Conductametric studies of some organotellurium(IV) trihalides

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Abstract: The electrical conductance of a series of aryl tellurium trihalides (i.e. p-RC₆H₄TeX₃: R= H, OCH₃, Cl; X= Cl, Br, I) has been measured in dimethylsulphoxide (DMSO) and dimethylformamide (DMF) at 298K. The results indicated that their behavior was as weak electrolytes. The conductance data were analyzed by a minimization technique using complete and modified equations of Pitt (P) and Fuoss - Hsia (F/H) equations. The variation in the three parameters KA, Ao and a was fully investigated.

Keywords: Electrical conductance, Aryl tellurium trihalides, Weak electrolytes, Fouss-Hsia equation.

Introduction

Our previous works[1,2] on the conductance studies of some organotellurium dihalides showed that these compounds are dissociated as weakly ionic compounds in DMF and DMSO solution [1,2]. The present work describes the electrical conductance of a series of aryltellurium trihalides (i.e. p-RC₆H₄TeX₃, R=H, OCH₃, Cl) in order to explore electrical behavior of this series. An iteration method (minimization technique) was applied using the complete and modified forms of both Pitts (P)[3,4] and Fuoss-Hsia (F/H) [5,6] equations.

Experimental

Synthesis

Diphenyl ditelluride[7] , bis(p-methoxyphenyl) ditelluride[8], bis(p-chloro phenyl) ditelluride[8] , phenyltellurium tribromide[9] and phenyltellurium tri chloride[9] were prepared according to literature methods. Phenyltellurium triiodide, p-methoxyphenyltellurium triiodide and p-chlorophenyltellurium tri iodide were prepared according to previous methods [10, 11].
Conductivity measurements

Conductivity measurements were carried out by using a Wayne-Kerr autobalance precision model B331. The bridge was calibrated against a standard low inductance resistance box; its sensitivity and reproducibility were found to be better than ±0.01% over the range 10^3-10^6 ohm. The temperature of the water-filled thermostat used in the conductivity measurements was maintained at 25.00±0.05 °C and was monitored by digital thermometer. The conductance cell and method used for measuring conductance have been described previously [12]. The cell constant was found to be 0.16623±0.0001cm⁻¹. All experiments were carried out under a dry nitrogen atmosphere. DMSO and DMF were purified and dried as described in the literature [13, 14]. All solvent and stock solutions (for conductivity measurements) were prepared by weight, and all measurements were made by the weight dilution technique. The solvent properties were taken from the literature [13,14].

Results and Discussion

The measured molar conductance (Λ_{exp}) and the corresponding concentrations (mol dm⁻³) were analyzed by means of the complete and modified of Fuoss-Hsia (F/H)[5,6] and Pitts (P)[3,4] equations. For the interpretation of the characteristic parameters of an electrolyte solution from conductance data, a minimization technique was used [15-17] in terms of K_A, Λ_o and α. The results of the best-fit values are listed in Table 1 together with the corresponding values of the standard deviation σ, given by:

\[ \sigma = \left[ \frac{S^2}{N} \right]^{1/2} \]  

Where \( S^2 \) is obtained by:

\[ S^2 = \sum_{j=1}^{N} (\Lambda_{\text{calculated}} - \Lambda_j)^2 \]  

\( \Lambda_j \) is the experimental value at \( j = 1,2,3,...N \) (N represents the number of the measured points).

The K_A values (Table 1) for compounds 1, 2, 4 and 5 indicate that these compounds are weak electrolytes and undergo more ion-pair formation in DMSO solvent than in DMF solvent which agrees well with our previous work [1,2]. Compound 3 has higher K_A value in DMF than in DMSO, Table 1.
Table 1. The best fit parameters $\Lambda_0$, $K_A$ and $a$ together with the standard deviations ($\sigma$) for the organotellurium(IV) compounds

| Compound | Parameter | DMF | DMSO |
|----------|-----------|-----|------|
|         |           | F/H complete | F/H modified | Pitts complete | Pitts modified | F/H complete | F/H modified | Pitts complete | Pitts modified |
| (1)     | $a$       | 14.5 | 14.5 | 14 | 14.5 | 14 | 14.5 | 10 | 14.5 |
|         | $\Lambda_0$ | 134 | 135 | 120 | 135 | 76 | 78 | 73 | 75 |
|         | $K_A$     | 72   | 71   | 68  | 1221 | 1151 | 1493 | 1095 |
|         | $\sigma$  | 0.91 | 1.10 | 0.62 | 1.19 | 1.18 | 0.98 | 1.17 | 1.34 |
| (2)     | $a$       | 5    | 7    | 3   | 15  | 14.5 | 3 | 14 |
|         | $\Lambda_0$ | 108 | 108 | 97 | 108 | 70 | 78 | 77 | 73 |
|         | $K_A$     | 91   | 94   | 80  | 9702 | 5381 | 11600 | 10259 |
|         | $\sigma$  | 0.43 | 0.43 | 1.95 | 0.43 | 1.40 | 1.54 | 2.20 | 1.82 |
| (3)     | $a$       | 15   | 15   | 15  | 14.5 | 14.5 | 3 | 14 |
|         | $\Lambda_0$ | 57  | 56   | 52  | 55  | 71 | 72 | 83 | 83 |
|         | $K_A$     | 49101 | 44850 | 44400 | 39555 | 3034 | 2801 | 6190 | 5638 |
|         | $\sigma$  | 0.83 | 0.84 | 0.76 | 0.69 | 2.38 | 2.18 | 2.20 | 3.05 |
| (4)     | $a$       | 15   | 15   | 13  | 14.05 | 14.5 | 14 | 14 |
|         | $\Lambda_0$ | 55  | 56.50 | 53  | 57.50 | 60 | 64 | 73 | 61 |
|         | $K_A$     | 116  | 219  | 1159 | 208 | 492 | 601 | 1515 | 483 |
|         | $\sigma$  | 0.90 | 0.96 | 0.88 | 1.27 | 1.42 | 1.27 | 1.56 | 1.54 |
| (5)     | $a$       | 14.5 | 2    | 10  | 6   | 15 | 15 | 7 | 15 |
|         | $\Lambda_0$ | 54  | 57.80 | 55.8 | 56  | 58 | 59 | 60 | 56 |
|         | $K_A$     | 920  | 1197 | 3170 | 877 | 7872 | 7872 | 10260 | 8050 |
|         | $\sigma$  | 1.98 | 1.53 | 1.65 | 1.95 | 0.98 | 1.00 | 0.73 | 1.01 |

$\Lambda_0$ (ohm$^{-1}$cm$^2$mol$^{-1}$); $K_A$(dm$^3$/mol$^{-1}$); $a$ (A$^+$)
The conductivities of compounds 1 and 2 in DMF are greater than those in DMSO (Fig. 1 and 2) which may be attributed to the tendency of aryltellurium triiodide to form polymeric compounds in DMSO[18]. It appears that the substituents on the aryl group is largely effect the conductance of compounds 1, 2, and 3. Table 1. The viscosity and high dielectric constant of DMSO also may be considered as additional reasons [19]. Furthermore, iodide ion is as a good leaving group which leading to weak interaction with tellurium atom. On the other hand, a reaction between solute and solvent may occurred[20,21]. By contrast, in DMSO, compounds 1 and 2 have high $K_A$ values, which means that these compounds are much more ionic in DMF than in DMSO, Table 1. Compound 3 has high conductivity values in DMSO than in DMF. This may be due to the presence of chloro substituent on para position of benzene ring increases the positive charge on tellurium atom which lead to high interaction between anion and cation forming ion pairs or due to its ability to form a polymeric structure [1,2]. The plot of $\Lambda$ against (concentration)$^{1/2}$ (Fig. 3) shows that equivalent conductance of 3 in DMSO decreasing at the beginning until reaching about $3.8 \times 10^{-4}$ M after which it increases again. The reason for such behavior may be attributed to the formation of ionic species or ionic complexes at definite range of concentration.

The conductivity of compound 4 in DMSO is greater than that in DMF (Fig. 4) due to the probability of its association in DMF; in fact, this is a general trend of phenyltellurium tribromide compounds to form polymeric molecular structure[18] via secondary intermolecular bonding through bridging halides. On the other hand, a coordination may occurs between DMSO solvent molecules through the oxygen atom with the organic tellurium ion [22], as shown in scheme 1.

![Scheme 1: probable coordination occurrence between DMSO and Te ion](image)

The $K_A$ values for compound 5 in DMSO is greater than that in DMF which means that this compound is more ionic in DMF. The increase and deviation of $S^2$ value for compound 5 in DMSO may be attributed to formation of additional ion-pair, Table 1.
It is clear from the Table 1 and Figure 5 that conductivity of compound 5 in both DMSO and DMF solvents is nearly the same. This may be attributed to the molecular association of the compound in both solvents [23], as it is known that a thermodynamic equilibrium occurs between association and dissociation of trichlorides, according to the following equation:

\[
\text{ArTeCl}_2^+ \text{Cl}^- \rightleftharpoons \text{ArTeCl}_2^+ + \text{Cl}^- \quad \text{.................(3)}
\]

So it is concluded that the conductivity of aryltellurium trihalides are as follow:

\[
\text{ArTeI}_3 > \text{ArTeBr}_3 > \text{ArTeCl}_3
\]
Figure 3: Plots of experimental molar conductance against (concentration $1/2$) for compound 3 in DMF and DMSO at 25°C.

Figure 4: Plots of experimental molar conductance against (concentration $1/2$) for compound 4 in DMF and DMSO at 25°C.

Figure 5: Plots of experimental molar conductance against (concentration $1/2$) for compound 5 in DMF and DMSO at 25°C.
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