[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Redistribution Reactions in the Halides of Carbon, Silicon, Germanium and Tin

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

The fundamental papers of Urey and co-workers on isotopic exchange equilibria[1,2,3] emphasize the fact that not even units so closely similar as isotopic atoms attain a truly random distribution among similar molecules. These investigators have set up general equations for calculation of equilibrium constants based on the distribution functions of diatomic and polyatomic molecules, and have quantitatively predicted those important deviations from random distribution which have served them so well in their separations of isotopes. One might expect *a priori* that any exchange reactions involving different organic groups, or even different halogen atoms, would exhibit substantial deviations from simple probability laws.

An important series of papers by Calingaert and co-workers[4,5,6,7,8,9] reports, however, that random exhange of organic radicals occurs within experimental error among certain alkyls, chloroalkyls and esters, likewise different halogen atoms among ethylene halides. From the laws of probability alone they work out a general equation for quantitative prediction of equilibria in such reactions, and stress the absence of chemical or energy factors affecting random distribution. They emphasize that "the redistribution reaction is adaptable as a new method of organic synthesis".[10]

It would seem that inorganic chemists have long possessed at least an instinctive realization of the possibilities of the redistribution reaction, especially in the synthesis of mixed halides containing a single atom of a quadrivalent element. For instance, Besson[11] obtained all the chloroiodides of silicon by passing iodine monochloride over silicon heated to redness. He found that if a silicon chloroiodide (plus iodine) was passed over heated silicon, silicon tetrachloride was one of the products, and he astutely remarks "... this is not surprising if one takes account of the partial dissociation of chloroiodides under the action of heat." Subsequently[12] he obtained mixed halides from the action of hydrogen bromide on phosphoryl chloride. He points out that the boiling point of $POClBr_2$, when distilled at normal pressure, is not fixed, since at this temperature (about 165°) it undergoes a progressive decomposition according to the equations

$$2POClBr_2 = POCl_2Br + POBr_3$$
$$\text{and } 3POClBr_2 = POCl_3 + 2POBr_3$$

Lecompte, Volkringer and Tchakirian,[13] improving a procedure of Besson,[14] heated chloroform with bromine in a sealed tube at successively higher temperatures up to 250°, allowing hydrogen bromide to escape after each heating. By fractional freezing, in addition to distillation, all the mixed halides were obtained.

Raeder[15] measured molar elevations of boiling points and molar depressions of freezing points in a great number of solutions made by dissolving a given halide of a given element from a middle group of the periodic system in excess of a second halide in the same category. By plotting $\pm\Delta T$/mole against mole per cent. of the first halide, he arrived at the following conclusions. The halides of phosphorus, arsenic, antimony, titanium, tin (and by prediction germanium as well) easily exchange their halogen atoms so as to enter into readily mobile equilibria and form mixed halides incapable of isolation in the solid or in the gaseous phase. On the other hand, the tetrahalides of carbon and silicon, which are characterized by great chemical inertness, form mixed halides only with difficulty and only under special conditions. Once formed, however, they can be isolated as pure compounds. Raeder cites Trümpy's analyses of Raman spectra of such systems[16] as confirmation of the above interpretations.

Papers of references 1 to 14 do not contain quantitative data on yields, so that closeness of approach to random distribution cannot be figured. Our interest in the stabilities of halides, cyanates and thiocyanates prompted a survey of the redistribution problem over Group IVA of the periodic system, in which at least the mixed chlorides of four elements enjoy some measure of stability. A subsequent paper by Anderson[17] describes the preparation and properties of three new compounds, $SiCl_3NCO$, $SiCl_2(NCO)_2$ and $SiCl(NCO)_3$ and shows that these, as well as mixtures of the end members of the series, attain at elevated temperatures distributions random within experimental error. In the present paper it is shown that their behavior fits into a larger scheme of relative stabilities.

Carbon Chlorobromides.—No reaction between carbon tetrachloride and tetrabromide was detected after seven hours in a sealed tube at 170°, or in a second experiment in which dry aluminum chloride was added. In the three

---

(1) Urey and Rittenberg, *J. Chem. Phys.*, **1**, 137 (1933).

(2) Rittenberg, Bleakney and Urey, *ibid.*, **2**, 48 (1934).

(3) Urey and Greiff, THIS JOURNAL, **57**, 321 (1935).

(4) to (7) *ibid.*, **61**, 2748, 2755, 2758, 3300 (1939).

(8) and (9) *ibid.*, **62**, 1099, 1104 (1940).

(10) Reference 4, p. 2754.

(11) Besson, *Compt. rend.*, **112**, 1314 (1891).

(12) Besson, *ibid.*, **122**, 814 (1896).

(13) Lecompte, Volkringer and Tchakirian, *ibid.*, **204**, 1927 (1937).

(14) Besson, *ibid.*, **114**, 222 (1892).

(15) Raeder, *Z. anorg. allgem. Chem.*, **210**, 145 (1933); from *Det. Kgl. Norske Vidensk Selsk. Skrifter*, **8**, 1 (1929).

(16) Trümpy, *Z. Physik*, **66**, 790 (1930); **68**, 675 (1931).

(17) Anderson, THIS JOURNAL, **66**, 934 (1944).

TABLE I

REDISTRIBUTION OF THE CARBON CHLOROBROMIDES; $AlCl_3$ CATALYST

	Compounds	Mole, % Cl		% CCl_4	CCl_3Br	CCl_2Br_2	$CClBr_3$	CBr_4
3	CCl_4, CBr_4	0.723	obs.	29.6	38.6	23.5	6.8	1.5 ±
			calc.[4]	27.3	41.9	24.1	6.1	0.6
4	CCl_4, CBr_4	0.623	obs.	12.9	38.8	34.5	12.1	1.7 ±
			calc.[4]	15.1	36.5	33.1	13.3	2.0
5	CCl_3Br, CCl_2Br_2	0.67	obs.	19	41	28	11	1 ±
			calc.[4]	20.2	39.7	29.3	9.6	1.2

TABLE II

REDISTRIBUTION OF THE SILICON CHLOROBROMIDES; NO CATALYST

	Compounds	Mole, % Cl		% $SiCl_4$	$SiCl_3Br$	$SiCl_2Br_2$	$SiClBr_3$	$SiBr_4$
1	$SiCl_4$, $SiBr_4$	0.50	(obs.	15.3	22.5	25.1	22.5	14.6)
			calc.	6.25	25.0	37.5	25.0	6.25
2	$SiCl_3Br$	0.75	obs.	31.0	39.8	26.5	2.7	(0)
			calc.	31.6	42.2	21.1	4.7	0.4
3	$SiCl_3Br$, $SiClBr_3$	0.60	obs.	12.1	38.8	28.4	19.0	1.8 ±
			calc.	12.96	34.56	34.56	15.36	2.56

experiments listed in Table I, slightly moistened aluminum chloride was used as a catalyst, and the pressure of hydrogen chloride in the sealed tube was apparent. Random distribution was now attained within experimental error. The calculated mole percentages in Table I are figured from Calingaert's equations.[4] We have found no previous record of a direct reaction between carbon tetrachloride and carbon tetrabromide.

Experimental.—Carbon tetrabromide was precipitated from a water solution containing 25 g. of sodium hydroxide, 1 cc. of acetone and 5 cc. of bromine per liter as recommended by Wallach.[18] About 120 g. of crude product was recovered, washed, dried by suction and fused. A mixture with carbon tetrachloride in a known mole ratio was heated in a sealed tube at 170° for seven hours. Decomposition of carbon tetrabromide would have been excessive at higher temperatures or over longer periods. The reaction, if any, was less than 10% of the whole. A second experiment, with introduction of dry aluminum chloride, generated no pressure in the tube and appeared to yield no chlorobromides. In the succeeding experiments the aluminum chloride was spread out on paper, and breathed upon to activate it, presumably through formation of hydrogen chloride. Redistribution now occurred readily. After washing with caustic solution and drying with calcium chloride, the liquid mixture, 5–7 ml. in volume, was distilled using a column 30 cm. high and 7 mm. in diameter with a spiral of No. 22 copper wire having 80 turns, and was surrounded with a vapor jacket. Simultaneous readings were made of temperature, and of the depth of liquid collected in small flat-bottomed tubes backed by a millimeter scale. Satisfactory "flats" were observed at the boiling points of the first four members of the series, namely, 77°, 104°, 134°, and 160°. The cuts were made half-way between these temperatures. Small corrections were applied to the fractions for the estimated molar volumes of the respective chlorobromides. We encountered difficulties in separating the last of the chlorotribromide from tetrabromide in the last, very small, fraction. Our system was further complicated by presence of the compounds C_2Br_4 and C_2Br_6. In Experiment 3, presence of carbon tetrabromide was established qualitatively, but the figures in the last column indicate nothing beyond orders of magnitude. The other volumes, read within 0.05 ml., yielded mole percentages significant, we believe, within 2%.

Silicon Chlorobromides.—Silicon tetrachloride and tetrabromide were heated for seventy hours in a sealed tube at 140° without a catalyst. The physical properties of the fractionated products were measured, or remeasured to improve previously existing data. The figures are being submitted for separate publication in THIS JOURNAL. For redistribution studies, however, the different reactants in known mole ratios were passed through a tube at 600° approximately. Equilibrium was established quite rapidly, but the first experiment was evidently too hurried, so that mixtures 2 and 3 were passed at a half and a quarter of this rate, respectively. Table II summarizes the results. Corrections for the respective molar volumes have been applied.

Experimental.—In Experiment 1, 12 ml. of mixed liquids passed through a tube of 17-ml. volume at about 600° in forty-five minutes, but about 20% of the reactants escaped reaction. Table II shows that the second and third rates were not too rapid at the temperatures prevailing. During distillation in the apparatus described above, the temperature moved very slowly, over considerable volume intervals, in the vicinity of the boiling points of the five pure compounds, 57°, 80°, 104.5°, 128° and 153°, respectively. The last half of fraction 4 in Experiment 3 boiled at an average temperature of 132° instead of 128°, indicating the presence of some 16% of silicon tetrabromide. The volumes of tetrabromide in Experiments 2 and 3 indicate orders of magnitude only.

Since the members of the series carbon tetrachloride through carbon tetrabromide require a catalyst for rearrangement at 170°, while the members of the corresponding silicon series rearrange without a catalyst, it appears that carbon tetrahalides are much more stable with respect to rearrangement than those of silicon.

Silicon Chloroiodides.—Treatment of silicon tetrachloride with fused potassium iodide yielded a relatively small amount of $SiCl_3I$. Upon passage through a hot tube, a mixture of all five members of the series was obtained. At 58°, 114° and 172°, the boiling points of the first three members, the "flats" were especially sharp. The fractions in Table III approximate random distribution.

TABLE III

	$SiCl_4$	$SiCl_3I$	$SiCl_2I_2$	$SiClI_3$	SiI_4
Mole % observed	30.4	42.7	22.0	3.7	1.2
Mole % calculated	31.6	42.2	21.1	4.7	0.4

Silicon chlorobromides, chloroiodides and chlorocyanates attain random distribution without a catalyst. If fractionation of such mixtures is complete within a few hours,

---

[18] Wallach, *Ann.*, **275**, 149 (1893).

the products are separated without appreciable rearrangement.

Germanium Chlorobromides.—Booth and Morris[19] prepared the closely related germanium fluorochlorides. Held at −78°, these rearranged to the extent of 60% within two weeks. We passed an equimolar mixture of tetrachloride and tetrabromide, prepared separately from the elements, through a hot tube at 600°. Five milliliters of the liquid product was distilled through the column described above, but more rapidly than the carbon and silicon chlorides. The initial rise in the actual distillation curve (Fig. 1) is consistent with a small percentage of tetrachloride and a low reflux ratio. Next, $GeCl_4$ and $GeCl_3Br$ are formed at the expense of higher chlorobromides and bled off. The first intermediate, $GeCl_3Br$, evidently distills off at 112°, between 25 and 36 atom per cent. of bromine allowing for products already distilled. Its calculated boiling point, 109°, is one-quarter of the way between 83° and 186.5°, the boiling points of the end members. On the whole the separate existence of germanium trichlorobromide, boiling point 111 ± 3°, is supported by the data. Redistillation of 12 ml. of distillate collected between 96° and 122° yielded relatively little at 109°, and large fractions approximating the end members. Evidently rearrangement is quite rapid between these temperatures. In another distillation, still more rapid, inconclusive retardations of the temperature rise seemed to occur near 135° and 161°, but we are reluctant to offer these in evidence. The upper half of the actual distillation curve shown in Fig. 1 resembles a curve for a mixture of stable end members.

Mixed Stannic Halides.—Besson[20] found it impossible to separate stannic chlorobromides from each other by repeated fractionation even under greatly diminished pressure. He states that this would result in total decomposition of the desired products into stannic chloride and stannic bromide. By fractional freezing he then obtained three products which he held to be the three chlorobromides of tin—quite nearly pure.

Raeder's freezing point curves for the systems $SnBr_4 + SnI_4$[21] and $SnCl_4 + SnBr_4$[22] indicated continuous series of mixed crystals without compound formation. He showed[22] why Besson's procedure led to fractions having the properties observed by him. In the system $SnCl_4 + SnI_4$, however, he found evidence of the compound $SnCl_2I_2$[22] having an incongruent melting point, and stable only below −47°.

As we were disinclined to undertake a further study of this problem, we merely passed equal volumes of stannic chloride and bromide through the hot tube, and redistilled the condensate in the same apparatus as used with the other chlorobromides, over a half-hour period. The distillation curve (Fig. 1) shows no retardations of temperature increase at any of the calculated boiling points of the chlorobromides. Its initial slope suggests rapid replacement of tetrachloride at the expense of chlorobromides. It lacks the steep middle portion to be expected, in this apparatus, of two non-reacting liquids boiling at 114° and 202°, respectively. Extrapolating the findings for carbon, silicon and germanium, one would predict a random mixture of all members of the tin series, very rapidly rearranging at all the distillation temperatures, in harmony with Raeder's conclusions. It would be of interest to determine whether mixed tin halides containing one or more fluorine atoms could be isolated.

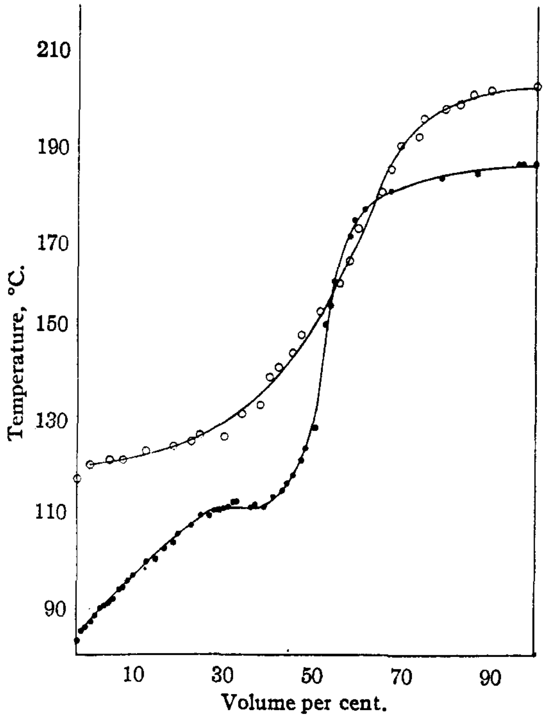

Fig. 1.—Distillation curves of germanium (●) and stannic (○) chlorobromides.

Summary

Mixtures of carbon tetrachloride and tetrabromide, as well as the carbon chlorobromides, rearrange in seven hours at 170° with slightly moistened aluminum chloride as a catalyst, until halogen atoms are distributed among the five members of the series according to the laws of probability

The corresponding rearrangements in the silicon series (chlorobromides and chloroiodides) in seven hours at 140° without catalyst are partial, but complete after passage through a tube at 600°. These random mixtures can be fully separated by fractional distillation at normal pressure without appreciable rearrangement.

Distillation curves of the hot tube product from germanium tetrachloride and tetrabromide show definite indications of the new compound $GeCl_3Br$ at 112° approximately. Upon redistillation of such a fraction, rapid redistribution takes place.

The slope of a distillation curve of the stannic chlorobromides showed no irregularities near the boiling points calculated for the mixed compounds. Some indication of redistribution was obtained, although the individual compounds could not be isolated, presumably because of redistribution during distillation.

None of the phenomena observed were inconsistent with the hypothesis that all possible members of the germanium and tin chlorobromide series coexisted in random distribution.

The stability, against rearrangement, of the chlorobromides of Group IVA decreases steadily from carbon to tin.

CAMBRIDGE, MASS. RECEIVED JANUARY 24, 1944

---

[19] Booth and Morris, THIS JOURNAL, **58**, 90 (1936).

[20] Besson, *Compt. rend.*, **124**, 683 (1897).

[21] Raeder, *Z. anorg. allgem. Chem.*, **130**, 325 (1923).

[22] Raeder, *ibid.*, **162**, 222 (1927).