New Reactions of Precious Metals and their Binary Compounds in Solvents containing Carbon Halides

Neale R. C. Jackson, W. David Harrison, and David C. Goodall*

Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

Several precious metals and their binary compounds react with CCl_4, CBr_4, CPh_2Cl_2, $CPhCl_3$, or $C(CN)_2Cl_2$ in dimethyl sulphoxide, dimethylformamide, or dimethylacetamide, and with carbon halides in ethanol or acetaldehyde containing added ligand.

Precious metals are well known for their general resistance to attack by solvents. We report several new reactions which precious metals and their binary compounds undergo with the solvents dimethyl sulphoxide (dmso), dimethylformamide (dmf), and dimethylacetamide (dma) containing dissolved CCl_4, CBr_4, CPh_2Cl_2, $CPhCl_3$, or $C(CN)_2Cl_2$. Parker[1] has described how redox reactions involving copper(II) or iron (III) allow the ready dissolution of silver and gold in dmso or dmf.

We find that addition of CCl_4 speeds up the reaction of Ag or Ag_2O with oxidants Cu^{II}, Fe^{III}, Ru^{III}, Rh^{III}, and Ir^{IV} in dmso or dmf in the presence of added halide. The oxidant is continuously regenerated under such conditions, even in the absence of added halide, with consumption of CCl_4, according to Scheme 1. In the case of Ag_2O, oxygen is evolved.

Solutions of CCl_4 in a range of solvents oxidise Cu^{I} to Cu^{II} (see ref. 2) and also oxidise many base metals.[3] At slightly elevated temperatures, we have found that solutions containing carbon halides react directly with several precious metals and their compounds. Ag reacts readily with CCl_4 or CBr_4 in dmso at 80 °C to form AgX_2^- (X = Cl, Br), but Au reacts only with CBr_4 in dmso, forming $AuBr_4^-$. Pd reacts slowly with CCl_4 in dmso, forming $PdCl_2 \cdot 2dmso$, and with CBr_4 in dmf, forming $PdBr_2 \cdot 2dmf$. The carbon halide solutions do not react with Ru, Rh, or Pt. PdO and PtO_2 react slowly with CBr_4 in dmf at 100 °C, forming $PdBr_2 \cdot 2dmf$ and $PtBr_4 \cdot 2dmf$, respectively. Ag_2O, Ag_2S, Ag_2Se, and Ag_2Te react with CBr_4 in dmf, forming $AgBr_2^-$. Au_2O_3 also reacts with CBr_4 in dmf, to form $AuBr_4^-$. No reaction was observed between CCl_4 in dmf and Ru, Rh, Rh_2O_3, Rh_2S_3, Ir_2S_3, PdO, PdS, PtO_2, PtS_2, Ag_2S, Ag_2Se, or Ag_2Te, or between CBr_4 in dmf and Rh_2O_3, Rh_2S_3, Ir_2O_3, Ir_2S_3, PdS, or PtS_2.

$$Ag + M^x \xrightarrow[CCl_4]{dmso} AgX_2^- + M^y$$

Scheme 1. For Cu, x = II, y = I; for Fe, Ru, x = III, y = II; for Rh, x = III, y = I; for Ir, x = IV, y = III.

CPh_2Cl_2 in dma at 110 °C reacts with Rh, Pd, Pt, and Ag, forming $RhCl_3 \cdot 3dma$, $PdCl_2 \cdot 2dma$, $PtCl_2 \cdot 2dma$, and $AgCl_2^-$, respectively. This system also reacts with PdO and PtO_2, forming $PdCl_2 \cdot 2dma$ and $PtCl_4 \cdot 2dma$, but no reaction was observed with Ru, Rh_2O_3, or Ir_2O_3. CPh_2Cl_2 in dma at 60 °C reacts readily with Ag_2O, Ag_2S, and Au_2O_3. CPh_2Cl_2 in dmf reacts readily with Ag_2Se and Ag_2Te, forming $AgCl_2^-$, but no reaction was observed with Rh_2S_3, Ir_2S_3, PdS, or PtS_2. Pd dissolves in a solution of CPh_2Cl_2 in thiophene, forming $PdCl_2 \cdot 2(C_4H_4S)$, but no reaction occurs when a solution of CPh_2Cl_2 in tetrahydrofuran is used.

Ag_2O reacts very readily with $CPhCl_3$ in dma, but not with CPh_3Cl in dma. $C(CN)_2Cl_2$ in dmf at 100 °C reacts with Rh, PdO, Pt, and PtO_2, forming $RhCl_3 \cdot 3dmf$, $PdCl_2 \cdot 2dmf$, $PtCl_2 \cdot 2dmf$, and $PtCl_4 \cdot 2dmf$, respectively, but no reaction occurs with Ru, Rh_2O_3, or Ir_2O_3.

PdO, PtO_2, and Ag_2O dissolve in solvents such as EtOH or MeCHO containing CCl_4 and a ligand such as 1,10-phenanthroline (phen) or triphenylphosphine (tpp), forming complexes $PdCl_2 \cdot tpp$, $PtCl_2 \cdot 2tpp$, $AgCl \cdot tpp$, $PdCl_2 \cdot phen$, $PtCl_4 \cdot phen$, and $2AgCl \cdot phen$. No reaction was observed in the case of RuO_2, RuS_2, Rh_2O_3, Rh_2S_3, Ir_2O_3, Ir_2S_3, PdS, PtS_2, Ag_2S, or Ag_2Se.

Kleinberg[2] originally referred to the possible involvement of a carbene in the reaction of copper(I) with dmso–CCl_4, and Tezuka[4] recently supported this idea. We have isolated tetraphenylethylene from reactions of metals with dma–CPh_2Cl_2 and *trans*-dichlorostilbene from reactions of metals with dma–$CPhCl_3$, in the absence of oxygen. This indicates that reaction proceeds through a carbene intermediate. In the presence of oxygen or air, reaction products include CO and

CO_2, Ph_2CO, and PhCOCl from solvents containing CCl_4, CPh_2Cl_2, and $CPhCl_3$, respectively.

We are grateful to the S.E.R.C. for the award of a CASE studentship (to N. R. C. J.), and to the British Petroleum Company P.L.C. for their support as the Co-operating Body.

Received, 28th January 1988; Com. 8/00312B

References

1 A. J. Parker, Australian Patent PCT/AU81/00096.
2 R. R. Lavine, R. T. Iwamoto, and J. Kleinberg, *J. Am. Chem. Soc.*, 1966, **88**, 4304.
3 I. P. Lavrentev and M. L. Khidekel, *Inst. Khim. Fiz. Cherngalavka*, 1983, **52**, 337.
4 Y. Tezuka, M. Miya, A. Hashimoto, and K. Imai, *J. Chem. Soc., Chem. Commun.*, 1987, 1642.