COMPLEXES OF ORGANOMETALLIC COMPOUNDS

VII. PAPER ELECTROPHORESIS OF $(C_2H_5)_2Pb^{2+}$ AND $(C_2H_5)_3Pb^+$ IN CHLORIDE SOLUTIONS

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The present work deals with the paper electrophoresis of the organometallic cations $(C_2H_5)_3Pb^+$ and $(C_2H_5)_2Pb^{2+}$, in aqueous LiCl solutions of varying molarity. It has been undertaken in order to investigate the applicability of paper electrophoresis to these organo-lead cations, and in particular to study, by this technique, the possibility of the cations forming reversible chloride complexes.

It is well known that the study of reversible complexes in aqueous solutions, and at high ligand concentration, can be carried out by means of ion exchange resins[1]. We have demonstrated that it is possible to study the reversible chloride complexes of organo-lead cations by anion exchange[2], and that useful results can be obtained in this field by the employment of anion exchange papers[3]. The results of the research given in refs. 2 and 3 strongly support the hypothesis of the formation of the complexes $(C_2H_5)_2PbCl_n^{2-n}$ (n ranging from 1 to 4) and $(C_2H_5)_3PbCl_n^{1-n}$ (n ranging from 0 to 3); the values of n are functions of the ligand activity in solution.

On the other hand, it must be kept in mind that the experimental distribution curves of $(C_2H_5)_2PbCl_2$ and $(C_2H_5)_3PbCl$ between resin and aqueous solutions containing the ligand Cl⁻, at pH $\simeq$ 7, are continuously increasing with the increase of ligand concentration in solution[2]. Distributions of this kind are often not attributed to anion exchange of negatively charged complexes (see ref. 3).

We have carried out the paper electrophoretic studies reported in this paper, in order to throw some light on this subject. If an eventual agreement of results were obtained with anion exchange and paper electrophoresis, *viz.* with two substantially different techniques, any reasonable doubt as to the existence of reversible chloride complexes of organo-lead cations in neutral solutions would be removed.

In conclusion our work showed that with the electrophoretic technique it is possible to obtain a rapid and accurate separation of $(C_2H_5)_2PbCl_2$ from $(C_2H_5)_3PbCl$. That is why we have also studied the electrophoretic behaviour of Pb^{2+}, since it is the principal decomposition product of organo-lead compounds.

EXPERIMENTAL

The diethyl-lead dichloride and the triethyl-lead chloride used were prepared, stored, checked for purity, and purified as described in earlier papers[a].

Paper electrophoresis was carried out using the technique and apparatus as described by LEDERER AND WARD[4].

Strips of Whatman No. 1 paper (5.5 × 40 cm) were employed. In order to avoid photochemical decomposition during the trials with organo-lead compounds, the sheets of glass containing each strip were enveloped in black paper.

Each electrophoresis was carried out simultaneously on amounts of about 50 γ of each organo-lead chloride (or $PbCl_2$) and on the same quantity of H_2O_2. These compounds were dissolved in aqueous LiCl solutions which were also employed in the electrophoresis. H_2O_2 was used to measure the electro-osmotic flow.

Previous experiments showed that the best results are obtained by employing a potential difference of 135 V for 2 h. The highest current intensity was about 60 mA for concentrated solutions, but in general it was 20–30 mA.

The location of organo-lead cations, after electrophoresis, was revealed by oxidation to Pb^{2+} with Br_2, followed by spraying with potassium rhodizonate. The H_2O_2 was located with KI.

Experiments on electrophoretic separations of solutions of $PbCl_2$ + $(C_2H_5)_2 PbCl_2$ + $(C_2H_5)_3PbCl$ mixture were also carried out.

RESULTS

The data obtained are reported in Table I, which indicates in mm the displacement (corrected for electro-osmotic flow) of the spot centre from the application point towards the cathode or towards the anode. It must be remembered that $(C_2H_5)_2PbCl_2$ and $PbCl_2$ are adsorbed on Whatman No. 1 paper in LiCl solutions of concentrations < 0.5 M, while $(C_2H_5)_3PbCl$ is adsorbed in [LiCl] > 4 M. A tail formation can be observed for these molarities (see Table I).

Partial decomposition, probably thermal, of the compound $(C_2H_5)_2PbCl_2$ occurred sometimes, during electrophoresis in concentrated LiCl solutions.

The best separation of the components in $PbCl_2$ + $(C_2H_5)_2PbCl_2$ + $(C_2H_5)_3PbCl$ mixtures was obtained using LiCl concentrations between 2 and 3 M. (see Table I).

DISCUSSION

The results obtained and reported in Table I show that paper electrophoresis may be used to study electrolytic solutions of organo-lead chlorides. The displacement observed is in fact very clear and reproducible.

From the data given in Table I, it is possible to deduce the formation of reversible complexes between Cl^- and organo-lead cations. The mean number of ligands, determining the charge of the complex, seems to be a function of the concentration of the supporting electrolyte which supplies the ligand. Similar results were obtained for Pb^{2+} (see Table I), which forms the well-known reversible chloride complexes $PbCl_n^{2-n}$.

The isoelectric points for $(C_2H_5)_2PbCl_2$, $(C_2H_5)_3PbCl$ and $PbCl_2$ are at LiCl $\simeq$

TABLE I

PAPER ELECTROPHORESIS OF $(C_2H_5)_2PbCl_2$, $(C_2H_5)_3PbCl$ AND $PbCl_2$

Supporting electrolyte: aqueous LiCl. Applied potential: 135 V for 2 h. The distances travelled are corrected for electro-osmotic flow.

Molarity of LiCl	Distances travelled in mm*		
	Et_2PbCl_2	Et_3PbCl	$PbCl_2$
3.24	—22	— 9	—34
2.14	—24	— 9	—30
1.47	—20	— 5	—20
1.00	—20	— 4	— 8
0.94	—16	— 3	— 5
0.825	—16	— 1	— 1.5
0.75	—11	0	+ 2
0.69	— 9	0	+ 4
0.54	— 9	+ 3	+ 8
0.45	— 8	+ 3	+ 9**
0.38	0	+ 7	+16**
0.276	+ 4**	+ 8	+22**
0.14	+15**	+16	+22**

* + indicates movement towards the cathode, — towards the anode.
** Tail produced by adsorption on cellulose.

0.4 M; LiCl $\simeq$ 0.75 M; LiCl $\simeq$ 0.8 M, respectively. If the isoelectric point corresponds to the presence of an electrically neutral complex, it follows that the complexes $PbCl_n^{2-n}$ (with the average number of ligands $\bar{n} = 2$), $(C_2H_5)_3PbCl_n^{1-n}$ (with $\bar{n} = 1$) and $(C_2H_5)_2PbCl_n^{2-n}$ (with $\bar{n} = 2$) are present at the LiCl concentrations corresponding to the isoelectric point.

In LiCl solutions with a lower concentration than that corresponding to the isoelectric point, cationic complexes or the respective cations (migrating towards the negative pole, cf. Table I) would exist, while in more concentrated LiCl solutions, there are anionic complexes (migrating to the positive pole, cf. Table I).

These deductions are in accordance with the data reported in ref. 2 for the distribution between aqueous LiCl and an anion exchange resin, corrected according to MARCUS AND CORYELL[5] for the "invasion" of the resin by the electrolyte supplying the ligand.

It is worth while pointing out that the agreement between the electrophoresis data and corrected anion exchange data pertaining to each organo-lead cation, is better for some corrected distribution curves than for others, which in theory are equally probable.

From the investigations reported in ref. 2, two deductions can be made.

(a) In the case of $(C_2H_5)_3PbCl_n^{1-n}$, the neutral complex $(C_2H_5)_3PbCl$ is preponderantly present (that is, $\bar{n} = 1$) in about 2.7 M LiCl. This holds only if we assume $n = 2$ for the complex which exchanges with the resin sites, applying a correction for experimental distribution according to MARCUS AND CORYELL. On the other hand, if we assume $n = 3$ in the correction, then $\bar{n} = 1$ for ca. 1 M LiCl. Values of 2 and 3 for n are both probable on the basis of the usual coordination numbers of lead, and according to anion exchange data neither can be preferred.

(b) In the case of $(C_2H_5)_2PbCl_n^{2-n}$, assuming $n = 3$ for the complex which exchanges with the resin sites, $\bar{n}$ becomes 2 for LiCl $\simeq$ 1 M; if, however, a value of 4

for n is assumed, $\bar{n}$ becomes 2 for LiCl $\simeq$ 0.65 M. The choice of the actual value of n between these two probable values cannot be made by anion exchange data.

By comparing these results with the isoelectric points obtained from electrophoresis, it can be concluded that the corrected anion exchange distribution curves that are in better accordance with the electrophoretic findings, are those obtained by assuming $(C_2H_5)_2PbCl_4^{2-}$ and $(C_2H_5)_3PbCl_3^{2-}$ as the complexes exchanging with the resin sites (see ref. 2). Following the MARCUS AND CORYELL theory for anion exchange distributions, these assumptions lead to the conclusion that the complexes that are fully coordinated are $(C_2H_5)_2PbCl_4^{2-}$ and $(C_2H_5)_3PbCl_3^{2-}$ (see ref. 2).

From these considerations it seems possible that paper electrophoresis will provide qualitative evidence of the formation of organo-lead chloride complexes. This evidence together with corrected anion exchange measurements, should lead to the actual determination of the fully coordinated complexes. Paper electrophoresis is thus useful also in determining the complexes exchanging with the resin sites.

It must be remembered that it is often impossible to obtain the data regarding these complexes necessary for the application of the MARCUS AND CORYELL theory.

In the case of $PbCl_n^{2-n}$, it was not possible to obtain any information about the type of fully coordinated complex by comparing distribution data between resin and solution[6] with the electrophoretic experiments reported above. In fact, if this last complex is either $PbCl_5^{3-}$ or $PbCl_4^{2-}$, corrected anion exchange data show that the respective isoelectric points are at LiCl $\simeq$ 0.7 M and LiCl $\simeq$ 0.95 M, while the isoelectric point obtained by the electrophoretic method is at LiCl $\simeq$ 0.8 M.

A further conclusion is that the electrophoretic method is also useful for the analytical separation of mixtures containing $(C_2H_5)_2PbCl_2$, $(C_2H_5)_3PbCl$ and $PbCl_2$.

SUMMARY

The compounds $(C_2H_5)_2PbCl_2$, $(C_2H_5)_3PbCl$ and $PbCl_2$ were studied by paper electrophoresis in aqueous LiCl solutions of various molarities. Determination was made of the formation of chloride complexes in which the electric charge was a function of ligand concentration in the solution. From the results of these experiments, and from a comparative examination of anion exchange data obtained in previous researches, useful information is obtained for determining the ligand concentrations relative to the preponderance of cationic, neutral and anionic complexes in the aqueous solutions. From this information it is possible to assume $(C_2H_5)_2PbCl_4^{2-}$ and $(C_2H_5)_3PbCl_3^{2-}$ as the fully coordinated complexes in aqueous solutions of LiCl. The electrophoretic method is also useful for separating the components of mixtures of $(C_2H_5)_2PbCl_2$, $(C_2H_5)_3PbCl$ and $PbCl_2$.

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