# Electrochemical Study of the Heterogeneously Catalysed Reaction between N,N-Dimethyl-p-phenylenediamine and Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> at Monometallic and Bimetallic Surfaces of Silver and Gold

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The mechanism of the heterogeneously catalysed reaction between N,N-dimethyl-p-phenylenediamine and Co<sup>111</sup>(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> at silver, gold and silver-on-gold (Ag/Au) discs has been studied by means of electrochemical methods. Both the mixed (or mixture) potentials and the mixture currents were determined by recording the current–potential curves of the reactants. Silver halide, formed during the reaction, was determined by sub-sequent galvanostatic reduction. The reaction at silver was strongly inhibited by the formation of silver halide whereas the reaction at gold was inhibited by adsorption of the organic compounds as well as by iodide. At Ag/Au discs almost no inhibition occurred. The explanation is that the reduction of the cobalt complex takes place predominantly at the silver surface whereas the simultaneous oxidation of the p-phenylenediamine occurs on the gold. In this way the formation of inhibiting silver halide is suppressed as well as the inhibition caused by the adsorption of p-phenylenediamine.

In a heterogeneously catalysed redox reaction between an oxidant (Ox) and a reductant (Red), the metal acts as a conductor of electrons from Red to Ox. In contrast to normal heterogeneous reactions, no direct contact of the reactants at the surface of the metal need take place.<sup>1-4</sup> Contrary to electrochemical reactions no external power supply is necessary to cause the transfer of electrons through the metal/solution interface. The general mechanism of reactions of this kind is schematically displayed in Fig. 1.

A suitable model system to study both the kinetics and the mechanism of such catalytic reactions is the oxidation of N,N-dimethyl-*p*-phenylenediamine (PPD) by Co<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup>. This reaction has been thoroughly studied by taking as catalyst silver and gold discs as well as the colloids of these noble metals.<sup>1-5</sup> The reaction occurs irreversibly because of the rapid hydrolysis of the reduced cobalt complex.<sup>5</sup> The first oxidation product of PPD is *p*-semiquinonediimine (SQDI<sup>+</sup>), an intensely coloured ion radical. SQDI<sup>+</sup> may give *p*-quinonediimine (QDI<sup>+</sup>) either by further oxidation or by disproportionation.<sup>6,7</sup> The most important redox reactions are summarized in Scheme 1.

Experiments carried out with both noble metal colloids and large noble metal discs have shown that silver is a better catalyst than gold,<sup>5,8</sup> but at the surface of silver the reduction of  $Co^{III}(NH_3)_5Cl^{2+}$  was found to become inhibited because of the oxidative formation of silver chloride.<sup>3,9,10</sup> Chloride released from the reduced cobalt complex according to eqn. (4) was usually sufficient to slow down the reaction rate considerably. This silver halide formation corresponds to the photographic bleaching process. On the other hand, silver



Fig. 1 Schematic representation of the mechanism by which a noble metal catalyses a redox reaction

chloride could be partially or completely reduced by *p*phenylenediamines, a reaction which is used to develop photographic material. This process, too, depends on the kind and concentration of halide ions  $(X^-)$  present in the solution. Scheme 2 summarizes the most important reactions responsible for both the formation and the reduction of silver halide on the surface of silver.

The higher the concentration of halide ions the more easily does silver halide formation occur.<sup>1,9</sup> Owing to the different solubility products, bromide is more effective than chloride but less than iodide. On the other hand, the reduction of silver halide becomes more difficult with increasing concen-

$$PPD + Co^{II}(NH_3)_5 Cl^{2+} \xrightarrow{\text{noble metal}} SQDI^+ + Co^{II}(NH_3)_5 Cl^+$$
(1)

$$SQDI^{+} + Co^{II}(NH_3)_5Cl^{2+} \xrightarrow{\text{noble metal}} QDI^{+} + Co^{II}(NH_3)_5Cl^{+} + H^{+}$$
(2)

$$PPD + QDI^+ + H^+ \longrightarrow 2SQDI^+$$
(3)

$$\operatorname{Co}^{II}(\mathrm{NH}_3)_5\mathrm{Cl}^+ \longrightarrow \operatorname{Co}^{II}_{aq} + 5\mathrm{NH}_3 + \mathrm{Cl}^-$$
 (4)

$$Ag^{0} + Co^{II}(NH_{3})_{5}Cl^{2+} \longrightarrow Ag^{+} + Co^{II}(NH_{3})_{5}Cl^{+}$$
 (5)

$$Ag^+ + X^- \longrightarrow AgX$$
 (6)

$$AgX + PPD \longrightarrow Ag^{o} + SQDI^{+} + X^{-}$$
 (7)

Scheme 2

tration of halide ions. Iodide disturbs more than bromide and much more than chloride. The addition of halide ions therefore strongly influences the silver-electrocatalysed reaction between N,N-dimethyl-*p*-phenylenediamine and  $Co^{II}(NH_3)_5Cl^{2+,1}$ 

The gold-catalysed reaction should not be influenced by the addition of halide ions because no insoluble gold salts are formed. However, with iodide an inhibition due to the adsorption of iodide at gold was found.<sup>8,11</sup> This effect has also been observed with related catalytic systems.<sup>12,13</sup>

Experiments carried out recently with a mixture of silver and gold colloids have shown a superadditive effect.<sup>8</sup> Under certain conditions the inhibition could be almost completely suppressed. In order to obtain more information about the mechanism of reactions of this kind, the oxidation of N,Ndimethyl-*p*-phenylenediamine with Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> has now been investigated by using metal discs. This paper deals with electrochemical studies on both the chemical and the electrochemical formation of silver halide at silver and Ag/Au discs. The formation of the silver salt was studied indirectly by subsequent electrochemical reduction.<sup>1,9</sup> The experimental results were compared with the data obtained from the current–potential curves of the reactants and discussed in terms of the theory of mixture potential and mixture current.<sup>4,14</sup>

#### Experimental

Rotating silver and gold discs of 4 mm diameter were taken for the study of both the oxidative formation of silver halide and the recording of the current-potential curves of N,Ndimethyl-p-phenylenediamine and [Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>. The silver halide was formed either electrochemically or chemically with the cobalt complex. The discs were carefully polished for at least 1 min with 0.25 µm diamond paste before each experiment and then thoroughly washed with water. Usually a rotation speed of 800 rpm was chosen. The zerocurrent potential was measured against a calomel reference electrode (0.1 mol dm<sup>-3</sup> KCl). The Luggin capillary was filled with 0.1 mol dm<sup>-3</sup> KNO<sub>3</sub>. The silver halide formed on the disc by chemical oxidation with [Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> was determined by subsequent galvanostatic reduction,<sup>1,9</sup> taking the disc as a cathode in an electrochemical cell with a platinum counter-electrode and a calomel reference electrode (0.1 mol dm<sup>-3</sup> KCl). Usually 0.1 mol dm<sup>-3</sup> KNO<sub>3</sub> + 0.01 mol dm<sup>-3</sup> KCl was chosen as electrolyte in an electrochemical cell. The current-potential curves for both the oxidation of N,N-dimethyl-p-phenylenediamine and the reduction of  $Co^{III}(NH_3)_5Cl^{2+}$  were recorded in the same electrochemical cell, the noble metal discs being taken as either anode or cathode, as appropriate.

Ag/Au discs were prepared by inserting the gold disc as cathode into a solution of 0.001 mol dm<sup>-3</sup> AgNO<sub>3</sub> and applying a current of  $-100 \,\mu\text{A}$  for 0.5, 1, 2, 5 or 10 s. Thus, a total charge of 0.05 mC up to 1.00 mC was passed. A simple calculation shows that 0.10 mC deposits  $6.2 \times 10^{14}$  silver atoms which corresponds to about three silver monolayers on the disc of 4 mm diameter. The thickness of a monolayer is about 0.288 nm according to the diameter of silver.<sup>15</sup>

The electrochemical measurements were performed with the potentiostat-galvanostat HEKA PG 284.

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The N,N-dimethyl-p-phenylenediamine  $\cdot$  2HCl, the halides and the buffer substances Na<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> were p.a. reagents from Merck. The cobalt complex [Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> was synthesized according to Schlessinger.<sup>16</sup> All solutions were prepared with doubly distilled water which had been degassed by ultrasound under water jet-pump vacuum and saturated with nitrogen. The phosphate buffers were prepared according to Sørensen, but diluted 1 : 2 with water in order to avoid the formation of silver phosphate. All experiments were carried out under an argon atmosphere at 20 °C.

## **Results and Discussion**

# Experiments with Silver and Gold Discs

Fig. 2 shows some current-potential curves for the electrochemical oxidation of N,N-dimethyl-p-phenylenediamine. All curves of this kind were recorded at the gold disc in order to avoid any disturbance because of the formation of silver oxide. For comparison the measurements were also carried out at a glassy carbon electrode. Almost the same results were obtained. The position of the curves depended on the pH. With increasing pH the curves were shifted to more negative potentials until a limiting value was obtained which is near the first protonation constant of N,N-dimethyl-pphenylenediamine (pK = 6.3).<sup>17</sup> The insert figure shows the pH dependence of the half-wave potential.<sup>18</sup>

Fig. 2 also shows several current-potential curves for the electrochemical reduction of  $[Co^{III}(NH_3)_5Cl]Cl_2$ . The results recorded at the silver disc electrode are indicated by 'S', while those obtained at the gold disc electrode are designated with 'G'. The position of these curves does not depend on the pH but does depend strongly on the kind of electrode material and on the kind and concentration of added halide ions. The higher the concentration of a given halide the more the curves shift cathodically. It is obvious that with silver as electrode the formation of silver halide is responsible for this shift.

The electrochemical reactions for both the reversible oxidation of PPD and the reduction of  $\text{Co}^{III}(\text{NH}_3)_5 \text{Cl}^{2+}$  are summarized in Scheme 3.

$$PPD \longrightarrow SQDI^+ + e^- \qquad (8a)$$

(8b)

 $SQDI^+ \longrightarrow QDI^+ + e^-$ 

$$\operatorname{Co^{III}(NH_3)_5Cl^{2+}} + e^{-} \longrightarrow \operatorname{Co^{II}(NH_3)_5Cl^+}$$
 (9)



Fig. 2 Current-potential curves of both N,N-dimethyl-p-phenylenediamine  $(5 \times 10^{-4} \text{ mol } \text{dm}^{-3})$  at three different pHs and  $\text{Co}^{III}(\text{NH}_3)_5\text{Cl}^{2+}$   $(5 \times 10^{-4} \text{ mol } \text{dm}^{-3})$  at pH 6.0 in the presence of the additional halide on a rotating silver disc (S1–S4) or a rotating gold disc (G1–G4); 800 rpm, scan rate 10 mV s<sup>-1</sup>; (—) no additional halide;  $(-\cdot -) 0.1 \text{ mol } \text{dm}^{-3} \text{ KCl}$ ;  $(---) 10^{-3} \text{ mol } \text{dm}^{-3} \text{ KBr}$ ;  $(\cdot \cdots \cdot) 10^{-3} \text{ mol } \text{dm}^{-3} \text{ KI}$ . (a) pH 4.5, (b) pH 5.6, (c) pH 7.0.

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Addition of eqn. (8a) and (9) gives eqn. (1) in Scheme 1, while addition of eqn. (8b) and (9) gives eqn. (2). The reactions (8) and (9) also take place at the surface of the noble metal in the absence of an external power supply if both redox couples are present in the solution together. The noble metal surface then takes up a mixed or mixture potential ( $E_{mix}$ ) so that it can act simultaneously as an anode for couple (8) and as a cathode for couple (9). An example is shown in Fig. 2. The mixture potential should not be confused with the zero-current potential which is measured for a single redox system.

At  $E_{mix}$  the net current is zero, owing to a balance between the anodic current resulting from the oxidation of PPD and the cathodic current produced by the reduction of Co<sup>III</sup>. These two currents, termed mixture currents ( $I_{mix}$ ), are indicated by dashed vertical lines in Fig. 2. By Faraday's law,  $I_{mix}$ is directly proportional to the reaction rate at the surface ( $v_{cat}$ /mol m<sup>-2</sup> s<sup>-1</sup>) and is given by eqn. (I):<sup>2,14,19</sup>

$$v_{\rm cat} = I_{\rm mix}/nFA \tag{I}$$

where F is the Faraday constant, n the number of electrons and A the surface area of the catalyst (in m<sup>2</sup>). As long as the initial concentration of PPD exceeds that of the cobalt(III) complex the mixture current is likely to be in the region of the limiting current of  $Co^{III}(NH_3)_5Cl^{2+}$ . Under these conditions the kinetics were consistent with diffusion control, and both the mixture current and the measured reaction rate were proportional to the  $[Co^{III}(NH_3)_5Cl]^{2+}$  concentration but independent of the concentration of N,N-dimethyl-p-phenylenediamine. The heterogeneous reaction rate at both silver and gold discs is then given by eqn. (II):<sup>2.5</sup>

$$v_{\text{sat}} = k_{\text{het}} [\text{Co}^{\text{III}} (\text{NH}_3)_5 \text{Cl}^{2+}]$$
 (II)

The curves displayed in Fig. 2 clearly show that the mixture current, and thus the heterogeneous reaction rate constant  $(k_{hel}/m \text{ s}^{-1})$ , depends on several factors. Most important is the kind of noble metal used as catalyst but also the kind and concentration of halide can strongly influence the position of the mixture potential and the value of the mixture current. Some values of the mixture potential and the mixture current, calculated from current–potential curves, are listed in Table 1.

For the system presented in Fig. 2, the maximum mixture current and therefore the maximum reaction rate were obtained with the gold disc at pH > 4.5 (as can be seen by comparing the lengths of the dashed vertical lines). At the silver disc this reaction rate was obtained only at pH  $\ge$  7 and in the absence of additional halide ions. The initial reaction rate, however, was high also at a lower pH. The decrease of the reaction rate, *i.e.* the amount of inhibition, was found to depend on the relative position of the current-potential curves of PPD,  $\operatorname{Co}^{II}(\mathrm{NH}_3)_5 \mathrm{Cl}^{2+}$  and silver halide.

The shift of the current-potential curves S1-S4 to more negative potentials is caused by the formation of silver halide. Inspection of the curve S1 in Fig. 2 shows that in the absence 619

of additional halide ions the formation of silver chloride began at about +100 mV (vs. 0.1 mol dm<sup>-3</sup> calomel electrode). The necessary chloride ions were provided by the counter-ions of the salts employed. As at pH > 7 the mixture potential of the p-phenylenediamine and cobalt complex redox couples was considerably more negative, almost no inhibition occurred, but in the presence of additional halide the shift of the current-potential curve of  $Co^{III}(NH_3)_5 Cl^{2+}$  to more negative potentials caused a dramatic decrease of the mixture current (cf. Table 1). The more negative the resulting mixture potential, the more difficult was the reduction of silver halide by PPD, because the mixture current for this catalytic process also became very small. In the presence of iodide the mixture current becomes zero. Indeed, the small amount of oxidized p-phenylenediamine present in the solution was then able to oxidize silver! Particularly strong inhibition of the silver-catalysed reaction between PPD and  $Co^{III}(NH_3)_5 Cl^{2+}$  took place at low pH (because of the positive shift of the current-potential curve of the p-phenylenediamine), in the presence of a high concentration of chloride (shifting the current-potential curve of the cobalt complex to more negative potentials due to the formation of silver halide), and even more so in the presence of bromide and iodide (which shifted the cathodic current-potential curve to still more negative positions).

The influence of additional halide on the current-potential curves of  $\text{Co}^{III}(\text{NH}_3)_5\text{Cl}^{2+}$  recorded at a gold disc electrode is also displayed in Fig. 2 (curves G1-G4). In contrast to silver, the mixture current was not decreased by the addition of chloride and bromide, because  $E_{\text{mix}}$  remained in the region of the limiting current for  $\text{Co}^{III}(\text{NH}_3)_5\text{Cl}^{2+}$  except when the pH became lower than 4 (see also Table 1). However, as with the silver curve S4, the mixture current decreased strongly in the presence of iodide (curve G4). This was probably caused by inhibition of the electron transfer by adsorption of iodide on the surface of gold.<sup>11,13,20</sup> The desorption of iodide only occurred at a rather negative potential.

However, not only iodide but also N,N-dimethyl-p-phenylenediamine itself and its oxidation products inhibited the catalysis due to an adsorption effect.<sup>21</sup> The current-potential curves G2 and G3 in Fig. 3 show the strong shift of curve G1 to more negative positions after a short treatment of the gold disc with the solution of the p-phenylenediamine. The corresponding values of  $E_{mix}$  and  $I_{mix}$  obtained from these curves are summarized in Table 2 (left-hand column). The curves SG refer to Ag/Au experiments and will be discussed later. Because of the decrease of the mixture current the rate of the catalytic reaction between N,N-dimethyl-p-phenylenediamine and Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> should also decrease. In fact, this decrease was found both at large gold discs and with colloids.<sup>2,8</sup> In the absence of additional halide and at pH > 5the reaction rate between PPD and Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> was usually considerably slower on the surface of gold than on the surface of silver.2,8

**Table 1** Values of  $E_{\text{mix}}$  and  $I_{\text{mix}}$  under different pH conditions and with additional halide ( $[Co^{III}]_0 = 0.5 \text{ mmol dm}^{-3}$  and  $[PPD]_0 = 0.5 \text{ mmol dm}^{-3}$  at 800 rpm)

pН	[KCl]/mol dm <sup>-3</sup>	[KBr]/mmol dm <sup>-3</sup>	[KI]/mmol dm <sup>-3</sup>	Ag disc		Au disc	
				$E_{mix}/mV$	I <sub>mix</sub> /μA	$E_{mix}/mV$	I <sub>mix</sub> /μA
4.5				95	4	210	28
5.6				90	15	140	28
7.0	_			65	28	65	28
6.0				90	25	90	25
6.0	0.1			-20	5	90	25
6.0		1.0		- 50	4	90	25
6.0	—	_	1.0	none	0	-85	2

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Fig. 3 Influence of the adsorption of N,N-dimethyl-p-phenylenediamine on the mixture current of the redox system N,N-dimethyl-pphenylenediamine  $(5 \times 10^{-4} \text{ mol dm}^{-3})$ -Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>) at pH 6.0 on a rotating Au disc (G1-G3) and a rotating Ag/Au disc (SG1-SG3); 800 rpm, scan rate 10 mV s<sup>-1</sup>. The Ag/Au disc was obtained by inserting a gold disc into a solution of 10<sup>-3</sup> mol dm<sup>-3</sup> AgNO<sub>3</sub> and galvanostatically reducing it for 10 s at -100 µA. Both Au and Ag/Au discs were pretreated with 0.1 mol dm<sup>-3</sup> PPD for 0 s (full lines, G1 and SG1), 10 s (dashed lines, G2 and SG2) and 30 s (dotted lines G3 and SG3), respectively.

## Experiments with Ag/Au Discs

4 shows some current-potential curves for Fig. [Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> recorded at several Ag/Au disc electrodes. At very negative potentials only the reduction of the cobalt complex took place, but when the potential became more positive, a parallel reaction set in: the oxidative formation of silver chloride. Thus, the cathodic current decreased or the net current even became anodic. Because of the limited amount of silver deposited on the gold disc this oxidative formation of silver chloride stopped when all the silver had been transformed into silver chloride. As the potential rose still further, the only electrode process was again the reduction of the cobalt complex. The more silver had been deposited on the gold disc electrode, the higher was the resulting anodic peak. The amount of AgCl could be determined from the total area of each peak in these curves; it was proportional to the amount of silver deposited on gold (see insert in Fig. 4), but independent of the concentration of chloride present in the solution or released from the cobalt complex. This is shown by the dashed curve, which corresponds to the conditions of Fig. 4, curve 2, but was recorded in the presence of  $0.1 \text{ mol dm}^{-3}$  KCl. The addition of chloride only shifted the peak cathodically, i.e. the formation of silver chloride began at a lower potential.

As the formed silver chloride is porous,<sup>10</sup> the deposition of AgCl on the gold disc decreased the limiting current  $(I_{\min})$  for the reduction of Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> only a little. In spite of a

Table 2 Values of  $E_{mix}$  and  $I_{mix}$  obtained from the current-potential curves displayed in Fig. 3

	Au	tisc	Ag/Au disc		
$\tau^a/s$	$E_{mix}/mV$	$I_{\rm mix}/\mu A$	$E_{\rm mix}/{\rm mV}$	$I_{mix}/\mu A$	
none	90	25	90	25	
10	0	6	90	25	
30	-40	3	50	20	

Discs were pretreated with 0.1 mol dm<sup>-3</sup> N,N-dimethyl-p-phenylenediamine (PPD) at pH 6. "  $\tau$  is the pretreatment time of the disc with PPD.



**Fig. 4** Influence of both the amount of deposited silver and the addition of chloride ion on the electrochemical reduction of  $Co^{III}(NH_3)_5Cl^{2+}$  (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>) at pH 5.6 on Ag/Au discs rotating at 800 rpm, scan rate 10 mV s<sup>-1</sup>. The amounts of silver deposited on gold discs 1–3 were 0.05, 0.10 and 0.20 mC, respectively. (----) No additional halide; (---) 0.1 mol dm<sup>-3</sup> KCl (with 0.10 mC silver on the Ag/Au disc). Insert: Dependence of the AgCl formed ( $Q_{AgCl}$ ) on the amount of silver ( $Q_{Ag}$ ) obtained from curves 1–3.  $Q_{AgCl}$  was calculated from the total areas of the corresponding peaks.

thin silver chloride layer, the electrocatalytic reaction between PPD and  $Co^{III}(NH_3)_5Cl^{2+}$  can therefore remain diffusion-controlled. The limiting current which under certain conditions (*e.g.* at pH > 5 and with an excess of PPD) equals the mixture current (see Fig. 2) is given by the relation (III)

$$I_{\rm lim} = nFD_{\rm Co} A[{\rm Co}^{\rm III}({\rm NH}_3)_5 {\rm Cl}^{2+}]/\delta$$
(III)

where  $D_{Co}$  (in m<sup>2</sup> s<sup>-1</sup>) is the tracer diffusion coefficient of the cobalt complex in the phosphate buffer and  $[Co^{III}(NH_3)_5Cl^{2+}]$  is the concentration of the cobalt complex in the bulk. At a rotated disc the diffusion layer thickness  $\delta$  (in m) is given by the Levich equation:<sup>22</sup>

$$\delta = 0.643 D_{\rm Co}^{1/3} v^{1/6} f^{-1/2} \tag{IV}$$

where v is the kinematic viscosity of the solution (in aqueous solution *ca.*  $10^{-6}$  m<sup>2</sup> s<sup>-1</sup>) and *f* is the rotation frequency of the disc (in s<sup>-1</sup>).

Fig. 5 shows some examples for the dependence of the limiting current  $(I_{lim})$  on the square root of the rotation frequency (f) for the reduction of Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> at an Ag/Au disc. The value of the diffusion coefficient  $(D_{Co})$  was obtained



Fig. 5 Dependence of the limiting current  $(I_{\rm lim})$  at two potentials on the speed of rotation of a rotating Ag/Au disc for the reduction of  $\rm Co^{III}(NH_3)_5 Cl^{2+}$  (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>) at pH 5.6; scan rate 10 mV s<sup>-1</sup>. The amount of silver deposited on the gold disc was 0.10 mC. (a) 400, (b) 800 and (c) 2000 rpm.

from eqn. (III), taking  $I_{\rm lim}$  at -100 and and +220 mV, respectively (indicated by the dashed line). At -100 mV a value of  $D_{\rm Co} = 7.16 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup> was obtained, and at +220 mV the slightly lower value of  $6.63 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>. The first value corresponds very well to the values obtained in previous papers in the absence of any phosphate buffer  $(7.24 \times 10^{-10}$  m<sup>2</sup> s<sup>-110</sup> and  $7.30 \times 10^{-10}$  m<sup>2</sup> s<sup>-19</sup>). As the diffusion coefficient should not depend on the potential of the electrode in this potential range, it can be assumed that the electron transfer through the interface of Ag/Au and of AgCl/Au is similar to that through the surface of pure silver or gold<sup>2.9</sup> and that the deviation in the value of  $D_{\rm Co}$  is only caused by a slight decrease of the active surface area of the disc.

Similar results were obtained when the concentration of  $[Co^{III}(NH_3)_5Cl]Cl_2$  was varied between 0.2 and 0.5 mmol dm<sup>-3</sup>. The amount of electrochemically formed AgCl did not depend on the concentration of  $[Co^{III}(NH_3)_5Cl]Cl_2$ , but only on the amount of silver deposited on the surface of gold. In accordance with eqn. (III), the limiting current was proportional to the concentration of the cobalt complex.

By combining eqn. (I) and (II), the rate constant  $k_{het}/m \text{ s}^{-1}$  could be calculated:

$$k_{\rm het} = I_{\rm mix} / \{ nFA [\operatorname{Co}(\mathrm{NH}_3)_5 \mathrm{Cl}^{2+}] \}$$
 (V)

A value of  $k_{het} = 5.0 \times 10^{-5}$  m s<sup>-1</sup> was obtained. This value is somewhat higher than that of  $3.6 \times 10^{-5}$  m s<sup>-1</sup> reported previously.<sup>2</sup> The difference can be explained by the slightly higher value of the mixture current obtained at the Ag/Au disc, because it more closely approached the limiting current for the reduction of the cobalt complex. It should be mentioned, however, that this value is obtained only if the mixture current equals the limiting current of the cobalt complex reduction, *i.e.* in the presence of an excess of PPD.

Fig. 6 shows some current-potential curves for the

(b)

0.6

0.2

٥

0.2 0.4 0.6 0

 $Q_{Ag}/mC$ 

200

Ě 0.4

O<sub>AgCI</sub>

0

(a)

600

200

400

678

400

/m/



7

-200

reduction of silver chloride deposited on an Ag/Au disc and for comparison the current-potential curves for the oxidation of N,N-dimethyl-p-phenylenediamine at two different pH values. The silver had been deposited on the gold disc galvanostatically as described above and the silver chloride was formed by subsequent chemical oxidation of the silver with  $Co^{III}(NH_3)_5Cl^{2+}$ . The more silver had been deposited, the more silver chloride could be formed during the chemical oxidation, but as the oxidation time was kept constant at 15 s, any large amount of silver deposited on the gold disc could not be completely converted into silver chloride. In order to avoid any dissolution of the silver chloride formed, the Au/ Ag/AgCl disc was then rinsed with water containing  $10^{-3}$ mol dm<sup>-3</sup> potassium chloride. The current-potential curves were carried out in a cathodic direction, starting from the zero-current potential. It can be seen from the insert figure that the zero-current potential depended on the amount of silver deposited on the surface of gold.

The silver chloride formed on the Ag/Au discs was determined from the total area of the cathodic peaks in Fig. 6. When only a small amount of silver had been deposited on the surface of the gold, the silver was almost completely converted into silver chloride by the subsequent chemical oxidation. Under this condition, the activity of the residual silver  $(a_{Ag})$  was much smaller than unity because of the dominant gold surface. If, however, a relatively large amount of silver had been deposited, so that the silver had not been completely converted into silver chloride, the activity of the silver could approach the value for pure silver, *i.e.*  $a_{Ag} \approx 1$ . Assuming the validity of the Nernst equation for this gold/ silver/silver chloride electrode, the zero-current potential  $(E_{Ag/Ag^+})$  is given by

$$E_{\mathbf{Ag}^{0}/\mathbf{Ag}^{+}} = E_{\mathbf{Ag}^{0}/\mathbf{Ag}^{+}}^{\circ} + \frac{RT}{F} \ln \frac{a_{\mathbf{Ag}^{+}}}{a_{\mathbf{Ag}^{0}}}$$
(VIa)  
$$= E_{\mathbf{Ag}^{0}/\mathbf{Ag}^{+}}^{\circ} + \frac{RT}{F} \ln L_{\mathbf{Ag}\mathbf{X}}$$
$$- \frac{RT}{F} \ln a_{\mathbf{Ag}^{0}} - \frac{RT}{F} \ln a_{\mathbf{X}^{-}}$$
(VIb)

where R is the gas constant, T the temperature in K and  $L_{AgX}$  the solubility product of AgX. The zero-current potential,  $E_{Ag^0/Ag^+}$ , at the Ag/Au disc can therefore be much more positive than at the surface of pure silver if the amount of silver is very small. In fact, the insert in Fig. 6 shows a strong dependence of the zero-current potential on the amount of silver deposited on gold. The points 1-4 correspond to the situation where the chemical oxidation time was sufficient to convert almost all the silver into silver chloride. The points 6-8 refer to the situation where the oxidation time was not sufficient to convert all the silver into silver chloride.

Although the zero-current potentials for runs 1-4 are strongly shifted to more positive values, the peaks in the current-potential curves are shifted much less. Nevertheless, the shift can be sufficient to allow reduction of silver chloride by PPD even at a relatively low pH. Fig. 6 shows that at pH 4.5 a mixture current is possible for experiments 1-3, but not for experiment 7. Therefore, at suitable Ag/Au surfaces the formation of silver chloride can be prevented in the presence of PPD as long as the pH is not too low.

The influence of the kind and amount of halide ion in solution on the position of the half-wave potentials  $(E_{1/2})$  of the  $Co^{III}(NH_3)_5Cl^{2+}$  reduction curves is demonstrated in Fig. 7. The full-line curves were recorded at a silver disc and the dashed-line curves at an Ag/Au disc. All sweeps were carried out in the anodic direction, as in Fig. 4. Numbers 2 and 3 refer to experiments in which small concentrations of

→ / anod/μA

I<sub>cath</sub>/μA ←

20

-20

-40

-60

-80

-100

-400

**Table 3**  $E_{1/2}$  values of 0.5 mmol dm<sup>-3</sup> Co<sup>III</sup> in the presence of halide at pH 5.6 obtained at a silver, a gold and an Ag/Au disc (with 1.00 mC of silver deposited on it)

	[KBr]/mmol dm <sup>-3</sup>	[KI]/mmol dm <sup>-3</sup>		$E_{1/2}/\mathrm{mV}$	
[KCl]/mol dm <sup>-3</sup>			Ag	Au	Ag/Au
			100	330	110, 150, 350
0.1	_		-10	290	10, 40, 250
	1.0		- 50	280	-20, 20, 200
		1.0	-250	150	-240



Fig. 7 Current-potential curves of  $Co^{III}(NH_3)_5Cl^{2+}$  (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>) at pH 5.6 on both Ag (----) and Ag/Au (---) discs in the presence of halide; scan rate of 10 mV s<sup>-1</sup>; 1, no additional halide; 2, 10<sup>-3</sup> mol dm<sup>-3</sup> KBr; 3, 10<sup>-3</sup> mol dm<sup>-3</sup> KI.

bromide and iodide were added to the solution. The amount of silver bromide formed depended on the amount of silver deposited on the surface of gold, but it was independent of the concentration of bromide in the solution. The same was true for iodide. Some values of  $E_{1/2}$  are listed in Table 3. These results can be explained with eqn. (VI) taking  $a_{Ag} < 1$ at the Ag/Au disc. The potential was shifted to a more negative value at an Ag/AgBr disc than at an Ag/Au/AgBr disc. Therefore, as with the results obtained with chloride, the reduction of silver bromide occurred more easily on the Ag/Au interface than on the surface of pure silver.

As mentioned in the previous section, strong inhibition of the  $Co^{III}(NH_3)_5 Cl^{2+}$  reduction occurred at the gold electrode after treating it with a solution of PPD (cf. the currentpotential curves G2 and G3 in Fig. 3). At an Ag/Au electrode, however, no inhibition of this kind was observed after pretreating it with N,N-dimethyl-p-phenylenediamine. The curves SG1-SG3 in Fig. 3 are similar to those displayed in Fig. 4 and 5; only the amount of silver chloride formed subsequently decreased a little. Inhibition due to the adsorption of PPD was avoided because of the rapid reduction of  $Co^{III}(NH_3)_5 Cl^{2+}$  at the silver surface and the simultaneous oxidation of PPD adsorbed at gold. This reaction began immediately after the addition of the cobalt complex and before recording of the current-potential curves. Thus, compared with the situation at pure gold discs, a less negative shift of the potential occurred and as a result the mixture current was greater. Some results are summarized in the right-hand column of Table 2.

It is clear from the above results that Ag/Au discs display different and catalytically useful properties compared with those of pure silver or gold discs. The introduction of a foreign metal into a metallic catalyst is a well established procedure for modifying surface electronic and geometric structures in order to manipulate catalytic selectivity.<sup>13,23</sup> Usually the electrocatalytic properties of the bimetallic interfaces are strongly dependent on the relative strengths of the interaction between the reactant and the individual components of the mixed-metal surface.<sup>24–26</sup> Silver and gold have very similar physical properties (e.g. similar atomic radius and lattice structure).<sup>15,25</sup> The experiments described above have shown that deposition of silver on the surface of gold resulted in a superadditive or synergistic effect. The reduction of  $Co^{III}(NH_3)_5Cl^{2+}$  occurred more rapidly at the surface of silver than at gold while the silver halide, formed according to eqn. (6), could be continuously reduced because PPD could inject electrons into the catalyst at the free surface of gold. The noble metal acting in reactions (1) and (2) is therefore predominantly silver, whereas the noble metal acting in reaction (7) is gold. The evidence obtained in the present paper thus explains why the inhibition caused by chloride and bromide ions in the catalysis of reactions (1) and (2) by colloidal silver could be overcome by taking a mixture of silver and gold colloids, or better by using Ag/Au particles.<sup>5,8</sup>

## Conclusion

The bimetallic interface consisting of silver islands on a gold substrate possesses unique catalytic properties distinct from those of the pure metals. The formation of silver halide, which is the main autoinhibiting effect in silver-catalysed reactions, can be avoided by electron transfer from the organic reducing agent via the free gold surface. Thus, even silver halide which has already been formed may be reduced. Moreover, the irreversible adsorption of the organic reactant, which is the most important inhibiting effect in gold-catalysed reactions, can be avoided by oxidation of the adsorbed compound via the silver surface. This mutual cancellation of inhibiting effects has already been used to accelerate the colloid-catalysed oxidation of p-phenylenediamines by  $[Co^{II}(NH_3)_5C1]Cl_2$ .

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