Physicochemical Studies of the Solvolysed Products from Various Lewis Acids in Tribromoacetic Acid as Solvent

J. K. PURI*, ASHU MIGLANI, MOHINI MALHOTRA and V. K. SHARMA

Department of Chemistry, Panjab University, Chandigarh-160014 (India)

(Received June 19, 1989; revised November 6, 1989)

Abstract

Lewis acids when refluxed with excess of tri-bromoacetic acid as solvent form the solid compounds $SnCl_2(CBr_3COO)_2$, $Ti(CBr_3COO)_4$, $Zr(CBr_3COO)_4$, $ZrO(CBr_3COO)_2CBr_3COOH$, $Th(CBr_3COO)_4$, $U(CBr_3COO)_4$, $Si_2O(CBr_3COO)_6$, $SbCl_2(CBr_3COO)_3$, $Al(CBr_3COO)_3$, $Fe(CBr_3COO)_3$ and $FeCl(CBr_3COO)_2$. The structures of these new compounds have been established by their elemental analysis, conductance, infrared, reflectance, NMR and FAB mass spectrometry. In solution the tribromoacetate groups are readily lost. The Lewis acid character of these newly isolated compounds was established by preparing and characterising their complexes with organic bases.

Introduction

Several studies on the solution chemistry of mono and dibromoacetic acid have recently been reported [1–5]. EPR studies of tribromoacetates of Cu(II) have been discussed by Uggla and Melnik [6]. During thermal decomposition of tribromoacetates of neodymium and erbium with 1:10 phenanthroline and 2,2'-bipyridyl the base molecules are lost in three stages [7]. Organotin tribromoacetate of the type $Me_3SnOCOCBr_3$ has also been reported in the literature [8].

In the present studies we explored the solvolytic studies of various Lewis acids in tribromoacetic acid as solvent as well as the complex formation of the resulting solvolysed products with organic bases.

Experimental

Tribromoacetic acid (Aldrich) was purified by the earlier reported method [1]. Lewis acids were commercially available samples and were purified by the

---

*Author to whom correspondence should be addressed.

usual methods before use. Partial solvolysis of Lewis acids with tribromoacetic acid occurred at nearly 100 °C. However, the completely solvolysed products of these Lewis acids were obtained and purified in an analogous manner to that reported in ref. 4. Complexes of these tribromoacetates of Lewis acids with organic bases were prepared and purified by the usual methods.

The molar conductance of millimolar solutions of these newly isolated compounds in acetonitrile and nitrobenzene was measured using a cell having a cell constant of 0.5996 cm^{-1} and a Beckman (RC-18) conductivity bridge.

Infrared spectra of the new compounds were measured between KBr plates using Perkin-Elmer 337 and 225 spectrophotometers. Solution spectra were obtained with the 225 Analat-6160 FTIR system. Mass spectra of these compounds were taken on a Kratos MS-30 double beam double focussing mass spectrophotometer. Analyses of metals, halogens, carbon, hydrogen and nitrogen were carried out in the Chemistry Department, Panjab University and Centre of Instrumental Lab at Panjab University, Chandigarh. ^{13}C NMR spectra were obtained on a Bruker WP-60 FT NMR system.

Results and Discussion

Titanium, zirconium, uranium and thorium tetrachlorides form the completely solvolysed products as tetrakis-tribromoacetates whereas silicon and tin tetrachlorides form the compounds $Si_2O(CBr_3COO)_6$ and $SnCl_2(CBr_3COO)_2$. Attempts to prepare their tetrakis-tribromoacetate derivatives were unsuccessful. Unlike Mehrotra and coworkers [9] who reported the formation of $OTi_2(OAc)_6$ when titanium tetrachloride was refluxed with excess of acetic acid, in the present studies a completely solvolysed product, $Ti(CBr_3COO)_4$, was prepared by an analogous method already reported [2, 4].

In the case of titanium, thorium and uranium tetrachlorides tetrasubstituted products are obtained, while in the case of tin, only the disubstituted

product is obtained, even if tin(IV) chloride is refluxed with excess of tribromoacetic acid for 4—5 days. A similar observation was made by Sara and Taugbol [10] with formic, acetic and trifluoroacetic acids. A possible mode of reaction is proposed

$$MCl_4 + CBr_3COOH \rightleftharpoons MCl_4 \cdot CBr_3COOH \longrightarrow$$

$$MCl_3(CBr_3COO) + HCl\uparrow$$
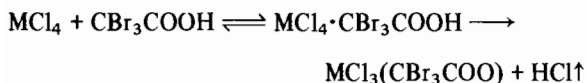
Eventually, all the chloride groups may be replaced by the tribromoacetate group, since hydrogen chloride in tribromoacetic acid escapes at higher temperatures. It is, therefore, expected that the reaction goes to completion. No attempts have been made to isolate the partially solvolysed products. In the case of silicon tetrachloride a new product has been obtained. The reaction of silicon tetrachloride with tribromoacetic acid may involve a straightforward reaction at first but a side reaction of the type shown below probably occurred giving the oxygen bridged compound disiloxane - hexayl-hexakis (tribromoacetate)

$$SiCl(CBr_3COO)_3 + Si(CBr_3COO)_4 \longrightarrow$$

$$O[Si(CBr_3COO)_3]_2 + CBr_3COCl$$
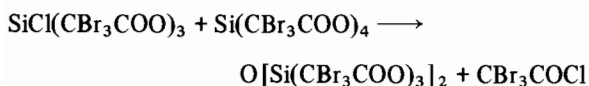
All attempts to prepare silicon tetrakis-tribromo-acetate from silicon tetrachloride and sodium tribromoacetate failed [11].

The position and the difference between the asymmetric and symmetric stretching modes of the carboxylate group in the region 1400—1600 cm^{-1} have been helpful in determining whether the tribromoacetate group behaves as a monodentate, bidentate or as bridging group [12] in these compounds. The intense bands at 1630 and 1365 cm^{-1} assigned to asymmetric and symmetric stretching modes of the carboxylate group are found at lower positions as compared to those of sodium tribromoacetate [13] suggesting that the carboxylate group in these compounds acts as a bidentate and the metal thus acquires hexa-coordination. The other important bands observed at 415 cm^{-1} may be assigned to the νSn—O mode while the bands at 330 and 625 cm^{-1} may be assigned to the νSn—Cl modes in an octahedral environment [14]. Since the spectral bands due to Sn—Cl stretching modes are simple, it is assumed that the chlorine atoms are *trans* to each other [15].

In the infrared spectra of Ti(CBr_3COO)_4, Th(CBr_3-COO)_4 and U(CBr_3COO)_4, no bands appeared in the region 250 to 350 cm^{-1}, which could be assigned to metal chlorine stretching modes. This suggests the complete solvolysis of tetrachlorides of titanium, thorium and uranium in tribromoacetic acid. No band which could be assigned to the ν(O—H) mode is observed in the region 3300—3500 cm^{-1} in these carboxylates. In all these compounds, the tribromo-acetate group is acting as a bidentate ligand. The presence of intense bands around 1580—1650 cm^{-1} suggests that some of the carboxylate groups are acting as a bridging group as well. The other important bands present in the far infrared spectra of these compounds are due to the metal—oxygen stretching modes. They are found in the region 350—500 cm^{-1}. In the case of the titanium compound the M—O mode is observed at 360 cm^{-1}, for thorium at 355 cm^{-1} and for uranium at 380 cm^{-1}. From the above limited information, it is assumed that the tribromoacetate group acts as a bidentate symmetrical chelating as well as a bridging group and that these compounds are polymeric in nature. However, with the present limited data, it is not possible to postulate any structure for these compounds. By analogy with the known structure of some of the transition metal carboxylates [16—18], a similar complexed structure may be proposed for the present compounds. All other important bands are listed in Table 1.

Stable compounds Zr(CBr_3COO)_4 and ZrO(CBr_3-COO)_2·CBr_3COOH have also been isolated and found to be stable to moisture. The molar conductance values of their millimolar solutions in nitrobenzene show that these compounds in solution are covalent or ion paired.

Of all these compounds prepared for this study, only Zr(CBr_3COO)_4 and Fe(CBr_3COO)_3 gave weak metal bromoacetate ions, e.g. [Zr(CBr_3COO)]⁺, [Fe(CBr_3COO)]⁺ and [Fe(CBr_3COO)_2]⁺, in their FAB mass spectra using 15 crown-5/Triglyme as matrix liquid. The others decompose under both EI and FAB conditions.

The infrared spectra of both these compounds show intense absorption bands for $\nu(COO)^-_{asym}$ at 1550 cm^{-1} for Zr(CBr_3COO)_4 and 1362 cm^{-1} for ZrO(CBr_3COO)_2·CBr_3COOH. The $\nu(COO)^-$ values are quite comparable to that of ionic tribromo-acetate. It is difficult to distinguish between the ionic and the covalent chelate structures from these values, but it is expected that zirconium will have a bridging or bidentate tribromoacetate group so as to enable it to acquire a coordination number as high as eight. Further evidence for this has been obtained by observing bands in the region below 700 cm^{-1} which are not present in the spectrum of ionic tribromoacetate and therefore can be assigned to Zr—O vibrations. On the other hand, the absence of sharp intense bands in the region 900—1100 cm^{-1} corresponding to a discrete multiple band Zr=O or a broad medium intensity band at 890 cm^{-1}, characteristic of infinite O—Zr—O—Zr—O chains containing bands with a bond order greater than one, indicate the absence of these species in our compounds [19]. The presence of narrow intense bands around 640, 465 and 365 cm^{-1} may be assigned to the Zr—O vibrations. The band at 665 cm^{-1} which is present only in the compound ZrO(CBr_3COO)_2CBr_3COOH

TABLE 1. Important infrared spectral bands and their assignments (cm^{-1})

Compound	COO^- asymmetric	symmetric	(M–O)	(M–Cl)
$Zr(CBr_3COO)_4$	1650, 1570, 1550	1362	465, 455	
$ZrO(CBr_3COO)_2 \cdot CBr_3COOH$	1645, 1585, 1535	1365	640, 465, 458	365
$Si_2O(CBr_3COO)_6$	1692, 1555, 1530	1365	355	
$Ti(CBr_3COO)_4$	1650, 1575, 1540	1385	360	
$Th(CBr_3COO)_4$	1630, 1565, 1535	1402	355	
$U(CBr_3COO)_4$	1655, 1542	1375	665, 555, 380	
$SbCl_2(CBr_3COO)_3$	1625, 1580, 1545	1400	435	320
$SnCl_2(CBr_3COO)_2$	1570, 1545	1388	415	
$Fe(CBr_3COO)_3$	1662, 1615	1182	465	
$FeCl(CBr_3COO)_2$	1695, 1615	1190, 1125	418	435
$Al(CBr_3COO)_3$	1660, 1625, 1525	1225	492	
$Zr(CBr_3COO)_4 \cdot 4PY$	1608, 1562, 1535	1345	350	
$Ti(CBr_3COO)_4 \cdot 2PY$	1635, 1570, 1530	1380	365	
$SbCl_2(CBr_3COO)_3 \cdot 2PY$	1595, 1570, 1535	1380	428	312
$SnCl_2(CBr_3COO)_2 \cdot 4PY$	1580, 1525	1375	375	322

may be assigned to Zr===O vibrations of the oxo group, its slightly high value suggesting the presence of a relatively high band order. The other bands at 465 and 365 cm^{-1} for $Zr(CBr_3(COO)_4$ and 458 and 365 cm^{-1} for $ZrO(CBr_3COO)_2 \cdot CBr_3COOH$ may be assigned to Zr–O single band stretching modes arising from the formation of bonds between zirconium and the oxygen atom of the tribromoacetate group. A special feature of the infrared spectra of ZrO-$(CBr_3COO)_2 \cdot CBr_3COOH$ is the presence of a strong band at 3380 cm^{-1} which may be assigned to the stretching vibrations of an –OH group of fused tribromoacetic acid which is coordinated to the central metal atom.

The possibility of these solvolysed products acting as Lewis acids has been investigated by reacting them with pyridine. Solid complexes of cobalt(III) bromoacetate have already been reported [20]. Uggla and Melnik [6] have elucidated the structure of cupric acetate complexes with pyridine and picoline Cu(II) bromoacetates and its adducts with dioxane. Lever and Ogden [21] have reported the complexes of tertiary organic bases with the haloacetates of cobalt-(II), nickel(II) and copper(II). Begnall and Lopez [22] have reported the formation of dichloroacetates of thorium(IV) and uranium(IV) and complexes with amides. Doedens et al. have recently reported that Cu(II) tribromoacetate complexes with 2,2',6,6'-tetramethylpiperidinyl-1-oxy (tempo) have a dimeric structure [23]. The reaction products from our solvolysed species and pyridine are shown in Table 2. The compounds are soluble in dimethylformamide. Molar conductance values of their millimolar solutions are quite high. It is of interest to note that there is no substitution of the less basic tribromoacetate group by the more basic pyridine.

In these compounds, the separation of the symmetric and antisymmetric O–C–O band stretching frequencies and the shift of the symmetric O–C–O stretch from values in the pure compounds suggest that tribromoacetate coordination becomes monodentate. The possibility of a five-coordination structure for these compounds is ruled out as it would give two symmetric O–C–O stretching bands. The probability of a polymeric structure is low. On complex formation with organic bases, the ν_{asym}-(O–C–O) and ν_{sym}(O–C–O) stretching frequencies shift to the higher and the lower frequency region respectively, which suggests nitrogen donation to the central metal atom. Similar observations have already been reported by Kitchens and Bear [24].

Solvolytic reactions have also been carried out between trichlorides of aluminium, iron and pentachlorides of antimony. Compounds $Al(CBr_3COO)_3$, $Fe(CBr_3COO)_3$, $FeCl(CBr_3COO)_2$ and $SbCl_2(CBr_3COO)_2$ have been isolated. These compounds are less hygroscopic than the corresponding metal chlorides. They are insoluble in many non-polar organic solvents but soluble in polar solvents such as nitrobenzene, nitromethane and acetonitrile. Molar conductance values for their millimolar solutions in these solvents exclude ionic dissociation. However, ^{13}C NMR, IR and solution spectra suggest free rather than covalently bound tribromoacetate groups. The conductivity data would thus suggest ion pairing. Solvolytic reactions of ferric chloride and aluminium chloride in acetic acid forms compounds of composition $[Fe_3(OAc)_6Cl_3] \cdot AcOH$ and $Al(OAc)_3 \cdot 2AlO$-(OAc) respectively [25] but no compounds of such composition have been isolated in the present studies.

The infrared spectra of these compounds especially in the region of asymmetric and symmetric

TABLE 2. Elemental analysis of various metal tribromoacetates and their complexes

Compound	Physical state		Metal (%)		Halogen (%)		Carbon (%)		Hydrogen (%)		Nitrogen (%)		Molar conductance
	Colour	Melting point (°C)	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	CH_3CN (ohm^{-1} cm^{-1} mol^{-1})
Zr(CBr$_3$COO)$_4$	white	above 310	6.9	7.152	73.98	75.28	7.13	7.528	0.158				0.0215[a]
Zr(CBr$_3$COO)$_2$·CBr$_3$COOH	white	250	8.75	9.155	70.29	72.27	8.002	7.227	0.325	0.10			1.025[a]
Si$_2$O(CBr$_3$COO)$_6$	white	decomposed at 120	2.98	3.02	76.85	77.29	7.392	7.729					14.85
Ti(CBr$_3$COO)$_4$	light yellow		3.216	3.886	75.73	77.93	6.78	7.793	0.273				9.21[a]
Th(CBr$_3$COO)$_4$	white	decomposed at 310	15.5	16.38	65.23	67.79	6.02	6.779	0.389				22.5[a]
U(CBr$_3$COO)$_4$	yellow	decomposed at 255	15.49	16.74	69.89	67.51	5.98	6.751	0.512				10.2[a]
SbCl$_2$(CBr$_3$COO)$_3$	white	195–198	10.28	11.26 Cl	69.59 / 5.69	66.62 / 6.57	6.53	6.662	0.459				24.48
SnCl$_2$(CBr$_3$COO)$_2$	white	163	14.32	15.18	58.73	61.41	5.43	6.141					6.45
Fe(CBr$_3$COO)$_3$	reddish	229	4.761	5.932	75.29	76.27	6.987	7.627					16.74
FeCl(CBr$_3$COO)$_2$	reddish brown	decomposed	7.98	8.193	69.89	70.226	6.927	7.0226					13.24
Al(CBr$_3$COO)$_3$	white		1.56	2.948	76.987	78.69	6.78	7.869		0.775			10.35
Zr(CBr$_3$COO)$_4$·4PY	light yellow		4.64	5.732	59.39	60.33	19.28	20.12	2.579	1.257	3.41	3.519	184.02[a]
Ti(CBr$_3$COO)$_4$·2PY	light yellow		3.82	3.445	58.75	69.06	13.69	15.54	1.98	0.7195	1.98	2.015	168.64[a]
SbCl$_2$(CBr$_3$COO)$_2$·2PY	white	280	17.68	18.88	10.67	11.01	32.69	33.69	33.50		0.017		
SnCl$_2$(CBr$_3$COO)$_2$·4PY	white	decomposed	11.64	10.812 Cl	42.3 / 5.98	43.728 / 6.648	25.48	26.24	0.665	1.822	4.38	5.102	196.20[a]

[a] = Nitrobenzene.

carboxylate group vibrations are similar to those of transition metal acetates where the acetate groups are supposed to act as bidentate chelating and bridging groups. The intense sharp bands observed in the range 1620–1570 cm^{-1} may be assigned to the bridging groups. Bands at 1520 and 1390 cm^{-1} though of low intensity, are shifted to lower frequency and the difference in the asymmetric and symmetric stretching modes is also reduced suggesting that there are also bidentate carboxylate groups.

A polymeric structure for these carboxylates cannot be ruled out but the extent of bridging must be small as the compounds are soluble in aprotic solvents. The other important band in the case of Al(CBr$_3$COO)$_3$ is observed at 495 cm^{-1} which may be assigned to the aluminium–oxygen stretching mode [26]. No band that could be assigned to the Al–Cl stretching mode is present. In the case of Fe(CBr$_3$COO)$_3$ no band that could be assigned to the iron chlorine stretching mode is present, while in the case of FeCl(CBr$_3$COO)$_2$ a metal–chlorine stretching band is observed at 432 cm^{-1} which could be assigned to a bridging chlorine, not to a terminal one, since the bridging stretching modes are expected to be at a lower frequency than the terminal metal–chlorine stretching modes. A possible hexa-coordinate structure around iron for both these compounds is to be attempted.

Attempts to observe the fast atom bombardment mass spectra of all these compounds in this work were unsuccessful, the bromoacetate group always being displaced by the FAB matrix liquid, except for Zr and iron mentioned previously.

References

1 J. K. Puri, J. Kaur and V. Sharma, *Polyhedron, 2* (1983) 1287.

2 J. K. Puri and V. K. Vats, *Inorg. Chim. Acta, 97* (1985) 205.

3 J. K. Puri, J. Kaur and V. Sharma, *Polyhedron, 4* (1985) 1253.

4 J. K. Puri and J. M. Miller, *Inorg. Chim. Acta, 101* (1985) 135.

5 J. K. Puri, V. K. Vats and V. Sharma, *Indian J. Chem., 25* (1986) 565.

6 R. Uggla and M. Melnik, *Suom Kemistvlethi, 44B* (1970) 6.

7 V. Yu. Kokunov and E. l. Segal, *Rev. Roum. Chem., 16* (1947) 1647.

8 C. Pander and R. J. Sams, *J. Organomet. Chem., 19* (1969) 67.

9 R. N. Kapoor, K. C. Pande and R. C. Mehrotra, *J. Indian Chem. Soc., 35* (1958) 157.

10 A. N. Sara and K. Taugbol, *J. Inorg. Nucl. Chem., 35* (1973) 1827.

11 Yu. K. Yurev, Z. V. Belyakova and V. P. Volkov, *Zh. Obshch. Khim., 29* (1959) 3652.

12 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963, p. 197.

13 E. Spinner, *J. Chem. Soc.*, (1969) 4217.

14 T. L. Brown and M. Kubota, *J. Am. Chem. Soc., 83* (1961) 4175.

15 R. J. H. Clark, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, (1962) 2460.

16 J. D. Donaldenn and A. Jelen, *J. Chem. Soc.*, (1968) 2245.

17 M. Kato, H. B. Janassen and J. C. Fannings, *Chem. Rev., 64* (1964) 99.

18 B. W. Skelton, T. N. Waters and N. F. Curtis, *J. Chem. Soc.*, (1970) 2133.

19 C. G. Barralough, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, (1959) 3352.

20 Kuo King wen and M. K. Stanley, *Inorg. Chem., 83* (1969) 1580.

21 A. B. P. Lever and D. Ogden, *J. Chem. Soc. A*, (1967) 2041.

22 K. W. Bagnall and O. Velasquez Lopez, *J. Chem. Soc., Dalton Trans.*, (1976) 1109.

23 L. C. Porter, M. H. Dickman and R. J. Doedens, *Inorg. Chem., 25* (1986) 678.

24 K. Kitchens and J. L. Bear, *J. Inorg. Nucl. Chem., 31* (1969) 2415.

25 H. Funk and M. Demmel, *Z. Anorg. Allg. Chem., 227* (1936) 94.

26 K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc., 83* (1961) 1066, 1272.