Heterogeneous Catalysis in Solution. Part XII.[1] Racemisation of $(+)_{589}$-Tris(ethylenediamine)cobalt(III) by a Carbon Black, and Kinetics of Reacting Systems involving Racemisation

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The McKay equation for radioactive exchange has been applied to optical-isomerisation reactions. A modified equation has been derived to take into account a first-order chemical side reaction. All these processes show first-order kinetics and concentration-dependence studies are required to establish the mechanism. An equation has also been derived to describe the redistribution of optical activity between bulk and adsorbed states. Experiments carried out on the racemisation of $(+)_{589}$-tris(ethylenediamine)cobalt(III) tri-iodide in aqueous solution at 40 °C catalysed by a carbon black have shown the surface reaction to be rate determining. The rate is second order in adsorbed $[Co(en)_3{}^{3+}]$ and first order in adsorbed $[I^-]$. The racemisation does not proceed through a cobalt(II) intermediate under the experimental conditions employed.

THE catalytic effect of charcoal and other solids on the racemisation of optically active compounds is widely attested,[2] yet few attempts have been made to determine the kinetics of this process. We report here a detailed investigation in which the concomitant adsorption and reduction processes have been followed as well as the racemisation itself. The system chosen was the racemisation of the salt $(+)_{589}[Co(en)_3]I_3$ in water at 40 °C catalysed by the carbon Black Pearls 2 (bp).† As bp adsorbed a considerable proportion of the reactant ions, it was possible to relate the racemisation rate directly to the 'concentrations' of $[Co(en)_3]^{3+}$ and I^- ions on the carbon surface. The kinetics of the accompanying reduction of $[Co(en)_3]^{3+}$ to Co^{II} by iodide ions on the same carbon surface have been reported in the preceding paper.[1]

RESULTS AND DISCUSSION

The Kinetics of Optical Racemisation Reactions.—We begin by deriving a general equation for the rate of racemisation of optically active compounds. It is based on McKay's approach [3-5] to the kinetics of isotopic exchange reactions such as (1). The McKay equation

$$AX + BX^* \rightleftharpoons AX^* + BX \qquad (1)$$

predicts that the rate of appearance of isotopically labelled AX, AX*, always follows a first-order expression, regardless of the actual mechanism of the exchange reaction. This is because there are no overall changes in the concentrations of the chemical components during the reaction, which in turn leads to a constant rate of overall exchange of X (without regard as to whether it is active or not).

It does not appear to have been recognised that racemisation reactions of type (2) bear a close formal similarity

$$\text{D-(A)} \rightleftharpoons \text{L-(A)} \qquad (2)$$

to exchange reactions. During the course of such a racemisation reaction, the D isomer (say) of compound (A) is progressively converted into the L isomer until such a time as equal distribution of the two forms is attained and no net optical activity remains. Whatever the mechanism, and several have been suggested,[6] the overall concentration of (A) must remain constant throughout provided that only racemisation occurs and *no net chemical changes take place.* {It must be emphasised that so-called 'racemisations,' such as the loss of optical activity [7] of a methanolic solution of the ion *cis*-(+)-$[Co(en)_2Cl_2]^+$ where the product contains only 30% of a racemic mixture of the *cis*-form and the remainder is the geometric *trans*-isomer, do not constitute true racemisation reactions.} With the above proviso, the rate v of the process leading to change in configuration must remain constant during the course of a given run. The rate equation for racemisation can then be derived.

Consider reaction (2), with a molecular process responsible for racemisation of rate v (in mol dm^{-3} s^{-1}). The concentration of the constituents can be denoted by c_D and c_L:

$$\begin{array}{lcc} & \text{D-(A)} \rightleftharpoons & \text{L-(A)} \qquad (2) \\ \text{at time } t = 0: & c_0 & 0 \\ \text{at time } t = t: & c_0 - c_L = c_D & c_L \end{array}$$

The sum $c_0 = c_L + c_D$ is always constant. Now:

$$\begin{aligned} dc_L/dt &= -dc_D/dt \\ &= \text{rate of production of L-(A)} - \text{rate of destruction of L-(A)} \\ &= v(c_D/c_0) - v(c_L/c_0) \qquad (3) \end{aligned}$$

Here c_D/c_0 and c_L/c_0 are the fractions of the total reactant that are in the D- and L-forms respectively. Equation (3) is analogous to the first step in the derivation of the McKay equation, and like that step, will be true regardless of the mechanism as no mechanistic assumptions have been made. From (3) it follows that:

$$-dc_D/dt = v[(2c_D - c_0)/c_0]$$

$$\text{whence} \quad \ln\left(\frac{c_0}{2c_D - c_0}\right) = \ln\left(\frac{c_D + c_L}{c_D - c_L}\right) = \frac{2vt}{c_0} \qquad (4)$$

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† Throughout this paper, the prefix (+) refers to the type of rotation at the sodium D line, 589 nm.

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

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

[3] H. A. C. McKay, *Nature*, 1938, **43**, 142; *J. Amer. Chem. Soc.*, 1943, **65**, 702.

[4] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, pp. 192—193.

[5] G. Friedlander, J. W. Kennedy, and J. M. Miller, 'Nuclear and Radiochemistry,' 2nd edn., Wiley, New York, 1964, pp. 196—198.

[6] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, pp. 290—334.

[7] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 1953, 2680; D. D. Brown and R. S. Nyholm, *ibid.*, p. 2696.

Optical properties which enable the reaction to be followed, such as the optical rotation α, are proportional to the net excess of one isomer, in this case to $(c_{\mathrm{D}} - c_{\mathrm{L}})$. Equation (4) then becomes (5), where α_0 and α_t are the

$$\ln(\alpha_0/\alpha_t) = 2vt/c_0 \qquad (5)$$

optical activities at times zero and t, respectively. The rate v can be conveniently determined by establishing the length of time required for α_t to fall to half its initial value. When $\alpha_t = \frac{1}{2}\alpha_0$, $(c_{\mathrm{D}} + c_{\mathrm{L}})/(c_{\mathrm{D}} - c_{\mathrm{L}}) = 2$ or $c_{\mathrm{D}} = 3c_{\mathrm{L}} = 3c_0/4$. If this time be denoted as $t_{\frac{1}{2}}$, then we obtain equation (6). An intriguing aspect of equation

$$v = (c_0/2t_{\frac{1}{2}})\ln 2 = 0{\cdot}3466c_0/t_{\frac{1}{2}} \qquad (6)$$

(6) is that it predicts, again in close analogy with the case of isotopic exchange, that a first-order rate law will be obeyed regardless of the mechanism of the racemisation. It may be noted that in all papers[6] in which the kinetics of homogeneous racemisations have been studied, the quoted rate constants are first-order ones. However, experimental first-order plots do not constitute evidence for a first-order racemisation process. As in the case of isotopic exchange reactions, the true mechanism can only be deduced by a study of the functional dependence of v on the concentrations of the reactants concerned.

The McKay equation was originally derived for exchange reactions in homogeneous solution. Zimens[8] showed that equivalent equations apply for exchange reactions that occur on a solid–liquid interface, and Jonasson and Stranks[9] and Hasany[10] successfully applied the McKay equation to isotopic exchange reactions in solution catalysed by various solids. The close analogy between the McKay equation and equation (5) justifies using the latter for the surface racemisation reaction under study here.

Kinetics of Optical Racemisations Accompanied by Other Reactions.—If the racemisation is accompanied by some simultaneous chemical reaction, such as geometrical isomerisation or reduction, the above equations must be modified. Analogy can again be drawn with an isotopic exchange reaction, now complicated by the occurrence of a side reaction. A good example is the exchange reaction between labelled I$^-$ ions and MeI complicated by the slow decay of the radioactive isotope. Swart and Le Roux[11] and Moelwyn-Hughes[12] showed how the rate of decay may be incorporated into the exchange rate equation, instead of the more usual practice of correcting individual activity measurements for radioactive decay and then applying the McKay equation to the corrected data.[5] It was assumed in the derivation that the exchange reaction is first order in [MeI] and [I$^-$].

We now derive a rate equation for racemisation occurring together with another process. Consider the reactions (7) and (8) with the assumptions that racemisation

$$\textsc{d}\text{-(A)} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \textsc{l}\text{-(A)} \qquad (7)$$

$$\textsc{d}\text{-(A)} \xrightarrow{\kappa_1} \text{(B)} \qquad (8a)$$

$$\textsc{l}\text{-(A)} \xrightarrow{\kappa_1} \text{(B)} \qquad (8b)$$

is a first-order process with rate constant k_1, and that side reaction (8) is first order in [(A)] with rate constant κ_1. [The subscripts of these rate constants indicate the order of the reaction with respect to the appropriate form of (A).] Although we have chosen to designate the side reaction as first order in [(A)], these kinetics are not arbitrary as they can be determined independently of the racemisation process. The concentrations of the species involved can now be written:

at time $t = 0$: $[\textsc{d}\text{-(A)}] = c_0$, $[\textsc{l}\text{-(A)}] = 0$, $[\text{(B)}] = 0$
at time $t = t$: $[\textsc{d}\text{-(A)}] = c_{\mathrm{D}} = c_0 - c_{\mathrm{L}} - c_1 - c_2 = c_0 - \beta$, $[\textsc{l}\text{-(A)}] = c_{\mathrm{L}}$, $[\text{(B)}] = c_1 + c_2 = \beta - c_{\mathrm{L}}$

Here c_1 is the concentration of product formed from D-(A), c_2 that formed from L-(A), $\beta = c_{\mathrm{L}} + c_1 + c_2$. Equations (9)—(12) are then obtained.

$$\mathrm{d}c_{\mathrm{L}}/\mathrm{d}t = k_1(c_0 - \beta) - c_{\mathrm{L}}(\kappa_1 + k_1) \qquad (9)$$

$$\mathrm{d}c_1/\mathrm{d}t = \kappa_1(c_0 - \beta) \qquad (10)$$

$$\mathrm{d}c_2/\mathrm{d}t = \kappa_1 c_{\mathrm{L}} \qquad (11)$$

$$\therefore\ \mathrm{d}(c_1 + c_2)/\mathrm{d}t = \mathrm{d}(\beta - c_{\mathrm{L}})/\mathrm{d}t = \kappa_1[c_0 - (\beta - c_{\mathrm{L}})]$$

$$\text{Hence } c_1 + c_2 = \beta - c_{\mathrm{L}} = c_0[1 - \exp(-\kappa_1 t)] \qquad (12)$$

Combination of (12) and (9) eliminates β. Equation (13)

$$\mathrm{d}c_{\mathrm{L}}/\mathrm{d}t = -c_{\mathrm{L}}(2k_1 + \kappa_1) + k_1 c_0 \exp(-\kappa_1 t) \qquad (13)$$

is a linear first-order differential which may be integrated by the standard technique of multiplying throughout by $\exp[(2k_1 + \kappa_1)t]$, to yield (14) since $c_{\mathrm{L}} = 0$ at $t = 0$.

$$c_{\mathrm{L}} = \tfrac{1}{2}c_0\{\exp(-\kappa_1 t) - \exp[-(2k_1 + \kappa_1)t]\} \qquad (14)$$

From (12) and (14) we can solve for β. Since $c_{\mathrm{D}} = c_0 - \beta$ we obtain (16), and from (16) and (14), equation

$$\beta = c_0\{1 - \tfrac{1}{2}\exp[-(2k_1 + \kappa_1)t] - \tfrac{1}{2}\exp(-\kappa_1 t)\} \qquad (15)$$

$$c_{\mathrm{D}} = c_0\{\tfrac{1}{2}\exp[-(2k_1 + \kappa_1)t] + \tfrac{1}{2}\exp(-\kappa_1 t)\} \qquad (16)$$

(17) is derived. Plots of ln $(c_{\mathrm{D}} - c_{\mathrm{L}})$, or ln (optical activity), against time should therefore yield straight lines as before, but of gradient $-(2k_1 + k_1)$. The

$$(c_{\mathrm{D}} - c_{\mathrm{L}})/c_0 = \exp[-(2k_1 + \kappa_1)t] \qquad (17)$$

value of κ_1 can be obtained from equation (12) by analysing for the product (B). If $\kappa_1 \ll k_1$, equation (17) simplifies to (18) which is equivalent to (4)

$$(c_{\mathrm{D}} - c_{\mathrm{L}})/c_0 = \exp(-2k_1 t) \qquad (18)$$

with $v = k_1 c_0$.

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[8] K. E. Zimens, *Arkiv. Kemi, Mineral. Geol.*, 1945, **A20**, No. 18; 1946, **A21**, No. 16.

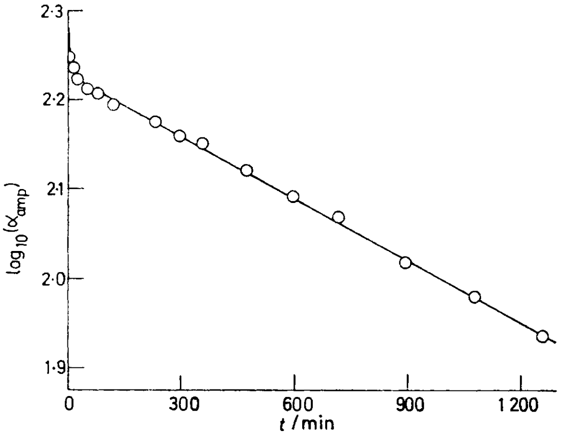
[9] I. R. Jonasson and D. R. Stranks, *Electrochim. Acta*, 1968, **13**, 1147.

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

[11] E. R. Swart and L. J. Le Roux, *J. Chem. Soc.*, 1956, 2110; 1957, 406.

[12] E. A. Moelwyn-Hughes, 'Chemical Statics and Dynamics of Solutions,' Academic Press, London, 1971, pp. 152—156, 515—519. Moelwyn-Hughes rightly points out that the original papers of Swart and Le Roux contain a number of editorial and typographical errors.

Equation (18) will obviously apply also where the side reaction is pseudo-first order in [(A)] (*e.g.* solvolysis), or where several parallel first-order reactions occur leading to different products (κ_1 is then the sum of the rate constants of these side reactions). In principle, it should be possible to solve the kinetic equations that arise from other assumptions about the orders of the racemisations and side reactions, but such solutions are not relevant to the present paper.



Variation of $\log_{10}(\alpha_{amp})$ with time in a typical experiment. At $t = 0$, $\log_{10}(\alpha_{amp}) = 2{\cdot}42$

Overall Kinetic Behaviour and Comparison with Literature Results.—No racemisation whatever was detected for the salt $(+)[Co(en)_3]I_3$ in water, even after 29 d at 40 °C, in the absence of a catalyst. On addition of bp carbon to the solution, the optical activity varied with time as depicted in the Figure. The initial rapid decrease in α_{amp} (see Experimental section) was caused by adsorption on the carbon of considerable amounts of the complex ion, at a rate much greater than the reduction of the complex[1] or its racemisation. The subsequent slower loss of optical activity gave linear log (α_{amp}) against time plots without serious deviation from linearity at up to four half-lives of racemisation. Rates of racemisation v were calculated from equation (6) using quarter-lives obtained from these plots and spectrophotometrically determined values (at 462 nm) of the bulk concentration c_0. These rates were generally more than an order of magnitude greater than the rates of reduction v_{Red} (Table 1). Even where v was no more than four times greater than v_{Red}, no significant deviation from linearity was observed in the log (α_{amp}) against time plots [*cf.* equations (17) and (18)] and equation (6) was applied without further correction.

TABLE 1

Racemisation at 40 °C of the salt $(+)[Co(en)_3]I_3$ by bp carbon in water (25 cm^3)

Run	$10^3[Co(en)_3I_3]_0$	m_{cat}	$10^3[Co(en)_3{}^{3+}]_\infty$ ($=c_0$)	$10^3[Co(en)_3{}^{3+}]_{ads}$ ($=A$)	$10^3[I^-]_{ads}$ ($=B$)	$10^{-3}t_{\frac{1}{2}}$	10^9v	$10^{10}v_{Red}$
	M	g	M	M	M	s	mol dm^{-3} s^{-1}	mol dm^{-3} s^{-1}
(1)	0·50	0·250	0·075 ± 0·02	0·425 ± 0·02	0·664 ± 0·013	201·4 ± 0·6	0·13 ± 0·10	*ca.* 0
(2)	0·75	0·250	0·22 ± 0·02	0·53 ± 0·02	0·97 ± 0·02	138·1 ± 0·6	0·54 ± 0·10	*ca.* 0
(3)	1·00	0·250	0·39 ± 0·02	0·61 ± 0·02	1·10 ± 0·02	122·0 ± 0·6	1·10 ± 0·20	0·56 ± 0·20
(4)	1·50	0·250	0·77 ± 0·02	0·73 ± 0·02	1·45 ± 0·02	92·9 ± 0·6	2·89 ± 0·20	1·72 ± 0·20
(5)	2·00	0·250	1·15 ± 0·02	0·85 ± 0·02	1·77 ± 0·02	77·0 ± 0·6	5·17 ± 0·20	3·60 ± 0·20
(6)	2·50	0·250	1·54 ± 0·02	0·96 ± 0·02	2·13 ± 0·02	61·2 ± 0·6	8·70 ± 0·20	5·59 ± 0·20
(7)	2·00	0·125	1·51 ± 0·02	0·49 ± 0·02	0·93 ± 0·02	124·7 ± 0·6	4·18 ± 0·20	2·57 ± 0·20
(8)	2·00	0·375	0·87 ± 0·02	1·13 ± 0·02	2·53 ± 0·02	67·7 ± 0·6	4·46 ± 0·20	3·10 ± 0·20
(9)	2·00	0·500	0·66 ± 0·02	1·34 ± 0·02	3·12 ± 0·02	72·0 ± 0·6	3·16 ± 0·20	2·46 ± 0·20
(10) [a]	1·00	0·250	0·32 ± 0·02	0·68 ± 0·02		139·0 ± 0·6	0·81 ± 0·20	2·18 ± 0·20
(11) [a]	2·00	0·250	1·05 ± 0·02	0·95 ± 0·02	1·82 ± 0·03	75·4 ± 0·6	4·88 ± 0·20	8·26 ± 0·20
(12) [b]	1·00	0·250	0·28 ± 0·02	0·72 ± 0·02		137·9 ± 0·6	0·70 ± 0·20	0·53 ± 0·20
(13) [b]	2·00	0·250	1·02 ± 0·02	0·98 ± 0·02	2·23 ± 0·03	72·2 ± 0·6	4·90 ± 0·20	1·98 ± 0·20
(14) [c]	1·00	0·250	0·39 ± 0·02	0·61 ± 0·02		115·9 ± 0·6	1·16 ± 0·20	0·67 ± 0·20
(15) [c]	2·00	0·250	1·15 ± 0·02	0·85 ± 0·02		76·1 ± 0·6	5·23 ± 0·20	3·55 ± 0·20

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

The predicted first-order kinetics found in the present work may be compared with results of Douglas and his co-workers for the racemisation of the salt K[Co(edta)] (edta = ethylenediaminetetra-acetato) by activated wood and sugar charcoal[13] and of $[Co(en)_3]Cl_3$ by activated wood charcoal.[14] First-order behaviour was observed for the racemisation of K[Co(edta)] on wood carbon but not in the other two cases. For these (second-order) plots of the reciprocal of the optical activity against time were linear if the same weights of carbon and complex were used, but not if their weights were different. When an excess (by weight) of either complex or carbon was used, linear second-order plots were obtained by[14] ' expressing the concentration of active complex as the observed rotation, and the " concentration " of carbon as the rotation of an equal weight of complex.' This suggests, they say,[14] ' that the carbon " reacts " stoichiometrically ' although they add that ' it is remarkable that such heterogeneous reactions seem to follow simple second-order kinetics.' We fully concur with the last comment, for solids cannot be assigned concentrations as if they were dissolved reagents.

Douglas and his co-workers[13,14] did not give tables of actual measurements, but their diagrams indicate that in many cases not more than *ca.* 35% of the reaction was followed. Within the limits of our crude estimation of their experimental values, first-order plots of log (optical activity) against time do not deviate sufficiently from linearity to enable one convincingly to differentiate reaction orders. Some of their lines extrapolated back to zero time yield intercepts appreciably different from the value used for the solution to which presumably no carbon had been added. As adsorption of complex on the carbons is probable, the initial points should not have

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[13] W. C. Erdman and B. E. Douglas, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1355.

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

been included in the plots. This may account for some of the curvature Douglas and his co-workers observed in trying to represent their data in a first-order form (*cf.* the Figure of our results). As the authors did not measure the surface areas of their carbons, one cannot estimate the degree of adsorption of their cobalt(III) complexes. Finally, it seems highly probable [1,15] that the adsorbed cobalt(III) complex ions were partially converted to cobalt(II) during the racemisations, although the experiments of Douglas and his co-workers would appear to rule out any large-scale reduction.

Rate Equation for Racemisation of the Ion $(+)[Co(en)_3]^{3+}$.—At constant mass of catalyst, the rate of racemisation v was found to depend on the concentrations of adsorbed complex ion, A, and adsorbed iodide ion, B, according to equation (19), where A and B are

$$v = k'A^2B - \text{constant} = k'(A^2B - A_1{}^2B_1) \quad (19)$$

defined in the previous paper [1] and $k'A_1{}^2B_1$ is a convenient way of describing the intercept in the v against A^2B plot. Numerically, $k' = 4{\cdot}6 \pm 0{\cdot}2$ dm^6 mol^{-2} s^{-1} and $A_1{}^2B_1 = (0{\cdot}11 \pm 0{\cdot}01) \times 10^{-9}$ mol^3 dm^{-9}. The rate equation for the accompanying redox reaction between adsorbed $[Co(en)_3]^{3+}$ and I^- ions included [1] an analogous x axis intercept which was interpreted [1] as due to the adsorption of reactants on sites that were catalytically inactive towards the redox process. The term $A_1{}^2B_1$ can similarly be regarded as representing species adsorbed on sites that are unable to catalyse the racemisation, possibly for geometric reasons.

Rate of Desorption.—Adsorption of $[Co(en)_3]^{3+}$ ions has been shown [1] to be much faster than the racemisation: we still have to demonstrate that desorption is faster than racemisation before concluding that the surface reaction is rate controlling. When a sample of bp carbon, on which optically active complex had been adsorbed, was filtered off and suspended in water, no desorption occurred. However, when the solid was suspended in a solution containing optically inactive complex, an increase in the optical activity of the solution showed that adsorption–desorption *exchange* was taking place. We now derive a kinetic equation for this exchange.

In the experiment under consideration, there is no net change in concentration of either adsorbed or bulk species, but simply a redistribution of the optically active form between the two states. Again there is a strong formal resemblance to an isotopic exchange reaction, with the ' doctoring ' of the solution equivalent to the introduction of the isotopic ' spike.' Let c_{ads} and c_{bulk} denote the concentrations of the complex (A) in the two states respectively, and let ‡ indicate the optically active form of (A). The reaction under consideration is (20).

$$(A_{\text{ads}})^{\ddagger} + (A_{\text{bulk}}) \rightleftharpoons (A_{\text{ads}}) + (A_{\text{bulk}})^{\ddagger} \quad (20)$$

Let $c_{\text{ads}}{}^{\ddagger} + c_{\text{ads}} = a$, $c_{\text{ads}}{}^{\ddagger} = y$, $c_{\text{bulk}}{}^{\ddagger} + c_{\text{bulk}} = b$, and $c_{\text{bulk}}{}^{\ddagger} = x$. Then $c_{\text{bulk}} = b - x$ and $c_{\text{ads}} = a - y$. Now from the definition of c_{ads} in the previous paper,[1] $x + y = x_\infty + y_\infty = d$, where the subscript ∞ denotes the value at infinite time, *i.e.* when exchange equilibrium has been reached. At this stage, moreover, $x_\infty/y_\infty = b/a$, so that $x_\infty = b(x_\infty + y_\infty)/(a + b) = bd/(a + b)$. Then equation (21) is obtained, where v_{ex} is the overall rate of

$$\frac{dx}{dt} = -\frac{dy}{dt} = v_{\text{ex}}\left[\left(\frac{y}{a}\right)\left(\frac{b-x}{b}\right) - \left(\frac{a-y}{a}\right)\left(\frac{x}{b}\right)\right]$$
$$= v_{\text{ex}}\left(\frac{a+b}{ab}\right)(x_\infty - x) \quad (21)$$

exchange taking into account both optically active and inactive species (A). Equation (21) integrates to (22),

$$\ln[(x_\infty - x_0)/(x_\infty - x_t)] = v_{\text{ex}}t(a + b)/ab \quad (22)$$

where x_0 and x_t are the values of x at zero time and at time t. Once more a kinetically first-order equation has emerged, one very similar in form to the McKay equation.[3]

In a typical desorption experiment under the conditions of run (5) (Table 1) for which $a = 0{\cdot}85 \times 10^{-3}$ and $b = 1{\cdot}15 \times 10^{-3}$M, v_{ex} was found to be $2{\cdot}0 \times 10^{-7}$ mol dm^{-3} s^{-1}, 40 times faster than the appropriate rate of racemisation ($5{\cdot}17 \times 10^{-9}$). The surface reaction is therefore the slow step in the racemisation.

Variation of Rate with Mass of Catalyst.—The rates of racemisation v were found to pass through a maximum as the mass of catalyst, m_{cat}, was varied [runs (7), (5), (8), and (9) in Table 1]. This phenomenon was also encountered in the reduction of $[Co(en)_3]^{3+}$ by I^- ions on bp carbon,[1] and with certain reactions of cobalt complexes catalysed by polyelectrolytes.[16] Morawetz *et al.*[16] suggested that the rise in rate up to the maximum reflects increasing adsorption until virtually all the reagents are adsorbed, while the rate decrease at higher catalyst concentrations is due to effective ' dilution ' of the adsorbed species over a greater area. Similar reasoning might apply here.

On the assumption that the value of $A_1{}^2B_1$ in equation (19) is independent of m_{cat}, the relation between v and m_{cat} was found to be (23) with $n = 2{\cdot}9$. With n rounded

$$v = \frac{k''}{m_{\text{cat}}{}^n}(A^2B - A_1{}^2B_1) \quad (23)$$

off to 3·0, $k'' = 0{\cdot}076$ dm^6 mol^{-2} s^{-1} g^3. Alternatively, following the same reasoning as for the redox reaction,[1] we may assume that the number of strongly adsorbing yet catalytically inactive sites is proportional to the surface area available. Multiplication of the $A_1{}^2B_1$ term in equation (23) by (m/0·250 g) led to best fit values of $n = 2{\cdot}6$ and $k'' = 0{\cdot}11$ dm^6 mol^{-2} s^{-1} g$^{2\cdot6}$. The changes in n and k'' are fairly small because $A_1{}^2B_1$ is a relatively small quantity. At first sight equation (23) appears to represent a third-order surface reaction, second order in the surface concentration of $[Co(en)_3]^{3+}$ and first order in that of iodide. In reality, values of v determined at constant volume of solution must obey a relation of the kind (24). Thus, if equation (23) holds, this suggests a

$$v \propto m_{\text{cat}}\,\text{f(surface concentrations)} \quad (24)$$

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

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

fourth-order surface reaction involving a constant amount of some other and unknown species spread over the surface. If, however, the intercept $k''A_1^2B_1$ increases with increasing m_{cat}, the surface reaction may be genuinely third order.

Effect of Changes in Reaction Conditions.—Washing the bp carbon as previously described[1] changed neither A nor the rate of racemisation [runs (3) and (14), (5) and (15), in Table 1]. This was true also[1] for the reduction of the ion $[\mathrm{Co(en)_3}]^{3+}$, and indicates that the carbon dioxide removed during washing had not affected the catalytic activity of the surface.

Under both nitrogen and oxygen atmospheres, the rate of racemisation decreased, more significantly so at the lower initial $[\mathrm{Co(en)_3}]\mathrm{I_3}$ concentration of 1mM (Table 1). This is surprising in the light of equation (19) since the value of A was greater under nitrogen or oxygen than under air, and the same was true for B where this was determined. The subject was not pursued further because experiments under controlled atmospheres were difficult and time consuming.

We now compare the rates of racemisation, v, and of reduction,[1] v_{Red}, of the ion $[\mathrm{Co(en)_3}]^{3+}$ under different atmospheres. The following rates (in mol dm^{-3} s^{-1}) refer to 2mM-$[\mathrm{Co(en)_3}]\mathrm{I_3}$ runs.

	Atmosphere		
	N_2	air	O_2
$10^{10}v_{\mathrm{Red}}$	8·26	3·60	1·98
$10^{10}v$	48·8	51·7	49·0
$10^{10}v'$	48·8	47·0	42·7

The observed net rates of reduction decrease in the order $N_2 > \text{air} > O_2$, which was attributed[1] to partial reoxidation of the $\mathrm{Co^{II}}$ formed. This reoxidation to $[\mathrm{Co(en)_3}]^{3+}$ provides a route to racemisation, but the racemisation rates do not increase in the reverse order $O_2 > \text{air} > N_2$. Furthermore, the values of v are an order of magnitude greater than those of v_{Red} so that the reoxidation mechanism can only make a marginal contribution to the overall racemisation rates. This contribution can be allowed for by subtracting from each value of v the difference $(v_{\mathrm{Red}})_{N_2} - (v_{\mathrm{Red}})_{\mathrm{atm}}$, to give the values of v' in the Table above. The sequence of these corrected racemisation rates v' is now $N_2 > \text{air} > O_2$, qualitatively the same as the net rates of reduction. Quantitatively, however, the values of v' and v_{Red} are by no means proportional to each other. A close mechanistic link between the redox and the racemisation reactions is therefore unlikely, particularly since a similar analysis of the 1mM series yields a sequence for v' that differs even qualitatively from that for v_{Red}.

Effect on the Rate of Added Reduction Products.—Table 2 lists the results of experiments carried out with cobalt(II) and $\mathrm{H_2en^{2+}}$ added, separately or together, as described previously.[1] Values of A remained the same as those in water, except for a small increase in run (23). The racemisation rate was not significantly affected by extra cobalt(II), but v decreased in the presence of extra $\mathrm{H_2en^{2+}}$ and decreased still further when both products were introduced. Yet Table 2 shows that part of the added cobalt(II) was adsorbed on the carbon surface. Cobalt(II), therefore, played no mechanistically important role: had it been the intermediate in the racemisation, its addition would have markedly enhanced the racemisation rate. Dwyer and Sargeson[17] provide evidence that the racemisation does proceed *via* a cobalt(II) intermediate under quite different reaction conditions (0·24M-en solution under nitrogen). Their mechanism is further discussed below.

Effect of Added Electrolytes.—The observed decreases in the rates of racemisation in Table 2 may be due to adsorption on the carbon of co-ions of the added salts. For this reason, the influence of adding certain simple electrolytes was investigated (Table 3). In the presence of perchloric acid, the rate of racemisation decreased appreciably. This was not due to changes in A (values of B were not determined), but pH measurements before (typically 2·00) and after (typically 2·30) introduction of bp carbon showed that hydrogen ions had been adsorbed. Perhaps this influenced the amount of iodide adsorbed and hence the rate. Whatever the reason, it is significant that the acid conditions that favoured reduction[1] retarded the racemisation. This further supports the idea that the two mechanisms are not interrelated. Other workers have observed a decrease in the racemisation rate of the salt $[\mathrm{Co(en)_3}]\mathrm{Cl_3}$ in the presence of perchloric[18] and sulphuric acids.[17,18]

TABLE 2

Rates of racemisation at 40 °C of the salt $(+)[\mathrm{Co(en)_3}]\mathrm{I_3}$ in water (25 cm^3) in the presence of bp (0·250 g) and the reduction products of the reaction

Run	$10^3[\mathrm{Co(en)_3I_3}]_0$ M	Medium	$10^3[\mathrm{Co(en)_3}^{3+}]_\infty$ $(=c_0)$ M	$10^3[\mathrm{Co(en)_3}^{3+}]_{\mathrm{ads}}$ $(=A)$ M	$10^4[\mathrm{Co^{II}}]_{\mathrm{ads}}$ M	$10^{-3}t_{\frac{1}{2}}$ s	$10^9 v$ mol dm^{-3} s^{-1}	$10^{10}v_{\mathrm{Red}}$ mol dm^{-3} s^{-1}
(3)	1·00	$\mathrm{H_2O}$	0·39 ± 0·02	0·61 ± 0·02		122·0 ± 0·6	1·10 ± 0·20	0·56 ± 0·20
(18)	1·00	0·5 × 10^{-4}M-$\mathrm{Co^{II}}$	0·36 ± 0·02	0·64 ± 0·02	0·33 ± 0·02	128·9 ± 0·6	0·95 ± 0·20	0·93 ± 0·30
(19)	1·00	4·5 × 10^{-4}M-$[\mathrm{H_2en}][\mathrm{ClO_4}]_2$	0·38 ± 0·02	0·62 ± 0·02		194·9 ± 0·6	0·67 ± 0·20	0·84 ± 0·20
(20)	1·00	combined (18) & (19)	0·39 ± 0·02	0·61 ± 0·02	0·15 ± 0·02	220·7 ± 0·6	0·61 ± 0·20	0·74 ± 0·30
(5)	2·00	$\mathrm{H_2O}$	1·15 ± 0·02	0·85 ± 0·02		77·0 ± 0·6	5·17 ± 0·20	3·60 ± 0·20
(21)	2·00	1·0 × 10^{-4}-M$\mathrm{Co^{II}}$	1·12 ± 0·02	0·88 ± 0·02	0·32 ± 0·02	74·3 ± 0·6	5·21 ± 0·20	3·60 ± 0·40
(22)	2·00	9·0 × 10^{-4}-M$[\mathrm{H_2en}][\mathrm{ClO_4}]_2$	1·11 ± 0·02	0·89 ± 0·02		77·4 ± 0·6	4·96 ± 0·20	3·84 ± 0·20
(23)	2·00	combined (21) & (22)	1·04 ± 0·02	0·96 ± 0·02	0·19 ± 0·02	100·6 ± 0·6	3·59 ± 0·20	3·60 ± 0·40

The rate of racemisation increased progressively with addition of sodium iodide and decreased monotonically with addition of sodium perchlorate. With mixtures of these salts the effects were roughly superimposed. This

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

[18] H. E. Swift and B. E. Douglas, *J. Inorg. Nuclear Chem.*, 1964, **26**, 601.

behaviour parallels that found[1] for the accompanying redox reaction. Swift and Douglas reported[18] that both sodium salts accelerated racemisation of the salt $[Co(en)_3]Cl_3$. The difference in behaviour may be due to the higher electrolyte concentrations they used, or, more probably, to the different carbons employed. The effects of sodium iodide and perchlorate on the racemisation rate v can be expressed empirically by equation (25) with

$$v = (A^2B - A_1^2B_1)/\{(p[\mathrm{Na^+}]_{ads}/B) + q\} \quad (25)$$

$p = 0.69$ and $q = 0.22_5$ mol² dm⁻⁶ s. Equation (25) reduces as required to (19) when $[\mathrm{Na^+}]_{ads} = 0$, with good agreement between k' and $1/q$. The form of equation (25) suggests competition for surface sites between Na^+ and I^- ions. The positive Na^+ ions, whether directly adsorbed or held in the Helmholtz layer, would electrostatically hinder the conjunction of two adsorbed $[Co(en)_3]^{3+}$ and one I^- ions implied by the A^2B term. This term also suggests that an adsorbed anion is required to enable two adsorbed $[Co(en)_3]^{3+}$ cations to approach each other sufficiently closely for racemisation to occur: iodide ions can act in this capacity since they are adsorbed on the carbon whereas perchlorate ions are not.[1] The zero rate in run (35) with the salt $[Co(en)_3][ClO_4]_3$ is thereby explained.

TABLE 3

Rates of racemisation at 40 °C of the salt $(+)[Co(en)_3]I_3$ in solution (25 cm³) containing bp carbon (0·250 g) and various added electrolytes

Run	$10^3[Co(en)_3I_3]_0$ M	Medium	$10^3[Co(en)_3{}^{3+}]_\infty$ $(=c_0)$ M	$10^3[Co(en)_3{}^{3+}]_{ads}$ $(=A)$ M	$10^3[I^-]_{ads}$ $(=B)$ M	$10^3[Na^+]_{ads}$ M	$[Na^+]_{ads}/[I^-]_{ads}$	$10^{-3}t_{\frac{1}{2}}$ s	10^9v mol dm⁻³ s⁻¹	$10^{10}v_{Red}$ mol dm⁻³ s⁻¹
(16)	1·00	0.5×10^{-2}M-$HClO_4$	0·42 ± 0·02	0·58 ± 0·02				192·6 ± 0·6	0·75 ± 0·20	1·05 ± 0·20
(17)	2·00	1.0×10^{-2}M-$HClO_4$	1·18 ± 0·02	0·82 ± 0·02				102·8 ± 0·6	3·99 ± 0·20	5·42 ± 0·20
(24)	1·00	0.5×10^{-3}M-$NaClO_4$	0·31 ± 0·02	0·69 ± 0·02				149·4 ± 0·6	0·72 ± 0·20	0·70 ± 0·20
(25)	2·00	1.0×10^{-2}M-$NaClO_4$	0·98 ± 0·02	1·02 ± 0·02				90·4 ± 0·6	3·42 ± 0·20	2·99 ± 0·20
(26)	2·00	1.5×10^{-2}M-$NaClO_4$	0·89 ± 0·02	1·11 ± 0·02	1·47 ± 0·02	0·60 ± 0·05	0·41	97·0 ± 0·6	3·19 ± 0·20	2·76 ± 0·20
(27)	1·00	2.5×10^{-3}M-NaI	0·30 ± 0·02	0·70 ± 0·02	2·02 ± 0·02			58·5 ± 0·6	1·75 ± 0·20	1·23 ± 0·20
(28)	1·00	5.0×10^{-3}M-NaI	0·27 ± 0·02	0·73 ± 0·02	2·69 ± 0·02			36·0 ± 0·6	2·59 ± 0·20	1·95 ± 0·20
(29)	1·00	7.5×10^{-3}M-NaI	0·20 ± 0·02	0·80 ± 0·02	3·36 ± 0·02			30·2 ± 0·6	2·34 ± 0·20	2·14 ± 0·20
(30)	2·00	0.5×10^{-2}M-NaI	0·90 ± 0·02	1·10 ± 0·02	3·25 ± 0·02	1·0 ± 0·1	0·31	36·4 ± 0·6	8·59 ± 0·20	7·03 ± 0·20
(31)	2·00	1.0×10^{-2}M-NaI	0·84 ± 0·02	1·16 ± 0·02	4·56 ± 0·02	2·2 ± 0·1	0·48	24·5 ± 0·6	11·88 ± 0·20	8·10 ± 0·20
(32)	2·00	1.5×10^{-2}M-NaI	0·78 ± 0·02	1·22 ± 0·02	5·81 ± 0·02	3·6 ± 0·1	0·62	20·5 ± 0·6	13·17 ± 0·20	9·26 ± 0·20
(33)	2·00	combined (25) & (30)	0·85 ± 0·02	1·15 ± 0·02	3·05 ± 0·02	1·3 ± 0·1	0·43	44·6 ± 0·6	6·59 ± 0·20	5·58 ± 0·20
(34)	2·00	combined (24) & (31)	0·81 ± 0·02	1·19 ± 0·02	4·52 ± 0·02	2·4 ± 0·1	0·53	25·2 ± 0·6	11·08 ± 0·20	8·35 ± 0·20
(35)	2·00 [a]	H_2O	1·12 ± 0·02	0·88 ± 0·02				∞	0	0
(36)	2·00 [a]	6×10^{-3}M-NaI	0·94 ± 0·02	1·06 ± 0·02				99·7 ± 0·6	3·29 ± 0·20	2·71 ± 0·20

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

Is a Cobalt(II) *Intermediate Involved?*—Dwyer and Sargeson[17] proposed the mechanism in equations (26)—(29) for their carbon-catalysed racemisation. Carbon

$$[Co(en)_3]^{3+}\ (\text{low-spin}) \rightleftharpoons [Co(en)_3]^{3+}\ (\text{high-spin}) \quad (26)$$

$$[Co(en)_3]^{3+}\ (\text{high-spin}) + e^- \rightleftharpoons [Co(en)_3]^{2+}\ (\text{high-spin}) \quad (27)$$

$$\text{D-}[Co(en)_3]^{3+}\ (\text{high-spin}) + \text{L-}[Co(en)_3]^{2+}\ (\text{high-spin}) \longrightarrow \text{L-}[Co(en)_3]^{3+} + \text{D-}[Co(en)_3]^{2+} \quad (28)$$

$$\text{D-}[Co(en)_3]^{2+} \rightleftharpoons \text{L-}[Co(en)_3]^{2+} \quad (29)$$

was viewed as catalysing (26), (28), and (29), and as acting as the reductant in (27). The essential ingredient in this scheme is the optically labile $[Co(en)_3]^{2+}$. That its formation by step (28) is rapid has recently received electrochemical support, for the exchange current density of the $[Co(en)_3]^{3+}$–$[Co(en)_3]^{2+}$ couple was found[19] to be high on platinum and is therefore probably[20] high on carbon also. Certainly cobalt(II) was produced in our experiments,[1] although the $[Co(en)_3]^{3+}$ ions were found to be reduced by I^- rather than by carbon as postulated above. Calculations showed,[1] however, that the concentration of the species $[Co(en)_3]^{2+}$ was exceedingly small (*ca.* 10^{-30}M), most of the cobalt(II) being present as $[Co(en)(H_2O)_4]^{2+}$ and $[Co(H_2O)_6]^{2+}$. Now the electrochemical experiments established[19] that electron exchange on platinum is fast only between the species $[Co(en)_3]^{3+}$ and $[Co(en)_3]^{2+}$, while cobalt(II)–ethylenediamine complexes of other stoicheiometries were electrochemically inactive. We must therefore conclude that Dwyer and Sargeson's mechanism does not apply under our experimental conditions. Only in solutions containing an appreciable concentration of the ion $[Co(en)_3]^{2+}$ can the electron exchange path be the main road to racemisation.

The form of the kinetics themselves provides a further argument against Dwyer and Sargeson's mechanism. If it held, one would expect a rate expression for step (28), and hence for the reaction, of type (30). Cobalt(II)

$$v = k'''[Co(en)_3{}^{3+}]_{ads}[Co^{II}]_{ads} = k'''A[Co^{II}]_{ads} \quad (30)$$

ions were generated according to the rate law[1] (31), so

$$v_{Red} = d[Co^{II}]/dt = k(AB - A_0B_0) \quad (31)$$

that the bulk cobalt(II) concentration at any time t is given by (32). Addition of cobalt(II) ions to the solution

$$[Co^{II}] = k(AB - A_0B_0)t \quad (32)$$

caused increased adsorption of these ions: thus $[Co^{II}]_{ads}$, like $[Co^{II}]$, would increase with time, and so would v. However, we detected no sign of autocatalytic behaviour.

Other evidence that the reduction of the ion $(+)$-$[Co(en)_3]^{3+}$ and its racemisation proceed along parallel but substantially independent paths has been described

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

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

in the preceding sections. Thus the two rates (studied with the same chemicals in the same laboratory) varied in a different way under nitrogen and oxygen atmospheres, and showed opposite responses in the presence of perchloric acid. Most convincing of all was the fact that adding extra cobalt(II), either alone or accompanied by en, failed to increase the rate of racemisation.

Mechanism of the Racemisation.—Intramolecular racemisation involves either rhombic [6] or trigonal [21] twisting without bond rupture, or else rupture of one Co–N linkage (or two such linkages involving different chelate rings). The latter case can lead [6] at low pH to protonation of the dechelated nitrogen followed by rapid elimination of the bidentate ligand from the complex. However, no aqua-products were detected spectrophotometrically in the reaction mixtures. The form of the rate law (19) also indicates that the catalysed racemisation is not purely intramolecular.

The intercept in equation (19) could be due to adsorption that for geometric or other reasons does not lead to racemisation. The third-order term suggests that the reaction proceeds by interaction on the carbon surface between two adsorbed $[Co(en)_3]^{3+}$ ions and one adsorbed I^- ion. Simple ligand exchange may be ruled out since Sen and Fernelius [22] have shown that over charcoal, and over platinum black, the rate of exchange of labelled en with $[Co(en)_3]^{3+}$ (as the iodide) is slower than the rate of racemisation. One may postulate, however, intermolecular links of the type $Co{-}NH_2 \cdots NH_2{-}Co$ to facilitate rearrangement or dissociation of other en groups. Kinetic data in the literature do not even exclude the possibility of rates second order in $[Co(en)_3{}^{3+}]$ in homogeneous racemisations. In these studies (*e.g.* that of Odell and Shooter [23]), first-order behaviour was inferred from linear first-order plots. However, as shown in our theoretical section, this is insufficient without the confirmatory evidence of the first-order rate constant so obtained being invariant with concentration.

Runs (35) and (36) in Table 3 point to the importance of adsorbed iodide. Its role may be electrostatic, enabling two complex ions to be adsorbed sufficiently close to one another to interact. Alternatively, its role may be to stabilise a bond-ruptured complex by forming an iodide bridge between the two cobalt atoms. Bridging halide ligands are well known in binuclear complexes, and bridged intermediates are involved in some substitution [24] and electron-exchange [25] reactions. Swift and Douglas [18] found racemisation of the salt $[Co(en)_3]Cl_3$ on wood charcoal to be accelerated by sodium salts in the order $NaClO_4$, $NaI > NaBr > NaCl > NaF$ (NaF actually retarded the reaction slightly). The position of the perchlorate looks anomalous in the light of our own measurements, but the remaining sequence probably reflects the degree to which the different halide ions are adsorbed on the carbon surface. What is not known is the sequence of catalysed racemisation rates per *adsorbed* halide ion, *i.e.* the sequence of k' values if the rate equation (19) holds for all halides. It may be added that association between one I^- and *one* $(+)[Co(en)_3]^{3+}$ ion is insufficient to cause racemisation: no homogeneous racemisation of aqueous $(+)[Co(en)_3]I_3$ was detected although ion-pairs were present.[26]

EXPERIMENTAL

Materials.—The salts $[Co(en)_3]I_3$ and $[Co(en)_3][ClO_4]_3$ were prepared and resolved as described before.[2] The carbon black bp was Black Pearls 2 of surface area 850 $m^2\,g^{-1}$ (B.E.T. N_2) supplied by Cabot Corporation. Sodium iodide was recrystallised twice from warm water, 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 employed throughout.

Method.—The experimental method was described in the previous papers.[1,2] The racemisation reaction was followed by measuring the amplitude (α_{amp}) of the optical rotatory dispersion curve for the ion $(+)[Co(en)_3]^{3+}$ between the rotation extrema at 518 and 461 nm. The instrument employed was a Bellingham and Stanley Polarmatic 62 spectropolarimeter fitted with a Hewlett–Packard 7035B X-Y recorder, with a cell of 1 cm optical path length.

Each desorption experiment was started by introducing bp carbon (0·250 g) into a solution (25 cm^3) of the salt $(+)$-$[Co(en)_3]I_3$. After 1 h, the sample bottle was removed from the rotating wheel on which it was agitated at 40 °C and the contents allowed to settle. A measured volume (17·5 cm^3) was removed from the supernatant liquid and filtered to ensure complete separation of solid. The optical absorbance of this filtrate was measured at 462 nm, and a solution of racemic $[Co(en)_3]I_3$ was prepared which had the same absorbance. Then the same volume (17·5 cm^3) of this racemic solution was pipetted into the bottle which was agitated for a further 2 h. Finally the optical activity of the solution was remeasured. It was corrected for the concomitant slow racemisation process (*cf.* the correction for radioactive decay [5]). It took *ca.* 10 min to replace the optically active solution (17·5 cm^3) with the same volume of inactive solution, and no racemisation correction was made for this interval.

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[21] J. C. Bailar, Jr., *J. Inorg. Nuclear Chem.*, 1958, **8**, 165.

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

[23] A. L. Odell and D. Shooter, *J.C.S. Dalton*, 1972, 135.

[24] D. S. Martin, Jr., *Inorg. Chim. Acta Rev.*, 1967, **1**, 87.

[25] Ref. 6, ch. 6.

[26] L. Johansson, *Acta Chem. Scand.*, 1971, **25**, 3752.