

Heterogeneous Catalysis in Solution. Part X.¹ Racemisation and Reduction by Solids of (+)₅₈₉-Tris(ethylenediamine)cobalt(III)

By Roland J. Mureinik and Michael Spiro,* Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

The effect of over 50 different solids (including sulphides, halides, oxides, metals, and non-metals) on aqueous solutions of the salts (+)₅₈₉[Co(en)₃]X₃ (X = I or ClO₄) has been investigated. The degrees of racemisation, adsorption, and reduction of the complex ion have all been followed. Thermodynamic arguments are presented that help to explain the role of the anion. The catalytic efficacies of the solids have been examined in the light of Pearson's theory of soft and hard acids and bases.

ALTHOUGH solids have often been observed²⁻¹¹ to hasten racemisation of optically active transition-metal complexes, the phenomenon has received little detailed study. Charcoal has proved to be the most successful catalyst of the few tried so far. Both intramolecular^{4,8} and electron-exchange⁷ processes have been suggested as the mechanism of racemisation, but considerable uncertainty still surrounds this subject. It was therefore thought desirable to carry out a more systematic investigation of the effect on racemisation of a wide variety of solids. The ion (+)₅₈₉[Co(en)₃]³⁺ was chosen as substrate because of its central position in the literature to date. It is also quite inert to racemisation in homogeneous solution^{2,12} at 100 °C. We found no racemisation at all in aqueous solutions at 40 °C even after 29 d, so that there was never any need to subtract the contribution of the homogeneous reaction. The choice of solid was limited to substances insoluble in water but was otherwise extensive. Not only were optical rotations measured after interaction with the solids, but also the optical absorbances in order to test for adsorption or decomposition processes. In many cases the extent of reduction to Co^{II} was determined also.

RESULTS AND DISCUSSION

Results of experiments with the salts [Co(en)₃]X₃ (X = I or ClO₄) and over 50 different solids are listed in Tables 1 and 2. Inspection shows that in most cases in which racemisation occurred it was accompanied by some degree of adsorption and/or reduction. In a few instances only reduction or only adsorption was observed. Thus zinc and brass, as expected on thermodynamic grounds (see below), completely reduced the complex. Zeolite Y, not surprisingly, strongly adsorbed the complex, and silicon carbide and talc partially adsorbed it, without apparent reduction or racemisation. First-order rate constants for the disappearance of optical activity, by whatever reaction, were estimated from gradients of log (α_{amp}) against time plots for the first 2–4 h of reaction (see Experimental section). Where

¹ Part IX, R. J. Mureinik, A. M. Feltham, and M. Spiro, *J.C.S. Dalton*, 1972, 1981.

² B. E. Douglas, *J. Amer. Chem. Soc.*, 1954, **76**, 1020.

³ W. C. Erdman and B. E. Douglas, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1355.

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

⁵ B. E. Douglas and H. E. Swift, *Nature*, 1962, **193**, 1173.

⁶ H. E. Swift and B. E. Douglas, *J. Inorg. Nuclear Chem.*, 1964, **26**, 601.

an induction period was observed, the rate constant was determined from the initial value of the gradient after the induction time.

Effect of the Anion.—Whether the perchlorate or the iodide salt was used had a strong bearing on the ease of racemisation of the complex ion. In some cases [Ag₂S, Hg₂Cl₂, AgI, Hg(OH)₂, Tl₂O₃, and Hg] no reaction occurred unless the complex was present as the iodide. In the presence of BiS, HgS, TlI, and Ag, and both forms of the carbon black Black Pearls 2, iodide increased the extent of racemisation and of reduction compared to perchlorate. The ungraphitised Black Pearls 2 partially adsorbed the complex ion from [Co(en)₃][ClO₄]₃ but caused no racemisation or reduction. All three processes, however, took place when Black Pearls 2 came into contact with the salt [Co(en)₃]I₃. (It will be shown in the following papers¹³ that adsorption of I⁻ on the carbon plays an essential role, and that in the case of reduction of the complex ion to Co^{II} the complementary oxidation process is the conversion of iodide to iodine. Perchlorate, of course, can perform no such service.) The experiments with HgS provided another good illustration. In its presence, the salt [Co(en)₃][ClO₄]₃ had undergone no change after 22 h. At this stage as much iodide (as sodium iodide) was added to the solution as it would have contained had the starting material been [Co(en)₃]I₃. After a further 24 h, appreciable racemisation (ca. 50%) and reduction (ca. 5%) had taken place. The only exception to the rule of greater reactivity for the iodide than the perchlorate salt was found using silicon powder. This, however, was differently treated before use in the two experiments [Table 1(e)].

The Nature of the Solid.—For a given substrate, the extent of catalysis depended on the physical nature of the catalyst. Thus some forms of carbon [Table 1(e)] caused racemisation while others did not. The specific area is obviously important: the catalytic effect by graphitised carbon blacks increased through the series Sterling FT, Graphon, and Black Pearls 2 with specific

⁷ F. P. Dwyer and A. M. Sargeson, *Nature*, 1960, **187**, 1022.

⁸ D. Sen and W. C. Fernelius, *J. Inorg. Nuclear Chem.*, 1959, **10**, 269.

⁹ F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, 1959, **81**, 290.

¹⁰ M. H. Ghandehari, T. N. Andersen, D. R. Boone, and H. Eyring, *J. Amer. Chem. Soc.*, 1970, **92**, 6466.

¹¹ B. E. Douglas and S.-M. Ho, *J. Inorg. Nuclear Chem.*, 1964, **26**, 609.

¹² A. Werner, *Ber.*, 1912, **45**, 121.

¹³ R. J. Mureinik and M. Spiro, following papers.

areas 7.7, 89.7, and 212 m² g⁻¹, respectively. But the area is not the only variable of importance. The charcoal Carbolac, with a greater specific area (950 m² g⁻¹) than any other solid investigated, exhibited no catalysis. No valid comparisons can be made between our results using carbon catalysts and those cited in the

literature²⁻¹¹ as the latter were all carried out at different temperatures and/or with different salts.

Inspection of the list of catalysts shows that no obvious predictions can be made as to the likelihood of an untried solid effecting catalysis. Thus, among the metal sulphides, those of silver(I) and mercury(II)

TABLE I

Effect of 0.500 g of various solids on 50 cm³ of 0.002M-[Co(en)₃]X₃ solution after 22 h at 40 °C

Solid and source	Area m ² g ⁻¹	X	% Loss of optical activity by					10 ⁵ k _{obs} s ⁻¹	Comments
			% Decrease in α _{amp}	% Decrease in A ₄₆₂	reduc- tion	adsorp- tion	racemis- ation		
Ag ₂ S (B.D.H.)	0.46	I	27	0	1	0	26	0.58	
		ClO ₄	0	0				0	
Sb ₂ S ₃ (B.D.H.)	0.36	I	54	30	14	16	24	1.23	New peak in absorption spectrum at ca. 342 nm
BiS (B.D.H.)	0.22	I	54			ca. 9 ^a		4.3	
		ClO ₄	31					2.4	An induction period of ca. 35 min occurred before loss of activity began
HgS (B.D.H.)	<i>b</i>	I	70			ca. 0 ^a		2.6	
		ClO ₄	0 ^c					0	
		ClO ₄ + I	55	6	5	ca. 1	ca. 50	0.64	New peak at ca. 342 nm
CdS (B.D.H.)		I	17 at 80 min	17	0	17	0	0	No further change after 80 min
PbS (B.D.H.)	0.15	I	15 at 6 min	15	0	15	0	0	No further change after 6 min
Tl ₂ S ₃ (metathesis)		ClO ₄	23	16			≠ 7	1.15	Spectrum considerably altered in 340—320 nm region
ZnS (metathesis)		ClO ₄	87	80			≠ 7	253	Extensive spectral changes
CuS (B.D.H.)		I	0	0				0	Cu ²⁺ detected in solution
MoS ₂ (unknown)		I	0					0	
(b) Effect of heavy-metal halides									
Hg ₂ I ₂ (B.D.H.)		I	59	7	3	ca. 4	ca. 52	5.1	New peak at ca. 342 nm
Hg ₂ Br ₂ (B.D.H.)		I	0					0	
Hg ₂ Cl ₂ (H. & W.)	<i>d</i>	I	29		12	14 ^a	≠ 3	1.5	Colour of solid Hg ₂ Cl ₂ changed from white to yellow, probably due to anion exchange on surface forming Hg ₂ I ₂
		ClO ₄	0					0	
AgI (freshly precipitated)		I	40	38	1	37	≠ 2		Adsorption was very slow
		ClO ₄	0					0	
AgBr (B.D.H.)	0.09	I	0					0	
AgBr (freshly precipitated)		I	0					0	
		ClO ₄	0					0	
AgCl (freshly precipitated)		I	0					0	
		ClO ₄	0					0	
TlI (metathesis)	<i>d</i>	ClO ₄	2						
		I	7		3		≠ 4		
CuBr (B.D.H.)		I	0					0	
(c) Effect of various oxides and hydroxides									
TiO ₂ (B.D.H.)		I	34	0				3.7	Strong new peak at 345 nm
Hg(OH) ₂ (metathesis)		I	13		0	ca. 0 ^a	ca. 13	0.82	
		ClO ₄	0					0	
SiO ₂ -Al ₂ O ₃ (Esso)	600	I	30	22	<1	21	8	0.88	Esso 3A cracking catalyst
Al ₂ O ₃ (Linde)		ClO ₄	0					0	Abrasive Alumina Linde B 0.05 μm; no change on addition of I ⁻
SiO ₂ (B.D.H.)	<i>d</i>	I	0					0	
Be(OH) ₂ (metathesis)		I	0					0	
		ClO ₄	0					0	
Cr(OH) ₂ .H ₂ O (metathesis)		ClO ₄	0					0	
Tl ₂ O ₃ (B.D.H.)	<i>d</i>	ClO ₄	0					0	
		I	4		0		≠ 4		
Ag ₂ O (B.D.H.)		I	1				1 (?)		
MnO ₂ (B.D.H.)		I	8				≠ 8		
SnO ₂ (B.D.H.)		ClO ₄	84	83			≠ 1	2.1	Induction period of ca. 20 min; strong peak below 300 nm

TABLE I (Continued)

(d) Effect of metals									
Metal	$\frac{10^4 \text{Area}}{\text{m}^2 \text{g}^{-1}}$	X	% Decrease in α_{amp}	% Decrease in A_{462}	% reduction	% adsorption	% Loss of optical activity by racemisation	$\frac{10^5 k_{\text{obs}}}{\text{s}^{-1}}$	Comments
Cu (clippings) (H. & W.)	6.27	I	14	peak distorted			≥ 14 (?)	≥ 6 ≤ 16	Both peaks in spectrum considerably distorted. α_{amp} against time plot scattered. No reduction detected by chloride method
	$\frac{10^4 \text{Area}}{\text{m}^2}$								
Zn (H. & W. powder)		I	100	100	100				After 2 h
Brass (turnings)		I	100	100	100				After 3 h
Ag (H. & W. powder)		ClO ₄	6	0			6		
		I	100	ca. 2	1.5		ca. 98	42	Colour changes on solid suggest AgI formation
Hg (distilled)		ClO ₄	0				0		
		I	100	0	2.5	0	97.5	8.1	Metal lost its sheen giving a yellow powder
Bright Pt (rotating disc) ^e	25.16	ClO ₄	0	0		0	0	0	
		ClO ₄ + I	0	0		0	0	0	[NaI] = 0.006M
		I	0			0	0	0	
Platinised Pt (rotating disc) ^e	7.500	ClO ₄	0	0	0	0	0	0	
		I	0	0	0	0	0	0	
(e) Effect of non-metals									
Solid and source	$\frac{\text{Area}}{\text{m}^2 \text{g}^{-1}}$	X	% Decrease in α_{amp}	% Decrease in A_{462}	% reduction	% adsorption	% Loss of optical activity by racemisation		Comments
Si (B.D.H.)		I	42	Peak masked					Strong new peak at 380 nm, large decrease at 330 nm peak. Si used as received.
		ClO ₄	90	Peak masked	0 (?)				Strong new peak at 380 nm, large decrease at 330 nm peak. No Co ^{II} detected by chloride method. Si boiled in dilute HCl before use to try to remove possible Fe impurities
Se (B.D.H., AnalaR)		I	0				0		
		ClO ₄	0				0		
Carbons and Graphites: Carbolac	950	I	8 at 10 min	ca. 10		8	≥ 2		At 25 °C
		I	6 at 10 min	ca. 7		7	≥ 1		
		I	25			12	≥ 13		[Co(en) ₃ I ₃] = 0.015M: 12% decrease in α_{amp} at 10 min attributed to adsorption
Decolorising charcoal		I	7				≥ 7		[Co(en) ₃ I ₃] = 0.015M ^f
Graphon (Cabot)	89.7	I	45						A graphitised carbon black ^f
Sterling FT (Cabot)	7.7	I	0			0	0		A graphitised carbon black ^f
Synthetic graphite (Thos. Hill-Jones)		I	0			0	0		[Co(en) ₃ I ₃] = 0.00135M
Sugar charcoal		I	8	0		0	8		Prepared by method of Douglas <i>et al.</i> ³
Black Pearls 2 graphitised (Cabot)	212	I	78						53% decrease in α_{amp} in 90 min with [Co(en) ₃ I ₃] = 0.015M
		ClO ₄	34	18	0	18	16		No Co ^{II} detected by chloride method: I = 1M(NaClO ₄)
Black Pearls 2 ungraphitised (Cabot)	850	I	65	43	1	43	21		See following papers ¹³ for detailed study
		ClO ₄	36	35.4	0	35.4	ca. 0		

^a Estimated by extrapolation of $\log(\alpha_{\text{amp}})$ against time plots back to zero time. ^b A sample of this compound from the same batch, washed with 1M-HNO₃, was found to have an area of $2.5 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$ [M. D. Archer and M. Spiro, *J. Chem. Soc. (A)*, 1970, 68]. It is probable that the untreated sample was of similar area. ^c After 166 h α_{amp} had fallen by 14%. At this stage sufficient NaI was added to make the solution 0.006M in I⁻. The numbers in the next line refer to 24 h after this addition. ^d Particles not resolved under optical microscope. ^e A platinum disc of 5.66 cm diameter was rotated at 400 rev. min⁻¹ in 200 cm³ of 0.002M-[Co(en)₃]X₃ solution at 25 °C. Bright platinum discs were pretreated by the method of Archer and Spiro,²⁵ platinised discs by the method of Gilman.²⁶ ^f Complete racemisation and extensive reduction occurred on boiling.

caused extensive racemisation with relatively little reduction, that of antimony(III) produced considerable racemisation and reduction, whereas the prime action of the sulphides of thallium(III) and zinc(II) was to cause reduction. Molybdenum(IV) and copper(II) sulphides had no effect on the complex, while cadmium(II) and

lead(II) sulphides did no more than adsorb appreciable amounts of complex ion.

Pearson's theory of hard and soft acids and bases¹⁴ has been used to rationalise why certain solids are more

¹⁴ R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; *Chem. in Britain*, 1967, **3**, 103.

TABLE 2

Various oxo-anion salts and other miscellaneous solids, 0.500 g of which had little or no effect on 50 cm³ of 0.002M-[Co(en)₃]X₃ solution after 22 h at 40 °C

Solid and source	X	% Decrease in α_{amp}	% Decrease in A_{462}	% Loss in optical activity by		
				reduction	adsorption	racemisation
BPO ₄ (Alfa Inorganics)	I	0			0	0
CdCO ₃ (B.D.H.)	I	0			0	0
	ClO ₄	0			0	0
BaSO ₄ (B.D.H.)	I	0			0	0
	ClO ₄	0			0	0
Pb ₃ (PO ₄) ₂ (B.D.H.)	I	0			0	0
	ClO ₄	0			0	0
ZnCrO ₄ (metathesis)	ClO ₄	4 ^a			4	
CaF ₂ (B.D.H.)	ClO ₄	0			0	0
	I	1 ^a			1	
NiC ₂ O ₄ (metathesis)	ClO ₄	3 ^a			3	
BN (B.D.H.)	I	1 ^a			1	
SiC (Carborundum)	I	13	15		15	
Perspex ^b (shavings)	I	0			0	0
Zeolite Y (Na form) ^c	ClO ₄	100	100		100	
Asbestos (H. & W.)	I	4	4		4	0
	ClO ₄	0			0	0
Talc (H. & W.)	ClO ₄	1 ^d				
	I	65 ^e	64		64	

^a After 5–10 min; no further change occurred for up to 22 h. These changes in optical activity were ascribed to adsorption. ^b Checked because the filtration apparatus was made of Perspex. ^c Complex not desorbed by 1M-NaClO₄. ^d No change on addition of I⁻. ^e Adsorption very slow.

effective than others in catalysing the reaction between ethyl iodide and silver(I) nitrate.¹⁵ The application of the theory is not obvious here. Sulphide is a soft base on the Pearson classification and so too, as acids, are mercury(II), thallium(III), and silver(I) whose sulphides were all active as catalysts. However, cadmium(II) is also soft but cadmium(II) sulphide was not a catalyst. Zinc(II), lead(II), copper(II), antimony(III), and bismuth(III) are all classed as borderline in softness. Zinc(II) sulphide caused extensive reduction, antimony(III) sulphide catalysed reduction and racemisation, but lead(II) and copper(II) sulphides were inactive.

The halides of mercury(I) and silver(I) appeared to improve as racemisation catalysts as the halide became softer. Thus, only silver(I) iodide of the silver(I) halides was a catalyst. Mercury(I) iodide was a good catalyst, mercury(I) bromide did not catalyse at all, and mercury(I) chloride probably functioned as a catalyst through ion exchange of surface chloride for iodide since the colour of the catalyst changed during the course of reaction. It is interesting that mercury(II) hydroxide was a reasonable catalyst, since OH⁻ is a hard base and mercury(II) a soft acid. One might be tempted to ascribe the effect to the large pH change at the hydroxide surface were it not for the fact that the similar substance Ag₂O caused no racemisation.

Bulk metals are capable of behaving¹⁴ either as soft acids or bases (so may charcoal, whose catalytic action has already been discussed). The complete reduction of the complex ion in iodide solution in the presence of zinc and brass obscured any catalytic role they may play in racemisation. Some chemical interaction in iodide solution was also observed with copper, silver, and mercury (see thermodynamic treatment below). The last two metals appeared to be good racemisation

catalysts. An unexpected finding was the failure of either bright or platinised platinum at 25 °C to catalyse racemisation even of the iodide salt. Perhaps this was due to a high activation energy, since Sen and Fernelius⁸ obtained complete racemisation on boiling the salt [Co(en)₃]I₃ for a few minutes with platinum black. Dwyer and Sargeson⁷ found platinum black to be a catalyst for racemisation of [Co(en)₃]Cl₃ only in the presence of added reductant such as sulphite, alcohol, or adsorbed hydrogen. They gave no experimental details so that a direct comparison of results is not possible. If indeed a reducing agent is necessary on platinum surfaces, then it seems likely that the iodide counter-ion fulfilled this role in the experiment of Sen and Fernelius.⁸

Despite differences in behaviour within groups of compounds of differing softness, it seems that at least one centre of softness is required for catalysis since compounds of hard acids and bases were not catalysts [Tables 1(c) and 2]. However, the presence of a soft site is not a sufficient condition for racemisation catalysis, as evidenced by the catalytic inertness of silver(I) oxide, silver(I) chloride, and platinum. We can rationalise these results as follows. The Co³⁺ ion is a hard acid and amines are hard bases. The complex formed from these two hard components, however, is a new and larger entity which presents six CH₂ groups to the world, and [Co(en)₃]³⁺ should therefore be softer than the parent ion. (Association constants between the complex ion and Cl⁻, Br⁻, and I⁻ in aqueous solution are not too dissimilar when allowance is made for the variation between the results of different workers, even those using the same physical method.^{16,17}) Thus [Co(en)₃]³⁺ ions might find the relatively large soft-base sites on the solid quite congenial. The presence on the solid of soft-acid

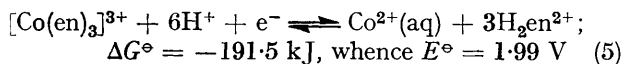
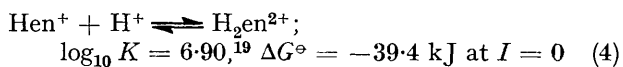
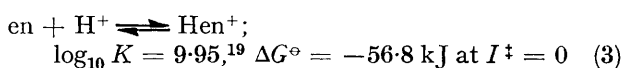
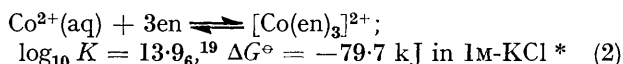
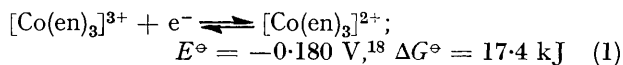
¹⁵ P. S. Walton and M. Spiro, *J. Chem. Soc. (B)*, 1969, 42.

¹⁶ M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, 1953, 49, 363.

¹⁷ N. Tanaka, Y. Kobayashi, and M. Kamada, *Bull. Chem. Soc. Japan*, 1967, 40, 2839.

sites would permit adsorption of soft-base co-ions such as I^- . As the following papers show,¹³ co-ion adsorption leads to further $[Co(en)_3]^{3+}$ adsorption, partly at least for electrostatic reasons. Undoubtedly geometrical and other factors also play their role in determining the degrees of adsorption and of catalysis and reduction.

Thermodynamic Considerations.—It has been amply demonstrated that reduction of the ion $[Co(en)_3]^{3+}$ occurs. The question now arises as to the nature of the complementary oxidation process. To evaluate the standard Gibbs free-energy change for the reduction of $[Co(en)_3]^{3+}$ we proceed as follows. Combination of

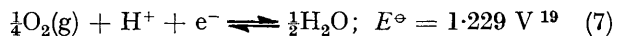


equations (1)—(4) gives (5). As for the $[Co(NH_3)_5Br]^{2+}$ — Co^{2+} couple,¹ the high potential derives essentially from the large decrease in free energy associated with protonation of the ligand nitrogen atoms. At pH *ca.* 6, a typical value in homogeneous $[Co(en)_3]I_3$ solutions, the formal potential of couple (5) drops to -0.14 V. The real potential is of course much higher if only a small amount of reduction takes place. If less acidic solutions are considered (pH ≥ 7), where the liberated en will exist predominantly in the monoprotonated form, we must instead combine equations (1)—(3) to give (6).

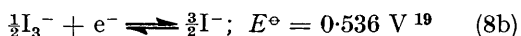
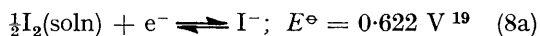


At pH 7 the formal potential of couple (6) becomes -0.48 V.

Thermodynamically, couple (5) is capable of oxidising the solvent in acid solutions [equation (7)]. Electro-



chemical measurements have shown¹³ that when carbon is the catalyst its potential in the solution is 0.54 V. Oxidation of the solvent on this solid is therefore impossible and, by analogy, seems unlikely to occur in similar systems. A more probable half-reaction is the oxidation of iodide to iodine [equations (8a) and (8b)]



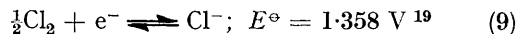
* $1M = 1 \text{ mol dm}^{-3}$.

† $I =$ ionic strength.

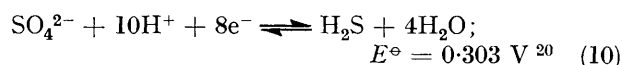
¹⁸ J. J. Kim and P. A. Rock, *Inorg. Chem.*, 1969, **8**, 563.

¹⁹ 'Stability Constants of Metal-ion Complexes,' eds. L. G. Sillén and A. E. Martell, Chem. Soc. Special Publ., Nos. 17 (1967) and 25 (1971).

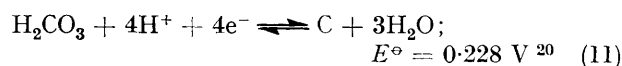
which is feasible thermodynamically as the complementary oxidation process for either (5) or (6). That reaction (8) does in fact occur is proved in the following paper.¹³ The calculation thus explains why a variety of solids brings about more reduction to Co^{II} in the presence of $[Co(en)_3]I_3$ than in that of the perchlorate salt, for ClO_4^- can be oxidised only with difficulty. More reduction of the ion $[Co(en)_3]^{3+}$ would also be expected with the iodide salt than with the chloride [*cf.* equation (9)].



Since in some cases reduction of the ion $[Co(en)_3]^{3+}$ to Co^{II} was noted with the perchlorate salt, other oxidation processes must be available also. One of these is oxidation of sulphide ions from sulphide catalysts (in acidic solutions) by reaction (10). In principle, charcoal

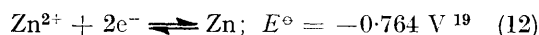


could also be oxidised by a process such as (11). In the

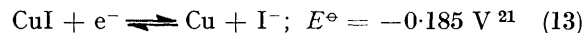


subsequent study,¹³ however, we found no reason to invoke reaction (11).

In view of their low electrode potentials, it is obvious why zinc (and brass) are readily oxidised [equation (12)].



Similarly, copper would be expected to be oxidised (E° for $Cu^{2+}/Cu = 0.337$ V), especially in iodide media where there is the possibility of stabilisation through complexation or formation of copper(I) iodide. The



potentials¹⁹ of silver and mercury are also much lower in the presence of the insoluble iodide salts (E° for $Ag^+/Ag = 0.799$ V but for $AgI/Ag, I^-$ it is -0.152 V; E° for $Hg_2^{2+}/Hg = 0.793$ V but for $Hg_2I_2/Hg, I^-$ it is -0.04 V). It will be noted from Table 1(d) that some reduction of $[Co(en)_3]^{3+}$ occurs with the iodide salt but not with the perchlorate, although one would find difficulty in distinguishing experimentally between direct oxidation of metal by $[Co(en)_3]^{3+}$ and indirect oxidation *via* iodine.

All the above calculations refer to values at 25°C , whereas most of the experimental work was carried out at 40°C . Exact calculations cannot be made for 40°C because of a paucity of data, but the figures available suggest that a rise of 15°C will usually affect the E° values by *ca.* 0.01 V. This change is small compared to the differences in potential between the various couples.

A Mechanistic Point.—Many of the solids brought

²⁰ M. Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solution,' Pergamon Press, Oxford, 1966, sections 17.1 and 19.2.

²¹ 'The Encyclopedia of Electrochemistry,' ed. C. A. Hampel, Reinhold, New York, 1964, p. 417.

about not only partial racemisation of the ion $(+)\text{Co(en)}_3^{3+}$, but also some degree of reduction to Co^{II} as well as adsorption on the solid. A knowledge of all three processes is necessary before any definite conclusions can be drawn regarding the mechanism. Detailed discussion¹³ of the action of the carbon Black Pearls 2 on this ion illustrates the inter-relation of the three processes.

EXPERIMENTAL

Materials.—The salt $[\text{Co(en)}_3]\text{I}_3 \cdot \text{H}_2\text{O}$ was prepared and resolved by the method of Broomhead *et al.*;²² $(+)\text{Co(en)}_3[\text{ClO}_4]_3$ was prepared by recrystallisation of the iodide from concentrated perchloric acid. Racemic $[\text{Co(en)}_3]\text{I}_3 \cdot \text{H}_2\text{O}$ was most conveniently obtained from the racemic chloride prepared by Work's method²³ by recrystallising from concentrated sodium iodide solutions. All the complexes analysed satisfactorily. Values of $\alpha_{m(589)}$ of $+89.2$ and -86.0° were found for $(+)$ - and $(-)$ - $[\text{Co(en)}_3]\text{I}_3 \cdot \text{H}_2\text{O}$ respectively, in good agreement with those of Broomhead *et al.*²² Sodium iodide (Hopkin and Williams) was recrystallised twice from warm water, and dried and stored *in vacuo* over silica gel. Sodium perchlorate, perchloric acid, and hydrochloric acid were of AnalaR quality. Doubly distilled water was used throughout.

Most of the solids whose catalytic effect was investigated were commercially available and were used as supplied unless otherwise stated: their sources are listed in Tables 1 and 2. Others were prepared by metathetic reaction of the appropriate salts, and dried *in vacuo* over silica gel. The surface areas of those solids that were found to have a catalytic effect were estimated using an optical microscope (Watson) with a calibrated eyepiece. The samples were dispersed in glycerol and average particle sizes estimated assuming spherical geometry after the method of van den Hul and Lyklema.²⁴ Many solids were too finely divided for the particles to be resolved under the optical microscope. Some surface areas were quoted by the suppliers and these are indicated in the Tables.

Method.—For experiments with powders, the solid was weighed into a conical flask (100 cm³), and a magnetic follower added. The flask was then immersed to its neck in a thermostat at $40.0 \pm 0.1^\circ\text{C}$. Solutions of complex of known concentration (0.002M unless otherwise stated) were separately equilibrated; at times t_0 they were added to the solid, and an immovable magnetic stirrer (Rank Bros., Bottisham, Cambridge) under the flask started at such a speed that all the powder was continuously agitated. Small aliquot portions were taken at various time intervals, filtered through a sintered glass disc (porosity 3), and their optical activities measured as described below. It was found for all the solids that racemisation and reduction, if any, ceased as soon as the solid was removed. This therefore provided a convenient method of quenching the reaction so that samples could be processed at leisure without a correction having to be applied for any homogeneous contribution to the rate.

For experiments using platinum discs, the rotating-disc

²² J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *Inorg. Synth.*, 1960, **6**, 183.

²³ J. B. Work, *Inorg. Synth.*, 1946, **2**, 221.

²⁴ H. J. van den Hul and J. Lyklema, *J. Amer. Chem. Soc.*, 1968, **90**, 3010.

²⁵ M. D. Archer and M. Spiro, *J. Chem. Soc. (A)*, 1970, 78.

²⁶ S. Gilman, *Adv. Electroanalyt. Chem.*, 1967, **2**, 111.

apparatus was set up as previously described.²⁵ Bright platinum discs were electrically pretreated by the method of Archer and Spiro.²⁵ Platinum discs, electrically cleaned according to the potential sequence of Gilman,²⁶ were platinised at 30 mA cm⁻² for 10 min from an aqueous solution 3.5 wt% in hexachloroplatinic(IV) acid, 0.005% in lead acetate, and 2M in hydrochloric acid.²⁷ All dissolvable lead from the surface layers was removed by soaking overnight in 1M-HClO₄.²⁸ Before use the platinised platinum disc was again pretreated using Gilman's method. The surface area was determined (by Dr A. M. Feltham) from the length of the hydrogen arrest of the galvanostatic charging curve in 1M-HClO₄.²⁹ The disc was rotated in a known volume of solution in a flanged QF Pyrex beaker (500 cm³) fitted with a Perspex lid. At time t_0 , a known volume of a concentrated $[\text{Co(en)}_3]\text{X}_3$ solution was added to give the required concentration. Small aliquot portions were periodically removed and their optical activities monitored using the α_{amp} function described below.

Optical-activity Measurements.—The optical rotatory dispersion (o.r.d.) and circular dichroism (c.d.) of optically active $[\text{Co(en)}_3]^{3+}$ have been well characterised.³⁰ The o.r.d. curve of the $(+)\text{Co(en)}_3$ form exhibits a positive extremum at 518 nm and a negative one at 461 nm. If α_{518} and $|\alpha_{461}|$ represent the magnitudes of the observed rotations at these wavelengths, and $\alpha_{m(518)}$ and $|\alpha_{m(461)}|$ the magnitudes of the specific rotations at these wavelengths, then equation (14) is applicable, where l is the pathlength in decimeters

$$(\alpha_{518} + |\alpha_{461}|) = (\alpha_{m(518)} + |\alpha_{m(461)}|)cl/100 \quad (14)$$

(0.1 dm here) and c the concentration in g solute per 100 cm³ solution. The bracketed term on the left represents the amplitude of the o.r.d. curve between the two extrema, since the signs of the rotations at the two wavelengths are opposite. Equation (14) can therefore be written as (15)

$$\alpha_{\text{amp}} = \alpha_{m(\text{amp})}cl/100 \quad (15)$$

where the subscript amp refers to the sum of the amplitudes at the two wavelengths. Equation (15) was tested in the concentration range used in these experiments and found to be obeyed within smaller error limits than measurements made at either extremum or at 270 nm where $(+)\text{Co(en)}_3^{3+}$ exhibits large negative rotation. This was due to the elimination of the error in the baseline position which must be determined if rotations at a single wavelength are used. In the instrument employed, the error introduced by the irreproducibility of the baseline was at least equal to the error in measurement at either extremum. The spectrum was therefore scanned over a wavelength range to include the two extrema, a procedure which eliminated the need to determine accurately the baseline position each time. In this way the sensitivity of the measurements was enhanced and the optical activity could be determined at low concentrations. For $(+)\text{Co(en)}_3[\text{ClO}_4]_3 \cdot \text{H}_2\text{O}$ the magnitude of $\alpha_{m(\text{amp})}$ is $1113^\circ\text{cm}^3\text{dm}^{-1}\text{g}^{-1}$ or $71.0^\circ\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$, more than ten times the value at 589 nm.

Optical activity measurements were made on a Bellingham and Stanley Polaromatic 62 spectropolarimeter, fitted with a Hewlett-Packard 7035B X-Y recorder. The optical

²⁷ A. M. Feltham and M. Spiro, *Chem. Rev.*, 1971, **71**, 177.

²⁸ A. M. Feltham and M. Spiro, *J. Electroanalyt. Chem.*, 1970, **28**, 151.

²⁹ A. M. Feltham and M. Spiro, *J. Electroanalyt. Chem.*, 1972, **35**, 181.

³⁰ R. D. Gillard and P. R. Mitchell, *Structure and Bonding*, 1970, **7**, 46, and refs. therein.

pathlength used was 1 cm. Absorbance measurements were made on a Hitachi-Perkin-Elmer model 124 spectrophotometer in matched quartz cells with optical pathlength of 1 cm.

Analysis for Cobalt(II).—In preliminary runs, aliquot portions were diluted with concentrated hydrochloric acid to give a $[\text{Cl}^-] : [\text{Co}^{II}]$ ratio of at least $10^4 : 1$, and the cobalt(II) content estimated from the absorbance at 690 nm (ϵ 450 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). For more sensitive determinations, the

³¹ K. W. Ellis and N. A. Gibson, *Analyt. Chim. Acta*, 1953, **9**, 275.

method of Ellis and Gibson,³¹ modified as described previously,¹ was used. Unless otherwise stated, values quoted in the Tables refer to determination by the latter method.

We thank the S.R.C. for a research grant for the purchase of the spectropolarimeter and for the award of a post-doctoral research assistantship (to R. J. M.), the South African Council for Scientific and Industrial Research for a travel grant (to R. J. M.), and Dr. A. M. Feltham for a preliminary literature survey.

[3/2223 Received, 29th October, 1973]
