Influence of Electrolyte Dissociation upon Rates of Reactions. Part VII.[1] Effects of Sulphate and some Dicarboxylate Media upon Rates of Aquation of Halogenopenta-amminecobalt(III) Complexes and the Rate of Base Hydrolysis of the Acetatopenta-amminecobalt(III) Complex

By **M. B. M. Campbell, M. R. Wendt,** and **C. B. Monk,*** Edward Davies Chemical Laboratory, University College of Wales, Aberystwyth SY23 1NE

Accelerations to the rates of aquation of chloropenta-amminecobalt(III) (at 35 °C) and bromopenta-amminecobalt(III) (at 25 °C) complexes caused by some ion-pairing dicarboxylates and sulphate have been studied by spectrophotometry. Similar work with iodopenta-amminecobalt(III) has been carried out at 25 °C by means of ^{125}I release. The results are analysed in terms of ion-pair rate constants of aquation. The ratios of these rate constants to those of the free cobalt(III) ions are in the range 2—3·1 : 1, being mainly independent of the halide component and only slightly related to the ion-pair dissociation constants. The rate of base hydrolysis of the acetatopenta-amminecobalt(III) complex at 25 °C, obtained by following the rate of release of [1-^{14}C]acetate, is retarded in dicarboxylate and sulphate media. There is a distinct proportionality between corresponding ion-pair rate and dissociation constants. The latter have been calculated from e.m.f. measurements on a glass electrode–calomel electrode cell (for dicarboxylate media) and from solubility measurements (for sulphate media).

PART III [2] dealt with accelerated rates of aquation of the chloropenta-amminecobalt(III) complex caused by certain ion-pairing ligands, and was based on the measurement of rates of release of ^{36}Cl from the complex. This work has now been repeated and extended by using absorption spectrophotometry for both the chloro- and bromo-complexes and (mainly) the rate of release of ^{125}I from the iodo-complex. In addition, the retarding effects of sulphate and some dicarboxylate media upon the rate of base hydrolysis of the acetatopenta-ammine-

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[1] Part VI, P. A. Jones and C. B. Monk, *J. Chem. Soc.* (*A*), 1971, 971.

[2] Part III, S. H. Laurie and C. B. Monk, *J. Chem. Soc.*, 1965, 274.

cobalt(III) complex have been measured by means of release rates of [1-^{14}C]acetate. This extends similar work described in Part V[3] on the halogeno-species.

RESULTS

The Chloropenta-amminecobalt(III) *Complex*.—The rate constant of aquation of the free ion at 35 °C was evaluated from direct spectrophotometric measurements at 300 and 540 nm. Rate constants in the presence of sulphate were likewise obtained at 540 nm and are given in Table 1. The method gave unsatisfactory results when dicarboxylate media were tried for the absorbance changes with time were less than those obtained in the absence of such media. This feature was caused by the production of traces of highly absorbing products such as the hydroxopenta-ammine-cobalt(III) complex at the pH values (*ca.* 5) of the dicarboxylate media. Thus the absorbance of a solution of the aquopenta-amminecobalt(III) complex in water at 35 °C increased with time whereas in 0·01M-perchloric acid no change occurred. Accordingly the reaction rates (Table 1) were assessed from the changes in absorbance with time of acidified samples.

TABLE 1

Rate constants at 35 °C for the aquation of the chloropenta-amminecobalt(III) complex and some of its ion-pairs. All measurements were made at 300 nm unless otherwise stated. Mean $k_1^0 = 652 \times 10^{-8}$ s^{-1}

$10^5 C_1$/mol dm^{-3}	10^5[Acid] mol dm^{-3}	10^5[NaOH] mol dm^{-3}	$10^8 k_{obs}$/s^{-1}	$10^7 k_{ip}^0$/s^{-1}
1583	1000 [a]		648 ± 6	
1605	500 [a]		657 ± 7	
1569	1500 [a]		652 ± 8	
1581	990 [a]	827 [f]	755 ± 7	127
1594	990 [a]	1086 [f]	775 ± 13	125
1553	990 [a]	1637 [f]	828 ± 17	128
1409	727 [b]	1211	846 ± 12	187
1413	1453 [b]	2423	981 ± 17	186
1411	2180 [b]	3634	1090 ± 12	189
1403	722 [c]	1211	730 ± 12	129
1407	1443 [c]	2422	794 ± 16	133
1408	2165 [c]	3634	829 ± 13	130
1392	726 [d]	1211	855 ± 16	201
1402	1090 [d]	1817	924 ± 14	197
1395	1453 [d]	2423	1010 ± 13	206
1403	1635 [d]	2726	1030 ± 17	200
1398	2179 [d]	3634	1090 ± 20	198
1404	723 [e]	1211	725 ± 17	143
1397	1447 [e]	2423	787 ± 21	150
1402	1809 [e]	3029	802 ± 16	146
1401	2170 [e]	3634	824 ± 17	149
585	800 [a]		658 ± 12 [g]	
591	1600 [a]		658 ± 10 [g]	

[a] Perchloric. [b] Phthalic. [c] Malonic. [d] Maleic. [e] Tartaric. [f] [Na_2SO_4]. [g] At 540 nm.

The Bromopenta-amminecobalt(III) *Complex*.—Rate constants at 25 °C in dilute acid and in sulphate and dicarboxylate solutions were evaluated from direct spectrophotometric measurements at 560 and 362 nm. This was possible since conversion of the aquo-form to the hydroxo-form was negligible at 25 °C. Absorbances with time at 560 nm of acidified samples gave rate constants that agreed well with those derived from direct absorbance measurements (Table 2).

It was found that the dicarboxylate media enhanced the absorptions of the aquo-complex below 400 nm. Down to about 320 nm such enhancements were small and could be allowed for by measuring the ' infinity ' absorbances from mixtures of aquo- and dicarboxylate-ions. These enhancements are due partly to the ligand charge-transfer spectra and partly to complex–dicarboxylate ion-pairing. Below 320 nm the enhancement caused by ion-pairing increases rapidly.

In contrast, below 330 nm, the dicarboxylate media produce small decreases in the absorbance of the bromo-complex. This ' medium ' effect was allowed for by obtaining absorbances at zero time for each run (as described later).

The Iodopenta-amminecobalt(III) *Complex*.—Yalman[4] obtained aquation rate constants for the free ion at an ionic strength of 1·0M from optical density measurements at 288 nm on chilled aliquots containing sulphite, thiosulphate, or arsenic(III). These additives were used to prevent oxidation of the liberated iodide, iodine absorbing strongly around 288 nm. Yalman found that free iodide reduces the iodo-complex and $<1 \times 10^{-3}$ mol dm^{-3} of the latter must be used to avoid this process. We were able to apply direct spectrophotometry with 4×10^{-4} mol dm^{-3} of free complex ion in the absence of reducing agents, but in the presence of dicarboxylates liberated iodide was oxidised to iodine. This could not be annulled by reducing agents since these could cause secondary ion-pair effects and also sulphite and thiosulphate liberated colloidal sulphur by decomposition. The use of reducing agents in chilled aliquot portions also introduces some uncertainty due to the time required for cooling and measuring the optical densities. We therefore used the method described previously[3] for base-hydrolysis studies of the iodo-complex, namely following the rate of release of ^{125}I after rapid filtration through a cation exchange resin of aliquot portions withdrawn at given intervals. The results are shown in Table 3.

The Acetatopenta-amminecobalt(III) *Complex*.—Previous reports on rates of base hydrolysis of carboxylatopenta-amminecobalt(III) ions are based upon acid-base titrations or optical density changes. Direct titrations of unchanged hydroxide or back-titrations after adding an excess of acid have been tried, using indicators and potentiometry. The relatively low solubilities of the complex ions meant using low concentrations of hydroxide ion with these methods in order to obtain significant changes of hydroxide concentration and since many of the reactions are slow, only about 5—10% of a reaction could be followed in a convenient time period. Basolo *et al.*,[5] for example, titrated unreacted hydroxide with hydrochloric acid, using Thymol Blue indicator. The reproducibility was only about ±10% and they pointed out that extra hydroxide consumption occurred after a certain time due to elimination of ammonia from the initial hydroxopenta-amminecobalt(III) product. Illuminati and Aprile,[6] and Jones and Thomas,[7] back titrated an excess of acid by potentiometry, but again only after about 5—10% reaction and the reproducibility was ±10%. Spectrophotometry[8-10] has been used for following either

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[3] Part V, M. R. Wendt and C. B. Monk, *J. Chem. Soc.* (*A*), 1969, 1624.

[4] R. G. Yalman, *J. Amer. Chem. Soc.*, 1953, **75**, 1842; *Inorg. Chem.*, 1962, **1**, 16.

[5] F. Basolo, J. G. Bergmann, and R. G. Pearson, *J. Phys. Chem.*, 1952, **56**, 22

[6] G. Illuminati and F. Aprile, *Ricerca sci.*, 1958, **28**, 1489.

[7] W. E. Jones and J. D. R. Thomas, *J. Chem. Soc.* (*A*), 1966, 1481.

[8] R. B. Jordan and H. Taube, *J. Amer. Chem. Soc.*, 1964, **86**, 3890; 1966, **88**, 4406.

[9] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 1967, **6**, 379.

[10] F. Monacelli, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1079.

the direct formation of the hydroxo-product or the aquo-form after quenching with acid. The former is subject to error in that the hydroxo-form undergoes decomposition so that absorbance changes are bigger than they should be. The method is successful when the rate of hydrolysis is much greater than the rate of decomposition, as with the halogenopenta-amminecobalt(III) ions [3] but this does not apply to the carboxylato-series. The latter process of conversion to the aquo-form does not overcome the problem since decomposition is irreversible and cobalt(III) oxide forms.

TABLE 2

Rate constants at 25 °C for the aquation of the bromopenta-amminecobalt(III) complex and some of its ion-pairs. All measurements made at (a) 560 nm, mean $k_1^0 = 625 \times 10^{-8}$ s^{-1} (b) 362 nm, $k_1^0 = 619 \times 10^{-8}$ s^{-1}

(*a*)

10^5C_1/ mol dm^{-3}	10^3[Acid] / mol dm^{-3}	10^5[NaOH] / mol dm^{-3}	10^8k_{obs}/ s^{-1}	$10^7k_{\text{ip}}^0$/ s^{-1}
1692	495^{a}		617 ± 12	
1472	990^{a}		630 ± 15	
1502	1979^{a}		628 ± 8	
1673		1200	823 ± 17	136
1407		1375^{f}	867 ± 12	138
1474	990^{a}	1602^{f}	838 ± 12	135
1210	990^{a}	1514^{f}	850 ± 10	138
1510	689^{c}	1201	715 ± 12	135
1492	1034^{c}	1802	745 ± 12	132
1501	1378^{c}	2402	780 ± 13	135
1522	1723^{c}	3003	802 ± 13	134
1544	2918^{c}	4804	838 ± 17	132
1486	731^{b}	1201	793 ± 8	175
1377	1097^{b}	1801	870 ± 10	175
1461	1462^{b}	2402	910 ± 13	171
1364	2194^{b}	3603	1010 ± 12	172
1525	717^{d}	1201	778 ± 8	169
1470	1076^{d}	1802	853 ± 10	176
1492	1434^{d}	2403	893 ± 13	170
1196	1463^{d}	2401	920 ± 8	173
1447	1793^{d}	3004	948 ± 10	172
1467	2151^{d}	3604	1000 ± 17	177
1377	728^{d}	1201	713 ± 7	158
1370	1456^{e}	2403	772 ± 12	155
1312	1492^{e}	2401	765 ± 12	153
1453	2184^{e}	3603	818 ± 8	158
1384	2912^{e}	4806	855 ± 10	158

(*b*)

10^5C_1/ mol dm^{-3}	10^3[Acid] / mol dm^{-3}	10^5[NaOH] / mol dm^{-3}	10^8k_{obs}/ s^{-1}	$10^7k_{\text{ip}}^0$/ s^{-1}
482			617 ± 10	
178	1000^{a}		617 ± 10	
488	500^{a}		622 ± 15	
486	785^{c}	1201	737 ± 8	132
491	1178^{c}	1802	772 ± 13	132
486	2355^{c}	3603	828 ± 22	129
486	1570^{c}	2402	802 ± 13	133
486	1963^{c}	3002	813 ± 10	130
491	1068^{d}	1789	942 ± 13	167
489	1424^{d}	2386	978 ± 15	164
488	1780^{d}	2982	1040 ± 13	169
494	2492^{d}	4175	1080 ± 8	166
489		590^{f}	838 ± 13	143
495		1180^{f}	912 ± 13	141
500		1770^{f}	975 ± 15	141
504		2360^{f}	1010 ± 18	142
489	746^{e}	1193	757 ± 8	167
489	1119^{e}	1789	792 ± 15	164
491	1492^{e}	2386	823 ± 8	164
490	1865^{e}	2982	845 ± 12	162
493	2984^{e}	4772	903 ± 10	164
488	733^{b}	1193	887 ± 8	168
488	1099^{b}	1789	975 ± 15	173
489	1466^{b}	2386	1020 ± 8	170
488	1832^{b}	2982	1060 ± 7	169
488	2199^{b}	3579	1100 ± 15	171

For footnotes see Table 1.

We have therefore tried following the rate of release of [1-^{14}C]acetate and have found that up to 30% reaction could be followed with average uncertainties of about ±3% in the experimental rate constants (Table 4). This method has the advantage that it is independent of the stabilities of the reaction products. As in a previous paper,[3] the retarding effects of sulphate and some dicarboxylate media have been ascertained and assessed in terms of ion-pair rate constants. This has entailed estimating the equilibrium constants for dissociation of the ion-pairs and this has been done by means of a glass electrode–calomel electrode e.m.f. cell (for the dicarboxylate media) and solubility measurements (for the sulphate media). The results are given in Table 5.

TABLE 3

Rate constants for the aquation of the iodopenta-amminecobalt(III) complex and some of its ion-pairs. All measurements made at (a) 25 °C using ^{125}I release, mean $k_1^0 = 767 \times 10^{-8}$ s^{-1} (b) 320 nm

(*a*)

10^5C_1/ mol dm^{-3}	10^5[Acid] / mol dm^{-3}	10^5[NaOH] / mol dm^{-3}	10^8k_{obs}/s^{-1}	$10^7k_{\text{ip}}^0$/ s^{-1}
300	1000^{a}		771 ± 20	
312	1000^{a}		770 ± 7	
332	1000^{a}		760 ± 22	
308	1000^{a}	1063^{f}	1030 ± 10	161
303	1000^{a}	1056^{f}	1035 ± 27	162
308	1000^{a}	2120^{f}	1150 ± 16	166
305	1000^{a}	2112^{f}	1135 ± 12	162
308	1000^{a}	1571^{f}	1100 ± 15	164
309	1800^{e}	3000	992 ± 13	167
307	2400^{e}	4000	1040 ± 14	170
308	3000^{e}	5000	1040 ± 20	166
426	3345^{e}	5434	1052 ± 13	171
416	3330^{e}	4643	987 ± 23	167
304	1200^{c}	2000	993 ± 17	157
304	1800^{c}	3000	1040 ± 16	158
304	2400^{c}	4000	1080 ± 18	162
305	3000^{c}	5000	1080 ± 19	154
302	3600^{c}	6000	1130 ± 15	162
308	612^{d}	1000	1150 ± 16	237
308	1206^{d}	2000	1320 ± 16	235
310	1813^{d}	3000	1410 ± 16	234
310	2399^{d}	4000	1480 ± 7	234
311	3004^{d}	5000	1520 ± 15	234
270	2412^{b}	3000	1220 ± 19	230
317	3136^{b}	4000	1310 ± 24	231
328	594^{b}	1000	1180 ± 11	235
329	1219^{b}	2000	1350 ± 25	235
328	1809^{b}	3000	1470 ± 14	237

(*b*)

10^5C_1/ mol dm^{-3}	10^5[Acid] / mol dm^{-3}	10^5[NaOH] / mol dm^{-3}	10^8k_{obs}/s^{-1}	$10^7k_{\text{ip}}^0$/ s^{-1}
418	1000^{a}		780 ± 15	
424	1000^{a}		750 ± 18	
436	1000^{a}	1000^{g}	750 ± 5	
430	1000^{a}	500^{g}	762 ± 20	
424	1000^{a}	1000^{h}	783 ± 20	
28·0	1000^{a}		3450 ± 120^{i}	
35·0	1000^{a}		3400 ± 90^{i}	
28·0	1000^{a}		12,800 ± 200^{j}	
26·0	1000^{a}		12,830 ± 300^{j}	

$^{a-f}$ See Table 1. ^{g} [NaCl]. ^{h} [NaClO$_4$]. ^{i} At 35 °C. ^{j} At 45 °C.

In Tables 1 and 2, and the second part of Table 3, the k_{obs} values were calculated by application of the standard expression (1), where A_∞ is the absorbance of the aquo-form,

$$k_{\text{obs}}\,t = \ln\,[(A_\infty - A_0)/(A_\infty - A)] \qquad (1)$$

A that of the reacting solution at time t, and A_0 that at $t = 0$ (*i.e.* that of the halogeno-species). A preliminary value of A_0 was obtained by extrapolating a plot of A against time over a short range of t back to $t = 0$. It was then adjusted slightly until the deviations in the k_{obs} values obtained with larger ranges of t were at a minimum. For the iodide- and acetate-labelled runs, the concentration, x, of complex which had reacted at time t was calculated from equation (2), where C_1 represents the initial total concentration of complex, and R count-rates of unit volumes. R_0 Was obtained by extrapolating a plot of R against time over a short range of t, and R_∞ after destruction of samples with an excess of hydroxide. Since $(R_\infty - R_0)$ was relatively large, adjustments to R_0 for minimum deviations in k_{obs} (Table 3) and second-order rate constants k_{2obs} (Table 4) were found to be unnecessary.

$$x = C_1(R - R_0)/(R_\infty - R_0) \qquad (2)$$

TABLE 4

Base hydrolysis rate constants at 25 °C for the acetatopenta-amminecobalt(III) complex and some of its ion-pairs. Mean $k_2^0 = (965 \pm 7) \times 10^{-6}$ mol^{-1} dm^{-3} s^{-1}

10^5C_1/ mol dm^{-3}	10^5[NaOH] / mol dm^{-3}	10^5[Sodium salt] / mol dm^{-3}	10^6k_{2obs}/ mol dm^{-3} s^{-1}	10^5[CpL] / mol dm^{-3}	$10^6k_2{}^0{}_{ip}$/ mol dm^{-3} s^{-1}
616	4001		426 ± 8		
639	5008		403 ± 10		
643	5008	3206 [a]	363 ± 11		
639	4006	3206 [a]	380 ± 8		
781	3970	329 [b]	373 ± 12	110	165
764	3970	658 [b]	334 ± 9	195	145
782	3970	987 [b]	310 ± 9	260	155
651	4006	390 [c]	404 ± 7	70	370
649	4006	780 [c]	374 ± 9	125	295
662	4006	1170 [c]	369 ± 6	165	340
620	3992	392 [d]	383 ± 8	95	220
616	3992	785 [d]	346 ± 7	160	200
603	3992	1106 [d]	326 ± 9	205	215
630	3992	1583 [d]	296 ± 5	245	180
932	3992	415 [e]	399 ± 10	85	440
747	3992	830 [e]	385 ± 8	125	375
796	3992	1245 [e]	387 ± 9	175	435
644	4006	486 [f]	399 ± 7	90	360
631	4006	810 [f]	376 ± 8	130	310
638	4006	1296 [f]	372 ± 6	180	360
613	4006	1759 [f]	352 ± 7	205	330
691	3992	339 [g]	410 ± 8	50	440
694	3992	798 [g]	406 ± 8	100	510
585	3992	1202 [g]	399 ± 8	115	480
570	3992	1596 [g]	387 ± 6	135	450
853	4006	452 [h]	408 ± 10	75	530
729	4006	892 [h]	397 ± 9	115	460
664	4006	1513 [h]	393 ± 8	150	480
654	5008	371 [i]	368 ± 8	90	200
629	5008	619 [i]	346 ± 8	135	185
632	5008	926 [i]	323 ± 7	180	180
619	5008	1260 [i]	316 ± 8	210	210

[a] Perchlorate. [b] Phthalate. [c] Oxalate. [d] Maleate. [e] Tartrate. [f] Malonate. [g] Succinate. [h] Malate. [i] Sulphate.

DISCUSSION

Acid Hydrolysis.—In Tables 1—3, k_1^0 represents the unimolecular rate constant for the free ion and k_{ip}^0 that of the ion-pair. The method of estimating k_{ip}^0 has been given in previous papers [1,2] and is based upon the treatment of Wyatt and Davies.[11] The relevant expression is that of (3). Values of [CpL], the concentration of the ion-pairs at $t = 0$, were calculated by an iterative procedure [2,12] using the known dissociation constants [13] of the chloro-ion-pairs for all three halogeno-complex series (see Table 6). The dissociation constants of the dicarboxylic acids, which were required for these calculations and the acetato-studies described subsequently, were taken from the tables of Robinson and Stokes [14] and of Kortum *et al.*[15]

$$k_{obs}C_1 = k_1^0(C_1 - [\mathrm{CpL}]) + k_{ip}^0[\mathrm{CpL}] \qquad (3)$$

TABLE 5

Dissociation constants of some acetatopenta-amminecobalt(III) ion-pairs at zero ionic strength at 25 °C; (a) from e.m.f. measurements (b) from solubilities

(*a*)

	10^5K/mol dm^{-3}					
Run	1	2	3	4	5	Average
Phthalate	326 ±8	230 ±4	241 ±6	241 ±6		235 ±8
Tartrate	567 ±8	559 ±6	553 ±8	556 ±11	544 ±8	555 ±10
Malonate	438 ±4	443 ±4	442 ±5	433 ±5	441 ±6	440 ±7
Maleate	301 ±2	302 ±3	306 ±3	306 ±2	304 ±2	305 ±3
Succinate	693 ±10	701 ±3	696 ±9	698 ±6	697 ±10	695 ±10
Malate	673 ±10	673 ±5	664 ±9	659 ±8	661 ±12	665 ±10
Oxalate	468 ±4	470 ±3	464 ±6	466 ±4		465 ±6

(*b*)

10^5C_1/ mol dm^{-3}	10^5[Na$_2$SO$_4$] / mol dm^{-3}	10^4I/ mol dm^{-3}	10^4K/ mol dm^{-3}
3460		1040	
3565	376	1085	25
3615	564	1110	25
3905	1662	1288	27

It seems justifiable to use the dissociation constants of the chloro-complexes for the bromo- and iodo-calculations since the three complex ions are of the same type and size, and since some related dissociation constants are of the same order as those of the chloro-species. Thus Prue *et al.*[16] have calculated that K is 0·00272 mol dm^{-3} at 25 °C for the nitropenta-amminecobalt(III), sulphate ion-pair from the conductivity measurements of Masterton and Brierly.[17] Values for the same ion-pairs with the acetatopenta-amminecobalt(III) ion (Table 7) are of the same order (about 20% lower) as those in Table 6 and so also are those of the chloropenta-amminechromium(III) ion with sulphate, malonate, phthalate, and tartrate.[12] In addition the values of

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[13] D. W. Archer, D. A. East, and C. B. Monk, *J. Chem. Soc.*, 1965, 720.

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[15] G. Kortum, W. Vogel, and K. Andrussow, 'Dissociation Constants of Organic Acids in Aqueous Solutions,' Butterworths, London, 1961.

[16] E. M. Hanna, A. D. Pethybridge, and J. E. Prue, *J. Phys. Chem.*, 1971, **75**, 291.

[17] W. L. Masterton and T. Brierly, *J. Phys. Chem.*, 1970, **74**, 139.

TABLE 6

Average aquation rate constants ($\times 10^8$, s^{-1}) [a] for the chloro-, bromo-, and iodo-penta-amminecobalt(III) complexes and their ion-pairs

	Chloro (35 °C)		Bromo (25 °C)		Iodo (25 °C)	
	300 nm	540 nm	560 nm	362 nm	^{125}I	320 nm
Free-ion (k_1^0)	652	658	625	619	767	765 [b]
Sulphate ion-pair (k_{ip}^0)		1270	1360	1420	1630	
Malonate ion-pair (k_{ip}^0)	1310		1340	1310	1590	
Tartrate ion-pair (k_{ip}^0)	1470		1560	1640	1680	
Phthalate ion-pair (k_{ip}^0)	1870		1730	1700	2330	
Maleate ion-pair (k_{ip}^0)	2000		1730	1670	2350	

Rate constant ratios and dissociation constants

	k_{ip}^0/k_1^0			
	Chloro	Bromo	Iodo	K/mol dm^{-3}
Sulphate	1·95	2·25	2·1	0·0035
Malonate	2·0	2·1	2·1	0·0048
Tartrate	2·25	2·55	2·2	0·0075
Phthalate	2·85	2·8	3·0	0·0030
Maleate	3·05	2·75	3·1	0·0034

[a] Previous results ($10^8 k_1^0$, s^{-1}) are: 633 (ref. 2), 670 (C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, 1960, **187**, 477), 667 in 0·1M-HNO_3 (R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, 1955, **59**, 304) for the chloro-ion at 35 °C; 620 (M. D. Archer and M. Spiro, *J. Chem. Soc.* (*A*), 1970, 68), 600 (A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261) for the bromo-ion at 25 °C; and 830 in 1M-NH_4ClO_4 (ref. 4) for the iodo-ion. [b] At 35 and 45 °C, $k_1^0 = 3430 \times 10^{-8}$ and $12{,}800 \times 10^{-8}$ s^{-1} respectively.

k_{ip}^0 are not very sensitive to the values of K, an error of 10% in K only effecting k_{ip}^0 by about 4%.

The average values of k_1^0 and k_{ip}^0 obtained in the present work are given in Table 6. This Table also lists k_{ip}^0/k_1^0 values and the average dissociation constants K. These figures show two features, namely that the k_{ip}^0/k_1^0 values for a particular ion-pairing ligand are largely independent of the halide contained in the complex ions, and that these ratios tend to increase for decreasing values of K. The second feature is only a broad generalisation however, for example k_{ip}^0/k_1^0 is in the region of 2—2·5 for both malonate ($K = 0{\cdot}0048$ mol dm^{-3}) and tartrate ($K = 0{\cdot}0075$ mol dm^{-3}). In addition the organic ligands seem to have a slightly greater effect, in terms of ion-association, than does sulphate. (This comment has been made previously [2,12] from an examination of more limited data.) The two reactions involve the aquation of free ions with two positive charges and the aquation of ion-pairs of zero charge. Since the latter are the faster, the effect of ion-pairing could be to weaken the cobalt(III)–halide bond (S_N2) in either the ion-pair or the activated complex, or to favour halide-dissociation (S_N1) through electrostatic repulsion between the halide and the ion-pairing ligand. Whatever the mechanism, the ion-pairing effect on the cobalt(III)–halide bond is more important than the different charges (2+, 0; 0, 0) on the reactants in the two reactions when the common reactant (water) is a neutral species. On these grounds, as stated previously,[12] the localised charges on the dicarboxylate ions should cause a greater effect than that of the uniformly charged sulphate ion, which is the case.

Jones *et al.*[18,19] have studied the effects of a series of ion-pairing ligands on the aquation of halogenopenta-amminechromium(III) complexes (the chloro-, bromo-, and fluoro-species). Some of their conclusions are that the increased rates of aquation obtained are indications of an S_N1 solvent-assisted mechanism, and that there is a good relationship between the k_{ip}/k_i and K values for a series of dicarboxylates. If this is so, it would appear that the central metal atom of the complex ion plays an important role, but from a limited study [12] of the aquation of the chloropenta-amminechromium(III) complex in sulphate, malonate, phthalate, and tartrate solutions in which the present analysis was applied, the same conclusion was reached as with the present cobalt(III) studies, namely the k_{ip}/k_i–K relationship is a tenuous one. Our findings are similar in many respects to those of Tanner and Higginson [20] concerning the catalysis by metal ions of chloride-elimination from chloro(ethylenediaminetriacetatoacetate)cobaltate(III). They formed the opinion that where outer-sphere association is likely, the ion-pair rate constant–dissociation constant relation is poor due to weak bonding forces. The values of the dissociation constants obtained or used in the present work are in the range usually found where ion-pairing is regarded as a consequence of electrostatic interaction, or outer-sphere association occurs without much disturbance of the solvation shells of the associating ions. Nevertheless there are many instances where definite relationships between k_{ip}/k_i and K are found. These occur when at least one of the reactants is a charged species (*i.e.*, considering free ions and ion-pairs reacting with a common reagent) and some examples are discussed in the following section.

Base Hydrolysis.—The dissociation constants of the dicarboxylate ion-pairs which have been derived at zero ionic strength from the present measurements are given in Table 5. The procedure for determining the standard potential of the cell for each run and of calculating the dissociation constants of the acetatopenta-amminecobalt(III) dicarboxylates has been described previously.[21] Our assessment of the dissociation constant of the sulphate ion-pair at zero ionic strength was obtained from solubilities since the relatively large dissociation constant of the HSO_4^- ion renders the present e.m.f. method too insensitive. The method of calculation follows that described by Davies.[22] It was assumed that the nitrate of the complex dissociates completely; slight association is possible but the consequences of this should largely cancel out by using the same assumption throughout the calculations.

The values of $k_2{}^0{}_{ip}$, the second-order ion-pair rate constants at zero ionic strength (Table 4), have been

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[18] J. P. Jones, W. E. Harris, and W. J. Wallace, *Canad. J. Chem.*, 1961, **39**, 2371.

[19] T. P. Jones and J. K. Phillips, *J. Chem. Soc.* (*A*), 1968, 674.

[20] S. P. Tanner and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1969, 1164.

[21] C. B. Monk, *J. Chem. Soc.*, 1965, 2456.

[22] C. W. Davies, 'Ion Association,' Butterworths, London, 1962.

derived from the Wyatt–Davies treatment [11] by application of equation (4), where $k_{2\mathrm{obs}}$ is the experimental

$$k_{2\mathrm{obs}}C_1 = k_2{}^0(C_1 - [\mathrm{CpL}])(f_1f_2/f_{12} + k_2{}^0{}_{\mathrm{ip}}[\mathrm{CpL}](f_{\mathrm{ip}}f_1/f_{2\mathrm{ip}}) \quad (4)$$

second-order rate constant and $k_2{}^0$ is the rate constant of the free ion–hydroxide reaction at zero ionic strength. f_1, f_2, And f_{12} are the activity coefficients of the hydroxide and complex ions and the corresponding transition state, f_{ip}, $f_{2\mathrm{ip}}$ those of the ion-pair and the transition state formed between the ion-pair and hydroxide (both unity). An alternative version of equation (4) is that of (5), where k_2 is the rate constant of the

$$k_{2\mathrm{obs}}C_1 = k_2(C_1 - [\mathrm{CpL}]) + k_{2\mathrm{ip}}[\mathrm{CpL}] \quad (5)$$

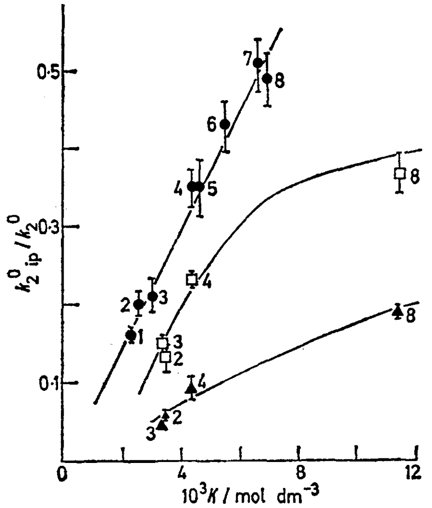
complex ion–hydroxide ion reaction at the ionic strength of a run and $k_{2\mathrm{ip}}$ is the corresponding constant for the ion-pair reaction with hydroxide. In the present case $k_{2\mathrm{ip}} = k_2{}^0{}_{\mathrm{ip}}$. As in previous work,[3] the activity-coefficient expression of Davies [22] has been used and the values of [CpL] and $k_{2\mathrm{ip}}$ obtained by iteration, using appropriate computer programs. Davies and Williams[23] have used the above treatment to analyse the results of Olson and Simonson [24] which are concerned with the effect of sulphate upon the rate of base hydrolysis of the bromopenta-amminecobalt(III) complex. A similar examination has been made [3] of the retarding effects of sulphate and some dicarboxylate media on the rates of base hydrolysis of some halogenopenta-amminecobalt(III) ions.

Table 7 gives the average dissociation constants (K) and $k_2{}^0{}_{\mathrm{ip}}$ values, and the quantity $k_2{}^0{}_{\mathrm{ip}}/k_2{}^0$. The latter decreases as K becomes smaller and, as the Figure shows, there is almost a linear relationship. Similar plots are shown for the base hydrolyses [3] of the chloro- and of bromo-penta-amminecobalt(III) complexes; for these the trends in $k_2{}^0{}_{\mathrm{ip}}/k_2{}^0$ are less than in the acetato-series but the general pattern is the same. On electrostatic grounds one would expect $k_2{}^0$ to be greater than $k_2{}^0{}_{\mathrm{ip}}$, but it is not obvious why greater retardation of base hydrolysis occurs as K becomes smaller. The values of K suggest that electrostatic or outer-sphere association occurs but the variations in K for the dicarboxylate ions could indicate that ion-association is dependent to some extent upon the localised charges on the carboxyl groups. As K decreases in value the cobalt(III)–dicarboxylate bond strengthens in that the ligand charge is brought closer to the cobalt(III) ion. This should promote repulsion of hydroxide ions from the centre of attack, *i.e.* cause increasing retardation of the base hydrolysis. A second feature is that, for a given value of K, the quantity $k_2{}^0{}_{\mathrm{ip}}/k_2{}^0$ is nearer to unity for the acetato-series than it is for the two halogeno-species. This could be attributed to the fact that acetate is more strongly bonded in the complex than are the halides, as judged by both the relative rates of aquation (about 1 : 50) and of base hydrolysis (about 1 : 10⁴).

TABLE 7

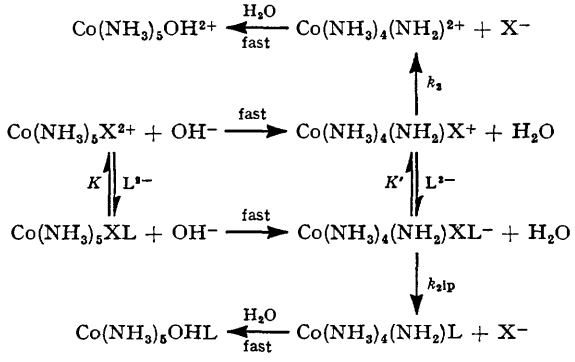
Average dissociation and base hydrolysis rate constants for the acetatopenta-amminecobalt(III) complex at 25 °C; $k_2{}^0 = 965 \times 10^{-6}$ mol⁻¹ dm⁻³ s⁻¹

	$10^6k_2{}^0{}_{\mathrm{ip}}$/ mol⁻¹ dm³ s⁻¹	K/mol dm⁻³	$k_2{}^0{}_{\mathrm{ip}}/k_2{}^0$
Phthalate	155 ± 10	0·00235	0·16
Sulphate	195 ± 10	0·0026	0·20
Maleate	205 ± 15	0·00305	0·21
Malonate	340 ± 20	0·00440	0·35
Oxalate	335 ± 30	0·00465	0·35
Tartrate	415 ± 30	0·00555	0·43
Malate	490 ± 30	0·00665	0·51
Succinate	470 ± 30	0·00695	0·49



Plots of the quantity $k_2{}^0{}_{\mathrm{ip}}/k_2{}^0$ against the ion-pair dissociation constant K for the base hydrolysis at 25 °C of the acetato (●)-, chloro (□)-, and bromo (▲)-penta-amminecobalt(III) complexes and their corresponding ion-pairs with: 1, phthalate; 2, sulphate; 3, maleate; 4, malonate; 5, oxalate; 6, tartrate; 7, malate; and 8, succinate

An alternative analysis is possible [25] in terms of an S_N1cB mechanism. This can be discussed by reference to the following scheme.



SCHEME

The smaller is the value of K, the higher is the fraction of complex that forms the intermediate $Co(NH_3)_4(NH_2)XL^-$.

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[23] C. W. Davies and I. W. Williams, *Trans. Faraday Soc.*, 1958, **54**, 1547.

[24] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, 1949, **17**, 1167.

[25] W. C. E. Higginson, personal communication.

From what is known about ion-association between singly charged cations and dicarboxylate ligands, the dissociation constant K' of this intermediate should be relatively large and mainly independent of the nature of L^{2-}, so this equilibrium should not have much influence on the relative rates of base hydrolysis. The criteria are therefore whether or not this intermediate dissociates more slowly than does $Co(NH_3)_4(NH_2)X^+$ and whether the nature of L^{2-} influences the rate of dissociation of $Co(NH_3)_4(NH_2)XL^-$. The negative charge of the latter should favour its rate of dissociation through repulsion of X^-. The rates of base hydrolysis of bromo- and fluoro-penta-amminechromium(III) complexes are also retarded by ion-pairing ligands such as pyrophosphate. In their report, Jones and Phillips [26] stated that if bond breaking is important in the rate-determining step, as implied by the above mechanism, then addition of anions such as pyrophosphate would be expected to increase the rate through outer-sphere complex formation. If the mechanism with bond formation to the incoming hydroxide ion is important in the transition state, then outer-sphere complex formation will tend to decrease the rate of reaction.

These views leave out of consideration a major factor that governs rates of reaction, namely that of the charges on the reactants. Any ion-pairing with cations gives a species with less positive charge so, on electrostatic grounds, reactions with negative ions should be slower irrespective of the mechanism. Davies [22] has reviewed many examples of substitution reactions where ion-association effects occur. In many of these both the initial reactants are ions (*i.e.* before introducing ion-associating ligands), and relationships between k_{2ip}/k_i and K are found. One example is the reaction of thiosulphate and bromoacetate ions in the presence of the cations of magnesium, calcium, and barium.[11] These cations cause a large increase in the reaction rate (450—900-fold) and Davies proposed that the cation influence is not exerted through any intimate effect on the reaction mechanism, but through the reduction in the charge of the activated complex. There should thus be a parallelism between log (k_{2ip}/k_2) values and the free-energy change for the association of a bivalent cation with the (bromoacetate, thiosulphate)$^{3-}$ activated complex. This is demonstrated by the close accord of log (k_{2ip}/k_2) and log K values for the alkaline-earth cyanoferrate(III) complexes. The dissociation-constant values (and those of the corresponding thiosulphate complexes) follow the order of size of the hydrated cations, *i.e.* $Mg^{2+} > Ca^{2+} > Ba^{2+}$ so that the ion-pairing process is essentially due to electrostatic interaction (outer-sphere association). We note that the K values of the thiosulphate ion-pairs [22] also follow the order of the k_{2ip}/k_2 values.

Metal-ion catalysis of the decarboxylation of a number of keto-acid anions in hydroxide solutions also shows relationships between rate and dissociation constants. With 3-oxopentanedioic acid [27] a plot of log k against log K(malonates) for a series of transition-metal ions follows the Irving–Williams order [28] and Prue [27] visualises a transition state in which a cation stabilises a chelate structure comparable with that formed with malonates. Lanthanum(III) and hexa-amminecobalt(III) ions do not fit into this scheme. The rate constant for the former, as judged by the dissociation constant of lanthanum(III) malonate, falls well below the plot while the cobalt(III) ion does not catalyse the reaction. These two ions apparently do not chelate with the transition state, *i.e.* there is outer-sphere association. Pederson's studies [29] of the metal-ion catalysis of nitroacetate follow the same sort of pattern. This series also shows the effect of the alkaline-earth cations in the order of the sizes of the hydrated cations, but in the decarboxylation of oxalatoacetate the results of Gelles and Clayton [30] show that the log k, log K relationship (which is roughly linear) is in the order of the bare cation sizes. The ion-association forces are strong enough for inner-sphere co-ordination or chelation to occur.

Thus in both anion and cation catalysis ion-association, either with a reactant or the transition state, seems to depend to a marked degree upon localised charge or inner-sphere effects as well as upon ion–ion and ion–dipole forces between the reactants.

EXPERIMENTAL

Chloropenta-amminecobalt(III) chloride, bromopenta-amminecobalt(III) perchlorate and iodopenta-amminecobalt(III) perchlorate, including samples containing ^{125}I, were prepared by standard methods with certain modifications.[3] Carbonatopenta-amminecobalt(III) nitrate, prepared and recrystallised by a published method,[31] was converted into acetatopenta-amminecobalt(III) nitrate; this was recrystallised and dried in accordance with the directions of Basolo *et al.* [1-^{14}C]Acetatopenta-amminecobalt(III) nitrate was prepared similarly by treating the carbonate salt (5 g), [1-^{14}C]acetic acid (0·5 mCi in 10 cm^3 water), and acetic acid (5 cm^3) on a steam-bath for 90 min. It was recrystallised and dried. Stock solutions of sodium sulphate and of the dicarboxylic acids were made up by weight from analytical or Reagent-grade materials. The concentrations of the dicarboxylic acid solutions were checked by titration with standard carbonate-free sodium hydroxide solution.

Absorbance measurements were made with 1 cm cells on a Pye Unicam SP 3000 spectrophotometer fitted with a time programmer, output typer, and water circulator controlled to ±0·1 °C. Water was used in the reference cell. When using this method for a kinetic run, a sample of the complex was weighed into a dry conical flask while the reactant solution was prepared in a graduated flask. The flasks were then equilibrated in a thermostat bath at 25 or 35 ± 0·05 °C before mixing. The complex dissolved in a few seconds; this was taken as the zero time. For direct spectrophoto-

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[26] T. P. Jones and J. K. Phillips, *J. Chem. Soc.* (*A*), 1971, 1881.

[27] J. E. Prue, *J. Chem. Soc.*, 1952, 2331.

[28] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.

[29] K. J. Pederson, *Acta Chem. Scand.*, 1949, **3**, 676.

[30] E. Gelles and J. P. Clayton, *Trans. Faraday Soc.*, 1956, **52**, 353.

[31] F. Basolo and R. K. Murmann, 'Inorganic Syntheses,' ed. J. C. Bailar, McGraw-Hill, New York, 1953, vol. IV, p. 172.

metry a cell was placed in position and filled as quickly as possible. For studies of the chloro-complex in dicarboxylate media, aliquot portions (20 cm^3) were withdrawn at timed intervals and ejected into perchloric acid (1 cm^3). The absorbances were measured as quickly as possible and followed for a short time in order to extrapolate the measurements back to the withdrawal times. ' Infinity ' readings were obtained with solutions of the aquo-complex containing the same concentrations of the other reagents as used in the rate studies. The two cells in the spectrophotometer were not disturbed until all measurements on a run had been made, ensuring that any cell difference remained constant.

The procedures used for the kinetic studies on the labelled iodo-complex have been described previously.[3] For the kinetics of aquation of the acetato-complex, the labelled complex (0·4 g) was weighed into a 500 cm^3 conical flask and the solvent (200 cm^3) placed in a second flask. The two were then equilibrated at 25 ± 0·05 °C before mixing. Aliquot portions (10 cm^3) were withdrawn at timed intervals and filtered through pads consisting of three discs of Amberlite SA2 cation-exchange paper. The first few cm^3 of filtrate were rejected, complete filtration taking 90—120 s. For an ' infinity ' sample, 20 cm^3 was heated on a water-bath until ammonia expulsion was complete, the coagulated cobalt hydroxide filtered off, and the filtrate diluted to 50 cm^3. Samples (1 cm^3) were taken with a calibrated pipette and mixed with scintillator solution [7 cm^3 DPO (0·6%)–POPOP (0·01%) in AnalaR dioxan] in counting vials. Samples were counted with an automatic coincidence counter (Nuclear Enterprises Ltd.) and sufficient counts were obtained for statistical variations to be <1%.

E.m.f. values of the glass electrode–calomel electrode cell for the dissociation-constant studies on the acetato-complex ion-pairs were measured to ±0·1 mV with a Beckmann Research pH-meter. The glass electrode was soaked overnight in a portion of the carboxylic acid–sodium hydroxide solution to be used in the cell. Readings on such solutions were taken until they were constant for at least 30 min before addition of up to eight portions of the stock solution of the acetato-complex in each run. For other details see elsewhere.[13]

Solubility measurements for evaluating the dissociation constant of the acetato-complex–sulphate ion-pair were based on optical-density measurements at 435 nm compared with that of a known concentration of an unsaturated solution of the nitrate salt. Saturated solutions in water and in sodium sulphate solutions at 25 °C were obtained by shaking (2 h) an excess of the nitrate salt with the solvent (*ca.* 50 cm^3) in stoppered tubes held on a rocker built into a thermostat bath. Samples were withdrawn with a warmed pipette fitted with a small length of polythene tube containing a cotton-wool plug. The spectrophotometer cell holder was kept at 25 °C.

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