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Solvolytic Reactions of Lewis Acids in Monobromoacetic Acid and the Nature of the Solvolysed Products

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Abstract

Solid compounds of composition $SnCl_2(CH_2BrCOO)_2$, $Ti(CH_2BrCOO)_4$, $Zr(CH_2BrCOO)_4$, $Th(CH_2BrCOO)_4$, $Si_2O(CH_2BrCOO)_6$ have been isolated when the respective tetrachlorides are refluxed with excess of monobromoacetic acid. Zirconylchloride forms the compound $ZrO(CH_2BrCOO)_2 \cdot CH_2BrCOOH$ in a similar manner. These compounds have been characterized by their elemental analysis, molar conductance and by infrared studies, NMR and FAB mass spectrometry. In solution, the bromoacetate groups 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 $SbCl_2(CH_2BrCOO)_3$, $Al(CH_2BrCOO)_3$, $FeCl(CH_2BrCOO)_2$ and $Fe(CH_2BrCOO)_3$ when refluxed with excess of the solvent and these have been characterized by infrared studies.

Introduction

Solvolytic behaviour and solubilities of various inorganic compounds, Lewis acids and bases have been reported [1] in fused monobromoacetic acid. A few adducts of very strong Lewis acids with monobromoacetic acid were isolated which were found to be very strong Bronsted acids. Reactions of metal carbonates, -oxides, -formates, -nitrates, *etc.* have been carried out in fused monobromoacetic acid [2] forming the respective monobromoacetates. Similar reactions have been carried out in various other solvents and show the existence of ionic species resulting from their autoionization [3–5]. Solvolytic reactions have also been carried out in acetic acid [6, 7], acetic anhydride [8, 9] and acetyl chloride [10, 11]. In our present studies, the solvolytic behaviour of Lewis acids in fused monobromoacetic acid has been investigated and an attempt has been made to elucidate the nature of the solvolysed products.

Experimental

Monobromoacetic acid was purifed by the method reported earlier [1]. Lewis acids were commercially available samples and were purified by standard methods before use. Partial solvolysis of some of the Lewis acids could be brought about at 100 °C by thoroughly mixing them with monobromoacetic acid. However, in the majority of cases the following method was adopted for complete solvolysis. The Lewis acid (2–3 g) was added to monobromoacetic acid (20 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 monobromoacetic acid and then dried under vacuum and analysed.

Additional compounds of completely or partially bromoacetate substituted Lewis acids were prepared in an inert solvent with tertiary organic bases by mixing a known weight of acid with excess base while 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 mili-molar solutions were determined in acetonitrile, nitrobenzene and dimethylformamide 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 potassium bromide plates using Perkin Elmer 337 and 225 spectrophotometers. Solution spectra were obtained with the 225 and an analect 6160 FTIR system. Analysis of metals, halogen, carbon, hydrogen and nitrogen were done

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

Compound	Physical colour	State M. Pt. (°C)	% Br		% C		% H		% Metal		Molar Cond. in CH_3CN (ohm^{-1} cm^{-1} mol^{-1})
			Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.	
$Zr(CH_2BrCOO)_4$	White	270	50.10	49.70	14.42	14.93	1.50	1.24	14.25	14.18	0.25[a]
$ZrO(CH_2BrCOO)_2 \cdot CH_2BrCOOH$	White	>260	46.10	45.98	13.84	13.79	1.56	1.40	17.39	17.47	0.21[a]
$Si_2O(CH_2BrCOO)_6$	White	110–12	53.73	53.25	16.02	15.99	1.45	1.33	6.33	6.24	13.22
$Ti(CH_2BrCOO)_4$	Light yellow	41–42	53.48	53.27	16.01	16.00	1.44	1.33	8.14	7.98	9.83[b]
$Th(CH_2BrCOO)_4$	White	185–87	40.51	40.92	12.78	12.30	1.32	1.02	29.65	29.70	25.61[a]
$Al(CH_2BrCOO)_3$	White	>260	54.55	54.39	16.36	16.32	1.45	1.36	6.22	6.12	27.95
$Fe(CH_2BrCOO)_3$	Reddish Brown	105–7	51.42	51.01	15.44	15.32	1.17	1.27	11.96	11.87	18.09
$SbCl_2(CH_2BrCOO)_3$	White	105	39.35 11.73 (%Cl)	39.50 11.70	11.64	11.92	1.27	0.99	19.75	20.02	27.95
$SnCl_2(CH_2BrCOO)_2$	White	>230	34.24 15.07 (%Cl)	34.31 15.27	10.39	10.30	0.96	0.85	25.65	25.48	9.37
$FeCl(CH_2BrCOO)_2$	Reddish	>230	43.13 9.65 (%Cl)	43.52 9.66	13.05	13.08	1.03	1.09	15.39	15.31	12.13
$Zr(CH_2BrCOO)_4 \cdot 4py$	Light yellow	185–87	32.68	33.30	34.86	34.00	3.48 5.63 (%N)	2.91 5.0	10.05	9.51	194.20[a]
$SnCl_2(CH_2BrCOO)_2 \cdot 4py$	White	>250	20.90 8.97 (%Cl)	20.44 9.08	36.05	36.84	3.58 5.95 (%N)	3.07 7.16 (%N)			231.60[a]
$Ti(CH_2BrCOO)_4 \cdot 2py$	Light yellow	172–73	42.38	42.17	29.29	28.50	2.65 3.28 (%N)	2.37 3.69 (%N)			178.64[a]
$SbCl_2(CH_2BrCOO)_3 \cdot 5py$	Brown	178–80	23.57 6.73 (%Cl)	23.93 7.09	37.68	37.13	3.45 6.88 (%N)	3.09 6.99			219.12[b]

[a] In DMF. [b] In Nitrobenzene.

by the Chemistry Department, Panjab University, Chandigarh, India and Guelph Chemical Laboratories Ltd., Guelph, Ontario Canada. ^{13}C NMR were obtained on a Bruker WP-60 FT NMR system.

Results and Discussion

Many metal chlorides, on solvolysis in acetic acid, give anhydrous acetates. Rhenium trichloride, on heating in acetic acid under nitrogen, gives an orange coloured precipitate of $ReCl(OAc)_2$ while a compound of composition $ReCl_3 \cdot 2AcOH$ could be obtained from the mother liquor [12]. Anhydrous iron trichloride forms colourless crystals of $Fe_3(OAc)_6Cl_3 \cdot AcOH$ while vanadium trichloride forms $V_3(OAc)_8OH$ when refluxed with acetic acid [13]. Similar observations have been made in the case of chromium trichloride.

In the present studies, tetrachlorides of tin, titanium, zirconium, thorium and silicon and dichloroxozirconium(IV) have been solvolysed in monobromoacetic acid and the products thus obtained are listed 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 tetrabromoacetates. Zirconylchloride when solvolysed with monobromoacetic acid forms a compound with the composition, $ZrO(CH_2BrCOO)_2$. $CH_2BrCOOH$ analogous to the acetic acid solvent system [14]. Silicon tetrachloride and tin tetrachloride form $Si_2O(CH_2BrCOO)_6$ and $SnCl_2(CH_2BrCOO)_2$, respectively. All attempts to obtain their tetra(monobromoacetates) 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 mili-molar solutions in these solvents exclude ionic dissociation. However ^{13}C NMR and solution IR data suggest free rather than covalently bound bromoacetate, as the conductivity data would suggest ion pairing. It is interesting to note that while Mehrotra and coworkers [15] obtained a compound of composition $OTi_2(OAc)_6$ when titanium tetrachloride was refluxed in acetic acid, we obtained the completely solvolysed product in monobromoacetic acid. Possibly chlorotitanium trismonobromoacetate is fairly stable and does not react with dichlorotitanium-bismonobromoacetate to form $OTi_2(CH_2BrCOO)_6$, but rather it reacts with an excess of the solvent to form titanium tetra(monobromoacetate). It is further of interest to note that unlike zirconium tetra-acetate [15], zirconium tetra(monobromoacetate) does not undergo decomposition to form $ZrO(CH_2BrCOO)_2$. It may be that the basic disubstituted product is kinetically less stable than the trisubstituted products. In the case of tin tetrachloride, dichlorotin-bismonobromoacetate is obtained. Even refluxing tin tetrachloride with excess of monobromoacetic acid for 7 days yields only $SnCl_2(CH_2BrCOO)_2$ which suggests a comparatively high kinetic stability of the disubstituted products. A similar observation has been made by Sara and coworkers [16] with formic acid and trifluoroacetic acid. A possible course of reaction is:

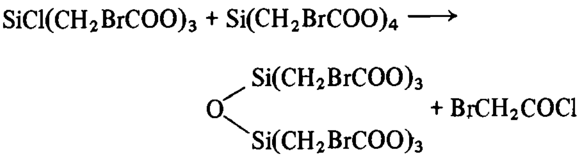
$$MCl_4 + CH_2BrCOOH \rightleftharpoons MCl_4 \cdot CH_2BrCOOH$$

$$\downarrow$$

$$MCl_3(CH_2BrCOO) + HCl$$

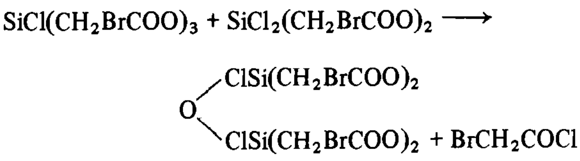
Similarly all the chlorine atoms may be replaced by monobromoacetate groups. Since hydrogen chloride in monobromoacetic acid escapes at higher temperature, it is reasonable to expect the reaction to go to completion. No attempt has been made to isolate the partially solvolysed products.

Bradley and coworkers [17] have already reported that silicon, zirconium and titanium exhibit a gradual variation in their reactivity towards alcohols. Similarly it has been shown by Mehrotra and coworkers [15] that these elements behave differently with acetic acid. The reaction of silicon tetrachloride with monobromoacetic acid is a straight forward reaction at first but side reactions of the type shown below begin to take place giving the basic acetate.

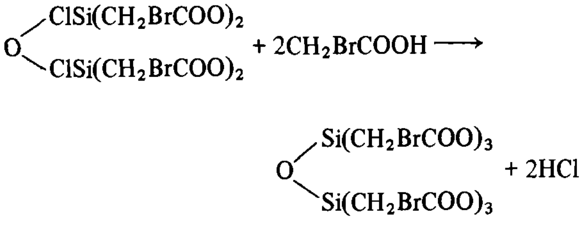


$$SiCl(CH_2BrCOO)_3 + Si(CH_2BrCOO)_4 \longrightarrow O\begin{matrix}\diagup Si(CH_2BrCOO)_3 \\ \diagdown Si(CH_2BrCOO)_3\end{matrix} + BrCH_2COCl$$

The other possible reaction leading to the formation of basic silicon tri(monobromoacetate) may be,



$$SiCl(CH_2BrCOO)_3 + SiCl_2(CH_2BrCOO)_2 \longrightarrow O\begin{matrix}\diagup ClSi(CH_2BrCOO)_2 \\ \diagdown ClSi(CH_2BrCOO)_2\end{matrix} + BrCH_2COCl$$



$$O\begin{matrix}\diagup ClSi(CH_2BrCOO)_2 \\ \diagdown ClSi(CH_2BrCOO)_2\end{matrix} + 2CH_2BrCOOH \longrightarrow O\begin{matrix}\diagup Si(CH_2BrCOO)_3 \\ \diagdown Si(CH_2BrCOO)_3\end{matrix} + 2HCl$$

TABLE II. Important Infrared Spectral Bands and their Assignments (cm^{-1}).

Compound	ν asymmetric COO$^-$	ν symmetric COO$^-$	ν(M–O)	ν(M–Cl)
$Zr(CH_2BrCOO)_4$	1645, 1572, 1552	1385	355, 465	
$ZrO(CH_2BrCOO)_2 \cdot CH_2BrCOOH$	1640, 1590, 1535	1365	665, 458	365
$Si_2O(CH_2BrCOO)_6$	1690, 1550, 1530	1395	355	
$Ti(CH_2BrCOO)_4$	1645, 1575, 1540	1382	360	
$SbCl_2(CH_2BrCOO)_3$	1610, 1580, 1545	1390	435	320
$Th(CH_2BrCOO)_4$	1625, 1565, 1535	1405	355	
$SnCl_2(CH_2BrCOO)_2$	1576, 1542	1388	405	332
$Al(CH_2BrCOO)_3$	1622, 1568, 1527	1400	490	
$FeCl(CH_2BrCOO)_2$	1610, 1570, 1538	1390	418	435
$Fe(CH_2BrCOO)_3$	1620, 1575, 1544	1385	425	
$Zr(CH_2BrCOO)_4 \cdot 4py$	1605, 1565, 1530	1348	350	
$SnCl_2(CH_2BrCOO)_2 \cdot 4py$	1572, 1527	1378	378	322
$Ti(CH_2BrCOO)_4 \cdot 2py$	1632, 1568, 1528	1378	365	
$SbCl_2(CH_2BrCOO)_3 \cdot 5py$	1598, 1572, 1532	1378	427	312

The material distilled off (b.p. 127–28 °C) was found to be bromoacetylchloride. All attempts to prepare the tetra(monobromoacetate) of silicon with sodium monobromoacetate have also failed though a monosubstituted derivative is known [18]. However, the solvolysis reaction of tin tetraiodide in acetic anhydride gives the tetraacetate [19].

Infrared spectral studies of these solid 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 determine whether monobromoacetate behaves as monodentate, bidentate chelating or bidentate bridging group in a particular compound [20]. In the case of $SnCl_2(CH_2BrCOO)_2$ no band has been observed in the region of 1720 cm^{-1} suggesting that no free carbonyl group is present. The intense absorption bands at 1542 and 1388 cm^{-1}, suggest that the carboxylate group in this compound is bidentate and the central atom is hexacoordinated. The band at 405 cm^{-1} was assigned to tin–oxygen stretching mode [20], while the band at 332 was assigned to the tin–chlorine stretching mode [21]. Since there is only one tin–chlorine stretching frequency observed [22], it is assumed that the chlorines are *trans* to each other.

In the far infrared spectra of the compounds $Ti(CH_2BrCOO)_4$, and $Th(CH_2BrCOO)_4$, there are no bands in the 250–300 cm^{-1} region which could be assigned to metal–chlorine stretching mode, thus confirming that complete solvolysis of tetrachloride of titanium, and thorium has taken place. No attempts have been made to arrest the reaction and isolate intermediate products. In both these compounds, the presence of intense bands around 1645–1620 cm^{-1} suggests that some of the carboxylate groups are acting as bridging groups as well. The other important bands present in the far infrared spectra of these compounds are due to metal oxygen stretching modes. They are found in the 500–340 cm^{-1} region. In the case of the titanium compounds, Ti–O is observed in the range 390–360 cm^{-1} and in the case of thorium Th–O is observed in the range 360–350 cm^{-1}. All the important bands are included in Table II.

Compounds of composition $Zr(OOCCH_2Br)_4$ and $ZrO(OOCCH_2Br)_2 \cdot CH_2BrCOOH$ have also been isolated and found to be stable to moisture. The molar conductance values of their milimolar solutions in nitrobenzene show that these compounds in solution are covalent or ion paired in nature. Of all the compounds prepared for this study, only $Zr(OOCCH_2Br)_4$ gave significant zirconium bromoacetate ion in the FAB mass spectra $[Zr(OOCCH_2Br)_2]^+$.

The important characteristic vibrational bands of these compounds are recorded in Table II. The difference between the ν_{asym} and ν_{symm} vibrations of the COO$^-$ groups has been generally employed to characterize the nature of bands between the bromoacetate group and the metal [23]. The spectra of these compounds show intense absorption bands for $\nu(COO^-)_{asym}$ at 1552 cm^{-1} for $Zr(OOCCH_2Br)_4$ and 1535 cm^{-1} for $ZrO(OOCCH_2Br)_2 \cdot CH_2BrCOOH$ and $\nu(COO^-)_{symm}$ at (1385 cm^{-1} for $Zr(OOCCH_2Br)_4$ and 1365 cm^{-1} for $ZrO(OOCCH_2Br)_2 \cdot CH_2BrCOOH$. The $\Delta\nu(COO^-)$ values are quite comparable to that in ionic monobromoacetate. 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 coordination 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 monobromoacetate, 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 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 [24]. The presence of narrow intense bands around 660 cm^{-1}, 465 cm^{-1}, and 355 cm^{-1} may be assigned to the Zr–O vibrations. The band at 665 cm^{-1} which is present only in the compound $ZrO(OOCCH_2Br)_2 \cdot CH_2BrCOOH$ may be assigned to the Zr···O vibrations of the oxo group. Its slightly high value suggests the presence of a relatively high bond order. The other bands at (465 cm^{-1} and 355 cm^{-1} for $Zr(OOCCH_2Br)_4$ and 458 cm^{-1} and 365 cm^{-1} for $ZrO(OOCCH_2Br)_2 \cdot CH_2BrCOOH$ may be assigned to Zr–O single band stretching modes arising from the formation of bonds between Zr and the oxygen atoms of the bromoacetate group. A special feature of the infrared spectra of $ZrO(OOCCH_2Br)_2 \cdot CH_2BrCOOH$ 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 monobromoacetic acid which is coordinated to the central metal atom.

We have explored the possibility of these solvolysed products acting as Lewis acids. Solid complexes of cobalt(III) bromoacetate have already been reported [25]. Melnik and his coworkers have elucidated the structure of cupric acetate complexes with pyridine and picoline Cu(II) bromoacetates and its adducts with dioxane [26]. Lever and coworkers [27] have reported the complexes of tertiary organic bases with the haloacetates of cobalt(II), nickel(II) and copper(II). The reaction products of the metal bromoacetate 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 monobromoacetate group by the more basic pyridine (analysis in Table I).

In these compounds the separation of the symmetric and antisymmetric O–C–O bond stretching frequencies and the shift of the symmetric O–C–O stretch from the values in the pure compounds suggest that bromoacetate coordination becomes monodentate. The possibility of a five coordinate structure for these compounds is ruled out as it would give two symmetric O–C–O stretching bands. The possibility of a polymeric structure in the solid state can be discounted in view of the high solubility in highly solvating solvents. On complex formation with tertiary 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 and coworkers [28].

Solvolytic reactions have been extended to the trichlorides of aluminium, iron and pentachlorides of antimony. Compounds of composition $Al(CH_2BrCOO)_3$, $Fe(CH_2BrCOO)_3$, $FeCl(CH_2BrCOO)_2$ and $SbCl_2(CH_2BrCOO)_3$ have been isolated. These compounds are less hygroscopic than the corresponding metal chlorides. They are insoluble in many nonpolar 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 $[Fe_2(OAc)_6]Cl_3 \cdot AcOH$ and $Al(OAc)_3 \cdot 2AlO(OAc)$, respectively [29], 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 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 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 $Al(CH_2BrCOO)_3$ is observed at 490 cm^{-1} which may be assigned to the aluminium–oxygen stretching mode [30]. No band that could be assigned to aluminium–chlorine stretching mode is present. In the case of $Fe(CH_2BrCOO)_3$ and $FeCl(CH_2BrCOO)_2$, no band that could be assigned to iron–chlorine stretching mode is present in the former while for the latter a metal–chlorine stretching band is observed at 435 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 hexacoordinated structure around iron for both the compounds may be postulated. The X-ray crystal structures of some of these compounds are 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 ion and is inconsistent with the ^{13}C solution NMR and solution IR data.

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