57. Acetyl Chloride as a Polar Solvent. Part III.[1] Formation of Acid–Base Neutralization Complexes in Acetyl Chloride.

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Titanium tetrachloride, stannic chloride, zirconium tetrachloride, and tellurium tetrachloride, which act as solvoacids in acetyl chloride, react with ansolvobases (benzyltrimethylammonium chloride and benzyldimethylphenylammonium chloride) and solvobases (quinoline, α-picoline, and dimethylaniline) to yield the acid–base neutralization complexes in acetyl chloride. The mode of their formation and the constitution of acidic and basic solutions in acetyl chloride are discussed.

DISSOCIATION of acetyl chloride, $AcCl \rightleftharpoons Ac^+ + Cl^-$, is supported by study of solubilities, solvate formation, and solvolytic reactions in it.[1-4] According to modern theory of acids and bases,[5] those substances which increase the concentration of the acetylium ions and of chloride ions, respectively, are acids and bases in acetyl chloride solution. The formation of solvates by Lewis acids and organic tertiary bases, and the conductivity of their solutions, have indicated the existence of acidic and basic species in this solvent.[3] Owing to their strong tendency to acquire a higher covalency by combining with chloride ions,[5,6] the Lewis acids indirectly increase the concentration of acetylium ions and thus will act as solvoacids in acetyl chloride.

Organic tertiary bases such as pyridine and quinoline can combine with acetylium ions to form acetylpyridinium and acetylquinolinium ions. Thus, they indirectly increase the concentration of the chloride ions in acetyl chloride and will act as solvobases.

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[1] Part II, preceding paper.
[2] Paul and Sandhu, *Proc. Chem. Soc.*, 1957, 262.
[3] Paul, Singh, and Sandhu, Part I, *J.*, 1959, 315.
[4] Manhas, Paul, and Sandhu, Part IV, following paper.
[5] Smith, *Chem. Rev.*, 1938, **23**, 165.
[6] Gutmann, *Monatsh.*, 1954, **85**, 404.

On the other hand, the quaternary ammonium chlorides which are soluble in acetyl chloride will directly increase the chloride-ion concentration in solution and therefore act as ansolvobases. As the chlorides of alkali and alkaline-earth metals are insoluble in acetyl chloride, benzyltrimethylammonium and benzyldimethylphenylammonium chlorides, which are more soluble than tetramethylammonium chloride, have been used as ansolvobases to study the neutralization reactions with the Lewis acids titanium tetrachloride, stannic chloride, zirconium tetrachloride, and tellurium tetrachloride.

Both of these quaternary ammonium chlorides react with these Lewis acids in acetyl chloride when mixed in a molar ratio of 2 : 1 to yield insoluble crystalline precipitates of the type $[NR^1{}_2R^2R^3]_2MCl_6$ (M = Ti, Sn, Zr, or Te). The precipitation of these complexes can be explained on the basis of the formation of solvoacids by the four Lewis acids in acetyl chloride. Titanium tetrachloride, which forms a monosolvate in acetyl chloride and gives conducting solutions,[3] can be regarded as existing in solution as $TiCl_4,AcCl + AcCl \rightleftharpoons 2Ac^+ + TiCl_6{}^{2-}$.

Stannic chloride gives conducting solutions in acetyl chloride.[3] Therefore, on the basis of the formation of hexachlorostannate ions,[7] its ionization in acetyl chloride can be represented as $SnCl_4 + 2AcCl \rightleftharpoons 2Ac^+ + SnCl_6{}^{2-}$. Although the conductivities of zirconium tetrachloride and tellerium tetrachloride solutions in acetyl chloride have not been measured, yet from their general behaviour,[8, 9] one can predict the existence of acetylium ions in their solutions in exactly the same way.

The formation of the neutralization complexes between Lewis acids and quaternary ammonium chlorides is due to combination of Ac^+ and Cl^- ions to give only feebly ionized acetyl chloride. A typical neutralization reaction in acetyl chloride can be represented as $2QCl + Ac_2MCl_6 \longrightarrow Q_2MCl_6 + 2AcCl$. In these complexes the ratio of the Lewis acid to the base is 1 : 2, so they are regarded as normal salts. On addition of an excess of the acid solution, the complex dissolves completely when the acid to base molar ratio is 1 : 1. This has been noticed with the complexes of titanium tetrachloride and stannic chloride, and may be attributed to the formation of very soluble acid salts. The formation of an acid salt by the dissolution of the normal salt can be expressed as $Q_2MCl_6 + Ac_2MCl_6 \longrightarrow 2QMCl_6Ac$. The existence of the acid and the normal salts of benzyltrimethyl- and benzyldimethylphenyl-ammonium chlorides with titanium tetrachloride and stannic chloride has been proved conductometrically.[4]

Quinoline acts as a solvobase as indicated by the high specific conductivity of its solutions in acetyl chloride.[3] It forms two complexes with titanium tetrachloride in acetyl chloride. The normal salt, $[C_9H_7NAc]_2TiCl_6$, loses acetyl chloride under vacuum, giving the desolvated complex, $(C_9H_7N)_2TiCl_4$. The acid salt $[C_9H_7NAc]AcTiCl_6$, has been isolated in the partly desolvated form $[C_9H_7NAc]TiCl_5$. The formation of these complexes can be represented as under:

$$B + AcCl \longrightarrow (B,Ac)^+ + Cl^- \quad \ldots \quad (1)$$

$$2B,AcCl + Ac_2MCl_6 \longrightarrow (B,Ac)_2MCl_6 + 2AcCl \quad \ldots \quad (2)$$

$$(B,Ac)_2MCl_6 - 2AcCl \longrightarrow B_2MCl_4 \quad \ldots \quad (3)$$

$$(B,Ac)_2MCl_6 + Ac_2MCl_6 \longrightarrow 2(B,Ac)AcMCl_6 \quad \ldots \quad (4)$$

$$(B,Ac)AcMCl_6 - AcCl \longrightarrow (B,Ac)MCl_5 \quad \ldots \quad (5)$$

The formation of the acid and the normal salt by quinoline with titanium tetrachloride in acetyl chloride has been verified conductometrically.[4]

Quinoline and zirconium tetrachloride, both dissolved in acetyl chloride, react to yield a white precipitate which is considered to be an equimolecular mixture of the normal and the acid salt, $(C_9H_7NAc)_3Ac(ZrCl_6)_2$. This complex is invariably formed when the acid solution is added to the base in acetyl chloride. Quinoline also reacts with tellurium

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[7] Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 276.

[8] Gutmann and Himml, *Z. anorg. Chem.*, 1956, **287**, 199.

[9] Groeneveld and Zuur, *Rec. Trav. chim.*, 1953, **72**, 617.

tetrachloride in acetyl chloride when equimolecular solutions of the two are mixed, to form $(C_9H_7NAc)TeCl_5$. All these complexes smell of acetyl chloride; being hygroscopic, their m. p.s could not be determined.

α-Picoline, a stronger base than pyridine, forms a solid solvate with acetyl chloride. With titanium tetrachloride it yields a precipitate of the composition $(C_6H_7N)_2TiCl_4$ which is the completely desolvated normal complex. α-Picoline also reacts with stannic chloride when equimolecular quantities of the two substances are mixed in acetyl chloride. On chilling the mixture and adding dry light petroleum (b. p. 40—60°), a precipitate of $(C_6H_7NAc)AcSnCl_6,AcCl$ has been obtained. The formation of these complexes of α-picoline with titanium tetrachloride and stannic chloride follows the general equations (2)—(4).

Although dimethylaniline does not form a solid solvate with acetyl chloride, it yields conducting solutions.[3] It reacts with titanium tetrachloride in acetyl chloride to yield a complex, $(C_8H_{11}N)_2TiCl_4,AcCl$, and with stannic chloride forms a complex, $(C_8H_{11}N)_2SnCl_4,AcCl$, as expressed by the general equation (2) followed by a partial desolvation: $(B{\cdot}Ac)_2MCl_6 - AcCl \longrightarrow B_2MCl_4,AcCl$. The formation of all these complexes has been confirmed conductometrically.[4]

EXPERIMENTAL

Reagents.—Acetyl chloride was purified as described in previous papers. Titanium tetrachloride and stannic chloride were treated with copper turnings and tin pieces, respectively, and fractionated in a current of dry nitrogen, fractions of b. p. 130°/745 mm. and 112·5—113°/743 mm. respectively being collected. Tellurium tetrachloride was resublimed before use. Zirconium tetrachloride supplied by Messrs. Johnson Matthey & Co. Ltd., London, was used as received.

The quaternary ammonium chlorides were recrystallized from lime-dried alcohol, and the purity of the dried samples was checked by analysis. The organic tertiary bases were fractionally distilled over potassium hydroxide pellets in a current of dry nitrogen and the fractions boiling at the following temperatures were collected: α-picoline, 125·5—126·5°/735 mm.; quinoline, 228—230°/740 mm.; dimethylaniline, 193—194°/736 mm.

Transfers of materials were carried out in a dry box and exposure was kept to a minimum. Filtrations were carried out in sintered-glass funnels in a dry atmosphere, and samples were kept under vacuum before analysis.

			Metal (%)		Chlorine (%)		Nitrogen (%)	
Complex	Colour	M. p.†	Found	Calc.	Found	Calc.	Found	Calc.
$[(CH_3)_3N{\cdot}C_7H_7]_2TiCl_6$	Yellow	165—170°	8·05	8·6	37·8	38·0	4·5	5·0
$[(CH_3)_3N{\cdot}C_7H_7]_2SnCl_6$	White	200—204	18·7	18·8	33·0	33·7	4·1	4·4
$[(CH_3)_3N{\cdot}C_7H_7]_2ZrCl_6$	White	285—290	14·2	14·4	35·3	35·3	4·4	4·6
$[(CH_3)_3N{\cdot}C_7H_7]_2TeCl_6,\frac{1}{2}CH_3{\cdot}COCl$	Yellow	214	18·7	18·8	33·7	33·9	4·4	4·4
$[(CH_3)_2N{\cdot}C_6H_5(C_7H_7)]_2TiCl_6$	Yellow	175—180	7·4	7·0	31·2	31·1	3·8	4·1
$[(CH_3)_2N{\cdot}C_6H_5(C_7H_7)]_2SnCl_6,CH_3{\cdot}COCl$	White	214	14·8	14·2	29·7	29·8	3·6	3·8
$[(CH_3)_2N{\cdot}C_6H_5(C_7H_7)]_2ZrCl_6$	White	115—116	12·9	12·55	29·2	29·25	3·55	3·8
$[(CH_3)_2N{\cdot}C_6H_5(C_7H_7)]_2TeCl_6$	Yellow	170—185	16·7	16·7	28·3	27·85	3·45	3·7
$[C_9H_7N{\cdot}CH_3{\cdot}CO]_2TiCl_6,\frac{1}{2}CH_3{\cdot}COCl$	Yellow	186	7·3	7·45	35·8	35·8	3·9	4·35
$[C_9H_7N]_2TiCl_4$ *	Light yellow	—	10·5	10·7	31·3	31·7	5·9	6·25
$[C_9H_7N{\cdot}CH_3{\cdot}CO]TiCl_5$	Yellow	‡	12·05	12·3	44·9	45·5	3·6	3·6
$[C_9H_7N{\cdot}CH_3{\cdot}CO]_3[CH_3{\cdot}CO][ZrCl_6]_2$	White	‡	15·85	15·6	36·5	36·5	3·4	3·6
$[C_9H_7N{\cdot}CH_3{\cdot}CO]TeCl_5$	Yellow	‡	26·75	26·7	37·2	37·3	2·9	2·9
$[C_6H_7N{\cdot}CH_3{\cdot}CO][CH_3{\cdot}CO]SnCl_6,CH_3{\cdot}COCl$	Orange-yellow	‡	19·7	20·1	42·2	42·3		
$[C_6H_7N]_2TiCl_4$	Orange	135	12·4	12·8	37·25	37·8		
$[C_8H_{11}N]_2TiCl_4,CH_3{\cdot}COCl$	Yellow	‡	9·6	9·4	34·2	34·8		
$[C_8H_{11}N]_2SnCl_4,CH_3{\cdot}COCl$	Dirty white	‡	20·9	20·35	30·6	30·9		

* This was obtained by keeping the preceding compound in a vacuum for 48 hr.

† All with decomposition. ‡ Hygroscopic.

General Procedure for the Preparation of Complexes of Quaternary Ammonium Chlorides.—The normal complexes of different acids with quaternary ammonium chlorides were prepared by adding solutions of the acids to solutions of quaternary ammonium chlorides in acetyl chlorides. The amounts of acids and quaternary ammonium chlorides were in a molar ratio of 1 : 2. Owing to their sparing solubility, the normal complexes separated out and after ½ hr. in an ice-bath were filtered off, washed with acetyl chloride, and dried in a vacuum.

Preparation of Complexes of Organic Tertiary Bases.—The normal complexes of organic tertiary bases and the acids were prepared according to the procedure given for the complexes of quaternary ammonium chlorides. For preparation of acid salts, the solution of the base was added to that of 1 mol. of the acid. On account of their high solubility, the acid salts were generally precipitated by addition of dry light petroleum (b. p. 40—60°). The mixture was kept at a low temperature, and the complex filtered off in absence of moist air and kept in a vacuum desiccator before analysis.

Nitrogen in salts of quaternary ammonium chlorides was determined commercially, that in the remaining samples was determined by Jackson and Smith's method.[10]

The formation of the complexes (except those of tellurium and zirconium tetrachloride) has been confirmed conductometrically.

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[10] Jackson and Smith, *J. Amer. Chem. Soc.*, 1940, **62**, 544.