

Dibromoacetic Acid: As Non-Aqueous Solvent

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ABSTRACT

Water on account of several unique properties has been used as an ideal solvent for ionic compounds in the last three decades. This was the main reason that the solvents other than water took so long to develop. It has been only since the late twenties that solution chemistry in non-aqueous solvents has been recognized as a separate and specialized branch of chemistry. Reactions of compounds susceptible to hydrolytic attack and even some routine chemical synthesis are now being extensively carried out in non-aqueous media. A large number of non-aqueous solvents have been successfully explored and amongst them, mention may be made of such solvents as liquid ammonia, liquid sulphur dioxide, acetic anhydride, methyl alcohol etc. Acid base reactions have been carried out in ethylacetate, methyl formate and ethylchloroformate to explain the role played by auto-ionization of the solvent. Mixed solvents are also used frequently in acid-base titrations and also in studying solvent-solute interactions. A systematic study of electrolytic solvent using mixed organic solvents has been carried out. Acetic anhydride in mixture with nitromethane, acetonitrile, acetic acid and chloroform has been conveniently used for the estimation of weak bases.

KEYWORDS

Dibromoacetic acid,
non-aqueous solvent,
solvolytic reactions,
redox reactions,
electrolytic solvent,
organic solvent

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INTRODUCTION

A large number of non-aqueous solvents have been successfully explored and amongst them, mention may be made of such solvents as liquid ammonia (Franklin, 1905, 1912; Jander, 1966), liquid sulphur dioxide (Jander, 1937; Waddington, 1966; Elving, 1960), acetic anhydride (Usanovich, 1942; Jander, 1938; Schmidt, 1947), methyl alcohol (Gues, 1940, Hammet, 1936) etc. Acid base reactions have been carried out in ethylacetate (Paul, 1963; 1963), methyl formate (Paul, 1969) and ethylchloroformate (Paul, 1977; Vasisht, 1970) to explain the role played by auto-ionization of the solvent. Mixed solvents are also used frequently in acid-base titrations and also in studying solvent-solute interactions. A systematic study of electrolytic solvent using mixed organic solvents has been carried out (Fuoss, 1955). Acetic anhydride in mixture with nitromethane (Fritz, 1953), acetonitrile (Marcus, 1953), acetic acid and chloroform (Salvesin, 1958) has been conveniently used for the estimation of weak bases (Cundoff, 1952).

Organic acid halides constitute an interesting class of compounds which have been extensively used as a non-aqueous media. These include acid halides such as selenyl (Jackson, 1940; Gutmann, 1956), phosphoryl (Lewis, 1957; Gutmann, 1952), nitrosyl (Lewis, 1955; Burg, 1952), nitryl (Paul, 1969), sulphuryl (Spandau, 1952; Gutmann, 1954), thionyl (Sandhu, 1962; Spandau, 1955), acetyl (Paul, 1977; Singh, 1959) and benzoyl (Goel, 1959; Paul, 1958) chlorides. There are few

references concerning to the use of these compounds in synthetic organic and inorganic chemistry (Macgookin, 1951).

Solubility of a particular solute in a solvent usually depends upon the specific forces of solvation. Since the solubility phenomenon of an ionic or covalent compound may be considered as donor-acceptor reaction, the donor number of the solvent will be of particular importance. Ionic compounds most probably indicate increasing solubility with increasing donor number of the solvent. Steric factors also require mention when an ionic solute dissolves in a polar solvent, its ion gets associated with the solvent molecules and it may be followed by a chemical change. This mechanism is ultimately selected to the capacity of the solute to behave either as an electron pair donor or as an electron pair acceptor for the solvent molecules.

Another important factor i.e. dielectric constant of the solvent also plays a major role in rendering the solvent potentialities. Bernet and Thompson rule suggests that the forces holding the ions of a molecule together are electrical in origin and get diminished when the molecule is surrounded by a solute of high inductive capacity. For the separation of charged particles (ions), it is essential to apply a solvent layer between them or to surround one or both of them which reduces their attraction for each other. The solvent having low dielectric constant possesses greater residual attractive forces of the ions for each other and as a result the greater is the tendency of such ions to agglomerate into inactive ion pairs. Sulphur dioxide

possessing low dielectric constant suggests that this solvent possess limited potentialities towards the dissolution of various solutes. On the other hand it contains some unusual capabilities towards the covalent halides which exist as electrolytes in liquid sulphur dioxide (Fuoss, 1959; Audriath, 1953). A high dipole moment, high polarizability and the electron acceptor character further suggest that the solvent having good solvent properties, the high solubility of alcohols, olefins and aromatic hydrocarbons in liquid sulphur dioxide may be assigned to the formation of charge transfer complexes.

Many investigators have already reported in literature (Davidson, 1928; Kolling, 1962; Crausz, 1963) the detailed solubility studies of various solutes in glacial acetic acid. Although the solvent properties of acetic acid are much inferior as compared to water and dimethylsulphoxide, yet it dissolves a large number of solutes. Compounds which are soluble in acetic acid are found soluble in water but the reverse is not true. Solubility of many transition metal salts in acetic acid usually results in the formation of solvates. On account of low dielectric constant, the great bulk of the electrolytes is present in the form of ion pairs or higher ionic agglomerates. Paul and his coworkers (Paul, 1959, 1958) reported the solubility of large number of ionic and covalent compound in acyl halides which are solvents of moderate dielectric constant and it has been reported that strongly ionic compounds are insoluble in them only those compounds which form solvates dissolve in these solvents.

It is observed from the Table I that strongly ionic compounds $MnCl_2$, $BaCl_2$, $AgCl$, $PbCl_2$, $NiCl_2$, $CuCl_2$ etc. do not dissolve in fused dibromoacetic acid. Iodides and thiocyanates of manganese, barium, silver, cobalt, nickel and copper get dissolved fairly as compared to chlorides and bromides of these metals. Moreover, anhydrous chlorides of lithium, sodium, potassium, ammonium, calcium, strontium and barium are found to be insoluble in it. Dibromoacetic acid having low dielectric constant possesses poor solvent potentialities for ionic compounds. Non-metals like carbon, sulphur, selenium, tellurium, phosphorus, aluminium, chromium, copper and lead are found to be insoluble in fused dibromoacetic acid.

From the dissolution of alkali metals, magnesium and aluminium ethoxides in dibromoacetic acid, it has been observed that all of them are insoluble in this solvent. Anhydrous acetates of cadmium get quickly dissolved in this solvent, whereas the acetates of calcium, magnesium, strontium, zinc etc. are found to be insoluble in fused dibromoacetic acid.

Tetramethylammonium chloride and bromide are observed to be highly soluble in it. When these compounds are dissolved in excess, formation of

dibromoacetates of these compounds took place. Chlorides of zinc, calcium and magnesium form adducts of composition $MCl_2 \cdot 2CHBr_2COOH$ when dissolved in fused dibromoacetic acid. Phosphorus trichloride/bromide and arsenic trichloride/tribromide yet miscible with fused dibromoacetic acid in all proportion without the formation of any compound, whereas trichlorides of bismuth and antimony form solid adducts of composition $MCl_3 \cdot CHBr_2COOH$ [where $M = As(III), Sb(III)$].

Selenium and tellurium tetrachlorides undergo reduction with the formation of black powder on heating with fused dibromoacetic acid. Anhydrous ferric chloride and aluminium chloride are highly soluble in this solvent. Tin tetrachloride, titanium tetrachloride and pentachlorides of antimony and phosphorus get completely miscible with it in all proportions. The compounds which get fully dissolved are generally the Lewis acids. Some of the Lewis acids produce coloured solutions probably due to the formation of solvates or complexes which is shown by conductance measurements of their solutions in fused dibromoacetic acid. From their qualitative tests it has been observed that the solubility of most of the compounds increases with increasing temperature. Only strong Lewis acids form adducts with fused dibromoacetic acid.

Pyridine, quinoline, isoquinoline, β , β' , β'' picoline, dimethyl and diethylamines, aniline, piperidine, morpholine, triethylamine, n-propylamine, n-butylamine, 1,10-phenanthroline, pyridine-N-oxide, 2,2'-bipyridal etc. are highly soluble in fused dibromoacetic acid with the evolution of heat during their reaction mechanism. Solid compounds of bases with dibromoacetic acid have been separated out from their solutions in carbon tetrachloride which will be explained in the following chapters. Dibromoacetates of alkali metals are highly soluble in dibromoacetic acid whereas dibromoacetates of alkaline earth metals are only sparingly soluble.

Solvolytic reactions/solvate formations

The mechanism of solvation which resembles to the term hydration in water, results in the attachment of solvent molecule or the molecules to the cation, the anion or the molecule of the solute as a whole through coordination or ion-dipole interaction. This results in the formation of stable solvates, which are the compounds containing solvents of crystallization.

Solvate formation is not limited to water alone. Most of the polar ionizing solvents react with the solutes resulting in the formation of crystalline solvates. For example in case of selenoyl chloride (Gutmann, 1956), acetyl chloride (Cook, 1962), benzoyl chloride (McIntosh, 1906), carbonyl chloride (Martin, 1949), acetic anhydride (Malhotra, 1974; Paul, 1964), sulphur dioxide (Burg, 1943; Jander, 1937) and ethylacetate

(Paul, 1963; Greenwood, 1953) solvate formation with Lewis acid and bases is reported. Lewis acids and bases are also known to form solvates with acetic acid (Chikhorakii, 1966; Venkatesan, 1927; Stranathan, 1927; Usanovich, 1951; Paul, 1962; Kotelnickov, 1958). Puri and his coworkers have also reported the formation of solvates of Lewis acids in fused monobromoacetic acid (Puri, 1983). In most of the cases, those solvates separate out as crystalline solids and in other cases the formation of such solvates has been shown by physical measurements of the solution of these solutes in fused monobromoacetic acid. Amphoteric character of fused dibromoacetic acid induces it to form coordination compounds with metal halides, organic bases and some other compounds. Many adducts of lewis acids/bases with fused dibromoacetic have been prepared and are shown in Table II and III.

Acetic acid is a very weak donor molecule and forms solvates of composition $\text{SbCl}_3 \cdot \text{CH}_3\text{COOH}$ (Kotelnickov, 1958) and $\text{SnBr}_4 \cdot \text{CH}_3\text{COOH}$ (Usanovich, 1955) only with various acceptor molecules. Infrared spectra of the donor-acceptor systems $\text{CH}_3\text{COOH} \cdot \text{SbCl}_5$, $\text{CH}_3\text{COOH} \cdot \text{SnCl}_4$ and $\text{CH}_3\text{COOH} \cdot \text{SbCl}_3$ indicates that carbonyl oxygen is the donor site (Zacksisson, 1961) and that the strong acceptor molecule like antimony pentachloride forms an adduct with the monomeric acids in which the hydrogen bonded structure of the parent acid is ruptured. It has been further observed that hydrogen bonds are retained in the adducts of weaker acceptors like tin tetrachloride and antimony trichloride. Boron trifluoride forms 1:1 addition compound with acetic acid which gets ionized in the molten state and the compound has been formulated as $\text{H}^+(\text{F}_3\text{B} \cdot \text{OOCCH}_3)^-$ (Bowlus, 1931). Though formic acid is not a strong electron donor yet it forms stable addition compounds with Lewis acids.

Aluminium trichloride and tribromide are known to form monosolvates with acetyl chloride (Boseken, 1901), benzoyl chloride (Pearson, 1934), phosphoryl chloride (Gerding, 1960), thiophosphoryl chloride (Paul, 1960), acetic acid (Funk, 1931), acetic anhydride (Malhotra, 1974) and ethylacetate (Lapport, 1961). Both these compounds are found fairly soluble in fused dibromoacetic acid and give conducting solutions.

Sulphur trioxide is known as a strong electron acceptor molecule (Paul, 1961, 1964, 1965, 1965 (a)). It is found to be miscible with fused dibromoacetic acid.

Trihalides of phosphorus and arsenic when dissolved in fused dibromoacetic acid get completely miscible in solution without showing any increase in their conductance which suggests that there is no interaction between them. Similar observations have been reported by Sumarokova and his coworkers (Sumarkova, 1951) in the viscosity and density measurements of these solutions. Bismuth trichloride

has a very limited solubility in fused dibromoacetic acid and conductance measurements of the system $\text{BiCl}_3 \cdot \text{CHBr}_2\text{COOH}$ could not be made. Although, the dilute solutions so obtained are found highly conducting.

In comparison to acetic acid dibromoacetic acid is a poor donor, therefore, very few adducts of lewis acids with it may be prepared. It has been observed that very strong lewis acids form solid adducts with dibromoacetic acid which could be prepared from liquid sulphur dioxide. The preparation and characterization of these adducts in the solid state would throw some light on the nature of the ions present in the solution. Stoichiometric compositions of the compounds prepared in the present paper has been determined by the elemental analysis and are reported in Table II. All these compounds are found extremely hygroscopic in nature and have fairly high melting points. All these compounds are insoluble in polar solvents but are soluble in various aprotic solvents. Molar conductance value of the millimolar solutions indicate them to be fairly ionic in nature.

Evidence regarding the adducts formation of lewis acids with carboxylic acids are available in literature but infrared studies in support of adduct formation is very lacking. Therefore, infrared spectra have been carried out in order to throw more light on the nature of these adducts. Dibromoacetic acid has a sharp intense absorption band at 1735 cm^{-1} which is assigned to the carboxyl stretching mode. It has a broad absorption band at 1310 cm^{-1} due to hydrogen bonded OH group. The spectra of pure carboxylic acids are known to have peaks around 1405 cm^{-1} and 1310 cm^{-1} , which arise from O-C vibrations but coupled with OH vibrations in a plane formation vibrations. It is therefore not possible to study the O-C stretching vibrations of these adducts as has been reported in the case of adducts of the esters (Lapport, 1961). Attention has, therefore, been mainly focused on the changes in the absorption frequencies due to the carbonyl group of the ligand on adduct formation.

It is interesting to note that in the lewis acid adduct formation, broad absorption band due to the OH group of the dibromoacetic acid becomes very sharp. Except in the case of very weak acceptor molecules like ZnCl_2 and SbCl_3 , the stretching frequency for the -OH group for the various adducts is at the same position as has been reported for the -OH group frequency for the monomeric acid i.e.; there is no hydrogen bonded structure in these adducts. It seems that in these adducts the intermolecular hydrogen bonded structure of the ligand is ruptured, as on adduct-formation, withdrawal of electrons from the carbonyl oxygen weakens the hydrogen bond and strengthens the adjacent OH bond.

In aldehydes (Beattie, 1963), ketones (Paul, 1966, 1965), amides (Paul, 1967, 1964) and esters (Lapport, 1961) the carbonyl stretching frequency moves to lower absorption regions on complex formation with various acceptor molecules. With the drainage of electrons from the carbonyl group, the double bond character of the carbonyl group is reduced and the carbonyl stretching mode is lowered.

In the case of the adducts of lewis acids and esters, the decrease is accompanied by a corresponding increase in the other O-C stretching mode. Related effects are expected for the acid adducts also if carbonyl oxygen is the donor atom. But if the ethereal oxygen is the donor site, the reverse effect would be observed. In the present investigations it has been observed that there is a decrease in the (C=O) stretching mode of the ligand and the carbonyl oxygen of dibromoacetic acid is the donor site. If the lowering of the $\nu(\text{C-O})$ stretching mode is a measure of the acceptor strength of the lewis acids, then from Table IV, it is quite clear that the order of the acceptor strength is,

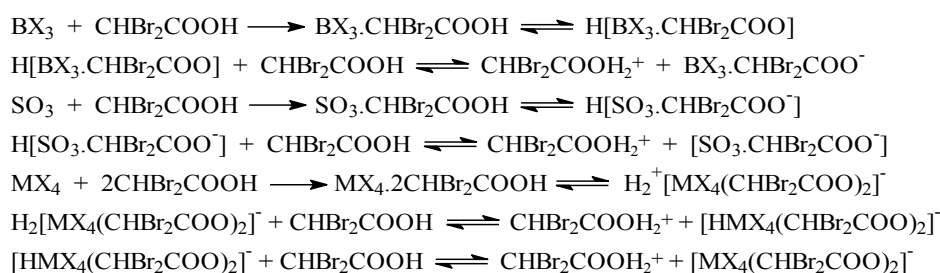


Similar trend about the lowering of carbonyl stretching mode on adduct formation has been reported by Lapport, Paul and his coworkers in their investigations of theoretical studies in various non-aqueous solvents.

Infrared spectral studies of these resulting compounds further support the formation of these adducts with lewis acids. In case of boron trihalide adducts, a new doublets at 525 cm^{-1} and 540 cm^{-1} is observed. The band at 540 cm^{-1} is analogous to the degenerate at ν_4 (B-Cl) bending mode in BCl_4^- (Waddington, 1960). This doublet can be attributed to the change in the local symmetry from T_d to C_{3v} for the boron atom. In both these compounds a strong new absorption band is observed around 1100 cm^{-1} which can be assigned to a B-X stretching mode analogous to ν_4 but this is coupled with the B-O stretching mode which also occurs in the same region (Janas, 1966). In the case of antimony pentachloride adduct, a new absorption band, not present in the ligand, appears at 410 cm^{-1} which has been assigned to the antimony-oxygen stretching mode (Malhotra, 1974). The

absorption bands at 345 cm^{-1} and 630 cm^{-1} may be assigned to the antimony-chlorine stretching mode in an octahedral environment by combining with the carbonyl oxygen of the dibromoacetic acid. In the case of the adducts of tetrachlorides of tin and titanium, the metal-oxygen stretching modes are observed at 395 cm^{-1} and 465 cm^{-1} respectively. These stretching modes are present in the same region as has been reported in literature (Matsuhayshi, 1968; Tanaka, 1968). The metal-chlorine stretching mode in these adducts are quite complex one. In the case of tin tetrachloride adduct, the tin-chlorine stretching mode is observed at 385 cm^{-1} with a shoulder at 365 cm^{-1} . A sharp absorption band at 298 cm^{-1} may also be assigned to tin-chlorine stretching mode. Since the tin-oxygen stretching mode of the spectrum is simpler than tin-chlorine stretching mode, therefore, the ligands are disposed in the trans position to each other (Beattie, 1963). It is therefore concluded that the tetrachlorides of tin and titanium acquire a coordination number of six by combining with two molecules of dibromoacetic acid and a possible trans disposition of the ligand around the metal is suggested.

Ionic character of the adducts of lewis acids with dibromoacetic acid has been further elucidated by determining the equivalent conductance of the solutions of lewis acids in dibromoacetic acid. Specific conductance values of lewis acids at a particular concentration in fused dibromoacetic acid, for which no solid adduct has been formed. It is quite clear from the Table V that the solution of lewis acids in fused dibromoacetic acid are found highly conducting. Comparatively high conductance values of these solution is quite significant when compared with the conductance of either of the components. A reasoning for the high conductivity values of these solutions of lewis acids in fused dibromoacetic acid can be accounted only on the basis of the existence of solvates which exhibit ions in the solvent. Similar explanation has already been reported in case of adducts of acetic acid with lewis acids i.e., $\text{SnCl}_4 \cdot 2\text{CH}_3\text{COOH}$ etc., that the possible ions present are $\text{H}_2[\text{SnCl}_4(\text{OAc})_2] = 2\text{H}^+ + [\text{SnCl}_4(\text{OAc})_2]^{2-}$. On analogy with the adduct of acetic acid and infrared spectral studies of the adducts of dibromoacetic acid, the possible ions present in these adducts of lewis acids with fused dibromoacetic acid may be formulated as,



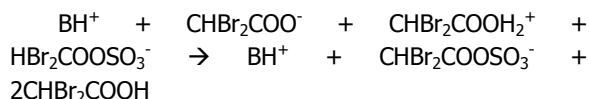
Formation of ions as suggested above finds support from the fact that these adducts behave as strong acids in fused dibromoacetic acid.

A detailed investigation on the compounds $\text{SeO}_3 \cdot \text{CHBr}_2\text{COOH}$ and $\text{SO}_3 \cdot \text{CHBr}_2\text{COOH}$ have been carried out. As explained earlier; there is a weakening of the $-\text{OH}$ bond of the ligand on adduct formation which shows the proton donor character of these adducts. Both these compounds are acidic in nature when dissolved in fluorosulphuric acid, there is a little change in the conductance of the solution i.e., these compounds have very little tendency to accept a proton, whereas fused dibromoacetic acid as such is known to behave as strong base of the solvosystem fluorosulphuric acid (loc.cit) and gets completely protonated and ionized. These adducts when dissolved in sulphuric acid, behave as weak bases in it. Their conductance in sulphuric acid is almost of the same magnitude as that of the solvent. For comparison the conductance of some mineral acids in sulphuric acid already known have been included. Since in the solvosystem sulphuric acid, the ions H_3^+SO_4 and HSO_4^- have abnormal mobilities, therefore, the conductance is the measure of the acidic or basic strength of various solutes dissolved in it. It is therefore, concluded that the adduct $\text{CHBr}_2\text{COOH} \cdot \text{SeO}_3$ and $\text{CHBr}_2\text{COOH} \cdot \text{SO}_3$ are fairly acidic in nature though presently behaves as weak bases in sulphuric acid.

Further attempts have been made to compare the acidic strength of the adducts of lewis acids with dibromoacetic acid with other strong mineral acids by comparing their equivalent conductance at very low concentration in acetic acid. Acetic acid is known to behave as differentiating solvent for acids (Kolthoff, 1934; Emeleus, 1955) and naturally suppresses the ionization of protonic acids to some extent in it. Only very strong proton donors shall protonate acetic acid. The equivalent conductances of the acids $\text{CHBr}_2\text{COOH} \cdot \text{SeO}_3$, $\text{CHBr}_2\text{COOH} \cdot \text{SO}_3$, $\text{CHBr}_2\text{COOH} \cdot \text{SbCl}_5$ and $\text{CHBr}_2\text{COOH} \cdot \text{BBr}_3$ have been plotted against the square root of concentration. It is quite clear that these adducts are fairly strong proton donor molecules and their order of decreasing acidic strength is, $\text{HSO}_3\text{F} > \text{HClO}_4 > \text{HSO}_3\text{Cl} > \text{BBr}_3 \cdot \text{CHBr}_2\text{COOH} > \text{SbCl}_5 \cdot \text{CHBr}_2\text{COOH} > \text{SO}_3 \cdot \text{CHBr}_2\text{COOH} > \text{HBr} > \text{SeO}_3 \cdot \text{CHBr}_2\text{COOH} > \text{H}_2\text{SO}_4 > \text{HCl}$

Nevertheless the compound $\text{SO}_3 \cdot \text{CHBr}_2\text{COOH}$ has been found to be a sufficiently strong Bronsted acid and has been successfully used as acidic titrant to estimate tertiary nitrogenous bases in acetic acid. Paul and his coworkers have used acetous sulphur trioxide as titrant for the estimations of nitrogenous bases in acetic acid (loc.cit). In the present studies, estimations of nitrogenous bases have been carried out in fused dibromoacetic acid conductometrically and with the help of visual indicators. Conductance-composition curves indicate sharp breaks at molar ratio acid/base of

1:1. The possible mode of reactions may be suggested as;



These estimations have also been successfully carried out with the help of visual indicators such as crystal violet and malachite green. The colour of the indicators in the solution of the acid is just the same as found in the case of the solutions of other protonic acids (Paul, 1958, 1959) in acetic acid, suggesting its proton donor character. Crystal violet when used as indicator produces violet colour to the solutions of a base in acetic acid. On further addition of acidic solutions, the colour changes to bluish green, green and finally yellow with a very sharp end points. Reverse titrations also give good results with a colour change from yellow to violet through green. The indicator malachite green has been used as internal indicator giving yellow and green colour in acidic and basic solutions respectively. The colour changes near the end points are very sharp. In all these visual titrations, the end point corresponds to the acid/base molar ratio 1:1. The results are given in Table VI. It is quite clear from the Table the adducts $\text{SO}_3 \cdot \text{CHBr}_2\text{COOH}$ and $\text{SO}_3 \cdot 2\text{CHBr}_2\text{COOH}$ can be used as the acidic titrant for the estimation of nitrogenous bases in non-aqueous solvent.

Coordination compounds formed by the interaction of zinc (II), cadmium (II) and mercury (II) and psudohalides with pyridine and its ring substituted methyl and dimethyl derivatives have gained considerable attention. X-ray crystallography (Gardenic, 1955) studies of some of these compounds have established their structures. The vibrational spectra of pyridine and its methyl derivatives have been extensively investigated. The most outstanding features of the infrared spectral studies of mercury (II) halide complexes is found in close agreement with the spectra of the corresponding free bases (Ahuja, 1972). This is found in accordance with the previous results on pyridine complexes with the exception of relatively minor shifts and the splitting of some bands (Frank, 1966), the fundamental frequencies of the pyridine molecules undergo little change of coordination to heavy metals. This close resemblance may be further assigned to considerable back-bonding from the d-orbital of the metal to the π^* -electronic system of the heterocyclic base. Greenwood and his coworkers (Greenwood, 1960) have prepared the adducts of pyridine with hydrogen chloride and have discussed in details the infrared spectra of similar compounds. Formation of the adducts of acyl halides with organic bases have been reported by Paul and his coworkers (Paul, 1966) and supported by infrared spectral studies the formation of the ions of the type $\text{B} \cdot \text{CH}_3\text{COO}^+ + \text{X}^-$. But the adducts of organic tertiary bases with

phosphoryl chloride (Paul, 1968), carbonyl, thionyl chloride (Paul, 1969) do not show any ion formation, rather these adducts have been observed to be a simple donor acceptor complexes which doubted the modes of autoionization of these solvents.

Trichlorides of bismuth (Paul, 1971) and antimony also form adducts with organic tertiary bases and infrared spectral studies of their solution supported the formation of ions as $[MX_2.B_2]^+ X^-$. Selenium and tellurium tetrachlorides are also known to form adducts with organic tertiary bases. From X-ray and spectral studies the formation of the ions $[MX_3.B_2]^+ + X^-$ have been reported (Paul, 1968; Gordes, 1964). Sulphur trioxide and selenium trioxide are very well-known to form addition compounds with organic tertiary bases and these adducts have been gainfully used for the controlled and the specific sulphonation of organic compounds (Scully, 1954; Dostan, 1956; Hinschelwood, 1939; Katistayana, 1947).

In the present investigations, a large number of addition compounds of dibromoacetic acid with pyridine, quinoline, β , β' -picoline, triethyl amine, aniline, diethylaniline, morpholine, piperidine, piperazine and substituted morpholine and piperazine etc., in carbon tetrachloride is prepared. The formation of all these adducts have been confirmed by their elemental analysis shown in Table III. All these adducts are susceptible to hydrolytic attack and are insoluble in the non-polar solvents yet dissolved in various aprotic solvents. Molar conductance values of their millimolar solutions in nitrobenzene indicate them to be fairly ionic. Molecular weight determination of their adducts suggest that they are present as monomers. On analogy with the adducts of organic tertiary bases with strong protonic acids, the possible ions present in these addition compounds may be proposed as; $BH^+ + CHBr_2COO^-$.

A good example of contradictory literature reports, is the case of pyridine-acetic acid system (Swanger, 1934; Naumova, 1949). Melting points composition diagram indicate the evidence for the formation of $Py.HOAc$ and $Py.4HOAc$ complexes in the binary mixture but conductance studies show the latter compound only while the viscosity measurements do not indicate any compound formation. From the refractive index measurements (Pushion, 1932), a compound of composition $Py.3HOAc$ is reported while freezing point measurements show that acetic acid combines only in equimolar proportions. In the case of fused dibromoacetic acid only the addition compounds having the composition $CHBr_2COOH.3C_5H_5N$ is prepared and is reported in this paper. Infrared and spectral investigations of all these above mentioned addition compounds of dibromoacetic acid/bases have been made to elucidate their structures. The main absorption frequencies of these adducts which undergo change

using adduct formation are discussed and presented in Table VII.

Upon complex formation, there are large perturbations of various bands present in the donor as well as in the acceptor molecules. As a result of complex formation, there is drainage of electrons from the nitrogen atom of organic bases to the proton of the acid. A study of the Table VII suggests that the changes in various bands are similar to the one observed for pyridine upon complex formation with metal and non-metal halides and acid halides (loc. cit). The lowering of the frequencies and the shifts of the bands are in the same directions as has been observed in the case of the above mentioned adducts.

From the Table VII it is observed that the C-H stretching frequency of pyridine shifts to lower spectral region in its adduct with fused dibromoacetic acid. Greenwood and Wade (Greenwood, 1958) and Paul and his coworkers (Paul, 1969) have examined the infrared spectra of the adducts of pyridine with a variety of acceptor molecules and it has been pointed out that this band shifts to the lower spectral region in these addition compounds. The lowering of this band has been attributed mainly to the coordination of pyridine through the nitrogen atom. In the present case, this band is observed as a broad band at 2725 cm^{-1} . In pure pyridine, this band is observed at 3010 cm^{-1} . A broad band at 2945 cm^{-1} is due to -CH- group of dibromoacetic acid. The strong bands at 1585 cm^{-1} , 1575 cm^{-1} , 1485 cm^{-1} and 1440 cm^{-1} in pyridine are due to C=C and C=N symmetric and antisymmetric stretching vibrations. It is quite clear that the donation will increase the double bond character of C=C and C=N bands because of the reduction of electron density on the nitrogen. The C=C and C=N frequencies shift to higher region because of donation of lone pair of electrons and hence increasing the double bond character. The new bands observed in the complex at 1625 cm^{-1} , 1610 cm^{-1} , 1505 cm^{-1} and 1480 cm^{-1} are nearly at the same position as found for the pyridinium ions (George, 1967). Pyridine has a very weak absorption at 1387 cm^{-1} , which is intensified and shifts a little in the pyridinium ion complex. A new band is observed at 1435 cm^{-1} in the complex which may be assigned to the N-H stretching frequency.

Infrared stretching frequencies obtained in the complex at 1255 cm^{-1} , 1205 cm^{-1} and 1165 cm^{-1} may be assigned to C-H in plane deformation of pyridine, which are observed at 1220 cm^{-1} , 1155 cm^{-1} and 1070 cm^{-1} in the free base. The shift to higher frequency is due to the withdrawal of electron density from the C-H bond. These above mentioned bands are present at the same position as those for the pyridinium ion in pyridinium hydrogen chloride. The other bands obtained at 1055 cm^{-1} , 1030 cm^{-1} and 1005 cm^{-1} in the complex are also at similar positions of the pyridinium ion. These bands arising from the deformation of the pyridine ring appear

at 1030 cm^{-1} and 995 cm^{-1} on complex formation. A strong band at 895 cm^{-1} in the spectrum of the complex is present at 890 cm^{-1} as a weak band. Two bands at 752 cm^{-1} and 682 cm^{-1} in the complex are observed at the same position as in $\text{Py.H}^+\text{Cl}^-$ (i.e. 753 cm^{-1} and 680 cm^{-1}) while pure pyridine absorbs at 784 cm^{-1} and 705 cm^{-1} . Therefore all the changes occurring in the spectra may be attributed to the formation of pyridinium ion.

In the case of the addition compounds of fused dibromoacetic acid with quinoline, picoline, the observed changes in the principal spectra are analogous to those observed in the case of pyridine. The bands due to ν (C-H), ν (C=N) and ν (C=C) and the aromatic ring frequencies are lowered down on complex formation. The magnitude of the lowering is also similar to those observed in case of pyridine adducts. Similarly in case of addition compounds of isoquinoline, diethylaniline and ν -picoline, same type of changes in their infrared bands are observed.

A yellow coloured compound having composition $\text{CHBr}_2\text{COOH.C}_{10}\text{H}_8\text{N}_2$ has been isolated on mixing 2,2'-bipyridine with fused dibromoacetic acid in liquid sulphur dioxide as solvent. The compound is susceptible to hydrolytic attack but is quite stable in dry atmosphere. Molar conductance values of their millimolar solutions show it to be ionic compound. 2,2'-bipyridine is basically a 2-substituted pyridine with pyridine being the substituted group. Consequently the hydrogen bonding vibrations should be comparable to those of 2-substituted pyridine (Katritzky, 1959). Besides from its pyridine character, it possesses certain inter ring motion similar to those of biphenyl (Geiss, 1966). There are four bands corresponding to C-H stretching modes between 3000 cm^{-1} to 3100 cm^{-1} , which upon complex formation move to the higher region but the shift is of 25 cm^{-1} only. Four characteristic phenyl-nuclear modes are observed between 1300 cm^{-1} to 1610 cm^{-1} . In pyridine (loc. cit) these are observed at 1585 cm^{-1} , 1565 cm^{-1} , 1485 cm^{-1} and 1445 cm^{-1} while in bipyridine these are observed at lower region i.e. 1580 cm^{-1} , 1555 cm^{-1} , 1452 cm^{-1} and 1410 cm^{-1} indicating the effect of substitution on the latter three absorption bands. All these bands shift to higher spectral region by 45 cm^{-1} upon complex formation. There are two bands at 1065 cm^{-1} and 1045 cm^{-1} attributed to inplane hydrogen bonding motion (Sinha, 1964) which do not change upon complex formation. The ring breaking motion at 992 cm^{-1} is shifted 38 cm^{-1} to higher region in the complex. This observation is similar to the one observed in the case of pyridine adducts (loc. cit). There is also one intense absorption band at 760 cm^{-1} and a weak band at 740 cm^{-1} which is due to aromatic out of plane substituted dependent hydrogen modes. The ring bending motion exists between 672 cm^{-1} to 630 cm^{-1} (Gill, 1961). However, the most intense absorption band is obtained

at 648 cm^{-1} . All these spectral changes suggest that 2,2'-bipyridinium ion is formed on complex formation with fused dibromoacetic acid. From the limiting infrared spectral data, it is very difficult to see why 2,2'-bipyridine acts as a monodentate ligand. All other important bands of 2,2'-bipyridine along with those of the complex are shown in Table VIII.

Tough 1,10'-phenanthroline is known to possess electron donating property, yet it forms a few adducts. Unlike, 2,2'-bipyridine, 1,10'-phenanthroline exists in the cis-form and has a very high dipole moment and is therefore an interesting donor molecule. Many 1:1 adducts of 1,10'-phenanthroline with trihalides of arsenic, antimony and bismuth are prepared. Electron spin complexes of 1,10'-phenanthroline have been examined wherein divalent metal cations have been shown in stable tetrahedral environment (Brown, 1963). Structural studies of 1:1 adducts of tin tetrachloride with 1,10'-phenanthroline have also been carried out.

A white compound of composition $\text{CHBr}_2\text{COOH.C}_{12}\text{H}_8\text{N}$ is obtained when 1,10'-phenanthroline is mixed with fused dibromoacetic acid in carbon tetrachloride at room temperature. The resulting compound is quite hygroscopic in nature. It is soluble in fluorosulphuric acid, disulphuric acid and chlorosulphuric acid and gives highly conducting solution. The conductance in fluorosulphuric acid is comparable to two fluorosulphate ions and in both disulphuric acid and chlorosulphuric acids give $2\text{HS}_3\text{O}_{10}^-$, $2\text{SO}_3\text{Cl}^-$ ions respectively suggesting that weaker acid (CHBr_2COOH) is replaced by a stronger acid (H^+). Principle infrared absorption bands of 1,10'-phenanthroline and its adducts with acid are shown in Table IX. In the spectra of 1,10-phenanthroline strong bands are obtained in two frequency regions i.e., 700 cm^{-1} and 860 cm^{-1} are due to the out of the plane motions of the hydrogen atom on heterocyclic rings and to the hydrogen on the central ring respectively. The band at 740 cm^{-1} resembles the ν_{11} modes of pyridine molecule. This band is shifted to 710 cm^{-1} on complex formation with the acid.

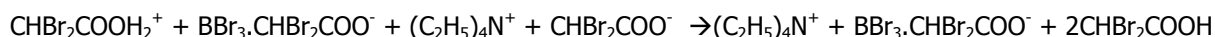
There is a decrease in the frequency upon coordination but the absorption bands present at 860 cm^{-1} does not undergo significant changes upon coordination. This is quite expected as the primary effect of coordination is on the nitrogen atom and the central ring has no nitrogen atom to provide any donor site. A medium intensity band at 992 cm^{-1} present in the pure ligand moves to 1010 cm^{-1} in the adduct. The bands in the region 1130 cm^{-1} to 1355 cm^{-1} attributed to the inplane hydrogen deformation motions or possibly the ring vibrations move to higher spectral region upon coordination.

Other important intense and characteristic bands in the vibrational spectrum of 1,10'-phenanthroline

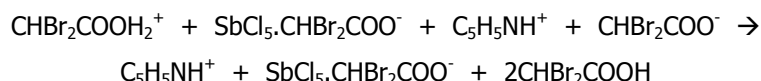
appear in the region 1400 cm^{-1} to 1610 cm^{-1} . An almost parallel behaviour is observed for pyridine and 1,10'-phenanthroline bands in this region. All the bands involve C=C and C=N stretching modes. A very strong band at 1418 cm^{-1} resembles ν_{14} mode of pyridine and is not disturbed on complex formation. The bands at 1452 cm^{-1} , 1505 cm^{-1} , 1565 cm^{-1} and 1580 cm^{-1} (antisymmetric and symmetric vibrations) closely resemble similar modes of pyridine molecule. All of these bands move to higher spectral regions on coordination. It may, therefore, be concluded that all inplane vibrations increase upon coordination whereas out of plane vibrations decrease. The largest shift in frequency is found with the vibrations involving C=C and C=N stretching modes. This is quite expected as the coordination takes place at nitrogen and the effect is transmitted throughout the region resulting into the readjustment of electron density. Upon the basis of the magnitude of the frequency shift on coordination, it may

be concluded that dibromoacetic acid is a weak proton donor molecule.

From the above studies, it is quite clear that the adducts of acids and bases with fused dibromoacetic acid are ionic in nature and it is reasonable to assume that ions are formed when these solutes are dissolved in fused dibromoacetic acid and both behave as solvo-acids and solvo-bases providing ions specific to the autoionization of the solvent. It is, therefore, of interest to carry out acid-base titrations in fused dibromoacetic acid. These titrations have been carried out conductometrically and with the help of visual indicators. Crystal violet, malachite green, benzathrone have been used to detect the end points in the case of visual titrations. Changes in the colour of the indicators near the end points are very sharp. The results are reproducible and the indicators can act reversibly. Acid-base neutralization reactions may be suggested as;



Similarly in the case of antimony pentachloride the reaction may be suggested as;



Decrease in the conductance of the solution with the addition of the acid solution may be accounted for the removal of $\text{CHBr}_2\text{COO}^-$ ions. When the molar ratio of acid/base of 1:1 is reached i.e., after complete removal of $\text{CHBr}_2\text{COO}^-$ ions further addition of $\text{CHBr}_2\text{COOH}_2^+$ ions causes an increase in the conductance of the solution.

In case of adducts of SnCl_4 and TiCl_4 with fused dibromoacetic acid, there are two breaks in the conductance-composition curves which corresponds to the molar ratio of acid/base of 1:1 and 1:2 suggesting the dibasic character of these adducts which may ionize as;



and subsequently ionizes as;



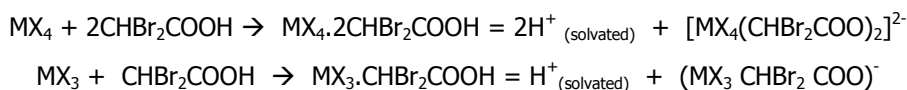
All these observations suggest the ionic character of the medium and its autoionization may be postulated as;



As compared to acetic acid, dibromoacetic acid is a better proton donor molecule. Its dielectric constant and dipole moment values are higher than those of acetic acid but its solvent potentialities have not yet been explored. In the present studies, its use as a non-aqueous medium has been investigated. The first step in the study of a solvent involves the solubility determinations. Solubilities of a large number of compounds, both organic and inorganic, have been determined at $60 \pm 0.5^\circ\text{C}$ in it. It is observed that as compared to ionic compounds, covalent compounds are more soluble in it. Iodides have been found to be more soluble than the bromides and chlorides of the same metal. Lewis acids and bases are either completely miscible or highly soluble in this medium. Tetraalkyl ammonium salts are highly soluble in it and when they are added in excess, corresponding dibromoacetates are obtained. Tetrachlorides of selenium and tellurium undergo reduction in it to form black powder.

Dibromoacetic acid forms solvates with a large number of compounds including lewis acids and organic tertiary bases. The solvate formation has been established by actual isolation of the solvates and also by conductometric measurements. The solutions of lewis acids and organic tertiary bases have been found to be highly conducting which

shows the presence of ions in the solutions. From infra-red spectra and solution chemistry of these compounds in various aprotic and protonic solvents, possible structure of these adducts have been proposed. In the case of the adducts of lewis acids, carbonyl oxygen of dibromoacetic acid has been shown to be the donor site and the possible ions present in the solid state and in solutions are:



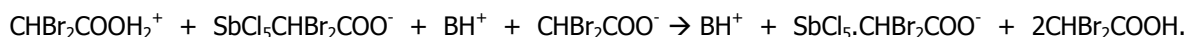
The compounds $\text{BBr}_3 \cdot \text{CHBr}_2 \text{COOH}$ and $\text{SbCl}_5 \cdot \text{CHBr}_2 \text{COOH}$ have been found to be fairly strong protonated acids. By determining the equivalent conductance values of these compounds in acetic acid at low concentrations, their relative acid strength with other minerals acids has been compared. The order of their decreasing acid strength is:



In the case of the adducts of organic tertiary bases with fused dibromoacetic acid, conductance and infrared spectral studies show the presence of ions as;



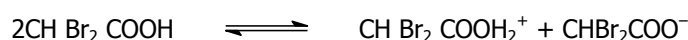
Acid base titrations between antimony pentachloride and pyridine have been carried out in fused dibromoacetic acid. These titrations have been followed conductometrically, potentiometrically and with the help of visual indicators to prove the role played by the autoionization of the solvent. A typical acid-base reaction in fused dibromoacetic acid can be explained as,



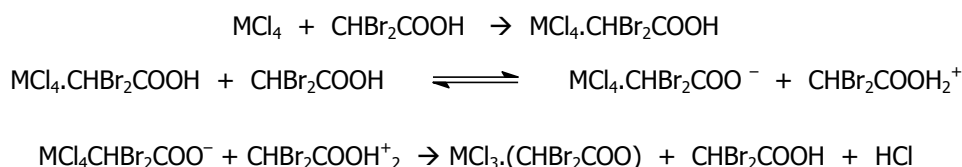
Solvolytic reactions between fused dibromoacetic acid and oxides, carbonates, oxalates, formates, sulphites, nitrites, nitrates and chlorides of metals, form the corresponding dibromoacetates. Oxides of zinc, cadmium and mercury form the dibromoacetates of composition $\text{M}(\text{CHBr}_2\text{COO})_2 \cdot \text{CHBr}_2\text{COOH}$. From infrared and conductance studies, it is observed that the carboxylate group acts as bridging as well as chelating group and the central metal atom acquires a coordination number of six. Oxides of nickel, cobalt and copper form the corresponding dibromoacetate of composition $\text{M}(\text{CHBr}_2\text{COO})_2$ and the central atom is found to have a tetrahedral structure. Adducts of Pyridine N-Oxide and triphenyl phosphineoxide with dibromoacetates of cobalt and nickel have been isolated and characterized. Trichlorides of Phosphorous, arsenic, antimony and bismuth form the compound $\text{P}_3(\text{CHBr}_2\text{COO})_2$, $\text{As}(\text{CHBr}_2\text{COO})_3$, $\text{SbCl}_2(\text{CHBr}_2\text{COO})$ and $\text{BiCl}_2(\text{CHBr}_2\text{COO})$ when refluxed with excess dibromoacetic acid for 12 to 15 hrs. The compound $\text{P}_3(\text{CHBr}_2\text{COO})_2$ could not be characterized while the compound $\text{As}(\text{CHBr}_2\text{COO})_3$ has been found to be covalent one where arsenic does not seem to acquire a coordination number of four or six. The compounds $\text{SbCl}_2(\text{CHBr}_2\text{COO})$ and $\text{BiCl}_2(\text{CHBr}_2 \text{COO})$ have tetra coordinated central metal atom. When the trichlorides are refluxed for longer period then compounds of composition $\text{Sb}(\text{CHBr}_2\text{COO})_3 \cdot \text{CHBr}_2\text{COOH}$ and $\text{Bi}(\text{CHBr}_2\text{COO})_3 \cdot \text{CHBr}_2\text{COOH}$ are obtained. The possible reactions for the formation of these dibromoacetates from the metal chlorides involving the ions of the solvent may be formulated as:



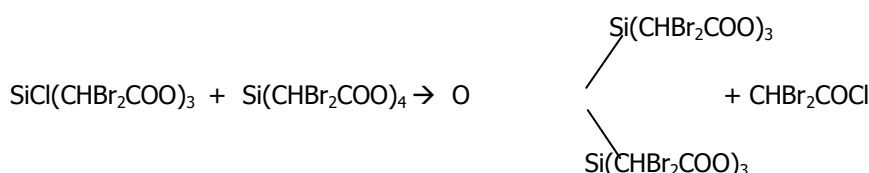
Further refluxing of the intermediates in excess of the solvent replace the other chlorine atoms bonded to the metal and the final product is a completely solvolysed compound $\text{M}(\text{CHBr}_2\text{COO})_3$. All these reactions, described above through the existence of $\text{CHBr}_2\text{COO}^-$ ions in solution supporting the auto ionisation of fused dibromoacetic acid as:



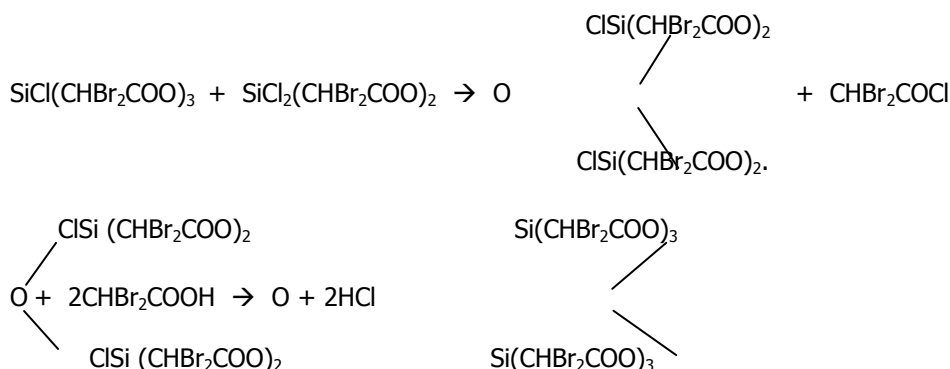
Solvolytic reactions of tetrachlorides of tin titanium, zirconium, thorium and silicon with excess of fused dibromoacetic acid have been carried out and compounds of composition $\text{SnCl}_2(\text{CHBr}_2\text{COO})_2$, $\text{Ti}(\text{CHBr}_2\text{CO})_4$, $\text{Zr}(\text{CHBr}_2\text{COO})_4$, $\text{Th}(\text{CHBr}_2\text{COO})_2$ and $\text{Si}_2\text{O}(\text{CHBr}_2\text{COO})_6$ have been isolated. From infrared, molecular weight and conductance studies, their structures have been elucidated. Their Lewis acid character has been established by isolating and characterization of their adducts with organic tertiary bases. Antimony pentachloride, aluminium trichloride and ferric chloride form compounds of composition $\text{SbCl}_2(\text{CHBr}_2\text{COO})_3$, $\text{Al}(\text{CHBr}_2\text{COO})_3$, $\text{FeCl}(\text{CHBr}_2\text{COO})_2$ and $\text{Fe}(\text{CHBr}_2\text{COO})_3$ when refluxed with excess of the solvent and these compounds have been characterized by conductance and infrared spectral studies. A possible course of reactions involving the liberation of HCl may be proposed as:



Similarly other chlorine atoms may be replaced by dibromoacetate groups. In the case of silicon tetrachloride basic dibromoacetate $\text{Si}_2\text{O}(\text{CHBr}_2\text{COO})_6$ is formed. In the beginning the reaction is straight forward but the side reactions of the type shown below also take place:



The other possible reaction leading to the formation of basic dibromoacetate may be



Redox Reactions in Dibromoacetic acid

In aqueous solutions the oxidation-reduction reactions have been carried out for many years by using various quantitative thermodynamic treatments. The aqueous chemistry of any element can be studied quantitatively in terms of the standard redox potentials. The overall treatment is, however, thermodynamic in itself and cannot account for any activation effects. Thus, although potassium permanganate should oxidize water under acidic condition, yet the aqueous solution is stable for all practical purposes. This is because of the

high over-voltage necessary to liberate oxygen which makes the rate of the reaction exceedingly slow. With a change in the reaction medium it is very likely that the various redox potentials may also change. Thus, the values for various non-aqueous media have to be reported again. Most of the available information relating to these systems are empirical so far.

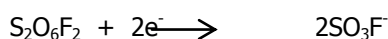
On account of the difference of redox potentials in aqueous and non-aqueous solutions for a particular element, it is possible to reduce an element in non-aqueous solutions to a state unknown in aqueous

solutions. It is very likely that a suitable solvent for this will be one, which is less acidic than water, i.e., with a lower concentration of the hydrogen ions. Thus the alkali metals dissolve in liquid ammonia at -33°C to form highly reducing solutions. These solutions have been extensively used for reduction processes for example tetracyanonickelate (II) and hexacyanocobaltate (II) ions are reduced to nickel (I) and cobalt (I) cyano-metallates respectively. Further reduction to nickel (0), cobalt (0) also takes place but the process is very slow. The salts of zinc, cadmium and mercury (II) are directly reduced to the metal.

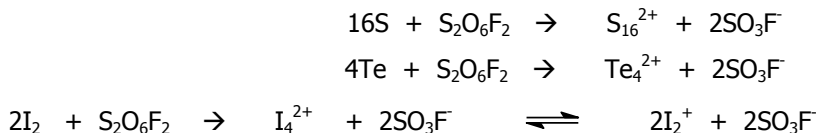
Apart from liquid ammonia, redox reactions have also been carried out in liquid sulphur dioxide which merely acts as an inert medium. Iodine oxidizes tetramethylammonium sulphite very rapidly to the corresponding sulphate and a solution of ferric chloride oxidizes potassium iodide to iodine. Even antimony pentachloride is known to oxidize potassium iodide to iodine. Also in liquid sulphur dioxide, the azides are reduced to nitrogen and the nitrosyl compounds oxidize various iodides to elemental iodine. Soal and his coworkers (Soal, 1951) have studied the reactions of

nitrosyl compounds with potassium and tetraethylammonium iodide in sulphur dioxide. Ethyl nitrite oxidizes iodide to iodine. Paul and his coworkers (Paul, 1969) have carried out redox reactions in formamide and have used lead tetraformamide as an oxidizing agent and elements such as tin (II), antimony (III) and arsenic (III) have been oxidized to their higher oxidation states. Potassium dichromate has also been used successfully as an oxidizing agent.

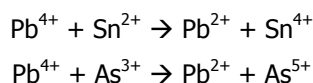
Redox reactions have been extended to highly acidic media such as hydrochloric acid (Iqbal, 1968) and fluorosulphuric acid (Paul, 1972). Waddington and his coworkers (Salhouse, 1967) have used successfully nitrosyl chloride, iodine monochloride, chlorine and bromine as the oxidizing agents in liquid hydrogen chloride solvent and have oxidized phosphorus (III) and arsenic (III) compounds to their higher oxidation states. Some of the metal carbonyls have been oxidized in this solvent and it has been observed that chlorine replaces the bridging carbon monoxide group. Gillespie and his coworkers (Gillespie, 1966) have used peroxydisulphuryl difluoride as an oxidizing agent in fluorosulphuric acid as;



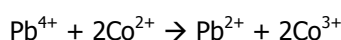
Metals and non-metals have been oxidized to various unusual oxidation states in this highly acidic medium as;



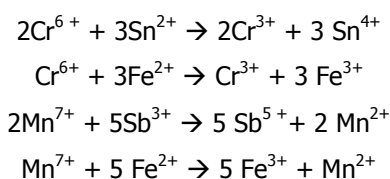
Redox reactions in fused dibromo acetic acid and some reducing agents such as thiourea, phenylhydrazine, ascorbic acid when titrated against some oxidizing agents as potassium permanganate, potassium dichromate, bromine, iodine monochloride, potassium ferricyanide could easily be estimated in it. Some elements has also been oxidized to the higher oxidation states with the help of these oxidizing agents. Lead tetradi-bromoacetate has been used to oxidise tin (II), antimony (III), arsenic (III) and phosphorous (III) to higher oxidation states as :



It also oxidizes cobalt (II) and nickel (II) to (III) oxidation states as:

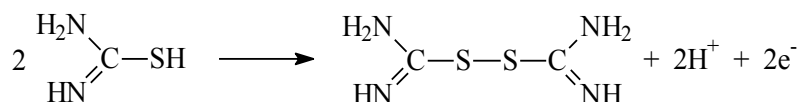


Similarly iodine has been successfully developed as oxidizing agent in this medium. Potassium permanganate and potassium dichromate act as fairly good oxidizing agent for the redox reactions in this solvent. These redox reactions have been followed potentiometrically. From the potential jumps the following reactions have been proposed as :

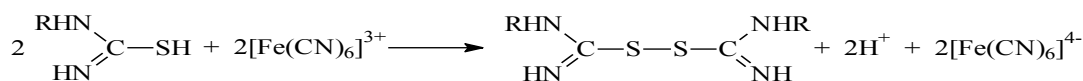
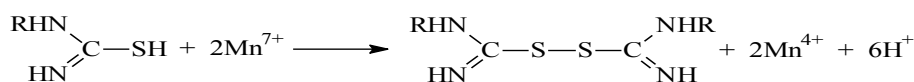
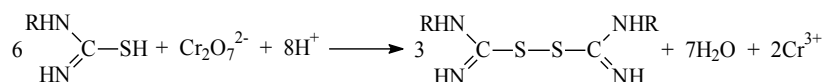
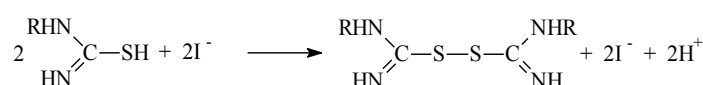
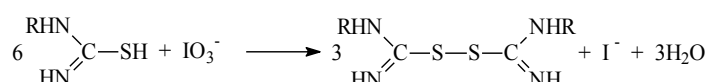


Thiourea and its alkyl or phenyl derivatives have been estimated in this solvent with the help of various oxidizing agents. The results obtained are within the experimental error and are reversible.

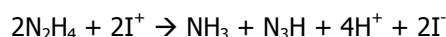
Oxidizing agents used are potassium iodate, iodine halides, potassium permanganate, potassium dichromate, potassium bromate and potassium ferricyanide. These oxidizing agents oxidize thiourea to yield thiourea formadine disulphide as:



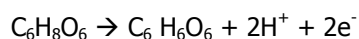
The corresponding reactions with other oxidising agents have been proposed as:



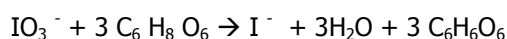
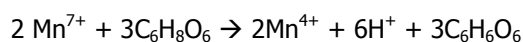
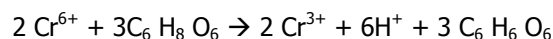
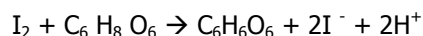
Hydrazine has been estimated with the help of various oxidizing agents. The potential jumps near the end point are quite high. The possible redox reactions for various oxidizing agents have been proposed as:



Ascorbic acid, which is powerful reducing agent, oxidized itself to dehydron ascorbic acid as.



Ascorbic acid has also been estimated quantitatively with the help of various oxidising agents potentiometrically. The possible reactions could be explained as:



From the above observations it may be concluded that fused dibromoacetic acid is a fairly good solvent for the estimation of weak bases. Redox reactions can also be conveniently carried out in it.

Table I :Solubility's of Various Solutes in Dibromoacetic acid at 60±0.5° C

Solute	Solubility in gm/100 gm of the solvent	Colour of Solution
AlCl ₃	18.72	Colourless
AlBr ₃	10.54	Light Yellow
SnCl ₄	Miscible	Colourless
SnBr ₄	8.22	Yellow
TiCl ₄	Miscible	Light Yellow
FeCl ₃	6.42	Yellow
ZrCl ₄	Insoluble	Light Yellow
ICl ₃	20.24	Reddish Brown
HgCl ₂	Insoluble	Colourless
HgBr ₂	Insoluble	Colourless
HgI ₂	Insoluble	Colourless
CdCl ₂	2.12	Colourless
CdBr ₂	2.48	Light Yellow
CdI₂		
ZnCl ₂	1.88	Colourless
ZnBr ₂	2.44	Reddish Brown
ZnI ₂	4.24	Red
BiCl ₃	6.84	Light Yellow
AsCl ₃	Miscible	Light Yellow
SbCl ₃	13.24	Yellow
PCl ₃	Miscible	Colourless
PBr ₃	Miscible	Colourless
SCl ₂	Miscible	Light Yellow
S ₂ Cl ₂	Miscible	Red
SOCl ₂	Miscible	Dark Red
PCl ₅	24.18	Colourless
SbCl ₅	Miscible	Light Yellow
Pyridine	Miscible	Light Pink
Quinoline	Miscible	Colourless
Dimethyl aniline	Miscible	Colourless
Triethylamine	Miscible	Colourless
Picoline	Miscible	Colourless
(C ₂ H ₅) ₄ NI	76.28	Dark Brown
(CH ₃) ₄ NCl	87.24	Colourless
(CH ₃) ₄ NBr	59.98	Yellow
(C ₂ H ₅) ₄ NBr	22.46	Light Yellow
ICl	Miscible	Brown
Br ₂	Miscible	Reddish Brown
SO ₃	Miscible	Colourless
KI	22.28	Reddish Brown
CoCl ₂	Insoluble	----
NiCl ₂	Insoluble	Colourless
CuCl ₂	Insoluble	----
CaCl ₂	1.22	Colourless
CaBr ₂	1.84	Colourless
MgCl ₂	0.48	Colourless
MgBr ₂	0.72	Colourless
BaCl ₂	Insoluble	----
SrCl ₂	Insoluble	----
NaCl	0.89	Colourless
KI	3.26	Colourless
NH ₄ Cl	2.74	Colourless
PbI ₂	Insoluble	----
NH ₄ CNS	8.64	Colourless
TeCl ₄	0.48	Colourless

Table I continued...

Solute	Solubility in gm/100 gm of the solvent	Colour of Solution
C ₆ H ₅ NO ₂	Miscible	Light Yellow
K ₂ Cr ₂ O ₇	9.87	Brownish Yellow
KMnO ₄	7.98	Pink
KBrO ₃	4.48	Light Yellow
KIO ₃	7.64	Brown
C ₆ H ₅ NO ₂	Miscible	Light Yellow
CHBr ₂ COONa	10.24	Colourless
CHBr ₂ COOK	11.16	Colourless
(CHBr ₂ COO) ₂ Ca	10.18	Colourless
1,10'-Phenanthroline	20.42	Colourless
2,2'-Bipyridine	26.84	Light Pink
Iodine	0.84	Dark Brown
Pyridine N-oxide	4.82	Colourless
POCl ₃	Miscible	Colourless
PSCl ₃	Miscible	Colourless
CH ₃ CONH ₂	28.46	Pale Yellow
HCON(CH ₃) ₂	Miscible	Colourless
(C ₆ H ₅) ₃ P	3.42	Colourless
(C ₆ H ₅) ₃ Sb	3.64	Colourless
Morpholine	Miscible	Colourless
Ethylacetate	Miscible	Colourless

Table II :Elemental analysis of the adducts of Lewis acids with fused dibromoacetic acid

[Compound]	Physical state		Elemental Analysis						Molar Conductance in DMF/Acetonitrile (S cm ² mol ⁻¹)[
			% Found			% Required			
	Colour	M. Pt. °C	Halogen		Metal	Halogen		Metal	
TiCl ₄ .2CHBr ₂ COOH	Solid light yellow	98-100	Cl	Br	Metal	Cl	Br	Metal	38.44 [#]
SnCl ₄ .2CHBr ₂ COOH	Solid white	82-84	24.08	53.24	8.12	22.67	51.10	7.66	24.42
SbCl ₅ .CHBr ₂ COOH	Solid grey	30-32	22.16	46.64	18.62	20.37	45.91	17.05	35.52
AlBr ₃ .CHBr ₂ COOH	Solid pale yellow	130-132	36.28	32.04	24.84	34.29	30.92	23.55	104.62
BBr ₃ .CHBr ₂ COOH	Solid yellow	119-121	----	84.98	6.24	----	82.45	5.57	48.20
FeCl ₃ .CHBr ₂ COOH	Semisolid reddish	----	87.62	2.02	----	85.30	2.31	29.64 [#]	29.64 [#]
SbCl ₃ .CHBr ₂ COOH	Solid white	38-40	28.86	43.54	15.12	27.91	42.05	14.69	28.48*
AlCl ₃ .CHBr ₂ COOH	Solid white	141-142	24.84	37.26	28.44	23.87	35.87	27.32	36.29*
			31.94	47.68	7.38	30.28	45.51	7.68	

*Nitrobenzene, [#]Acetonitrile

Table III :Elemental analysis of adducts of bases and fused dibromoacetic acid

Compound	Physical state and colour		Elemental Analysis				Molar Conductance In DMF/Acetonitrile (S cm ² mol ⁻¹)
			% Found Required		% Required		
	Colour	M. Pt. °C	Br	N	Br	N	
(C ₅ H ₅ N) ₃ .CHBr ₂ COOH	Solid white	180-182	51.24	4.45	53.82	4.72	74.52
C ₉ H ₇ .CHBr ₂ COOH	Solid light brown	30-32	43.85	3.98	46.05	4.04	3042*
·-C ₆ H ₇ .CHBr ₂ COOH	Liquid straw yellow	135-138 (B.Pt.)	54.72	4.34	57.39	4.50	88.78
C ₆ H ₅ NH ₂ .CHBr ₂ COOH	Solid light yellow	91-92	49.22	4.42	51.39	4.50	38.42*
C ₆ H ₅ NHNH ₂ .CHBr ₂ COOH	Solid yellow	116-118	47.48	4.19	49.17	4.30	59.48
C ₈ H ₁₁ N.CHBr ₂ COOH	Viscous orange liquid	----	45.34	3.98	47.14	4.13	68.46
(C ₂ H ₅) ₃ N.(CHBr ₂ COOH) ₂	Liquid dirty yellow	148-150 (B.Pt.)	28.41	2.45	29.77	2.61	24.16*
C ₅ H ₁₁ N.CHBr ₂ COOH	Solid white	144 ^D	49.98	4.48	52.74	4.62	66.24
C ₁₀ H ₈ N ₂ .CHBr ₂ COOH	Pink Liquid	76-78 (B.Pt.)	40.42	7.26	42.73	7.49	48.34

Table IV: Shift of carboxyl stretching frequencies in fused dibromoacetic acid on complex formation

Compound	Observed carboxyl frequency (cm ⁻¹)	· · cm ⁻¹
AlBr ₃ .CHBr ₂ COOH	1650	65
AlCl ₃ .CHBr ₂ COOH	1680	30
BBr ₃ .CHBr ₂ COOH	1635	70
TiCl ₄ .2CHBr ₂ COOH	1650	60
SnCl ₄ .2CHBr ₂ COOH	1685	28
SbCl ₅ .CHBr ₂ COOH	1630	80
FeCl ₃ .CHBr ₂ COOH	1695	15
BCl ₃ .CHBr ₂ COOH	1665	45

Table V: Specific conductance of various compounds in fused dibromoacetic acid at 60±0.5° C

Compound	Amount of compound gm/moles/litre	Specific conductance (S S cm ⁻¹)
TiCl ₄	0.01214	0.4426 × 10 ⁻⁴
SbCl ₅	0.01248	0.22086 × 10 ⁻³
FeCl ₃	0.00082	0.42264 × 10 ⁻⁴
SnCl ₄	0.01174	0.7248 × 10 ⁻⁴
BBr ₃	0.00622	0.1846 × 10 ⁻³
AlBr ₃	0.00988	0.1326 × 10 ⁻³
(C ₂ H ₅) ₄ NBr	0.001614	0.2124 × 10 ⁻³
(CH ₃) ₄ NBr	0.001214	0.1886 × 10 ⁻³
C ₆ H ₅ CH ₂ NH ₂	0.031812	0.6422 × 10 ⁻³
CH ₂ (CH ₂) ₄ NH	0.003842	1.5448 × 10 ⁻³
C ₅ H ₅ N	0.14884	0.7242 × 10 ⁻³
C ₆ H ₅ NH ₂	0.005428	0.2248 × 10 ⁻³
CHBr ₂ COONa	0.005428	1.4268 × 10 ⁻³
CHBr ₂ COOK	0.005644	1.2824 × 10 ⁻³

Table VI: Visual titrations of SO₃.CHBr₂COOH and SeO₃.CHBr₂COOH with various organic bases

Titrant	Substance	Titrant concn Gm eq/litre	Wt. of substance	Gm. Equivalent		% Error	Colour of indicator at the end point
				Expt × 10 ⁴	Theort × 10 ⁴		
Malachite Green							
SO ₃ .CHBr ₂ COOH	Pyridine	0.3842	0.041	8.64	8.65	+0.11	Yellow
SO ₃ .CHBr ₂ COOH	Quinoline	0.6848	0.045	5.87	5.85	-0.34	"
SO ₃ .CHBr ₂ COOH	--Picoline	0.5204	0.051	8.07	8.07	0.00	"
SO ₃ .CHBr ₂ COOH	Diethylamine	0.5048	0.048	10.96	10.98	+0.18	"
SeO ₃ .CHBr ₂ COOH	Pyridine	0.5242	0.034	6.81	6.80	-0.14	"
SeO ₃ .CHBr ₂ COOH	Quinoline	0.3304	0.055	7.12	7.10	-0.28	"
SeO ₃ .CHBr ₂ COOH	--Picoline	0.4924	0.038	6.64	6.64	0.00	"
Crystal Violet							
SO ₃ .CHBr ₂ COOH	Pyridine	0.5242	0.038	8.58	8.58	0.00	Greenish blue
SO ₃ .CHBr ₂ COOH	Dimethylamine	0.4224	0.042	9.95	10.03	+0.79	"
SeO ₃ .CHBr ₂ COOH	Diethylamine	0.5308	0.071	16.90	16.89	-0.05	"
SeO ₃ .CHBr ₂ COOH	Dimethylamine	0.6214	0.042	6.00	6.02	+0.32	"

Table VII: Principal infrared bands (cm⁻¹) of the compounds of fused dibromoacetic acid with organic tertiary bases

Pyridine	Quinoline	--Picoline	Piperidine
2949s	2950s	2946s	2944s
2725s	2710s	2715s	2726s
2142s	2205m	2132m	2155m
1625s	1645s	1655s	1650s
1610	1630s	1635s	1635s
1505	1610s	1625s	1610s
1480s	1565m	1605s	1440s

Table VII: Continued...

Pyridine	Quinoline	--Picoline	Piperidine
1435s	1430s	1445s	1438s
1387m	1388m	1395m	1405m
1325s	1320s	1322s	1310s
1255s	1240s	1235s	1220s
1225s			
1205s			
1165s	1175m	1170m	1160m
1080m	1070m	1065m	1062m
1055s	1045s	1045s	1040s
1030s	1025s	1030s	1025s
1005s	1006s	1110s	1008s
995			
895s	890s	892s	895s
752·s	748·s	745·s	742·s
682·s	690·s	685·s	625·s

Table VIII :Infrared spectra of the adducts of 2,2'-bipyridine with fused dibromoacetic acid

2,2'-bipyridine		C ₁₀ H ₈ N ₂ .CHBr ₂ COOH
3085	C-H stretching modes	3110
3072		3098
3060		3085
3056		3080
1580	Phenyl nuclear stretching modes	1625
1565		1600
1452		1496
1410		1455
1065	In plane hydrogen bonding	1065
1045		1045
992	Ring breathing	1030
760	Ring-H out of plane band	772
740		730
672	Ring band	648
630		

Table IX: Infrared spectral band (cm⁻¹) of the adduct of 1,10'-Phenanthroline with fused dibromoacetic acid

C ₁₂ H ₈ N ₂		C ₁₂ H ₈ N ₂ .CHBr ₂ COOH
3402	C-H	3580
3075		3105
1580	C=C and C=N stretching mode	1625
1565		1592
1505		1525
1452		1470
1418	Ring vibrations	1355
		1260
		1225
		1150
992		1010
860	Out of plane (C-H) on heterocyclic ring	858
740	Out of plane (C-H) of centre ring	710

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