Solvolytic Reactions of Lewis Acids in Dibromoacetic Acid and the Characterization of the Solvolysed Products

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Abstract

Solid Compounds, $SnCl_2(CHBr_2COO)_2$, $Ti(CHBr_2COO)_4$, $Zr(CHBr_2COO)_4$, $Th(CHBr_2COO)_4$, $U(CHBr_2COO)_4$ and $Si_2O(CHBr_2COO)_6$ have been isolated when the respective tetrachlorides are refluxed with excess of dibromoacetic acid. Zirconyl chloride forms $ZrO(CHBr_2COO)_2 \cdot CHBr_2COOH$. These compounds have been characterized by their elemental analysis, molar conductance, and infra-red, NMR and FAB mass spectra. In solution, the bromoacetate group is readily lost. Their Lewis acid character was established by isolating and characterizing their adducts with organic tertiary bases. Antimony pentachloride, aluminium trichloride and ferric chloride form compounds of composition $SbCl_2(CHBr_2COO)_3$, $Al(CHBr_2COO)_3$, $FeCl(CHBr_2COO)_2$ and $Fe(CHBr_2COO)_3$ when refluxed with excess of the solvent and these have been characterized by infrared studies.

Introduction

Solvolytic reactions of lewis acids have been reported in ionizing solvents, postulated as being a result of their autoionization. Such solvolytic reactions have been carried out in acetic acid [1], monobromoacetic acid [2], acetic anhydride [3], acetyl chloride [4], dimethylformamide [5], sulphur dioxide [6], methane sulphuric acid [7], and alcohols [8]. These types of reactions constitute a simple method for the preparation of anhydrous acetates, chlorides, dimethylformamidyls and alkoxides. Silicon, zirconium, titanium and thorium exhibit a gradual variation in the reactivity of their compounds towards alcohols [9] and acids [10]. It is therefore, of interest to investigate the behaviour of the tetrachlorides of tin, titanium, thorium, zirconium, uranium and silicon etc. in dibromoacetic acid.

Experimental

Dibromoacetic acid (Aldrich) was purified by the method analogous to monobromoacetic acid reported earlier [11]. Lewis acids used were purified by the standard methods. Partial solvolysis of some of the lewis acids could be achieved at 80 °C by thoroughly mixing them with dibromoacetic acid. However, in the majority of cases the following method was adopted for complete solvolysis. The lewis acid (3–4 g) was added to dibromoacetic acid (30 g) in a 100 ml flask fitted with an air condensor and a silica gel guard tube. The reaction mixture was refluxed for a time varying from a few hours to days depending upon the rate of the reaction. The final products were washed a number of times with hot benzene to remove excess of dibromoacetic acid and then dried under vacuum and analysed.

Addition compounds of completely or partially dibromoacetate substituted lewis acids were prepared in an inert solvent with tertiary organic bases by mixing a known weight of acid with excess base, stirring until solid compounds separated. These were filtered in a dry atmosphere, washed 3–4 times with hot benzene and dried under vacuum.

Molar conductance of milimolar solutions were determined in acetonitrile, nitrobenzene and dimethyl formamide using a cell having a cell constant of $0.5996 \, cm^{-1}$ and a Beckman (RC-18) conductivity bridge.

Infra-red spectra of the new compounds were measured between potassium bromide plates using Perkin Elmer 337 and 225 spectrophotometers. Solution spectra were obtained with the PE 225 and an Analect 6160 FTIR system. Analysis of halogen, carbon, hydrogen and nitrogen were done by the Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. ^{13}C NMR spectra were obtained on a Bruker WP-60 FT. NMR system at 15 MHz.

Results and Discussion

Tetrachlorides of tin, titanium, zirconium, thorium and uranium and silicon have been solvolysed

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TABLE I. Analytical Data of the Solvolysed Products and Their Compounds with Pyridine.

| Compound	Physical state Colour M.P. (°C)		Elemental Analysis						Molar Conductance in CH$_3$CN (ohm^{-1} cm^2 mol^{-1})
			Percentage Found			Percentage Required			
			C	H	Br	C	H	Br	
Ti(CHBr$_2$COO)$_4$	light yellow	34–35	10.13	0.62	67.98	10.50	0.44	69.85	4.56[a]
Si$_2$O(CHBr$_2$COO)$_6$	white	>270	9.98	0.52	68.58	10.57	0.44	70.48	9.84
Zr(CHBr$_2$COO)$_4$	white	>270	10.05	0.40	66.38	10.01	0.42	66.69	2.34[b]
ZrO(CHBr$_2$COO)$_2$·CHBr$_2$COOH	white	>270	8.66	0.42	59.05	8.88	0.37	59.09	1.96[b]
Th(CHBr$_2$COO)$_4$	white	>270	8.75	0.37	58.42	8.74	0.36	58.14	11.62[b]
U(CHBr$_2$COO)$_4$	light green	342–45(D)[c]	8.38	0.43	57.54	8.68	0.36	57.85	8.43[b]
Al(CHBr$_2$COO)$_3$	white	>270	9.84	0.59	69.90	10.64	0.44	70.76	24.34
SbCl$_2$(CHBr$_2$COO)$_3$	orange/yellow	100–101	8.14	0.48	55.94 / 9.06(Cl)	8.55	0.36	56.87 / 8.41(Cl)	23.66
Fe(CHBr$_2$COO)$_3$	reddish/brown	235–37	9.79	0.80	66.38	10.18	0.64	67.90	16.27
SnCl$_2$(CHBr$_2$COO)$_2$	white	>270	7.28	0.27	52.12 / 11.51(Cl)	7.69	0.32	51.24 / 11.38(Cl)	7.82
FeCl(CHBr$_2$COO)$_2$	reddish	125–27	10.12	0.61	64.22 / 6.94(Cl)	9.73	0.40	64.86 / 7.10(Cl)	14.74
Zr(CHBr$_2$COO)$_4$·2py	light yellow	109–111	19.02	1.03 / 2.17(N)	56.78	19.34	1.25 / 2.51(N)	57.25	172.86[b]
Ti(CHBr$_2$COO)$_4$·2py	light yellow	81–82	19.65	1.12 / 2.34(N)	58.85	20.13	1.30 / 2.61(N)	59.56	163.94[a]
SnCl$_2$(CHBr$_2$COO)$_2$·4py	white	>270	29.96	2.17 / 5.34(N)	33.64 / 7.08(Cl)	30.65	2.34 / 5.96(N)	34.01 / 7.55(Cl)	213.43[b]
SbCl$_2$(CHBr$_2$COO)$_3$·5py	brown	85–87	29.53	1.95 / 5.02(N)	38.16 / 5.28(Cl)	30.05	2.26 / 5.65(N)	38.72 / 5.73(Cl)	196.24[a]

[a] Nitrobenzene.　[b] DMF.　[c] D: Decomposed.

in dibromoacetic acid. The products obtained are shown in Table I. The stoichiometric compositions have been determined by elemental analysis (Table I). It is quite clear from the table that the tetrachlorides of zirconium and titanium undergo complete solvolysis to form the corresponding tetra(-dibromoacetates). Zirconylchloride when reacted with dibromoacetic acid forms a compound with the composition, $ZrO(CHBr_2COO)_2 \cdot CHBr_2COOH$ analogous to the acetic acid solvent system [12]. Silicon tetrachloride and tin tetrachloride form $Si_2O(CHBr_2COO)_6$ and $SnCl_2(CHBr_2COO)_2$ respectively. All attempts to obtain their tetra(-dibromoacetates) have failed. It is also observed that no solvent is attached to these products. All have fairly high melting points and are insoluble in most polar solvents with the exception of acetonitrile, dimethylformamide and nitrobenzene. Molar conductance values of their milimolar solutions in these solvents exclude ionic dissociation. However, ^{13}C NMR and solution IR data suggest free rather than covalently bound dibromoacetate groups. The conductivity data would thus suggest ion pairing. It is interesting to note that while Mehrotra *et al.* [13] obtained a compound of composition $OTi_2(OAC)_6$ when titanium tetrachloride was refluxed in acetic acid but we obtained the completely solvolysed product in dibromoacetic acid. A compound of similar composition was obtained in monobromoacetic acid solvo-system [14]. In the case of zirconium, thorium and uranium, tetrasubstituted products are obtained while in the case of tin only a disubstituted product is obtained even if it is refluxed with excess of dibromoacetic acid for seven days. A similar observation has been made by Sara *et al.* [15] with formic, acetic and trifluoroacetic acids. A possible course of reaction is,

$$MCl_4 + CHBr_2COOH \rightleftharpoons MCl_4 \cdot CHBr_2COOH$$
$$\Updownarrow$$
$$MCl_3(CHBr_2COO) + HCl$$
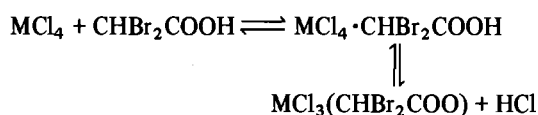
Eventually all the chlorine atoms are replaced by dibromoacetate groups. Since hydrogen chloride in dibromoacetic acid escapes at higher temperature, it is therefore, reasonable to expect the reaction to go to completion. No attempt has been made to isolate the partially solvolysed products.

Bradley *et al.* [9] have already reported that silicon, zirconium and titanium exhibit a gradual variation in their reactivity towards alcohols. Similarly it has been shown by Mehrotra *et al.* [13] that these elements behave differently with acetic acid. The reaction of silicon tetrachloride with dibromoacetic acid is a straight forward reaction at first but side reaction of the type shown below probably occurs giving the oxygen-bridged compound, disiloxanehexayl hexabis (dibromoacetate):

$$SiCl(CHBr_2COO)_3 + Si(CHBr_2COO)_4 \longrightarrow$$
$$O[Si(CHBr_2COO)_3]_2 + CHBr_2COCl$$
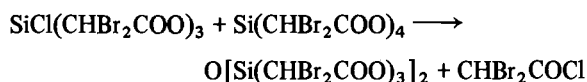
All attempts to prepare tetradibromoacetates of silicon with sodium dibromoacetate failed.

Infra-red studies of these carboxylates have been carried out to elucidate their structures. The positions of the asymmetric and symmetric stretching modes in the region $1400-1600$ cm^{-1} have been used to decide whether the dibromoacetate group behaves as a monodentate, a bidentate symmetrical chelating or a bidentate bridging group in a particular compound [16]. In the case of the compound $SnCl_2(CHBr_2COO)_2$, no bands have been observed in the region 1720 cm^{-1} suggesting that no free carbonyl group is present. The asymmetric and symmetric absorption bands at 1535 and 1385 cm^{-1}, suggest that the carboxylate group in this compound is bidentate and the central metal atom is hexa-coordinated. The band at 405 cm^{-1} was assigned to tin—oxygen stretching mode [17], while the band at 332 and 625 cm^{-1} may be assigned to tin—chlorine stretching modes [18]. Since the spectral bands due to tin—chlorine stretching modes are simple, it is assumed that the chlorine atoms are *trans* to each other [19].

In the infra-red spectra of $Ti(CHBr_2COO)_4$, $Zr(CHBr_2COO)_4$ and $Th(CHBr_2COO)_4$, $U(CHBr_2COO)_4$ there are no bands in the region $250-300$ cm^{-1} which could be assigned to metal—chlorine stretching modes. This suggests that complete solvolysis of the tetrachlorides of titanium, zirconium, thorium and uranium has taken place in dibromoacetic acid. In all these compounds, the dibromoacetate group is acting as a bidentate ligand. The presence of the intense bands around $1650-1580$ cm^{-1} suggest that some of the carboxylate groups are acting as bridging groups as well. The other important bands present in the far infra-red spectra of these compounds are due to metal—oxygen stretching modes. They are found in the region $350-500$ cm^{-1}. In the case of the compound $Ti(CHBr_2COO)_4$ the titanium—oxygen stretching mode is observed at 368 cm^{-1} and in the case of thorium—oxygen is observed at 355 cm^{-1} and for uranium—oxygen is observed at 387 cm^{-1}. From the above limited information, it is assumed that the dibromoacetate group acts as a bidentate symmetrical chelating as well as bridging group and that these compounds are polymeric in nature. With the present limited data, it is not possible to postulate any structure for these compounds. By analogy with the structures of some of the transition metal carboxylates, a similar complexed structure may be proposed for the present compounds. All the important bands are included in Table II.

Compounds of composition $Zr(CHBr_2COO)_4$ and $ZrO(CHBr_2COO)_2 \cdot CHBr_2COOH$ have also been isolated and found to be stable to moisture. The

TABLE II. Important Infra-Red Spectral Bands and Their Assignments (cm^{-1}).

Compound	ν_{asymm}	ν_{symm}	$\nu(M-O)$	$\nu(M-Cl)$
$Ti(CHBr_2COO)_4$	1658, 1580, 1548	1385	368	–
$Si_2O(CHBr_2COO)_6$	1690, 1555, 1530	1400	356	–
$Zr(CHBr_2COO)_4$	1650, 1580, 1550	1408	465, 355	–
$ZrO(CHBr_2COO)_2 \cdot CHBr_2COOH$	1640, 1580, 1540	1365	665, 455, 359	–
$Th(CHBr_2COO)_4$	1629, 1568, 1536	1425	355	–
$U(CHBr_2COO)_4$	1658, 1572, 1536	1376	387	–
$Al(CHBr_2COO)_3$	1620, 1572, 1542	1402	492	–
$Fe(CHBr_2COO)_3$	1640, 1571, 1555, 1535	1376	425	–
$SbCl_2(CHBr_2COO)_3$	1640, 1575, 1535	1382	417	325
$SnCl_2(CHBr_2COO)_2$	1570, 1535	1385	405	332
$FeCl(CHBr_2COO)_2$	1611, 1564, 1545	1392	412	432
$Zr(CHBr_2COO)_4 \cdot 2py$	1605, 1565, 1530	1375	358	–
$SnCl_2(CHBr_2COO)_2 \cdot 4py$	1580, 1545, 1535	1395	396	325
$Ti(CHBr_2COO)_4 \cdot 2py$	1632, 1555, 1528	1410	374	329
$SbCl_2(CHBr_2COO)_3 5py$	1610, 1562, 1518	1395	402	332

molar conductance values of their milimolar solutions in nitrobenzene show that these compounds in solution are covalent or ion paired.

Of all these compounds prepared for this study, only $Zr(CHBr_2COO)_4$ and $Fe(CHBr_2COO)_3$ gave weak metal—bromoacetate ions, e.g. $[Zr(CHBr_2-COO)]^+$ and $[Fe(CHBr_2COO)]^+$ and $[Fe(CHBr_2-COO)_2]^+$, in their FAB mass spectra using 15 crown-5/triglyme as a matrix liquid. The others decompose under both EI and FAB conditions.

The important characteristic bands of these compounds are recorded in Table II. The difference between the ν-asymmetric and ν-symmetric vibrations of the COO^- groups has been generally employed to characterize the nature of the bands between the dibromoacetate groups and the metal [20]. The spectra of these compounds show intense absorption bands for $\nu(COO)^-$ asymmetric at 1500 cm^{-1} for $Zr(CHBr_2COO)_4$ and 1540 cm^{-1} for $ZrO(CHBr_2-COO)_2$. $CHBr_2COOH$ and $\nu(COO)^-$ symm. at 1408 cm^{-1} for $Zr(CHBr_2COO)_4$ and 1365 cm^{-1} for $ZrO-(CHBr_2COO)_2 \cdot CHBr_2COOH$. The $\Delta\nu(COO)^-$ values are quite comparable to that in ionic dibromoacetate. It is difficult to distinguish between the ionic and the covalent chelate structure from these values, but it is expected that zirconium will have bridging or bidentate bromoacetate groups so as to enable it to acquire a co-ordination number as high as eight. Further evidence in this regard has been obtained by observing bands in the region below 700 cm^{-1} which are not present in the spectrum of ionic dibromo-acetate, 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 discrete multiple bond 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 band order greater than one, indicate the absence of these species in our compounds [21]. The presence of narrow intense bands around 665 cm^{-1}, 455 cm^{-1} and 359 cm^{-1} may be assigned to the Zr—O vibrations. The band at 665 cm^{-1} which is present only in the compound $ZrO(OOCCHBr_2) \cdot CHBr_2COOH$ may be assigned to the Zr⋯O vibrations of the oxo-group, its slightly high value suggests the presence of a relatively high band order. The other bands at (465 cm^{-1} and 355 cm^{-1} for $Zr(OOCCHBr_2)$ and 455 cm^{-1} and 359 cm^{-1} for $ZrO(OOCCHBr_2)_2 \cdot CHBr_2-COOH$ may be assigned to Zr—O single band stretching modes arising from the formation of bonds between Zr and the oxygen atoms of the bromo-acetate group. A special feature of the infra-red spectra of $ZrO(OOCCHBr_2) \cdot CHBr_2COOH$ 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 dibromoacetic acid which is co-ordinated to the central metal atom.

We have explored the possibility of these sol-volysed products acting as Lewis acids by reacting them with pyridine. Solid complexes of cobalt(III) bromoacetate have already been reported [22]. Melnik et al. [23] have elucidated the structure of cupric acetate complexes with pyridine and picoline Cu(II) bromoacetates and its adducts with dioxane. Lever et al. [24] have reported the complexes of tertiary organic bases with the haloacetates of cobalt-(II), nickel(II) and copper(II). Kenneth et al. [25] have recently reported the formation of dichloro-acetates of thorium(IV) and uranium(IV) and complexes with amides. The reaction products from our solvolysed species and pyridine are shown in Table I. The compounds are soluble in dimethylformamide.

Molar conductance values of their milimolar solutions are quite high. It is of interest to note that there is no substitution of the less basic dibromoacetate group by the more basic pyridine.

In these compounds, the separation of the symmetric and anti-symmetric O–C–O band stretching frequencies and the shift of the symmetric O–C–O stretch from values in the pure compounds suggest that dibromoacetate co-ordination becomes monodentate. The possibility of a five co-ordinate structure for these compounds is ruled out as it would give two symmetric O–C–O stretching bands. Probability of a polymeric-structure is low. On complex formation with tertiary organic bases the ν_{asym} (O–C–O) and ν_{symm} (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 *et al.* [26].

Solvolytic reactions have been extended to the trichlorides of aluminium, iron and pentachlorides of antimony. Compounds of composition Al-(CHBr₂COO)₃, Fe(CHBr₂COO)₃, FeCl(CHBr₂COO)₂ and SbCl₂(CHBr₂COO)₃ 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 value for their solutions indicate them to be fairly ionic compounds. Solvolytic reactions of ferric chloride and aluminium chloride in acetic acid forms compounds of composition [Fe₃(OAC)₆]Cl₃·AcOH and Al(OAC)₃· 2AlO(OAC) respectively [27], but no compounds of such composition have been isolated in the present studies.

The infra-red spectra of these compounds, especially in the region of asymmetric and symmetric carboxylate group vibrations, are similar to those of transition metal acetates where the acetate groups are supposed to act as bidentate chelating and bridging group. 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 the 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 bands in the case of Al(CHBr₂COO)₃ is observed at 492 cm⁻¹ which may be assigned to the aluminium–oxygen stretching mode [28]. No band that could be assigned to aluminium–chlorine stretching mode is present. In the case of Fe(CHBr₂COO)₃ no band that could be assigned to iron–chlorine stretching mode is present,

while in the case of FeCl(CHBr₂COO)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 lower frequency than the terminal metal–chlorine stretching modes. A possible hexa co-ordinated 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 Fe mentioned previously.

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