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Silver and Gold(I) Complexes with Thiomorpholin-3-one: Kinetics of Reduction of Gold(III)

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White, crystalline, diamagnetic complexes $[AuXT]$ *(where* $X=Cl$, *Br, and* $T=\underline{S\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CO\text{-}CH_2}$*) where obtained by reduction of* $[AuX_4]^-$ *with T. The kinetic study has been carried out by absorbance and pH measurements in 0.5* M *KX in 50/50 (vol.)* $EtOH/H_2O$. *The mechanism is dominated by a preliminary hydrolysis equilibrium. After the addition of T the ligand replaces the hydroxyl ion and, after another hydrolysis step, reduces the metal to gold(I). The k and* ΔE^* *values are reported. A white, crystalline, diamagnetic complex* $[AgT]NO_3$ *was obtained from the reaction between* $AgNO_3$ *and T. All complexes are S—bonded to the metal.*

Introduction

In previous papers[1-6] we have described the *trans*-planar complexes $[MX_2T_2]$ (where $M=Pt^{II}$ and Pd^{II}; T = thiomorpholin-3-one; X = Cl, Br, and OH), the octahedral or *pseudo*-octahedral $[CoT_6]X_2 . 2H_2O$ and $[M(CO)_4T_2]$ (where $M=Cr^0$, Mo^0, or W^0), and the *pseudo*-tetrahedral $[Pt(Ph_3P)_2T_2]$. In all cases the ligand is S-bonded to the metal and the thiomorpholin-3-one behaves as a soft base. Generally, this ligand stabilizes the lower oxidation state of the metal, as in the very stable complexes $[Pt(Ph_3P)_2T_2]$ or $[M(CO)_4T_2]$. Furthermore, Pt^{IV} and Pd^{IV} are reduced by T to Pt^{II} and Pd^{II}, with separation in the former case of insoluble $[PtCl_2T_2]$ and, in the latter, with formation of $[Pd(OH)_2T_2]$. The mechanism of reduction of Pt^{IV} obeys a second order rate law, while for Pd^{IV} the process is more complicated. The first step is, in our interpretation, the hydrolysis equilibrium between $[PdCl_6]^{2-}$ and $[PdCl_5OH]^{2-}$ followed, after the addition of T, by a substitution reaction of the ligand to the hydroxyl ion with formation of the complex $[PdCl_5T]^-$. This is followed by some hydrolysis and substitution reactions by the formation of the complex $[PdCl_3(OH)T_2]$. The latter reacts with the ligand with reduction to *trans*—$[PdCl_2T_2]$ and, by two additional hydrolytic stages, to *trans*—$[Pd(OH)_2T_2]$.

It is remarkable that, as shown by the pH measurements, in the first part of this process the ligand T replaces the hydroxyl ion rather then the halogen.

The aim of the present work is to verify this scheme by kinetic investigation of the reduction of gold(III) by T.

Starting with $AgNO_3$ we obtaine a white, crystalline, diamagnetic complex $[AgT]NO_3$ by reaction at room temperature in a concentrated aqueous alcoholic solution ($EtOH/H_2O = 50/50$). This complex is stable, slightly soluble in water or acetonitrile. The conductance measurements show that it is a uni-univalent eletrolyte. In the i.r. spectra between 4000 and 600 cm^{-1} only the absorption bands of the free ligand are present, and at 1035 and 715 cm^{-1} the ν_1 and ν_4 vibration modes of the NO_3 group.[7] In the region below 600 cm^{-1} three strong bands at 463, 422 and 372 cm^{-1} are present. The first is typical of the ligand while the other two are, tentatively, attributable to the ineracion Ag-S. This assignment is uncertain at present because there are no values for ν(Ag–S) reported in the literature.

Starting with $M[AuX_4]$ (where M = Na, K, and X = Cl, Br) we obtained the white complexes $[AuXT]$ by reaction with T in $EtOH/H_2O = 50/50$ solution. In aqueous solutions the process results in the formation of metal gold. The uptake of T is two moles for one mole of $[AuX_4]^-$, where one of these is obviously used for the reduction of the metal.

The analytical data and some physical properties of $[AuXT]$ are reported in Table I.

The electronic spectra of the compounds in the solid state[8] show, in the near infrared region, only some vibrational bands typical of the ligand.

The principal absorption bands in the i.r. region are reported in Table II and correspond above 650 cm^{-1}, to the principal absorptions bands of the free ligand. Furthermore, in the range 650-200 cm^{-1}, a few bands due to the interactions of the metal with T and X are present. The bands present in the spectra of $[AuClT]$ at 337.5 and 317.5 (sh) cm^{-1} are atributable to ν(Au–Cl). In fact, for linear two-coordinate Au-LX (where X = Cl and $L=SMe_2$) the metal-halogen stretching frequencies are at 324.5 and 319.6 (sh)

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(1) D. De Filippo and C. Preti, *Gazz. Chim. It.*, *98*, 64 (1968).

(2) C. Preti and D. De Filippo, *Annual Meeting of Inorg. Chem.*, 137 (1968).

(3) D. De Filippo and C. Preti, *Inorg. Chim. Acta*, *3*, 287 (1969).

(4) D. De Filippo, F Devillanova, and C. Preti, *Inorg. Chim. Acta*, *3*, 341 (1969).

(5) D. De Filippo and. C. Preti, *Ann. Soc. Nat. e Mat., Modena*, *100*, 3 (1969).

(6) C. Preti and D. De Filippo, *J. Chem. Soc.* (*A*) 1901 (1970).

(7) M. G. Miles, J. H Patterson, C. W. Hobbs, M. J. Hopper, J. Overend, and R. S. Tobias, *Inorg. Chem.*, *7*, 1721 (1968).

(8) M. T. Halfpenny, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.* (A) 627 (1967).

Table I. Analytical data and some physical properties.

Compound	Colour	Dec. temp.	Λ ohm^{-1}cm^2	M found	M calc.	C found	C calc.	H found	H calc.
[AuClT]	white	157-8	—	56.5	56.4	13.3	13.7	2.2	1.6
[AuBrT]	white	104-6	—	49.9	50.0	12.2	12.2	1.8	1.8
[AgT]NO$_3$	white	198-9	131.5	37.2	37.6	16.9	16.7	2.6	2.5

Method of preparation: reaction of T with $[AuX_4]^-$ or $AgNO_3$ in EtOH/H_2O = 50/50 concentrated solutions at room temperature. *Solubility*: [AuXT] very slightly soluble in H_2O and EtOH; insoluble in the other most common solvents; [AgT]NO$_3$ soluble in water and acetonitrile. *Conductance of [AgT]NO$_3$*: for a 10^{-3} *M* acqueous solution at 25°C; Λ = 136.6 for a 10^{-2} *M* solution in acetonitrile at the same temperature. *Magnetism*: all compounds are diamagnetic.

Table II. Principal infrared absorption bands (4000-200 cm^{-1})

thiomorpholin-3-one	3220s, 2880ms, 2650m, 1970w, 1620s, 1340s, 1280vw, 1240-30m, 1220-10m, 1125vw 1160m, 1115-05s, 1010-05s, 953s, 926m, 862m, 824vw, 770s, 692vw, 643s, 562s, 452s, 405vw.
[AuClT]	3180w, 1640s, 1348s, 1290w, 1150m, 1110s, 1015s, 948s, 920s, 864m, 820w, 758m, 720s, 523s, 457s, 417s, 412.5s, 374s, 337.5m, 317.5s
[AuBrT]	3180m, 1662s, 1348s, 1285w, 1246m, 1152w, 1120m, 1022s, 952s, 918s, 845m, 820w, 752w, 718s, 527m, 472s, 428s, 375m, < 225.
[AgT]NO$_3$	3260w, 3180s, 2720m, 2660w, 1745m, 1660s, 1305m, 1240w, 1220w, 1180w, 1160m, 1110s, 1035m, 1015s, 970m, 945s, 920m, 860ms, 810ms, 790w, 760m, 715s, 685m, 463s, 422s, 372ms.

cm^{-1}.[9] For ν(Au–Br) the value 228 cm^{-1} is reported in the literature whereas our compound absorbos below 225 cm^{-1}, but this absorption could be masked by an unresolved band in this region near to the limit of measurement. The bands present at 417; 412.5; 374 cm^{-1} and at 428; 375 cm^{-1} in the spectra of [AuClT] and [AuBrT] respectively, are tentatively attributable to the prevalent contribution of the stretching of the Au–S bond. The literature contains no informations concerning the value of ν(Au–S) for gold(I) complexes, whereas for complexes of the type $[Au(SCN)_4]^-$ the absorption bands attributed to ν(Au–S) are at 314-308 and 294-292 cm^{-1}.[10]

The examination of the ν(N–H) region and of the region between 1700 and 1600 cm^{-1} allows us to exclude the possibility of coordination *via* oxygen or nitrogen atoms. Furthermore, the weak band present in the spectra of the free ligand at 560 cm^{-1}, chiefly attributable to the contribution of the C–S bond vibrations, is shifted to 523 and 527 cm^{-1} for [AuClT] and [AuBrT] respectively.

The compounds are very stable and only slightly soluble in polar solvents; the diamagnetism is consistent with a d^{10} configuration of the metal.

Kinetics

In the visible region the spectra of $[AuCl_4]^-$ and $[AuBr_4]^-$ show strong bands at 319 and 389 mμ respectively (ε = 4550 for $[AuCl_4]^-$ and ε = 4700 for $[AuBr_4]^-$). These bands disappear by the reaction with T and it is possible to study the mechanism of the reaction by means of absorbance measurements in these regions. Furthermore, the reaction is accompanied by an increase in the acidity of the solution. In fact, when the process is complete, two moles of HX are liberated for each mole of $[AuX_4]^-$ used. The uptake of T is two moles for one mole of [AuXT] produced.

The initial pH of the solution falls below 7 for the complete hydrolysis of $[AuX_4]^-$ to $[AuX_3OH]^-$; the pK$_h$ values, obtained by pH measurements in solutions free from T and 0.5 *M* in KX, are reported *versus* 1/T in Figure 1. The excess of halide ion keeps constant the value of [X$^-$] and partially suppresses the hydrolysis equilibrium.

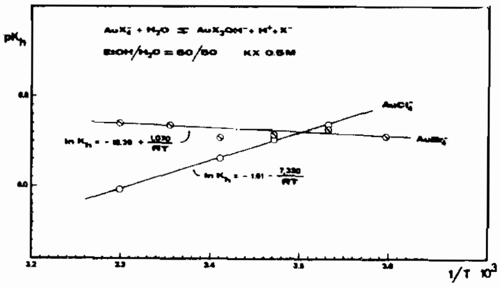

Figure 1. pK$_h$ values against 1/T.

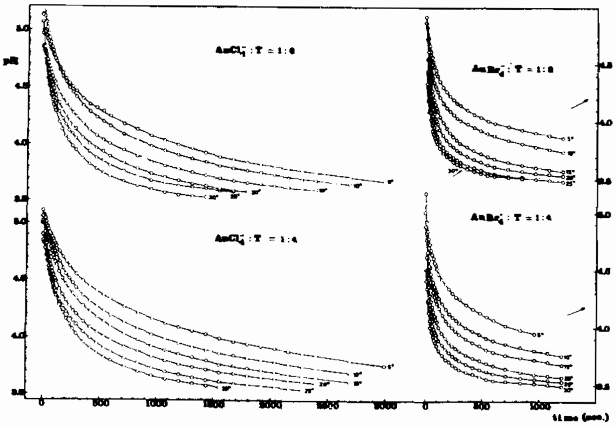

Figure 2. pH values against time.

The variation of pH and absorbance with time, obtained using a 3.33 10^{-4} *M* solution of $[AuX_4]^-$ in

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(9) G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).
(10) D. M. Adams, *Metal ligand and related vibrations*, 326, E. Arnold Ltd, London (1967).

EtOH/$H_2O = 50/50$, are reported in Figures 2 and 3 for the temperatures 5, 10, 15, 20, 25, 30°C and for molar ratios with $[AuX_4^-]:T$ of 1:4 and 1:6.

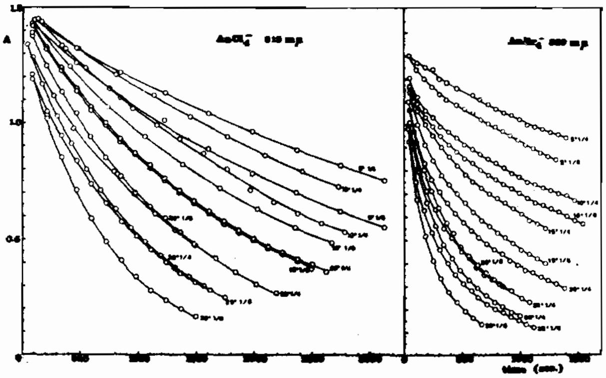

Figure 3. Absorbance values against time.

The rate of the reaction increases with increasing concentration of the ligand and with increasing temperature.

At temperatures below 5°C and with $[AuX_4^-] = 10^{-3}$ *M* and $[T] = 2 \times 10^{-3}$ *M* the pH of the solution increases by only one or two hundredths of a unit within the first ten seconds after mixing the reagents.

The ratio $([H^+]_t - [H^+]_o) / ([AuX_4^-]_o - [AuX_4^-]_t)$, where the suffixes refer to initial concentrations and concentrations after time t, increases from unity at the beginning of the reaction to a limiting value of 2. This observation excludes a simple mechanism with a unique rate-determining step, such as

$$[AuX_4]^- + 2T + H_2O \longrightarrow [AuXT] + TO + 3X^- + 2H^+$$

because, in this case, the ratio would always be equal to 2.

Alternatively we could suggest a mechanism similar to the reduction of $[PdCl_6]^{2-}$ with T, *e.g.*

$$[AuX_4]^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} [AuX_3OH]^- + H^+ + X^- \qquad (1)$$

$$[AuX_3OH]^- + T \xrightarrow{fast} [AuX_3T] + OH^- \qquad (2)$$

$$[AuX_3T] + H_2O \xrightarrow{fast} [AuX_2OHT] + H^+ + X^- \qquad (3)$$

$$[AuX_2OHT] + T \xrightarrow{k_3} [AuXT] + TO + H^+ + X^- \qquad (4)$$

In our interpretation the process depends on the initial hydrolysis equilibrium of the salt $M[AuX_4]$ followed by the substitution of the hydroxyl ion by the ligand. It would be possible to suggest an alternative mechanism in which the rate-determining step consists in the direct substitution of the halide ion by the ligand, such as

$$[AuX_4]^- + T \longrightarrow [AuX_3T] + X^- \qquad (5)$$

This interpretation is inconsistent with the experimental results. In fact the reaction becomes almost instantaneous in the absence of KX when the hydrolysis is almost complete. This means that the reagent species after the addition of T is $[AuX_3OH]^-$ and not $[AuX_4]^-$.

In stages [1–3] the production of one mole of HX occurs for each mole of $[AuX_4]^-$ hydrolysed. At the beginning of the reaction the increase in the solution acidity due to the fourth step is negligible. After some time, this contribution is no longer negligible and the ratio $([H^+]_t - [H^+]_o) / ([AuX_4^-]_o - [AuX_4^-]_t)$ becomes > 1.

Then, the difference between $[H^+]$ produced and $[AuX_4^-]$ consumed is equal to the $[AuXT]$ produced

$$[AuXT]_t = ([H^+]_t - [H^+]_o) - ([AuX_4^-]_o - [AuX_4^-]_t) \qquad (6)$$

Working on this hypothesis, in order to collate the experimental data according to the suggested interpretation of the mechanism, the following rate and stoichiometric equations could be applied:

$$-\frac{d[AuX_4^-]}{dt} = k_1[AuX_4^-] - k_2[X^-][AuX_3OH^-][H^+] \qquad (7)$$

$$\frac{d[AuXT]}{dt} = k_3[AuX_2OHT][T] \qquad (8)$$

$$\frac{d[AuX_2OHT]}{dt} = k_1[AuX_4^-] - k_2[X^-][AuX_3OH^-][H^+] - k_3[AuX_2OHT][T] \qquad (9)$$

$$[T]_o = [T]_t + [AuX_2OHT] + 2[AuXT] \qquad (10)$$

$$[AuX_4^-]_o = [AuX_4^-]_t + [AuX_3OH^-] + [AuX_2OHT] + [AuXT] \qquad (11)$$

$$[X^-]_t = [KX] + [AuX_3OH^-] + 2[AuX_2OHT] + 3[AuXT] \qquad (12)$$

$$[H^+]_t = [H^+]_o + [AuX_3OH^-] + (AuX_2OHT] + 2[AuXT] \qquad (13)$$

$$\frac{k_1}{k_2} = \frac{[X^-][AuX_3OH^-][H^+]}{[AuX_4^-]} = K_h \qquad (14)$$

If the steady state hypothesis is applied for the species $[AuX_2OHT]$, the left-hand side of equation (9) is equal to zero and, considering that stages (2-3) are faster than (1) and (4), it can be shown that

$$\frac{d[AuXT]}{dt} = \frac{k_1 k_3 K_h [AuX_4^-][T]}{k_1[H^+][X^-] + k_3 K_h [T]} \qquad (15)$$

All the other processes, from $[AuX_3OH]^-$ to $[AuX_2OHT]$ are considered to be without influence on the kinetic behaviour of the reaction, although the substitution of the hydroxyl ion by T will be slow if compared with the subsequent hydrolytic step. This behaviour is explained if the strong M–S bond labilizes the trans M–X bond, thus favouring a new hydrolytic attack.

Processing the data

As a first approximation we place $[X^-] = 0.5$ *M*, *i.e.* equal to the concentration of KX. The error involved is negligible because the ratio between [KX] and $[AuX_4^-]$ is over 1000: 1 for t=0. At the end, when $[AuX_4^-]$ is completely transformed to [AuXT], the total concentration of X^- is about 0.501 *M* and the error is still less than 0.2%.

As far as the absorbance data are concerned, it is necessary to take into account the contribution to the total absorbance due to the species $[AuX_3OH]^-$ and $[AuX_2OHT]$. In fact the total absorbance of the solution is defined by

$$A = \varepsilon_1[AuX_4^-] + \varepsilon_2[AuX_3OH^-] + \varepsilon_3[AuX_2OHT] \quad (16)$$

where ε_1, ε_2, and ε_3 are the molar extinction coefficients at 319 and 389 mμ for $[AuCl_4]^-$ and $[AuBr_4]^-$ respectively. Also assuming that $\varepsilon_1 \simeq \varepsilon_2 \simeq \varepsilon_3$ at least in the first and in the middle parts of the reaction then the relation $[AuX_4^-] > [AuX_2OHT] \gtrsim [AuX_3OH^-]$ applies. In fact, the high concentration of X^- ion represses almost completely the initial hydrolysis equilibrium and the concentration of $[AuX_3OH]^-$ is lower than 10^{-5} *M* during the whole reaction; the $[AuX_2OHT]$ has been evaluated to be lower than 10^{-4} *M* for the ratio of 1:6 between the reagents at 30°C. When this condition is applicable then the error due to the approximation.

$$A = \varepsilon_1[AuX_4^-] \quad (17)$$

is small enough for a first evaluation of the experimental data.

As far as the pH measurements are concerned, working in $EtOH/H_2O = 50/50$ (vol.) solution, with KX 0.5 *M*, it is necessary to determine a calibration curve. This was done by carrying out pH measurements on standardized solutions of HCl and HBr under the same experimental conditions. The equations of the least squares lines for the conversion of the pH values in H^+ concentrations at the various temperatures are reported in Table III.

Table III. Parameters for the equation $pH_{EtOH/H_2O} = A + BpH_{H_2O}$

t °C	$[AuCl_4]^-$ A	$[AuCl_4]^-$ B	$[AuBr_4]^-$ A	$[AuBr_4]^-$ B
30	−0.091	1.121	−0.048	1.111
25	−0.190	1.135	−0.180	1.146
20	−0.200	1.135	−0.178	1.143
15	−0.253	1.142	−0.263	1.162
10	−0.287	1.148	−0.295	1.171
5	−0.288	1.142	−0.521	1.222

Working with the equations (6-15) a special programme for an IBM 1620 computer was set up using as input data absorbance, pH, time and K_h values. The k_1. k_3 and concentration values for the intermeme. An example of the behaviour of the concentratdiate species were obtained for each value of the tiion values is reported in Figure 4 for 30°C and for a molar ratio of the reagents equal to 1:6.

In the initial stages the concentration of the species AuX_2OHT shows a maximum. After a few seconds this value becomes almost constant. It is then possible to apply the steady state hypothesis using equation (15).

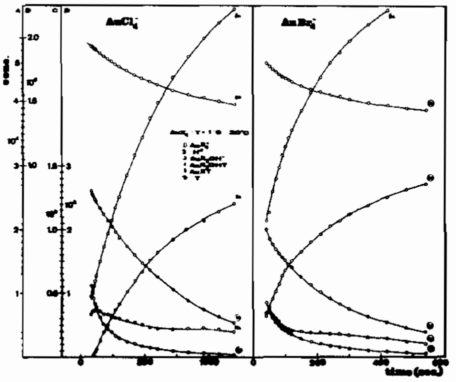

Figure 4. The diagram shows an example of concentration variation against time. These values were obtained as follows: $[AuX_4^-]$ and $[H^+]$ from the experimental data and the others from the equations [6, 10, 11, 14].

Discussion of the Results

The *k* values obtained are reported in Table IV and in Figure 5. Energy profiles of the reactions are reported in Figure 6.

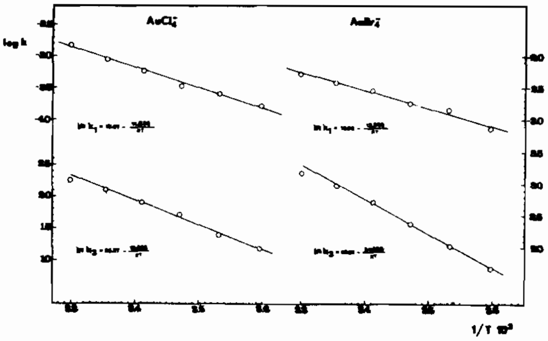

Figure 5. Correlation between *k* values and 1/T.

As far as the hydrolysis equilibria of $[AuX_4]^-$ are concerned, both ΔE^* values are of the same order of magnitude. Also, the pK_h value obtained by us at 20°C for $[AuCl_4]^-$ is in very good agreement with the value reported in the literature (6.16 against 6.07).[11,12]

The *k* values for the reduction of the chloride derivative are much lower than the corresponding values for the reduction of the bromide and this is in agreement with the experimental results. In fact the bromide derivative undergoes reduction much faster than the chloride inspite of the higher value of ΔE^*.

Comparing these results with those obtained in the kinetic study of the reduction of palladium(IV) to palladium(II)[4] by the same ligand it appears that the mechanism suggested are very similar.

(11) H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 2464 (1932).
(12) N. Bjerrum, *Bl. Soc. Chim. Belg.*, *57*, 432 (1948).

Table IV. Rate constants and activation parameters

Reaction	t °C	*k* (1)	ΔH*[13]	ΔS*[13]
$AuCl_4^- + H_2O \rightarrow AuCl_3OH^- + HCl$	30	14.8×10^{-4}(2)	14.3	—24.6
	25	8.9		
	20	5.8		
	15	3.4		
	10	2.6		
	5	1.6		
$AuCl_2OHT + T \rightarrow AuClT + TO + HCl$	30	17.5×10^{1}(3)	17.4	9.6
	25	12.6		
	20	7.8		
	15	5.1		
	10	2.4		
	5	1.5		
$AuBr_4^- + H_2O \rightarrow AuBr_3OH^- + HBr$	30	5.4×10^{-3}(2)	12.7	—26.8
	25	3.9		
	20	2.9		
	15	1.8		
	10	1.4		
	5	0.7		
$AuBr_2OHT + T \rightarrow AuBrT + TO + HBr$	30	14.7×10^{2}(3)	24.2	36.5
	25	9.2		
	20	5.2		
	15	2.4		
	10	1.1		
	5	0.5		

(1) each value is the average of two runs (2) sec^{-1}; (3) $l.mole^{-1}\ sec^{-1}$.

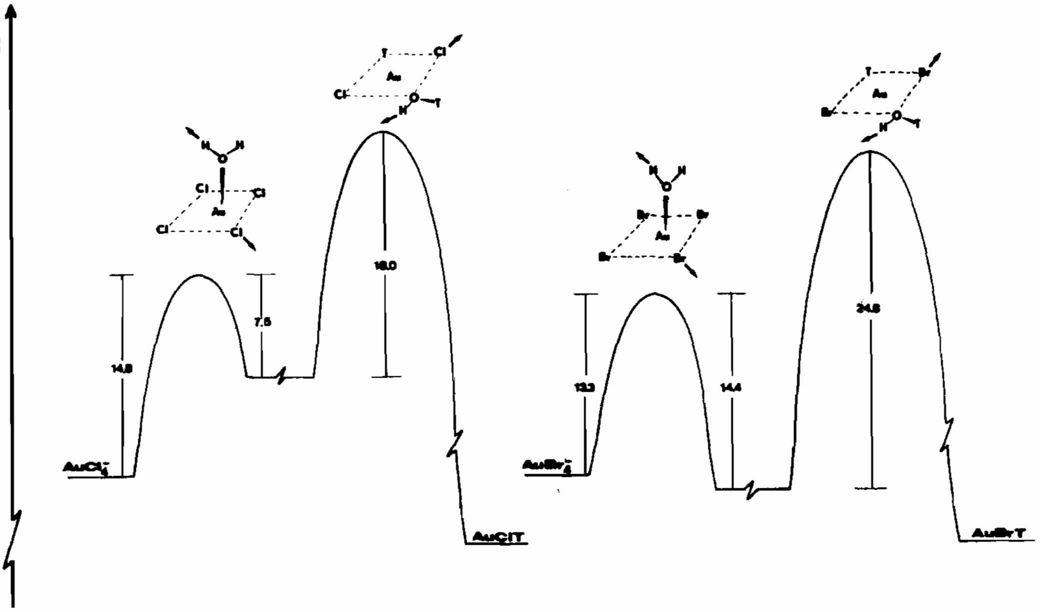

Figure 6. Energy profile of reactions (ΔE* values are in Kcal/mole).

Furthermore, the substitution step of the hydroxyl ion by T in the reduction of gold(III) is faster and does not influence the kinetic behaviour. This is also true for the reduction of palladium(IV).

The ΔE* values for the hydrolysis reaction of $[AuX_4]^-$ are about 60% of the corresponding value for the same process with $[PdCl_6]^{2-}$. The ΔE* values for the reduction of $[AuX_4]^-$ are of the same order of magnitude as the value for the reduction of $[PdCl_6]^{2-}$.

A kinetic study of the reduction of iridium, rhodium, ruthenium and osmium complexes by the same ligand and with selenomorpholin-3-one is now in progress. In order to avoid possible errors resulting from the use of different solutions for the pH and absorbance measurements, this study will be carried out recording simultaneously pH and absorbance data by a silica cell fitted with a micro-glass electrode.

Experimental Section

Materials. The salts $Na[AuCl_4]$ and $K[AuBr_4]$ were supplied by Fluka. The thiomorpholin-3-one was supplied by Aldrich and was purified by extraction with ethyl ether and recrystallisation. Samples of NaCl or KBr and HCl or HBr (CGS, supplied by C. Erba) were used in all experiments. The solutions were prepared with double-distilled water ($\chi = 2.3\ 10^{-6}$ ohm^{-1} cm^{-1}) and absolute ethanol.

Preparation of the Compounds. The compounds [AuXT] and [AgT]NO_3 were obtained starting from a concentrated solution of M[AuX_4] or $AgNO_3$ in EtOH/H_2O = 50/50 and adding, at room temperature, a solution of T in the same solvent, with a molar ratio of 1:2 and 1:1, respectively. In the former case, the colour of the solution disappeared in few minutes and the white crystalline product was separated. It is very stable and insoluble in the more common solvents.

In aqueous solutions the reduction of gold(III) goes almost quantitatively to gold(0).

The analytical data, reported in Table I, were obtained by determining Au% as metal, Ag% by Volhard's method, C% and H% by combustion.

Kinetics. The kinetics were followed by recording absorbance and pH. The absorbance data were recorded with a Perkin Elmer Mod. 402 spectrophotometer working between 270 and 350 mμ for $[AuCl_4]^-$ and between 350 and 430 mμ for $[AuBr_4]^-$. The degree of precision in the absorbance measurements was ±0.01 unit.

The pH measurements were recorded using a DAT 2002 digital pH meter and a glass electrode (ref. Ag/AgCl) which results in a degree of precision of ±0.01 pH units. The readings were recorded manually or using a Bausch and Lomb recorder.

The solutions were thermostated at the required temperature (±0.02°C) by a Lauda K2RD electronic apparatus.

Solutions of Na[$AuCl_4$] and K[$AuBr_4$] ($3\times33\ 10^{-4}$ *M*) were used in solvents consisting of 0.5 *M* solutions of NaCl or KBr respectively in EtOH/H_2O = 50/50 (vol.). The solutions of T in the same solvent each had a concentration of 4×10^{-2} *M* in order to minimize the concentration changes resulting from the mixing of the reagents. All the solutions were pre-thermostated at the required temperaure. The time necessary for a complete mixing, under vigorous stirring, has been estimated as seven or eight seconds and it does not affect the kinetic calculations.

Infrared measurements. The i.r. spectra (recorded with Perkin Elmer Mod. 225 and 621 spectrophotometers) were measured as nujol mulls supported between sodium chloride discs in the rock salt region or in KBr discs. In the range 400-200 cm^{-1} the spectra were recorded as nujol mulls supported between thin polyethylene sheets or in CsI discs. The principal absorption bands are reported in Table II.

Magnetic Measurements. Magnetic measurements were carried out by Gouy's method.

Conductance Measurements. Conductance measurements were carried out with a WTW type LBR bridge at 25°C±0.05 on solutions of [AgT]NO_3 in water or acetonitrile.

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(13) A. A. Frost and R. G. Pearson, *Kinetics and mechanism*, 2nd edition J. Wiley and Sons Inc., p. 98-101, (1963).