56. *Acetyl Chloride as a Polar Solvent. Part II.* Solvolytic Reactions in Acetyl Chloride.*

By RAM CHAND PAUL, DULA SINGH, and SARJIT SINGH SANDHU.

Solvolysis of a number of oxides, carbonates, nitrates, nitrites, acetates, and sulphates has been studied quantitatively in acetyl chloride. A mechanism for the solvolysis of these compounds, based on the ionization of acetyl chloride, has been suggested.

THE literature contains scattered references to the solvolytic properties of acetyl chloride. McGookin and Page[1] used organic acid chlorides and metallic oxides to synthesize the acid anhydrides. Mackenzie and Winter[2] reported formation of acetyl perchlorate from silver perchlorate and acetyl chloride in acetic anhydride. Chrétien and Oechsel[3] prepared pervanadyl chloride, uranyl chloride, and manganese tetrachloride from vanadium pentoxide, uranium trioxide, and manganese dioxide by treating them with acetyl chloride. Recently, a method for the preparation of anhydrous chlorides has been suggested[4] in which hydrated salts of metals are treated with the requisite quantity of acetyl chloride in benzene.

However, the solvolytic properties of acetyl chloride have not hitherto been systematically studied. Most of the anhydrous chlorides are insoluble in acetyl chloride and thus these reactions constitute a very convenient method for their preparation. Oxides, oxychlorides, nitrates, nitrites, acetates, and sulphates are solvolysed by acetyl chloride; the results are given in the Table. The calcium oxide solvate when heated at 150° gives an equimolecular mixture of calcium chloride and calcium oxide. At higher temperatures an equilibrium is set up due to the back reaction,[5] *i.e.*, formation of acetyl chloride from calcium chloride and acetic anhydride.

Antimony and bismuth oxychlorides formed solvates of the corresponding trichloride and acetic anhydride. The constitution of these solvates was proved by comparison of their α-picoline complexes with those made directly from the corresponding trichloride and α-picoline in acetyl chloride.

Tellurium dioxide and acetyl chloride gave only a solution from which a mixture of

---

* Part I, preceding paper.

[1] McGookin and Page, *J.*, 1951, 2769.

[2] Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159.

[3] Chretien and Oechsel, *Compt. rend.*, 1938, **206**, 254.

[4] Watt, Gentile, and Helvenston, *J. Amer. Chem. Soc.*, 1955, **77**, 2752.

[5] Gmunder, *Helv. Chim. Acta*, 1953, **36**, 2021.

products was obtained on removal of solvent. Morgan and Drew[6] reported formation of acids from tellurium tetrachloride and acetic anhydride, which could be the initial products of solvolysis of the dioxide.

Compound	Solvolysed product	Colour of product	Temp.	Time (hr.)	Analysis % Found	Calc.
CuO	$CuO,3CuCl_2,2AcCl$	Brown	Room	24	Cl 38·0	38·4
					Cu 34·8	34·3
	$CuCl_2$	,,	Reflux	8	Cl 51·1	52·8
					Cu 46·1	47·2
HgO	$HgCl_2$	White	Room	~500	Cl 25·3	26·2
					Hg 72·1	73·8
	$HgCl_2$	,,	Reflux	9	Cl 25·7	26·0
					Hg 71·2	73·8
SeO_2	$SeCl_4$	Light yellow	Room	20	Cl 63·5	64·25
					Se 35·25	35·75
CaO	$CaO,2AcCl$	White	Room	24	Cl 33·5	33·3
					Ca 18·7	18·8
	$CaO,CaCl_2$	,,	Reflux	12	Cl 43·4	43·1
ZnO	$3ZnCl_2,2Ac_2O$	Reddish-brown *	Room	24	Cl 34·8	34·8
					Zn 31·7	31·9
Fe_2O_3	$2FeCl_3,3Ac_2O$	Reddish-brown *	Reflux	4	Cl 35·8	33·8
					Fe 18·5	17·8
Bi_2O_3	$2BiCl_3,Ac_2O$	Dark red	Room	24	Cl 29·65	29·1
					Bi 56·65	57·0
Sb_2O_5	$2SbCl_5,5Ac_2O$	Dark red	Room	24	Cl 32·1	32·0
					Sb 21·6	22·1
BiOCl	$BiCl_3,Ac_2O$	Dark red *	Room	24	Cl 25·6	25·5
					Bi 50·2	50·1
SbOCl	$SbCl_3,Ac_2O$	Orange-yellow †	Room	24	Cl 32·2	32·3
					Sb 37·2	36·85
$AgNO_3$	AgCl	White	Reflux	3	Ag 73·6	75·3
KNO_3	KCl	White	Reflux	3	Cl 45·4	47·0
$NaNO_3$	NaCl	White	Reflux	2	Cl 57·9	60·7
$Hg(AcO)_2$	$HgCl_2$	Brown	Reflux	8	Cl 23·9	26·2
					Hg 70·0	73·8
$CuCO_3$	$CuCl_2$	Brown	Reflux	6	Cl 50·7	52·8
					Cu 45·7	47·2
$CdCO_3$	$CdCl_2,Ac_2O$	Yellow	Reflux	8	Cl 30·65	30·3
					Cd 47·9	47·9
$HgSO_4$	$4HgCl_2,HgSO_4$	Dirty white	Reflux	12	Cl 20·5	20·9
					Hg 70·4	72·5

* Viscous liquid. † Liquid.

Note: Where results for chlorine or metals are low, the possibility of incomplete solvolysis due to the formation of a protective layer of the insoluble chloride on the unsolvolysed product is presumed, and certain chlorides contain some inert matter formed as a result of side reactions.

Aluminium oxide resists solvolysis in acetyl chloride, and lead dioxide is solvolysed very slowly.

The solvolysis of silver nitrate in benzoyl chloride has been reported.[7] In acetyl chloride it is slowly converted into silver chloride, reaction being retarded by the insolubility of the reagents and the formation on it of a layer of silver chloride. At room temperature, copious brown fumes of oxides of nitrogen are evolved, but to ensure completion of the reaction, the reactants were refluxed for 3 hr.

Acetyl chloride is believed to ionize thus: $AcCl \rightleftharpoons Ac^+ + Cl^-$.[8] The mode of these solvolytic reactions in acetyl chloride can then be expressed as follows:

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^- \text{ (slightly soluble and feebly ionized)}$$

$$Ac^+ + Cl^- + Ag^+ + NO_3^- \longrightarrow AgCl + AcNO_3$$

---

[6] Morgan and Drew, *J.*, 1925, **127**, 531.
[7] Francis, *Ber.*, 1906, **39**, 3798.
[8] Preceding paper; Paul and Sandhu, *Proc. Chem. Soc.*, 1957, 262.

Acetyl nitrate formed during this reaction may decompose to produce nitrogen dioxide or nitrosyl chloride and other products in the presence of excess of acetyl chloride: [9]

$$4AcNO_3 \longrightarrow 2Ac_2O + 4NO_2 + O_2$$
$$2AcNO_3 + 6AcCl \longrightarrow 4Ac_2O + 2NOCl + 2Cl_2$$

Carbonates and nitrites are similarly solvolysed, carbon dioxide and oxides of nitrogen being evolved.

Mercuric acetate reacts to produce mercuric chloride and acetic anhydride: $Hg^{++} + 2AcO^- + 2Ac^+ + 2Cl^- \longrightarrow HgCl_2 + 2Ac_2O$. McGookin and Page [1] assumed that the primary reaction between an oxide and an acid chloride is the formation of an addition compound which rearranges to produce acid anhydride and metallic chloride: $SeO_2 + 4AcCl \longrightarrow SeO_2,4AcCl \longrightarrow SeCl_4 + 2Ac_2O$. In certain cases the addition product of acetic anhydride and metallic chloride is obtained: $Fe_2O_3 + 6AcCl \longrightarrow Fe_2O_3,6AcCl \longrightarrow 2FeCl_3,3Ac_2O$. The existence of an intermediate compound has been shown in the case of incomplete solvolysis of cupric oxide (see above) and supports these views.

EXPERIMENTAL

Reagents.—Acetyl chloride was prepared and stored as described in the preceding paper. Oxides and other salts were dried before use and, if necessary, to remove traces of moisture and carbonate, the oxide was heated to an appropriate temperature. A dry box and calcium chloride guard-tubes were used to avoid contact of the reactants with damp air.

General Procedure.—Compounds could be partially solvolysed by keeping a mixture with enough acetyl chloride in a sealed ampoule at room temperature for a few days. In some cases the solvolysis went to completion even at room temperature but more often, to attain complete or maximum solvolysis, the following procedure was adopted: Well-dried solid (3·5 g.) was added to acetyl chloride (30 ml.) and the mixture was refluxed with the exclusion of moisture for 4—12 hr. and acetyl chloride was occasionally replenished. The solid was filtered off, washed with dry light petroleum (b. p. 40—60°), kept under vacuum, and analysed.

Sometimes the solvolyzed product went into solution, from which it was isolated either by addition of solvents such as dry light petroleum and carbon tetrachloride, or by removal of excess of solvent. The product so obtained was analysed by following the usual procedure. If the solvolysed product was liquid, it was purified by repeated washing with dry light petroleum and keeping it under vacuum.

Reaction of Zinc Chloride with Acetic Anhydride.—Zinc chloride (4 g.) was refluxed with acetic anhydride (20 ml.) for 3 hr. A dark red solution, similar to one obtained from zinc oxide and acetyl chloride, was formed; this solution was distilled under reduced pressure (45 mm.) at 120° to remove the excess of acetic anhydride. The residual liquid was washed and stored (as above) before analysis (Found: Cl, 29·0. $ZnCl_2,Ac_2O$ requires Cl, 29·8%).

This *compound* was then heated on an oil-bath at 150° under reduced pressure; heating was stopped when gas evolution ceased, and the sample was analysed (Found: Cl, 34·5; Zn, 31·6. $3ZnCl_2,2Ac_2O$ requires Cl, 34·8; Zn, 31·9%).

Reaction of Antimony Pentachloride with Acetic Anhydride.—Antimony pentachloride (2 ml.) was added dropwise to ice-cold acetic anhydride (5 ml.); heat was evolved and a dark red solution obtained. This liquid was thoroughly washed with carbon tetrachloride and kept under vacuum (Found: Cl, 30·35; Sb, 20·5. $SbCl_5,3Ac_2O$ requires Cl, 29·3; Sb, 20·1%). This dark red, thick liquid was kept under vacuum for about a week. The viscous liquid so obtained was analysed (Found: Cl, 32·7. $2SbCl_5,5Ac_2O$ requires Cl, 32·0%).

Solvolysis of Bismuth Oxychloride.—A compound $BiOCl,2AcCl$ was obtained from bismuth oxychloride or bismuth oxide with acetyl chloride. It can also be represented as $BiCl_3,Ac_2O$, and this structure was confirmed by the following experiment.

Reaction with α-picoline. To the compound (4 g.) in acetyl chloride (10 ml.), α-picoline (1 g.) in acetyl chloride (10 ml.) was added dropwise. The solution was triturated and the yellowish crystals were washed with acetyl chloride, followed by light petroleum, and kept under vacuum (yield, 4 g.) (Found: Cl, 31·0; Bi, 37·55. $[C_6H_7NAc]BiCl_4,AcCl$ requires Cl, 31·4; Bi, 37·0%).

---

[9] Diels and Okada, *Ber.*, 1911, **44**, 3333.

Its m. p. (91°) was not depressed on mixing with the sample obtained directly by the interaction of bismuth trichloride and α-picoline in acetyl chloride.

Solvolysis of Antimony Oxychloride.—A compound, $SbOCl,2AcCl$ or $SbCl_3,Ac_2O$, was similarly treated with α-picoline; the resulting reddish liquid was triturated with three portions of acetyl chloride, and yellowish-brown solid obtained, m. p. 94° (Found: Cl, 36·9; Sb, 25·4. $[C_6H_7NAc]SbCl_4,AcCl$ requires Cl, 37·1; Sb, 25·4%). An identical *compound* (mixed m. p.) was obtained by the interaction of antimony trichloride and α-picoline in acetyl chloride.

Solvolysis of Bismuth Oxide.—Bismuth oxide yielded crystalline $BiO,BiCl_4,2AcCl$ or $2BiCl_3,Ac_2O$ together with a product similar to that obtained from bismuth oxychloride in solution. The following experiments were performed to decide the nature of present product.

Supposed reaction of bismuth trichloride with bismuth oxychloride. Dry bismuth oxychloride (2 g.) was added to a saturated solution (15 ml.) of bismuth trichloride in acetyl chloride. A reddish solution was obtained and heat was evolved, but no solid separated on chilling or overnight. This solution, on addition of dry light petroleum (b. p. 40—60°), gave only a liquid resembling the product obtained from bismuth oxide and acetyl chloride in the liquid phase.

Reaction of bismuth trichloride with acetic anhydride. Dry bismuth trichloride (30 g.) and acetic anhydride (25 ml.) were refluxed for 7 hr. to give a thick, dark red liquid which was washed with dry carbon tetrachloride and kept under vacuum (Found: Cl, 24·7; Bi, 53·7. Calc. for $BiCl_3,Ac_2O$: Cl, 25·4; Bi, 50·1%. Calc. for $BiCl_2OAc$: Cl, 20·9; Bi, 60·65%). The solvolysis of bismuth trichloride in acetic anhydride has been reported,[10] but the failure of the first reaction and a partial success of this one lead to the probability that the product is $BiCl_3,Ac_2O$ contaminated with a little $BiCl_2OAc$.

PANJAB UNIVERSITY, HOSHIARPUR, INDIA.

[*Received, February* 11*th*, 1958.]

---

[10] Schmidt, Blohm, and Jander, *Angew. Chem.*, 1947, **59**, 233.