Extraction of Ruthenium(III) by Tri-n-octyl-phosphine from Hydrochloric Acid Solutions

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It is shown for the first time that tertiary phosphines like tri-n-octylphosphine can be used for investigating liquid anion exchange behaviour of halometal complexes such as RuCl₃. The relevant chemical parameters of such studies are also discussed.

THE extraction of ruthenium in different oxidation states by long chain amines from acid solutions has been studied earlier. Moore¹ reported that ruthenium(IV) could be efficiently extracted from hydrochloric acid solutions by triisooctylamine in xylene. Shanker et al.² have investigated in detail the extraction of Ru(III) by primary, secondary and tertiary amines from sulphuric acid solutions. Saraiya et al.³ have studied the antagonistic effects of n-octanol, cyclohexanol and chloroform on the reverse phase partition and extraction of Ru(III) from hydrochloric acid solutions.

Venkateswarlu and Kishore⁴ have reported the extraction of mineral acids by tri-n-octylphosphine (TOP). Similar to the behaviour of tri-n-alkyl amines, one would expect TOP to combine with the proton of the acid, or H₃O⁺, to form a phosphonium cation, RaPH⁺. Such a cation in the organic phase would necessarily be balanced by the presence of an anion like perchlorate. Thus, in principle the extraction of acids from aqueous solutions by TOP should follow the familiar pattern of amine extraction.

Since no work has been reported on the extraction properties of TOP, specially with halometal acids like RuCl₃, it was thought worthwhile to study the extraction of Ru(III) from hydrochloric acid solutions by TOP.

Materials and Methods

Tri-n-octylphosphine (TOP, Aldrich Chemical Co) was used as such. All the acids and diluents used were either of AR or GR grade.

Ruthenium chloride (E. Merck extra pure) contained ruthenium principally in trivalent and to a small extent in other oxidation states. It was, therefore, essential to chemically treat the sample so that one was dealing with Ru(III) alone. Repeated evaporation (four times) of the sample with conc. hydrochloric acid to near dryness and dissolution in conc hydrochloric acid gave all the ruthenium in trivalent form as an anionic chloro complex. During the process of evaporation the solution was labelled with ¹⁰³Ru as a tracer. Such a sample of ruthenium was stored at low temperature (~5°C) in conc. HCl under N₂ atmosphere.

In all solvent extraction experiments, the extracting agent in a suitable diluent, pre-equilibrated with the aqueous phase of appropriate acidity, served as the organic phase. Solvent extraction was carried out by batch equilibration for at least 20 min in a mechanical shaker. The two phases were separated and centrifuged. Equal volumes of both the phases were pipetted out into glass vials and ¹⁰³Ru in each aliquot determined on a NaI(Tl) scintillation counting assembly. The extraction coefficient (E) was determined from these data.

Results and Discussion

Effect of diluents on the extraction — When an anion like RuCl₃ is extracted into the organic phase containing either a protonated trialkylammonium or protonated trialkylphosphonium or a tetraalkylammonium cation, the species in the organic phase can exist either in the form of an ion-pair or as dissociated ions. To determine the class to which the extracted species belongs, the effect of different diluents was studied. In this set of experiments the diluents were so chosen as to give a wide variation both in their dielectric constants and their chemical nature. Three groups of diluents were selected for this purpose, viz. (i) aromatics such as benzene, toluene, xylene and nitrobenzene, (ii) cyclic compounds such as cyclohexane and cyclohexanol and (iii) chlorocarbons like chloroform, carbon tetrachloride and tetrachloroethylene.

It was expected that compounds like cyclohexane and carbon tetrachloride would merely provide a medium for extraction without in anyway influencing the extraction process and would thus serve as reference diluents. However, these could only be used if a higher percentage of the extractant was used.

10 ml portions of 1×10⁻⁴M ruthenium chloro complex solution in 3M HCl were equilibrated for 45 min with an equal volume of extractants in
Different diluents. The extraction data are presented in Table 1.

It is apparent from Table 1 that the aromatic diluents as a rule favour extraction, even though there is a wide variation of the dielectric constant within this group i.e. the dielectric constant of nitrobenzene is much greater than that of benzene. This behaviour could be explained on the following basis.

In their studies on the extraction of RuCl₄ by chloroform, Venkateswarlu and Kishore⁴ have shown that while HClO₄ was present as an ion pair in TOP-benzene phase, it was present as dissociated ions in TOP-nitrobenzene phase because of the high dielectric constant of the latter diluent. If we assume that a similar situation exists in the extraction of RuCl₄ also, one can expect the formation of ion pairs in the benzene phase (R₃PH⁺ . . . . RuCl₄⁻). In nitrobenzene phase, it then will exist as dissociated ions (R₃PH)⁺ and (RuCl₄)⁻. As the aqueous phase contains 3M hydrochloric acid, chloride ions will compete in the extraction process and this will be easy if dissociated ions are present in the organic phase. Thus the combined effect of dissociation in the organic phase and competition from chloride ions will lead to a somewhat lower percentage in extractions with nitrobenzene as compared to benzene.

There is not much difference in the dielectric constants of benzene, toluene and xylene and the differences in percentage extraction noticed with these diluents in Table 1 can be ascribed to their chemical nature. The π-electron character of the aromatic ring which leads to stabilization of cations like R₃NH⁺ or R₃PH⁺ will decrease due to the presence of alkyl substituents on the benzene ring. This will result in a lowering of extraction of RuCl₄.

Considering the data on the two non aromatic cyclic compounds, the higher dielectric constant of cyclohexanol relative to cyclohexane does not favour extraction. It has been shown in an earlier paper by Saraiya et al.⁴ that cyclohexanol has marked antagonistic effect due to its interaction with different extractants like tertiary amines, quaternary ammonium halides, etc., in addition to phosphines and phosphine oxides. Among the chlorocarbons even though the dielectric constants of carbon tetrachloride and tetrachloroethylene are fairly close to each other, there is a marked difference in their extraction characteristics. One would be tempted to associate the higher extraction of RuCl₄ with π-electron availability in tetrachloroethylene. The behaviour of chloroform is understandable, in view of its slightly acidic hydrogen and a higher dielectric constant as compared to the other two. Possible coordination or solvation of the anion, RuCl₄⁻ by chloroform, besides its higher dielectric constant may be responsible for the differences noticed between chloroform and carbon tetrachloride. Such a situation was noticed in the amine extraction of RuCl₄ also⁵.

It is clear from the above that the selection of diluent is an important criterion which has to be judged by considering all the different parameters involved. One would like to study the extraction behaviour with minimum interference from the diluents. Probably carbon tetrachloride is ideal for this. However, in this particular case, the amount of TOP available on hand imposed a limitation. It was found difficult to employ 2.5% (wt/v) solutions of TOP in carbon tetrachloride. As a compromise the least interfering aromatic compound, namely xylene was chosen as the diluent. One could then employ 0.4% (wt/v) solutions, so that a larger amount of data could be collected with the limited supply of TOP. In all subsequent experiments xylene was employed as the diluent.

### Table 1 — Extraction of Ru(III) Chloro Complex by Tri-n-octylphosphine (TOP) from 3M Hydrochloric Acid

<table>
<thead>
<tr>
<th>Diluent</th>
<th>Dielectric constant</th>
<th>Extraction (%) using TOP* (wt/vol.)</th>
<th>0.4%</th>
<th>2.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.28</td>
<td>88.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.43</td>
<td>76.6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Xylene</td>
<td>2.37</td>
<td>44.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>3.74</td>
<td>70.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.02</td>
<td>—</td>
<td>83.5</td>
<td>—</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>15.00</td>
<td>2.8</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.80</td>
<td>72.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.24</td>
<td>—</td>
<td>24.4</td>
<td>—</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>2.50</td>
<td>—</td>
<td>86.1</td>
<td>—</td>
</tr>
</tbody>
</table>

*TOP being a highly viscous liquid, it was difficult to have the concentration specified as v/v, hence it was taken as wt/vol.
Extraction dependence on TOP concentration—
In this set of experiments the conditions in the aqueous phase were kept constant by keeping ruthenium concentration at $1.5 \times 10^{-3}$ M in $3M$ HCl. The concentration of TOP in the organic phase was varied from $0.12$ to $1.20$ % (wt/v) in xylene. Pre-equilibration of the organic phase with aqueous HCl phase at $3M$ always constituted the first step in the experiment.

A plot of $\log E$ against $\log$ per cent TOP, shown in Fig. 2, gives a slope of 1.1. This indicates that at $3M$ HCl the major ruthenium species extracted has a single negative charge, that is, the species is $\text{RuCl}_4^-$.

It is clear from the observations reported by the authors earlier, as well as from the similarity expected between the extraction properties of tri-$n$-alkylphosphine and tri-$n$-alkylamines, that the equilibria (1-5) may be written for the extraction process.

\[
\begin{align*}
\text{RuCl}_4(aq) + \text{HCl}(aq) & \rightleftharpoons \text{HRuCl}_4(aq) \quad \ldots(1) \\
\text{HRuCl}_4(aq) + \text{HCl}(aq) & \rightleftharpoons \text{H}_2\text{RuCl}_6(aq) \quad \ldots(2) \\
\left[\text{C}_8\text{H}_{18} \text{P} \right]_{\text{org}} + \text{HCl}(aq) & \rightleftharpoons \left[\text{C}_8\text{H}_{18} \text{P} + \text{Cl}^- \right]_{\text{org}} \quad \ldots(3) \\
\left[\text{C}_8\text{H}_{18} \text{P} + \text{H}^+ \text{Cl}^- \right]_{\text{org}} + \text{HCl}(aq) & \rightleftharpoons \left[\text{C}_8\text{H}_{18} \text{P} + \text{Cl}^- \right]_{\text{org}} + \text{HCl}(aq) \quad \ldots(4) \\
2\left[\text{C}_8\text{H}_{18} \text{P} + \text{Cl}^- \right]_{\text{org}} + \text{H}_2\text{RuCl}_6(aq) & \rightleftharpoons \left[\text{C}_8\text{H}_{18} \text{P} + \text{RuCl}_4^-. \right]_{\text{org}} + 2\text{HCl}(aq) \quad \ldots(5)
\end{align*}
\]

The equilibrium (4) is the dominating one at lower molarity of HCl. The solvent dependency of 1.1 supports this and indicates that a small fraction of the extraction is due to equilibrium (5).

In conclusion, this study has shown that tertiary phosphines can also be used for investigating liquid anion exchange behaviour of halometal complexes.

References