# Heterogeneous Catalysis in Solution. Part XI.[1] Reduction of Tris(ethylenediamine)cobalt(III) by a Carbon Black

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The reduction of $[Co(en)_3]^{3+}$ ions in the presence of carbon black has been studied at 40 °C in aqueous solutions containing iodide ions. The reduction is accompanied by the oxidation of iodide ions, and no cobalt(II) is produced in their absence. Measurements have been made of the amounts of $[Co(en)_3]^{3+}$ and of $I^-$ ions adsorbed on the carbon surface, the variation of pH, and the effects of adding various electrolytes.

SEVERAL workers [1-4] have noted that small amounts of cobalt(II) or other decomposition products are formed during the charcoal-catalysed racemisation of the ion $[Co(en)_3]^{3+}$ (en = ethylenediamine). Although one of the proposed mechanisms for the racemisation involves cobalt(II) intermediates,[2] the reduction process itself has never been investigated. We have therefore carried out a detailed study of the reduction of $[Co(en)_3]^{3+}$ ion by a carbon black to shed light on the mechanism of the racemisation reaction. The carbon black chosen, Black Pearls 2 (bp), possessed a high surface area (850 m$^2$ g$^{-1}$) so that appreciable amounts of the complex were adsorbed. The extent of adsorption could then be measured spectrophotometrically. With solid catalysts of low surface area,[5-7] the nature of the adsorption process has to be inferred from the kinetic data.

## RESULTS AND DISCUSSION

Homogeneous solutions of the salt $[Co(en)_3]I_3$ were quite stable, and only in the presence of bp did reaction occur. During a typical experiment, the following variables were monitored: bulk concentrations of the complex ion, the iodide ion, and the reduction product, and the pH. Three of these variables exhibited a fast first stage followed by a much slower second stage (Figure 1). However, plots of $[Co^{II}]$ against time were linear and passed through the origin unless cobalt(II) was added. Since even at the longest times measured no more than 5% of the initial amount of cobalt was present as cobalt(II), the gradients of these lines were used [8a] to evaluate the initial rates of reduction, $v_R$ (Tables 1 and 2).

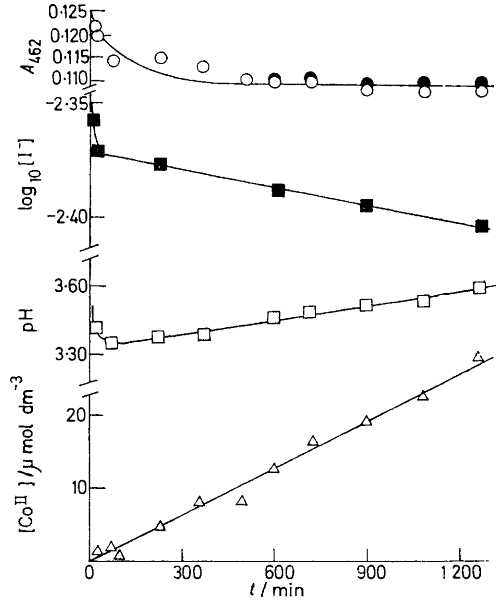

FIGURE 1 Typical variations with time of: (○), the optical absorbance at 462 nm of the ion $[Co(en)_3]^{3+}$ and (●), with corrections applied for reduction (see text); (■), $\log_{10}[I^-]$; (□), pH; and (△), $[Co^{II}]$. At $t = 0$ [run (5)] the values of these quantities were 0·185, −1·78, 6·10, and 0·0 respectively

*pH Behaviour*.—Suspensions of bp in water rapidly attained a pH of 3·78. Carbons that give acid reactions are well known; [9] in the case of bp the acidity is not due

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[1] Part X, R. J. Mureinik and M. Spiro, preceding paper.

[2] F. P. Dwyer and A. M. Sargeson, *Nature*, 1960, **87**, 1022.

[3] D. Sen and W. C. Fernelius, *J. Inorg. Nuclear Chem.*, 1959, **10**, 269.

[4] W. C. Erdman, H. E. Swift, and B. E. Douglas, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1365.

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

[6] I. R. Jonasson and D. R. Stranks, *Electrochim. Acta*, 1968, **13**, 1147.

[7] S. M. Hasany, Ph.D. Thesis, University of Adelaide, 1971.

[8] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1953 (*a*) p. 45, (*b*) p. 150.

[9] M. Smisek and S. Cerny, 'Active Carbon,' Elsevier, London, 1970, chs. 1—3.

to acid impurities[10] but to the surface itself. Since carbon blacks are generally prepared by burning organic substances of high carbon content in air, the solid on cooling contains surface oxygen–carbon complexes, surface oxides or carboxyl groups, or chemisorbed Experimental section). Thus bp contains adsorbed $CO_2$ to the extent expected if it had cooled down in an atmosphere of the gas. Washing progressively removed it until equilibrium with a normal atmosphere of low $CO_2$ content was attained.

TABLE 1

Rates of reduction of the ion $[Co(en)_3]^{3+}$ in the presence of bp carbon in aqueous solution (25 cm³) at 40 °C

| Run | $10^3[Co(en)_3I_3]_0$ / M | $m_{cat}$ / g | $10^3[Co(en)_3{}^{3+}]_\infty$ / M | $10^3[Co(en)_3{}^{3+}]_{ads}$ $(=A)$ / M | $10^3[I^-]_{ads}$ $(=B)$ / M | $10^6k_1$ / s⁻¹ | $10^9k_0$ / mol dm⁻³ s⁻¹ | $10^3k_{ads}$/s⁻¹ for I⁻ | $10^3k_{ads}$/s⁻¹ for $[Co(en)_3]^{3+}$ | $10^{10}v_{Red}$ / mol dm⁻³ s⁻¹ |
|---|---|---|---|---|---|---|---|---|---|---|
| (1) | 0·50 | 0·250 | 0·075 ± 0·02 | 0·425 ± 0·02 | 0·664 ± 0·013 | 2·85 ± 0·10 | 2·22 ± 0·10 | 4·3 ± 0·5 | 6·4 ± 0·5 | *ca.* 0 |
| (2) | 0·75 | 0·250 | 0·22 ± 0·02 | 0·53 ± 0·02 | 0·97 ± 0·02 | 1·33 ± 0·10 | 1·69 ± 0·10 | 3·6 ± 0·5 | | *ca.* 0 |
| (3) | 1·00 | 0·250 | 0·39 ± 0·02 | 0·61 ± 0·02 | 1·10 ± 0·02 | 1·92 ± 0·10 | 3·27 ± 0·10 | 4·1 ± 0·5 | 2·8 ± 0·5 | 0·56 ± 0·20 |
| (4) | 1·50 | 0·250 | 0·77 ± 0·02 | 0·73 ± 0·02 | 1·45 ± 0·02 | 1·18 ± 0·10 | 3·30 ± 0·10 | 3·5 ± 0·5 | 7·2 ± 0·5 | 1·72 ± 0·20 |
| (5) | 2·00 | 0·250 | 1·15 ± 0·02 | 0·85 ± 0·02 | 1·77 ± 0·02 | 0·88 ± 0·08 | 3·62 ± 0·10 | 4·1 ± 0·5 | 4·8 ± 0·5 | 3·60 ± 0·20 |
| (6) | 2·50 | 0·250 | 1·54 ± 0·02 | 0·96 ± 0·02 | 2·13 ± 0·02 | 1·33 ± 0·10 | 4·91 ± 0·10 | 3·9 ± 0·5 | 5·6 ± 0·5 | 5·59 ± 0·20 |
| (7) | 2·00 | 0·125 | 1·51 ± 0·02 | 0·49 ± 0·02 | 0·93 ± 0·02 | 7·36 ± 0·10 | 3·61 ± 0·10 | 5·7 ± 0·5 | 5·4 ± 0·5 | 2·57 ± 0·20 |
| (8) | 2·00 | 0·375 | 0·87 ± 0·02 | 1·13 ± 0·02 | 2·53 ± 0·02 | 3·30 ± 0·10 | 5·97 ± 0·10 | 3·7 ± 0·5 | 5·9 ± 0·5 | 3·10 ± 0·20 |
| (9) | 2·00 | 0·500 | 0·66 ± 0·02 | 1·34 ± 0·02 | 3·12 ± 0·02 | 0·71 ± 0·07 | 6·95 ± 0·10 | 3·8 ± 0·5 | 5·6 ± 0·5 | 2·46 ± 0·20 |
| (10) [a] | 2·00 | 0·250 | 1·05 ± 0·02 | 0·95 ± 0·02 | 1·82 ± 0·03 | 0·20 ± 0·05 | 0·93 ± 0·10 | | | 8·26 ± 0·20 |
| (11) [a] | 1·00 | 0·250 | 0·32 ± 0·02 | 0·68 ± 0·02 | | | | | | 2·18 ± 0·20 |
| (12) [b] | 2·00 | 0·250 | 1·02 ± 0·02 | 0·98 ± 0·02 | 2·23 ± 0·03 | 1·92 ± 0·10 | 6·56 ± 0·20 | | | 1·98 ± 0·20 |
| (13) [b] | 1·00 | 0·250 | 0·28 ± 0·02 | 0·72 ± 0·02 | | | | | | 0·53 ± 0·20 |
| (14) [c] | 2·00 | 0·250 | 1·15 ± 0·02 | 0·85 ± 0·02 | | | | | | 3·55 ± 0·20 |
| (15) [c] | 1·00 | 0·250 | 0·39 ± 0·02 | 0·61 ± 0·02 | | | | | | 0·67 ± 0·20 |

[a] Under nitrogen. [b] Under oxygen. [c] Using ' washed ' bp.

TABLE 2

Rates of reduction of the ion $[Co(en)_3]^{3+}$ at 40 °C in solution (25 cm³) containing bp (0·250 g) in the presence of various added electrolytes

| Run | $10^3[Co(en)_3I_3]_0$ / M | Medium | $10^3[Co(en)_3{}^{3+}]_\infty$ / M | $10^3[Co(en)_3{}^{3+}]_{ads}$ $(=A)$ / M | $10^3[I^-]_{ads}$ $(=B)$ / M | $10^4[Co^{II}]_{ads}$ / M | $10^3[Na^+]_{ads}$ / M | $[Na^+]_{ads}/[I^-]_{ads}$ | $10^{10}v_{Red}$ / mol dm⁻³ s⁻¹ |
|---|---|---|---|---|---|---|---|---|---|
| (3) | 1·00 | $H_2O$ | 0·39 ± 0·02 | 0·61 ± 0·02 | 1·10 ± 0·02 | | | | 0·56 ± 0·20 |
| (5) | 2·00 | $H_2O$ | 1·15 ± 0·02 | 0·85 ± 0·02 | 1·77 ± 0·02 | | | | 3·60 ± 0·20 |
| (16) | 2·00 | $1 \times 10^{-2}$M-$HClO_4$ | 1·18 ± 0·02 | 0·82 ± 0·02 | | | | | 5·42 ± 0·20 |
| (17) | 1·00 | $0·5 \times 10^{-2}$M-$HClO_4$ | 0·42 ± 0·02 | 0·58 ± 0·02 | | | | | 1·05 ± 0·20 |
| (18) | 2·00 | $1·0 \times 10^{-4}$M-$Co^{II}$ | 1·12 ± 0·02 | 0·88 ± 0·02 | | 0·32 ± 0·02 | | | 3·60 ± 0·40 |
| (19) | 2·00 | $9·0 \times 10^{-4}$M-$[H_2en][ClO_4]_2$ | 1·11 ± 0·02 | 0·89 ± 0·02 | | | | | 3·84 ± 0·20 |
| (20) | 2·00 | Combined (18) & (19) | 1·04 ± 0·02 | 0·96 ± 0·02 | | 0·19 ± 0·02 | | | 3·60 ± 0·40 |
| (21) | 1·00 | $0·5 \times 10^{-4}$M-$Co^{II}$ | 0·36 ± 0·02 | 0·64 ± 0·02 | | 0·33 ± 0·02 | | | 0·93 ± 0·30 |
| (22) | 1·00 | $4·5 \times 10^{-4}$M-$[H_2en][ClO_4]_2$ | 0·38 ± 0·02 | 0·62 ± 0·02 | | | | | 0·84 ± 0·20 |
| (23) | 1·00 | Combined (21) & (22) | 0·39 ± 0·02 | 0·61 ± 0·02 | | 0·15 ± 0·02 | | | 0·74 ± 0·30 |
| (24) | 2·00 | $1·0 \times 10^{-2}$M-$NaClO_4$ | 0·98 ± 0·02 | 1·02 ± 0·02 | | | | | 2·99 ± 0·20 |
| (25) | 2·00 | $1·5 \times 10^{-2}$M-$NaClO_4$ | 0·89 ± 0·02 | 1·11 ± 0·02 | 1·47 ± 0·02 | | 0·6 ± 0·05 | 0·41 | 2·76 ± 0·20 |
| (26) | 1·00 | $0·5 \times 10^{-2}$M-$NaClO_4$ | 0·31 ± 0·02 | 0·69 ± 0·02 | | | | | 0·70 ± 0·20 |
| (27) | 2·00 | $0·5 \times 10^{-2}$M-NaI | 0·90 ± 0·02 | 1·10 ± 0·02 | 3·25 ± 0·02 | | 1·0 ± 0·1 | 0·31 | 7·03 ± 0·20 |
| (28) | 2·00 | $1·0 \times 10^{-2}$M-NaI | 0·84 ± 0·02 | 1·16 ± 0·02 | 4·56 ± 0·02 | | 2·2 ± 0·1 | 0·48 | 8·10 ± 0·20 |
| (29) | 2·00 | $1·5 \times 10^{-2}$M-NaI | 0·78 ± 0·02 | 1·22 ± 0·02 | 5·81 ± 0·02 | | 3·6 ± 0·1 | 0·62 | 9·26 ± 0·20 |
| (30) | 1·00 | $2·5 \times 10^{-3}$M-NaI | 0·30 ± 0·02 | 0·70 ± 0·02 | 2·02 ± 0·02 | | | | 1·23 ± 0·20 |
| (31) | 1·00 | $5·0 \times 10^{-3}$M-NaI | 0·27 ± 0·02 | 0·73 ± 0·02 | 2·69 ± 0·02 | | | | 1·95 ± 0·20 |
| (32) | 1·00 | $7·5 \times 10^{-3}$M-NaI | 0·20 ± 0·02 | 0·80 ± 0·02 | 3·36 ± 0·02 | | | | 2·14 ± 0·20 |
| (33) | 2·00 | Combined (24) & (27) | 0·85 ± 0·02 | 1·15 ± 0·02 | 3·05 ± 0·02 | | 1·3 ± 0·1 | 0·43 | 5·58 ± 0·20 |
| (34) | 2·00 | Combined (26) & (28) | 0·81 ± 0·02 | 1·19 ± 0·02 | 4·52 ± 0·02 | | 2·4 ± 0·1 | 0·53 | 8·35 ± 0·20 |
| (35) | 2·00 [a] | $H_2O$ | 1·12 ± 0·02 | 0·88 ± 0·02 | | | | | 0 |
| (36) | 2·00 [a] | $6 \times 10^{-3}$M-NaI | 0·94 ± 0·02 | 1·06 ± 0·02 | 2·53 ± 0·02 | | | | 2·71 ± 0·20 |

[a] $10^3[Co(en)_3(ClO_4)_3]_0$.

oxygen.[9] Carbon dioxide will always be present, and considerable amounts of the gas can be removed by pumping at room temperature or by heating.[11,12] The gas dissolves when bp is introduced into water. From the equilibrium constant for reaction (1) and Henry's

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \qquad (1)$$

constant for the solubility of $CO_2$ at 25[13] or 40 °C,[14] the pH of water in equilibrium with 1 atm $CO_2$ can be calculated to be *ca.* 3·91 at 25 °C (*ca.* 3·95 at 40 °C) and, for an atmosphere containing 1% $CO_2$, *ca.* 4·91 at 25 °C (*ca.* 4·95 at 40 °C). These values are very similar to those found (3·8, 4·8) for the first and last centrifugates, respectively, after thoroughly washing the carbon (see

When bp was introduced into solutions of the salt $[Co(en)_3]I_3$ at 40 °C of pH between 5·60 and 6·20 (depending on concentration), the pH fell within 30 min to between 3·20 and 3·50 (depending on the concentration and mass of catalyst). Most of this change is explained by solution of $CO_2$ desorbed from the carbon. The increase in $[H^+]$ above that produced by the same amount of bp in water was much less than the increase expected if $[Co(en)_3]^{3+}$ ions, on adsorption, had liberated an equivalent number of $H^+$ ions. Furthermore, the extent of adsorption of complex ion, as well as the change in pH, were the same using ' washed ' or untreated bp despite the difference of 1 pH unit between their aqueous suspensions. This suggests that the solid

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[10] Cabot Corporation, Ellesmere Port, Cheshire, personal communication, 1971.

[11] W. D. Schaeffer, W. R. Smith, and M. H. Polley, *Ind. and Eng. Chem.*, 1953, **45**, 1721.

[12] W. R. Smith and M. H. Polley, *J. Phys. Chem.*, 1956, **60**, 689.

[13] D. A. MacInnes, ' Principles of Electrochemistry,' Reinhold, New York, 1939, pp. 206—211.

[14] H. S. Harned and B. B. Owen, ' The Physical Chemistry of Electrolytic Solutions,' 3rd edn., Reinhold, New York, 1958, pp. 690—692.

itself possessed a degree of buffering ability. It should therefore have been capable also of removing $H^+$ ions from an acid solution, and indeed addition of bp to perchloric acid media raised the pH from 2·00 to 2·30.

The pH of the reaction mixtures increased to 3·50—3·80 (depending on the concentration and mass of catalyst) after *ca.* 21 h. Two reactions contributed to this rise: the reduction of the complex ion, which under our experimental conditions involves the couple (2),

$$[\mathrm{Co(en)_3}]^{3+} + 6\mathrm{H}^+ + e^- \rightleftharpoons \mathrm{Co}^{2+} + 3\mathrm{H_2en}^{2+} \qquad (2)$$

and aerial oxidation of iodide [equation (3)]. Quantitative calculations of the pH change on the basis of

$$\mathrm{I}^- + \mathrm{H}^+ + \tfrac{1}{4}\mathrm{O}_2 \rightleftharpoons \tfrac{1}{2}\mathrm{I}_2 + \tfrac{1}{2}\mathrm{H_2O} \qquad (3)$$

equations (2) and (3) agreed with experiment only if the decrease in $[H^+]$ was less than *ca.* 2 × $10^{-4}$M (Table 3).* For larger decreases the observed changes were smaller than the calculated ones, due to the solid's ability to buffer the pH.

TABLE 3

Calculated and observed changes in $[H^+]$ during the course of the reaction in solution (25 $cm^3$) at 40 °C

| Run | $m_{cat}$/g | $10^4[\mathrm{Co^{II}}]$ [a]/M | $10^4[\mathrm{I^-}]$ [b]/M | $-10^4\Delta[\mathrm{H^+}]$/M Calc. [c] | $-10^4\Delta[\mathrm{H^+}]$/M Obs. |
|---|---|---|---|---|---|
| (1) | 0·250 | *ca.* 0 | 1·28 | 1·28 | 1·52 ± 0·50 |
| (2) | 0·250 | *ca.* 0 | 0·97 | 0·97 | 0·73 ± 0·50 |
| (3) | 0·250 | 0·03 | 1·88 | 2·03 | 2·00 ± 0·50 |
| (4) | 0·250 | 0·10 | 1·90 | 2·40 | 1·22 ± 0·50 |
| (5) | 0·250 | 0·21 | 2·09 | 3·14 | 1·48 ± 0·50 |
| (6) | 0·250 | 0·32 | 2·83 | 4·43 | 1·94 ± 0·50 |
| (7) | 0·125 | 0·15 | 2·08 | 2·83 | 1·88 ± 0·50 |
| (8) | 0·375 | 0·18 | 1·02 | 1·92 | 1·71 ± 0·50 |
| (9) | 0·500 | 0·14 | 4·00 | 4·70 | 2·42 ± 0·50 |
| (10) [d] | 0·250 | 0·40 | $\not>$0·45 | 2·45 | 0·70 ± 0·50 |
| (12) [e] | 0·250 | 0·10 | 3·40 | 3·90 | 1·68 ± 0·50 |

[a] Produced between $t$ = 240 and 1 200 min; $x$. [b] Lost between $t$ = 240 and 1 200 min; $y$. [c] $6x + (y - x) = 5x + y$. [d] Between $t$ = 420 and 1 230 min; under nitrogen. [e] Between $t$ = 395 and 1 260 min; under oxygen.

*The Iodide Concentration.*—The process responsible for the initial rapid decrease in iodide concentration (Figure 1) is adsorption, while the subsequent slower decrease is caused by chemical reactions (see below). Plots of $[I^-]$, or log $[I^-]$, against time were linear after the fast initial decrease, and from these lines zero-order, $k_0$, and first-order rate constants, $k_1$, were calculated (Table 1). An estimate of the first-order rate constant of the adsorption process was derived from equation (4),

$$k_{\mathrm{ads}} = (2{\cdot}303/t)\log_{10}\{([\mathrm{I^-}]_0 - [\mathrm{I^-}]_\infty)/([\mathrm{I^-}]_t - [\mathrm{I^-}]_\infty)\} \qquad (4)$$

where subscripts on the concentrations refer to values of time. The 'infinite-time' concentration was determined by extrapolating $[I^-]$ back to $t = 30$ min where adsorption was essentially complete. This procedure is equivalent to the technique of curve stripping [8b] applicable where the second (first-order) process is much slower than the first (first-order) one. Table 1 shows that $k_{\mathrm{ads}} \gg k_1$, and that $k_{\mathrm{ads}}$ is roughly constant.

Rate constants for the second, slower, process of iodide disappearance were greater by an order of magnitude than rates of reduction of the ion $[\mathrm{Co(en)_3}]^{3+}$ and thus could only be partly accounted for by reaction (5). Experiments carried out under a nitrogen

$$\mathrm{Co^{III}} + \mathrm{I}^- \rightleftharpoons \mathrm{Co^{II}} + \tfrac{1}{2}\mathrm{I}_2 \qquad (5)$$

atmosphere showed that, after allowance for the fast adsorption process, the amount of iodide lost ($\not>$4·5 × $10^{-5}$M) corresponded closely to the amount of cobalt(II) produced (4·0 × $10^{-5}$M). The extra iodide lost in runs exposed to air can therefore be attributed to the aerial-oxidation reaction (3). This reaction was extremely slow in homogeneous solution at 40 °C even at pH 2 but was catalysed by bp; carbon has previously been found to catalyse redox reactions in solution.[15] As expected, considerably more iodide was oxidised in runs under an oxygen atmosphere [runs (5), (10), and (12) in Table 3].

Two sources of evidence confirmed that oxidation of iodide caused its slow disappearance. First, although iodine is very strongly adsorbed on carbon, some iodine was detected when filtered bp solid from a spent reaction mixture was shaken with water for 24 h, and the water then shaken with $CCl_4$. Second, the potential taken up by the carbon particles was measured. In a solution containing two or more redox couples, the electron-conducting carbon will adopt a mixture potential (the potential at which the sum of the anodic or oxidation currents equals the sum of the cathodic or reduction currents) that lies closest to the Nernst potential of the most electrochemically reversible couple.[16] In our experiments, couples (2) ($E^\ominus = 1{\cdot}97$ V [1]), (6), and (7) are

$$\mathrm{O}_2 + 4\mathrm{H}^+ + 4e^- \rightleftharpoons 2\mathrm{H_2O};\ E^\ominus = 1{\cdot}229\ \mathrm{V}^{17} \qquad (6)$$

$$\tfrac{1}{2}\mathrm{I}_2 + e^- \rightleftharpoons \mathrm{I}^-;\ E^\ominus = 0{\cdot}536\ \mathrm{V}^{17} \qquad (7)$$

known to be present. Couple (7) is highly reversible at platinum electrodes,[18] and even if its exchange current density on carbon were one or two powers of ten smaller [19] it would still be classed as reversible. The oxygen couple is irreversible since oxygen evolution on carbon requires a high overpotential [20] and, for reasons discussed later, couple (2) is also expected to be highly irreversible. The mixture potential should therefore be close to the Nernst potential for couple (7). We found that a bp carbon electrode in the experimental solution took up a potential of 540 ± 4 mV, which supports the idea that iodide lost from the solution was oxidised to iodine.

*The Concentration of the Ion* $[\mathrm{Co(en)_3}]^{3+}$.—Rapid initial adsorption of complex ion (Figure 1) was followed by a very much slower reduction to $Co^{II}$. Beyond the initial period a plot of ($[\mathrm{Co(en)_3}^{3+}] + [\mathrm{Co^{II}}]$) against time was thus found to be horizontal (filled circles in Figure 1) and

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* 1M = 1 mol $dm^{-3}$.

[15] T. Groenewald, J. M. Austin, and M. Spiro, unpublished work.

[16] M. Spiro and A. B. Ravnö, *J. Chem. Soc.*, 1965, 78; M. Spiro and P. W. Griffin, *Chem. Comm.*, 1969, 262.

[17] 'The Encyclopaedia of Electrochemistry,' ed. C. A. Hampel, Reinhold, New York, 1964, pp. 415—421.

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

[19] Z. Galus and R. N. Adams, *J. Phys. Chem.*, 1963, **67**, 866.

[20] Ref. 17, p. 150.

yielded a value for the 'infinite-time' concentration of complex ion after completion of adsorption. First-order rate constants for adsorption of $[Co(en)_3]^{3+}$ were then calculated as for iodide with an equation analogous to (4), and are listed in Table 1. Their values are roughly constant, and suggest a reasonably fast adsorption process first-order in bulk concentration of adsorbate and with a half-life of *ca.* 2 min. This is in keeping with Hasany's observation[7] that the ions $[Co(en)_3]^{3+\text{ or }2+}$ and $[Co(edta)]^{1-\text{ or }2-}$ (edta = ethylenediaminetetra-acetato) attain adsorption equilibrium on platinised platinum within 5 min.

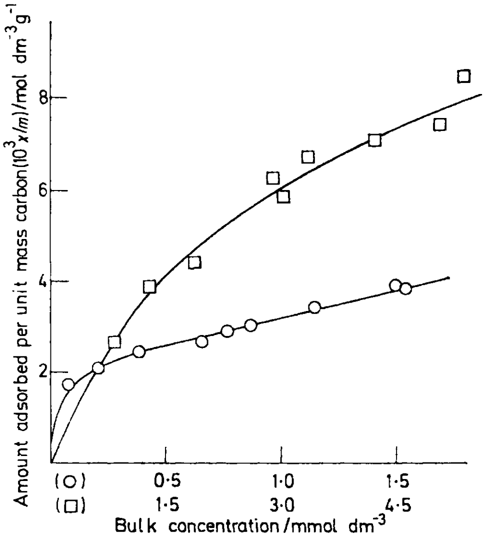

FIGURE 2 Adsorption isotherms on bp carbon for $[Co(en)_3]^{3+}$ (○) and $I^-$ (□) from solutions (25 cm³) at 40 °C containing only the $[Co(en)_3]I_3$ salt

*Adsorption Isotherms.*—For convenience, $[Co(en)_3{}^{3+}]_{ads}$ and $[I^-]_{ads}$ are defined as in equations (8) and (9), where

$$[Co(en)_3{}^{3+}]_{ads} = [Co(en)_3{}^{3+}]_0 - [Co(en)_3{}^{3+}]_\infty = A \qquad (8)$$

$$[I^-]_{ads} = [I^-]_0 - [I^-]_\infty = B \qquad (9)$$

the subscripts 0 and ∞ refer to time. Each adsorbed quantity has thus been defined as the extra molarity that would be obtained if all the adsorbate desorbed again into the volume of solution used. Multiplication of the 'concentration' of the adsorbates by 0·025 dm³ gives the number of moles adsorbed. Adsorption isotherms were plotted with the values of $A$ and $B$ for runs (1)—(9) in Table 1, and are shown in Figure 2. Neither species exhibited Langmuir adsorption behaviour, but the adsorption of both ions was satisfactorily described by the Freundlich equation (10). Here $x$ is the amount

$$\log(x/m) = \log k' + n \log c \qquad (10)$$

adsorbed ($A$ or $B$, in molarity units), $m$ the mass of bp carbon (in g), and $c$ the bulk molarity. The following values were found for the parameters $k'$ and $n$:

$$[Co(en)_3]^{3+}\colon\ k' = 0{\cdot}0178 \pm 0{\cdot}0018,\ n = 0{\cdot}250 \pm 0{\cdot}003$$

$$I^-\colon\ k' = 0{\cdot}20_3 \pm 0{\cdot}02,\ n = 0{\cdot}61 \pm 0{\cdot}06$$

Since the two exponents $n$ differ, the ratios in which the two ions were adsorbed from various $[Co(en)_3]I_3$ solutions differed also. In no case was this ratio close to 1 : 3.

In several earlier papers, the type of adsorption isotherm has been inferred from the form of the heterogeneous kinetics. In investigations of the effects of platinum,[21] mercury(II) sulphide,[5] and silver(I) bromide[5] on aqueous $[Co(NH_3)_5Br]^{2+}$, where the solids were later shown[22] to cause reduction of the complex ion, its absorption was best described by the Langmuir equation. On the other hand, catalysis by charcoal of the reaction between aqueous ethyl iodide and silver ions was more consistent with Freundlich adsorption.[23] It would seem the adsorbant rather than the adsorbate determines the type of isotherm.

*Rate Law for Reduction of the Ion* $[Co(en)_3]^{3+}$.—A plot of $v_{Red}$ against $AB$ was found to be linear, and we can write equation (11). At 40 °C, $k = (3{\cdot}61 \pm 0{\cdot}10) \times$

$$v_{Red} = kAB - \text{constant} = k(AB - A_0B_0) \qquad (11)$$

$10^{-4}$ dm³ mol⁻¹ s⁻¹ and $A_0B_0 = (0{\cdot}52 \pm 0{\cdot}02) \times 10^{-6}$ mol² dm⁻⁶. If the rate-determining step of reaction (5) is interaction between adsorbed $[Co(en)_3]^{3+}$ and $I^-$ ions, the rate would be expected to be proportional to the product $AB$. The intercept $kA_0B_0$ complicates this interpretation. No cobalt(II) ions were detected in the two most dilute solutions [runs (1) and (2) in Table 1] even after 90 h, probably because all the cobalt(II) ions were adsorbed (see below) or else reoxidised by air or by oxygen adsorbed on the carbon. Another explanation could be partial adsorption of the reacting ions on inactive sites, for the surface is probably heterogeneous both chemically and physically.[24,25] An analogous intercept was observed[26] for the rate equation for racemisation of $(+)_{589}[Co(en)_3]I_3$.

From the crystal structures of $[Co(en)_3]X_3,H_2O$ (X = Cl[27] and Br[28]), a value of *ca.* 4·15 Å can be calculated for the radius of the ion $[Co(en)_3]^{3+}$. The radius of the $I^-$ ion is[29] 2·16 Å. It can then be shown, from the results in Table 1, that both adsorbed species together occupy only *ca.* 5% of the total surface area. Much of this area may comprise micropores which were accessible to $N_2$ molecules in the Brunauer, Emmett, and Teller (B.E.T.) area determination but not to the larger species in our experiments. Nevertheless, the surface occupancy is low and suggests that average

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

[22] R. J. Mureinik, A. M. Feltham, and M. Spiro, *J.C.S. Dalton*, 1972, 1981.

[23] J. M. Austin, O. D. E.-S. Ibrahim, and M. Spiro, *J. Chem. Soc.* (*B*), 1969, 669.

[24] V. A. Garten and D. E. Weiss, *Rev. Pure Appl. Chem.*, 1957, **7**, 69.

[25] H. P. Boehm, E. Diehl, W. Heck, and R. Sappok, *Angew. Chem. Internat. Edn.*, 1964, **3**, 669; H. P. Boehm, *ibid.*, 1966, **5**, 533.

[26] R. J. Mureinik and M. Spiro, following paper.

[27] K. Nakatsu, *Bull. Chem. Soc. Japan*, 1962, **35**, 832.

[28] M. Iwata, K. Nakatsu, and Y. Saito, *Acta Cryst.*, 1969, **B25**, 2562.

[29] A. F. Wells, 'Structural Inorganic Chemistry,' Oxford University Press, 1946.

distances between adsorbed species are large. This may be the result of strong electrostatic repulsions between like-charged adsorbed species. Adsorption of $I^-$ ions will appreciably lessen the net repulsion between adsorbed $[Co(en)_3]^{3+}$ ions. It is significant that when reaction (5) was carried out in sodium iodide solutions, not only were more iodide ions adsorbed but also more ions of the complex (Table 2). The low coverage of the surface should not affect the rate constant since the electron transfer between adsorbed $[Co(en)_3]^{3+}$ and $I^-$ ions probably takes place through the electron-conducting carbon catalyst.[15,16] If any surface groups are not conjugated to the bulk carbon and hence do not conduct electrons, ions adsorbed on these sites should not react. Adsorption on inactive sites was suggested in the previous paragraph as a possible reason for the intercept in equation (11).

*Variation of Rate with Mass of Catalyst.*—As $m_{cat}$ increased, $v_{Red}$ passed through a maximum [runs (7), (5), (8), and (9) in Table 1]. A similar relation was observed by Morawetz *et al.*[30] for electron-transfer reactions catalysed by polyelectrolytes, but their explanation does not apply where the mechanism is one of electron transfer through the catalyst. Here, as more carbon is added, more $[Co(en)_3]^{3+}$ and $I^-$ ions are adsorbed and the rate rises. However, when more carbon is present there will also be more of the inactive sites postulated above to account for the intercept in equation (11). If these sites adsorb the reactants preferentially, the rate will fall again. The product of adsorbed and chemically reactive species is therefore given by $AB - (m_{cat}/0{\cdot}250\ g)A_0B_0$. This quantity, as the numbers show, is proportional to $v_{Red}(m_{cat})^2$ as in equation (12).

$$v_{Red} = \frac{k''}{(m_{cat})^2}\left(AB - \frac{m_{cat}}{0{\cdot}250} A_0B_0\right) \qquad (12)$$

The rate of the surface reaction is now expressed as the product of two effective surface concentrations. A complete analysis would also have to take into account the surface concentrations of the adsorbed product species $Co^{II}$ and $I_2$. However, the whole of the right-hand side of equation (12) should be proportional to $m_{cat}$ at constant volume of solution. That it is not could mean either that $m_{cat}^{-2}$ should really be written $m_{cat} . m_{cat}^{-3}$, with the involvement of another adsorbed species, or, more likely, that the interpretation of the rate law is more complex, as the following electrochemical considerations indicate.

*Electrochemical Aspects of the* $[Co(en)_3]^{3+}$–$Co^{II}$ *System.*—Several aspects of the electron-exchange reaction (13)

$$[Co(en)_3]^{3+} + e^- \rightleftharpoons [Co(en)_3]^{2+} \qquad (13)$$

have been investigated by different workers.[31-35] Under conditions where the complex $[Co(en)_3]^{2+}$ can exist (*i.e.* in the presence of excess of free en[32] and with rigorous exclusion of oxygen[34,35]), couple (13) is electrochemically reversible at a platinum electrode.[33] From reported values[33] of the electrochemical rate constant $k_{el}$ and cathodic transfer coefficient $\alpha$ at 25 °C, the exchange current density $j_0$ of couple (13) appropriate for the concentrations used in our work ($c_{Ox} = 1 \times 10^{-3}$, $c_{Red} = 1 \times 10^{-5}$M) may be calculated from equation (14)

$$j_0 = Fk_{el}c_{Ox}^{1-\alpha}c_{Red}^{\alpha} \qquad (14)$$

to be 6·7 A $m^{-2}$ ($F$ = Faraday's constant). At 40 °C $j_0$ would be greater; at a carbon instead of a platinum electrode it would be smaller.[19] These two influences will tend to cancel.

Under our experimental conditions (pH 3·50), the potential of couple (2) is 1·65 V. The mixture potential in the reacting solution was found to be 0·54 V (see above) so that the overpotential $\eta$ on the $[Co(en)_3]^{3+}$–$Co^{II}$ couple at the carbon surface is −1·11 V. The Tafel equation (15) then predicts a current density $j$ of

$$j = j_0 \exp(-\alpha F\eta/RT) \qquad (15)$$

*ca.* $1{\cdot}9 \times 10^5$ A $m^{-2}$. The observed rates of reduction (typically $3 \times 10^{-10}$ mol $dm^{-3}$ $s^{-1}$) correspond to a current density of $v_{Red}VF/A$ ($V$ = volume of solution, $A$ = surface area of solid) which equals *ca.* $4 \times 10^{-9}$ A $m^{-2}$. The main reason for this huge discrepancy of almost $10^{13}$ lies in the change in reaction conditions. From values[36] of the protonation constants of en and the stability constant of the ion $[Co(en)_3]^{2+}$, the concentration of the latter at pH 3·50 can be calculated to be *ca.* $10^{-30}$M. Bartelt and Skilandat showed[33] that only those ions of different oxidation states that possess the same stoicheiometry take part in electron exchange at platinum, and that $[Co(en)_2]^{2+}$ and $[Co(en)]^{2+}$ are electrochemically inactive. Thus couple (2), which is the one involved here, is highly irreversible compared to (13) and its $j_0$ value is considerably smaller. This is hardly surprising since reaction (2) involves cleavage of six Co–N bonds.

It is probable, none the less, that an electrochemical mechanism predominates in reaction (5), with the carbon at a mixture potential determined by the current–voltage curves of couples (2) and (7). For a full electrochemical interpretation it would be necessary to know these curves and their dependence on the concentrations of the relevant species.

*Effect of Added Electrolytes.*—Addition of perchloric acid at a constant ratio of acid to reactant significantly increased the reaction rates [Table 2: runs (5) and (16), (3) and (17)]. The *ca.* 20-fold increase in hydrogen-ion concentration would raise the potential of couple (2) by *ca.* $0{\cdot}062 \log_{10} (20)$[6] or 0·48 V. The couple would thus

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[30] H. Morawetz and B. Vogel, *J. Amer. Chem. Soc.*, 1969, **91**, 563; H. Morawetz and G. Gordimer, *ibid.*, 1970, **92**, 7532.

[31] W. B. Lewis, C. D. Coryell, and J. W. Irvine, *J. Chem. Soc.*, Suppl. No. 2, 1949, 386.

[32] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, 1961, **65**, 1892.

[33] H. Bartelt and H. Skilandat, *J. Electroanalyt. Chem.*, 1969, **23**, 407.

[34] P. Bijl and G. de Vries, *J.C.S. Dalton*, 1972, 303.

[35] U. Künkel, H. Bartelt, and R. Landsberg, *Z. phys. Chem. (Leipzig)*, 1970, **245**, 135.

[36] 'Stability Constants of Metal-ion Complexes,' eds. L. G. Sillén and A. E. Martell, *Chem. Soc. Special Publ.* Nos. 17 (1964) and 25 (1971).

be subject to a much greater overvoltage at the mixture potential, and this explains the enhancement in rate.

In runs (18)—(23) in Table 2, the effects of the products of the reaction on its rate were investigated. The products were added at constant ratio to the reactants, and experiments were conducted in the presence of excess of cobalt(II) [runs (18) and (21)], excess of $H_2en^{2+}$ [runs (19) and (22); en was added in this form so as to alter the pH as little as possible], and excess of both products together [runs (20) and (23)]. In experiments with added cobalt(II), plots of $[Co^{II}]$ against time were linear and, on extrapolation back to zero time, gave $[Co^{II}]$ intercepts smaller than the added concentrations. These low intercepts can be attributed to cobalt(II) adsorption on the bp carbon. {In the absence of $[Co(en)_3]I_3$, the amounts of cobalt(II) that had been added in these experiments were totally adsorbed by bp under the same conditions.} The extent of adsorption of the ion $[Co(en)_3]^{3+}$ was apparently unaffected, but iodide adsorption was not determined. At an initial $[Co(en)_3]I_3$ concentration of 2mM, addition of the two reduction products either separately or together had little effect on the rate. At the lower initial concentration of 1mM the rates did appear to increase, perhaps because relatively more cobalt(II) was adsorbed. If this and/or adsorption of $H_2en^{2+}$ enhanced the extent of adsorption of the oppositely charged iodide ions then the increases in rate would be explained [equation (11)].

These results suggested that the adsorption of ions other than the reactants and products could be important. In runs (24)—(34) in Table 2, experiments were carried out in which sodium perchlorate or sodium iodide, or both, were added to the reaction solution. Both $Na^+$ and $I^-$ were adsorbed on bp, but, within the experimental error of e.m.f. measurements with a perchlorate-sensitive electrode, $ClO_4^-$ ions were not adsorbed from solutions of sodium perchlorate. Perchlorate concentrations could not be monitored in the reaction solutions because iodide interfered, and it was assumed that no perchlorate ions were adsorbed from the reaction media either.

With increasing concentration of NaI, more iodide and sodium ions were adsorbed. The amount of adsorbed $[Co(en)_3]^{3+}$ rose also, presumably because of the extra iodide anions on the surface. There was a positive correlation between the concentration of NaI and the rate of reduction of the ion $[Co(en)_3]^{3+}$, as expected from equation (11). Addition of sodium perchlorate tended to decrease the rate of reduction. This was associated with a rise in the adsorption of sodium and $[Co(en)_3]^{3+}$ ions and a fall in the extent of iodide adsorption. If we assume that the value of $A_0B_0$ in (11) remains unchanged in the presence of sodium salts, the rates fit the empirical equation (16)

$$v_{\text{Red}} = (AB - A_0B_0)/\{(p[\text{Na}^+]_{\text{ads}}/B) + q\} \quad (16)$$

with $p = 6{\cdot}1_2 \times 10^3$ and $q = 2{\cdot}7_7 \times 10^3$ mol dm$^{-3}$ s. Equation (16) must reduce to (11) when $[Na^+]_{ads} = 0$, and indeed $1/q$ ($3{\cdot}6_1 \times 10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$) agrees excellently with $k$. The form of equation (16) suggests competition between sodium and iodide ions for surface sites. Since more iodide than sodium was adsorbed, the retarding effect on the rate of adsorbed sodium was swamped in NaI solutions and became apparent only when $NaClO_4$ was added. It now becomes possible to explain runs (35) and (36) in Table 2. In the complete absence of iodide ion there was no reduction of $[Co(en)_3]^{3+}$ at all, a strong indication that the bp carbon itself was not acting as reductant. Addition of enough NaI to the perchlorate salt to give the same iodide concentration as when the iodide salt was used, gave a lower rate of reaction than did the iodide salt itself [run (5)]. Clearly sodium ions added as part of NaI were partly adsorbed and decreased the rate of reduction.

## EXPERIMENTAL

*Materials.*—The complexes $[Co(en)_3]I_3,H_2O$ and $[Co(en)_3][ClO_4]_3$ were prepared [37,38] as before.[1] The carbon black was Black Pearls 2 (bp) of surface area 850 m$^2$ g$^{-1}$ (B.E.T. $N_2$) and was supplied by Cabot Corporation, Ellesmere Port, Cheshire. Sodium iodide (Hopkin and Williams) was recrystallised twice from warm water, and dried and stored *in vacuo* over silica gel. Ethylenediamine (B.D.H.) was used as supplied. All other reagents were of AnalaR grade. Doubly distilled water was used throughout.

*Method.*—All reactions were carried out with solutions (25 cm$^3$) in closed dark amber bottles (50 cm$^3$) rotated at 32 rev. min$^{-1}$ in a $40{\cdot}0 \pm 0{\cdot}1$ °C thermostat. Further details are given in ref. 22. Once the carbon had been filtered off there was no further reduction of complex.

Analysis for cobalt(II) was carried out by the modified method of Ellis and Gibson [39] described elsewhere.[22] The concentration of the ion $[Co(en)_3]^{3+}$ was monitored spectrophotometrically at 462 nm, where the absorption coefficient was found to be $93 \pm 2$ dm$^3$ mol$^{-1}$ cm$^{-1}$, using a Hitachi–Perkin-Elmer model 124 spectrophotometer. Iodide was determined by titration with standard sodium iodate.[40] Sodium was analysed with an Eel flame photometer. A Pye model 78 pH meter was used for pH measurements.

Perchlorate was determined with a perchlorate-ion selective electrode prepared in the following way. The dry body of a Corning No. 476041 calcium-selective electrode was filled with liquid ion-exchange resin (1 cm$^3$) for an Orion chloride electrode and allowed to stand in air for 6 h to enable the resin to permeate through the membrane under gravity. The electrode was then assembled and soaked in saturated potassium perchlorate solution for 2 h. After thorough external rinsing with water, the electrode behaved as a perchlorate-sensitive electrode in halide-free solutions. A saturated calomel electrode was used as reference and potentials were measured on a Unisol digital ion meter. Concentrations of perchlorate in test solutions were determined from a calibration curve constructed with standard sodium perchlorate solutions. The measurements were highly reproducible. A literature method [41] for

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[37] J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *Inorg. Synth.*, 1960, **6**, 183.

[38] J. B. Work, *Inorg. Synth.*, 1946, **2**, 221.

[39] K. W. Ellis and N. A. Gibson, *Analyt. Chim. Acta*, 1953, **9**, 275.

[40] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 1946, p. 441.

[41] H. Kurz and G. Renner, *Z. Analyt. Chem.*, 1962, **186**, 368.

estimating perchlorate by means of Nitron was tried and found wanting.

The potential taken up by carbon in the solution was determined by means of a ' bp electrode.' It was made by compressing bp carbon inside a 7 cm long glass tube so as to form a plane surface of bp at the open end. Electrical contact was provided by a platinum wire which had been previously sealed into the glass. The open end of the bp electrode was immersed in a stirred solution of the reaction mixture, and its potential measured relative to a saturated calomel electrode using a Radiometer 4 pH meter as a millivoltmeter. Steady readings were obtained within minutes of the electrodes being introduced into the solution.

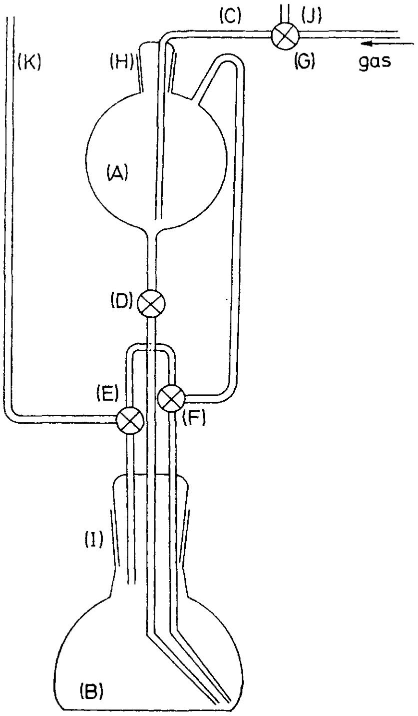

FIGURE 3 Apparatus used for conducting experiments under controlled atmospheres: (A), bulb for saturating the solution with the appropriate gas before reaction; (B), reaction flask; (C), gas inlet; (D), two-way tap; (E)—(G), three-way taps; (H), (I), ground-glass stoppers sealed with Apiezon L grease and springs; and (J), (K), exhaust tubes

Experiments in a controlled atmosphere were conducted in the reaction vessel depicted in Figure 3. A weighed amount of bp carbon was placed in the dry flask (B) together with a magnetic stirrer follower. The upper part of the apparatus was then inserted by means of stopper (I), and the whole vessel was seated on the floor of the thermostat. The height of the vessel was such that bulb (A) was then below the water level. An aqueous solution (25 cm$^3$) of complex at the appropriate concentration, thermally equilibrated, was introduced in to bulb (A), and tube (C) was set in place with stopper (H). The appropriate gas ($O_2$ or $N_2$), saturated with water vapour by passage through a water-filled gas bubbler immersed in the thermostat, was passed through the solution *via* tube (C) and thence through the reaction vessel *via* tap (F). After purging for 1 h, tap (D) was opened at time $t_0$ and the solution allowed to run under gas pressure into (B). The whole vessel was raised on to an immersible magnetic stirrer (Rank Bros., Bottisham, Cambridge), and the stirrer was started at such a speed that all the solid was continuously agitated. The gas was allowed to flow for a further 10 min through the solution and then taps (D)—(F) were closed, sealing off flask (B), and the gas flow stopped. After suitable time intervals, the whole apparatus was removed from the thermostat and the contents of (B) filtered as rapidly as possible. Runs without the solid present showed that the procedure prior to actual reaction caused no concentration change in a solution of the complex. Runs under a controlled atmosphere were extremely time consuming: at best three points on a concentration–time plot were obtained per week.

A washed sample of bp carbon was prepared as follows. Bp (0·250 g) was weighed into a reaction bottle, distilled water (25 cm$^3$) was added, and the whole weighed. The bottle was then rotated for 2 h after which the contents were centrifuged and as much centrifugate as possible removed without allowing the solid to dry out. All the solid was then washed back into the bottle and the difference in weight determined. This value was used to calculate the amount of water to be added to restore the contents to their original volume. The bottle was then rotated again and the whole procedure repeated until there was little change in the pH of successive centrifugates. Values for a typical sequence were 3·78, 4·10, 4·41, 4·65, and 4·83; after five washes, the pH converged to 4·70—4·90. Where washed solid was to be used as a catalyst in a kinetic run, the washed and centrifuged carbon was flushed back into the bottle and weighed. This weight was used to calculate the necessary volume of a concentrated solution of complex that, when added to the carbon, would give the desired total volume and concentration for the kinetic run. In an experiment to determine how much solid was lost in the washing procedure, no more than 0·010 g (4%) was unaccounted for after allowing the solid to dry in air.

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