Heterogeneous Catalysis in Solution. Part IX.[1] Reduction of Bromopenta-amminecobalt(III) and other Cobalt(III) Complexes in the Presence of Solids

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$Co(NH_3)_5Br^{2+}$ in aqueous acid solution reacts more rapidly in the presence of various solids. The only effect of platinized platinum is to cause reduction of the complex to cobalt(II). With mercury(II) sulphide or silver(I) bromide present, a significant fraction of the enhanced rate is due to reduction. Addition of charcoal in various forms brings about partial reduction of aqueous $Co(NO_2)_6^{3-}$ and of aqueous ammoniacal $Co(NH_3)_6^{3+}$.

THE aquation reaction (1) of $[Co(NH_3)_5X]^{2+}$ (RX^{2+} for short) is slow in homogeneous solution at 25 °C, with a

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^- (X = Cl \text{ or } Br) \quad (1)$$

first-order rate constant k_{hom}. In the presence of various solids the rate of disappearance of aqueous $[Co(NH_3)_5Br]Br_2$ was found [2] to be markedly enhanced, and could be formally described by writing

$$k_{obs} = k_{hom} + k_{het} \quad (2)$$

Kinetic studies showed that the rate constant, per unit area of surface, increased from silver bromide [3] to mercury(II) sulphide [3] to platinum.[1] In every case, the dependence of k_{het} on reactant concentration and area of catalyst was consistent with a mechanism of Langmuir-type adsorption of the complex ion followed by the rate-determining reaction of the adsorbed species. k_{het} Was high at very low concentrations of RX^{2+} and low at high concentrations, and so the total extent of extra reaction brought about by introducing the solid was never very large. It was therefore decided to follow the chemical reaction of RBr^{2+} in the presence of platinized platinum which provides a surface several hundred times greater in area [4] than those used before, and enables the surface reaction to be studied at higher concentrations. In particular, the possibility of reduction of RBr^{2+} to Co^{II}, as well as aquation, was examined. The results obtained prompted a reinvestigation of the solids studied previously.

Experiments with Platinized Platinum.—The reactant solution was always aqueous $[RBr]Br_2$ of initial concentration c_{init} mol dm^{-3} dissolved in 200 cm^3 of 0·01 mol dm^{-3} (0·01M) perchloric acid at 25 °C. In preliminary kinetic runs with 10^{-4}M $[RBr]Br_2$ exposed to a 1-in square piece of platinized platinum foil, k_{het} rose when the speed of a magnetic stirrer was changed from slow to very fast. This phenomenon was not unexpected: as the rate of the surface reaction depends on the real surface area (S) rather than the geometric surface area (A), the velocity of the reaction on a platinized surface could well become comparable with the rate of diffusion of reactant from the bulk solution. Subsequent work was therefore carried out with a trumpet-shaped platinized platinum rotating disc (diameter of platinum 5·66 cm, $A = 25·2$ cm^2, $S = 0·67$—$1·01$ m^2) which was never rotated at less than 400 r.p.m. The spectrophotometrically measured rates of disappearance of RBr^{2+} ($c_{init} = 1$—5×10^{-4}M) displayed no regular variation with changing disc rotation speed in the range 400—1000 r.p.m., indicating that the reaction was now essentially surface-controlled. This suggests that the whole of the platinized area was not immediately accessible to reactant as has been found with certain electrochemical processes also.[5] After all, the real surface area had been determined (see Experimental section) by utilizing the system

$$H^+ + e^- \rightleftharpoons H$$

whereas the reaction under study involved the bulky RBr^{2+} species which would penetrate much more slowly into narrow pores. The values of k_{het} themselves are consistent with this idea. Although k_{het} decreased as the mean RBr^{2+} concentration increased (compare runs 1 and 4 in Table 1), in qualitative agreement with the earlier results [1] obtained with bright platinum and interpreted on a Langmuir model, the absolute values of k_{het} were much lower and less reproducible than expected. Thus, at a mean RBr^{2+} concentration of 7×10^{-5}M, with a solution volume of 200 cm^3 and a platinized platinum area of 0·68 m^2, $k_{het} = 25 \times 10^{-6}$ s^{-1}. In comparison, with the same solution concentration, a volume of 500 cm^3 and an area of bright platinum of only 25·2 cm^2, Archer [6a] found $k_{het} = 4 \times 10^{-6}$ s^{-1}. These rates differ by a factor of only 6 whereas, very crudely, a ratio of $(6800/25·2) \times (500/200) \approx 680$ was anticipated. Experiment showed that the effect of the different electrochemical pretreatments of the bright and platinized surfaces was not responsible: it would not have altered the rates by more than a factor of 2 and was, in any event, in the wrong direction to explain the results (see runs 1 and 3 in Table 1).

After electrochemical pretreatment, the disc immersed in 0·01M-perchloric acid displayed potentials of 0·94 ± 0·02 V(NHE). Addition of $[RBr]Br_2$ caused a fairly

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[1] Part VIII, M. D. Archer and M. Spiro, *J. Chem. Soc.* (*A*), 1970, 78.

[2] M. D. Archer and M. Spiro, *J. Chem. Soc.* (*A*), 1970, 68.

[3] M. D. Archer and M. Spiro, *J. Chem. Soc.* (*A*), 1970, 73.

[4] A. M. Feltham and M. Spiro, *Chem. Rev.*, 1971, **71**, 177.

[5] E. A. Aikazyan and A. I. Fedorova, *Doklady Akad. Nauk S.S.S.R.*, 1952, **86**, 1137.

[6] M. D. Archer, Ph.D. Thesis, Univ. of London, 1968, (*a*) p. 209; (*b*) p. 87; (*c*) pp. 144, 178; (*d*) p. 140; (*e*) p. 83.

sharp rise to between 0·99 and 1·08 V(NHE), followed by a slow decline from the $E_{max.}$ value. Qualitatively, this behaviour resembled that reported [1] for bright platinum. So did the effect of holding the potential on the disc constant during a run. When a lower potential than usual was imposed (0·980 V), the rate of disappearance of RBr^{2+} increased more than 10-fold (run 5, Table 1). The application of a more anodic potential of 1·130 V, on the other hand, almost completely suppressed the rate enhancement (run 6, Table 1).

After the runs listed in Table 1, the reaction mixtures were analysed for Co^{II} by [2] complex formation with chloride and spectrophotometric measurements at 690 nm. Cobalt(II) was found after every run except no. 6, in which the disc was kept at an anodic potential. Some supporting evidence comes from experiment 4, which had deliberately been allowed to proceed for a much longer time than usual. Rapid titration after the run revealed a drop in the hydrogen ion concentration of *ca.* 8 × 10^{-4}M, consistent with liberation of ammonia as Co^{II} was formed. Comparison of columns 7 and 8 in Table 1 shows that in all runs except no. 4 the enhancement in reaction produced by the platinized platinum disc corresponds approximately to the amount of Co^{II} generated. It follows that at least the major part of the increased reaction rate in the presence of platinized platinum is due to reduction of RBr^{2+}. The reason for the unusually high concentration of cobalt(II) in run 4 is discussed in the next section.

TABLE 1

Effect of a platinized platinum disc rotating at 400 r.p.m. on the reaction of $[Co(NH_3)_5Br]Br_2$ in 200 cm³ of 0·01M-aqueous perchloric acid solution at 25 °C

Run	S/m²	Time/h	10^4c_{init}/M	10^4c_{fin}/M	$10^4\Delta c_{hom}$ [a] / M	$10^4\Delta c_{enh}$ [b] / M	$10^4[Co^{II}]_{fin}$ / M	10^6k_{het} / s^{-1}	E_{max} / V(NHE)
1	0·87	52·45	5·53	0·85	3·68	1·00	1·45	2·9	1·083
2	0·86	13·00	5·40	3·00	1·27	1·13	1·00	(5·4) [d]	—
3 [c]	0·76	13·00	5·36	3·39	1·26	0·71	0·65	2·6	1·078
4	0·80	108·25	13·08	1·30	11·71	0·07	3·20	~0	1·070
5	0·88	6·32	5·23	0·62	0·64	3·97	4·00	88	0·980 (const.)
6	0·87	8·35	5·35	4·32	0·86	0·17	0·00	~0	1·130 (const.)

[a] Calculated concentration of product that would be produced by homogeneous reaction alone. [b] $\Delta c_{enh} = c_{init} - c_{fin} - \Delta_{hom}$. It measures the total rate enhancement of the reaction produced by the presence of the platinum. [c] The electrochemical pretreatment of the disc in run 3 was the same as that used for bright platinum in ref. 1. [d] Only two readings of concentration were taken.

TABLE 2

Effect of a bright platinum disc rotating at 400 r.p.m. on the reactions of $[Co(NH_3)_5Br]^{2+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$ in 500 cm³ of 0·01M-aqueous perchloric acid solution at 25 °C

Run	Substrates [a] and 10^5c_{init}/M	Time/h	10^6k_{het} / s^{-1}	10^6k_{het} / s^{-1} from ref. 6*a*	$10^5[Co^{II}]_{calc}$ / M	$10^5[Co]^{II}_{obs}$ / M
1	9·74 $[RBr]Br_2$	24·7	3·6 ± 0·3	3·6	$2{\cdot}6_5$	4·4 ± 0·2
2	14·4 $[RBr]Br_2$	26	2·2 ± 0·2	2·4	$2{\cdot}7_2$	2·4 ± 0·2
3	10·0 $[R(H_2O)](ClO_4)_3$	30				0·0
4	10·0 $[R(H_2O)](ClO_4)_3$ + 25·0 KBr	27				1·3 ± 0·2

[a] R stands for $Co(NH_3)_5$.

The largest concentration of cobalt(II) was found in run 5, and this is consistent with its formation by electrolytic reduction. The disc in run 5 was under cathodic potentiostatic control, and the cathodic current flowing through the disc/solution interface fell rapidly from an initial value of 900 to 100 μA. Graphical current–time integration gave a total passage of 5·6 coulombs, corresponding to the reduction of 0·58 × 10^{-4} mol Co^{III} to Co^{II} in 200 cm³ solution, or a rise in Co^{II} concentration of 2·9 × 10^{-4}M. The observed rise was 4·0 × 10^{-4}M. By a similar argument, it is hardly surprising that no cobalt(II) was detected at the end of run 6 in which the disc had been under anodic potentiostatic control.

Experiments with Bright Platinum.—No cobalt(II) had been detected in previous work [1] with a bright platinum disc. It was therefore decided to repeat some of the earlier experiments, and to analyse for the presence of cobalt(II) by complexing it as $(MePh_3As)_2Co(NCS)_4$, extracting the complex in 1,2-dichlorobenzene, and examining the extract spectrophotometrically or by atomic absorption. The sensitivity of this analytical method is approximately ten times greater than that of the earlier procedure. Table 2 summarizes the results. The electrochemical pretreatment of the disc was exactly the same as that of Archer and Spiro,[1] and the kinetic rate constants agree very satisfactorily. The second-to-last column in Table 2 lists the concentrations of cobalt(II) expected to be present if the entire rate enhancement had caused reduction: comparison with the final column shows that the observed concentrations of cobalt(II) equal or even exceed these calculated amounts. The behaviour of bright and of platinized platinum is therefore essentially the same.

At the end of run 1 of Table 2 significantly more cobalt(II) was found than had been calculated from the rate of disappearance of RBr^{2+}. Could this have arisen from reduction at the platinum surface of the product ion $R(H_2O)^{3+}$? Run 3 demonstrates that the product ion alone is not sufficient, but $R(H_2O)^{3+}$ in the presence of bromide ions (run 4) certainly did produce cobalt(II) and in sufficient amount to explain the discrepancy in run 1. It seems highly likely that bromide ions were needed in order to participate in the corresponding oxidation reaction (see next section). This result also sheds considerable light on the very long platinized platinum run 4 in Table 1 in which far more cobalt(II) was discovered than could be accounted for on the basis of k_{het}. It is significant that in the second longest run in Table 1, run 1, the cobalt(II) concentration also appreciably exceeded that expected from the enhancement of the rate of reaction of RBr^{2+}. Moreover, an explanation is now provided for the curious finding by Archer and Spiro [1] that k_{het} at bright platinum is *increased* by adding to the solution either of the product ions of the aquation reaction (1), $R(H_2O)^{3+}$ or Br^-. Let us first consider the presence of $R(H_2O)^{3+}$. Under typical conditions previously used,[1] 100×10^{-5}M $[R(H_2O)](ClO_4)_3$ were added to a solution $2{\cdot}35 \times 10^{-5}$M in $[RBr]Br_2$. The extinction coefficients of these two substances at 253 nm, the wavelength at which the reaction was followed, were 86·3 and $1{\cdot}74_4 \times 10^4$ l mol^{-1} cm^{-1} respectively, and thus 17·4% of the initial absorbance of this solution was due to the aquo-ion. Reduction of $R(H_2O)^{3+}$ at platinum would diminish the absorbance at 253 nm and be interpreted as an enhancement in the rate of disappearance of RBr^{2+}. The reason that the reaction —now known to be a reduction—of RBr^{2+} was found [1] to be accelerated by the addition of KBr can be ascribed to the involvement of bromide ions in the complementary oxidation reaction. This subject will now be examined thermodynamically.

Thermodynamic and Electrochemical Considerations.— To evaluate the standard Gibbs free-energy change for the reduction of $Co(NH_3)_5Br^{2+}$ in acid solution we proceed as follows.

$$Co(NH_3)_5Br^{2+} + H_2O \rightleftharpoons Co(NH_3)_5(H_2O)^{3+} + Br^- \quad (3)$$

$$\Delta G°(3) = -4{\cdot}4 \text{ kJ (ref. 7) } [+0{\cdot}0_5 \text{ kJ (ref. 6}b)]$$

$$Co(NH_3)_5(H_2O)^{3+} + e^- \rightleftharpoons Co(NH_3)_5(H_2O)^{2+} \quad (4)$$

$E°(4) = 0{\cdot}35 \pm 0{\cdot}02$ V at an ionic strength of 1·0M,[8] whence $\Delta G°(4) = -33{\cdot}_8$ kJ.

$$Co(NH_3)_5(H_2O)^{2+} \rightleftharpoons Co^{2+} + 5NH_3 + H_2O \quad (5)$$

$$\log_{10} K(5) = -5{\cdot}35 \pm 0{\cdot}2,^9\ \Delta G°(5) = 30{\cdot}5 \text{ kJ}$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \quad (6)$$

$$\log_{10} K(6) = 9{\cdot}23,^9\ \Delta G°(6) = -52{\cdot}7 \text{ kJ}$$

Combination of equations (5) and (6) gives

$$Co(NH_3)_5(H_2O)^{2+} + 5H^+ \rightleftharpoons Co^{2+} + 5NH_4^+ + H_2O \quad (7)$$

$$\Delta G°(7) = -232{\cdot}9 \text{ kJ}$$

Finally, addition of (3), (4), and (7) yields

$$Co(NH_3)_5Br^{2+} + 5H^+ + e^- \rightleftharpoons Co^{2+} + 5NH_4^+ + Br^- \quad (8)$$

$$\Delta G°(8) = -271{\cdot}1 \text{ kJ, and hence } E°(8) = 2{\cdot}81 \text{ V}$$

This extremely high potential derives essentially from the large decrease in free energy associated with the protonation of the five liberated ammonia molecules. The same driving force produces a large standard potential for the reduction of $Co(NH_3)_5(H_2O)^{3+}$:

$$Co(NH_3)_5(H_2O)^{3+} + 5H^+ + e^- \rightleftharpoons Co^{2+} + 5NH_4^+ + H_2O \quad (9)$$

$$\Delta G°(9) = -266{\cdot}7 \text{ kJ, and thus } E°(9) = 2{\cdot}76 \text{ V}$$

Thermodynamically, couple (8) is capable of oxidizing the solvent since

$$\tfrac{1}{4}O_2(g) + H^+ + e^- \rightleftharpoons \tfrac{1}{2}H_2O \quad (10)$$

$$E°(10) = 1{\cdot}229 \text{ V},^9\ \Delta G°(10) = -118{\cdot}6 \text{ kJ}$$

If this were the case, the platinum disc in the solution would have adopted a mixed or mixture potential [10] that lies somewhere between those of couples (8) and (10). Since the observed maximum potential was 1·070—1·083 V (Table 1), well below that of either couple, we can entirely rule out solvent oxidation on the platinum surface. Another and more likely reaction is the partial oxidation of bromide ions to bromine:

$$\tfrac{1}{2}Br_2 + e^- \rightleftharpoons Br^- \quad (11)$$

$$E°(11) = 1{\cdot}086 \text{ V},^9\ \Delta G°(11) = -104{\cdot}8 \text{ kJ}$$

The mean bromine/bromide Nernst potential corresponding to the conditions in Table 1 would be *ca.* 1·14 V if all the bromine generated remains in solution, but if some is lost by vaporization and adsorption the potential could well fall below the observed mixture potentials in Table 1. These, as might be expected,[10] then lie much closer to that of the highly reversible Br_2/Br^- couple, with its large exchange current density,[11,12] than to that of the (almost certainly irreversible) RBr^{2+}/Co^{2+} couple. A third possibility is dissolution of platinum itself, its ions stabilized by complexing with bromide:

$$\tfrac{1}{2}PtBr_4^{2-} + e^- \rightleftharpoons \tfrac{1}{2}Pt(s) + 2Br^- \quad (12)$$

$$E°(12) = 0{\cdot}58 \text{ V},^9\ \Delta G°(12) = -56{\cdot}_0 \text{ kJ}$$

Platinum ions are known to be produced in 3·6M-hydrochloric acid by anodic polarization [13] and in 1M-sulphuric

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[7] M. Mori and R. Tsuchiya, *Bull. Chem. Soc. Japan*, 1960, **33**, 841.

[8] R. G. Yalman, *Inorg. Chem.*, 1962, **1**, 16.

[9] L. G. Sillén and A. E. Martell, 'Stability Constants of Metal-Ion Complexes,' Chem. Soc. Special Publns. No. 17, 1964, and No. 25, 1971.

[10] M. Spiro and A. B. Ravnö, *J. Chem. Soc.*, 1965, 78.

[11] M. Spiro, *Electrochim. Acta*, 1964, **9**, 1531.

[12] W. D. Cooper and R. Parsons, *Trans. Faraday Soc.*, 1970, **66**, 1698.

[13] T. Dickinson, R. C. Irwin, and W. F. K. Wynne-Jones, *J. Electroanalyt. Chem.*, 1964, **7**, 297.

acid by cyclic voltammetry,[14] as well as by chemical oxidants in various media.[15]

Whether (11) or (12), or both, are the oxidation processes corresponding to the reduction of RBr^{2+} in the presence of platinum, it is clear that bromide ions are involved. By similar reasoning, they are involved in the reduction of $R(H_2O)^{3+}$ at the platinum disc, and this explains the results of runs 3 and 4 in Table 2 where reduction of the aquo-ion is seen to occur only if bromide ions are present. Another previously puzzling feature is now clarified: the acceleration of the disappearance of RBr^{2+} when bromide ions—a product of the reaction—were added.[1] The greater the concentration of bromide the lower will be the Nernst potentials of couples (11) and (12) and the higher their partial anodic currents at any potential and, in particular, at the more negative mixture potential. At this point the increased anodic current equals a correspondingly increased cathodic current. The latter is equivalent to the rate of reduction of RBr^{2+} at the platinum surface, and thus RBr^{2+} reacts more rapidly when the bromide ion concentration is increased.

TABLE 3

Effect of mercury(II) sulphide and silver(I) bromide on the reaction of $[Co(NH_3)_5Br]Br_2$ in 500 cm³ of 0·01M-perchloric acid at 25 °C

Solid	10^5c_{init} / M	10^6k_{het} / s^{-1}	10^6k_{het} / s^{-1} from ref. 6c	Time/h	$10^5[Co^{II}]_{calc}$ / M	$10^5[Co^{II}]_{obs}$ / M
HgS	254·6	1·0	0·6	3·0	2·8	3·4 ± 0·2
(1·00 g)				6·0	5·5	4·3 ± 0·2
	134·7	2·8	1·2	3·0	4·0	2·5 ± 0·2
				6·0	7·9	3·2 ± 0·2
	100·0	1·7	1·0	6·0	3·7	2·5 ± 0·2
	31·0	4·3	3·9	4·0	1·9	1·0 ± 0·2
				20·5	8·4	2·9 ± 0·2
	3·87	29·0	$14{\cdot}_3$	19·0	3·3	1·5 ± 0·2
	[a]			23·0		$\ngtr$0·25 ± 0·2
AgBr	6·41	3·7	7·6	21·5	1·6	0·5 ± 0·2
(2·00 g)	5·03	4·6	9·6	21·5	1·5	0·5 ± 0·2

[a] This solution contained 50 × 10^{-5}M-$[Co(NH_3)_5(H_2O)](ClO_4)_3$, 110 × 10^{-5}M-KBr, and 0·01M-perchloric acid.

Experiments with Mercury(II) *Sulphide*.—The rate of disappearance of RBr^{2+} is accelerated in the presence of mercury(II) sulphide and silver(I) bromide,[2,3] though to a lesser degree than in the presence of platinum.[1] In view of the finding that platinum induces the formation of cobalt(II), some of the earlier experiments with mercuric sulphide and silver bromide were repeated under the same physical conditions as before and cobalt(II) was analysed for by the sensitive extraction technique described. The results are listed in Table 3.

The observed values of k_{het} using mercuric sulphide are consistently double those observed by Archer.[6c] This is attributable to the different batches of solids used in the two sets of experiments having different surface areas in spite of the fact that they were pre-treated in the same way. The values of $[Co^{II}]$ found are given in the last column and may be compared with those to be expected if the total rate enhancement were due to reduction of the complex. In seven out of eight cases the observed concentrations of cobalt(II) are less than those predicted on this basis. One run using the aquation product as its perchlorate salt, together with a 2·1 : 1 mol ratio of bromide, is also listed in Table 3. A very small amount of cobalt(II) was detected.

We conclude that the rate enhancement previously ascribed to heterogeneous catalysis of the aquation process is instead largely caused by reduction of RBr^{2+} to Co^{II}. The aquo-ion generated by the aquation is very slightly reduced in a solution containing bromide, and this by itself would have the effect of further enhancing the observed rate. However, in practice aquo-ions will compete with bromo-ions for the limited number of sites on the surface, and addition to the solution of the more slowly reacting aquo-ion should therefore decrease the overall rate. This has in fact been observed.[3] The increase of the first-order rate constant k_{het} with decreasing RBr^{2+} concentration suggests that both the catalysed aquation and the reduction conform to a mechanism [3] of adsorption pre-equilibrium followed by the rate-controlling surface reaction.

As in the case of platinum surfaces, the reduction of RBr^{2+} to Co^{II} could be accompanied by several possible oxidation processes. The conversion of bromide ions to bromine is one of these; another is the oxidation of sulphide ions by reaction (13) (in acid solution) whose standard potential is 0·303 V.[16] At extended times (4 days), tests for sulphate were slightly positive.[6d] We can write the partial dissolution of mercuric sulphide in a medium of pH 2 containing bromide ions as

$$SO_4^{2-} + 10H^+ + 8e^- \rightleftharpoons H_2S + 4H_2O \quad (13)$$

$$HgS(s) + 2H^+ + Br^- \rightleftharpoons HgBr^+ + H_2S \quad (14)$$

$K(14) = K_{so}K_{stab}/K_1K_2$, where K_{so} is the solubility product of HgS, K_{stab} the formation constant of $HgBr^+$, and K_1 and K_2 the dissociation constants of dissolved H_2S. From literature data,[9] $K(14) = 10^{-23}$ dm³ mol⁻¹. Combination of equations (8) and (13) shows that $[SO_4^{2-}]_{max.} = \frac{1}{8}[Co^{II}]_{max.} \doteqdot 10^{-5}$M (Table 3). It follows from equation (14) that $[HgBr^+]_{max.} \doteqdot 10^{-5}$M, and hence,

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[14] T. Biegler, *J. Electrochem. Soc.*, 1969, **116**, 1131.

[15] A. B. Ravnö and M. Spiro, *J. Chem. Soc.*, 1965, 97.

[16] M. Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solutions,' Pergamon Press, Oxford, 1966, Section 19.2.

using the known values of $K(14)$, pH, and $[\mathrm{Br}^-]$, $[\mathrm{H_2S}]_{\mathrm{min.}} = 3 \times 10^{-25}$M. The maximum Nernst potential of couple (13) is then 0·299 V, well below that of the $\mathrm{RBr^{2+}/Co^{II}}$ couple (8). The latter is therefore thermodynamically capable of producing sulphate ions from suspended mercuric sulphide.

Experiments with Silver Bromide.—Two runs were carried out with a sample of silver(I) bromide treated in the same way as batch 4 of Archer and Spiro.[3] The results are listed in Table 3. Observed rates of reaction were about half those determined previously,[6c] attributable to different photochemical and surface conditions. The amounts of cobalt(II) observed were only one third as large as those calculated from the measured enhancement of the rate, and most of the latter is therefore due to genuine heterogeneous catalysis of the aquation reaction. Such catalysis may well proceed *via* adsorbed cobalt(II) intermediates.[17]

Interaction between Carbon and $\mathrm{Co(NO_2)_6^{3-}}$.—Tomita and Tamai[18,19] have reported the effects of various carbons on reactions of two other cobalt(III) complex ions: ' hydrolysis ' of the anion $\mathrm{Co(NO_2)_6^{3-}}$ and hydroxylation of the cation $\mathrm{Co(NH_3)_6^{3+}}$. In neither case, however, did they test whether any reduction to cobalt(II) had occurred. Since we have found that the presence of carbon causes reduction of[2] $[\mathrm{Co(NH_3)_5Br}]^{2+}$ and of[20] $\mathrm{Co(en)_3^{3+}}$, it was decided to investigate the matter further.

Sodium cobaltinitrite has been shown[21,22] to undergo spontaneous reduction in solution even in the dark. It is also extensively photochemically reduced[21,22] in monochromatic light of wavelength 472·5, 565·0, and 730·4 nm, as well as in sunlight and under illumination from a 1000 W (presumably tungsten) lamp. Similar results have been obtained by more recent workers[23] using u.v. light (of unspecified wavelength) and γ-radiation.

It seemed likely that one consequence of the 'catalytic' effect of Tomita and Tamai[18] was to increase the rate of reduction of $\mathrm{Co(NO_2)_6^{3-}}$. We decided to test this hypothesis. As carbons of the type used by Tomita and Tamai were not available, three carbons of different properties were employed. The speed of photochemical reduction even in the homogeneous solution made it difficult at first to estimate the effect of carbon. For example, while a freshly prepared 10×10^{-3}M-$\mathrm{Na_3[Co(NO_2)_6]}$ solution in Pyrex glass gave no positive test for cobalt(II), after 10 min in normal laboratory light $0{\cdot}25 \times 10^{-3}$M cobalt(II), *i.e. ca.* 2·5% reduction, was observed. When in subsequent experiments we used dark amber bottles, insulated all the filtration and extraction apparatus for the cobalt(II) determination against light, and carried out the reactions in a darkened laboratory, homogeneous 10×10^{-3}M-solutions were reproducibly found to contain $0{\cdot}03 \times 10^{-3}$M-cobalt(II) after 2 h at 25°. Under identical conditions, considerably more cobalt(II) was found when the reactions were studied in the presence of any of the three carbons used (Table 4).

TABLE 4

Effect of various carbons on the reaction of 0·01M-$\mathrm{Na_3[Co(NO_2)_6]}$ in water at 25 °C in a darkened room

Type and mass of carbon	Volume/ $\mathrm{cm^3}$	$10^3[\mathrm{Co^{II}}]$/M after 16 min	120 min
None	250		0·03
BP (100 mg)	25	0·76	2·04
BP (100 mg)[a]	25		2·93
G (100 mg)	20		0·42
SFT (100 mg)	20		0·42

[a] This experiment was carried out at 30 °C.

To judge whether the reduction process formed a large or small part of the overall reaction we carried out a few kinetic experiments with dark amber bottles in a darkened room. The first-order homogeneous rate constant k_{hom} was $0{\cdot}4_5 \times 10^{-4}\ \mathrm{s^{-1}}$ at 25 °C and $1{\cdot}3_1 \times 10^{-4}\ \mathrm{s^{-1}}$ at 30 °C. Tomita and Tamai[18] give a higher figure of $1{\cdot}8_3 \times 10^{-4}\ \mathrm{s^{-1}}$ at 30 °C for the homogeneous reaction in amber tubes, but since they make no mention of darkening the laboratory their higher result may have been caused by photochemical action. With 100 mg of Black Pearls carbon in 25 cm³ solution we obtained a value of k_{het} [see equation (2)] of $3{\cdot}5 \times 10^{-4}\ \mathrm{s^{-1}}$ at 25 °C and of $8{\cdot}3 \times 10^{-4}\ \mathrm{s^{-1}}$ at 30 °C. The latter value is similar to Tomita and Tamai's rate constant of $6{\cdot}7 \times 10^{-4}\ \mathrm{s^{-1}}$ at 30 °C recorded with 100 mg of HAF carbon in an unstated volume of solution. It is clear from these figures that in the presence of BP carbon the reaction of $\mathrm{Co(NO_2)_6^{3-}}$ was virtually complete in 2 h, and the figures in Table 4 then show that the reduction to cobalt(II) accounted for 20% of the reaction at 25 °C and for 29% at 30 °C.

The Effect of Carbon on $\mathrm{Co(NH_3)_6^{3+}}$.—Reaction (15) is

$$\mathrm{Co(NH_3)_6^{3+} + OH^- \rightleftharpoons Co(NH_3)_5(OH)^{2+} + NH_3} \tag{15}$$

known to be catalysed by carbon.[24a] Tomita and Tamai[19] recently investigated the effect of pH and the nature of the carbon surface on the forward reaction. They concluded that in the presence of a carbon the concentration of $\mathrm{Co(NH_3)_6^{3+}}$, as monitored spectrophotometrically, decreased by two mechanisms, *viz*, ' irreversible adsorption ' on the carbon, and conversion into the hydroxo-complex.

The $\mathrm{Co(NH_3)_6^{3+}}$ ion has an absorbance peak at 474 nm and $\mathrm{Co(NH_3)_5(OH)^{2+}}$ at 503 nm. An overall pseudo-first order rate constant k_{obs} was determined[19] from the decrease in absorbance at 474 nm, and was equated to the

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sum of the first-order rate constants for adsorption and hydrolysis:

$$k_{\mathrm{obs}} = k_{\mathrm{ads}} + k_{\mathrm{hyd}} \qquad (16)$$

k_{ads} was evaluated as follows. Had only hydrolysis taken place, the sum of the concentrations of the two cobaltic ions (c_{sum}) calculated from the two absorbance peaks would have been constant and equal to the initial hexammine molarity (c_0). The difference (x) between c_0 and c_{sum} in the presence of carbon was ascribed[19] to irreversible adsorption and was used to work out a first-order adsorption rate constant:

$$k_{\mathrm{ads}}t = 2{\cdot}303 \log_{10} [c_0/(c_0 - x)] \qquad (17)$$

Plots of the right-hand side of equation (17) against time were linear except for the very initial region and showed small positive intercepts. These could be interpreted as rapid initial adsorption. The values of k_{ads}, however, are low (10^{-6} to 10^{-4} s^{-1}) compared with rates of adsorption obtained in this laboratory[20] for $Co(en)_3^{3+}$ on both graphitized and ungraphitized carbon black BP. Hasany,[25] too, has shown that the complexes $Co(en)_3^{3+}$, $Co(en)_3^{2+}$, $Co(EDTA)^{2-}$, and $Co(EDTA)^{3-}$ attain adsorption equilibrium on platinized platinum within 5 min. It may be significant that the calculation of k_{ads} assumes the absence of other soluble cobalt species, whether optically observable or not. The experiments described below show that this assumption is not correct.

TABLE 5

Effect of various carbons on the reactions of 0·01M-$[Co(NH_3)_6]Cl_3$ in 0·15M-NH_3 at 30 °C

Type and mass of carbon	Volume/cm³	Bottle colour	10^6d log A_{474}/dt / s^{-1}	10^6d log A_{503}/dt / s^{-1}	$10^5[Co^{II}]_{obs}$ after 2 h / M
None	20	Amber	4·7	6·7	0·0 ± 0·2
None	20	Clear			0·0 ± 0·2
BP (200 mg)	20	Amber	−200[a]	−152[a]	47·6[b] ± 0·2
BP (50 mg)	10	Clear			19·3[b] ± 0·2
G (200 mg)	20	Amber	1·0	4·0	0·9 ± 0·2
G (100 mg)	10	Clear			1·3 ± 0·2
SFT (200 mg)	20	Amber	2·2	4·2	0·4 ± 0·2
SFT (100 mg)	10	Clear			1·0 ± 0·2

[a] The corresponding first-order rate constants are 4·6 × 10^{-4} and 3·5 × 10^{-4} s^{-1}. [b] $10^5[Co^{II}]$/M after 1 h.

We reinvestigated the hydrolysis in ammoniacal solution of $Co(NH_3)_6^{3+}$ in order, primarily, to discover whether cobalt(II) was produced. Since the carbons originally used by Tomita and Tamai could not be obtained, less emphasis was placed on rate measurements. Reaction conditions were chosen to reproduce exactly those of the second run in Tomita and Tamai's[19] Table IV, and absorbances were monitored at 474 and 503 nm. The results are listed in Table 5.

In the homogeneous solution, if only the hydrolysis reaction occurs, a decrease in optical absorbance at 474 nm and an increase at 503 nm would be expected. Surprisingly, the absorbances increased at both wavelengths. No cobalt(II) was detected. These observations can be explained by the formation of the outer-sphere complex $Co(NH_3)_6^{3+},NH_3$. The existence of some new cobaltammine species in ammoniacal solutions of $Co(NH_3)_6^{3+}$ was suggested on spectral grounds by Nakatsuka,[26] and investigated more thoroughly by Larsson.[27] He determined the stability constant of the complex by solubility and by spectrophotometric measurements in the u.v. region, and from his value we calculate that in the medium of 0·15M-ammonia used here some 4% of the $Co(NH_3)_6^{3+}$ ions are present as an association pair with NH_3. In Tomita and Tamai's work the ammonia concentration was usually 1·5M and a large fraction of their cobalt(III) ions must have been associated with ammonia molecules. This may explain their observation of a rapid shift in the spectral peak to 488 nm when adsorption to carbon was slow. Larsson[27] examined the spectrum of ammoniacal $Co(NH_3)_6^{3+}$ solutions from 231 to 255 nm, and found that on addition of ammonia the absorbance increased more the greater the wavelength. Changes in the visible region have also been reported.[24b] It may be noted that no anomalous absorbance behaviour was observed when the hydrolysis of $Co(NH_3)_6^{3+}$ was studied in aqueous sodium hydroxide solution.[28,29]

When carbons G and SFT were added to the $[Co(NH_3)_6]Cl_3$ solution, absorbances at both 474 and 503 nm still increased but at a slower rate, and small amounts of cobalt(II) were detected (Table 5). Only when using carbon BP as catalyst were results found to be qualitatively of the form of Tomita and Tamai's, with the optical absorbances at both 474 and 503 nm decreasing. Rate constants based on the absorbances at the two wavelengths differ (Table 5) implying the occurrence of both adsorption and hydrolysis. Appreciable amounts of cobalt(II) were detected, corresponding after 1 h to *ca.* 4·5% of the total cobalt initially present and to *ca.* 5·5% of the amount of $Co(NH_3)_6^{3+}$ that had disappeared. The formation of cobalt(II) accounts, in part, for the ammonia that Tomita and Tamai found to be liberated during the reaction.

Thus all the carbons cause some reduction of the complex. For the two less-active carbons, the tendency of the carbon to reduce and cause hydrolysis is outweighed by the formation of the association pair. The

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[27] R. Larsson, *Acta Chem. Scand.*, 1958, **12**, 708.

[28] H. Yoneda, *Bull. Chem. Soc. Japan*, 1958, **31**, 74.

[29] J. H. Takemoto and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1970, **32**, 175.

highly active carbon BP completely swamps this effect. A few experiments showed that with all the carbons more reduction occurs in clear glass than in amber. The photoreduction of $Co(NH_3)_6^{3+}$ has been shown to have a relatively small quantum yield:[30] it is possible that carbon catalyses this process.

EXPERIMENTAL

Materials.—$[Co(NH_3)_5Br]Br_2$ and $[Co(NH_3)_5(H_2O)](ClO_4)_3$ were prepared by published methods[31,32] and had satisfactory analyses. $[Co(NH_3)_6]Cl_3$ (Hopkin and Williams) and $Na_3[Co(NO_2)_6]$ (B.D.H. AnalaR) were commercially available. Ammonium thiocyanate (B.D.H. AnalaR) and sodium thiocyanate (Hopkin and Williams) were recrystallized once from water. Triphenylmethylarsonium iodide (Koch–Light) and 1,2-dichlorobenzene (B.D.H.) were used as supplied. Perchloric acid and ammonia were of AnalaR grade. Doubly distilled water was employed throughout.

A batch of mercury(II) sulphide was prepared by washing the B.D.H. product in M-nitric acid, then washing until acid-free, and drying *in vacuo* over silica gel. Silver bromide was prepared in the same way as Archer and Spiro's[3] batch 4 sample: the B.D.H. product was sieved (<76 μm mesh), stirred for 30 min in 0·01M-nitric acid, filtered, washed, and dried at room temperature *in vacuo* over silica gel. Black Pearls 2 (abbreviated BP), a carbon black of surface area 850 $m^2 g^{-1}$ (BET N_2) was supplied by Cabot Corporation, Ellesmere Port, Cheshire. Sterling FT (SFT), 7·7 $m^2 g^{-1}$, and Graphon (G), 90 $m^2 g^{-1}$, both graphitized carbon blacks, were supplied by Cabot Corporation, Boston, Mass., U.S.A.

Platinized and Bright Platinum Discs.—The platinum disc and the apparatus for rotating it have been described previously.[1] Prior to platinization the platinum face of the disc was briefly abraded with 00 grade emery cloth, washed, and electrochemically cleaned in 0·2M-perchloric acid with a Chemical Electronics Co. TR70/2A potentiostat by the potential sequence:[33] 2 s at 1·8 V (RHE) with rotation at 300 r.p.m., 30 s at 1·2 V (RHE) at 300 r.p.m., and then, without stirring, 90 s at 1·2 V (RHE) followed by 10 s at 0·4 V (RHE). The reference electrode was quinhydrone. Platinization was carried out at 30 mA cm^{-2} for 10 min from an aqueous solution 3·5 wt % in chloroplatinic acid, 0·005% in lead acetate, and 2M in hydrochloric acid. The counter electrode was a lightly chloridized silver sheet placed horizontally under the disc; no gas was evolved from this electrode and the initial chloridization prevented oxidation of metallic silver by the chloroplatinate ions. To obtain a uniform black velvety deposit without gassing, the disc had to be rotated at 200 r.p.m. during the platinization, a speed at which the current density employed corresponds approximately to the diffusion limiting current. At 150 r.p.m. the deposition of platinum black was accompanied by hydrogen evolution, and at 300 r.p.m. a grey compact deposit was formed at the rim of the disc only and none at the centre. Newman[34] has predicted that, below the limiting current, the current density is higher at the edge of a rotating disc electrode than at the centre, and this has been confirmed for the electrodeposition of copper.[35,36]

After platinization the electrode was soaked overnight in 1M-perchloric acid to remove all the dissolvable lead from the surface layers.[37] The surface area S of the platinized disc was determined from the length of the hydrogen arrest of the galvanostatic charging curve[38] taken in a 1M-perchloric acid solution. The point where plots against current of the cathodic and anodic arrest lengths crossed was taken as characterizing the area. The result in C was converted into m^2 by dividing by 2·80. The area was periodically measured during the series of kinetic experiments, the average daily rate of decrease being 0·3%. This is of the order of magnitude expected from various observations in the literature.[4]

The bright platinum disc was pretreated by the method of Archer:[1] 15 min at 0·4 V (NHE) followed by 10 min at 1·11 V (NHE), the disc being rotated at 100 r.p.m. Quinhydrone served as reference electrode.

Kinetic Runs with Platinum Discs.—The disc was rotated in a known volume of 0·01M-perchloric acid in a flanged QF 500 cm^3 Pyrex beaker fitted with a Perspex lid and immersed in a thermostat bath at 25° ± 0·01 °C. At time t_0, a standard volume of concentrated $[Co(NH_3)_5Br]Br_2$ dissolved in 0·01M-perchloric acid was added so as to give 200 cm^3 of the required reactant concentration. Periodically samples of 1 cm^3 were removed and analysed in a Hitachi–Perkin-Elmer 124 spectrophotometer at 300 nm, using special 1-cm semi-micro cells with thick side walls made of black quartz (Hellma Ltd.). At 300 nm the extinction coefficient was found to be 973 ± 9 cm^{-1} l mol^{-1} (*cf.* 987[6e]). The homogeneous reaction was also followed to allow the actual starting concentration of the heterogeneous run to be determined: k_{hom} was $(5{\cdot}79 \pm 0{\cdot}07) \times 10^{-6}$ s^{-1} in 0·01M-perchloric acid (*cf.*[2] $6{\cdot}17 \times 10^{-6}$ s^{-1}).

The potential of the platinized disc was monitored against a quinhydrone reference electrode in 0·01M-perchloric acid connected by a Luggin capillary filled with 0·01M-perchloric acid. In two runs the platinum disc was held at constant potential using an accumulator and a 100 kΩ resistor. The counter electrode was a platinum foil, also immersed in 0·01M-perchloric acid and joined to the reaction solution *via* a ceramic porous plug from a Beckman remote junction glass electrode.

Kinetic Runs with Mercury(II) *Sulphide and Silver*(I) *Bromide.*—A weighed amount of catalyst and a magnetic stirrer were placed in a 500 cm^3 conical flask immersed in a thermostat at 25·0 °C. Perchloric acid (500 cm^3 of 0·01M) was separately equilibrated. At time t_0, a weighed amount of $[Co(NH_3)_5Br]Br_2$ was dissolved in the acid, and the solution was poured into the conical flask. The stirrer was maintained at a speed such that all the solid was continuously agitated in the liquid. Aliquots (5 cm^3) were removed at regular intervals, filtered through a sintered glass disc of porosity 3, and the reaction followed spectrophotometrically as for the runs involving platinum discs. Larger aliquots were used for estimation of Co^{II}.

Kinetic Runs with Carbons and $Na_3[Co(NO_2)_6]$.—To exclude the effects of photochemical reduction, the reactions

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were carried out in 50 cm^3 closed dark amber bottles in the dark. Weighed amounts of carbon were placed in the bottles. At times t_0, weighed amounts of $Na_3[Co(NO_2)_6]$ were dissolved in water previously equilibrated in a thermostat, and the appropriate volumes of solution were pipetted into the bottles. These were clamped in position on a wheel rotating in the thermostat at a speed such that all the solid was constantly agitated. At various times, a bottle was removed from the thermostat and the carbon filtered off with a ground glass disc of porosity 3. The concentration of $Co(NO_2)_6^{3-}$ in the filtrate was determined spectrophotometrically at 480 nm and the concentration of cobalt(II) by the extraction technique described below. Both the filtration and the extraction apparatus were lagged against stray light with insulation tape. The contents of any given bottle were used for measurements at one value of time only.

Kinetic Runs with Carbons and $[Co(NH_3)_6]Cl_3$.—The procedure was similar to that described above, except that both clear glass and dark amber bottles were employed in a normally illuminated laboratory. The salt was dissolved in thermally equilibrated 0·15M-ammonia solutions, and the reaction followed spectrophotometrically at 474 and 503 nm.

Analysis for Cobalt(II).—In the runs using platinized platinum, aliquots of solution were diluted with concentrated hydrochloric acid so that the ratio $[Cl^-]/[Co^{II}]$ was at least 10^4, and the cobalt(II) content was estimated [2] from the absorbance at 690 nm (extinction coefficient 450 l mol^{-1} cm^{-1}). In all other experiments, a modification of the analytical method of Ellis and Gibson [39] was employed. The pH of a 10 cm^3 aliquot of solution was adjusted, if necessary, to between 1 and 4 with 0·1M-perchloric acid. Ammonium thiocyanate, or sodium thiocyanate for the reaction of $Co(NO_2)_6^{3-}$ (1 cm^3 of 25% w/v) and triphenylmethylarsonium iodide (1 cm^3 of 2% w/v) were added, and the resulting $(MePh_3As)_2Co(NCS)_4$ complex was extracted into 1,2-dichlorobenzene (5 cm^3). The aqueous layer was extracted twice more with 1,2-dichlorobenzene (1 cm^3). A further 1 cm^3 triphenylmethylarsonium iodide solution was added and complex extracted with two fresh 1 cm^3 portions of organic solvent. The procedure in the last sentence was repeated once more. The organic fractions were combined, filtered if necessary, and made up to volume (25 cm^3). Experiments with standard cobalt(II) solutions showed that at low concentrations ($<$*ca.* 10^{-4}M) more than 97% of the initial cobalt(II) was removed by the first (5 + 2) cm^3 extract. For solutions weak in cobalt(II), therefore, the second and third extracts were eliminated, and volume made up to 10 cm^3. The sensitivity was thereby enhanced by a factor of 2·5 at a cost of introducing a maximum error of 3%. The solutions were analysed either spectrophotometrically using a Hitachi–Perkin-Elmer model 124 spectrophotometer, or by atomic absorption using a Perkin-Elmer 290B atomic absorption spectrophotometer. Calibration curves were constructed from the values of the absorbance at 627 nm (extinction coefficient 790 l mol^{-1} cm^{-1}) for extracts from solutions of known cobalt(II) concentration, or from the atomic absorption of these solutions at the 240·73 nm absorption line of cobalt. Agreement between the two techniques was excellent. The optical method, with scale expansion, allowed detection of less than 1×10^{-6}-M-cobalt(II).

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