

Recent investigations into the reactions of platinum metal compounds with formic acid have led to the discovery of a new and convenient method of preparing carbonyl halide complexes of osmium, ruthenium and iridium by refluxing the metal halide or halo-complex with 90 per cent formic acid (6). The compounds formed were initially recognised as carbonyl rather than formate complexes by infra-red spectroscopy in the 2000 cm^{-1} region.

The complexes that have so far been prepared and the reaction conditions are set out in the table opposite; all the compounds have been characterised by elemental analysis and their full infra-red spectra have been determined and recorded.

To isolate salts of the anionic species it was found necessary to use caesium as the cation since lighter atomic weight alkali metals yielded salts of very high solubility.

The reaction between sodium hexachlorosmate (IV) (used because of the low solubility of other $[\text{OsCl}_6]^{2-}$ salts) and formic acid is of particular interest since it takes place much more slowly than those between ruthenium and iridium compounds and formic acid. This has made it possible to identify by infra-red spectroscopy intermediate formato-halo species containing one and two monodentate formate groups. These species probably contain formally divalent osmium, that is $[\text{Os}^{\text{II}}(\text{COOH})\text{Cl}_5]^{4-}$ and $[\text{Os}^{\text{II}}(\text{COOH})_2\text{Cl}_4]^{4-}$,

and they further react to give the mono- and dicarbonyl species respectively. The reaction proceeds quickly to the diformate stage and the monocarbonyl complex is formed in small quantities only.

Triphenylphosphine derivatives are easily prepared by warming the complexes with triphenylphosphine in formic acid solution or, more conveniently, by treating the solutions prior to isolation of a carbonyl halide salt with triphenylphosphine. The complexes $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2\text{X}_2]$ and $[\text{Os}(\text{CO})_3(\text{PPh}_3)\text{X}_2]$ have been prepared from $\text{Cs}_2[\text{Os}(\text{CO})_2\text{X}_4]$ and $\text{Cs}[\text{Os}(\text{CO})_3\text{X}_3]$ respectively, while $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\text{X}_2]$ and $[\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2]$ have been prepared from $\text{Cs}_2[\text{Ru}(\text{CO})_2\text{X}_4]$ and $\text{Cs}_2[\text{Ru}(\text{CO})(\text{H}_2\text{O})\text{Cl}_4]$ respectively ($\text{X} = \text{Cl}, \text{Br}$).

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Performance of Platinised Titanium Anodes

The use of platinised titanium as a counter electrode in cathodic protection is well established, even though a detailed mechanism for the excellent performance of these anodes is not fully documented. A recent investigation of this subject by P. Van Laer and J. Van Muylder of CEBELCOR, presented as a paper to the CITCE colloquium on Corrosion and Electrochemical Thermodynamics held in Istanbul in September, is of some considerable help in this direction.

Anodic polarisation studies in synthetic sea-water, using current densities in the range 0 to 600 mA/cm^2 , showed that if corrosion of

the titanium is to be avoided the anodic potential must not exceed +7.0 V_{SCE} . Further, the authors state that at potentials above +2.1 V_{SCE} modification of the platinum surface occurs, and studies in the range +1.3 to 1.4 V_{SCE} suggest that oxidation of platinic oxide PtO_2 to perplatinic oxide PtO_3 may take place.

It was concluded that the long life of platinised titanium anodes in sea-water is due to the titanium surface being protected from high current densities by the platinised areas, thus ensuring that the potential does not exceed the threshold of danger. J. H.