The Existence of Carbonyl Fluorides of the Platinum Metals

By R. D. W. KEMMITT, R. D. PEACOCK,* and I. L. WILSON
(*Department of Chemistry, The University, Leicester*, LE1 7RH)

A NUMBER of years ago one of us investigated the action of carbon monoxide on ruthenium pentafluoride, and concluded that an amorphous, reactive form of ruthenium trifluoride was the probable product,[1] though it was not possible at that date to undertake physical studies. In 1963 this reaction was again examined very briefly, and it was shown that the product gave i.r. absorption frequencies characteristic of combined carbonyl groups.[2]

We now find that ruthenium pentafluoride reacts with carbon monoxide in a flow system at 200° to give a yellow-brown, moisture-sensitive, nonvolatile solid of composition $Ru(CO)F_{3 \cdot 5}$. The solid shows two i.r. absorption frequencies at 2196 and 2117 cm.$^{-1}$ in the region associated with carbonyl stretching modes. Other bands occur at 722m,sh, 655 broad s, and 555s cm.$^{-1}$. The strong frequency at 655 cm.$^{-1}$ is close to that observed in salts of the RuF_6^- ion.[3] The solid has a μ_{eff} at 25° of 3·0 B.M. per ruthenium atom. With water a vigorous reaction occurs with gas evolution, and the precipitation of part of the ruthenium as dioxide; a little of the ruthenium also appears as volatile RuO_4. The solid dissolves in hydrochloric acid to give a red solution from which the polymeric $[Ru(CO)_2Cl_2]_n$ was isolated. No inert solvent for the material has yet been found.

From these observations we conclude that the solid is probably a single phase, and that a possible formulation is $\{[Ru(CO)_2F]^+[RuF_6]^-\}_n$ or some related structure involving fluorine bridging. If it is assumed that a cation of low or zero paramagnetism is present, the magnetic moment of the ruthenium anion is about 4·1 B.M., a value close to those of RuF_5[4] and of RuF_6^-.[5] The evolution of RuO_4 from Ru(V) compounds has frequently been noted.[4,6]

Related carbonyl compounds of osmium and iridium also appear to exist.

During this work we have re-investigated the reaction of platinum tetrafluoride made by the bromine trifluoride method,[7] with carbon monoxide both in a flow system and under static pressure. The adduct $PtF_4,2BrF_3$ gives high yields of the volatile *cis*-$Pt(CO)_2Br_2$ (ν_{CO} 2178 and 2132 cm.$^{-1}$), and even when great care is taken to remove as much of the BrF_3 as possible at 200° under a high vacuum this compound is still formed, though in small yields, by reaction of the residue with carbon monoxide. Further treatment of the residue with fluorine at 200° does not remove the last traces of bromine. The material earlier reported to be $Pt(CO)_2F_8$[8] has properties identical to those of *cis*-$Pt(CO)_2Br_2$,† and it is concluded that the existence of carbonyl fluorides of platinum remains an open question. We find that the reaction of the adduct $PtF_4,2BrF_3$, or of the impure PtF_4 formed from it, with PF_3 leads to the analogous $Pt(PF_3)_2Br_2$.

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† The presence of bromine seriously interferes with certain analytical methods for fluorine determination. An authentic sample of $Pt(CO)_2Br_2$, reported to an analyst as containing Pt, CO, and F, gave a spurious fluorine result near that required for $Pt(CO)_2F_8$.

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