Heterogeneous Catalysis in Solution. Part 16.[1] Racemisation of $(+)_{589}$-Tris(ethylenediamine)cobalt(III) by a Carbon Black in Alkaline and Ethylenediamine Solutions

By **Peter D. Totterdell** and **Michael Spiro,*** Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

The rate of racemisation at 25 °C of aqueous $(+)_{589}[Co(en)_3][ClO_4]_3$ in the presence of Black Pearls 2 carbon increases sharply on the addition of sodium hydroxide. The catalytic reaction is first order in adsorbed $[OH^-]$, and the mechanism probably involves a conjugate base leading to a five-co-ordinated intermediate. The racemisation rate is also greatly increased by adding ethylenediamine (en), mainly due to the hydroxide ions formed by its hydrolysis. In en solutions a second and even faster pathway to racemisation appears when $[Co(en)_3]^{2+}$ ions are present. This redox pathway operates also on suitably preconditioned platinized platinum surfaces.

THE ion $(+)_{589}[Co(en)_3]^{3+}$(en = ethylenediamine) is remarkably stable in homogeneous aqueous solutions.[2,3] At ordinary temperatures it racemises without decomposition only in the presence of suitable solid catalysts, carbon being one of the best examples.[3] The kinetics of the catalysis by the carbon black bp (Black Pearls 2 ungraphitised) in slightly acid solutions [4] have recently been studied,[5,6] and the catalytic rate v_{II} of the surface reaction at 40 °C was found to fit equation (1). The

$$v_{II} = k[Co(en)_3{}^{3+}]_{II}{}^2[I^-]_{II} \qquad (1)$$

subscript II relates to properties in the surface layer in the two-phase model of heterogeneous catalysis.[6] These third-order kinetics suggest that the racemisation could proceed by interaction on the carbon surface between an adsorbed $[Co(en)_3]^{3+}I^-$ ion pair and an adsorbed $[Co(en)_3]^{3+}$ ion, followed by rate-determining rearrangement of the activated complex so formed. The I^- ion may play an electrostatic role by enabling two positively charged complex ions to adsorb closely enough for interaction, and/or a bridging role to stabilise a bond-ruptured intermediate.[5] Racemisation *via* the labile $[Co(en)_3]^{2+}$ ion, an idea which is plausible on mechanistic grounds,[7] is difficult to reconcile with the observed kinetics. Formally such an intermediate could be accommodated in the following modification of Dwyer and Sargeson's scheme: [8]

$$\text{D-}[Co(en)_3]_{II}{}^{3+}\ \text{(low-spin)} \longrightarrow \text{D-}[Co(en)_3]_{II}{}^{3+}\ \text{(high-spin)} \qquad (2)$$

$$\text{D-}[Co(en)_3]_{II}{}^{3+}\ \text{(high-spin)} + I_{II}{}^- \longrightarrow \text{D-}[Co(en)_3]_{II}{}^{2+}\ \text{(high-spin)} + I_{II} \qquad (3)$$

$$\text{D-}[Co(en)_3]_{II}{}^{2+}\ \text{(high-spin)} \rightleftharpoons \text{L-}[Co(en)_3]_{II}{}^{2+}\ \text{(high-spin)} \qquad (4)$$

$$\text{D-}[Co(en)_3]_{II}{}^{3+}\ \text{(low-spin)} + \text{L-}[Co(en)_3]_{II}{}^{2+}\ \text{(high-spin)} \longrightarrow \text{L-}[Co(en)_3]_{II}{}^{3+} + \text{D-}[Co(en)_3]_{II}{}^{2+} \qquad (5)$$

$$[Co(en)_3]_{II}{}^{2+} + I_{II} \longrightarrow [Co(en)_3]_{II}{}^{3+} + I_{II}{}^- \qquad (6)$$

Reactions (2)—(4) and (6) could by themselves explain racemisation but not the third-order kinetics. The latter would be consistent with equations (2)—(5) provided reaction (6) is slow or else if most adsorbed iodine atoms disappear as iodine or by reaction with reducing groups on the bp surface. However, the parallel and substantially independent redox reaction (7) is not sufficiently rapid.[4,5] Certainly, non-transient

$$Co^{III} + I^- \longrightarrow Co^{II} + \tfrac{1}{2}I_2 \qquad (7)$$

cobalt(II) species were not involved in the racemisation mechanism: there was no autocatalysis by the Co^{II} produced by reaction (7) and the racemisation rate was not increased by adding Co^{II} to the system.[5] The reason is that, in the slightly acid solutions employed, only a tiny fraction of Co^{II} was actually present as $[Co(en)_3]^{2+}$. Electrochemical evidence indicates [5] that both cobalt(III) and cobalt(II) ions must be in the $(en)_3$ form if the electron-transfer reaction (5) is to be fast on a metal [9] or carbon [10] surface. The same will be true for reactions (3) and (6).

The $[Co(en)_3]^{2+}$ pathway to racemisation is nevertheless such an attractive one mechanistically that it might be expected to prevail under conditions favouring the $[Co(en)_3]^{2+}$ form of Co^{II}, *i.e.* when there is excess of en in the solution. Dwyer and Sargeson [8] reported, briefly, that the racemisation of a mixture of $[Co(en)_3]^{3+}$, $[Co(en)_3]^{2+}$, and en at 25 °C was strongly catalysed by activated carbon although the rate was not measured in the absence of added $[Co(en)_3]^{2+}$. We therefore decided to carry out a series of experiments with the same carbon black bp as before,[3-5] and to study the rate of the catalysed racemisation in the presence of various concentrations of en. The study was extended to $Na[OH]$ solutions since en solutions themselves are alkaline. The complex was employed as the perchlorate salt.

The analysis of the kinetic and adsorption results will follow our previous practice [6] of assigning all adsorbed species to a surface layer II of volume $V_{II} = 0.705_5\ (m_{cat}/g)\ cm^3$.

RESULTS

Adsorption on to the Catalyst.—Before heterogeneous catalysis can occur, the reactant(s) must be adsorbed on the surface. Mureinik and Spiro [3] found that, in 25 cm^3 of a 0.002 mol dm^{-3} solution of $[Co(en)_3]^{3+}$, 0.25 g bp at 40 °C adsorbed 43% of the complex ion if the salt was in the iodide

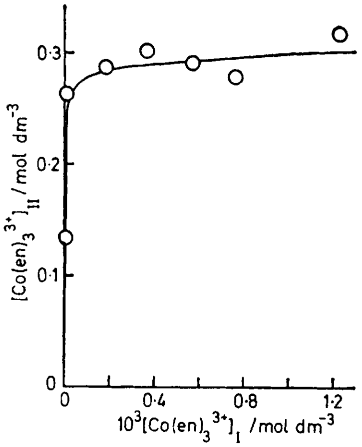

FIGURE 1 Adsorption isotherm of $[Co(en)_3]^{3+}$ on bp carbon (25 mg) from solutions (25 cm^3) of 0.001 mol dm^{-3} Na[OH] at 25 °C

form and 35% if it was in the perchlorate form. Since iodide ions were found to be adsorbed on bp whereas $[ClO_4]^-$ ions were not,[4] anion adsorption appeared to aid cation adsorption. This effect was highlighted in alkaline solutions where $[OH]^-$ and en adsorb strongly (see below). In 25 cm^3 of a 0.002 mol dm^{-3} solution of $[Co(en)_3][ClO_4]_3$, 0.25 g bp at 26 °C adsorbed 83% of the complex ion in the presence of 0.01 mol dm^{-3} Na[OH] and 93% with 0.1 mol dm^{-3} Na[OH]. From a similar solution at 40 °C, 0.25 g bp adsorbed 94% of the complex ion if 0.1 mol dm^{-3} en was added. Because adsorption was so pronounced in alkaline media, the experiments below were carried out instead with 0.025 g bp in 25 cm^3.

The adsorption of $[Co(en)_3]^{3+}$ on to bp at 40 °C from iodide solutions fitted a Freundlich isotherm.[4] In Na[OH] solutions, however, the adsorption at 25 °C appears to follow an asymptotic approach to monolayer coverage as Figure 1 illustrates, although the simultaneous adsorption of $[OH]^-$ ions complicates the interpretation of the diagram.

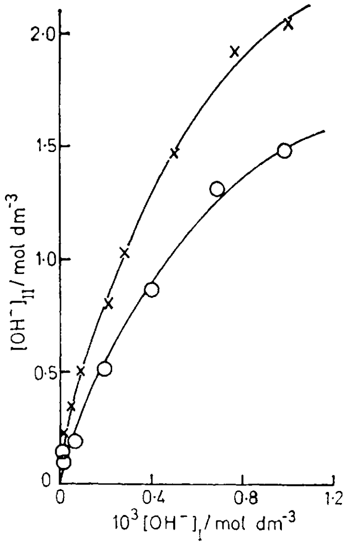

FIGURE 2 Adsorption isotherms for hydroxide ions on bp carbon (25 mg) at 25 °C from Na[OH] solutions (25 cm^3) without complex ions present (○) and with 0.001 5 mol dm^{-3} $[Co(en)_3][ClO_4]_3$ present (×)

The amount of complex ion adsorbed from a 0.002 mol dm^{-3} $[Co(en)_3][ClO_4]_3$ solution also increases with increasing Na[OH] concentration, and when the latter is of the order of 0.001 mol dm^{-3} the amount adsorbed approaches a plateau value of *ca.* 0.3 mol dm^{-3}. This figure, from the known dimensions of the $[Co(en)_3]^{3+}$ ion,[6] is equivalent to a 9% coverage of the B.E.T. area quoted for bp. This probably indicates monolayer coverage of the surface sites since the large complex ion will be unable to penetrate the smaller pores in the carbon black.

The results plotted in Figure 2 show that the hydroxide ions themselves are extensively adsorbed on a bp surface. The degree of adsorption is *ca.* 30% greater in the presence of 0.001 5 mol dm^{-3} $[Co(en)_3]^{3+}$, probably for electrostatic reasons. Corrections were made for atmospheric contamination (see Experimental). Both the curves in Figure 2 fitted Freundlich equations of type (8) with $n = 0.55 \pm$

$$[OH^-]_{II} = k_F[OH^-]_I{}^n \qquad (8)$$

0.03 (mean standard error). Adsorption of hydroxide ions is to be expected in view of the fact that carbon black surfaces [11-13] and bp in particular [14] possess attached quinoid, phenolic, and carboxyl groups as well as adsorbed carbon dioxide.

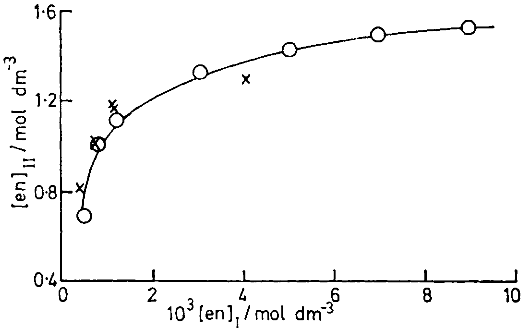

FIGURE 3 Adsorption isotherm for en on bp carbon (25 mg) at 25 °C from solutions (25 cm^3) containing no complex ions (○) and with 0.001 5 mol dm^{-3} $[Co(en)_3][ClO_4]_3$ present (×)

The adsorption isotherm of ethylenediamine is depicted in Figure 3. Except for the lowest point at 0.001 mol dm^{-3} the data fit a Langmuir equation. Addition of complex ions in this case has much less effect on the adsorption of the base which is understandable if en adsorbs in its neutral form. The extent of en adsorption on bp is of the same order of magnitude as that of $[OH]^-$. A few experiments with Norite had suggested [15] that here en was adsorbed more than $[OH]^-$.

The rate of adsorption of complex ion on to the bp surface was found to be fairly fast whereas that of $[OH]^-$ ions was much slower (>20 min). This slow equilibrium of base with carbon surfaces has been noted elsewhere.[12,14] The reasons may be gradual acid–base interactions, slow pore diffusion, and a breakdown of the bp aggregates which in stronger alkaline solutions produced almost a colloidal suspension. Equilibrium with hydroxide ions was reached more rapidly when complex ions were present. The kinetic runs were therefore arranged in such a way that bottles of bp in the appropriate Na[OH] or en solution were first equilibrated in a thermostat overnight, and the reaction started by addition of $[Co(en)_3][ClO_4]_3$ stock solution. Even so, several minutes elapsed before a new adsorption equilibrium had been established because the advent of complex ions on the bp surface slightly altered the extent of $[OH]^-$ adsorption.

Kinetic Experiments in Na[OH] *Solutions*.—According to equation (*1*), in slightly acid solutions the catalysed racemisation rate should be zero in the absence of iodide ions. Indeed, no racemisation was observed[5] with $[Co(en)_3][ClO_4]_3$ at 40 °C even in the presence of 0.25 g bp in 25 cm^3 solution. Addition of alkali, however, produced such a marked increase in the rate of racemisation that the experimental temperature had to be lowered to 25 °C and the mass of catalyst decreased tenfold. Even so, large first-order rates were recorded at higher alkali concentrations (Figure 4). The experiments were not extended beyond 0.025 mol dm^{-3} Na[OH] because the racemisation was then almost complete by the time all the solutes had reached adsorption equilibrium on the bp surface.

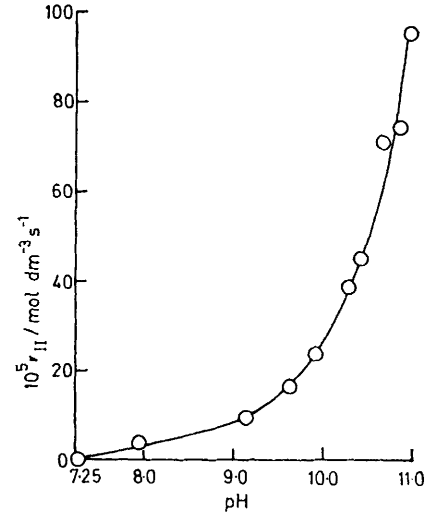

FIGURE 4 Variation of the catalysed rates of racemisation of $(+)_{589}[Co(en)_3][ClO_4]_3$ (0.001 5 mol dm^{-3}) in various Na[OH] solutions (25 cm^3) containing bp carbon (25 mg) at 25 °C, plotted against the observed pH of the reaction mixtures

The homogeneous racemisation was too slow to be measured: in a solution 0.001 5 mol dm^{-3} in complex perchlorate and 0.01 mol dm^{-3} in Na[OH] at 25 °C no significant change in optical rotation was noted after 1 week. The reaction therefore took place entirely on the catalyst surface. The rate v in this surface phase was calculated from the slope of the straightline plot against time of ln (α_0/α_t) according to[6] equation (9), where α is

$$\frac{d \ln (\alpha_0/\alpha_t)}{dt} = \frac{2v_{II}V_{II}}{[Co(en)_3{}^{3+}]_0 V_I} \qquad (9)$$

optical rotation, t is time, subscript 0 indicates the initial value, V_I is the volume of the bulk solution (25 cm^3), and V_{II} that of the surface layer (defined earlier).

The concentration of $[OH]^-$ ions in phase II was determined from the difference between the initial Na[OH] concentration and that derived from the pH of the bulk solution suitably corrected for atmospheric contamination and with allowance for the activity coefficient. It was assumed that the fraction of the analytical hydroxide concentration not affected by CO$_2$ from the bp surface or the atmosphere was the same in both the bulk and the surface phases. When the initial Na[OH] concentration ranged from 0.001 3 to 0.003 5 mol dm^{-3}, $[NaOH]_{II}$ varied from 0.22 to 2.05 mol dm^{-3}. Over the whole of this range, v_{II} was found to be directly proportional to $[OH^-]_{II}$ when the initial concentration of complex ion was held constant at 0.001 5 mol dm^{-3} [equation (10)] with $k_1 = 4.4 \times 10^{-4}$ s^{-1}.

$$v_{II} = k_1[OH^-]_{II} \qquad (10)$$

An alternative treatment incorporating the Freundlich adsorption isotherm (8) leads to (11). As expected, a plot

$$v_{II} = k_1 k_F[OH^-]_I{}^n \qquad (11)$$

of log v_{II} against log $[OH^-]_I$ gave a straight line, with a slope n of 0.64 ± 0.06 (s.e.). This agrees within the uncertainty limits with the slope found for the adsorption experiments. The catalytic racemisation is therefore first order in the concentration of adsorbed hydroxide ion.

The variation of the racemisation rate with $[Co(en)_3{}^{3+}]_{II}$ at constant $[NaOH]_0$ (0.001 mol dm^{-3}) was much more difficult to establish. When the initial concentration of complex salt was increased from 0.3×10^{-3} to 2.5×10^{-3} mol dm^{-3}, the concentration in phase II only rose from 0.24 to 0.40 mol dm^{-3}. The reason is obvious from the shape of the adsorption isotherm in Figure 1. The adsorbed concentrations, moreover, are subject to appreciable uncertainty as they depend on the often small differences between the optical absorbances of the initial solutions of complex ion and the absorbances of the reaction mixtures from which the catalyst has been removed. This uncertainty was confirmed by an alternative method of estimating $[Co(en)_3{}^{3+}]_{II}$. The linear sections of the plots of ln (α_0/α_t) against t were extrapolated back to zero time, and the intercepts were used to calculate the amount of optically active complex removed from the solution by adsorption at the beginning of the run (*cf.* the Figure in ref. 5). Only for one third of the runs did the results of these two procedures agree satisfactorily. It is therefore hardly surprising that the data did not show a consistent kinetic trend. Furthermore, on a theoretical point, such concentrated surface solutions of a triply charged species will not exhibit ideal behaviour as the concentration increases. Overall a zero-order dependence of rate on $[Co(en)_3{}^{3+}]_{II}$ appeared to fit the data best but one set of results was consistent with a first-order dependence. The latter conclusion is much the more likely on mechanistic grounds.

There was no definite trend in v_{II} with mass of catalyst when m_{cat} was changed to 12.5 and to 37.5 mg per 25 cm^3 solution. Although both these runs were slower than expected from the 25 mg runs, the rates were not noticeably outside the usual scatter of all the points around the line of log v_{II} *versus* log $[OH^-]_I$. Washing the catalyst before a run to remove some of the adsorbed CO$_2$ had no marked effect on the rate.

Normally, reactants and catalyst were continuously mixed by a bottle rotator inside the thermostat bath at 25 °C. In one run, however, the rotator was switched off during the second half of the reaction and in another run, lasting 5 h, the rotation was stopped for two separate 1-h periods. In both cases the plot of ln (α_0/α_t) against time was straight throughout the run, without any discontinuities or changes of slope during the quiescent periods. Thus the rate of the catalysed racemisation is not controlled by diffusion of reactants towards the surface, or by that of products away from it, but by the velocity of the surface reaction itself.

There was no evidence for a redox pathway *via* Co^{II} in these alkaline runs. In one experiment with 1.5×10^{-3} mol dm^{-3} $[Co(en)_3][ClO_4]_3$ and 0.01 mol dm^{-3} Na[OH] and the usual 25 mg bp in 25 cm^3 solution, the reaction mixture was tested periodically for the formation of Co^{II} by the sensitive analytical method described previously.[16] If any Co^{II} did form it was at the limit of detection of the method used. The high catalytic rates in alkali cannot therefore be attributed to the presence of Co^{II}. {This argument is strengthened by the fact that in a comparable $[Co(en)_3]I_3$ run in slightly acid solution, where appreciable amounts of Co^{II} are being continually formed,[4] the rate is several thousand times less.[5]} Moreover, in another run (with 0.001 mol dm^{-3} Na[OH]) the reaction mixture was degassed with N_2 to avoid aerial oxidation of Co^{II}: the rate was, if anything, lower than that of similar runs that were not degassed. The opposite result would have been expected had Co^{II} contributed to the catalytic mechanism.

In solutions of higher Na[OH] concentration, the orange hue of the complex ion in the solution became discoloured as the runs progressed and eventually turned purple. A run (no. 68) with 0.001 5 mol dm^{-3} $[Co(en)_3][ClO_4]_3$, 0.025 mol dm^{-3} Na[OH], and 25 mg bp was left at 25 °C over the weekend. After filtration, the spectrum showed two new peaks, at 369 and 519 nm. Comparison with literature spectra [15,17,18] for various hydroxo- and aquahydroxo-cobalt en complexes pointed to *cis*-$[Co(en)_2(OH)_2]^+$ as the most likely hydrolysis product. On the basis of the literature absorption coefficients, and making no allowance for adsorption on the bp carbon, the percentage hydrolysis of $[Co(en)_3]^{3+}$ at equilibrium was found to be negligible in 0.001 mol dm^{-3} Na[OH] and *ca.* 70% in 0.025 mol dm^{-3} Na[OH]. The latter figure may be compared with that of 55% calculated from Bjerrum and Rasmussen's published [15] equilibrium constant for reaction (12) in 1 mol dm^{-3} $Na[NO_3]$ solution. The rate of the hydrolysis could be

$$[Co(en)_3]^{3+} + 2[OH]^- \rightleftharpoons [Co(en)_2(OH)_2]^+ + en \qquad (12)$$

followed conveniently by the absorbance A at 260 nm where the hydrolysis product absorbs strongly, unlike the original complex ion. Plots of ln $(A_\infty - A_t)$ against t gave straight lines, and for run 68 with 0.025 mol dm^{-3} Na[OH] the hydrolysis rate constant was found to be 8.6×10^{-5} s^{-1}. The first-order racemisation rate constant for the same run was 74×10^{-5} s^{-1}. For a similar experiment with 0.002 5 mol dm^{-3} Na[OH] the figures were 4×10^{-5} and 34×10^{-5} s^{-1}, respectively. The hydrolysis is therefore 8.6 times slower than the racemisation, and formation of the hydrolysis product cannot be a prerequisite to racemisation. The two reactions probably proceed in parallel, possibly with the same rate-determining step involving interaction between adsorbed $[Co(en)_3]^{3+}$ and adsorbed $[OH]^-$.

Kinetic Experiments in Ethylenediamine Solutions.—In the absence of bp carbon the rate of racemisation was negligibly small, no change in rotation being observed after 1 week in a solution 0.001 5 mol dm^{-3} in $[Co(en)_3][ClO_4]_3$ and 0.01 mol dm^{-3} in en at 25 °C. All further experiments were then carried out with 25 mg bp in 25 cm^3 reaction mixture. The effect on the racemisation rate of varying the en concentration is depicted in Figure 5. At low base concentrations the increase in rate produced by adding en is similar to that produced by adding an equimolar amount of Na[OH], but higher en concentrations do not increase the rate as much as do higher Na[OH] concentrations. These facts are consistent with the hypothesis that the racemisation is promoted, not by en molecules, but by the hydroxide ions formed by the hydrolysis reactions (13) and (14). In

$$en + H_2O \rightleftharpoons [Hen]^+ + [OH]^- \qquad (13)$$

$$[Hen]^+ + H_2O \rightleftharpoons [H_2en]^{2+} + [OH]^- \qquad (14)$$

dilute base solutions these equilibria are shifted to the right, an effect accentuated by adsorption of $[OH]^-$ ions on to the bp surface. In concentrated en solutions the degree of homogeneous hydrolysis will be less and, moreover, the relative effect of adsorption will be smaller because the bp surface will tend to become ' saturated ' with $[OH]^-$ ions (Figure 2). The qualitative trends are thereby explained. For a more quantitative assessment, the rates v_{II} in various en and Na[OH] solutions can be compared when the experimental pH values of the reaction mixtures are the same. Throughout the range $[en]_0 = 0.001$—0.01 mol dm^{-3}, the racemisation rates in the corresponding Na[OH] solutions were found to be just over 80% of the rates in the en solutions. This figure should be corrected to *ca.* 70% if allowance is made for the absence of the presumably racemic hydrolysis products in the en runs [excess of en suppressed the hydrolysis reaction (12)]. Such a similarity of the rates over a more than 10-fold change in rate is striking. Most, if not all, of the catalysed racemisation rates in en solutions can thus be attributed to the hydroxide ions formed by en hydrolysis. The *ca.* 30% difference between the two sets of rates may be partly due to the experimental difficulties involved in working with alkaline solutions, and partly to differences in adsorption behaviour in $[OH]^-$ and en solutions. If there were an additional racemisation process that occurs only in en solutions, it would presumably involve adsorbed $[Co(en)_3]^{3+}$ and adsorbed en. No simple proportionality exists between v_{II} (or 30% of v_{II}) in en solutions and either $[en]_{II}$ or $[en]_{II}$-$[Co(en)_3{}^{3+}]_{II}$. Although the results can be formally fitted to equation (15) with $k_2 = 1.5 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and

$$v_{II} = k_2[Co(en)_3{}^{3+}]_{II}[en]_{II} - k_2' \qquad (15)$$

$k_2' = 3.5 \times 10^{-4}$ mol dm^{-3} s^{-1}, respectively, the large intercept k_2' cannot readily be explained.

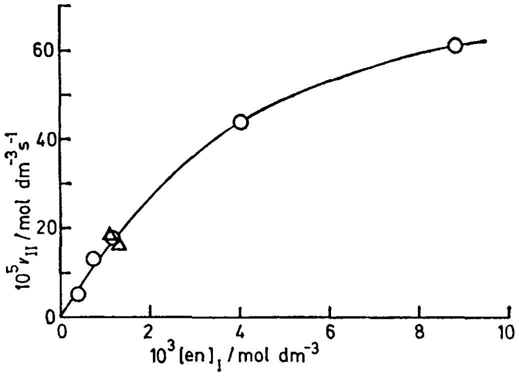

FIGURE 5 Variation of the catalysed rates of racemisation of $(+)_{589}[Co(en)_3][ClO_4]_3$ (0.001 5 mol dm^{-3}) in various en solutions (25 cm^3) containing bp carbon (25 mg) at 25 °C, plotted against bulk en concentration. In runs marked Δ, 4×10^{-5} mol dm^{-3} Co^{II} had been added to the reaction mixture

Since the rates in en solutions were not markedly higher than expected from the amount of hydroxide present, it seemed unlikely that racemisation was proceeding by a redox pathway as indicated by equations (4) and (5). When the filtrates of two runs with 0.1 mol dm^{-3} en were examined for the formation of Co^{II}, only trace amounts were detected at the limit of accuracy (of order 10^{-6} mol dm^{-3}) of the analytical method employed.[16] Two other runs with 0.002 mol dm^{-3} en had 4×10^{-5} mol dm^{-3} Co^{II} added initially: in one case before overnight equilibration, in the second case after this period. In neither run was the rate significantly affected (Figure 5), and in neither run was any Co^{II} detected in the filtrates of the reaction mixtures. The inference was that any Co^{II} present in the en solutions was rapidly oxidised by dissolved oxygen to $[Co(en)_3]^{3+}$. Such oxidation is well known.[19] A further experiment was consequently carried out with 0.001 5 mol dm^{-3} $[Co(en)_3][ClO_4]_3$ and 0.01 mol dm^{-3} en in which the solution was first degassed with nitrogen, and a much larger amount of Co^{II} (0.001 mol dm^{-3}) added initially. Again no Co^{II} could be detected in the final filtrate. The racemisation rate, however, increased dramatically. The reaction was too fast to time accurately but v_{II} certainly exceeded 2.8×10^{-3} mol dm^{-3} s^{-1}, a figure more than four times the rate obtained in a similar run without the addition of Co^{II} and degassing. Thus even though the Co^{II} disappeared rapidly through adsorption and/or oxidation, it was present for long enough to enhance the reaction rate considerably. A redox pathway does therefore exist for bp-catalysed racemisation in en solutions but only if Co^{II} is present and its existence in the solution is safeguarded.

The rate of the redox-path racemisation was too rapid for convenient measurement on the high-surface-area carbon employed. To estimate the order of magnitude of this rate in en solutions, a few exploratory runs were carried out with an aged disc of platinized platinum of much smaller area. Most good electron-conducting solids should permit reaction (5) to proceed rapidly: the electron-exchange reaction (5) is already known to be catalysed by platinum black[20] and the surface rate on carbon should be of the same order of magnitude.[10] The area of the platinum disc was not known precisely because of the effects of ageing and of the different surface pretreatments employed,[21] and the rates quoted below are therefore lower limits. When the disc was pretreated in 1 mol dm^{-3} $HClO_4$ by Gilman's potential sequence[22] which involves longer anodic than cathodic steps, no racemisation at all was observed with a solution 0.001 5 mol dm^{-3} in $[Co(en)_3]^{3+}$ and 0.01 mol dm^{-3} in en after 18 h. Addition of 10^{-4} mol dm^{-3} Co^{II} produced no change after 100 h, nor did addition of 0.001 mol dm^{-3} Co^{II} after a further 21 h. The last experiment was then repeated with the disc subjected to a strong cathodic pretreatment and with all solutions thoroughly degassed with nitrogen. Racemisation now took place. With the disc rotating at 400 r.p.m., v_{II} at 25 °C was found to be $\geqslant 1.2 \times 10^{-3}$ mol dm^{-3} s^{-1}. When [en] was raised to 0.1 mol dm^{-3}, v_{II} was $\geqslant 1.7 \times 10^{-3}$ mol dm^{-3} s^{-1}. This increase can be partly explained by the greater percentage of Co^{II} present in the form of $[Co(en)_3]^{2+}$. In these last two runs it was shown by cobalt(II) analyses that over 90% of the initial 0.001 mol dm^{-3} Co^{II} remained as such in the solution. The order of magnitude of the redox-path racemisation was therefore similar on bp and on platinum provided the latter had been appropriately preconditioned.

DISCUSSION

In homogeneous aqueous solution, the ion $(+)_{589}$-$[Co(en)_3]^{3+}$ is inert to racemisation in neutral solution at high temperatures as well as in alkaline or en solutions at room temperature.[2] However, alkaline or en solutions at high temperature do produce racemisation.[2] Three kinetic studies are relevant. Friend and Nunn[23] followed the homogeneous hydrolysis reaction (12) at 70 °C and above, finding it to be first order in the complex ion concentration and (if the ionic strength was kept constant) first order in $[OH^-]$. Gehman and Fernelius[2] also reported that at 85 °C the homogeneous racemisation rate was first order in complex ion concentration and first order in $[OH^-]$ or [en], respectively. They emphasized that the reaction with Na[OH] is actually a decomposition process [*cf.* equation (12)], and the rate constant with Na[OH] was more than 100 times greater than with en. In en media the formation of, and the catalysis by, $[Co(en)_3]^{2+}$ were excluded. The exchange rate between $[Co(en)_3]^{3+}$ and en was found to be somewhat slower than the racemisation rate but of the same order of magnitude. To explain the en-catalysed racemisation they postulated a seven-co-ordinated intermediate. A third homogeneous study by Dwyer and Sargeson[24] with en solutions of both $[Co(en)_3]^{3+}$ and $[Co(en)_3]^{2+}$ at 80 and 98 °C yielded the rate expression (16). The first term on the right-hand side could

$$v = k[Co^{III}][Co^{II}] + k'[Co^{III}][en] \qquad (16)$$

be identified with an electron-transfer mechanism [*cf.* equation (5)] while the second term was related to the findings of Gehman and Fernelius.[2]

No previous kinetic study had been undertaken on the heterogeneous racemisation under alkaline conditions. Only Searle *et al.*,[25] independently of ourselves, had ever observed that $[Co(en)_3][ClO_4]_3$ can be racemised in 0.01 mol dm^{-3} Na[OH] at room temperature in the presence of charcoal. From our kinetic work with bp carbon and the ensuing discussion, the heterogeneous racemisation rate in Na[OH] solutions may be represented by equation (17) with $k_2 = (9 \pm 1) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}

$$v_{II} = k_2[Co(en)_3{}^{3+}]_{II}[OH^-]_{II} \qquad (17)$$

at 25 °C. It seems likely that the mechanism follows the general pattern for homogeneous base hydrolysis of octahedral cobalt(III) amine complexes[25,26] [$S_N1(CB)$]. The absorbed $[OH]^-$ first removes a proton from the adsorbed $[Co(en)_3]^{3+}$, and in the conjugate base thus produced a Co–N bond is broken to form the adsorbed five-co-ordinated intermediate $[(en)_2Co(NH_2CH_2CH_2NH)]^{2+}$. Within this intermediate, probably of trigonal-bipyramidal shape, rearrangement then takes place. An intramolecular proton jump, for example, could result in the severance of another Co-N link and lead to racemisation very simply. Whatever the details of the rearrangement, an important role may well be played by the interaction of the dissociated ligand with the carbon surface. That reactions in which N is co-ordinated to Co are particularly susceptible to catalysis by charcoal has been noted long ago.[27,*]

In the en solutions our kinetic results indicated that most if not all the heterogeneous racemisation at 25 °C could be explained in terms of the hydroxide effect. The catalytic mechanism is then the same as that discussed above. In the presence of $[Co(en)_3]^{2+}$, however, the existence of Dwyer and Sargeson's redox route [8] was clearly confirmed. The fact that the velocities of the redox-path racemisations on bp carbon and on cathodically pretreated platinum are of the same order of magnitude lends added weight to the electron-transfer mechanism in equations (4) and (5). The redox route possesses a much higher heterogeneous racemisation rate than the hydroxyl route, and so will become the dominant mechanism if enough $[Co(en)_3]^{2+}$ ions are present.

To summarise, $(+)_{589}[Co(en)_3]^{3+}$ racemises in alkaline conditions by several mechanisms. In hot homogeneous Na[OH] solutions the loss of optical activity is just a consequence of the hydrolysis reaction (12), while in cool Na[OH] solutions and in the presence of carbon the hydrolysis makes a minor contribution. The major process here is heterogeneous racemisation proceeding, most likely, through the conjugate base and a five-co-ordinated intermediate. In ethylenediamine solutions, the racemisation mechanism found in the hot homogeneous medium appears to be largely absent under cool carbon-catalysed conditions. The heterogeneous catalysis in en solutions is chiefly due to the hydroxide ions present. Finally, in en solutions that also contain $[Co(en)_3]^{2+}$ ions, an electron-transfer path to racemisation operates both in homogeneous and in heterogeneous conditions provided the solid is a good electron conductor. The heterogeneous process is then much the faster.

EXPERIMENTAL

Materials.—The salt $(+)_{589}[Co(en)_3][ClO_4]_3$ was prepared as described earlier.[3] Cobalt(II) perchlorate was synthesized from B.D.H. AnalaR $Co[SO_4]$ and Hopkin & Williams $Ba[ClO_4]_2$. Sodium hydroxide solutions were made initially from AnalaR Na[OH] pellets and standardised by titration with HCl, and later by dilution from B.D.H. 0.5 mol dm^{-3} volumetric solutions. Standard HCl solutions were made up from various B.D.H. volumetric solution ampoules. Ethylenediamine from Jefferson Chemicals U.K. had been purified by Dr. M. C. Lima in this laboratory by distillation over calcium hydride. All solutions were prepared with doubly distilled water. The carbon black catalyst bp was Black Pearls 2 of B.E.T. (N_2) surface area 850 m^2 g^{-1} supplied by Cabot Corporation.

Analysis.—The optical rotations of the solutions were determined by the amplitude between the two extrema at 518 and 461 nm as described previously.[3] Output from the Bellingham and Stanley Polarmatic 62 spectropolarimeter was fed into a Perkin-Elmer 56 chart recorder. The 2-cm long Spectrosil cell was supplied by Lightpath Optical Co. Ltd. Concentrations of $[Co(en)_3]^{3+}$ in the filtered bulk solutions were monitored by optical absorbance readings at 464 nm using an absorption coefficient of 9.1 m^2 mol^{-1}. pH values were determined with a Pye–Unicam 401 EO7 combined glass–AgCl reference electrode and a Beckman Research pH meter. In the kinetic runs contamination by atmospheric carbon dioxide took place during the mixing of the reagents and during the filtration of the bp carbon from the alkaline aliquots. A series of blank pH experiments, similar to the kinetic ones, was therefore carried out over a range of known Na[OH] concentrations both with and without 0.001 5 mol dm^{-3} $[Co(en)_3][ClO_4]_3$. Plots were then drawn of measured pH and of expected pH against [NaOH], and subsequent experimental pH readings could be adjusted accordingly. The relatively small activity coefficient correction was calculated by the Güntelberg equation. In strong Na[OH] solutions the bp suspensions appeared to become almost colloidal and this may have affected the glass electrode readings.[29] Ethylenediamine solutions were analysed by pH titration with HCl solutions, the en concentrations being calculated from the second and sharper equivalence points.

Method.—For a typical kinetic run about 10 identical reaction mixtures (25 cm^3) were made up in closed amber screw-top bottles (capacity 50 cm^3) and were rotated on a large wheel in a thermostat held at 25 °C to better than ±0.1 °C. The bp and alkaline solutions were equilibrated together overnight, and the reaction started by adding stock solution of the complex salt. The microburette used for this purpose in early runs was later replaced by a Jencons Repette H9/2 syringe because of its speed and reproducibility. After suitable times bottles were taken out of the bath, and the bp catalyst removed by centrifuging or filtering. Removal of catalyst automatically 'froze' the racemisation. The filtrates were then analysed spectropolarimetrically and spectrophotometrically to determine the extents of racemisation and adsorption, respectively. Other tests [pH, cobalt(II) analysis] were often carried out as well. Reactions under nitrogen were studied in the apparatus described by Mureinik and Spiro.[4]

In the centrifugal removal of carbon, the filtrates were spun in Polythene tubes at *ca.* 4 000 r.p.m. in a Gallenkamp Junior Centrifuge for 5 min. However, this proved ineffective at higher alkali concentrations where the bp suspensions became almost colloidal. Filtration was more successful but took more than 10 min, the samples having to be passed first through a no. 3 sinter and then through a no. 5 sinter. The time required could be reduced to 1 min for 25 cm^3 by using a no. 3 sinter alone provided it had been cleaned only with distilled water. Carbon particles remaining in the sinter then increased the effectiveness of the filtration. O.r.d. and optical density measurements were the same as those found previously. This procedure also obviated the earlier difficulty of having to remove carbon from the sinter pores between each filtration by treatment with chromic and sulphuric acids.

The reproducibility of the results was improved by paying

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[*] *Note added at proof:* Hammershøi and Larsen [28] reported that the (Co–S)-linked $(-)_D$-*u-fac*-$[Co(daes)_2]Cl_3$ [daes = di-(2-aminoethyl) sulphide] was racemised by Norit W charcoal at 60 °C even in acid solutions. Like us, they detected no Co^{II} formation and found the rate of racemisation to be inversely proportional to $[H^+]$. They interpreted this as due to competition between the H^+ ions in acid solution and complex ions for the active sites on the charcoal. The racemisation was believed to occur through rupture of the weak Co–S bond on the charcoal surface. Our work suggests that racemisation of the more inert (Co–N)-linked $[Co(en)_3]^{3+}$ requires interaction on the carbon surface between the complex ion and a suitable adsorbed anion (I^-, OH^-).

attention to the way in which the bp catalyst was added. Drying the carbon at 150 °C overnight had little effect but sieving the material into ranges of particle sizes proved important. The range 152—250 μm was employed as it was most catalytically active even though only 10% of the suppliers' material was of this size. This behaviour is similar to that reported and explained by Morawetz[30] for polyelectrolyte catalysis. (The adsorption experiments, however, were done earlier and with unsieved bp.) To prevent the fine carbon powder floating on the solution or adhering to various glass surfaces, samples of the sieved bp (0.625 g) were first thoroughly stirred in alkali solution (250 cm^3) of the appropriate concentration at 25 °C. From the agitated suspension, aliquots (10 cm^3) were then pipetted into the reaction bottles and made up to 25 cm^3. For the ethylenediamine experiments, suspension samples of catalyst in water were pipetted into aqueous en mixtures inside the reaction bottles.

The platinum disc had been platinized by the recipe of Feltham and Spiro.[21] Kinetic runs with it were carried out as described previously.[16] The disc was estimated to have an effective surface area of $\leqslant 2.1$ m^2 and the volume of reaction solution was 150 cm^3.

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REFERENCES

[1] Part 15, M. Spiro, *J.C.S. Faraday I*, 1977, 1825.

[2] W. G. Gehman and W. C. Fernelius, *J. Inorg. Nuclear Chem.*, 1959, **9**, 71.

[3] R. J. Mureinik and M. Spiro, *J.C.S. Dalton*, 1974, 2480.

[4] R. J. Mureinik and M. Spiro, *J.C.S. Dalton*, 1974, 2486.

[5] R. J. Mureinik and M. Spiro, *J.C.S. Dalton*, 1974, 2493.

[6] P. D. Totterdell and M. Spiro, *J.C.S. Faraday I*, 1976, 1477.

[7] F. R. Hartley, personal communication, 1976.

[8] F. P. Dwyer and A. M. Sargeson, *Nature*, 1960, **187**, 1022.

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

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

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

[12] H.-P. Boehm, E. Diehl, W. Heck, and R. Sappock, *Angew. Chem. Internat. Edn.*, 1964, **3**, 669.

[13] R. E. Panzer and P. J. Elving, *Electrochim. Acta*, 1975, **20**, 635.

[14] R. E. Test and R. S. Hansen, Atomic Energy Comm. Document IS-341 (Chemistry), Iowa State University, 1961.

[15] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265.

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

[17] F. Basolo, *J. Amer. Chem. Soc.*, 1950, **72**, 4393.

[18] D. J. Francis and R. B. Jordan, *J. Amer. Chem. Soc.*, 1969, **91**, 6626.

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

[20] S. M. Hasany, Ph.D. Thesis, University of Adelaide, 1971, ch. III.

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

[22] S. Gilman, *Adv. Electroanalyt. Chem.*, 1967, **2**, 111.

[23] J. A. Friend and E. K. Nunn, *J. Chem. Soc.*, 1958, 1567.

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

[25] G. H. Searle, F. R. Keene, and S. F. Lincoln, *Inorg. Chem.*, 1978, **17**, 2362.

[26] M. L. Tobe, *Accounts Chem. Res.*, 1970, **3**, 377.

[27] J. C. Bailar, jun., and J. B. Work, *J. Amer. Chem. Soc.*, 1945, **67**, 176.

[28] A. Hammershøi and E. Larsen, *Acta Chem. Scand.*, 1978, **A32**, 485.

[29] R. G. Bates, in ' Reference Electrodes Theory and Practice,' eds. D. J. G. Ives and G. J. Janz, Academic Press, New York, 1961, p. 267.

[30] H. Morawetz, *Adv. Catalysis*, 1969, **20**, 341 (see p. 352).