an immediate reaction was observed to take place with the formation of large amounts of solid in agreement with Trost's reports, if unpurified components are mixed out in the open. It is suspected that a catalyzed reaction of some type takes place as a result of the presence of impurities, thus accounting for the differences in behavior observed.

Lastly, neither of Trost's higher complexes, $3Et_3N \cdot PCl_3$ and $5Et_3N \cdot 2PCl_5$, were found in this study under the experimental conditions employed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Reduction of Phosphorus and Antimony Chlorides by Trimethylarsine and Trimethylstibine[1]

BY ROBERT R. HOLMES AND EDGARD F. BERTAUT[2]

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Trimethylarsine formed 1:1 complexes with either phosphorus or antimony trichloride. With the corresponding pentachlorides, trimethylarsine acted to reduce them to the trichloride stage accompanied by the appearance of trimethylarsine dichloride. The reaction of trimethylstibine with both the tri- and pentachlorides led to complete reduction to the element and the formation of trimethylstibine dichloride in each case. The results suggested a four step mechanism for the over-all reduction process of the pentachlorides involving complex formation and the appearance of the trichloride as intermediate steps.

As shown in the previous paper,[3] when phosphorus or antimony chloride is treated with trimethylamine, triethylamine or trimethylphosphine, the primary result was complex formation. In only one instance did a reaction other than complex formation take place, namely, the reaction of phosphorus pentachloride with either trimethyl- or triethylamine. In the latter case reduction to the trichloride occurred. However, on going to heavier members of the series, trimethylarsine and trimethylstibine (concerning which prior literature is completely lacking), we found that reduction of the halide to the element became the predominant reaction. This action is particularly pronounced with trimethylstibine.

It was felt that an investigation of the path of the reduction might prove fruitful in allowing a general correlation to be made concerning the action of the various trimethyl derivatives of Group Vb on Group Vb chlorides.

Experimental

Apparatus and Procedures.—The apparatus and procedures for carrying out the reactions are the same as those reported in the previous paper,[3] the only significant modification being the construction of an additional reaction section so that two interactions could be studied simultaneously in the high vacuum system. This proved desirable because of the slowness with which the reduction reactions proceeded.

Materials.—The tri- and pentachlorides of phosphorus and antimony used in this study were purified in the same fashion as described in the previous paper.[3]

Trimethylarsine was prepared by variations of the methods outlined by Harris[4] and by Mann and Purdie.[5] This substance proved to be the most difficult of the trimethyl derivatives to prepare primarily because of the difficulty in isolating the trimethylarsine from the solvent used, diethyl ether. Harris used butyl ether as a solvent and separated trimethylarsine by a time consuming fractionation procedure. Mann and Purdie isolated the crude product using $(NH_4)_2PdCl_4$ to form $(Me_3As)_2PdCl_2$ and regenerated pure trimethylarsine by thermal decomposition of the latter complex *in vacuo*. We chose the latter course but discovered that the amount of trimethylarsine obtained depended considerably on the temperature at which the thermal decomposition was carried out. Mann and Purdie did not report any details concerning their preparation and we did not investigate this point fully. The yield we obtained was poor. To augment this, a sample prepared by Harris at Purdue University was used. The trimethylarsine was dried and purified in the line by a procedure similar to that described for trimethylphosphine in the previous paper.[3] Its vapor pressure at 0° was 101.0 mm.

Trimethylstibine was prepared by a procedure similar to that outlined by Harris[4] in which excess methylmagnesium chloride reacted with antimony trichloride in ethyl ether solution, the crude product being isolated by forming solid trimethylstibine dibromide, Me_3SbBr_2, with bromine. It melted with decomposition at 185.5–186.0°. Heating the dibromide with zinc metal in the presence of water freed the trimethylstibine. It was introduced into the line and dried in contact with phosphorus pentoxide and fractionated to a constant vapor pressure of 30.5 mm. at 0°.

Trimethylarsine Reactions. Me_3As–PCl_5.—Trimethylarsine (3.41 mmoles) reacted with phosphorus pentachloride (0.66 mmole) in the vacuum line at room temperature to form a white solid while giving off a volatile substance suspected to be phosphorus trichloride. After 15 days no further take up of trimethylarsine was observed. The volatile material recovered (3.20 mmoles; total vapor pressure, 88.5 mm. at 0°) from the reaction was condensed over KOH pellets to absorb the suspected phosphorus trichloride. Pure trimethylarsine remained (2.74 mmoles) as measured by its vapor pressure of 100.3 mm. at 0°. This corresponds to a mole ratio of 1.01 moles of trimethylarsine per mole of phosphorus pentachloride. The reaction occurring[6] would therefore be

$$Me_3As + PCl_5 \longrightarrow Me_3AsCl_2 + PCl_3$$

Me_3As–PCl_3.—The two liquid reactants, trimethylarsine (6.00 mmoles) and phosphorus trichloride (0.98 mmole), reacted rapidly at −29.5° to form a white solid, insoluble in excess trimethylarsine. On successive removal of small portions of the arsine, the vapor pressure remained constant at the vapor pressure of pure trimethylarsine (26.3 mm.) at this temperature until 5.03 mmoles had been removed. At this point the vapor pressure dropped to 8.8 mm. at −29.5° and remained constant with further arsine removal. The latter plateau corresponds to a reversible dissociation

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[1] Presented in part before the Physical Inorganic Division at the 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957. Based on a thesis submitted by Edgard F. Bertaut in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

[2] Research Corporation Fellow (1955–1957).

[3] R. R. Holmes and E. F. Bertaut, THIS JOURNAL, **80**, 2980 (1958).

[4] R. H. Harris, Ph.D. Thesis, Purdue University, 1952.

[5] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 873 (1936).

[6] The analysis shows the formation of 0.46 mmole of phosphorus trichloride (0.66 mmole expected). It was noted that phosphorus trichloride slowly reacts with mercury in the vacuum system, possibly accounting for the reduced amount of phosphorus trichloride.

of the solid of composition $(Me_3As)_{0.99}PCl_3$. On warming the solid to 0°, it liquefied with further dissociation.

Me_3As–$SbCl_5$.—Solid antimony pentachloride (1.50 mmoles) initially reacted rapidly with small amounts of trimethylarsine at 0°. A 1:1 white reaction product insoluble in excess trimethylarsine formed in approximately 10 hr. Further reaction took place, becoming complete after 180 hr. as evidenced by no further loss of trimethylarsine after 72 additional hr. The product composition corresponded to the reaction of 2.03 moles of trimethylarsine per mole of antimony pentachloride. The white product proved to be a mixture, part of which was soluble in carbon tetrachloride; the remainder dissolved in acetone. Both solids slowly turned gray in air, indicating decomposition and precluding effective analysis.

Me_3As–$SbCl_3$.—Treatment of solid antimony trichloride with excess trimethylarsine (3.49 mmoles) at room temperature resulted in a prolonged reaction coming to completion after 195 hr. A powdery white solid insoluble in excess trimethylarsine formed having the composition $(Me_3As)_{0.99}$-$SbCl_3$. The solid on recrystallization from acetone melted with decomposition at 145–146.5°. It slowly turned gray in air.

Trimethylstibine Reductions. Me_3Sb–PCl_5.—Phosphorus pentachloride (1.08 mmoles) slowly reacted with excess trimethylstibine (8.96 mmoles) at 0° to give first a green-yellow solid forming up to about a 1:1 mole ratio which then turned to a non-volatile mixture of an orange and a white solid on further reaction to a 2.31:1 mole ratio of the stibine to phosphorus pentachloride. The reaction was complete after 153 hr. as attested by successive interactions of the product with excess trimethylstibine. The product mixture was extracted with acetone. An orange insoluble solid remained on filtering, which latter was washed several times with fresh acetone and dried in air. The filtrate and washings were evaporated in air and yielded a white solid, which was recrystallized from acetone, melting point 228–229°. A 50:50 mixture of these crystals and a previously prepared sample of pure Me_3SbCl_2[7] melted similarly.

The orange solid dissolved readily in concentrated nitric acid. Qualitative tests[8] showed the presence of phosphorus and the absence of chlorine and mercury.

The above knowledge, combined with the stoichiometry obtained, shows that the reaction is

$$2.5Me_3Sb + PCl_5 \longrightarrow 2.5Me_3SbCl_2 + P$$

Me_3Sb–PCl_3.—Phosphorus trichloride (0.59 mmole) reacted rapidly with small additions of trimethylstibine at 0° up to a mole ratio of one and formed an orange-white solid. A slower reaction ensued with additional trimethylstibine until reaction was complete. A total of 0.86 mmole of trimethylstibine were taken up, corresponding to reaction of 1.46 moles of trimethylstibine per mole of phosphorus trichloride.

An exactly similar treatment of the orange-white solid as outlined above in the trimethylstibine–phosphorus pentachloride system was carried out. Again the products were found to be elemental phosphorus and trimethylstibine dichloride corresponding to the equation

$$1.5Me_3Sb + PCl_3 \longrightarrow 1.5Me_3SbCl_2 + P$$

Me_3Sb–$SbCl_5$.—Initially rapid reaction of antimony pentachloride (1.99 mmoles) was observed at 0° on additions of trimethylstibine, resulting in the formation of a white, non-volatile solid. The reaction rate began to slow up markedly after a mole ratio of 1:1 was reached. The white solid began turning black after the reaction was about 60% complete. The remaining part of the reaction was carried to completion at room temperature. Measurement of the unreacted trimethylstibine gave a total reaction of 2.47 moles of stibine per mole of pentachloride. The black insoluble material was washed with distilled water and dissolved in concentrated nitric acid. Qualitative tests showed it to be antimony. Analogous to phosphorus pentachloride the reaction postulated is

$$2.5Me_3Sb + SbCl_5 \longrightarrow 2.5Me_3SbCl_2 + Sb$$

Me_3Sb–$SbCl_3$.—Reaction of antimony trichloride (1.66 mmoles) with excess trimethylstibine (6.54 mmoles) at room temperature required a total of about 180 hr. for completion. A black insoluble product was produced. Measurement of the recovery of unreacted trimethylstibine gave a stibine to chloride mole ratio of 1.48:1.

Extraction of the black product with acetone produced on evaporation a white powder which on recrystallization from acetone and then absolute ether melted at 228–229°, the melting point of pure trimethylstibine dichloride. A 50:50 mixture melted at 228–228.5° showing no depression. A sample submitted for C, H and Cl analysis gave the following results: C, 16.0, 16.2; H, 3.6, 3.7; Cl, 30.2, 30.0. Calcd.: C, 15.2; H, 3.8; Cl, 29.8. A black solid insoluble in acetone tested qualitatively for antimony metal.

The reaction then is

$$1.5Me_3Sb + SbCl_3 \longrightarrow 1.5Me_3SbCl_2 + Sb$$

Results and Discussion

The results are summarized in Table I. There are listed the systems studied and reaction temperature, the product mole ratio of the trimethyl compound to the chlorides and the composition of the product as indicated by the experimental data.

TABLE I

SUMMARY OF DATA FOR THE REACTIONS OF PHOSPHORUS AND ANTIMONY CHLORIDES WITH TRIMETHYLARSINE AND TRIMETHYLSTIBINE

System	Reaction temp., °C.	Product mole ratio	Product composition
Me_3As–PCl_5	Room temp.	1.01	$Me_3AsCl_2 + PCl_3$
Me_3As–PCl_3	−29.5	0.99	$Me_3As \cdot PCl_3$[a]
Me_3As–$SbCl_5$	0.0	2.03	$Me_3AsCl_2 + Me_3As \cdot SbCl_3$[b]
Me_3As–$SbCl_3$	Room temp.	0.99	$Me_3As \cdot SbCl_3$[c]
Me_3Sb–PCl_5	0.0	2.31	$Me_3SbCl_2 + P$
Me_3Sb–PCl_3	.0	1.46	$Me_3SbCl_2 + P$
Me_3Sb–$SbCl_5$	.0, room temp.	2.47	$Me_3SbCl_2 + Sb$
Me_3Sb–$SbCl_3$	Room temp.	1.48	$Me_3SbCl_2 + Sb$

[a] Dissociates on warming to 0°. [b] The individual products were not separated from one another in this case. [c] M.p. 145–146.5°.

Examination of the data shows that reduction of Group Vb chlorides by trimethylarsine and trimethylstibine is the predominant reaction. This is in contrast with the action of trimethylamine or trimethylphosphine on chlorides[3] where complex formation was primarily observed.

In this study complex formation of the 1:1 variety is seen to take place with either phosphorus trichloride or antimony trichloride and trimethylarsine. With antimony pentachloride, however, both reduction and complex formation were observed, the antimony pentachloride being reduced to the trichloride which then complexed with excess trimethylarsine.

$$SbCl_5 + 2Me_3As \longrightarrow Me_3AsCl_2 + Me_3As \cdot SbCl_3$$

No acid–base complexes are seen to form with trimethylstibine. In the latter case both tri- and pentachlorides are reduced completely to the element and trimethylstibine dichloride.

$$MCl_5\ (M = P, Sb) + 2.5Me_3Sb \longrightarrow 2.5Me_3SbCl_2 + M$$
$$MCl_3 + 1.5Me_3Sb \longrightarrow 1.5Me_3SbCl_2 + M$$

It appears then that trimethylstibine is the strongest reducing agent of the trimethyl derivatives of the Group Vb elements, trimethylarsine shows a lesser reducing tendency which, however, is greater than that displayed by trimethylphosphine or trimethylamine.

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[7] Me_3SbCl_2 was prepared according to a method described by H. Hibbert, *Ber.*, **39**, 160 (1906). After synthesis and recrystallization from acetone it was found to melt at 228.2–229.0°. No previous melting point is listed in the literature.

[8] L. J. Curtman, "A Brief Course in Qualitative Chemical Analysis," The Macmillan Co., New York, N. Y., 1949.

In addition it is suspected that it is easier to reduce phosphorus pentachloride as compared to antimony pentachloride as evidenced by the lack of any reduction of the latter by either trimethylamine or triethylamine, whereas both amines did reduce phosphorus pentachloride to the trichloride.

More detailed examination of the reductions indicates that several steps are involved in the mechanism. Thus, in the reaction of antimony pentachloride with trimethylstibine, a fast initial reaction to give a white solid with essentially the composition $Me_3Sb–SbCl_5$ was followed by a slower reaction to give complete reduction. This change in reaction rate coupled with the observations that the trimethylstibine–antimony trichloride reaction was a slow one and both reactions led to the same products indicated that the complete reduction of the pentachloride involved the formation of the trichloride as an intermediate according to the equations

$$SbCl_5 + Me_3Sb \longrightarrow Me_3SbCl_2 + SbCl_3$$

$$SbCl_3 + 1.5Me_3Sb \longrightarrow 1.5Me_3SbCl_2 + Sb$$

With a weaker reducing agent, trimethylarsine, the reduction of a pentachloride to the trichloride appears to be the established course as seen from Table I.

Moreover, it is postulated that acid–base complex formation precedes both the reduction of the pentachloride and the reduction of the trichloride. The reason for the latter postulation is readily apparent. Whenever reduction does not occur in the systems studied in this paper and the preceding one,[3] complex formation is the end result, reduction being looked on as one step further. Hence, the complete mechanism postulated is

$$MCl_5\ (M = P,Sb) + Me_3Sb \longrightarrow Me_3Sb{\cdot}MCl_5 \quad (1)$$

$$Me_3Sb{\cdot}MCl_5 \longrightarrow Me_3SbCl_2 + MCl_3 \quad (2)$$

$$MCl_3 + Me_3Sb \longrightarrow Me_3Sb{\cdot}MCl_3 \quad (3)$$

$$Me_3Sb{\cdot}MCl_3 + .5Me_3Sb \longrightarrow 1.5Me_3SbCl_2 + M \quad (4)$$

Undoubtedly the second and fourth steps are much more complicated but resolution of the complete mechanism could not be attempted on the basis of the existing data.

The above mechanism is seen to correlate most of the results. Thus, the reaction of trimethylamine and antimony pentachloride is an example of the initial complex formation alone (step 1). The reaction of phosphorus pentachloride with trimethylarsine is an example of the complete initial reduction process (steps 1 and 2). Reaction through the initial reduction process and further to yield the second 1:1 complex is shown by the trimethylarsine–antimony pentachloride system (steps 1, 2 and 3). Trimethylstibine, indicated to be the strongest reducing agent in the series, then is the only trimethyl derivative to completely reduce either pentachloride (steps 1 through 4).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Hydrolysis of *t*-Alkyl Trifluoroacetates

BY ARLO MOFFAT AND HERSCHEL HUNT

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t-Alkyl trifluoroacetates were hydrolyzed in a mixture of acetone (70% by volume) and water. First-order rate constants, relative rates, % elimination, activation energies and activation entropies indicate that the hydrolyses of these *t*-alkyl trifluoroacetates are examples of the uncatalyzed ionization of esters to carbonium ions and carboxylate ions.

Introduction

Cohen and Schneider[1] have presented the following mechanism for the acid-catalyzed hydrolysis of most esters of tertiary alcohols

$$RCO_2R \overset{H^{\oplus}}{\rightleftharpoons} R\overset{\overset{\oplus OH}{\|}}{C}OR \rightleftharpoons RCO_2H + R^{\oplus} \quad (1)$$

$$\overset{\oplus}{R} + H_2O \rightleftharpoons \overset{\oplus}{R}OH_2 \rightleftharpoons ROH + H^{\oplus} \quad (2)$$

According to Hine,[2] "in order for this cleavage to occur without acid catalysis, the carbonium ion to be formed should be more stable or the anion to be formed should be less basic or both." Several examples of this type of uncatalyzed cleavage are known which involve the formation of a more stable carbonium ion (triphenylmethylcarbonium ion, for example).[3]

The object of this research was to study this same type of non-catalyzed cleavage where the anion formed is less basic (*i.e.*, the acid formed is a much stronger acid than benzoic or mesitoic acids, for example). The esters used were the *t*-butyl, the *t*-amyl and the 2-methyl-2-pentyl trifluoroacetates, which were hydrolyzed in 70% acetone–29% water by volume (1% ester).

Experimental

The esters were prepared from trifluoroacetyl chloride and the corresponding alcohols in the presence of pyridine. Alternate samples were prepared from trifluoroacetic anhydride and the corresponding alcohols. Purification was carried out as described previously.[4]

TABLE I

PROPERTIES OF ESTERS

Ester	B.p. °C.	B.p. Mm.	$n^{20}D$	Sapn. equiv.
$CF_3CO_2C(CH_3)_3$	45	145	1.3304	170
$CF_3CO_2C(CH_3)_2CH_2CH_3$	45	78	1.3469	183
$CF_3CO_2C(CH_3)_2CH_2CH_2CH_3$	46	40	1.3583	196

The reactions were followed conductimetrically in 70% acetone and 29% water (by volume) at 25, 35 and 45°.[4]

Olefin concentrations at various intervals of time were determined using a method similar to the one described by

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[1] S. G. Cohen and A. Schneider, THIS JOURNAL, **63**, 3382 (1941).

[2] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 271.

[3] G. S. Hammond and J. T. Rudesill, THIS JOURNAL, **72**, 2769 (1950).

[4] A. Moffat and H. Hunt, *ibid.*, **79**, 54 (1957).