Solvolytic Reactions of Group (IV) Halides in Trichloroacetic Acid

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Received 22 November 1978; revised 4 April 1979; accepted 21 May 1979

Compounds of compositions SnCl₂(CCl₃COO)₆, Ti(CCl₃COO)₆, Zr(CCl₃COO)₄, Th(CCl₃COO)₄ and Si₂O(CCl₃COO)₂ are obtained when the respective metal tetrachlorides are reacted with excess of trichloroacetic acid. Their structures have been proposed on the basis of elemental analyses, conductance and IR spectral studies. Lewis acid character of the solvolysed products has been established by isolating and characterising their adducts with pyridine, pyridine-N-oxide and triphenylphosphine oxide.

In continuation of our investigations on solution chemistry of monochloro- and dichloro-acetic acids¹⁻⁴, we have now extended our studies to trichloroacetic acid.

Trichloroacetic acid is known to form a variety of addition compounds with Lewis acids like, antimonytrichloroacetic acid. We report here the solvolytic reactions of group (IV) halides in trichloroacetic acid. We obtained the tetrakis-trichloroacetates while silicon and tin tetrahalides went into solution and the compounds were isolated by the addition of an inert solvent like petroleum ether and were filtered and dried in vacuo.

Materials and Methods

Trichloroacetic acid (Riedel) was distilled in an all glass apparatus under reduced pressure. The fraction distilling at 141-42°/50 mm was collected and recrystallised from pure and dry benzene. The sample melting at 58° was used. Lewis acids used were purified by standard methods. The solvolysed products were obtained by adding Lewis acid (6-7 g) to trichloroacetic acid (50 g) in a flask equipped with an air-condenser and a silica gel guard tube. The reaction mixture was refluxed until the evolution of hydrogen chloride gas takes place. The products isolated in the present study are listed in Table 1. All these compounds have fairly high melting points and are insoluble in most of the organic solvents. In the case of titanium, zirconium and thorium tetrachlorides, complete solvolysis has been observed resulting in the formation of corresponding tetrakis-trichloroacetates while silicon and tin tetrahalides formed compounds of the type Si₂O(CCl₃COO)₂ and SnCl₄(CCl₃COO)₂. Attempts to obtain their tetrakis-trichloroacetate derivatives have been unsuccessful. Unlike Mehrotra and his coworkers¹¹ who obtained OTi₂(OAc)₆ when titanium tetrachloride was refluxed with excess of acetic acid, we obtained a completely solvolysed product, Ti(CCl₃COO)₆, on refluxing titanium tetrachloride with excess of trichloroacetic acid.

Results and Discussion

Tetrachlorides of tin, titanium and silicon are miscible with trichloroacetic acid while tetrachlorides of zirconium and thorium are insoluble. But when the mixture is heated, solvolysis accompanied by evolution of hydrogen chloride gas takes place. The products isolated in the present study are listed in Table 1. In the case of titanium, zirconium and thorium tetrachlorides, complete solvolysis has been observed resulting in the formation of corresponding tetrakis-trichloroacetates while silicon and tin tetrachlorides form compounds of the type Si₂O(CCl₃COO)₂ and SnCl₄(CCl₃COO)₂. Attempts to obtain their tetrakis-trichloroacetate derivatives have been unsuccessful. Unlike Mehrotra and his coworkers¹¹ who obtained OTi₂(OAc)₆ when titanium tetrachloride was refluxed with excess of acetic acid, we obtained a completely solvolysed product, Ti(CCl₃COO)₆, on refluxing titanium tetrachloride with excess of trichloroacetic acid.
In the infrared spectra of Ti(CCl₃COO)₄, Zr(CCl₃COO)₄, and Th(CCl₃COO)₄, no band in the region 250-350 cm⁻¹, which could be assigned to metal-chlorine stretching modes, has been observed which suggests that complete solvolysis of tetrachlorides of titanium, zirconium and thorium in trichloroacetic acid has taken place. No band that could be assigned to νO-H mode is observed in the region 3300-3500 cm⁻¹ in these carboxylates. As discussed above, in all these compounds, trichloroacetate group acts as a bidentate chelating group. The presence of intense bands around 1625-1640 cm⁻¹ suggests that the carboxylate group acts as bridging group as well. In the case of titanium compound νM-O mode is observed at 360 cm⁻¹; for zirconium compound at 352 cm⁻¹ and for thorium compound it is observed at 335 cm⁻¹. From the above limited information, it is assumed that trichloroacetate group acts as a bidentate chelating as well as a bridging group and that these compounds are polymeric in nature. However, with the present data, it is not possible to postulate any structure for these compounds but by analogy with the known structures if some of the transition metal carboxylates, a similar type of complexed structure may be proposed or the present compounds.

Attempts have also been made to establish the Lewis acid character of these acetates by reacting ...
them with pyridine, pyridine N-oxide and triphenylphosphine oxide. There are reports of preparation of complexes of copper (II) dichloroacetate, trichloro- and trifluoroacetates with nitrogen donor ligands which have in general 1:2 molar ratio. Paul and coworkers have isolated the addition compounds of copper (II) and cobalt (II) monochloroacetate with oxygen donor ligands. Lever and his coworkers have reported the haloacetate complexes of (trichloroacetate) derivatives of tin(IV), titanium(IV), zirconium (IV) and thorium (IV) have been shown to act as potential Lewis acids and form stable addition compounds with those of the parent compounds.

Further, the (N-O) bending mode of pyridine N-oxide (PyO) in the complexes of composition M(CCl₃COO)₄.2PyO is suggested from the fact that vN-O of pure pyridine N-oxide which occurs at 1265 cm⁻¹ (ref. 25) is shifted to 1190, 1185 and 1175 cm⁻¹ in the spectra of titanium, zirconium and thorium complexes respectively. Such a lowering may be attributed to the coordination of the ligand through oxygen atom to the central metal. Furthermore, the (N-O) bending mode of pyridine N-oxide at 465 cm⁻¹ shifts to lower frequency (458, 450 and 452 cm⁻¹) and the C-H out-of-plane bending at 758 cm⁻¹ shifts to higher wave numbers (767, 763 and 760 cm⁻¹) in the case of titanium, zirconium and thorium adducts respectively. These shifts in the ligand bands on complex formation are as expected. There is no significant decrease in the νP=O mode of the ligand on complex formation as noted also by Cotton and his coworkers in the complexes of triphenylphosphine oxide with metal halides. In the case of pyridine complexes, the coordination of pyridine to the central metal of the acetate is indicated by the appearance of new bands at 1605, 1592, 1579, 1561, 1490, 1433, 1311, 1250, 1160, 785, 680, 642 and 425 cm⁻¹ which are due to coordinated pyridine. Thus, from the limited information, it can be concluded that these transition metal trichloroacetates are polymeric compounds wherein trichloroacetate groups are acting as chelating bidentate or bridging groups or both. However, the polymeric character decreases to some extent on forming complexes with bases as indicated by infrared spectra and slight solubility in organic solvents which is in accordance with earlier observations.

References