient and led to separation being based on differential vacuum-evaporation. This process depends only on the vapour-pressure characteristics of the system and could therefore be applied to any exchange system containing a volatile and an involatile reactant with or without a solvent. Exchange at zero time and incomplete separation, together with the errors involved in the calculation of exchange rates, are discussed below after the experimental method has been described.

#### EXPERIMENTAL

Halogenotrimethylsilanes were prepared by a published method.<sup>1</sup> Trimethylchlorosilane was fractionally distilled under dry nitrogen, purified in a vacuum to constant vapour pressure

<sup>1</sup> Voronkov, Dolgov, and Dmitrieva, *Doklady Akad. Nauk S.S.S.R.*, 1952, **84**, 959.

( $\pm 0.1$  mm.) by repeated passage through a trap at  $-78^\circ$ , and contained by an all-metal bellows valve (type 431, obtained from Hoke Inc., Englewood, N.J., U.S.A.) connecting to a glass storage bulb with a metal-to-glass seal.

*Antimony Trichloride.*—Commercial antimony trichloride, dried over phosphoric oxide, was twice distilled under dry nitrogen at 50 mm. After being degassed, the compound was twice sublimed, in a vacuum, to ampoules containing break-seals. It then melted sharply at  $73^\circ$  and its analysis agreed within 0.1% with that required by the formula.

*Labelling of Compounds.*— $^{36}\text{Cl}$  was obtained as  $\text{H}^{36}\text{Cl}$  in 2*N*-hydrochloric acid from the Radiochemical Centre, Amersham.  $^{82}\text{Br}$  was obtained by the Szilard-Chalmers process, by using slow neutrons produced during the operation of the Australian National University's 8 Mev cyclotron. Purified trimethylchlorosilane was labelled by equilibration, in a vacuum, with  $\text{Sb}^{36}\text{Cl}_3$ , and recovered by low-temperature evaporation. Equilibration with  $\text{Al}^{36}\text{Cl}_3$ , prepared by Wallace and Willard's method,<sup>2</sup> was also used.  $^{36}\text{Cl}_2$ , prepared by the method of Brown, Gillies, and Stevens,<sup>3</sup> was degassed and any remaining water was removed by several evaporations at  $-78^\circ$ .  $\text{Sb}^{36}\text{Cl}_3$  was prepared in a vacuum by direct combination, with final heating to 200–300° to ensure decomposition of any antimony pentachloride and complete combination of chlorine. After several vacuum-sublimations the trichloride was sealed in glass ampoules containing break-seals. Analysis gave values within 0.1% of these required by the formula.  $\text{Al}^{82}\text{Br}_3$ ,  $\text{Mg}^{82}\text{Br}_2$ , and  $\text{Sb}^{82}\text{Br}_3$  were synthesised for qualitative investigation of their exchange with the corresponding organosilicon bromides. These compound were prepared, under anhydrous conditions, by the action of bromine, containing  $^{82}\text{Br}$ , on the metals under ether or benzene.

Solvents were dried over liquid sodium-potassium alloy and fractionally distilled. Solutions were made up from degassed solvents stored in a vacuum over sodium-potassium alloy. The storage vessels were connected with the vacuum-system through a fine sintered-glass diaphragm to prevent carry-over of solid material and were closed with stopcocks lubricated with Silicone grease.

Nitrogen for the manipulation of anhydrous solutions or compounds was freed completely from oxygen, carbon dioxide, and moisture by passage through liquid sodium-potassium alloy.

*Reactant Solutions.*—A 250 ml. bulb was connected through a sintered-glass diaphragm to a limb to which were joined, through seal-off constrictions, two or three storage bulbs (A in Fig. 1) containing break-seals. The apparatus was dried by passage of heated nitrogen, and degassed at  $10^{-6}$  mm. Antimony trichloride was sublimed into the 250 ml. bulb, and an appropriate volume of hexane condensed and sealed in with it. For the highest concentrations used, the vessel was equilibrated one or two degrees below the reaction temperature, and the saturated solution poured through the sinter into the storage bulbs. These were then cooled simultaneously in liquid air and sealed, being subsequently joined to the reaction vessel.

*Trimethylchlorosilane Solution.*—The solution in benzene was prepared in a vacuum in a storage bulb placed vertically above two metal bellows valves, the evacuated space between them serving as an accurately defined delivery chamber (2.5 ml.  $\pm 0.1\%$  by weight of benzene delivered).

*Exchange Experiments.*—For hexane solutions the reaction vessel was as in Fig. 1. This apparatus depended on the use of a greaseless glass stopcock, G, obtained from the Springham Co., Harlow. It allowed the withdrawal, in a vacuum, of a number of samples of solution without contamination of the remainder. The general method was very satisfactory, although requiring considerable mechanical care in the preparation of reactant solutions, and allowed the reaction to be carried out in all-glass apparatus closed by a small surface (0.25 cm.<sup>2</sup>) of Polythene. In the form used (0.004" sheet), Polythene deforms slightly under pressure to give a high-vacuum seal against glass. Thin Teflon sheet was unsatisfactory because of wrinkling. After the reaction vessel had been dried, degassed, and pre-treated with trimethylchlorosilane, an appropriate amount of this reactant was condensed into it. Reaction was begun, after temperature equilibration, by dropping the striker S on to the adjacent break-seal and pouring the solution between A and B until the reactants were thoroughly mixed. The guard tube C kept fragments of glass from entering G. The vessel K was then placed in a thermostat bath as shown. The upper of the two o-rings served as a temporary water-seal until the lower one was fixed in position, and the two served as a stable,

<sup>2</sup> Wallace and Willard, *J. Amer. Chem. Soc.*, 1950, **72**, 5275.

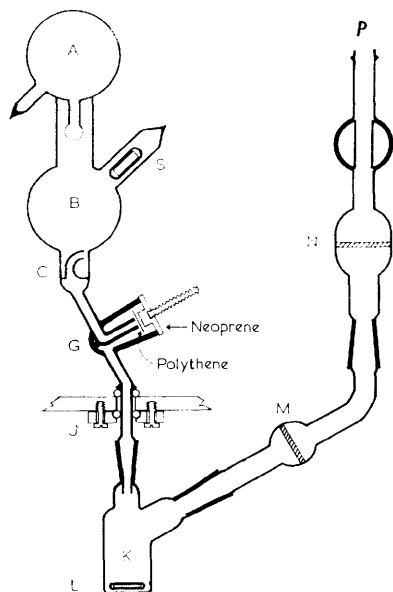
<sup>3</sup> Brown, Gillies, and Stevens, *Canad. J. Chem.*, 1953, **31**, 768.

flexible and water-tight support which allowed rotation and sliding of the vessel. The evaporation vessel K and the separation sinter-vessels were put in place, with the upper vessel connected to the vacuum-system at P by a short length of pressure tubing.

For experiments with benzene solutions, antimony trichloride solution was manipulated under dry nitrogen, and an aliquot part was degassed and mixed with an aliquot part of trimethylchlorosilane solution delivered in a vacuum. The whole of the reaction solution (5 ml.) was separated in each experiment, by a procedure similar to that for hexane solutions, but with the evaporation vessel in a thermostat bath.

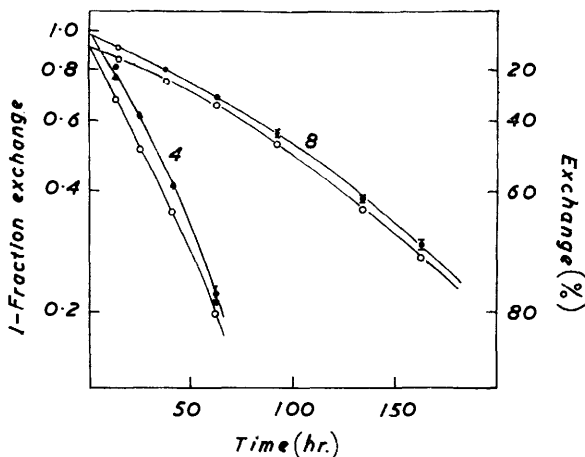
*Separation of Reactants.*—Antimony trichloride ( $p_{20}$   $10^{-1}$  mm.) and trimethylchlorosilane ( $p_{20}$  190 mm.) are readily separated by distillation at atmospheric pressure, and it was found

FIG. 1. *Reaction and separation vessels.*



A, Solution storage bulb. B, Reaction vessel. S, Glass-covered striker. C, Guard tube. G, Diaphragm valve. J, Thermostat bath base. K, Evaporation vessel. L, Magnetic stirrer. M, N, Coarse and fine glass sinters. P, Pressure tubing to hydrolysis trap.

FIG. 2. *Exchange in hexane at 30° and 20°, showing corrected and uncorrected curves.*



8, Exchange curve for 20°. 4, Exchange curve for 30° (Table 2).  $\blacktriangle$ ,  $\bullet$  Corrected data F for  $\text{SbCl}_3$  and  $\text{Me}_3\text{SiCl}$  respectively.  $\circ$  Uncorrected data.

that, from a solution of the two in benzene or hexane, the solvent and trimethylchlorosilane could be separated from the antimony trichloride by rapid vacuum-evaporation from the stirred solution held under its own vapour pressure provided that the evaporation rate was limited by a fine sintered-glass diaphragm in the separation line. The effects of exchange during separation and of incomplete separation were found to be small, and appropriate corrections could be made for them, as is shown below.

When valve G was opened, a sample (5–7 ml.) of solution was forced into the evacuated vessel K (held at a lower temperature) by the vapour pressure of the solution. With the magnetic stirrer L rotating rapidly, the evaporation vessel was opened to an evacuated hydrolysis trap with a surface of 100 cm.<sup>2</sup> cooled in liquid air, joined to the line through a stopcock and ground joint, and containing a measured volume of hydrolysis solution, frozen in liquid air. The evaporating solution was thus rapidly cooled, and the resultant quenching of the reaction makes variation in the time for complete evaporation unimportant. The hydrolysis trap was finally closed, and dry nitrogen admitted to the rest of the space. The vessels K and M were replaced by similar ones after the body of the valve had been flushed clean with benzene, and an aliquot part of hydrolysis solution was pipetted into K. The lower, coarse sinter M

prevented splashing and frothing of solution on to N, washings from the latter after one or more separations showing negligible activity.

*Analyses.*—Chloride ion was determined, in dilute acid solution, by differential potentiometric titration with silver nitrate, silver-silver chloride electrodes being used. Silicone-treated pipettes minimised the transfer error, and 0.2 milliequiv. or larger samples could be analysed within 0.1%.

Tervalent antimony in 2*N*-sulphuric acid was titrated potentiometrically with potassium bromate, the titrant solution being kept 1% with respect to potassium bromide. The arrangement was as described for the micro-determination of arsenite.<sup>4</sup> The bromate-antimony titration was found to be particularly precise, duplicate determinations of 0.05 milliequiv. samples agreeing within 0.1%, and of 2 microequivalent samples within 0.5%. Antimony trichloride and trimethylchlorosilane were hydrolysed with 10*N*-sulphuric acid, so that counting could be carried out in media of the same density and composition. Any fine suspensions of solvents in aqueous solutions were removed by centrifugation.

For total assay of the reaction solution, a sample was withdrawn into an evacuated, calibrated volume-apparatus, with provision for sealing off, and a stopcock and ground joint on a side-arm for connection to a separating funnel containing hydrolysis solution.

*Counting Procedure.*—<sup>36</sup>Cl was counted as chloride ion in 10 ml. portions of solution, with a thin glass-walled Geiger tube fitting through a ground joint into a liquid well, constant geometry being thus obtained. Standards were counted whenever sets of activities were to be compared; for each experiment, separated samples and the reaction solution total assay sample were counted contiguously. Counting rates were 2000—4000 c.p.m.; measured specific activities were reproducible within 0.6%.

*Exchange during Separation.*—Since separation was effected by a purely physical method and separation times were very short compared with half-times, induced exchange would not be expected to be important. (The amount of exchange occurring during separation should not be greater than that which would occur in the same time if the system were left undisturbed.) It is apparent that once trimethylchlorosilane and any antimony trichloride carried in the vapour phase have passed from the reaction solution any further exchange between them will not affect the specific activity of the chloride contained in the separated fraction.

Experimental observations confirmed these expectations. For benzene solutions, directly observed zero-time fractions of exchange, obtained by separating the reactants immediately after mixing, were 0.01—0.02. For hexane solutions, back-extrapolation gave the same range of values over all experiments.

*Effectiveness of Separation.*—The amounts of antimony trichloride (0.5—15%) transported with the vapour when 5 ml. were evaporated to dryness were sensibly constant for given initial conditions, and were not proportionately less for partial evaporation of the solution. For the evaporation vessel held in a thermostat bath at 40°, a typical rate of evaporation of benzene was 5 ml. in 60 sec and, even for 12 ml. of solution initially at 25°, all but a small fraction of a ml. evaporated without solidification. For separation from hexane solution, with the evaporation vessel in the air, rapid cooling of the solution occurred, with precipitation of antimony

TABLE 1. *Efficiency of separation by evaporation.*

SbCl <sub>3</sub>				SbCl <sub>3</sub>					
Temp.	Molarity	Ml.	Average % carried over	No. of obsns.	Temp.	Molarity	Ml.	Average % carried over	No. of obsns.
In benzene *					In hexane †				
40°	0.04	7.06	3.5 ± 1.3	6	40°	0.005	7	15.8 ± 1.8	6
40	0.03	4.7	1.2 ± 0.8	8	30	0.005	6	14.9 ± 2.1	4
			(lowest 0.15)		20	0.005	7	15.2 ± 1.7	6
25	0.03	4.7	2.5 ± 0.5	4	20	0.035	6	5.0 ± 0.8	6
25	0.27	6	0.27 ± 0.06	4					

\* A 3 cm. diameter no. 3 sinter at 40° and a no. 2 at 25°. † A 3 cm. diameter no. 3 sinter preceded by a 2.5 cm. no. 1 sinter at each temperature.

trichloride. It was necessary to heat the vessel with a lamp to keep the temperature above 0° c and accomplish evaporation in a reasonably short time, usually 3—5 min. for 5 ml. of solution. The amounts of antimony trichloride carried over during evaporation are shown in Table 1.

*Calculation of Results.*—Fraction of exchange was calculated with the usual definitions.<sup>5</sup>

<sup>4</sup> Reid, *Mikrochim. Acta*, 1958, 236.

<sup>5</sup> Stranks and Wilkins, *Chem. Rev.*, 1957, 57, 743.

The reaction was carried out and the samples were separated in such ways that the specific activities of separated samples could be directly compared with that of a completely hydrolysed sample of the reaction solution, and the fraction of exchange for the reactant not initially labelled was determined by the ratio of the two specific activities. Mass-balance checks were made by independent assay of the labelled reactant for specific activity, and by comparison of fractions of exchange for both reactants. The specific activity of the evaporated reactant was corrected for that of the involatile reactant carried over by simple consideration of activity sums, which leads to the expression

$$S_A = S_{obs} - (x/y)(S_B - S_{obs}) \quad \dots \quad (1)$$

where  $x/y$  is the ratio of chloride derived from the involatile component (component B) to that from the volatile (component A).  $S_B$  may be measured, or a first approximate value of the fraction of exchange assumed, and a first approximation to  $S_B$  can be made from the definition. Successive iteration (usually in 3 or 4 steps) leads to a constant value of  $F$ , which usually agreed closely with that determined from using, in equation 1, a measured value of  $S_B$ , and with the value based on  $S_B$ . The exchange curves obtained from the corrected values of  $F$  gave a smooth fit of experimental points to the curve, within small limits of error, and the curves based on the uncorrected value of  $F$  were parallel to them, as shown in Fig. 2. The data for the lower set of curves are given in Table 2, and similar agreement was observed in all cases where the comparisons were made.

TABLE 2. *Exchange in hexane at 30°.*

Sample no.	Time (hr.)	Fraction of exchange			
		SbCl <sub>3</sub>	Corr.	Me <sub>3</sub> SiCl Iterated	Uncorr.
1	13.25	0.236	0.194	0.186	0.323
2	25.0	0.390	0.387	0.387	0.491
3	41.0	0.582	0.583	0.584	0.646
4	62.1	0.784	0.778	0.778	0.802

$t_{\frac{1}{2}}$ : 28 hr.  $10^3k_2 = 3.2$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. Molarities: Me<sub>3</sub>SiCl, 0.644; Sb<sup>36</sup>Cl<sub>3</sub>, 0.00484.

While the exchange plots, illustrated in Fig. 2, are seen to have a downward curvature (similar over all concentration ranges), the fractions of exchange based on each reactant are self-consistent. In Part II a mechanism of accelerated exchange is discussed and it should be emphasised that the curvature is due to this and not to any inherent error in the experimental technique.

*Calculation of Errors.*—The limits of error shown in the exchange curves were calculated by compounding the individual errors determined from replicate measurements of the various quantities. The correction to the specific activity of the evaporated fraction was usually small and accurately determined, and hence error in its determination produced almost negligible error in  $F$ . The error produced by the correction procedure can, however, be calculated for a general case.

When the notation of equation (1) is used and all activity is assumed to be initially in the antimony trichloride, B, then

$$F = \frac{S_{obs} - (x/y)(S_B - S_{obs})}{S_{A\infty}} \quad \dots \quad (2)$$

Hence, in addition to the direct error in  $F$  due to error in the determination of  $S_{obs}$ , there will be an error  $dF$  for a given percentage error  $e$  in  $x/y$  of

$$dF = \frac{(A) + (B)}{(A)} \cdot \frac{e}{100} \cdot \frac{(x/y)(S_B - S_{obs})}{S_{Bo}} \quad \dots \quad (3)$$

This will be greatest for zero time, when  $S_B = S_{Bo}$ , with the error decreasing as the specific activities of the two reactants become more nearly equal. The diameters of the circles in Fig. 2 show the estimated limits of error for  $F = 0.5$ , with all sources of error included.

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