



## Direct Electrochemical Synthesis of Unique Organoaluminium Halides and Their Coordination Complexes at Sacrificial Aluminium Anode

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The method of direct electrochemical synthesis of organoaluminium halide involves the electrolysis of organic halide in acetonitrile (as solvent) and tetrabutylammonium chloride (as supporting electrolyte) using sacrificial aluminium anode and platinum cathode in H-type cell. The organic halide is bromoethane, 1-bromopropane, chlorobenzene and cyclopentadiene (Cp). The compounds conveniently isolated are  $(R)_2AlX$  and  $AlCp_3$ . On refluxing with nitrogen containing ligand (L) 2,2'-bipyridyl and 1,10-phenanthroline, these organoaluminium halides do not form coordination compounds. However, the coordination compounds with general formula  $(R)_2AlX \cdot L$  and  $AlCp_3 \cdot L$  have been synthesized electrochemically by addition of these ligand to the electrolysis phase. All these electrochemically synthesized organoaluminium halides have been characterized by physical measurements, elemental analysis and infrared spectroscopic studies. All these electrochemical products are associated with high current efficiencies.

**Keywords:** Electrochemical oxidation, Sacrificial aluminium anode, Organoaluminium halides, Current efficiencies.

### INTRODUCTION

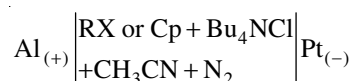
The electrochemical technique is one of the simplest and most direct methods to achieve the oxidation and reduction reactions since the removal or addition of electrons can be achieved without any complications. This technique has received a great deal of appreciation to number of scientists because of a broad spectrum of applications in inorganic [1-3], organic [4-6], environmental sciences [7], thin film coatings on metals [8], electro deposition [9], anticorrosion processes [10], pharmaceutical [11] or chemical industries [12] and it is used in development of biosensors [13], gold and silver nanoparticles [14,15]. The use of the direct electrochemical oxidation of metal in non-aqueous media has been proved to be effective route for the synthesis of organometallic halides of a number of main group metals. The continuation interest of our research group [16-22] in electrochemical synthesis of inorganic compounds on different metals like mercury, cadmium, zinc, antimony, copper and bismuth, so, in the present context, we have extended this direct electrochemical technique for the synthesis of organoaluminium halides and their coordination complexes by electrochemical dissolution of sacrificial aluminium anode. A sacrificial electrode is the electrode which in addition to acting as source or sink for electrons may also react with the species present in the solution or produced during the progress of the electrolysis.

### EXPERIMENTAL

Acetonitrile (Merck) was purified and dried over 4A molecular sieves and was kept for overnight. Then the sample was distilled [23] in the range of 81-82 °C and was used as solvent. Tetrabutylammonium chloride was crystallized from conductivity water, dried under reduced pressure at 100 °C and was used as a supporting electrolyte. Alkyl/aryl halides were used as supplied (Merck). Cyclopentadiene (Fluka) exists in dimer form. So, first of all dicyclopentadiene was broken down to monocyclopentadiene by refluxing for more than 8 h and then distilled cyclopentadiene which was kept in a tight stoppered flask and used as a reactant. Electrolysis has been carried out in an H-type cell made up of pyrex glass in which two compartments anodic and cathodic were separated from each other by a sintered glass disc of G-4 porosity. Platinum foil (1.0 cm × 1.0 cm) was used as inert cathode and aluminium plate (2.0 cm × 10 cm × 0.2 cm) as sacrificial anode. Direct current for electrochemical oxidation was obtained by using Toshniwal electrophoresis 'Perfit' power supply.

**Electrochemical procedure:** A reaction mixture of 3 mL of alkyl/aryl halides (RX) or cyclopentadiene (Cp) in 250 mL of acetonitrile using tetrabutylammonium chloride (1.0 g) as supporting electrolyte was prepared and transferred into the H-type electrolytic cell. The sacrificial aluminium electrode and inert platinum electrode were introduced into the anodic

and cathodic compartments of H-type cell respectively. The electrolytic cell was closed from both sides with the help of guard tubes (filled with dried calcium chloride and glass wool) so as to protect the reaction mixture from moisture. Direct current was obtained from an electrophoresis power supply. For the smooth dissolution of metal, the potential across the electrodes was so adjusted that a current of 20 mA passed through the anodic solution. During the electrolysis, nitrogen gas was bubbled through the solution to provide an inert atmosphere and magnetic bead using magnetic stirrer was used in order to stir the solution phase and remove the product adhering on the electrode. As electrolysis proceeded, the colour of the solution changed and hydrogen gas evolved from the cathode. The cell can be summarized as follows:



where:  $\text{Al}_{(+)}$  is sacrificial aluminium anode,  $\text{Pt}_{(-)}$  is inert platinum cathode,  $\text{Bu}_4\text{NCl}$  is tetrabutylammonium chloride,  $\text{CH}_3\text{CN}$  is acetonitrile,  $\text{N}_2$  is nitrogen gas bubbled through the system and  $\text{RX/Cp}$  is alkyl/aryl halides or cyclopentadiene.

Electrolysis was conducted for 5 h (with the bubbling of nitrogen gas) at a constant current of 20 mA so that enough product may be obtained in the anodic compartment. The solid product formed in the anodic compartment were filtered, washed with warm acetonitrile (10 mL) and diethyl ether (20 mL) and then finally dried *in vacuo*. All efforts were done to protect the product from air and moisture.

For the synthesis of coordination compounds of these products electrochemically, 1 g of ligand 2,2'-bipyridyl or 1,10-phenanthroline was also added in addition to above substrates before starting the electrolysis and electrolysis was done under the similar conditions. Melting point of all these products was determined using electrical device with a heating rate of 5 °C/min. Carbon, hydrogen and nitrogen (where applicable) contents in the products were determined through CHNS elemental analyzer 'Elementor Vario EL'. Aluminium contents in all these separated products were determined using oxine method [24]. The halide ion (Br/Cl) contents in these products were determined using Mohr's salt method [24]. Infrared spectra of the products were scanned on Perkin-Elmer spectrophotometer (FTIR) using KBr pallets in the region of 4000-400  $\text{cm}^{-1}$  and 400-30  $\text{cm}^{-1}$ . The current efficiencies (gram equivalents of metal dissolved per Faraday of electricity passed) of all these reactions were determined using Faraday's first law of electrolysis by electrolyzing the above systems for exactly 2 h at a constant current of 20 mA. After the electrolysis of

2 h, the solution in anode compartment was distilled in rotary film evaporator (Buchi) till 10 mL of contents were left in the flask. The contents were transferred to the beaker and heated to dryness. The theoretical value of aluminium was calculated by using Faraday's first law of electrolysis. The ratio of experimental and theoretical aluminium contents gives the electrochemical efficiency or current efficiency of the system.

## RESULTS AND DISCUSSION

**Synthesis of organoaluminium halides:** Electrochemical reactions of alkyl/aryl halides or cyclopentadiene have been conducted at sacrificial aluminium anode and inert platinum cathode in the presence of acetonitrile and tetrabutylammonium chloride. All the above synthesized electrochemical products are more sensitive to air or moisture. All these compounds are insoluble in most of the commonly used organic solvents like methanol, ethanol, acetone, benzene, chloroform, carbon tetrachloride, N,N-dimethyl formamide, dimethyl sulfoxide and carbon disulfide. It has also been observed that all these isolated complexes do not melt upto 300 °C, however, decompose in a temperature range of 200 to 240 °C. The decomposition of the products is indicated from the change in colour of these compounds. The composition of the electrochemical synthesized complexes was determined by analytical and elemental analytical data (Al, Cl, Br, C and H) which is summarized in Table-1. From this data, the complexes are proposed to have the general molecular formula  $(\text{R})_2\text{AlX}$  in case of alkyl/aryl halides and  $\text{AlCp}_3$  in case of cyclopentadiene aluminium complex. These compounds are highly hygroscopic and decompose in air. Therefore, these compounds have been handled in a dry box.

Infrared spectral data reveal that the characteristics absorption bands in all these products appear in the region of 638-560  $\text{cm}^{-1}$ , 352  $\text{cm}^{-1}$ , 238-230  $\text{cm}^{-1}$  and 158-156  $\text{cm}^{-1}$ . It is reported in literature studies [25-27] that  $\nu(\text{M-C})$  absorption bands appear in the range of 700-450  $\text{cm}^{-1}$ . So, in the present products, the absorption bands in the region of 638-560  $\text{cm}^{-1}$  corresponding to  $\nu(\text{Al-C})$  stretching vibrations. The presence of  $\nu(\text{Al-C})$  absorption bands in these complexes shows that these products are organoaluminium compounds. The moisture sensitivity of these products also supports that these are organoaluminium compounds. In literature, it is reported [28] that aluminium-halogen  $\nu(\text{Al-X})$  stretching vibrations for inorganic complexes are occur in the far infrared in the 500-200  $\text{cm}^{-1}$  region. The metal-bromine  $\nu(\text{M-Br})$  stretching vibrations in the far infrared region are reported [29] in the region of 254-210  $\text{cm}^{-1}$ . In literature, the  $\nu(\text{M-Br})$  peaks are also reported [30] in the region of 165-150  $\text{cm}^{-1}$ . The bands centered at 230

TABLE-I  
ELECTROLYSIS CHARACTERISTICS, ELEMENTAL ANALYSIS AND OTHER RELATED  
DATA OF ELECTROLYSIS OF ALKYL/ARYL HALIDES AT ALUMINIUM ANODE

System	Potential applied	Product	Colour	Elemental analysis (%): Found (calcd.)				Current efficiency (gram equivalents per Faraday)
				Al	C	H	X	
Bromoethane	42	$(\text{C}_2\text{H}_5)_2\text{AlBr}$	Grey	15.90 (16.37)	30.00 (29.11)	6.02 (6.06)	49.00 (48.45)	1.30
1-Bromopropane	40	$(\text{C}_3\text{H}_7)_2\text{AlBr}$	Grey	13.05 (13.99)	37.81 (37.33)	7.09 (7.26)	40.00 (41.42)	2.00
Chlorobenzene	35	$(\text{C}_6\text{H}_5)_2\text{AlCl}$	Grey	12.15 (12.47)	66.28 (66.51)	4.28 (4.62)	15.35 (16.40)	0.84
Cyclopentadiene	30	$(\text{C}_5\text{H}_5)_3\text{Al}$	Dark brown	12.35 (12.16)	81.00 (81.08)	6.22 (6.76)	–	0.81

(X) is halogen Cl, Br

$\text{cm}^{-1}$ ,  $156\text{ cm}^{-1}$  and  $238\text{ cm}^{-1}$ ,  $158\text{ cm}^{-1}$  in the present products are corresponding to  $\nu(\text{Al-Br})$  vibration. Survey of literature reveals [31,32] that for polymeric metal complexes  $\nu(\text{M-Cl})$  stretches are observed in the region of  $430\text{--}330\text{ cm}^{-1}$ . So, in the present products, the band centered at the  $352\text{ cm}^{-1}$  are assignable to  $\nu(\text{Al-Cl})$  stretching vibrations of organoaluminium halide compounds. Infrared spectrum of cyclopentadiene show absorption bands at  $2976\text{ cm}^{-1}$ ,  $1020\text{ cm}^{-1}$ ,  $832\text{ cm}^{-1}$  which can be assigned to  $\nu(\text{C-H})$  deformation [27,33] (out-of-plane and in-plane) and at  $1412\text{ cm}^{-1}$  are assigned to  $\nu(\text{C-C})$  deformation [32,33] of the cyclopentadienyl ring. Another medium intensity band assignable to  $\nu(\text{Al-ring})$  vibrations has been observed at  $410\text{ cm}^{-1}$  in this compound (*i.e.*  $\text{AlCp}_3$ ). The infrared data of all these products are shown in Table-2.

So, physical characteristics and infrared spectra of the present electrochemical products reveal that these compounds are organoaluminium halide compounds. All these organoaluminium halides are having high melting point and insoluble nature in all the commonly used organic solvents thereby indicating their unique polymeric nature. From the infrared data and physical measurements, the probable structure of the organoaluminium through halide bridges as shown below (Fig. 1).

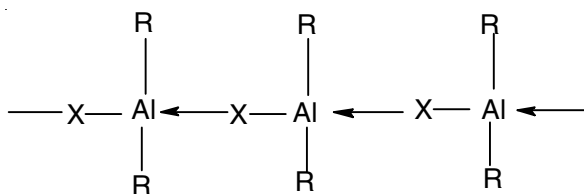
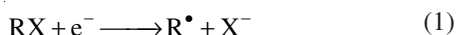


Fig. 1. Probable Structure of organoaluminium compounds through halide bridges

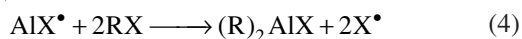
An interesting feature of these reactions is that current efficiencies of all these systems (Table-1) are very high (more than 100 % except chlorobenzene and cyclopentadiene). This unusual phenomenon has been explained on the basis of the mechanism discussed below:

**At cathode:**



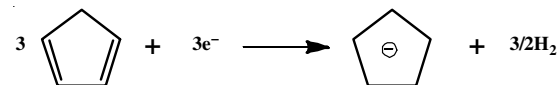
The halide ion formed at cathode migrates to the anode compartment under the influence of the applied potential and undergoes the following sequence of reactions:

**At anode:**

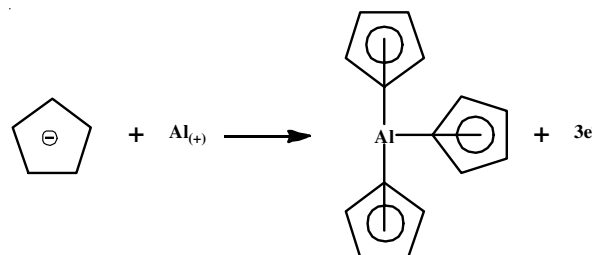


The reaction (3) and (4) constitute a chain process and proceed without the consumption of any current from the source and thus explain the high current efficiencies of these systems. High current efficiency of all these systems indicating the reaction leading to formation of  $(\text{R})_2\text{AlX}$  and  $\text{AlCp}_3$  is the predominant reaction of this system. The mode of this reaction is as follow:

**At cathode:**



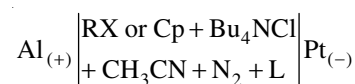
**At anode:**



**Coordination compounds of organoaluminium**

**halides:** The organoaluminium halides prepared have been refluxed with ligands 2,2'-bipyridyl and 1,10-phenanthroline in polar and non-polar solvents like methanol, ethanol, benzene and acetonitrile for 48 h in order to prepare coordination complexes of these compounds. However the analytical and IR data of these compounds showed that the ligand molecule could not be attached to these organoaluminium halides. It may be due to the reason that the metal atom in these organoaluminium halides have already achieved its favourable coordination number through halide bridging, therefore, further expansion of coordination sphere due to the addition of ligand could not be achieved. It was thus considered worthwhile that the ligand may be added to these organoaluminium halides before these form halides bridging and get polymerized. So, it was thought that the ligand molecule can be added electrochemically. So, the coordination compounds of these organoaluminium halides have been prepared by adding 1 g of 2,2'-bipyridyl and 1,10-phenanthroline in addition of the supporting electrolyte and reactant before starting the electrolysis process. The other details were essentially the same as discussed earlier for the synthesis of organoaluminium halides.

The cell can be represented as:



where L: 2,2'-bipyridyl or 1,10-phenanthroline and the other symbols have same meanings as discussed earlier.

TABLE-2  
SELECTED INFRARED ABSORPTION BANDS OF ELECTROLYSIS OF ALKYL/ARYL HALIDES AT ALUMINIUM ANODE

System	Possible assignment: Absorption bands ( $\text{cm}^{-1}$ )					
	$\nu(\text{Al-C})$	$\nu(\text{Al-Br})$	$\nu(\text{Al-Cl})$	$\nu(\text{C-H})$ of Cp	$\nu(\text{C-C})$ of Cp	$\nu(\text{Al-Cp})$
Bromoethane	560(s), 638(m)	230(m), 156(m)	—	—	—	—
1-Bromopropane	72(s), 625(m)	238(m), 158(m)	—	—	—	—
Chlorobenzene	63(s), 614(m)	—	352(m)	—	—	—
Cyclopentadiene	—	—	—	2976(s), 1020(m) 832(m)	1412(s)	410(m)

The term (s) and (m) represents the strong and medium intensity bands.

All these coordination compounds of these organoaluminium halides are having high melting point and insoluble in various commonly used organic solvents compounds. The compositions of the resulting products were established by analytical/elemental analysis (Table-3) and this data is best suited to the molecular formula  $(R)_2AlX \cdot L$  in the case of alkyl/aryl halides and  $AlCp_3 \cdot L$  in the case of cyclopentadiene. The absorption bands in the regions of  $632\text{--}598\text{ cm}^{-1}$  and  $448\text{--}423\text{ cm}^{-1}$  in the resulting products can be assigned to  $\nu(Al-C)$  stretching vibrations [25,26]. In the present study, the medium intensity absorption bands in the region of  $359\text{--}335\text{ cm}^{-1}$  are assignable to  $\nu(Al-Cl)$  stretching vibrations and in the region of  $242\text{--}224\text{ cm}^{-1}$  and  $162\text{--}152\text{ cm}^{-1}$  are corresponding to  $\nu(Al-Br)$  stretching vibrations of organoaluminium compounds respectively. In the case of cyclopentadiene-aluminium complex the persistence of bands at  $3028\text{ cm}^{-1}$ ,  $1416\text{ cm}^{-1}$ ,  $1020\text{ cm}^{-1}$ ,  $830\text{ cm}^{-1}$  are due to cyclopentadienyl rings. The additional bands appearing in the region of  $1611\text{--}1440\text{ cm}^{-1}$  are assigned due to stretching vibrations of the ligand molecules [34,35] and in the region of  $430\text{--}420\text{ cm}^{-1}$  are assigned to  $\nu(Al-Cp)$  ring vibrations. However, these bands appear at slightly lower region as compared to those reported in the pure ligand molecules and these bands are completely absent in the parent organoaluminium

halides, thereby conforming the attachment of the ligand. The infrared data of all these products are shown in Table-4.

All these coordination complexes of organoaluminium halides have also high current efficiencies (except chlorobenzene and cyclopentadiene). The reason of high current efficiencies of these coordination complexes is same as discussed earlier. High melting point, insoluble behaviour and the infrared data indicates that these coordination compounds may also be polymeric in nature like their parent organoaluminium halides.

The comparison of infrared data of coordination complexes of organoaluminium halides with their parent compounds show that there is blue shift in stretching vibrations of  $\nu(Al-C)$ ,  $\nu(Al-Cl)$  and  $\nu(Al-Br)$  and appearance of absorption bands due to ligand molecules  $\nu(C=C)$  and  $\nu(C=N)$  confirmed the attachment of the ligand which was also supported by the analytical data of these adducts.  $((R)_2AlX \cdot L$  and  $AlCp_3 \cdot L$ ).

### Conclusion

The present study thus reveals that electrochemical technique has proved to be the useful tool and a reliable, fast, low cost and a tuneable method for the synthesis of organoaluminium halides and their coordination complexes in a single step

TABLE-3  
ELECTROLYSIS CHARACTERISTICS, ELEMENTAL ANALYSIS AND OTHER RELATED DATA OF  
ELECTROLYSIS OF ALKYL/ARYL HALIDES + LIGAND SYSTEMS AT ALUMINIUM ANODE

System	Potential applied	Product	Colour	Elemental analysis (%): Found (calcd.)					Current efficiency (gram equivalents per Faraday)
				Al	C	H	N	X	
Bromoethane + 2,2'-bipyridyl	40	$(C_2H_5)_2AlBrC_{10}H_8N_2$	Light grey	8.33 (8.41)	52.28 (52.32)	5.59 (5.61)	8.76 (8.72)	23.78 (24.88)	1.60
1-Bromopropne + 2,2'-bipyridyl	30	$(C_3H_7)_2AlBrC_{10}H_8N_2$	Light grey	7.36 (7.73)	54.80 (55.00)	6.15 (6.30)	8.00 (8.02)	22.80 (22.89)	2.00
Chlorobenzene + 2,2'-bipyridyl	45	$(C_6H_5)_2AlClC_{10}H_8N_2$	Light grey	7.42 (7.24)	70.00 (70.08)	4.82 (4.83)	7.60 (7.51)	9.25 (9.53)	0.79
Cyclopentadiene + 2,2'-bipyridyl	45	$(C_5H_5)_3AlC_{10}H_8N_2$	Dark brown	7.11 (7.14)	79.00 (79.32)	5.78 (6.08)	7.90 (7.40)	—	0.82
Bromoethane + 1,10-phenanthroline	45	$(C_2H_5)_2AlBrC_{12}H_8N_2$	Brown	7.42 (7.82)	55.00 (55.63)	5.18 (5.22)	8.10 (8.11)	21.90 (23.15)	2.00
1-Bromopropne + 1,10-phenanthroline	25	$(C_3H_7)_2AlBrC_{12}H_8N_2$	Light brown	7.16 (7.24)	57.02 (57.89)	5.89 (5.90)	7.28 (7.50)	21.39 (21.41)	1.40
Chlorobenzene + 1,10-phenanthroline	55	$(C_6H_5)_2AlClC_{12}H_8N_2$	Light brown	7.18 (6.81)	71.53 (72.59)	4.49 (4.54)	7.42 (7.06)	8.94 (8.95)	0.82
Cyclopentadiene + 1,10-phenanthroline	40	$(C_5H_5)_3AlC_{12}H_8N_2$	Dark brown	7.00 (6.71)	79.26 (80.56)	5.34 (5.72)	6.29 (6.96)	—	0.76

TABLE-4  
SELECTED INFRARED ABSORPTION BANDS OF ELECTROLYSIS OF  
COORDINATION COMPLEXES OF ALKYL/ARYL HALIDES AT ALUMINIUM ANODE

System	Possible assignment: Absorption bands ( $\text{cm}^{-1}$ )			
	$\nu(Al-C)$	$\nu(Al-Br)$	$\nu(Al-Cl)$	$\nu(C=C)/\nu(C=N)$
Bromoethane + 2,2'-bipyridyl	432(s), 610(m)	224(m), 152(m)	—	1440, 1608
1-Bromopropne + 2,2'-bipyridyl	448(s), 622(m)	242(m), 158(m)	—	1448, 1600
Chlorobenzene + 2,2'-bipyridyl	429(s), 632(m)	—	359(m)	1452, 1605
Bromoethane + 1,10-phenanthroline	428(s), 598(m)	230(m), 162(m)	—	1464, 1600
1-Bromopropne + 1,10-phenanthroline	433(s), 602(m)	234(m), 160(m)	—	1460, 1602
Chlorobenzene + 1,10-phenanthroline	423(s), 625(m)	—	355(m)	1459, 1605
System	$\nu(C-H)$ of Cp	$\nu(C-C)$ of Cp	$\nu(Al-Cp)$	$\nu(C=C)/\nu(C=N)$
Cyclopentadiene + 2,2'-bipyridyl	3028(s), 1020(m), 830(m)	1416(s)	420(m)	1456, 1600
Cyclopentadiene + 1,10-phenanthroline	3030(s), 1028(m), 840(m)	1412(s)	430(m)	1456, 1611

The term (s) and (m) represents the strong and medium intensity bands.



as compared to other multi step methods. Current efficiency of all these systems is quite high. So, the technique offers a versatile approach for the commercial preparation of these compounds.

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