248. Oxidation – Reduction Reactions of Tetrachloroaurate(III) Anion with Triphenyl Derivatives of Group V Elements

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Summary. The reduction of the tetrachloroaurate (III) anion by L (L = PPh_3, $AsPh_3$, $SbPh_3$) is quantitative in non-aqueous solution. The products are the gold(I)-complexes AuClL (L = $AsPh_3$, $SbPh_3$) and $Au(PPh_3)_2^+$ together with the corresponding oxidation product LCl_2. Kinetic studies show that the reactions are first order in $AuCl_4^-$ and L. In addition a path independent of PPh_3 was found in dichloromethane. These data are interpreted in terms of mechanisms which involve reduction of $AuCl_4^-$ to $AuCl_2^-$, followed by equilibrium formation of AuClL for L = $AsPh_3$ and $SbPh_3$. For PPh_3, the data are consistent with a chloride replacement by PPh_3 to give $AuCl_3$ PPh_3, which is followed by a rapid reduction by a second mole of PPh_3. Equilibrium formation constants are reported for several Au(I) complexes.

1. Introduction. – The majority of kinetic studies of gold(III)-complexes deal with nucleophilic substitutions [1] and very few with reactions which involve redox processes. Except for the electrochemical reduction of $AuCl_4^-$ [2], reduction reactions of gold(III) to gold(I) have been poorly characterized, probably because of the ease of reduction into colloidal gold and the tendency of gold(I) to disproportionate in solution into Au(O) and Au(III). *Rich et al.* [3] have reported the catalytic reduction of $AuCl_4^-$ by Fe^{2+}; *De Filippo et al.* [4] have examined its reduction by thiomorpholine, and *Gibson et al.* [5] the reduction of $AuBr_3S(C_7H_7)_2$ by styrene.

To avoid the reduction into metallic gold, a logical choice is to use ligands which act as two electrons reducing agents and also form stable gold(I)-complexes. This is the case for the reaction of tetrachloroaurate(III) with triphenyl-phosphine, -arsine and -stibine in acetonitrile and other aprotic solvents. These reactions are conveniently followed by UV. spectrophotometry. As gold(I)-complexes are the products of the reduction, a quantitative evaluation of their stability in solution and of their spectral characteristics was undertaken.

2. Electronic absorption spectra of AuX_2^--complexes (X = Cl, Br, I). – The spectra of AuX_2^- (Fig. 1) were measured in acetonitrile at room temperature. The AuX_2^--solutions (X = Cl or Br) were prepared by making a 1:3 mixture of $[Au(MeCN)_2]ClO_4$ and Et_4NCl or Bu_4NBr respectively. For this ratio, $\log K_1K_2$ in Table 2 shows that AuX_2^- is the main gold species present. The spectra of $AuCl_2^-$ follow *Beer*'s law between 0.3 and 3.10^{-3} M. The solutions of $AuCl_2^-$ and of $AuBr_2^-$ were colorless and free of gold(III) ($AuCl_4^-$ would give maxima at 323 and 226 nm, $AuBr_4^-$ at 396 nm). The pale yellow AuI_2^--solutions were prepared by treating $AuBr_2^-$ with excess Bu_4NI. No maxima above 350 nm due to I_3^- or AuI_4^- were observed.

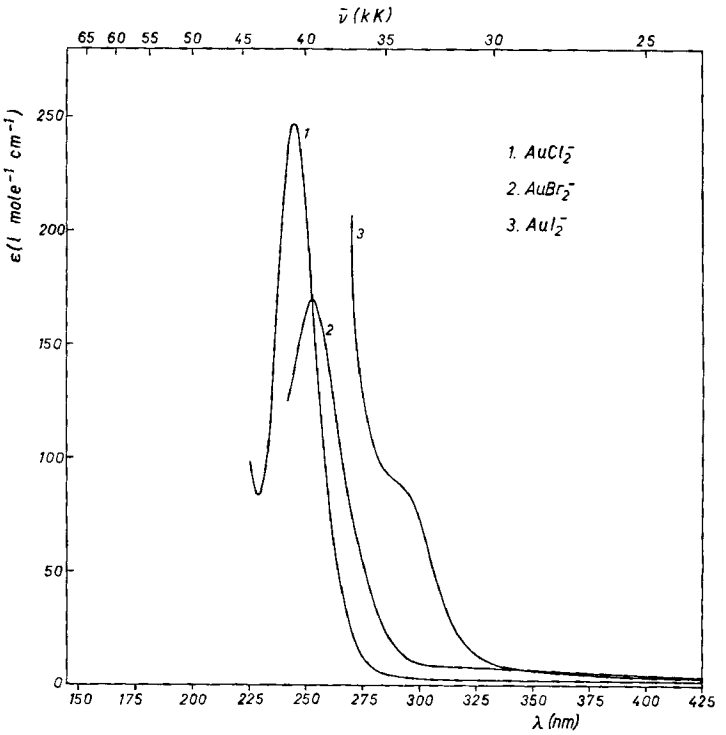


Fig. 1. *Electronic spectra of AuX_2^- in acetonitrile at 20°*

Table. 1. *Electronic spectra of dihalogold(I)-complexes in acetonitrile*

	$AuCl_2^-$	$AuBr_2^-$	AuI_2^-
λ_{max} (nm)	245	253	290
ε (M^{-1} cm^{-1})	247	170	90

The bands observed for AuX_2^- are too weak to be assigned to allowed charge-transfer transitions. Furthermore, a ligand to metal (L → M) process can be ruled out since the L → M systems in the isoelectronic HgX_2-complexes appear at higher energies [6]. The logical assignment for the spectra of AuX_2^- is a parity forbidden 5d → 6s transition, probably $5d_{z^2} \rightarrow 6s$ [$^1\Sigma_g^+ \rightarrow {}^1\Sigma_g^+$]. Such transitions have been assigned for related Ag(I)-complexes [7].

3. Stability of some gold(I) complexes in acetonitrile. – 3.1. *Potentiometric results.* The successive stability constants $K_1 = [AuL]/[Au][L]$ and $K_2 = [AuL_2]/[AuL][L]$ (L = ligand, charges omitted) were determined by direct or inverse titrations (see 5.2). The indicating gold electrode obeyed *Nernst*'s law ($E^0_{Au^+/Au} = +1.335$ V *vs.* SCE at 20°; *Goolsby et al.* found +1.338 V at 24° [2]). Thus, the constants were calculated by using the equation $E = E^0 + 0.058 \log c_{Au}/(1 + [L]K_1 + [L]^2K_1K_2)$ and the following approximations: 1. before the first equivalence point, AuL is the main complex in solution, 2. between the first and the second equivalence point, one has a mixture of AuL and AuL_2, 3. after the second equivalence point, AuL_2 is the main

species of gold(I). The identity of the complex was deduced from the abscissa of the drop in potential of the titration curves (Fig. 6). In the case of PPh_3, *Mutterties et al.* [8] have identified the complex $Au(PPh_3)_3^+$ in dichloromethane at $-80°$. However in acetonitrile and for ratios $2 < PPh_3/Au < 3$, this species seems to be present in negligible amount compared to $Au(PPh_3)_2^+$ (see 5.2).

Table 2. *Stability constants of some gold(I)-complexes in acetonitrile*
$T = 20.0 \pm 0.1°$, $\mu = 0.1$ (Et_4NClO_4)

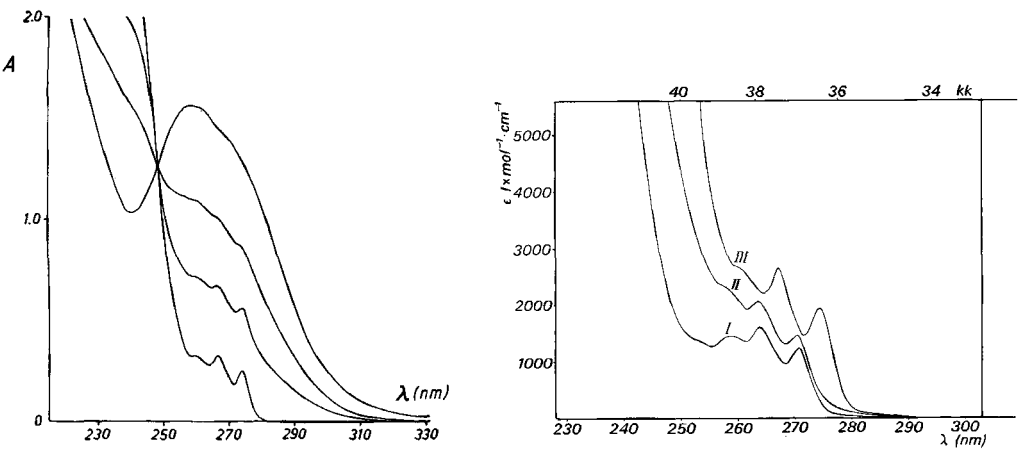
ligand	log K_1	log K_1K_2	ligand	log K_1K_2
Cl^-	12.0 [a]	20.2 (21.2 [b])	Me_2S	10.6
Br^-	12.0 [a]	20.6 (21.4 [b])	$C_6H_{11}NH_2$	19.6
I^-	17.1	23.8	$AsPh_3$	17.1
Ph_3PO		< 6	PPh_3	23.3

[a] Ref. [2]: at 24°, log $K_1K_2 = 19.9$ for $AuCl_2^-$ and 20.2 for $AuBr_2^-$; Ref. [15]: at 25°, log $K_1K_2 = 20.5$ for $AuCl_2^-$

[b] Corrected for ion pair formation using $K' = [Et_4N^+L^-]/[Et_4N^+][L^-] = 35$ for Cl^- and 22.4 for Br^-, and $K'' = [Et_4N^+ClO_4^-]/[Et_4N^+][ClO_4^-] = 11.2$ [15].

$Au(MeCN)_2^+$ is reduced into metallic gold by triphenylamine, -stibine and -bismuthine. Using some of *Goolsby & Sawyer*'s data [2] in addition to our results, one gets the following trends of increasing stability of the AuL_2-complexes: anionic complexes: $CNO^- < CNS^- \sim Cl^- < Br^- < I^- \ll CN^-$; cationic complexes: $Ph_3PO < Me_2S < py < AsPh_3 < NH_3 < C_6H_{11}NH_2 \ll PPh_3$. These trends are typical of a soft or class B acceptor.

3.2. *Equilibrium Constants for* $AuCl_2^- + L \rightleftarrows AuClL + Cl^-$ *(eq. 1)* ($L = PPh_3$, $AsPh_3$, $SbPh_3$). The knowledge of the position of these equilibria is necessary for the understanding of the kinetic results (part 4). As expected for a d^{10} substrate, the



a) b)

Fig. 2. a) *Absorbance of mixtures of* Et_4NAuCl_2 *and* PPh_3 *in various ratios in acetonitrile.* b) *Electronic spectrum of* $AuClAsPh_3$ (I), $AuClSbPh_3$ (*II*) *and* $AuClPPh_3$ (*III*)

substitution reactions of AuX_2^- are rapid (complete in the mixing time of 5 sec.). This is also true with amines (NH_3, cyclohexylamine). The constants $K = [AuClL][Cl^-]/[AuCl_2^-][L]$ were determined spectrophotometrically by using mixtures of the reactants in various ratios and also of the products in the case of $AsPh_3$ (L and AuClL follow *Beer*'s law). The identity of the mixed complexes was deduced by comparing the UV. spectrum of 1:1 mixtures of L and $AuCl_2^-$ with the spectrum of the corresponding AuClL-complex. Solid $AuClAsPh_3$ and $AuClPPh_3$ were isolated from the equilibrium mixtures at higher gold(I) concentration. In each case, good isosbestic points show that in the region examined only the absorption of L and AuClL have to considered. (Fig. 2). Knowing the extinction coefficients ε_L of L and ε_{AuClL} of AuClL, the total concentrations $[Au]_t$, $[L]_t$, $[Cl]_t$, and measuring the absorbance A at the corresponding wavelength, one obtains:

$$[AuClL] = x = (A - \varepsilon_L[L]_t)/(\varepsilon_{AuClL} - \varepsilon_L) \text{ and}$$

$$K = x\,([Cl]_t + x - 2\,[Au]_t)/([Au]_t - x)\,([Cl]_t - x)$$

Table 3. *Equilibrium constant of* $AuCl_2^- + L \rightleftarrows AuClL + Cl^-$ *in acetonitrile at 20.0 ± 0.1°* (mean of measurements)

ligand L	$SbPh_3$	$AsPh_3$	PPh_3
K	0.15 ± 0.05	13 ± 2	$>10^2$

An additional equilibrium becomes important in the presence of an excess of triphenylphosphine as $AuClPPh_3$ is then converted into $Au(PPh_3)_2^+$ [9].

4. Redox reactions of $AuCl_2^-$ with the triphenyl derivatives of group V elements. – 4.1. *Reactions on a preparative scale.* The reduction of gold(III) is quan-

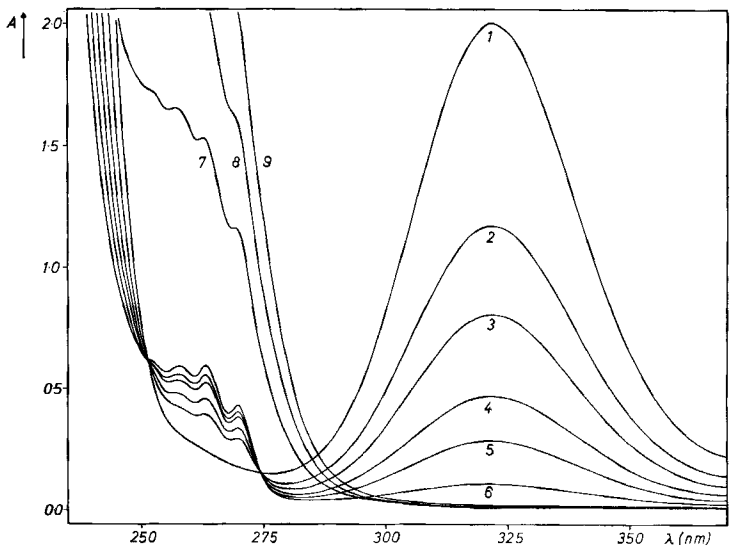


Fig. 3. *Electronic spectrum of equilibrium mixtures of* $AuCl_4^-$ *and* $SbPh_3$ *in acetonitrile at 20°.* $[AuCl_4^-]_t = 3.75 \cdot 10^{-4}$ M; $[SbPh_3]_t \cdot 10^4$ M = 0 (spectrum 1), 1.514 (2), 2.187 (3), 2.861 (4), 3.197 (5), 3.534 (6), 5.050 (7) and 5.720 (8) (see 5.1. for extinction coefficients)

titative when the ligand L (PPh_3, $AsPh_3$, $SbPh_3$) is added to an acetone solution of Bu_4NAuCl_4 in ratios L/Au > 2. The complex AuClL precipitates on adding ether. In the triphenylarsine case, the oxidation product is identified in the reaction mixture by thin layer chromatography as beeing Ph_3AsCl_2. The quantitative separation from $AsPh_3$, $AuClAsPh_3$ and Bu_4NCl was performed by partition chromatography (silica gel column, eluent: acetone/benzene 4:6, then ethanol). The alcoholysis product of Ph_3AsCl_2 was obtained and identified by its UV., IR. and ^{1}H-NMR.-spectra. The complex $AuCl_3AsPh_3$ was not present at any time in the reaction mixture in measurable amounts. Triphenylbismuthine was found to reduce $AuCl_4^-$ rapidly into metallic gold, and triphenylamine does not reduce $AuCl_4^-$ in acetone or acetonitrile but instead gives chloride substitution.

4.2. *Stoichiometry of the reaction* $AuCl_2^-$ + L *in acetonitrile* (L = PPh_3, $AsPh_3$, $SbPh_3$).

a) $L = SbPh_3$.

The variation of the absorbance at 322 nm where only $AuCl_4^-$ absorbs shows that the stoichiometry is 1:1:

Table 4. *Stoichiometry of the reaction* $AuCl_4^-$ + $SbPh_3$ (= L) *in acetonitrile*
$[AuCl_4^-]_t = 3.75 \cdot 10^{-4}$ M, $\varepsilon_{322} = 5360\ M^{-1} \cdot cm^{-1}$

spectrum	$[L]_t \cdot 10^4$ M	$100[L]_t/[AuCl_4^-]_t$	A_{322}	% $AuCl_4^-$ reduced	L/Au
1	0	0	2.013		
2	1.514	40.4	1.181	41.3	1.02
3	2.187	58.3	0.816	59.4	1.02
4	2.861	76.3	0.480	76.1	1.00
5	3.197	85.2	0.294	85.3	1.00
6	3.534	94.2	0.121	93.9	1.00

For ratios L/Au < 1 (spectra 1–6), the isosbestic points show that only one species P absorbs apart from $AuCl_4^-$. When analysing the curves at 263 (and 270) nm, the apparent extinction coefficient of P ($\varepsilon_P = A - \varepsilon[AuCl_4^-]/[P]$) was equal within 1% to the extinction coefficient of pure Ph_3SbCl_2 (see 5.1.). For ratios > 1, free triphenylstibine appeared in solution. Curves 7–8 show that the concentration of free $SbPh_3$ is lower than the theorical one. Thus, the gold(I) complex (assumed to be $AuCl_2^-$) reacts with the excess of $SbPh_3$ until the equilibrium (eq. 1) is reached. The hypothesis that $AuCl_2^-$ is an intermediate of the reaction is supported by calculating $K = [AuClSbPh_3][Cl^-]/[AuCl_2^-][SbPh_3]$ and comparing it with the result in Table 3. At a given wavelength, the difference in absorbance due to the presence of $SbPh_3$ (= L) and AuClL is:

$\Delta A = A - \varepsilon_{LCl_2}[LCl_2]$ ($[AuCl_4^-] = 0$). As each compound follows *Beer*'s law, one has:

$$[AuCl_4^-]_t = [LCl_2] = [AuCl_2^-] + [AuClL]$$

$$[L]_t = [L] + [LCl_2] + [AuClL] \quad \text{and} \quad [AuClL] = [Cl^-]$$

$$\Delta A = \varepsilon_{AuClL}[AuClL] + \varepsilon_L([L]_t - [AuCl_4^-]_t - [AuClL])$$

The substitution of [AuClL] in the three mass balances allows the determination of K.

Table 5. *Evaluation of K from mixtures of $AuCl_4^-$ and $SbPh_3$ (= L) in acetonitrile at 20°*
At 263 nm: $\varepsilon_L = 10130$, $\varepsilon_{AuClL} = 2040$, $\varepsilon_{LCl_2} = 1634\,M^{-1} \cdot cm^{-1}$; at 270 nm: $\varepsilon_L = 7770$, $\varepsilon_{AuClL} = 1438$, $\varepsilon_{LCl_2} = 1186$. Error of K: ±40%

λ(nm)	A	$[AuCl_4^-]_t \cdot 10^4\,M$	$[L]_t \cdot 10^4\,M$	ΔA	% $\varepsilon_{AuClL} \cdot [AuClL]/\Delta A$	K
270	1.580	3.75	5.72	1.134	20	0.10
270	1.148	3.75	5.05	0.703	20	0.09
263	1.530	3.75	5.05	0.917	11	0.09

This measure of K is in good agreement with the value in Table 3. obtained by direct equilibration of Et_4NAuCl_2 with $SbPh_3$.

Thus the identity of the redox reaction is:

$$AuCl_4^- + SbPh_3 \xrightarrow{\text{slow}} AuCl_2^- + Ph_3SbCl_2 \qquad \text{(eq. 2)}$$

$$AuCl_2^- + SbPh_3 \underset{\text{fast}}{\rightleftharpoons} AuClSbPh_3 + Cl^- \quad K = 0{,}1 \qquad \text{(eq. 3)}$$

b) $L = AsPh_3$.

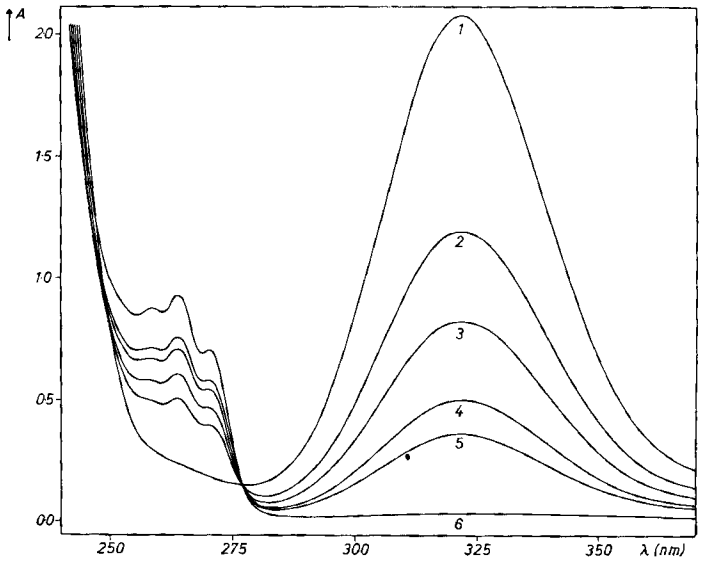


Fig. 4. *Electronic spectrum of equilibrium mixtures of $AuCl_4^-$ and $AsPh_3$ in acetonitrile at 20°.* $[AuCl_4^-]_t = 3.89 \cdot 10^{-4}\,M$; $[AsPh_3]_t \cdot 10^4\,M = 0$ (spectrum 1), 1.605 (2), 2.319 (3), 3.033 (4), 3.389 (5) and 4.282 (6) (see 5.1. for extinction coefficients)

The apparent stoichiometry is 1:1. The same procedure used in the triphenylstibine case showed that the oxidation product of $AsPh_3$ is Ph_3AsCl_2 (see 5.1.). For ratios $1 < L/Au < 2$, the absorbance was due only to Ph_3AsCl_2 and $AuClAsPh_3$.

Table 6. *Apparent stoichiometry of the reaction* $AuCl_4^-$ + $AsPh_3$ (= *L*) *in acetonitrile*
$[AuCl^-]_t = 3.89 \cdot 10^{-4}$ M; $\varepsilon_{322} = 5345\ M^{-1} \cdot cm^{-1}$

spectrum	$[L]_t \cdot 10^4$ M	100 $[L]_t/[AuCl_4^-]_t$	A_{322}	% $AuCl_4^-$ reduced	L/Au
1	0	0	2.079		
2	1.605	41.3	1.204	42.5	1.03
3	2.319	59.6	0.837	60.4	1.01
–	2.676	68.8	0.708	66.0	0.96
4	3.033	77.9	0.498	76.1	0.98
5	3.389	87.1	0.361	82.6	0.95

Free triphenylarsine appeared in solution for ratios L/Au > 2. Thus in presence of an excess of $AsPh_3$, the overall stoichiometry is 2:1 and the identity of the reaction is:

$$AuCl_4^- + AsPh_3 \xrightarrow{\text{slow}} AuCl_2^- + Ph_3AsCl_2 \qquad K_1 \gg K_2 \qquad \text{(eq. 4)}$$

$$AuCl_2^- + AsPh_3 \underset{\text{fast}}{\rightleftharpoons} AuClAsPh_3 + Cl^- \qquad K_2 = 13 \qquad \text{(eq. 5)}$$

The apparent contradiction with the result in Table 6 is explained by the fact that reaction (4), being a redox process, must have an equilibrium constant K_1 greater than K_2. Thus, for ratios L/Au smaller than one, $AuClAsPh_3$ reacts with the excess of $AuCl_4^-$ by eq. 6, giving an apparent stoichiometry 1:1:

$$AuCl_4^- + AuClAsPh_3 + Cl^- \rightarrow 2\,AuCl_2^- + Ph_3AsCl_2 \qquad K_3 = K_1/K_2 \gg 1 \qquad \text{(eq. 6)}$$

c) *L* = *PPh*$_3$.

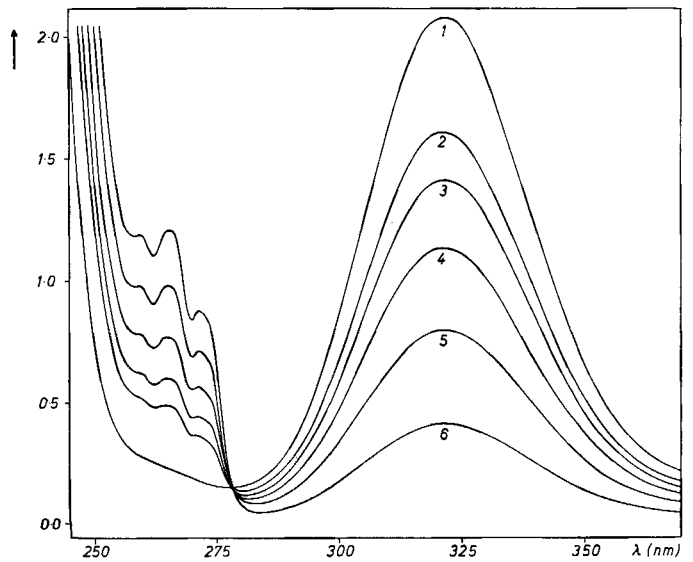


Fig. 5. *Electronic spectrum of equilibrium mixtures of* $AuCl_4^-$ *and* PPh_3 *in acetonitrile at 20°.*
$[AuCl_4^-]_t = 3.89 \cdot 10^{-4}$ M; $[PPh_3]_t \cdot 10^4$ M = 0 (spectrum 1), 1.681 (2), 2.428 (3), 3.175 (4), 4.857 (5) and 6.351 (6) (see 5.1. for extinction coefficients)

Table 7. *Stoichiometry of the reaction* $AuCl_4^- + PPh_3$ (= *L*) *in acetonitrile*
$[AuCl_4^-]_t = 3.89 \cdot 10^{-4}$ M

spectrum	$[L]_t \cdot 10^4$ M	$100\,[L]_t/[AuCl_4^-]_t$	A_{322}	% $AuCl_4^-$ reduced	L/Au
1	0	0	2.079		
2	1.681	43.1	1.608	22.5	1.92
3	2.428	62.2	1.414	31.8	1.96
4	3.175	81.3	1.228	40.8	1.99
–	4.483	114.8	0.894	56.9	2.02
5	4.857	124.3	0.840	61.4	2.02
6	6.351	162.1	0.410	80.3	2.01

The stoichiometry is 2:1. The analysis of curves 2–6 in the region 260–275 nm showed that the absorbance is the sum of three contributions by $AuCl_4^-$, Ph_3PCl_2 and $AuClPPh_3$ (see 5.1). The identity of the overall redox reaction is:

$$AuCl_4^- + 2\,PPh_3 \rightarrow AuClPPh_3 + Ph_3PCl_2 + Cl^- \qquad \text{(eq. 7)}$$

In presence of a great excess of PPh_3, the complex $Au(PPh_3)_2^+$ is formed [9]. The reaction scheme is probably different from those of $SbPh_3$ and $AsPh_3$. Indeed, for ratios $PPh_3/Au < 1$, one should observe a similar reaction as (6) and get an apparent 1:1 stoichiometry. As it is not the case, the first step is probably not the reduction of $AuCl_4^-$ into $AuCl_2^-$ (see 4.3).

4.3. *Kinetics of the redox reactions in acetonitrile.* a) *L = $SbPh_3$ and $AsPh_3$:* The reduction of $AuCl_4^-$ is relatively rapid in acetonitrile and could not be studied under pseudo first order conditions, but it could be followed by conventional UV. spectrophotometry if second order conditions were used. The disappearance of both reactants were recorded. For the general reaction scheme:

$$\begin{array}{lccccc} \text{1st step} & AuCl_4^- & + & L & \xrightarrow{k} & AuCl_2^- + LCl_2 \\ & (a-x) & & (b-x-y) & & (x-y) \quad x \\ \text{2nd step} & AuCl_2^- & + & L & \underset{}{\overset{K}{\rightleftharpoons}} & AuClL + Cl^- \\ & (x-y) & & (b-x-y) & & y \quad y \end{array},$$

the rate of formation of LCl_2 is given by: $dx/dt = k(a-x)(b-x-y)$ (eq. 8). The integrated rate equation may be simplified in the following way: in the case of triphenylstibine (K = 0.1), one adopts the approximation K = 0, and the integration of eq. 8 gives: $kt = x/a(a-x)$ (eq. 9) if $b/a = 1$, and $kt = 1/(b-a) \cdot \ln[a(b-x)/b(a-x)]$ (eq. 10) if $b/a > 1$. The rate of disappearance of $AuCl_4^-$ should be the same as that of $SbPh_3$. In the case of triphenylarsine, one adopts the approximation $K = \infty$. If $b/a = 2$: $kt = x/ma(a-x)$ (eq. 11) (m = 2 if $AuCl_4^-$ is followed at 322 nm; m = 4 for $AsPh_3$ at 270 nm). When an excess of chloride is present, equilibrium (3) is shifted towards the left and eq. 9–10 must be used. If $b/a > 2$: $kt = 1/(b-2a) \cdot \ln[a(b-2x)/b(a-x)]$ (eq. 12).

In the case of triphenylarsine, the exact kinetic expression obtained by integration of eq. 8 gives a function $kt = f(t)$ which is linear for $K = 15 \pm 4$. This value is in agreement with the direct measure of the equilibrium constant (Table 3).

Table 8. *Rate constants for the reaction of $AuCl_4^-$ + L (L = $SbPh_3$, $AsPh_3$) in acetonitrile at 20 ± 0.2°*

b/a	λ (nm)	$[ClO_4^-]$	$[Cl^-]$	k (M^{-1} s^{-1})	eq. used	L
1.06	322	0.10	–	162 ± 2 [a]	(9)	$SbPh_3$
1.06	270	–	–	161 ± 2	(9)	$SbPh_3$
1.03	322	0.08	0.02	163 ± 5	(9)	$SbPh_3$
2.14	322	0.05	0.05	163 ± 2	(10)	$SbPh_3$
2.19	322	–	0.10	161 ± 5	(10)	$SbPh_3$
1.00	322	–	0.10	55 ± 1	(9)	$AsPh_3$
2.55	322	–	0.10	55 ± 1	(10)	$AsPh_3$
2.53	322	0.05	0.05	59 ± 1	(10)	$AsPh_3$
2.56	322	0.08	0.02	63 ± 1	(10)	$AsPh_3$
2.09	270	0.10	–	61 ± 1	(11)	$AsPh_3$
2.01	322	–	–	62 ± 1	(11)	$AsPh_3$

[a] The reported error is calculated from the standard deviation. As it depends on the accuracy of a and b, the estimated relative error of k is 10%.

In acetonitrile the rate determining step is the reduction of $AuCl_4^-$ into $AuCl_2^-$. The reaction is of first order in gold(III) substrate and in reducing agent:

$$-d[AuCl_4^-]/dt = -d[SbPh_3]/dt = k[AuCl_4^-][SbPh_3]$$

$$-d[AuCl_4^-]/dt = -{}^1/_2 d[AsPh_3]/dt = k[AuCl_4^-][AsPh_3]$$

The chloride concentration has no effect no the rate but merely shifts equilibrium (3) in favor of $AuCl_2^-$.

b) *L = PPh_3.* Since the reaction of $AuCl_4^-$ with PPh_3 was much faster than with $SbPh_3$ or $AsPh_3$, it was necessary to use stopped-flow techniques. The reaction conditions consisted of excess PPh_3 and the rates were pseudo first order in gold(III). Good first order kinetics were observed over 75–90% of the reaction, which was followed at 322 nm.

Table 9. *Rate constants for the reaction of $AuCl_4^-$ + PPh_3 (= L) in acetonitrile* $[AuCl_4^-]_t = 9.2 \cdot 10^{-5}$ M

$10^3[L]_t$	k_{ob} (s^{-1}) 10^{-4}	k_2 (M^{-1} s^{-1})	$10^3[L]_t$	k_{ob} (s^{-1}) 10^{-4}	k_2 (M^{-1} s^{-1})
	3.0°			15°	
1.84	93.2	5.1	1.84	108	5.8
2.38	114	5.1	2.38	135	5.7
3.69	188	4.8	2.38	141	5.9
4.76	264	5.5	3.69	232	6.3
			3.69	248	6.7
	9.0°		4.76	296	6.2
1.84	102	5.5			
2.38	133	5.6			
3.69	208	5.6			
4.76	284	6.0			
4.76	290	6.1			

The rate data are consistent with the rate law ($k_2 = k_{ob}/[PPh_3]$):

$$-d[AuCl_4^-]/dt = k_2[AuCl_4^-][PPh_3].$$

Within experimental uncertainty, no term zero order in [PPh_3] was found. Therefore if a two term rate law is applicable (see studies in dichloromethane, 4.4), the value of k_1 is $0 \pm 20\ s^{-1}$ at 3–15°.

Activation parameters were calculated for the k_2 process from the temperature dependence of the rates: $\Delta H^* = 1.7 \pm 0{,}7$ kcal mol^{-1} and $\Delta S^* = -31 \pm 3$ cal deg^{-1} mol^{-1}.

4.4 *Kinetics in acetone and dichloromethane.* a) $L = SbPh_3$ *and* $AsPh_3$: Since the reduction of gold(III) is slower than in acetonitrile, higher concentrations of reducing agent were used and the disappearance of $AuCl_4^-$ was followed by UV. spectrophotometry at 340 nm. The slope of the graph $\ln(A_t - A_\infty) = f(t)$ is k_{ob}. As the conditions are not strictly of pseudo first order in L, the rate constant k of the rate determining step (eq. 2 and 4) is the slope of the graph $k_{ob} = f(b - ma)$ where $m = 1$ for $SbPh_3$ and 2 for $AsPh_3$. As this function is linear and passes through the origin, there is no parallel path independent of the L concentration. A stopped-flow experiment was performed in dichloromethane ($L = AsPh_3$) to look for a fast reaction which preceeds the reduction of gold(III) ($T = 17°$, $b/a = 18$, $\lambda = 323$ nm). The traces show only a decrease in transmittance on mixing due to the strongly absorbing $AuCl_4^-$ ion. Thus, there appears to be only one reaction with a half-life longer than about 1–2 msec.

b) $L = PPh_3$: The rates of the reduction were again much faster than for $SbPh_3$ and $AsPh_3$, and stopped-flow methods were employed. The rate data were gathered under pseudo first order conditions using an excess of PPh_3. The data in dichloromethane were consistent with the rate law ($k_{ob} = k_1 + k_2[PPh_3]$)

$$-d[AuCl_4^-]/dt = (k_1 + k_2[PPh_3])\,[AuCl_4^-] \qquad \text{(eq. 13)}$$

Table 10. *Rate constants of the reaction* $AuCl_4^- + L$

Ligand L	in dichloromethane				in acetone		
	T(°C)	b/a	k ($M^{-1}\,s^{-1}$)		T(°C)	b/a	k ($M^{-1}\,s^{-1}$)
$SbPh_3$	7	9–19	16 ±1		3	4–9	3.2 ±0.3
	11	11–21	19 ±1		10	7–14	4.5 ±0.2
	17	10–20	26.4 ±0.8		17	6–14	6.4 ±0.1
	19	8–16	28 ±1		24	4–27	8.9 ±0.1
	21	10–20	31 ±2				
$AsPh_3$	7	10–23	11.0 ±0.1		3	18–35	0.97 ±0.04 [a]
	15	10–21	15 ±1		10	20–45	1.36 ±0.06
	21	10–21	19.9 ±0.8		17	11–23	2.0 ±0.2
					20	12–26	2.19 ±0.06 [b]
					24	10–22	2.9 ±0.1
			k_1 (s^{-1})	k_2 ($M^{-1}\,s^{-1}$) · 10^{-4}			k_2 ($M^{-1}\,s^{-1}$) · 10^{-4}
PPh_3	3	20–52	1.4	2.3		16–52	9.6
	9	20–52	2.4	2.6		16–52	11.4
	15	20–52	3.9	3.0		16–52	12.8

[a] A kinetic run with $[Cl^-] = 0.2$ M (LiCl) gave $k = 1.1 \pm 0.1\ M^{-1}\,s^{-1}$

[b] For $b/a = 2$, $k = 2.1 \pm 0.4\ M^{-1}\,s^{-1}$.

In acetone, only the k_2 term was observed; if a k_1 path is applicable in this solvent, k_1 is $0 \pm 0.2\ s^{-1}$ at 3–15°.

Activation parameters were calculated from the temperature dependence of the rates and are given in Table 11.

Table 11. *Activation parameters of the rate determining step of the reduction of $AuCl_4^-$ by L*

Ligand L		in dichloromethane		in acetone	
		ΔH^* (kcal/mol)	ΔS^* (e.u)	ΔH^*	ΔS^*
APh_3	(k_1)	12.6 ± 0.1	-12 ± 1	– a	– a
$SsPh_3$	(k_2)	2.3 ± 0.8	-30 ± 3	3.1 ± 1.6	-34 ± 6
$PsPh_3$	(k)	~6	−31	7.7 ± 0.9	-30 ± 3
$AbPh_3$	(k)	7.0 ± 0.8	-28 ± 3	7.5 ± 0.5	-29 ± 2

a) k_1 path is zero within experimental error.

4.5. *Mechanism of the reduction of $AuCl_4^-$ by PPh_3, $AsPh_3$ and $SbPh_3$ (= L).* The triphenylarsine and -stibine systems react at very similar rates and both have similar activation parameters. However, the triphenylphosphine is more reactive and seems to behave differently. The lower activation enthalpy for PPh_3 is primarily responsible for the greater reactivity. In the case of $AsPh_3$ and $SbPh_3$, both the reaction stoichiometry and the rate data are consistent with a path which involves a slow reduction of $AuCl_4^-$ to $AuCl_2^-$ (eq. 2 or 4), followed by a rapid equilibrium formation of AuClL (eq. 3 or 5). An alternative path in which a chloride is replaced in $AuCl_4^-$ giving a reactive substitution product, $AuCl_3L$, as an intermediate is considered unlikely because we have noted that at least for $AsPh_3$, the complex $AuCl_3$ $AsPh_3$ is stable in acetonitrile. No evidence for such a species was found. Further the lack of dependence of the rates on the presence of excess chloride indicates that loss of chloride is not involved in the rate determining step. Since the rate laws are first order in both $AuCl_4^-$ and ligand, the mechanism undoubtedly involves associative activation.

The ligands are good nucleophiles towards d^8 substrates, and $AuCl_4^-$ has an empty p_z orbital suitable for use in the formation of a five-coordinate intermediate or transition state. Consequently, it is likely that the rate determining step for $AsPh_3$ and $SbPh_3$ involves first a nucleophilic attack perpendicular to the plane of the gold(III)-complex forming a redox reactive intermediate $[AuCl_4L]$. This step is then followed by a rapid intramolecular redox process which gives rise to products. The geometry of this five-coordinate $[AuCl_4L]$ species must be of considerable importance, since in the case of $AsPh_3$, the four-coordinate complex $AuCl_3AsPh_3$ is redox stable. The redox rearrangement may involve chlorine atom transfer to Sb or As, but a detailed description of the redox rearrangement would be speculative. It should be pointed out however, that since all the d^{10} complexes examined were very labile, any Au–Cl or Au–L bond breaking occuring after the electron transfer in the five-coordinate complex is not expected to be kinetically important.

In the case of PPh_3, the rate law in dichloromethane (eq. 13) strongly suggests that the rate determining step involves the formation of $AuCl_3PPh_3$ by the usual

associative square-planar substitution paths (k_1 and k_2). A rapid reduction reaction involving another mol of PPh_3 would then follow to give products. This kind of pathway is consistent with the reaction stoichiometry. That PPh_3 should behave differently than $SbPh_3$ and $AsPh_3$ is perhaps not too surprising since PPh_3 is a weaker reducing agent, yet still a very powerful nucleophile towards gold(III). Thus for PPh_3, chloride substitution is favored over a redox rearrangement process, at least for the first replacement. The redox process that follows the chloride replacement may well be quite similar to that visualized for $SbPh_3$ and $AsPh_3$.

The role the solvent plays in these redox reactions is not entirely clear. Two effects may be noted. First, the order of reactivity for the second-order path of all three ligands is acetonitrile > dichloromethane > acetone. This order does not parallel solvent polarity, but since there is little change in ionic charge in the transition states visualized for these reactions, only small contributions would be expected from differences in solvent polarity. The rate differences may reflect differences in solvent's ability to stabilize the transition states by some type of coordinative interaction with the soft metal and donor atom centers. Acetonitrile is the most reactive medium and is probably the best donor towards soft centers. Second, only for dichloromethane is a k_1 path observed for PPh_3, indicating that if the associative square-planar mechanism is applicable, the solvent reactivity order for the k_1 path is dichloromethane $\gg$ acetonitrile $\sim$ acetone. This effect can be rationalized by noting that dichloromethane has the lowest dielectric constant and is thus the poorest solvent for the ionic substrate $AuCl_4^-$ of the three. The solvation of $AuCl_4^-$ by acetonitrile and acetone is expected to be more efficient, and therefore the desolvation required to form a solvent complex transition state associated with the k_1 path will be less favorable than for dichloromethane.

5. Experimental Part

5.1. *Solvents and compounds.* All solvents and liquids were purified, dried by standard methods [10] and degassed with nitrogen for most of gold(I)-complexes are very prone to dismutation. The following compounds were prepared by published methods: $[Au(MeCN)_2]ClO_4$ [11]; AuClL [9] (UV. max. in MeCN for $AuClPPh_3$: 260 nm (ε = 2550 M^{-1} cm^{-1}), 267 (2590), 271 (2010); for $AuClAsPh_3$: 253 (1590), 258.5 (1570), 263.7 (1670), 270.5 (1260); for $AuClSbPh_3$: 256.5 (2370), 263.2 (2070), 270 (1440)); Bu_4NAuCl_4 [12] (UV. max: 225 (43400), 322 (5360)); LCl_2 [13] (UV. max. for Ph_3PCl_2: 254 (1080), 259 (1500), 271.5 (1560); for Ph_3AsCl_2: 259 (1890), 264.8 (1970), 271.2 (1430); for Ph_3SbCl_2: 258, 263 (1629), 270 (1196)). $AuCl_3L$-complexes: one mmol of AuClL was dissolved in the minimum amount of 1,1,2,2-tetrachloroethane and 2 mmol Cl_2 in CCl_4 were slowly added; the solid was washed with CCl_4, then with Et_2O, dried under vacuum and stored in sealed tubes; UV. max. for $AuCl_3PPh_3$ in CH_2Cl_2: 335 nm (12970), for $AuCl_3AsPh_3$: 342.5 (12680). The majority of gold(I)-complexes are very soluble and were not isolated in the solid state except $AuXNH_3$ (X = Cl, Br, I): 0.5 mmol $[Au(MeCN)_2]ClO_4$ and 1.5 mmol Et_4NX was dissolved in MeCN, and 2 mmol NH_3 in MeCN added; the white powder was filtered under nitrogen, washed with MeCN and dried over P_2O_5 (0.01 mmHg); IR.-spectra of $AuClNH_3$: ν(N–H) sym. and asym.: 3100–3300 cm^{-1}, δ(H–N–H): 1620 (as), 1278 (sym.), $\delta_r(NH_3)$: 800, ν(Au–N): 480, ν(Au–Cl): 320 cm^{-1}. Good elemental analysis were obtained for all the reported compounds.

5.2. *Potentiometric measurements in acetonitrile.* The titrations were performed under nitrogen at 20.0 $\pm$ 0.1° and μ = 0.1 (Et_4NClO_4) using a *Metrohm* E388 compensator and the cell Au/$[Au(MeCN)_2]ClO_4$ 10^{-3} M + L + Et_3NClO_4 0.1 M/Et_4NClO_4 0.1 M/$KClO_4$, KCl/Hg_2Cl_2/Hg. The reference electrode was built with the aid of *Bravo*'s and *Iwamoto*'s data [14]. Pure gold(I)-solutions were obtained by dissolving $[Au(MeCN)_2]ClO_4$ in acetonitrile or by constant potential anodic oxidation of a gold foil in presence of Et_4NClO_4 0.1 M (*McKee Pedersen* coulometer).

The approximations used (see 3.1) are: for $V < V_1$ (1st equivalent point): $E = E^{\circ}_{Au^+/Au} + 0.058 \log [c_{Au}/(1 + V/V_1 - V)]$; for $V_1 < V < V_2$ (2nd equiv. point): $E = E^{\circ}_{Au^+/Au} + 0.058 \log K_2/K_1 + 0.058 \log [c_{Au}/(x + x^2)]$ where $x = (V - V_1)/(2V_1 - V)$; for $V > V_2$: $E = E^{\circ}_{Au^+/Au} - 0.058 \log K_1K_2 + 0.058 \log [V_1(V_0 + V)/c_L(V - 2V_1)^2]$. The constancy of the calculated potentials is shown in the example of Table 12.

Table 12. *Potentiometric titration of* $Au(MeCN)_2^+$ *by* PPh_3 (= *L*)

$V_0 = 40$ ml; $V_1 = 0.399$ ml; $c_{Au} = [Au(MeCN)_2^+]_t = 2.10^{-3}$ M; $c_L = [L]_t = 0.2007$ M

V (ml)	E (Volt)	$V/(V_1 - V) = y$	$c_{Au} = [Au(MeCN)_2^+]_t$	$E^{\circ}_{Au^+/Au}$
0.04	1.176	0.111	1.800	1.335
0.08	1.173	0.251	1.599	1.335
0.16	1.166	0.669	1.198	1.335
		$(V - 2V_1)^2 10^2 = z$	$V_1(V_0 + V)/[L_t]_2$	$E^{\circ}_{Au^+/Au} - 0.058 \log K_1K_2$
0.90	0.037	1.040	7818	−0.189
0.94	0.020	2.016	4037	−0.189
0.96	0.014	2.624	3103	−0.189
1.00	0.004	4.080	1998	−0.187

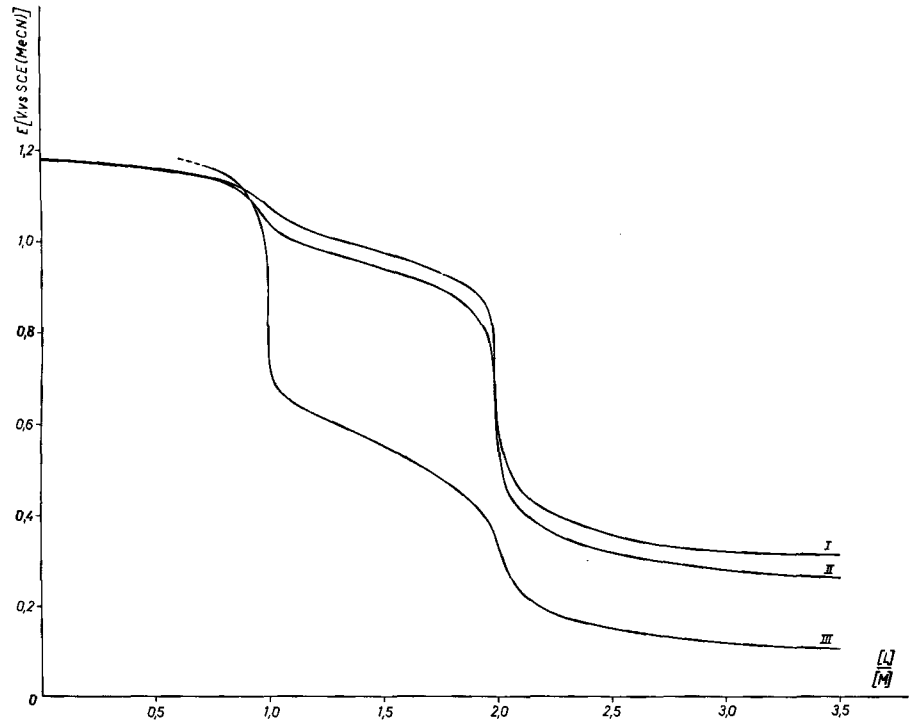


Fig. 6. *Potentiometric titration curves of* Au^+ *by* Cl^- (*I*), *Br* (*II*), *I* (*III*, *inverse titration*) *in acetonitrile at 20°,* $\mu = 0.1$ (Et_4NClO_4)

5.3. *Kinetic measurements by spectrophotometry.* We used a *Beckman* Acta V and a *Beckman* DBGT spectrophotometer with thermostated cells. The reaction $AuCl_4^- + L$ was followed by repetitive scannings or by monitoring the disappearance of one reactant at fixed wavelength. The

conversion of eq. 9–12 (see 4.3) in terms of absorbance is: $A_0-A_t/(A_t-A_\infty) = makt$ where $rom = 1$, 2, 4 for eq. 9 and 11, respectively; $1n[(b/a)(A_0-A_\infty) - m(A_0-A_t)/(b/a)(A_t-A_\infty)] = (b\text{-}ma)kt$ where $m = 1$ for eq. 10 and 2 for eq. 12.

5.4. *Stopped-flow measurements.* A *Durrum-Gibson* model D-110 stopped-flow spectrophotometer equipped with a thermostated valve block, drive syringes, and mixing chamber was used for the stopped flow measurements. Data acquisition and computation of rate constants has been described previously [16]. Pseudo-first-order rate constants, k_{ob}, were obtained with 1–2% standard deviations in almost all cases. Reproducibility of independent experiments was generally within $\pm 5\%$.

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249. Vinca Alkaloids XXXII[1]). Microbiological Conversions of Vindoline, a Major Alkaloid from *Vinca rosea* L[2])

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(30. VIII. 73)

Summary. Vindoline, a major alkaloid from *Vinca rosea* L was subjected to microbiological conversion using *Streptomyces* cultures.

Several new metabolites were isolated and their structures elucidated.

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1) Paper XXXI in this series, see [1].

2) Presented in part at the joint meeting of the American Academy of Pharmacognosy and Natural Products Section, Academy of Pharmaceutical Sciences Symposium on Biotransformations and Fermentations, Jekyll Island, Georgia, USA, July 15–20, 1973.