assuming a low degree of dissociation of the ferrous oxalate itself.

The low-oxalate, alkaline developers deposit ferric oxide along with the silver during development. If the silver is removed by suitable means, a ferric-oxide image remains behind. If the solution is sufficiently alkaline, ferric oxide is deposited even in the presence of considerable amounts of oxalate. At *p*H 8.7, strong oxide images were obtained even in the presence of 0.2 *M* oxalate, although little ferric oxide was in evidence at 0.6 *M* oxalate.

Summary

1. The rate of development in a dilute ferro-oxalate developer of low excess oxalate-ion concentration increases with *p*H in the range 8.0 to 8.5. The increase was observed with photographic films made with lime-process gelatin and with acid-process gelatin. The increase was not observed at high excess oxalate-ion concentration, where the development characteristics are those of development by a doubly charged agent.

2. At low excess oxalate-ion concentration and *p*H greater than 8.0, development shows no induction period and very little sensitivity to bromide-ion concentration. The general characteristics are those of development by an uncharged (or possibly a positively charged) agent.

3. It is suggested that ferrous hydroxide (or the $FeOH^+$ ion) is the active developing agent.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Rearrangements in Compounds of Carbon, Silicon, Germanium and Tin containing Halogens, Isocyanate and Thiocyanate

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

The redistribution reactions, long known qualitatively,[1] were first quantitatively shown to be random by Calingaert and co-workers[2] in certain alkyls, chloroalkyls and ethylene halides. A previous paper[3] demonstrated the same outcome in the silicon chloroisocyanates. Further we have shown in a recent report[4] that the chlorobromides of carbon, silicon, germanium and tin, also the chloroiodides of silicon, all tend toward random distribution. The halides of carbon require a catalyst such as slightly moistened aluminum chloride, while the mixed halides of each succeeding element of Group IVA react with greater speed at distillation temperatures. In these papers[3,4] we have discussed the redistribution reaction from qualitative and quantitative standpoints, and have cited typical papers upon the subject without any effort to make the list complete. Still more recently, Mayo and Dolnick[5] have studied catalyzed rearrangements, at equilibrium, of halogen atoms in dihaloethanes and in bromopropanes.

The purpose of this article is to describe a study from the same standpoint, of a greater variety of Group IVA compounds. These include methane derivatives containing two or three halogen atoms, the recently synthesized trichlorosilicon thiocyanate,[6] germanium chloroisocyanates, and in addition oxidation products of stannous oxide and stannous fluoride.

Experimental

Chloroform and Bromoform.—No previous record of a reaction between these compounds could be found. Under the conditions described below, approximately random distribution was attained, as shown in Table I. The hydrogen showed no perceptible tendency to migrate. To minimize separation of carbon, oxygen was displaced by carbon dioxide. This method is advantageous for preparation of the two intermediate chlorobromides.

Bromoform was prepared by gradual addition of bromine and sodium hydroxide to a water solution of acetone.[7] The crude product was washed, dried with calcium bromide, and purified by distillation with care to collect material boiling from 149 to 150° for use in redistribution studies. Bromoacetone, b. p. 136.5°, was present in traces only. Mixtures of chloroform and bromoform were heated in sealed tubes in presence of potassium chloride and aluminum chloride containing hydrochloric acid produced by partial hydrolysis. The crude product was washed with caustic solution, then with water and centrifuged to help the separation of the layers. After drying with calcium chloride the mixture was analyzed by distillation using the following procedure, typical of all the experiments with carbon and germanium compounds. A liquid mixture of 3–6 ml. was distilled using a column 20 cm. high made of tubing 7 mm. in outside diameter and having a spiral of no. 22 copper wire with 56 turns. Distillation curves of mixtures of *stable* components boiling 30° or more apart always consist of "flats" close to predicted boiling points connected by steep, almost linear sections. Readings of temperature and of volume were made simultaneously; the latter was measured to 0.01 ml. in special tubes of 1–2 ml. capacity graduated to 0.1 ml. These tubes were checked at several points by delivery of mercury from a standardized 0.1 ml. micropipet. Thus the volume of any particular fraction was known within 0.01–0.02 ml., or within 1% of the total volume of the reaction product,

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(1) See, for instance, Besson, *Compt. rend.*, **122**, 814 (1896).

(2) Calingaert and others, THIS JOURNAL, **61**, 2748, 2755, 2758, 3300 (1939); **62**, 1099, 1104 (1940).

(3) Anderson, *ibid.*, **66**, 934 (1944).

(4) Forbes and Anderson, *ibid.*, **66**, 931 (1944).

(5) Mayo and Dolnick, *ibid.*, **66**, 985 (1944).

(6) Anderson, *ibid.*, **67**, 223 (1945).

(7) L. Vanino, "Handbuch der präparativen Chemie," Vol. II, F. Enke, Stuttgart, 1937, p. 15.

3–6 ml. Cuts were made or interpolated at temperatures half way between the boiling points of the several compounds—$CHCl_3$, 61.3°; $CHCl_2Br$, 91–92°; $CHClBr_2$, 120° and $CHBr_3$, 149.5°. Satisfactory "flats" were observed close to 91.5 and 120.5°. Slight uncertainties were introduced by evaporation and by the assumption that division of the volume of a given fraction by the appropriate molar volume of a pure compound gave the number of moles of that compound. In the initial experiment air was not excluded and a temperature of 180° was maintained for sixteen hours. This treatment proved too drastic, for much black solid (carbon ?) was formed, and a high gas pressure was developed. A run of eighteen hours at 114° with catalyst (and air), starting with 4.8 ml. of $CHCl_3$ and 3.0 ml. of $CHBr_3$ went about 40% of the way to equilibrium (Table I, no. 1). The best result was obtained starting with 3.0 ml. of $CHCl_3$ and 2.1 ml. of $CHBr_3$ heated for fourteen hours at 135° in an atmosphere of carbon dioxide. Perhaps nitrogen would have been an even better atmosphere. The crude product contained little free carbon, and the redistribution (Table I, no. 2) is random within experimental error.

Methylene Chloride and Methylene Bromide or Iodide.—These reactions proceed easily upon heating the reactants in a sealed tube with 5–10% by weight of potassium chloride and moistened aluminum chloride as catalyst. The amounts of methylene chlorobromide and methylene chloroiodide correspond closely to random distribution (Table II) so that the method is practicable for small-scale preparations. Even in the presence of air little carbon is formed.

Methylene chloride and bromide, 5.7 and 3.8 ml., respectively, were heated sixteen hours at 180° with the catalyst described above. The purification of the crude product and its analysis by distillation were carried out as described in the previous experimental section. The boiling points are: CH_2Cl_2, 41.6°; CH_2ClBr, 68–69°; CH_2Br_2, 98°; the "flat" corresponding to CH_2ClBr occurred at 68.8° (uncor.). The mole fraction of chlorine was calculated from the mole ratio of the purified reaction products.

Methylene chloride and iodide, 4.2 and 3.0 ml., respectively, required only eighteen hours at 114° with the usual catalyst. The crude reaction product was quite dark. In this experiment the amount of methylene chloroiodide is 3% low, outside of the over-all experimental error of 1%, and indicates a somewhat insufficient period of heating. The boiling points are: CH_2Cl_2, 41.6°; CH_2ClI, 109° and CH_2I_2, 181° with partial decomposition. The "flat" corresponding to CH_2ClI was observed at 107–108° (uncor.).

Preliminary experiments with methylene bromide and methylene iodide were made. In the first run, with aluminum chloride catalyst, methylene chloride and chlorobromide were detected in the products. In the second run, 2 ml. of methylene bromide and 3.3 ml. of methylene iodide were heated in a sealed tube for twenty hours at 140° in air, with mercuric bromide as a catalyst. Distillation of the product after purification yielded 8% of methylene chloroiodide boiling close to 139°. Since this amounted to 16% reaction only, 150 hours at 140° would probably have been required for attainment of random distribution.

Preliminary Experiments on Chloroform and Iodoform.—Mixtures heated in sealed tubes with slightly moistened aluminum chloride in presence of air liberated much iodine. . Refluxing in hexane as a solvent in presence of the same catalyst also proved unsuccessful. The sealed tube method should be repeated with mercuric chloride in an atmosphere of nitrogen.

Disproportionation of Silicon Trichlorothiocyanate; Silicon Tetrachloride and Silicon Tetrathiocyanate.—It has been shown[6] that if silver thiocyanate is gradually added to a considerable excess of silicon tetrachloride in benzene solution, silicon trichlorothiocyanate is the only stable mixed compound obtainable by fractional distillation at either atmospheric or diminished pressure. A sample of the trichlorothiocyanate, after five months at room temperature, had rearranged to the extent of 35%.[6] Another sample sealed in glass after nineteen months at room temperature was now found to contain about 16% of silicon tetrathiocyanate, which implied that 37 mole per cent. of trichlorothiocyanate remained and that 47 mole per cent. of tetrachloride had been formed.

Vapors of trichlorothiocyanate, also mixed vapors of tetrachloride and tetrathiocyanate in the mole ratio of three to one, were passed through a hot tube at 600°. The composition of the products was the same within experimental error irrespective of the direction of the reaction: $SiCl_4$, 37.8 mole %; $SiCl_3(SCN)$, 49.5 mole %; $Si(SCN)_4$, 12.7 mole %. At the temperature where the reaction "froze," the equilibrium constant K_x in terms of mole fractions for the reaction $4SiCl_3SCN \rightleftarrows 3SiCl_4 + Si(SCN)_4$ is 0.11.

Convenience in manipulation of our hot-tube apparatus required that the reactant(s) be introduced dropwise. Therefore the two-phase mixture of tetrachloride and tetrathiocyanate, in the mole ratio three to one, had to be preheated in a closed tube for twenty-four hours at 112°. Through partial redistribution a liquid mixture was produced. Silicon trichlorothiocyanate was similarly preheated for twenty-four hours at 140°. At 600°, volatilization and attainment of equilibrium occurred immediately. The products were collected and analyzed by distillation. The bulb was weighed empty, then with the total sample. The loss in weight up to 93° was taken as the weight of tetrachloride. The subsequent loss in weight up to 200° represented trichlorothiocyanate. Finally, by subtraction of the weight of the empty bulb, the weight of the solid tetrathiocyanate resulted. Table III gives the mole fractions correct, we believe, to within about one per cent. of the entire sample.

Silicon isocyanate and thiocyanate were brought to equilibrium in a hot tube. Analysis by distillation at 760 mm. gave no evidence of a definite intermediate compound. The distillation curve at 28 mm., however, included a "flat" strongly indicative of the new compound $Si(NCO)_3SCN$ as explained in greater detail below. Although this fraction could hardly be altogether stable upon redistillation, we still entertain hopes of isolating silicon tetraisocyanatothiocyanate in a relatively pure state.

The reactants were heated together for forty hours at 140°. The original mixture contained 22.9 and 10.8 g. of the components respectively, or 26 mole per cent. of SCN. One weighed portion of the final mixture was analyzed by distillation at 760 mm. according to the volumetric method described above. In Fig. 1 boiling point is plotted against percentage distilled. Although the curve at 760 mm. shows no "flat," its shape is suggestive of at least one unstable intermediate component. A second portion was analyzed by distillation at 28 mm. For this experiment an all-glass system was constructed, including bulb, column,

TABLE I

(A) REDISTRIBUTION BETWEEN CHLOROFORM AND BROMOFORM

			$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Treatment
1	$CHCl_3 + CHBr_3$, %	Obs.	47	17	11	25	18 hrs. at 114°
2	$CHCl_3 + CHBr_3$, %	Obs.	17	43	31	9	14 hrs. at 135°
		Calcd.	17.4	41.4	32.6	8.6	(for Cl = 0.556)

(B) REDISTRIBUTION BETWEEN METHYLENE HALIDES

			CH_2Cl_2	CH_2ClBr	CH_2Br_2	Treatment
1	$CH_2Cl_2 + CH_2Br_2$, %	Obs.	33	50	18	16 hrs. at 180°
		Calcd.	33.0	48.9	18.2	(for Cl = 0.574)

			CH_2Cl_2	CH_2ClI	CH_2I_2	Treatment
2	$CH_2Cl_2 + CH_2I_2$, %	Obs.	33	46	21	18 hrs. at 114°
		Calcd.	31.5	49.2	19.3	(for Cl = 0.561)

(C) REDISTRIBUTION INVOLVING SILICON TRICHLOROTHIOCYANATE

			$SiCl_4$	$SiCl_3(SCN)$	$Si(SCN)_4$	Treatment
1	$SiCl_3(SCN)$, %	Obs.	37	50	13	600°
2	$3SiCl_4 + Si(SCN)_4$, %	Obsd.	39	49	12	600°

45° ground dripper, and beyond the head a Y tube. The lower end of the latter was sealed to a ground joint communicating with a piece of 8-mm. tubing backed by a millimeter scale. Simultaneous readings of volume distilled and temperature could thus be made. The small amount of silicon tetrathiocyanate remaining in the bulb was estimated. The distillation curve (Fig. 1) has a well-defined flat at 126° approximately which is plausibly ascribed to the compound $Si(NCO)_3SCN$, since the pure isocyanate boils at 98° under 28 mm.,[8] approximately. As the distillation pressures fluctuated slightly, the observed temperatures were all corrected back to 28 mm. by means of temperature-pressure data previously obtained by us, before plotting them upon the lower curve.

Germanium Chloride and Isocyanate.—In earlier experiments, by reaction of silver isocyanate with large excess of germanium tetrachloride in carbon disulfide solution, a product apparently containing trichloroisocyanate had been obtained. Several mixtures of chloride and isocyanate were now conducted through a hot tube at 500° with slight decomposition of the latter compound. The distillation of the first portion of the product was made at 760 mm. and occupied one hour. The corresponding plot merely suggested the presence of unstable intermediates. Distillations of two other portions, at 760 mm., and completed within ten minutes each, yielded curves closely resembling that for a mixture of germanium chloride and bromide previously passed through a hot tube.[4] The "flat" indicative of germanium trichloroisocyanate, $GeCl_3NCO$, occurred at 112°, just like that for germanium trichlorobromide, $GeCl_3Br$, in the earlier research. Upon redistillation at 760 mm. the fraction corresponding to trichloroisocyanate redistributed rapidly into chloride and isocyanate, in full agreement with the behavior of the trichlorobromide.[4] Further investigation of both these compounds is contemplated.

Stannous Oxide or Fluoride with Chlorine or Bromine.—Weber,[9] also M. Berthelot,[9] treated stannous oxide with chlorine and obtained stannic oxide and stannic chloride only. Berthelot postulated intermediate formation of a stannic oxychloride, $SnOCl_2$. The final outcome corresponded to oxidation followed by disproportionation. The same products were obtained by heating stannous chloride with oxygen in a sealed tube.

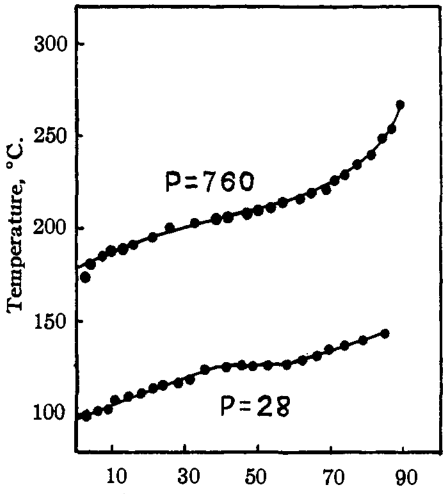

Fig. 1.—Stability of $Si(NCO)_3SCN$.

We thought it desirable to investigate additional reactions of the same type. In separate experiments, chlorine and bromine were passed over stannous oxide at 550 to 600°. The reactions were presumably

$$2SnO + 2Cl_2 \longrightarrow SnO_2 + SnCl_4$$
$$2SnO + 2Br_2 \longrightarrow SnO_2 + SnBr_4$$

for when the condensates were distilled their boiling points were those of stannic chloride and stannic bromide only. A crude sample of stannous fluoride, doubtless partially hydrolyzed and oxidized, was prepared by dissolving stannous oxide in hydrofluoric acid, evaporation, fusion and powdering. Portions of the resulting solid were

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(8) Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940).

(9) Weber, *Pogg. Ann.*, **112**, 619 (1861); M. Berthelot, *Ann. chim. phys.*, (5) **15**, 185 (1878).

treated separately with chlorine and with bromine. The essential reactions appeared to be

$$2SnF_2 + 2Cl_2 \longrightarrow SnF_4 + SnCl_4$$
$$2SnF_2 + 2Br_2 \longrightarrow SnF_4 + SnBr_4$$

Again, the boiling points of these condensates indicated stannic chloride and bromide only. The most vigorous of the four reactions was that between stannous fluoride and chlorine, as a flame, not visible in the other three, was observed. Bromine reacted more vigorously and, it seemed, more completely upon stannous fluoride than upon stannous oxide. As our interest was centered upon the volatile products, the solid residues were not investigated.

Discussion of Results

Our previous article[4] showed that random distribution can occur among the tetrahalides of carbon, silicon, germanium and tin. Silicon chloroiodides[4] and chloroisocyanates follow the same rule. If the data furnished by the present article are included, it becomes permissible to state that redistribution tends to occur in compounds of Group IVA elements with chlorine, bromine, isocyanate, thiocyanate and iodine. The readiness of rearrangement increases from carbon to tin and from chlorine to iodine, and is in general favored by increasing atomic volume, also by decreasing electronegativity of halogens and pseudohalogens. Many stable mixed substituted methanes but relatively few stable mixed substituted silanes are known. The latter include halides with isocyanate, oxyhalides and thiochlorides, and one mixed chlorothiocyanate, $SiCl_3SCN$.[6] The germanium fluorochlorides, subject to gradual rearrangement even at −78°, were isolated by Booth and Morris.[10] As shown above, germanium trichloroisocyanate, $GeCl_3NCO$, appears capable of existence, but rearranges quite rapidly at 112°. The same can be said of germanium trichlorobromide, $GeCl_3Br$, at the same temperature.

Ruff and Plato[11] isolated from a solution of stannic chloride in liquid hydrofluoric acid a solid having the empirical composition $SnCl_4 \cdot SnF_4$, which evolved stannic chloride at red heat. Raeder[12] showed that stannic dichlorodiiodide, $SnCl_2I_2$, appears to have an incongruent melting point at −47°. The lattice characteristics of stannic fluoride and oxide would seem to preclude existence of oxyhalides capable of being volatilized without decomposition.

Summary

1. Random distribution of halogen atoms occurs when certain pairs of halogen substituted methanes are heated to suitable temperatures with a suitable catalyst. These include methylene chloride and bromide, methylene chloride and iodide, also chloroform and bromoform. All these mixtures were heated with potassium chloride and partially hydrolyzed aluminum chloride. Partial rearrangement was obtained with methylene bromide and iodide in presence of mercuric bromide. This method offers some advantage for preparation of mixed methylene halides.

2. Equilibrium in the reaction $4\ SiCl_3SCN \rightleftarrows 3\ SiCl_4 + Si(SCN)_4$ has been approached from both sides at 600° or less. The equilibrium constant, in terms of mole fractions, is close to 0.11 in each instance.

3. Silicon isocyanate and thiocyanate when heated together in a sealed tube at 140° for forty hours undergo partial rearrangement. The distillation curve at 28 mm. pressure definitely indicates at 126° approximately the probable existence of the new compound silicon triisocyanatothiocyanate $Si(NCO)_3SCN$. Rearrangement at 760 mm. and 215° is very rapid, but isolation of the pure compound is still considered possible.

4. Germanium chloride and isocyanate were brought to reaction in a hot tube at 500°. The distillation curve of the product at atmospheric pressure indicated the probable existence of the new compound germanium trichloroisocyanate, $GeCl_3NCO$, boiling at 112° approximately, and subject to severe decomposition when redistilled.

5. Three new reactions were observed involving halogenation of stannous compounds followed by disproportionation. These include stannous oxide with bromine, stannous fluoride with chlorine and stannous fluoride with bromine. As in the previously known reaction between stannous oxide and chlorine, the products obtained upon distillation are binary stannic compounds only. The solid residues were not further investigated.

6. A further systematization of the stabilities of ternary compounds in Group IVA is attempted in the light of the above data.

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(10) Booth and Morris, THIS JOURNAL, **58**, 90 (1936).

(11) Ruff and Plato, *Ber.*, **37**, 681 (1904).

(12) Raeder, *Z. anorg. allgem. Chem.*, **162**, 222 (1927).