Influence of Electrolytic Dissociation upon Rates of Reactions. Part 9.† The Aquation of Chloro- and Bromo-penta-amminecobalt(III) and of -penta-amminechromium(III) in Aqueous and 10% Ethanol Solutions of Sulphate and Dicarboxylates

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Rate coefficients (k) for aquation of $[Co(NH_3)_5X]^{2+}$ (X = Br or Cl) in 10% ethanol solutions of some dicarboxylates and sulphate have been determined by spectrophotometry, potentiometric titrations, and e.m.f. changes with time of a cell comprising glass and silver halide electrodes. Similar work has been done with the corresponding complexes of chromium(III) in aqueous solutions. The dissociation constants of the ion pairs formed have been obtained from the e.m.f.s of a cell comprising glass and calomel electrodes. A wide range of values of k(ion), k(ion pair), and dissociation constants has been obtained and in general there is a correlation between k(ion pair)/k(ion) and the dissociation constants for the dicarboxylate series. That for the sulphate series is characteristic of this ligand.

SEVERAL Parts of the present series [1-3] have been concerned with enhanced rates of aquation of penta-amminehalogenocobalt(III) and penta-amminechlorochromium(III) caused by ion-pairing ligands, particularly some dicarboxylates and sulphate. There was some evidence that the rate coefficients of the ion pairs formed with a particular complex ion were broadly related to the corresponding ion-pair dissociation constants. The present work is an extension (and partly repetition by other methods) of this theme. Thus some studies were made of the chloro- and bromo-cobalt(III) complexes in 10% ethanol since greater ion association occurs in this solvent, thereby giving more favourable conditions for high-lighting any connection between ion-pair rate coefficient and dissociation constant.

For much of the previous work with the chloro- and bromo-cobalt(III) systems, visible and u.v. spectrophotometry were used but certain limitations were found.[3] Thus the u.v. band of the chloro-ion which starts at *ca.* 300 nm is overlapped by ligand absorption bands. A band which peaks at 540 nm is sufficiently different from that of the aquo-complex for kinetic studies, but when using dicarboxylate buffers traces of the highly absorbing hydroxy-complex could form. This meant taking timed measurements of acidified samples, but this particular problem has now been largely overcome by using slightly more acidic forms of these buffers and confining readings to regions where plots of ln $(A_t - A_\infty)$ against time were linear (A_t = absorption at time t, A_∞ = absorption of the aquo-ion in the same buffer).

Similar interference problems were also found with penta-amminehalogenochromium(III) systems. The u.v. band of the bromo-complex starts at *ca.* 320 nm. This rules out direct spectrophotometry with maleate and phthalate solutions and likewise all such work with dicarboxylates is ruled out with the chloro-complex since its u.v. band starts at 240 nm.

Other methods used include rates of radio-chloride release [2] to obtain aquation rates of penta-amminechlorochromium(III) in sulphate, malonate, phthalate, and tartrate solutions. This is time-consuming and can give uncertain results. Jones *et al.*[4] used polarography for similar studies with the bromo-complex, while Garrick [5] followed the aquation of penta-amminechlorocobalt(III) in sulphate solutions by potentiometric titration of released chloride.

We have used the method of Garrick,[5] together with u.v. spectrophotometry (where applicable), for our studies in 10% ethanol and have also applied timed e.m.f. measurements of the cell (I) (X^- = chloride or bromide).

$$\text{Glass electrode }|H_2L(c_1),\ Na[OH]\text{ or }Na_2[CO_3](c_2),\ [M(NH_3)_5X][ClO_4]_2(c_3),\ KX(c_4)|AgX,Ag \quad (I)$$

The concentration c_2 was sufficient for *ca.* 75% neutralisation of c_1. With M = Co^{III}, $X^- = Cl^-$, this proved to be a satisfactory procedure, but with $X = Br^-$ few reliable results were obtained. This appeared to be due to the released Br^- attacking the Pt, Ag, AgBr electrode, resulting in the Pt becoming stripped. A Ag,AgBr electrode proved to better but still inconsistent. With M = Cr^{III}, good results were obtained with $X = Cl^-$ and Br^-.

EXPERIMENTAL

Penta-amminechlorocobalt(III) and penta-amminebromocobalt(III) halides were made by published methods [6,7] and converted into perchlorates and nitrates by precipitation from warm acidified solutions of concentrated $Li[ClO_4]$ or $Na[NO_3]$ by cooling in ice–water. The products were washed free of acid with alcohol and diethyl ether. The chloro-salts were dried at 110 °C and the bromo-salts were air dried over silica gel. Chloro- and bromo-penta-amminechromium(III) halides were made by published methods,[8,9] converted into perchlorates, and dried as described above. AnalaR or laboratory-grade chemicals were used for making stock solutions of the ion-pairing ligands.

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† Part 8, P. A. Jones and C. B. Monk, *J.C.S. Dalton*, 1972, 1721.

To follow rates of aquation with cell (I), 200 cm^3 of solution were equilibrated in the cell. The solution was made from a stock solution of H_2L, three quarters neutralised by Na[OH] or $Na_2[CO_3]$, and from a stock solution of KX. The latter was added by weight pipette since an accurate assessment of $[X^-]$ is needed for the calculations. The solid complex salt (*ca.* 0.3—0.8 g) was weighed into the cell, stirred into solution (*ca.* 1 min needed), and the e.m.f.s obtained from a digital voltmeter system reading to 0.01 mV (described previously [10,11]). The readings changed rapidly for a few minutes before settling down to give steady changes with time. The same procedure and e.m.f. instrumentation was used for the dissociation-constant calculations from cell (II) measurements. For this work either a series of amounts of solid complex salt or of a stock solution were added to the cell, stirred in, and the readings followed until they were steady (*ca.* 5 min).

Timed spectrophotometric measurements were obtained from a Pye–Unicam SP 3000 instrument and stoppered 1 cm cells. Potentiometric titrations of released halide were based on a published method,[12] using timed samples cooled by ice–water.

RESULTS AND DISCUSSION

For rate coefficients from the e.m.f.s (E) of cell (I), plots of E against t (ignoring the rapid changes in E when t was small) were extrapolated to $t = 0$ to obtain E^0 from (1) where $[X^-] = c_4$. Equation (1) was then used to

$$E = E^0 - RT\ln[X^-]/F \qquad (1)$$

calculate $[X^-]$ values as the reaction proceeded and rate coefficients, k(obs.), were obtained from (2). The

$$k(\text{obs.}) = \ln\{c_3/(c_3 + c_4 - [X^-])\}/t \qquad (2)$$

k(obs.) values were then plotted against t and if the plots showed marked curvature near the commencement of aquation E^0 was adjusted until the plots were linear and k(obs.) obtained from the intercept on the ordinate. The k(obs.) values invariably decreased with time. This could be due to slight association of X^- with the aquo-ion and with slight pH changes due to greater association of the dicarboxylate ligands with the aquo-ion than with the original complex.

Values of k(obs.) were calculated from absorbances by linear least-mean-squares analysis of ln $(A_t - A_\infty)$, t data (A_t and A_∞ defined earlier) and so were the values from potentiometric titration (using c_t = concentration titrated at time t for A_t and c_∞ = concentration titrated at infinity for A_∞).

The dissociation constants of the ion pairs formed between the chloro- and bromo-complex ions and the dicarboxylate anions, K(CpL), were calculated from e.m.f.s of cell (II). Most of the method of calculating

Glass electrode $|H_2L(c_1)$, Na[OH] or $Na_2[CO_3](c_2)$,
complex perchlorate or nitrate $(c_3)|$
calomel electrode (II)

K(CpL) values has been described previously [13] but since a few modifications have been made, and also for later reference, the equations used are (3)—(10). Here K_1 and K_2 are the dissociation constants of the dicarboxylic acids H_2L at the appropriate temperature and in the appropriate solvent,[14,15] K_N is the dissociation constant of $CpNO_3^+$ (0.1 mol dm^{-3}), while Y 1 when c_2 is of Na[OH], $Y = 2$ when c_2 is of $Na_2[CO_3]$. The parameter of 1.3 in (5) is that derived from previous work.[11] The

$$E = E^0 - RT\ \ln[H^+]/F \qquad (3)$$

$$\log K_1 = \log([HL^-][H^+]/[H_2L]) - 2\,F(\mathrm{I}) \qquad (4)$$

$$F(\mathrm{I}) = -AZ_i^2[I^{\frac{1}{2}}/(I + 1.3I^{\frac{1}{2}}) - 0.3I] \qquad (5)$$

$$[HL^-] = 2c_1 - yc_2 - 2\,[H_2L] - [H^+] \qquad (6)$$

$$\log K_2 = \log([L^{2-}][H^+]/[HL^-]) - 4F(\mathrm{I}) \qquad (7)$$

$$\log(CpNO_3^+) = \log([Cp^{2+}][NO_3^-]) - \log K_N - 4F(\mathrm{I}) \qquad (8)$$

$$[CpL] = c_1 - [H_2L] - [HL^-] - [L^{2-}] \qquad (9)$$

$$\log K(CpL) = \log([Cp^{2+}][L^{2-}]/[CpL]) - 8F(\mathrm{I}) \qquad (10)$$

values of A used were 0.51 and 0.52 for water at 25 and 35 °C, and 0.54 and 0.58 in 10% ethanol at 25 and 40 °C.[15]

E^0 was determined by use of (3)—(7) and reiteration until $[H^+]$ was constant to $<1 \times 10^{-8}$ mol dm^{-3}. K(CpL) values were calculated when [CpL] was constant to $<1 \times 10^{-5}$ mol dm^{-3}.

The cell (III) was likewise used to obtain $K(CpSO_4)$

Glass electrode $|HCl(c_1)$, $Na_2[SO_4](c_2)$,
$Cp(ClO_4)_2(c_3)|$ calomel electrode (III)

values. Allowance was made for $NaSO_4^-$ with $K(NaSO_4^-) = 0.2$ mol dm^{-3} while $K(HSO_4^-)$ in 10% ethanol was found to be 0.005 9 at 25 °C and 0.003 75 mol dm^{-3} at 40 °C. For this purpose, E^0 was found with cell (III) when $c_2 = c_3 = 0$ before getting e.m.f.s on additions of $Na_2[SO_4]$ for $K(HSO_4^-)$. The concentrations of HSO_4^- and $NaSO_4^-$ were found by iterating until $[HSO_4^-]$ was constant to $<5 \times 10^{-9}$ mol dm^{-3}. To obtain $K(CpSO_4)$, E^0 was found with cell (III) when $c_3 = 0$ followed by calculating $[CpSO_4]$ on addition of $Cp(ClO_4)_2$ samples until $[CpSO_4]$ was steady to $<5 \times 10^{-6}$ mol dm^{-3}.

Rate coefficients, k(obs.), obtained in the present work are given in Tables 1 and 2. As in previous cases,[1-3] the information was analysed by the Wyatt–Davies treatment in the form (11) where x represents [CpL] or

$$k(\text{obs.})c_1 = k_i(c_1 - x) + k_{ip}x \qquad (11)$$

$[CpSO_4]$ at $t = 0$ and k_{ip} is the rate coefficient of aquation of these ion pairs. The method of calculating x has been described previously.[2] It is based on equations (4)—(10).

The present determinations of K(CpL) and $K(CpSO_4)$ are summarised in Table 3. Some previous results [13] for aqueous solutions at 25 and 35 °C are of the same order but were obtained with less precise e.m.f. equipment, and a few of the previous values are sufficiently different to warrant recalculation of previous kinetic data.[3] The new estimates are shown in Table 4 together with a summary of k_{ip}/k_i values. As on previous occasions [1-3] this is a convenient way of comparing information on series with widely different rate coefficients.

It has been assumed that the dissociation constants of the bromo-ion pairs are the same as those of the chloro-ion pairs under the same conditions of temperature and solvent. Some justification for this is shown by the figures in Table 3 where, within experimental limits, the dissociation constants of the two series are the same, in the case of cobalt, at 25 °C in water and in 10% ethanol. The aquation rates of penta-amminebromochromium(III) are too fast for obtaining the dissociation constants. Only one study proved successful: $K = 0.004\,3$ mol dm^{-3} for penta-amminebromochromium in sulphate was obtained at 25 °C in water (compared with 0.004 5 mol dm^{-3} for the chloro-salt, Table 3). With the dicarboxylates e.m.f. changes of cell (II) with time were too marked for such calculations.

TABLE 1

Rate coefficients (s^{-1}) of aquation of penta-amminechlorocobalt(III) and of penta-amminebromocobalt(III). Concentrations in mol dm^{-3}. Methods and ion-pairing ligands described in the footnotes

Method[a]	10^4c_1	10^4c_2	10^5c_3	10^5c_4	10^5 [CpL]	10^7k (obs.)	10^7k_{ip}
(*a*) Penta-amminechlorocobalt(III) in 10% ethanol at 40 °C							
A			314			94	
A			313			95	
A			324			95	
C			350			96	
A	480[b]	600[c]	321		77	126	225
A	164[b]	273[c]	350		84	118	190
B	509[b]	375[d]	615	36[e]	189	128	200
C	299[b]	219[d]	530		130	123	210
B	384[f]	280[d]	619	77[e]	234	175	305
C	385[f]	250[d]	480		149	162	310
A	400[g]	500[c]	348		110	140	240
B	463[g]	344[d]	594	51[e]	239	145	220
C	299[g]	217[d]	473		161	137	220
A	218[h]	363[c]	356		107	139	240
A	260[h]	450[c]	347		117	141	230
B	358[h]	267[d]	374		116	145	260
C	401[h]	268[d]	474		126	137	250
A	218[i]	363[c]	332		199	223	310
A	260[i]	450[c]	325		209	325	313
B	424[i]	310[d]	508	40[e]	306	220	300
A	436[j]	263[c]	354		269	261	310
A	520[j]	450[c]	318		260	270	310
C	41.7[k]	257[d]	479		445	172	180
C	52.2[k]	321[d]	468		441	179	185
(*b*) Penta-amminebromocobalt(III) in 10% ethanol at 40 °C							
A			305			320	
A			292			315	
C			432			325	
B	573[b]	428[d]	621	95[l]	204	480	810
C	299[b]	220[d]	492		123	440	800
C	385[f]	250[d]	451		139	560	1 100
C	578[f]	374[d]	430		155	610	1 110
A	145[g]	242[h]	286		95	430	815
C	369[g]	274[d]	455		173	500	795
C	301[h]	219[d]	458		126	482	910
A	450[g]	680[c]	282		183	890	1 200
A	260[i]	450[c]	273		176	910	1 240
B	466[i]	348[d]	578	90[l]	361	940	1 310
A	436[b]	363[c]	293		234	1 045	1 230
B	273[b]	67[d]	694	153[l]	429	900	1 260
C	56.3[k]	323[m]	440		415	785	815
C	56.3[k]	323[m]	448		442	830	860
(*c*) Penta-amminechlorocobalt(III) in water at 35 °C							
C	297[b]	216[d]	478		120	785	1 190
C	300[h]	216[d]	476		137	818	1 230
(*d*) Penta-amminebromocobalt(III) in water at 25 °C							
C	297[b]	216[d]	481		92	737	1 230
C	464[h]	315[d]	434		98	790	1 370

[a] A = Potentiometric titrations; B = e.m.f. measurements [cell (I)]; C = spectrophotometry at 300 (chloro-series) or 362 nm (bromo-series). [b] Succinic acid. [c] Sodium hydroxide. [d] Sodium carbonate. [e] Potassium chloride. [f] Malonic acid. [g] Tartaric acid. [h] Malic acid. Maleic acid. [j] Potassium hydrogenphthalate. [k] Perchloric acid. [l] Potassium bromide. [m] Sodium sulphate. [n] Phthalic acid.

TABLE 2

Rate coefficients (s^{-1}) of aquation of penta-amminechlorochromium(III) and of penta-amminebromochromium(III) in water at 25 °C. Details as in Table 1 (except D = radiochloride release)

Method[a]	10^4c_1	10^4c_2	10^5c_3	10^5c_4	10^5 [CpL]	10^7k (obs.)	10^7k_{ip}
(*a*) Chloro-series ($k_1 = 100 \times 10^{-7}$ s^{-1})							
B	768[b]	1 153[c]	899	64[e]	245	113	151
B	390[b]	583[c]	564	76[e]	115	114	170
B	719[f]	1 079[c]	770	150[e]	262	133	197
B	648[f]	973[c]	903	203[e]	289	127	184
B	752[g]	1 129[c]	941	154[e]	295	124	176
B	507[g]	762[c]	691	154[e]	183	124	190
B	788[h]	1 183[c]	902	67[e]	261	115	152
B	543[h]	816[c]	1 195	135[e]	275	120	187
B	678[i]	1 017[c]	835	135[e]	394	152	210
B	555[i]	834[c]	773	137[e]	340	146	205
D	300[i]	432[c]	507		319	117	210
B	490[j]	246[c]	1 089	308[e]	468	165	214
B	685[j]	343[c]	827	66[e]	420	166	230
D	478[n]	607[c]	505		160	146	245
C	66[c]	492[d]	430		371	146	152
(293 nm)							
D	1[k]	200[m]	534		400	129	139
D	1[k]	300[m]	527		431	144	154
D	100[c]	300[m]	506		393	134	144
(*b*) Bromo-series (280 nm for method C)							
C	108[k]		482			970	
C	540[k]		519			965	
C	1 080[k]		560			960	
B	730[b]	1 096[c]	642	59[l]	185	1 120	1 500
C	200[b]	282[c]	538		72	1 060	1 670
C	600[b]	845[c]	540		128	1 120	1 620
C	300[f]	415[c]	534		106	1 150	1 895
C	500[f]	691[c]	561		143	1 200	1 890
B	813[f]	1 202[c]	438	91[l]	159	1 280	1 830
B	769[g]	1 153[c]	341	94[l]	113	1 240	1 760
C	200[g]	282[c]	542		82	1 100	1 860
B	784[h]	1 177[c]	302	109[l]	91	1 130	1 510
C	500[h]	695[c]	540		113	1 060	1 420
C	700[h]	973[c]	537		132	1 250	1 550
B	760[i]	1 188[c]	703	92[l]	373	1 550	2 070
B	588[i]	881[c]	706	99[l]	323	1 500	2 130
B	696[j]	349[c]	536	104[l]	281	1 550	2 080
B	448[j]	223[c]	829	141[l]	357	1 460	2 110
C	108[k]	301[m]	533		412	1 360	1 480
C	108[k]	301[m]	594		457	1 320	1 430
C	54[k]	40[m]	511		142	1 100	1 450

The relationships between k_{ip}/k_i and K are illustrated by the Figure. There is a broad correlation, with two exceptions. First the sulphate data fall below the main trend given by the dicarboxylates. This is in line with

TABLE 3

Dissociation constants of penta-amminechlorocobalt(III), penta-amminebromocobalt(III), and penta-amminechlorochromium(III) ion pairs at zero ionic strength. Concentrations in mol dm^{-3} and dissociation constants in mol dm^{-3}

(*a*) Cobalt, example 1

$[Co(NH_3)_5Cl][NO_3]_2$ with malate in 10% ethanol at 25 °C. $K_1 = 2.52 \times 10^{-4}$, $K_2 = 8.07 \times 10^{-6}$, E^0 (calc.) = −0.353 20 V, E^0 (used) = −0.353 30 V

10^5c_1	5 437	4 943	4 728	4 531	4 438
$10^5c_2(Na_2[CO_3])$	4 046	3 346	3 201	3 067	3 005
10^5c_3	0	460	660	843	929
$-10^5 E/V$	5 976	6 120	6 180	6 230	6 250
$10^6 K$/mol dm^{-3}		684	678	696	750

example 2

$[Co(NH_3)_5Cl][ClO_4]_2$ with sulphate in 10% ethanol at 40 °C; $K(HSO_4^-)$ = 0.003 75, c_1 = 0.006 247 mol dm^{-3} HCl, c_2 = 0.034 05 mol dm^{-3} $Na_2[SO_4]$, E^0 (calc.) = −0.323 21 V, E° (used) = −0.323 26 V

$10^5 c_3$	0	551	1 168	1 541	1 892	2 299
$-10^5 E/V$	14 520	14 785	15 085	15 255	15 395	15 565
$10^6 K$/mol dm^{-3}		128	119	120	126	123

Summary of 10^4K/mol dm^{-3}

θ_c/°C	Solvent	Succinate	Malonate	Malate	Tartrate	Maleate	Phthalate	Sulphate
25	H_2O(chloro-)	110	60	100	72	35	27	25
25	H_2O(bromo-)	115		100	75	35	28	
35	H_2O(chloro-)	105	55	85	70	30	24	21
25	10% ethanol(chloro-)	85	52	70	60	27	21	19
25	10% ethanol(bromo-)			70	60	27	20	20
40	10% ethanol(chloro-)	63	35	54	40	15	11	13

(*b*) Chromium

$[Cr(NH_3)_5Cl][ClO_4]_2$ with malonate in water at 250 °C; $K_1 = 1.0 \times 10^{-3}$, $K_2 = 2.00 \times 10^{-6}$, E^0 (calc.) = E^0 (used) = −0.423 33 V, 10^5c_1 = 5 751, $10^5 c_2$ (Na[OH]) = 8 625 mol dm^{-3}

$10^5 c_3$	0	568	1 219	1 781	2 332	2 813
$-10^5 E/V$	10 415	10 610	10 823	10 988	11 140	11 260
$10^6 K$/mol dm^{-3}		887	856	866	873	881

Summary of 10^4K/mol dm ^{3} at 25 °C in water

	Succinate	Malonate	Malate	Tartrate	Maleate	Phthalate	Sulphate
1st run	122	87	125	105	46	45	45
2nd run	120	86	115	105	45	45	46

an earlier suggestion [2,3] that the uniform charge on sulphate has less effect on weakening the metal–halide bonds than has the localised charge of dicarboxylates. These localised charges in turn are influenced by factors such as ring size, chelation, double bonds, and dielectric constants of the medium and these are reflected in the values of the ion-pair rate coefficients and of the dissociation constants. The second exception concerns k_{ip}/k_i for penta-amminebromocobalt(III) ion pairs in 10% ethanol. These values are somewhat higher than those

TABLE 4

Average aquation rate coefficients ($10^7\ k/s^{-1}$) and k(ion pair)/k(ion) values

	Chloro-cobalt		Bromo-cobalt	
	35 °C, water	40 °C, 10% ethanol	25 °C, water	40 °C, 10% ethanol
Free ion (k_i)	65.5 [3]	95	625 [3]	320
Succinate (k_{ip})	119	205	123	805
Malonate (k_{ip})	136 *	310	144	1 100
Tartrate (k_{ip})	142 *	230	153	800
Malate (k_{ip})	123	240	131	910
Maleate (k_{ip})	185 *	290	169 *	1 280
Phthalate (k_{ip})	174 *	310	166 *	1 250
Sulphate (k_{ip})	111 *	180	125 *	840

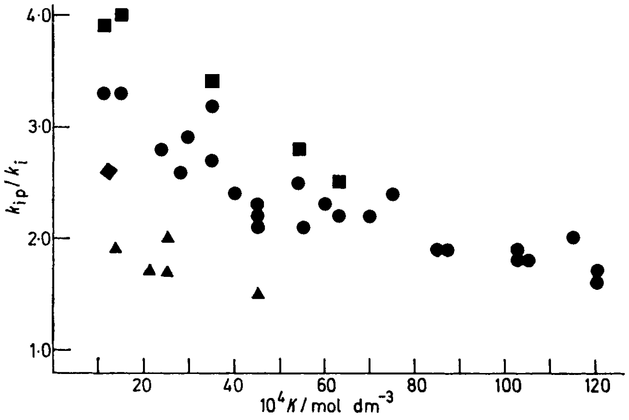
	Chloro-chromium (25 °C, water)	Bromo-chromium (25 °C, water)
Free ion (k_i)	100	965
Succinate (k_{ip})	160	1 600
Malonate (k_{ip})	187	1 870
Tartrate (k_{ip})	180	1 850
Malate (k_{ip})	170	1 530
Maleate (k_{ip})	210	1 850
Phthalate (k_{ip})	230	2 100
Sulphate (k_{ip})	150	1 450

* Recalculation of data from ref. 3.

	k_{ip}/k_i						
	Succinate	Malonate	Tartrate	Malate	Maleate	Phthalate	Sulphate
(*a*) Cobalt							
Chloro-series, 35 °C, H_2O	1.8	2.1 *	2.2 *	1.9	2.9 *	2.8 *	1.7 *
Chloro-series, 40 °C, 10% ethanol	2.2	3.2	2.4	2.5	3.3	3.3	1.9
Bromo-series, 25 °C, H_2O	2.0	2.3 *	2.4 *	2.2	2.7 *	2.6 *	2.0 *
Bromo-series, 40 °C, 10% ethanol	2.5	3.4	2.5	2.8	4.0	3.9	2.6
(*b*) Chromium							
Chloro-series, 25 °C, H_2O	1.6	1.9	1.8	1.7	2.1	2.3	1.5
Bromo-series, 25 °C, H_2O	1.7	1.9	1.9	1.6	2.2	2.2	1.5

of the main plot for the dicarboxylates and sulphates. The only apparent explanation is that it is the consequence of using a mixed solvent, but only further work with other organic solvents can refute or support this.

Jones *et al.*[4] analysed their figures for aquation rates of penta-amminebromochromium(III) in aqueous ligand solutions by plotting k(obs.) against ligand concentrations. Small ligand concentrations caused marked accelerations of the reaction and these were roughly linear with concentration until the concentration of ligand and complex were about the same. After this the rate of reaction increase was much less. These regions were extrapolated to zero ligand concentration to give k(extrap.) values. These were characteristic for each ligand and have the order succinate < malonate < phthalate < maleate (taking those ligands used in the present work). This is a somewhat different order to our k_{ip} values. Apart from the empirical nature of such plots, since sodium salts of the ligands were used, the dicarboxylate solutions would be alkaline so some base hydrolysis could have occurred. This would be greatest for maleate since the acid has the highest pK_2 of the series. This comment does not apply to sulphate but in this case the plot is in fact curved so that a reliable estimate of k(extrap.) is not really possible.



Plot of k_{ip}/k_i against K values for all series (●) except sulphate (▲), and penta-amminebromocobalt(III) with sulphate (♦) and dicarboxylates (■) (the two latter in 10% ethanol)

The authors also gave the slopes of the plots and these are in the order succinate < malonate < maleate < phthalate which is also the sequence of our k_{ip} values. Such slopes can be regarded as extents to which k(obs.) increases with ion pairing so this seems to be a more logical basis of comparison.

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