Kinetics and Thermodynamics of the Oxidative-addition Reaction of Iodine with the Dicyanoaurate(I) Ion in Aqueous Solution

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The equilibrium constant for the reaction $Au(CN)_2^- + I_2 \rightleftharpoons Au(CN)_2I_2^-$ has been measured. The reaction obeys the rate expression $d[Au(CN)_2I_2^-]/dt = k_2[Au(CN)_2^-][I_2] + k_2'[Au(CN)_2^-][I_3^-]$ with $k_2 = (2.8 \pm 0.2) \times 10^4$ l mol^{-1} s^{-1} and $k_2' = (4.40 \pm 0.08) \times 10^6$ l mol^{-1} s^{-1} at 25 °C and $\mu = 0.10$M, and is unusual in having $k_{I_2}/k_{I_3^-} = 0.0064$ (normally $k_{I_2}/k_{I_3^-} > 1$).

GOLD(I) usually has a co-ordination number of two whereas gold(III) is often four-co-ordinate with the ligands in a square-planar arrangement about the gold atom. Because of this difference in co-ordination number for the two oxidation states of gold, oxidation of gold(I) complexes to gold(III) by the halogens is accompanied by the incorporation of halide ions into the inner co-ordination sphere of gold(III). I.r. and Raman spectroscopic studies [1] of the products when $Au(CN)_2^-$ was oxidised by chlorine, bromine, and iodine in methanol showed that *trans*-$Au(CN)_2X_2^-$ ions were obtained [equation (1) (X = Cl, Br, or I)]. We report

$$Au(CN)_2^- + X_2 \longrightarrow trans\text{-}Au(CN)_2X_2^- \qquad (1)$$

values of the equilibrium constant for the reaction with iodine at four temperatures and the results of kinetic studies on the $Au(CN)_2^-$–I_2 and $Au(CN)_2^-$–I_3^- systems.

EXPERIMENTAL

Reagents.—All reagents were AnalaR grade except for potassium dicyanoaurate(I) (Hopkins and Williams) and sodium perchlorate (prepared by mixing AnalaR sodium hydroxide or sodium hydrogen carbonate with AnalaR perchloric acid). Potassium dicyanoaurate(I) was stored over P_2O_5 in a desiccator and then analysed for gold by decomposing the complex with warm sulphuric acid and weighing the metal; [2] the complex was found to be 99·3% pure. Standard concentrated solutions were prepared by weight; dilute solutions were estimated spectrophotometrically using extinction coefficients obtained in this work. The spectrum of $Au(CN)_2^-$ in 0·1M-$HClO_4$ was in reasonable agreement with published data: [3,4]

$\lambda_{max.}$/nm	204·3	211·1	230·2	239·7
$\varepsilon_{max.}$/ l mol^{-1} cm^{-1}	12,850 ± 104	10,230 ± 112	3663 ± 21	3441 ± 34

Sodium perchlorate solutions were analysed by passing them through a cation-exchange resin in the acid form and estimating the liberated acid by titration with standard alkali solution.

Aqueous iodine solutions (*ca.* 10^{-3}M) were prepared directly and were protected from the light. Solutions were estimated spectrophotometrically by adding a known volume to a deoxygenated solution of KI (*ca.* 1·0M) and measuring the absorption due to I_3^- at 353 nm ($\varepsilon_{max.}$ = 26,400 l mol^{-1} cm^{-1}).

Apparatus.—Preliminary kinetic results were obtained using a stopped- and continuous-flow apparatus built from a modified SP 500 spectrophotometer coupled to a chart recorder. Accurate kinetic studies were performed using a Durrum–Gibson stopped-flow spectrophotometer fitted with a Kel-F flow system and a deuterium lamp. Temperature control was ±0·05 °C.

RESULTS

Spectra of $Au(CN)_2X_2^-$ (X = Cl, Br, or I) *in Aqueous Solution.*—Solutions of $Au(CN)_2X_2^-$ were prepared from the solid compounds $KAu(CN)_2X_2,2H_2O$ and were estimated iodometrically. Consistent values for extinction co-efficients were obtained in the presence of $HClO_4$ and/or X^-. Some solutions slowly deposited AuCN, particularly in the presence of acid. A possible contribution by I_3^- to the 275 nm absorption of $Au(CN)_2I_2^-$ was excluded when identical absorbances were obtained in acid solution in the presence or absence of IO_3^-.

	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/l mol^{-1} cm^{-1}	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/l mol^{-1} cm^{-1}
$Au(CN)_2Cl_2^-$	217	21,000 ± 1000	287	960 ± 20
$Au(CN)_2Br_2^-$	241	34,000 ± 500	324	960 ± 10
$Au(CN)_2I_2^-$	275	43,100 ± 1000	380	5000 ± 200

The Equilibrium Constant for the Reaction $Au(CN)_2^- + I_2 \rightleftharpoons Au(CN)_2I_2^-$.—The equilibrium constant was determined by measuring the partition of iodine between carbon tetrachloride and water. The partition coefficient for iodine distribution between CCl_4 and water is a constant only under certain conditions and can vary very considerably with $[I_2]$, pH, and time of mixing.[5] In this work the $[I_2]$ in CCl_4 was determined spectrophotometrically ($\lambda_{max.}$ = 517 nm, $\varepsilon_{max.}$ = 930 l mol^{-1} cm^{-1}) after 2 h of shaking and was found not to vary significantly over the period used in the extrapolation described below. Partition coefficients, *P*, at four temperatures are listed in Table 1. As a check, we used these coefficients to calculate values of *K* for $I_2 + I^- \rightleftharpoons I_3^-$, from data obtained in the

TABLE 1

Equilibrium constants determined by partition for the reaction $Au(CN)_2^- + I_2 \rightleftharpoons Au(CN)_2I_2^-$. μ = 0·10M; $[H^+]$ = 0·10M

Temp./(°C)	*P*	Number of expts.	10^{-4} *K*/l mol^{-1}
5	81·6	4	2·11 ± 0·09
15	94·6	4	1·66 ± 0·06
25	81·1	9	1·33 ± 0·13
35	115·8	8	0·97 ± 0·05

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[1] L. H. Jones, *Inorg. Chem.*, 1964, **3**, 1581; 1965, **4**, 369, 1472.

[2] A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961.

[3] J. Brigando, *Bull. Soc. chim. France*, 1957, **24**, 511.

[4] C. K. Jorgensen, quoted in J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1963, **85**, 249.

[5] R. G. Wille and M. L. Good, *J. Amer. Chem. Soc.*, 1957, **79**, 1040.

presence of I^- at four temperatures, and obtained satisfactory agreement with literature values.[6]

Measurements were then made of the partition coefficient when known amounts of $KAu(CN)_2$ were dissolved in the aqueous layer. It was found that results were somewhat dependent on the duration of shaking and in some systems a precipitate of AuCN could be seen. A small correction was made for this decomposition by making measurements at several different times and obtaining an extrapolated value for zero-time which was used to calculate the equilibrium constant. The results are listed in Table 1. The plot of log K against $1/T$ was linear and yielded the values $\Delta H = -18{\cdot}0 \pm 1{\cdot}2$ kJ mol^{-1} and $\Delta S = 18{\cdot}0 \pm 1{\cdot}3$ J mol^{-1} K^{-1}.

The partition method was found to be unsuitable for measurements involving Cl_2 and Br_2. Potentiometric titrations of $Au(CN)_2^-$ solutions with Cl_2 or Br_2 solution and *vice-versa* yielded the K values: $(1{\cdot}8 \pm 0{\cdot}1) \times 10^{13}$ l mol^{-1} for $Au(CN)_2^- + Cl_2 \rightleftharpoons Au(CN)_2Cl_2^-$ and $(5{\cdot}3 \pm 0{\cdot}3) \times 10^8$ l mol^{-1} for $Au(CN)_2^- + Br_2 \rightleftharpoons Au(CN)_2Br_2^-$. The equilibrium constants, combined with literature values for the $X_2/2X^-$ (X = Cl, Br, or I) potentials, yield the following values of the half-cell potentials E^0 at 25 °C and $\mu = 0{\cdot}1$M: $Au(CN)_2I_2^- + 2e \longrightarrow Au(CN)_2^- + 2I^-$, $+0{\cdot}51$ V; $Au(CN)_2Br_2^- + 2e \longrightarrow Au(CN)_2^- + 2Br^-$, $+0{\cdot}83$ V and $Au(CN)_2Cl_2^- + 2e \longrightarrow Au(CN)_2^- + 2Cl^-$, $+1{\cdot}00$ V.

Kinetics of the Reaction $Au(CN)_2^- + I_2 \longrightarrow Au(CN)_2I_2^-$.—Detailed investigation showed that the rates of the reactions of $Au(CN)_2^-$ with Cl_2 and Br_2 were too rapid to be measured and that the dehydrolysis of halogen was rate-determining. Our results, interpreted in this way, yield third-order rate constants for the reactions $HOX + X^- + H^+ \longrightarrow H_2O + X_2$ (X = Cl or Br) which are in good agreement with published data.[7] However, it did prove possible to measure the rate of oxidation of $Au(CN)_2^-$ by iodine.

Kinetic measurements were made under conditions in which (i) the initial concentrations of iodine and $Au(CN)_2^-$ were equal and (ii) in which one reagent was present in at least a ten-fold excess over the other. When the initial concentrations were equal the data were treated using the integrated second-order expression (2) modified to take account of the fact that the reaction did not go to completion [a is the initial concentration of $Au(CN)_2^-$ and I_2^-,

$$Au(CN)_2^- + I_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} Au(CN)_2I_2^-$$

$$d[Au(CN)_2I_2^-]/dt = k_2(a - x)^2 - k_{-1}x$$

$$k_2(a^2 - x_e^2)t/x_e = 2{\cdot}303 \log x_e(a^2 - xx_e)/a^2(x_e - x) \qquad (2)$$

and x and x_e are the concentrations of $Au(CN)_2I_2^-$ at time t and at equilibrium]. Plots of log $(a^2 - xx_e)/(x_e - x)$ against time were linear to at least 70% reaction and the slopes yielded values of $k_2(a^2 - x_e^2)/2{\cdot}303x_e$ from which k_2 was calculated.

With one reagent in at least a ten-fold excess, pseudo-first-order conditions applied and the integrated first-order expression (3) (modified to take account of the equilibrium nature of the reaction) was employed:

$$d[Au(CN)_2I_2^-]/dt = k_1(a - x) - k_{-1}x$$

$$(k_1 + k_{-1})t = 2{\cdot}303 \log x_e/(x_e - x) \qquad (3)$$

Plots of log $x_e/(x_e - x)$ against time were linear to at least 75% reaction. The slopes yielded values of $(k_1 + k_{-1})$ from which k_2 was obtained using $k_2 = (k_1 + k_{-1})/b + 1/K$ and a value of K appropriate to the temperature (a and b represent the initial concentration of the reactants, with an excess of b over a). The results are listed in Tables 2 and 3.

TABLE 2

Rate constants for the $Au(CN)_2^- + I_2 \longrightarrow Au(CN)_2I_2^-$ reaction. $\mu = 0{\cdot}10$M; Temp. = 25·0 °C

$10^6[I_2]_0$ (M)	$10^6[Au(CN)_2^-]_0$ (M)	$10^6[Au(CN)_2I_2^-]_e$ (M)	$(k_1 + k_{-1})$/ s^{-1}	$10^{-4}k_2$/ l mol^{-1} s^{-1}
200	200	110		4·20
200	200	110		3·02
100	100	39·7		3·05
70	70	25·8		3·61
50	50	15·7		3·18
50	50	15·7		2·48
50	50	15·7		2·51 [a]
49	50	15·7		3·22
48	50	15·7		3·21 [a]
48	50	15·7		2·41 [a]
40	40	11·12		2·98
10·8	10·0	1·13		4·10
197·5	20·0	14·4	10·63	3·90
197·5	20·0	14·4	8·06	2·99
197·5	20·0	14·4	11·26	4·13
197·5	2·0	1·54	8·01	2·92
197·5	2·0	1·54	8·02	2·95
4·0	200	2·83	3·90	1·42
4·0	200	2·83	4·56	1·66
19·8	200	14·1	4·56	1·66

Average = 2·80 ± 0·20

$[\,]_0$ = Initial concentrations; $[\,]_e$ = calculated equilibrium concentrations.

[a] Ionic strength maintained using $NaClO_4$; $HClO_4$ used in all other runs.

TABLE 3

Rate constants for the $Au(CN)_2^- + I_2 \longrightarrow Au(CN)_2I_2^-$ reaction at different temperatures. $\mu = 0{\cdot}10$M; $[H^+] = 0{\cdot}10$M

Number of runs	Temp. (°C)	$10^{-4}k_2$/l mol^{-1} s^{-1}
10	5·0	1·09 ± 0·17
9	15·0	1·73 ± 0·32
20	25·0	2·80 ± 0·20
9	35·0	4·32 ± 0·34

Reasonably consistent values of k_2 were obtained over a very wide range of initial concentrations (initial rates varied by a factor of 400) and were measured at four temperatures. The plot of log k_2 against $1/T$ was linear; from the slope and intercept Arrhenius parameters were calculated (Table 4). Attempts to obtain a direct measurement of the rate constant for the reverse reaction, k_{-1}, were not successful (see below).

Kinetics of the Reaction $Au(CN)_2^- + I_3^- \longrightarrow Au(CN)_2I_2^- + I^-$.—We attempted to measure k_{-1} directly by preparing $Au(CN)_2I_2^-$ solutions [together with equilibrium amounts of $Au(CN)_2^-$ and I_2] and then mixing the solution with a substance X known to react rapidly with iodine [equations (4) and (5)], with the object of confirming

$$Au(CN)_2I_2^- \xrightarrow{k_{-1}} Au(CN)_2^- + I_2 \qquad (4)$$

$$I_2 + X \xrightarrow{\text{fast}} \text{Products} \qquad (5)$$

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[6] 'Stability Constants of Metal-Ion Complexes,' Special Publ. No. 17, The Chemical Society, London, 1964; *ibid.*, No. 25, 1971.

[7] M. Eigen and E. Kustin, *J. Amer. Chem. Soc.*, 1962, **84**, 1355.

our results obtained in the $Au(CN)_2^-$–I_2 study through using a simpler kinetic system in which reaction would be first order and would go to completion. We investigated a large number of possible organic compounds including phenol, aniline, dimethylaniline, allyl alcohol, phloroglucinol, m-phenylenediamine, pyrogallol, quinol, and resorcinol, but found that either $Au(CN)_2I_2^-$ reacted directly with each compound (presumably to give iodinated products), *i.e.* the observed first-order rate constant for the disappearance of $Au(CN)_2I_2^-$ depended on [X], or that the rate of reaction of I_2 with the compound was too small for reaction (4) to be rate-determining.

TABLE 4

Arrhenius parameters (25·0 °C)

Reaction	E_a / kJ mol^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}
$Au(CN)_2^- + I_2 \xrightarrow{k_2}$	33·4 ± 2·0	30·9 ± 2·0
$Au(CN)_2^- + I_2 + I^- \xrightarrow{k_3}$	9·0 ± 1·4	6·5 ± 1·4
$Au(CN)_2^- + I_3^- \xrightarrow{k_2'}$	24·4 ± 2·0	22·1 ± 2·0

Reaction	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$ / kJ mol^{-1}
$Au(CN)_2^- + I_2 \xrightarrow{k_2}$	−56·4 ± 6·6	47·8 ± 4·3
$Au(CN)_2^- + I_2 + I^- \xrightarrow{k_3}$	−41·3 ± 4·6	18·7 ± 1·3
$Au(CN)_2^- + I_3^- \xrightarrow{k_2'}$	−44·0 ± 6·3	35·2 ± 1·8

The $I_2 + I^- \longrightarrow I_3^-$ reaction is known to be very rapid and we performed some runs with $X = I^-$. Again we found that the rate of disappearance of $Au(CN)_2I_2^-$ depended on $[I^-]$ and this indicated that the rate of the forward reaction might also depend on $[I^-]$. We accordingly carried out an investigation into the effect of added iodide on the rate of the forward reaction. All runs were performed with $[Au(CN)_2^-] = [I_2]$ and second-order plots were linear to about 75% reaction. It was found that the observed second-order rate constants for the appearance of $Au(CN)_2I_2^-$ increased with increasing $[I^-]$ (Table 5). A plot was made of log $(k_{obs} - k_2)$ against log $[I^-]$ and gave a good straight line of slope 1·0 ± 0·04, the order of the catalysed reaction with respect to $[I^-]$. Therefore one can write the rate expression (6):

TABLE 5

Observed second-order rate constants for the appearance of $Au(CN)_2I_2^-$ at various iodide-ion concentrations. Temp. = 25·0 °C; μ = 0·10M; $[H^+]$ = 0·10M; $[Au(CN)_2^-]_0 = [I_2]_0 = 3{\cdot}0 \times 10^{-5}$M

$10^5[I^-]$/M	$10^{-4}k_{obs}$/l mol^{-1} s^{-1}	$10^{-4}(k_{obs} - k_2)$/ l mol^{-1} s^{-1}
0·0	3·1	0·0
0·1	3·8	0·7
0·2	4·2	1·1
0·4	4·5	1·4
0·6	5·7	2·6
0·9	7·1	4·0
1·6	9·5	6·4
2·0	11·1	8·0
3·0	13·9	10·8
4·0	17·0	13·9
6·0	22·9	19·8
7·0	26·1	23·0

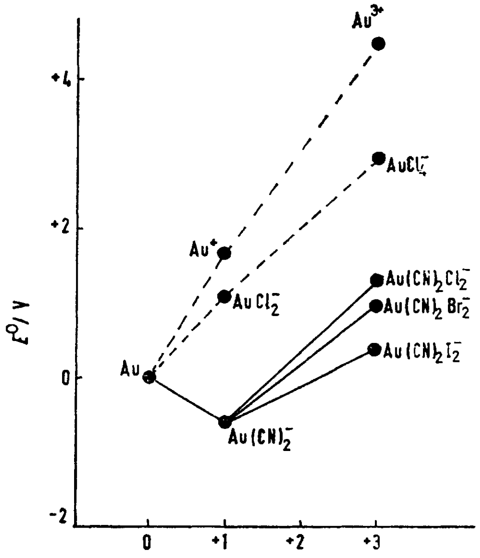
$$d[Au(CN)_2I_2^-]/dt = k_2[Au(CN)_2^-][I_2] + k_3[Au(CN)_2^-][I_2][I^-] \quad (6)$$

In view of the very low iodide ion concentrations used it is correct to assume that essentially all of the Au^I and iodine are in the forms $Au(CN)_2^-$ and I_2 rather than complexed (less than 5% of the total iodine is present as I_3^- at the highest $[I^-]$ used) and therefore a plot of k_{obs} against $[I^-]$ should be linear with an intercept of k_2 and a slope of k_3. Data obtained at four temperatures are listed in Table 6.

TABLE 6

Observed second-order rate constants at various iodide-ion concentrations and temperatures. μ = 0·10M; $[H^+]$ = 0·10M

	$10^{-4}k_{obs}$/l mol^{-1} s^{-1}			
$10^5[I^-]$/M	5 °C	15 °C	25 °C	35 °C
0	1·09	1·73	2·8	4·32
1·0	3·95	5·55	7·1	8·6
2·0	6·8	8·6	11·1	12·5
3·0	8·9	12·3	13·9	16·5
4·0	12·3	15·9	17·0	23·2
$10^{-9}k_3$/ l^2 mol^{-2} s^{-1}	2·72 ± 0·17	3·15 ± 0·22	3·25 ± 0·06	4·15 ± 0·21
$10^{-6}k_2'$/ l mol^{-1} s^{-1}	2·36 ± 0·15	3·33 ± 0·23	4·40 ± 0·08	7·03 ± 0·36



Oxidation-state diagram for gold

The values of the intercepts agreed within experimental error with the values of k_2 measured in the absence of added iodide (Table 3) and the values of the third-order rate constants (k_3) obtained are listed in Table 6. Plots of log k_2 and log k_3 against $1/T$ were linear and from the slopes and intercepts Arrhenius parameters were calculated (Table 4).

DISCUSSION

The E^0 data obtained in this work for the $Au(CN)_2X_2^- + 2e \longrightarrow Au(CN)_2^- + 2X^-$ (X = Cl, Br, or I) half-cell reactions are the first such data for mixed complexes of gold(III). The results are shown in the oxidation-state diagram together with other E^0 data from the literature.[6] The, as yet unknown, complex ion $Au(CN)_2(H_2O)_2^+$ is clearly a 'soft' acid (class b), with the equilibrium constants for the reactions $Au(CN)_2(H_2O)_2^+ + 2X^- \rightleftharpoons Au(CN)_2X_2^- + 2H_2O$ (X = Cl, Br, or I) in the order $I^- > Br^- > Cl^-$. The unusual stability conferred on Au^I by the two cyanide ligands [$Au(CN)_2^- + e \longrightarrow Au + 2CN^-$, ($E^0 = -0{\cdot}61$ V is the only Au^I–Au^0 couple to have a negative value for E^0] is maintained practically unchanged in Au^{III} complexes; the Au^{III}–Au^I potentials are very similar for ions containing only halide ions as ligands or a mixture of CN^- and X^- [$AuBr_4^- + 2e \longrightarrow AuBr_2^- + 2Br^-$, $E^0 = +0{\cdot}8$ V; $Au(CN)_2Br_2^- + 2e \longrightarrow Au(CN)_2^- + 2Br^-$, $E^0 = +0{\cdot}83$ V; $AuCl_4^- + 2e \longrightarrow AuCl_2^- + 2Cl^-$, $E^0 = +0{\cdot}93$ V; $Au(CN)_2Cl_2^- + 2e \longrightarrow Au(CN)_2^- + 2Cl^-$, $E^0 = +1{\cdot}00$ V], a result similar to that obtained[8] for $Pt(NH_3)_4X_2^{2+} + 2e \longrightarrow Pt(NH_3)_4^{2+} + 2X^-$ but not for[9] $Pt(CN)_4X_2^{2-} + 2e \longrightarrow Pt(CN)_4^{2-} + 2X^-$ compared with $PtX_6^{2-} + 2e \longrightarrow PtX_4^{2-} + 2X^-$.

The term $k_3[Au(CN)_2^-][I_2][I^-]$ in the rate expression could in principle arise from any or all of the three mechanisms (7)—(9):

$$
\begin{aligned}
&Au(CN)_2^- + I^- \overset{K_1}{\rightleftharpoons} Au(CN)_2I^{2-} \\
&Au(CN)_2I^{2-} + I_2 \xrightarrow{k_4} Au(CN)_2I_2^- + I^- \qquad (7)\\
&\text{with } k_3 = K_1k_4
\end{aligned}
$$

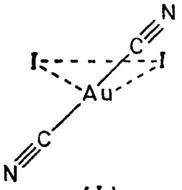
$$
\begin{aligned}
&I_2 + I^- \overset{K_2}{\rightleftharpoons} I_3^- \\
&Au(CN)_2^- + I_3^- \xrightarrow{k_2'} \\
&\qquad Au(CN)_2I_2^- + I^-, \text{ with } k_3 = K_2k'_2 \qquad (8)
\end{aligned}
$$

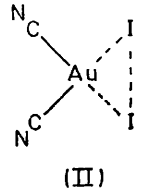
$$
\begin{aligned}
&Au(CN)_2^- + I_2 + I^- \xrightarrow{k_3} \\
&\qquad Au(CN)_2I_2^- + I^-, \text{ termolecular} \qquad (9)
\end{aligned}
$$

There is no evidence that complexes of the type $Au(CN)_2I^{2-}$ are formed in aqueous solution and this suggests that K_1 must be very small. This would require k_4 to be impossibly large in order to explain the observed catalysis (K_1 would have to exceed 10^{-1} for k_4 to be less than the collision frequency). k_3 Is probably much too big for the reaction to be termolecular so it is very probable that the I_3^- path (8) is the correct one. Using literature values[6] for K_2 we have calculated values for k_2' (Table 6) and the corresponding Arrhenius parameters are listed in Table 4.

The apparent lack of any acid dependence exhibited by the reaction (established by the data in Table 2 for reactions performed in 0·10M-$HClO_4$ and 0·10M-$NaClO_4$) suggests that $HAu(CN)_2$ and $Au(CN)_2^-$ react at similar rates with iodine. Available evidence[3,10] suggests that $HAu(CN)_2$ is a reasonably strong acid. We prepared a fresh solution of $HAu(CN)_2$ (0·01M), using a cation-exchange resin in the acid form, and titrated it with NaOH solution (0·01M). The pH of half-neutralisation was 2·35, corresponding to a dissociation constant of $4{\cdot}5 \times 10^{-3}$ mol l^{-1} for $HAu(CN)_2$. Thus $HAu(CN)_2$ will be almost entirely undissociated in $[H^+] = 0{\cdot}10$M, but extensively dissociated at concentrations of 10^{-5}M in 0·10M-$NaClO_4$.

There is no experimental evidence that suggests other than that the reaction $Au(CN)_2^- + I_2 \longrightarrow$ *trans*-$Au(CN)_2I_2^-$ proceeds in a single step. This means (*a*) that the reaction must be inner sphere, and (*b*) that the transition state for the reaction must resemble (I) with the I–I axis normal to the C–Au–C axis. An outer-sphere mechanism would yield $Au(CN)_2(H_2O)_2^+$ or $Au(CN)_2(OH)_2^-$ as immediate products while alternative transition states such as (II) or (III) would give, as intermediates, *cis*-$Au(CN)_2I_2^-$ and *trans*-$Au(CN)_2(H_2O)I$ or *trans*-$Au(CN)_2(OH)I^-$ respectively. Substitution reactions at Au^{III} are generally *not* very rapid[11] and the formation of any of these intermediates would have been detected in this work, but were not, before they were converted into the presumably thermodynamically preferred final product, *trans*-$Au(CN)_2I_2^-$.


(I)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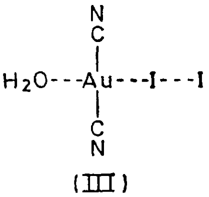
(III)

The marked catalysis of the reaction by iodide and the result derived from this, that I_3^- reacts much more rapidly than I_2 with $Au(CN)_2^-$, are unusual features of this system. Some data on the relative rates of oxidation by I_2 and I_3^- from the literature are given in Table 7, where it will be seen that commonly I_3^- reacts *less* rapidly than I_2. [The kinetic results for the oxidation of V^{III} and $Fe(CN)_6^{4-}$, and aromatic substitution for pyrroles and azulene were interpreted satisfactorily assuming that the rate for I_3^- was negligibly small

TABLE 7

Relative rates of oxidation by I_2 and I_3^-

Reaction	Species being oxidised	$k_{I_2}/k_{I_3^-}$
V^{III}–V^{IV}	VOH^{2+}	>1000? [a]
Fe^{II}–Fe^{III}	$Fe(CN)_6^{4-}$	>1000? [b]
Aromatic substitution		>1000? [c]
Ti^{III}–Ti^{IV}	$TiOH^{2+}$	600 [d]
As^{III}–As^V	$H_2AsO_3^-$	31 [e]
Fe^{II}–Fe^{III}	Fe^{2+}	0·63 [f]
Au^I–Au^{III}	$Au(CN)_2^-$	0·0064 [g]

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compared with that for I_2. We interpret this conservatively as implying a difference in rates of at least a factor of 10^3.] The unusual result obtained with $Au(CN)_2^-$ may originate from the fact that oxidative addition rather than oxidation is taking place (with the other inorganic systems in Table 7 it is likely that iodide is *not* complexed in the product, even temporarily) and therefore the size of the oxidant may be important. The I_3^- ion is, of course, much longer than the I_2 molecule and the two terminal atoms could more easily bond to gold in the transition state required by the *trans*-product. Alternatively, neighbouring iodine atoms in I_3^- could bond to gold in the transition state more readily because the I–I distance is somewhat greater in I_3^- than in I_2 (2·91 and 2·68 Å respectively) and the I–I bond is somewhat weaker. It appears from the results that this dimensional effect more than outweighs the expected kinetic consequences of I_3^- being a slightly less powerful oxidising agent than I_2, thermodynamically.

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