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Kinetic Salt Effects on the Reaction between the [1,3,6,8,10,13,16,19-Octa-azabicyclo(666)icosane]Cobalt(III) Ion, Co(sep)$^{3+}$, and the Hexa-aquochromium(II) Ion

Francesco Ferranti and Antonio Indelli*
Department of Physical and Inorganic Chemistry, University of Bologna, Italy

Highly specific effects are shown by different salts on the title reaction. Some salts increase the rate by a factor between *ca.* two and four, whereas for others the increase is between 30 and over a 1000 times. This is attributed to the formation of highly reactive ion pairs (or triplets), whose formation constants have been evaluated, in some cases, from the kinetic data at constant ionic strength. These ion pairs involve essentially the Cr^{II} reactant, and their high reactivity is related to the rate of formation of the precursor complex and/or to the rate of electron transfer within the precursor complex.

The kinetics of the title reaction have been studied by Boucher *et al.*,† but, apparently, only at an ionic strength, I, of 0.5 mol dm^{-3} of NaClO$_4$. Reactions between ions of like charge often show peculiar salt effects,[2] and some examples have been studied recently.[3] We considered that it would be interesting to re-examine this reaction, particularly in the presence of anions capable of acting as bridges[4] in reactions of the inner-sphere type, and in the presence of multicharged anions.

Experimental

Materials

Co(sep)Cl$_3$ was prepared as described in the literature.[5] Co(sep)(ClO$_4$)$_3$ was obtained by metathesis with AgClO$_4$ and recrystallized. Cr(ClO$_4$)$_3$ was prepared by reduction of CrO$_3$ with H$_2$O$_2$ in diluted HClO$_4$, and recrystallized. Solutions of Cr(ClO$_4$)$_2$ were obtained by reduction under N$_2$ with amalgamated Zn. NaCF$_3$SO$_3$ and NaNH$_2$SO$_3$ were prepared by neutralization of the corresponding acids, and crystallized. Na$_3$P$_3$O$_9$ and Na$_4$P$_4$O$_{12}$ were obtained as described elsewhere.[6] All other chemicals were commercial products of high purity.

Procedure

The reaction was followed measuring the decrease in optical density at 340 nm, where the extinction coefficient of Co(sep)$^{3+}$ is much larger than that of all the other reactants or products. In almost all runs a tenfold excess of Cr^{II} over Co(sep)$^{3+}$ was used, and pseudo-first-order, or second-order, plots were used to calculate the rates. These plots, except where indicated, were linear for at least 50% of the reaction. The reaction solution was kept under N$_2$, and contained, besides the reactants and the salts under investigation, Zn(ClO$_4$)$_2$, coming from the reduction of Cr^{III}, and 0.01 mol dm^{-3} HClO$_4$, to prevent the hydrolysis of Cr^{III} produced. In the absence of complexing anions, the reaction has been confirmed as second order, *i.e.* first order with respect to Co(sep)$^{3+}$ and also with respect to Cr^{II}. See, for instance, the first three entries of table 2 (later).

† Reported by A. M. Sargeson in ref. (1).

Table 1. Second-order rate constants in the presence of different concentrations of added salts

salt	concentration /mol dm^{-3}	$10^3\ k_{obs}$ /dm^3 mol^{-1} s^{-1}	salt	concentration /mol dm^{-3}	$10^3\ k_{obs}$ /dm^3 mol^{-1} s^{-1}
—	—	0.273	NaF	0.01	52
$NaClO_4$	0.05	0.384		0.02	152
	0.1	0.50		0.03	272
	0.2	0.61		0.04	415
	0.3	0.72		0.05	705
	0.337	0.76		0.06	910
$NaCF_3SO_3$	0.1	0.57		0.07	1250
	0.2	0.50	$Ba(ClO_4)_2$	0.1	0.47
	0.4	0.44	$La(ClO_4)_3$	0.0667	0.68
$NaNH_2SO_3$	0.05	0.43	Na_2SO_4	0.01	6.43
	0.1	0.57		0.05	10.6
	0.2	0.93		0.1	9.45
	0.4	1.01		0.2	8.50
NaCl	0.05	6.40		0.4	7.34
	0.1	11.2	$Na_3P_3O_9$	0.005	27
	0.2	18.2		0.01	55
	0.4	27.4		0.0167	75
NaBr	0.1	5.8		0.0333	122
	0.2	9.1		0.1	137
NaI	0.1	5.8		0.133	121
	0.2	8.1		0.2	119
			$Na_4P_4O_{12}$	0.0025	116[a]
				0.005	304[a]
				0.0125	715[a]

[a] Pseudo-first-order plots were linear for 10–20% reaction only. k_{obs} is the initial rate divided by the initial $Cr(ClO_4)_2$ and $Co(sep)Cl_3$ concentrations. Co(sep) $[(ClO_4)_3] = 0.003$, $[Cr(ClO_4)_2] = 0.03$, $[HClO_4] = 0.01$ and $[Zn(ClO_4)_2] = 0.015$ mol dm^{-3}.

Results and Discussion

Table 1 reports the results obtained in the presence of several added salts. In the presence of $NaClO_4$, $NaCF_3SO_3$ and $NaNH_2SO_3$ the increase in salt concentration, and therefore of I, produces an increase in rate which is in fair agreement with the predictions of the classic theories of kinetic salt effects.[7] In fig. 1 second-order rate constants are plotted against anion concentration. The continuous line has been calculated interpolating the results for $NaClO_4$ by means of the equation:

$$\log k_{obs} = \log k_o + a\sqrt{I}/(1+\sqrt{I}) + bI \qquad (1)$$

the adjustable parameters, $\log k_o = \log 2.6 \times 10^{-6}$, $a = 8.0$, and $b = -1.75$ being obtained by a least-squares method. The value of a is not very different from the value of 6.1 which is predicted for a reaction between two ions of charge +3 and +2.[7] The negative and rather high value of b is due, at least partly, to the fact that the average distance of closest approach between ions is certainly larger than 304 pm [which is the value corresponding to the $(1+\sqrt{I})$ denominator in eqn (1)].

In the presence of $Ba(ClO_4)_2$ and of $La(ClO_4)_3$ the values of k_{obs} are little different from those for $NaClO_4$ at the same anion concentration, despite the much higher value of the ionic strength. This is in agreement with the usual observation[2] that for reactions between ions of the same sign the correlation with the concentrations of the ions of the opposite sign is much better than the correlation with the ionic strength.[7] In the case of $Ba(ClO_4)_2$ the rate is slower than it is in the presence of $NaClO_4$, due to the increase in ionic strength. A similar effect has been observed in other cases as well,[8] and can be predicted by the Mayer theory (DHLL + B_2)[9] when the distance of closest approach is very small.[10]

The specific effects, observed in the presence of $CF_3SO_3^-$ and $NH_2SO_3^-$, could be related to their different Setchenov coefficients, on the solubility of non-electrolytes, which are a measurement of their relative hydrophilic, or hydrophobic, character. These coefficients increase in the order $NaCF_3SO_3 < NaClO_4 < NaNH_2SO_3$.[11]

The large increases in rate observed in the presence of the other salts suggest that the formation of highly reactive ion pairs is the main reason for these effects. The fact that the stability of the halo-aquo complexes of Cr^{III} decreases in the order $F^- > Cl^- > Br^- \approx I^-$ is in agreement with this interpretation.[4] Anyway, in this case as well, a qualitative correlation with the Setchenov coefficients is apparent.[11] However, a neglect of the change in the ionic environment, accompanying the addition of these salts, does not appear reasonable. Therefore some measurements were repeated at constant I (0.5 mol dm^{-3}), obtained by addition of $NaClO_4$. Table 2 reports the results.

For NaCl the results are in agreement with the equation:

$$k_{obs} = (k_1 + k_2 K_1[X])/(1 + K_1[X]) \tag{2}$$

where [X] is the anion concentration, which is the usual expression when ion pairs and free ions give parallel reaction paths. One mechanism therefore could be:

$$Cr^{II} + Co^{III} \xrightarrow{k_1} Cr^{III} + Co^{II} \tag{3}$$

$$Cr^{II} + X \overset{K_1}{\rightleftharpoons} Cr^{II}X \tag{4}$$

$$Cr^{II}X + Co^{III} \xrightarrow{k_2} Cr^{III}X + Co^{II}. \tag{5}$$

From the experimental k_{obs} values the following values for the parameters of eqn (2) are obtained:

$$k_1 = 0.77 \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1};\ k_2 = 76 \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1}\ \text{and}\ K_1 = 1.46\ dm^3\ mol^{-1}.$$

We believe that the cation forming the ion pair (or the labile ionic complex) is $Cr(H_2O)_6^{2+}$. The stability of complexes of Cl^- with Cr^{III} is well known, whereas there are no indications for complexes with $Co(sep)^{3+}$.[13] The value of K_1 is the same as that in the literature,[14] obtained from kinetic measurements on a reaction of Cr^{II} with a neutral molecule. Moreover, at the end of the reaction, the visible spectrum of the solution shows that Cr^{III} has Cl^- in its first coordination sphere. The value of $0.76 \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$, obtained in the absence of Cl^-, or that of 0.77×10^{-3}, extrapolated at $[Cl^-] = 0$, can be compared with the value of $8.5 \times 10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$ given by Sargeson.[1]

The large value of the ratio k_2/k_1, which is *ca.* 100, cannot be due only to the difference in the charge of the reactants. According to Eigen's treatment,[15] both step (3) and step (5) should happen through the mechanism (6)–(8), k_{obs} being equal to $(k_d/k_{-d}) \times k_t$:

$$Co^{III} + Cr^{II} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} Co^{III}Cr^{II} \quad \text{precursor complex} \tag{6}$$

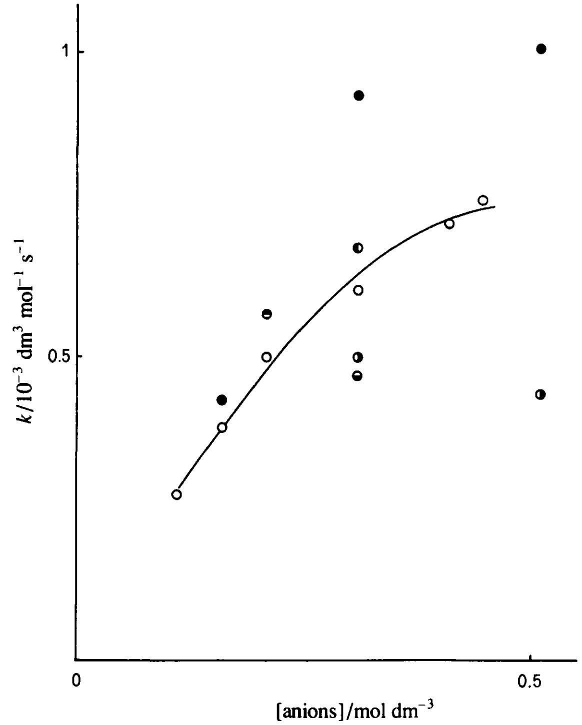

Fig. 1. Rate constants as a function of the anion concentration for different salts. (○), $NaClO_4$; (◒), $Ba(ClO_4)_2$; (◐), $La(ClO_4)_3$; (●), $NaNH_2SO_3$; (◑), $NaCF_3SO_3$. The continuous curve has been drawn using eqn (1) with the following parameters: $10^3 k_0 = 0.0026$, $a = 8.0$, $b = -1.75$. For I the values for $NaClO_4$ were taken.

$$Co^{III}Cr^{II} \xrightarrow{k_t} Co^{II}Cr^{III} \quad \text{electron transfer} \tag{7}$$

$$Co^{II}Cr^{III} \xrightarrow{\text{fast}} Co^{II} + Cr^{III} \quad \text{products.} \tag{8}$$

The intervention of one Cl^-, associated with Cr^{II}, should increase the formation constant of the precursor complex, k_d/k_{-d}, since the product of the charges of the reactants, $Z_a Z_b$, decreases from +6 to +3. Assuming that the distance of reaction, r, is of the order of 600 pm, and that the change in the energy of the electrostatic repulsion at $I = 0$, $Z_A Z_B e^2/Dr$, is equal to the change in the free energy of formation of the precursor complex, the ratio k_2/k_1 should be *ca.* 35. At $I = 0.5$ mol dm^{-3}, the electrostatic repulsion is reduced by a factor of *ca.* 0.5, because of the screening due to the ionic cloud, so that k_2/k_1 should be even smaller. Therefore, the effect of the addition of Cl^- consists, at least partly, of an increase in k_t. This is to be expected, since the products of the reactions (3) and (5) are different. ΔG° of reaction (5) is more negative, because of the known stability of the $[Cr(H_2O)_5Cl]^{2+}$ ion. According to the Marcus cross-relation:[16]

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} \tag{9}$$

an increase in K_{12} should parallel an increase in k_{12}, provided that the other parameters are comparable and that we are far from the 'inverted region'.[17] It should be noticed that if Cl^- were associated with $Co(sep)^{3+}$ (as could appear reasonable, in view of the

Table 2. Second order rate constants, k_{obs}, in the presence of different concentrations of added salts, at constant ionic strength, $I = 0.5$ mol dm^{-3} (NaClO$_4$)

salt	concentration /mol dm^{-3}	$10^3\ k_{obs}$ /dm^3 mol^{-1} s^{-1}	$10^3\ k_{cal}$ /dm^3 mol^{-1} s^{-1}
NaCl	0	0.76	0.77
	0	0.78[a]	0.77
	0	0.76[b]	0.77
	0.02	2.83	2.82[c]
	0.05	5.7	5.7
	0.10	10.0	10.0
	0.15	13.9	13.9
	0.20	17.3	17.3
NaF	0.01	10.8	5.7[d]
	0.02	33.4	38.1[d]
	0.03	118	110[d]
	0.04	225	218[d]
	0.05	345	355[d]
	0.06	505	518[d]
	0.07	710	703[d]
	0.08	916	906[d]
	0.09	1120	1123[d]
	0.10	1350	1352[d]
$Na_3P_3O_9$	0.005	12.5	—
	0.01	27.6	—
	0.02	56.5	—
	0.03	86	—
	0.04	112	—
	0.05	133	—

[Co(sep) (ClO$_4$)$_3$] = 0.003, [Cr(ClO$_4$)$_2$] = 0.03, [HClO$_4$] = 0.01 and [Zn(ClO$_4$)$_2$] = 0.015 mol dm^{-3}. [a] [Cr(ClO$_4$)$_2$] = 0.06 mol dm^{-3}; [b] [Co(sep)Cl$_3$] = 0.006, [Cr(ClO$_4$)$_2$] = 0.06 mol dm^{-3}. [c] Parameters of eqn (2): $10^3\ k_1 = 0.77$ dm^3 mol^{-1} s^{-1}, $10^3\ k_2 = 76$ dm^3 mol^{-1} s^{-1} and $K_1 = 1.46$ dm^3 mol^{-1}. [d] Parameters of eqn (10): $10^3\ k_1 = 0.76$ dm^3 mol^{-1} s^{-1} (assumed), $K_1 = 7.3$ dm^3 mol^{-1} (assumed), $k_2 = 0.13$ dm^3 mol^{-1} s^{-1} (calculated), $k_3 = 19$ dm^3 mol^{-1} s^{-1} (calculated), $K_2 = 2.6$ dm^3 mol^{-1} (calculated), p$K_{HF} = 2.91$ (assumed), ref. (12). When using eqn (2) and (10) the concentrations of the anions have been corrected for the association.

higher charge of the cation) the electrostatic effect should be even smaller, since $Z_A Z_B$ becomes 4.

In the presence of NaF a plot of the second-order rate constants against [F$^-$] shows an upward curvature, so that a term proportional to [F$^-$]^2 is suggested. Apparently, besides the intervention of CrF$^+$, with a formation constant of K_1 and a rate constant k_2, a triplet CrF$_2$, with a formation constant K_2 and a rate constant k_3, gives an appreciable contribution to the total rate. The results are not accurate enough to evaluate independently all the constants at the same time. However, taking for k_1 the value of 0.76×10^{-3} dm^3 mol^{-1} s^{-1}, obtained in the absence of F$^-$ and for K_1 the value of 7.3 dm^3 mol^{-1} given by the literature,[14] the equation

$$k_{obs} = (k_1 + k_2 K_1[F^-] + k_3 K_1 K_2[F^-]^2)/(1 + K_1[F^-] + K_1 K_2[F^-]^2) \tag{10}$$

Table 3. Second-order rate constants [first order with respect to $Co(sep)^{3+}$ and also with respect to either $P_4O_{12}^{4-}$ or Cr^{II}, whichever is present in trace amounts]

$[Cr(ClO_4)_2]$ /mol dm^{-3}	$[Co(sep)(ClO_4)_3]$ /mol dm^{-3}	$[Na_4P_4O_{12}]$ /mol dm^{-3}	k' /dm^3 mol^{-1} s^{-1}
0.03	0.003	0.002	1.12
0.03	0.003	0.005	1.12
0.03	0.003	0.0075	1.18
0.03	0.003	0.01	1.31
0.03	0.003	0.0125	1.43
0.03	0.003	0.015	1.60
0.06	0.003	0.005	1.15
0.03	0.0015	0.005	1.12
0.0033	0.006	0.005	1.11
0.03	0.006	0.005	1.03
0.06	0.006	0.005	0.97

$[HClO_4] = 0.01$, $[Zn(ClO_4)_2] = 0.015$ mol dm^{-3} and $I = 0.5$ mol dm^{-3} ($NaClO_4$).

represents satisfactorily the data (last column of table 2). For the adjustable parameters the following values are obtained:

$$k_2 = 0.13\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1},\ k_3 = 19\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\quad \text{and}\ K_2 = 2.6\ \text{dm}^3\ \text{mol}^{-1}.$$

We are inclined to rule out the association of F^- with $Co(sep)^{3+}$ for the same reasons as in the case of Cl^-. The ratios k_2/k_1 and k_3/k_2 are so large that, in this case as well, the increase in rate must be attributed mainly to the change in k_t, and only in a minor part to electrostatic effects. It is reassuring that K_2 is smaller than K_1, although of the same order of magnitude. However the uncertainty of the calculated parameters does not warrant a more detailed discussion.

The reason why the order of the accelerating effects of the halogens in this reaction follows the 'inverted order', instead of the 'normal order',[4] is not well understood.

In the presence of $Na_3P_3O_9$, the increase in k_{obs} when increasing $[P_3O_9^{3-}]$ is almost linear, in contrast to the case at variable ionic strength. Application of eqn (2) allows us to calculate approximate values of 1 dm^3 mol^{-1} s^{-1} for k_2 and 3 dm^3 mol^{-1} for K_1, and a contribution of the free ions which is negligible in comparison to that of the ion pairs. In fact, when the contribution of free ions is comparable with that of the ion pairs, $[P_3O_9^{3-}]$ should be of the order of 10^{-4} mol dm^{-3}, and at such low concentrations the results become uncertain. In this case, anyway, the electrostatic effect seems to be sufficient to explain the increase in rate, although the poor accuracy of the parameters prevents a detailed discussion.

In the presence of $Na_4P_4O_{12}$, pseudo-first-order, or second-order [with respect to $Co(sep)^{3+}$ and Cr^{II}, respectively] plots are linear only for a small, and not significant, part of the reaction. This also happens in the absence of $NaClO_4$ (see foot-note of table 1). However, second order plots are reasonably linear, provided that the orders are taken as one with respect to $Co(sep)^{3+}$ and with respect to the reactant $P_4O_{12}^{4-}$ or Cr^{II} which is present in trace amounts. This proves that the reaction in reality is:

$$Co(sep)^{3+} + Cr^{II}\,P_4O_{12}^{2-} \xrightarrow{k'} Co(sep)^{2+} + Cr^{III}\,P_4O_{12}^{-} \qquad (11)$$

so that in this case as well the cation which is associated with the multivalent anion is

Cr^{II}, despite the higher charge of $Co(sep)^{3+}$. Apparently this association is quantitative, and the product, $Cr^{III}\ P_4O_{12}^-$, seems to be inert. The ratio k'/k_1, which is *ca.* 1500, is in reasonable agreement with that predicted from the electrostatic effect. For concentrations of Cr^{II} of 0.03 mol dm^{-3} and of $P_4O_{12}^{4-} > 0.005$ mol dm^{-3}, there is a definite increase in k', suggesting the intervention of a second $P_4O_{12}^{4-}$, which gives an appreciable contribution to the reaction rate.

Note that in the presence of these salts, which give very large salt effects, the addition of $NaClO_4$ produces a decrease, rather than an increase, in the rate. This is in agreement with the assumption of the intervention of ion pairs. In the case of Cl^-, F^-, and perhaps $P_3O_9^{3-}$, the association constants should decrease with increasing the ionic strength. On the other hand, in the case of $P_4O_{12}^{4-}$ and that of $P_3O_9^{3-}$, the association changes the reaction from one between two ions of the same sign into one between two ions of opposite sign.

This decrease in the rate could explain the fact that the rate, at variable ionic strength, shows a maximum for certain concentrations of Na_2SO_4 and $Na_3P_3O_9$: at low concentrations the effect of the ion pairing prevails, but then at higher concentrations the effect of I becomes dominant.

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