Inorganica Chimica Acta, 64 (1982) L187

The Effect of Ligands on the Gold(III)–Promoted Hydrolysis of *S*-Amides

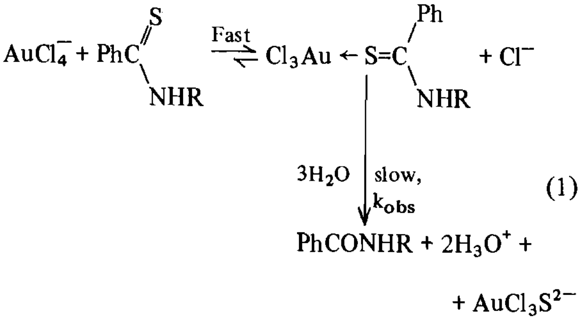
JACOB V. MICALLEF and DEREK P. N. SATCHELL

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

Received November 9, 1981

We recently reported on the kinetics and mechanisms of the hydrolyses of *N*-substituted *S*-benzamides [1] and of various *S*-esters [2, 3] promoted by the tetrachlorogold(III) ion. We present now the results of a study of the effects of a variety of other ligands attached to the gold atom on the rate of the promoted hydrolysis of *N*-cyclohexyl thiobenzamide, (I).

In aqueous solution an excess of tetrachlorogold(III) ions react [1] very rapidly and quantitatively with (I) to give a 1:1-adduct by displacement of chloride. There follows the process we observe kinetically: the hydrolytic decomposition of the adduct (eqn. 1). An important part of the process must be the formation of increased gold-sulphur bonding.



(1)

Mechanisms similar to that of eqn. (1) are found for each of the species $AuBr_4^-$, *trans*-$Au(CN)_2Br_2^-$, $Au(dien\text{-}H)Cl^+$, $Au(dien)Cl^{2+}$, and $[Au(NH_3)_4]^{3+}$, except that for $[Au(NH_3)_4]^{3+}$ an ammonia molecule is displaced in the pre-equilibrium. A comparison of the first-order rate constants (k_{obs}) observed with the different gold species provides therefore a direct indication of the effects of ligands on the rate of hydrolytic decomposition of the gold-*S*-amide adduct. At 25 °C we find the relative reactivity sequence:

$$\underset{1}{AuCl_3(S\text{-amide})} < \underset{13}{[Au(dien\text{-}H)(S\text{-amide})]^{2+}} < \underset{28}{[Au(NH_3)_3(S\text{-amide})]^{3+}} \gtrsim \underset{30}{AuBr_3(S\text{-amide})} < \underset{48}{[Au(dien)(S\text{-amide})]^{3+}} < \underset{\sim 600}{[Au(CN)_2Br(S\text{-amide})]}.$$

This sequence shows that (i) an increase in positive charge on the gold atom and (ii) an increase in the softness of attached ligands are both factors which favour the hydrolysis of the adduct. The softness effect appears to be the more important of these two factors.

The species $[Au(phen)Cl_2]^+$ also promotes the hydrolysis of (I) but here a different mechanism is involved. Little adduct formation is detectable, the overall reaction is kinetically of the first-order in the concentrations of both (I) and $[Au(phen)Cl_2]^+$, and, at constant ionic strength, k_{obs} is little affected by added chloride ions. These facts suggest the mechanism of eqn. (2). This involves a rate-determining substitution of Cl^- (rather than slow adduct decomposition) and is similar to that identified recently for certain Au(III)-promoted *S*-ester hydrolyses [2]. $[Au(phen)Cl_2]^+$ is a species known [4] to lead to relatively stable 5-coordinate structures,

$$\begin{aligned}&[Au(phen)Cl_2]^+ + S\text{-amide} \rightleftharpoons\\ &\quad [Au(phen)Cl_2(S\text{-amide})]^+ \xrightarrow{\text{slow}}\\ &\quad [Au(phen)Cl(S\text{-amide})]^{2+} + Cl^- \xrightarrow[3H_2O]{\text{fast}}\\ &\qquad O\text{-amide} + 2H_3O^+ + Cl^- + [Au(phen)ClS]\end{aligned} \qquad (2)$$

a fact in keeping with eqn. (2). The soft phenanthroline ligand will also, in the light of our findings with the other gold(III) derivatives, facilitate the hydrolysis step, a circumstance also in keeping with eqn. (2).

References

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