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COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XLI. ANION-EXCHANGE PAPER CHROMATOGRAPHY OF ORGANO-THALLIUM(III) CYANIDES

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SUMMARY

The chromatography of $\text{Me}_2\text{Tl}^{\text{III}}$, $\text{Ph}_2\text{Tl}^{\text{III}}$, PhTl^{III} and iodide on anion-exchange papers and potassium cyanide-containing eluents has been carried out. The results for the organothallium moieties are discussed in terms of the formation of cyanide complexes in solution.

INTRODUCTION

Anion-exchange paper chromatography has been widely employed to investigate the formation of reversible complexes in solution¹⁻⁸. This technique, in conjunction with paper electrophoresis, allowed, *inter alia*, the detection of complex species formed by the organothallium moieties $\text{R}_2\text{Tl}^{\text{III}}$ ($\text{R} = \text{Me}, \text{Ph}$) and PhTl^{III} in presence of thiocyanate ligand⁷. Findings concerning the ranges of ligand concentration where cationic, neutral and anionic $\text{Ph}_2\text{Tl}(\text{CNS})_n^{1-n}$ and $\text{PhTl}(\text{CNS})_n^{2-n}$ species predominate were successively confirmed by equilibration studies employing anion-exchange resins⁹.

In this work we have investigated the chromatographic behaviour of organothallium(III) moieties on exchange papers with cyanide-containing eluents, and the results are interpreted in terms of the formation of organothallium cyanide complexes.

EXPERIMENTAL

The compounds R_2TlNO_3 ($\text{R} = \text{Me}, \text{Ph}$) were prepared as described elsewhere^{10,11}. Solutions of $\text{PhTl}(\text{NO}_3)_2$ were obtained from PhTlCl_2 (ref. 12) and silver nitrate. All chemicals were analytical-grade reagents.

The following commercial anion-exchange papers were employed: SB-2 paper

(Rohm & Haas, Philadelphia, Pa., U.S.A.) impregnated with Amberlite IRA-400, a quaternary ammonium resin; AE-30 (Whatman, Maidstone, Great Britain), aminoethylcellulose paper; and DE-20 (Whatman), diethylaminoethylcellulose paper. The papers, which were originally in the Cl^- form, were converted into the cyanide form by percolating 2 *M* potassium cyanide solution through them, and then washed with distilled water and air dried at room temperature.

Ascending chromatographic development¹⁻⁸ of the organothallium derivatives was carried out on paper strips (17 × 1.7 cm) in closed glass tubes with eluents consisting of solutions of potassium cyanide (at known concentrations in the range 0.01–1 *M*) in methanol–water (1:1). About 50–150 μg of organothallium nitrates, from solutions having the same composition of the eluents, were chromatographed. After development, the $\text{R}_2\text{Tl}^{\text{III}}$ compounds were located by spraying the papers with aqueous potassium rhodizonate; in the case of PhTl^{III} , the strips were exposed to bromine vapour, warmed to eliminate the excess of bromine, and then sprayed with aqueous sodium sulphide.

In order to evaluate the retention due to the cellulose network of the anion-exchange papers, the compounds were also chromatographed on Whatman No. 1 (pure cellulose) paper, employing the same eluent solutions. Further, we followed the chromatographic behaviour of iodide anions on the DE-20 paper (in the CN^- form), eluted under the same conditions as the organothallium derivatives; this was accomplished placing potassium iodide on the paper strips and spraying with aqueous lead nitrate as detection reagent.

RESULTS AND DISCUSSION

Fig. 1 shows the R_F values measured for the different systems as a function of the potassium cyanide concentration in the eluent.

Water–methanol was employed because when pure aqueous eluents were used organothallium derivatives showed appreciable retention (and tailed spots) on cellulose; possibly this can be partially ascribed to hydrolysis which, in the aqueous medium, is not sufficiently repressed by the formation of cyanide complexes. This disadvantage is reduced to a limited extent with the water–methanol eluent employed as it appears from the R_F values close to unity on the Whatman No. 1 paper.

The weak retention displayed by $\text{Me}_2\text{Tl}^{\text{III}}$ apparently does not depend on factors such as the specific exchange capacity or the basicity of the exchanger group of the chromatographic papers, and is ascribed to a low tendency of $\text{Me}_2\text{Tl}^{\text{III}}$ to form $\text{Me}_2\text{Tl}(\text{CN})_n^{3-n}$ complexes. The chromatographic behaviour is similar to that displayed by dimethylthallium with thiocyanate-containing eluents⁷ and it can be related to the consistent ionic character observed for many dimethylthallium compounds, as well as for Me_2TlCN itself¹³. Nevertheless, electrophoresis experiments showed that $\text{Me}_2\text{Tl}^{\text{III}}$ may form anionic thiocyanate species at suitable ligand concentrations⁷, and we do not exclude the possible formation of cyanide complexes, at least into the exchanger phase, as being responsible, for instance, for the retention observed on the AE-30 paper.

The R_F values for the $\text{Ph}_2\text{Tl}^{\text{III}}$ and PhTl^{III} systems are compatible with formation of complex cyanide species in both the exchanger and the solution phases. The high adsorption on the SB-2 paper may be partially due to the greater exchange capac-

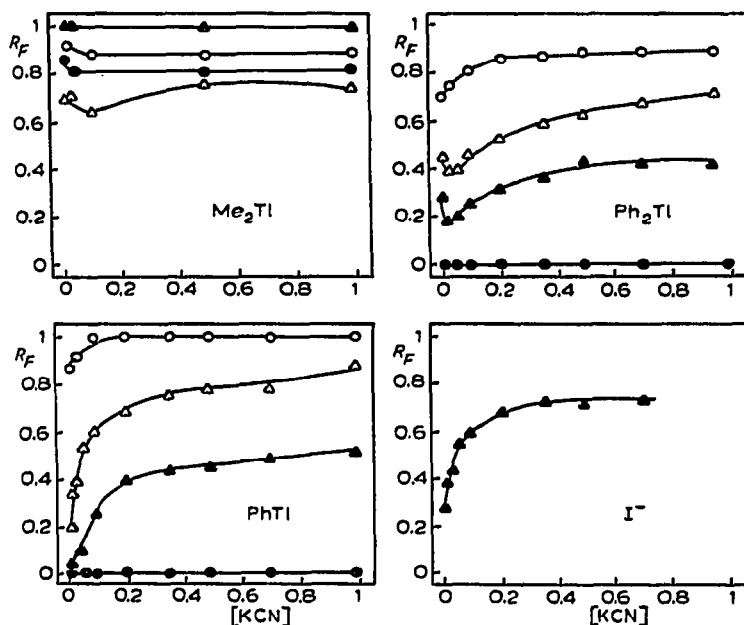


Fig. 1. R_F values of chromatographed compounds on various papers plotted against the concentration of potassium cyanide. \circ , W-1; Δ , AE-30; \blacktriangle , DE-20; \bullet , SB-2.

ity of this paper, but it is likely that the main contribution derives from non-specific interactions between the organic residues linked to thallium and the resinous matrix of the exchanger.

The R_F data on AE-30 and DE-20 papers provide useful information for planning further anion-exchange research on such systems employing cellulosic anion exchangers, simply by taking into account the relationship between R_F and D , the distribution coefficient based on a unit volume of exchanger bed:

$$D = \left(\frac{1}{R_F} - 1 \right) A_L/A_S \quad (1)$$

where A_L and A_S are the cross-sectional amounts of mobile and stationary phases, respectively¹⁴. In this respect, a DE-type exchanger should give values of D in the best range to be measured through standard column or equilibration techniques.

However, preliminary information about the coordination number of the species in solution may be derived by applying the anion-exchange theory¹⁵ to the D values calculated from eqn. 1 for the DE-20 exchanger. From eqn. 1, defining $R_M = \log(1/R_F - 1)$, one obtains:

$$\frac{dR_M}{d(\log \text{ activity of } CN^-)} = \bar{i} \quad (2)$$

i.e., the average charge of complexes in solution, on the assumption that the ratio A_L/A_S is independent of the cyanide activity.

In Fig. 2, R_M values are plotted against $\log[\text{KCN}]$ for the $\text{Ph}_2\text{Tl-DE}$ and PhTI-DE systems. Obviously, these curves are affected by the inherent approximations concerning the use of concentrations instead of activities and the fact that in the treatment the "invasion" of the exchanger phase by the supporting electrolyte has not been considered¹⁵. In principle, it should be possible to take these effects into account by using appropriate activity coefficients and calculating the "invasion" correction function from the data for iodide on the same DE exchanger paper. For such a uninegative ion, the theory¹⁵ predicts a distribution curve behaving as a straight line with a slope of -1 , whereas the experimental R_M vs. $\log [\text{KCN}]$ curve (Fig. 2) shows first a linear region (with slope > -1), and then the tendency to curve upwards, in a manner typically ascribable to the occurrence of "invasion".

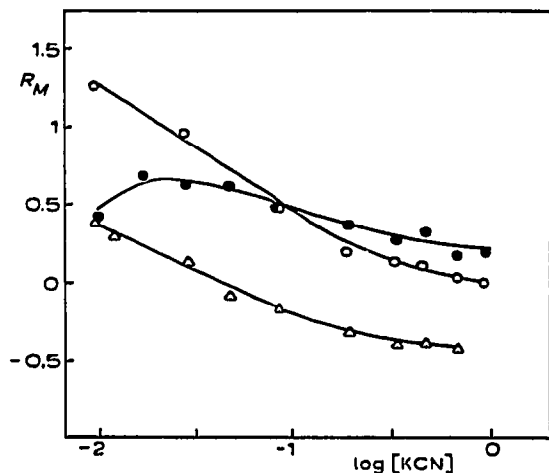


Fig. 2. R_M vs. $\log[\text{KCN}]$ for PhTI^{III} (○), $\text{Ph}_2\text{Tl}^{\text{III}}$ (●) and I^- (△) on DE-20 paper.

Although distortions of the same type will affect the R_M curves for $\text{Ph}_2\text{Tl}^{\text{III}}$ and PhTI^{III} , it may be noticed that these differ appreciably in the region of low CN^- concentrations. From eqn. 2, one can infer that the negative slope of the PhTI^{III} curve indicates the predominance of negatively charged species even in this ligand concentration range, where $\text{Ph}_2\text{Tl}^{\text{III}}$ shows the presence of cationic (Ph_2Tl^+) or neutral (Ph_2TlCN) species. These results are in agreement with the observed higher acceptor ability of PhTI^{III} with respect to $\text{Ph}_2\text{Tl}^{\text{III}}$ ^{17,9,16}, and with the existence of $\text{PhTI}(\text{CN})_3^-$ in the solid state¹⁷. At high ligand concentrations, PhTI^{III} displays a slope more negative than that for $\text{Ph}_2\text{Tl}^{\text{III}}$ (and that for I^-), which probably indicates $\text{PhTI}(\text{CN})_4^{2-}$ and $\text{Ph}_2\text{Tl}(\text{CN})_2^-$ as the coordinately saturated complexes. The latter would correspond to the organothallium thiocyanate species detected in aqueous solution⁹.

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