*Inorganica Chimica Acta*, 54 (1981) L97–L98

# Slow Metal Transfer in Hydrolyses Promoted by Gold(III) Ions

G. PATEL, R. S. SATCHELL

*Department of Chemistry, Queen, Elizabeth College, Campden Hill Road, London W8 7AH, U.K.*

and (in part) D. P. N. SATCHELL

*Department of Chemistry, King's College, Strand, London WC2R 2LS, U.K.*

Received April 1, 1981

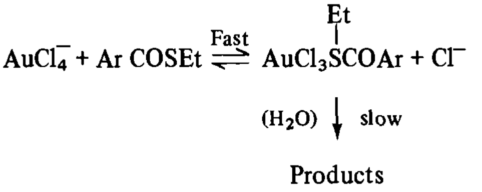
Very few heterolytic reactions promoted by metal ions have been found which involve slow metal transfer (the analogue of slow proton transfer in catalysis by hydrogen ions); almost all have been found to involve a rapid pre-equilibrium between the metal ion and substrate, followed by some slow step or steps [1]. We report now a probable example of slow metal transfer involving gold(III) ions.

In aqueous solution gold(III) ions (typically $AuCl_4^-$) promote the hydrolysis of various sulphur-containing compounds. In the known examples [2, 3] the substrate rapidly coordinates (*via* its S-atom) to the metal, displacing a chloride ion; the adduct formed then undergoes either a slow unimolecular decomposition followed by rapid attack of water (A1- scheme) or a slow reaction involving attack by water (A-2 scheme). We find now, however, that the promoted hydrolysis of thiol esters (*e.g.* eqn. 1) follows a different course.

$$ArCOSEt + AuCl_4^- + 2H_2O \rightarrow ArCO_2H + AuCl_3SEt^- + Cl^- + H_3O^+ \qquad (1)$$

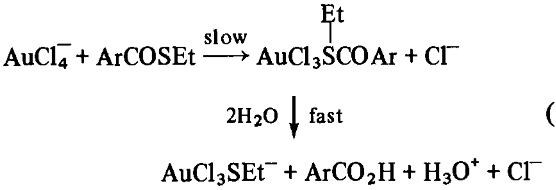
The hydrolysis can be monitored by observing the loss of ester by u.v. spectroscopy in the 260–290 nm region. Kinetic and spectroscopic studies, mostly at 25 °C, with *S*-ethyl-*p*-methoxy- and *S*-ethyl-*p*-nitrothiol benzoates (initial concentration *ca.* $10^{-4}$ *M*) using solutions containing known concentrations of added chloride and/or hydrogen ions at constant ionic strength, show (i) that the rates of the spontaneous and the hydrogen ion-catalysed hydrolyses are negligible compared with the gold-promoted rates, (ii) that, for the latter, using a 10-fold (or greater) excess of gold(III) ions (added as $NaAuCl_4$) the reaction is of the first order both in thiol ester and in gold(III) ions, (iii) that little (if any) adduct formation occurs between the thiol ester and gold(III) species, (iv) that at ambient chloride and hydrogen ion concentrations such that [4, 5] virtually all (>96%) of the added gold(III) ions exist in solution as $AuCl_4^-$, added chloride ions produce no common ion effect, (v) that the entropies of activation for the promoted hydrolysis of both esters have values ($\Delta S^{\ddagger} = -60$ to $-80$ J mol$^{-1}$ K$^{-1}$) characteristic of reactions involving a slow bimolecular step, (vi) that the *p*-methoxy ester is *ca.* 50-fold more reactive in the presence of $AuCl_4^-$ than is the *p*-nitro derivative, (vii) that the promoted rates in $D_2O$ are within ±3% of those in $H_2O$ and (viii) that an increase in ionic strength retards the reaction.

Mechanisms, such as eqn. (2), involving a pre-equilibrium square planar substitution, with concomitant displacement of a chloride ion from gold, appear unlikely owing (a) to



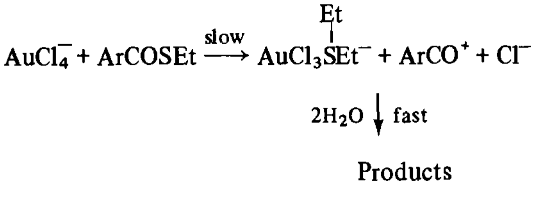
$$\begin{array}{c} AuCl_4^- + Ar\,COSEt \overset{Fast}{\rightleftharpoons} AuCl_3\overset{\overset{Et}{|}}{S}COAr + Cl^- \\ (H_2O)\downarrow \text{slow} \\ \text{Products} \end{array} \qquad (2)$$

the absence of a common ion effect by chloride and (b) to the bimolecular nature of the slow step, which the isotope effect suggests [6, 7] does not involve water as a nucleophile. The actual mechanism therefore probably involves a square planar substitution as, or as part of, the slow step. The mechanism of equation (3) is compatible with all the facts [8].



$$\begin{array}{c} AuCl_4^- + ArCOSEt \xrightarrow{slow} AuCl_3\overset{\overset{Et}{|}}{S}COAr + Cl^- \\ 2H_2O\downarrow \text{fast} \\ AuCl_3SEt^- + ArCO_2H + H_3O^+ + Cl^- \end{array} \qquad (3)$$

The relative reactivity of the *p*-methoxy and the *p*-nitro derivatives, the $\Delta S^{\ddagger}$ values and the ionic strength effect, all suggest [9] that little breakdown of the ester (*e.g.* eqn. (4) occurs during the square planar substitution.



$$\begin{array}{c} AuCl_4^- + ArCOSEt \xrightarrow{slow} AuCl_3\overset{\overset{Et}{|}}{S}Et^- + ArCO^+ + Cl^- \\ 2H_2O\downarrow \text{fast} \\ \text{Products} \end{array} \qquad (4)$$

## References

1 D. P. N. Satchell and R. S. Satchell, *Ann. Rep. Chem. Soc., A,* 25 (1978).

2 A. J. Hall and D. P. N. Satchell, *J. Chem. Soc. Perkin II,* 1351 (1975).

3 A. J. Hall and D. P. N. Satchell, *J. Chem. Soc. Perkin II,* 1278 (1976).

4 P. van Z. Bekker and W. Robb, *Inorg. Nucl. Chem. Lett., 8,* 849 (1972).

5 B. I. Peshchevitskii, V. I. Belevantsev and N. V. Kurbatova, *Russ. J. Inorg. Chem., 16,* 1007 (1971).

6 P. M. Laughton and B. E. Robertson, in 'Solute–Solvent Interactions', Ed. J. F. Coetzee and C. D. Ritchie, Marcel Decker, New York, 1969, Vol. 1, p. 400.

7 R. L. Schowen, *Prog. Phys. Org. Chem., 9,* 295 (1972).

8 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', J. Wiley, New York, 2nd Edition, 1967, Chap. 5.

9 D. P. N. Satchell and I. I. Secemski, *J. Chem. Soc. (B),* 1306 (1970).