201. A Unified Interpretation of Kinetic Data on the Acid-Induced Cleavage and of Product-Analysis Data on Spontaneous Cleavage of the Mono-ol Cation μ-Hydroxo-bis[pentaamminecobalt(III)] ($[(NH_3)_5CoOHCo(NH_3)_5]^{5+}$)

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Recent work on the spontaneous (= acid-independent) cleavage of the mono-ol cation, *i.e.*

$$[(NH_3)_5CoOHCo(NH_3)_5]^{5+} + H_2O \rightarrow [(NH_3)_5CoOH_2]^{3+} + [(NH_3)_5CoOH]^{2+}$$

$$[(NH_3)_5CoOH]^{2+} + H^+ \rightarrow [(NH_3)_5CoOH_2]^{3+} \text{ (fast)},$$

in Cl^-/ClO_4^- and NO_3^-/ClO_4^- mixed-electrolyte media has established (by analysis of anion-competition experiments) the existence of reactive ion pairs of the mono-ol cation with Cl^- and NO_3^-. Their existence must be allowed for in the analysis of the rate data for the acid-induced cleavage (pH 0–1) of the mono-ol cation in these mixed-electrolyte media. Thus, previous data for acidic Cl^-/ClO_4^- media have been re-interpreted in this work, and new data for NO_3^-/ClO_4^- media have been analyzed in the same sense. This analysis removes an apparent discrepancy in the orders of magnitude of ion aggregate stability constants between the mono-ol and similar binuclear cations.

Introduction. – The mono-ol cation $[(NH_3)_5CoOHCo(NH_3)_5]^{5+}$ has aroused sustained interest in connection with three related, general problems: (*i*) This kinetically inert, binuclear cation has served as a simple model for studying the feasibility of uncatalyzed (= spontaneous) and acid-catalyzed cleavage of single hydroxide bridges in polynuclear complexes [1] [2]. (*ii*) Both spontaneous and acid-induced cleavage of this cation may lead to the coordinatively unsaturated intermediate $[(NH_3)_5Co]^{3+}$ [3] [4]. These reactions have provided valuable alternatives to the classical ways [5–7] of producing this intermediate. (*iii*) The mono-ol cation has proved useful in the study of the influence of ion pairing (or, more generally, anion aggregation) on the reactivity of highly charged reactants (5+ in spontaneous, and 6+ in acid-induced cleavage) [2–4].

The present communication is mainly concerned with the third aspect. Previous kinetic studies have demonstrated the formation of anion aggregates (ion pairs and ion triplets) in both spontaneous and acid-induced cleavage [3] [4]. Ion aggregates with added anions Y^- were found to be more reactive than the unaggregated reactant (or its aggregates with ClO_4^- from the background electrolyte) in acid-induced cleavage [3]. In contrast, *reactive* as well as *unreactive* ion aggregates were detected in spontaneous cleavage. However, the differences in reactivity for all these different species are small, as expected, and in some cases, the rate differences were near or below the limit of detection by kinetic methods. The difficulties in detecting these species kinetically were partly due to experimental problems and also to accidental cancellation or approximative cancella-

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tion of numerator and denominator terms in the rate law (see *Footnote 25* in [4]). However, clear evidence for the postulated reactive ion aggregates in spontaneous cleavage arose from product analysis in competition experiments [4] (see below).

The results of these competition studies impose a bias on the selection of the 'best' empirical rate law: the best fit to the kinetic data is now subject to the constraint that *all* species detectable by product analysis are also included in the fitting procedure, unless the resulting fit is statistically significantly inferior to any other fit that excludes these species. However, this last restriction is not likely to apply here, since the reactivities and stabilities of the species are expected to be very similar.

In this communication, the conclusions reached in the detailed study of the spontaneous cleavage of $[(NH_3)_5CoOHCo(NH_3)_5]^{5+}$ [4] are extended to incorporate the acid-induced cleavage. In particular, the rate law for the acid-induced mono-ol cleavage in the presence of Cl^- is reinterpreted, allowing for a reactive ion pair and an unreactive ion triplet in spontaneous aquation. In addition, preliminary data on the acid-induced cleavage in NO_3^-/ClO_4^- media are reported in order to complement the spontaneous-cleavage kinetics in this medium.

Results and Discussion. – *Reaction Scheme and Rate Laws.* A general overview of the pathways for both acid-induced and spontaneous cleavage is given in the *Scheme*. *Eqn. 1* is the general form of the derived rate law for this reaction scheme. This expression has been derived for preequilibrium addition of protons at the OH^- bridge and of anions to the second coordination sphere of the mono-ol cation. Thus far, in no case were all parameters of rate law *1* observed. First, all denominator terms first order in $[H^+]$ are negligible under the experimental conditions ($[H^+] < 1\,\text{M}$), and this is due to the low basicity ($K_H \ll 1$) of the bridging ligand in this 5+ cation. Furthermore, the form of the empirical rate law depends also on the stability and reactivity of each individual species, *i.e.* on the relative magnitude of each K or k parameter.

The parameters of *Eqn. 1* are such that clear experimental distinction is possible between the H^+-independent- and acid-induced-cleavage pathways. Thus, the observed rate constant k_{obs} as a function of $[Y^-]$ may be represented (henceforth omitting charges in all rate expressions) by:

$$k_{obs}([Y], [H]) = f_0([Y]) + f_1([Y]) \cdot [H],$$

where

$$f_0 = \frac{k_0 + k_Y K_Y[Y] + \ldots}{1 + K_Y[Y] + K_{Y_2}K_Y[Y]^2 + \ldots}$$

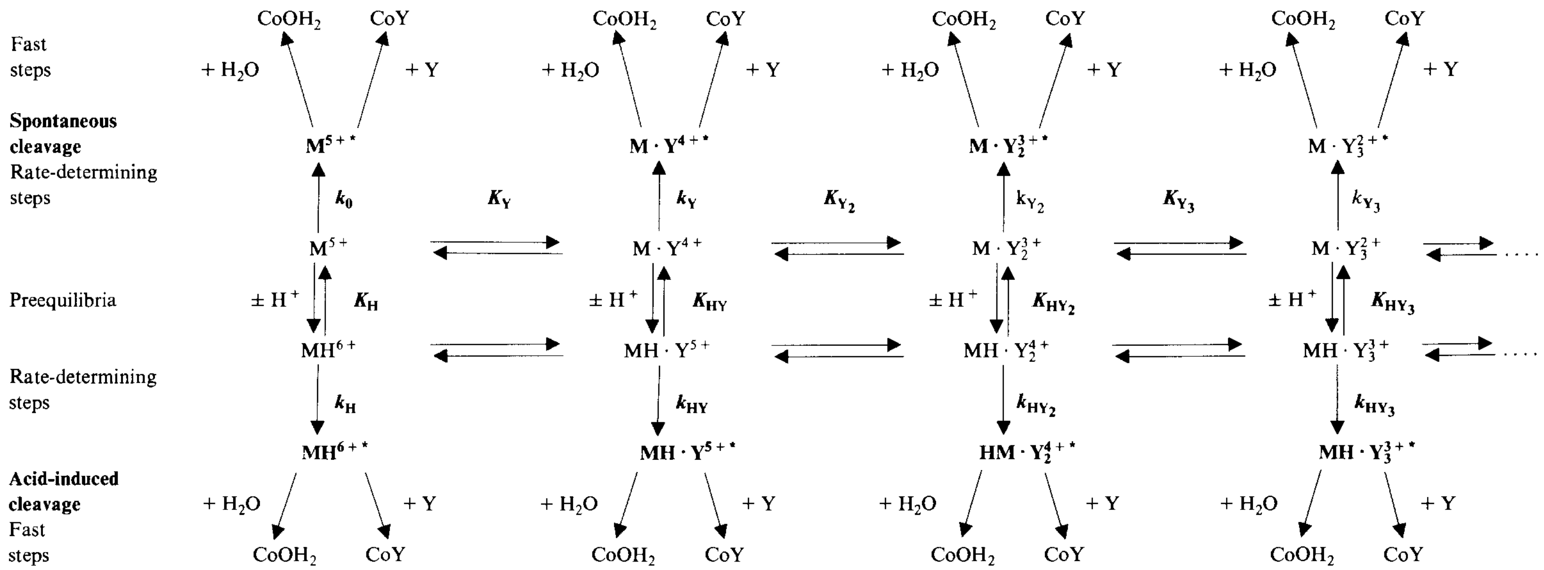
and

$$f_1 = \frac{k_H K_H + k_{HY}K_{HY}K_Y[Y] + k_{HY_2}K_{HY_2}K_{Y_2}K_Y[Y]^2 + \ldots}{1 + K_Y[Y] + K_{Y_2}K_Y[Y]^2 + \ldots}.$$

Depending on the acidity, either the f_0 term (at pH 3–4) or the f_1 term (at pH 0–1) can be the major contributor to the overall rate [3].

Eqns. 2 and *3* are the empirical rate laws for spontaneous cleavage alone. Here, all numerator and denominator terms first order in [H] are negligible [4]. *Eqn. 2* holds for spontaneous cleavage in ClO_4^- media in the presence of added anions Y(= Cl^-, $CH_3SO_3^-$) [3]. This rate law does *not* account for a reactive ion pair in spontaneous cleavage.

Scheme[a])



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[a]) $M^{5+} = [(NH_3)_5CoOHCo(NH_3)_5]^{5+}$, $MH^{6+} = [(NH_3)_5CoOH_2Co(NH_3)_5]^{6+}$, $CoOH_2 = [(NH_3)_5CoOH_2]^{3+}$, $CoY = [(NH_3)_5CoY]^{2+}$; in bold-face: species, equilibria, and pathways observed. Starred species: transition states of rate-determining steps.

Rate Expressions (charges omitted)

$$-\mathrm{d[mono\text{-}ol]}/\mathrm{d}t = k_{\mathrm{obs}}\mathrm{[mono\text{-}ol]};$$

$$k_{\mathrm{obs}} = \frac{k_0 + k_{\mathrm{Y}}K_{\mathrm{Y}}[\mathrm{Y}] + k_{\mathrm{Y}_2}K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{Y}]^2 + \cdots + k_{\mathrm{H}}K_{\mathrm{H}}[\mathrm{H}] + k_{\mathrm{HY}}K_{\mathrm{HY}}K_{\mathrm{Y}}[\mathrm{H}][\mathrm{Y}] + k_{\mathrm{HY}_2}K_{\mathrm{HY}_2}K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{H}][\mathrm{Y}]^2 + k_{\mathrm{HY}_3}K_{\mathrm{HY}_3}K_{\mathrm{Y}}K_{\mathrm{Y}_2}K_{\mathrm{Y}_3}[\mathrm{H}][\mathrm{Y}]^3 + \cdots}{1 + K_{\mathrm{Y}}[\mathrm{Y}] + K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{Y}]^2 + \cdots + K_{\mathrm{H}}[\mathrm{H}] + K_{\mathrm{HY}}K_{\mathrm{Y}}[\mathrm{H}][\mathrm{Y}] + K_{\mathrm{HY}_2}K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{H}][\mathrm{Y}]^2 + K_{\mathrm{HY}_3}K_{\mathrm{Y}}K_{\mathrm{Y}_2}K_{\mathrm{Y}_3}[\mathrm{H}][\mathrm{Y}]^3 + \cdots} \tag{1}$$

$$k_{\mathrm{obs}} = \frac{k_0}{1 + K_{\mathrm{Y}}[\mathrm{Y}]} \tag{2}$$

$$k_{\mathrm{obs}} = \frac{k_0 + k_{\mathrm{Y}}K_{\mathrm{Y}}[\mathrm{Y}]}{1 + K_{\mathrm{Y}}[\mathrm{Y}] + K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{Y}]^2} \tag{3}$$

$$k_{\mathrm{obs}} = \frac{k_0 + k_{\mathrm{H}}K_{\mathrm{H}}[\mathrm{H}] + k_{\mathrm{HY}}K_{\mathrm{HY}}K_{\mathrm{Y}}[\mathrm{H}][\mathrm{Y}] + k_{\mathrm{HY}_2}K_{\mathrm{HY}_2}K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{H}][\mathrm{Y}]^2}{1 + K_{\mathrm{Y}}[\mathrm{Y}]} \tag{4}$$

$$k_{\mathrm{obs}} = \frac{k_0 + k_{\mathrm{Y}}K_{\mathrm{Y}}[\mathrm{Y}] + k_{\mathrm{H}}K_{\mathrm{H}}[\mathrm{H}] + k_{\mathrm{HY}}K_{\mathrm{HY}}K_{\mathrm{Y}}[\mathrm{H}][\mathrm{Y}] + k_{\mathrm{HY}_2}K_{\mathrm{HY}_2}K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{H}][\mathrm{Y}]^2 + k_{\mathrm{HY}_3}K_{\mathrm{HY}_3}K_{\mathrm{Y}}K_{\mathrm{Y}_2}K_{\mathrm{Y}_3}[\mathrm{H}][\mathrm{Y}]^3}{1 + K_{\mathrm{Y}}[\mathrm{Y}] + K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{Y}]^2} \tag{5}$$

$$k_{\mathrm{obs}} = \frac{k_0 + k_{\mathrm{H}}K_{\mathrm{H}}[\mathrm{H}] + k_{\mathrm{HY}}K_{\mathrm{HY}}K_{\mathrm{Y}}[\mathrm{H}][\mathrm{Y}] + k_{\mathrm{HY}_2}K_{\mathrm{HY}_2}K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{H}][\mathrm{Y}]^2 + k_{\mathrm{HY}_3}K_{\mathrm{HY}_3}K_{\mathrm{Y}}K_{\mathrm{Y}_2}K_{\mathrm{Y}_3}[\mathrm{H}][\mathrm{Y}]^3}{1 + K_{\mathrm{Y}}[\mathrm{Y}]} \tag{6}$$

$$k_{\mathrm{obs}} = \frac{k_0 + k_{\mathrm{H}}K_{\mathrm{H}}[\mathrm{H}] + k_{\mathrm{HY}}K_{\mathrm{HY}}K_{\mathrm{Y}}[\mathrm{H}][\mathrm{Y}] + k_{\mathrm{HY}_2}K_{\mathrm{HY}_2}K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{H}][\mathrm{Y}]^2 + k_{\mathrm{HY}_3}K_{\mathrm{HY}_3}K_{\mathrm{Y}}K_{\mathrm{Y}_2}K_{\mathrm{Y}_3}[\mathrm{H}][\mathrm{Y}]^3 + k_{\mathrm{HY}_4}K_{\mathrm{HY}_4}K_{\mathrm{Y}}K_{\mathrm{Y}_2}K_{\mathrm{Y}_3}K_{\mathrm{Y}_4}[\mathrm{H}][\mathrm{Y}]^4}{1 + K_{\mathrm{Y}}[\mathrm{Y}] + K_{\mathrm{Y}}K_{\mathrm{Y}_2}[\mathrm{Y}]^2} \tag{7}$$

Table 1. *Kinetics of Cleavage of* $[(NH_3)_5CoOHCo(NH_3)_5]^{5+}$ *in* Cl^-/ClO_4^- *Medium at 25°C and* $\mu = 1.0$ M *(*Na^+*,* Cl^-/ClO_4^-*)*

$[Cl^-]$ [M]	$[H^+]$ [M]	$10^3 \cdot k_{obs}$[a]) $[s^{-1}]$	$10^3 \cdot k_{calc}$ $[s^{-1}]$	
			Eqn. 4[b])	*Eqn. 5*[c])
0.0	$10^{-3.5}$	3.96	4.0	4.05
	0.25	5.52	5.6	5.63
	0.5	7.12	7.2	7.21
0.1	$10^{-3.5}$	3.3	3.1	3.17
	0.1	6.0	6.9	6.81
	0.6	22.2	26	25.1
	1.0	38.2	41	39.7
0.2	$10^{-3.5}$	2.57	2.5	2.60
0.25	$10^{-3.5}$	2.46	2.3	2.39
	0.25	23.5	23.7	22.8
	0.5	46.6	45.1	43.3
	1.0	93.9	88	84.3
0.4	$10^{-3.5}$	1.86	1.85	1.94
0.5	$10^{-3.5}$	1.65	1.63	1.72
	0.2	32.5	34	33.2
	0.5	78.0	84	80.4
	1.0	162	165	159
0.6	$10^{-3.5}$	1.46	1.46	1.56
	0.2	39.5	40.5	39.1
	0.6	121	118	114
	1.0	204	196	189
0.75	$10^{-3.5}$	1.27	1.26	1.37
	0.25	62.4	61.7	59.6
	0.5	123	122	118
	1.0	249	243	235
0.9	$10^{-3.5}$	1.09	1.1	1.23
	0.25	69.4	73	70.8
	0.5	144	145	140
	0.9	260	261	252
	1.0	289	289	280
1.0	$10^{-3.5}$	1.03	1.02	1.15
	0.1	27.3	33	32.0
	0.25	74.9	81	78.3
	0.5	151	161	156
	0.75	226	241	233
	1.0	291	321	310

[a]) Data from [3].

[b]) Calculated using $k_O = 4.0 \cdot 10^{-3} s^{-1}$, $K_{Cl} = 2.9 M^{-1}$, $k_H = 6.2 \cdot 10^{-3} M^{-1} s^{-1}$, $k_{HCl} K_{HCl} K_{Cl} = 0.34 M^{-2} s^{-1}$, $k_{HCl_2} K_{HCl_2} K_{Cl_2} K_{Cl} = 0.90 M^{-3} s^{-1}$, and $R = 0.040$.

[c]) Calculated using $k_O = 4.05 \cdot 10^{-3} s^{-1}$, $k_{Cl} = 3.38 \cdot 10^{-3} s^{-1}$, $K_{Cl} = 17.1 M^{-1}$, $K_{Cl_2} = 2.37 M^{-1}$, $k_H = 6.2 \cdot 10^{-3} M^{-1} s^{-1}$, $k_{HCl} K_{HCl} K_{Cl} = 0.41 M^{-2} s^{-1}$, $k_{HCl_2} K_{HCl_2} K_{Cl_2} K_{Cl} = 5.42 M^{-3} s^{-1}$, $k_{HCl_3} K_{HCl_3} K_{Cl_3} K_{Cl_2} K_{Cl} = 12.3 M^{-4} s^{-1}$, and $R = 0.046$.

However, in NO_3^-/ClO_4^- media, spontaneous cleavage was no longer adequately described by Eqn. 2. Rate law *3* was only slightly (but statistically significantly) preferred over rate law *2* [4], but the inferred existence of a reactive ion pair $M \cdot NO_3^{4+}$ (giving rise to the terms $k_Y K_Y[Y]$ and $K_Y[Y]$, for $Y = NO_3^-$) and of an unreactive ion triplet $M \cdot (NO_3)_2^{3+}$ (giving rise to the denominator term $K_Y K_{Y_2}[Y]^2$ with $Y = NO_3^-$), received clear support from an analysis of the product-distribution function $F([\mathrm{Y}]) = [\mathrm{CoY}]_\infty/[\text{starting material}]_0$. In the mono-ol cleavage reactions, the pentaammine fragment CoY ($\mathrm{Y} = \mathrm{NO_3^-}$) arises from *scavenging of Y by a coordinatively unsaturated intermediate*, and not through subsequent anation of $\mathrm{CoOH_2}$ [3] [4]. The same analysis was carried out also for $\mathrm{Cl^-/ClO_4^-}$ media. Again, clear support for reactive $\mathrm{M\cdot Cl^{4+}}$ and unreactive $\mathrm{M\cdot Cl_2^{3+}}$ in spontaneous cleavage was obtained from the amount of competition product as a function of [Y].

Eqn. 4 is the empirical rate law incorporating both acid-induced and spontaneous cleavage in $\mathrm{Cl^-/ClO_4^-}$ media. Although this rate expression is statistically the best on the basis of the kinetic data *alone*, it must be replaced by one that accounts for the presence of reactive $\mathrm{M\cdot Cl^{4+}}$ and unreactive $\mathrm{M\cdot Cl_2^{3+}}$ (see above). The simplest rate law consistent with the participation of these species is *Eqn. 5*. This expression features an additional reactive species, *viz.* the ion quartet $\mathrm{MH\cdot Cl_3^{3+}}$, giving rise to the numerator term $k_{\mathrm{HY_3}}K_{\mathrm{HY_3}}K_{\mathrm{Y}}K_{\mathrm{Y_2}}K_{\mathrm{Y_3}}[\mathrm{H}][\mathrm{Y}]^3$.

Table 1 shows the measured values of k_{obs} [3] and the calculated values for rate laws *4* and *5*. The best values of the rate and stability constants are given in the *Footnotes*. The quality of the fit may be estimated from the *R* factors

$$R = \frac{\sum\limits_{i=1}^{N} [k^i_{\mathrm{obs}} - k^i_{\mathrm{calc}}]^2}{\sum\limits_{i=1}^{N} k^i_{\mathrm{obs}}}$$

where k^i_{obs} is the i-th measured rate constant k_{obs}. The k_{calc} are the calculated rate constants for a given set of parameters. Since rate law *4* for the acid-induced cleavage gave a satisfactory fit, rate law *5* must be related to *4* in good approximation by a factor common to numerator and denominator of *Eqn. 5*. (Conversely, *Eqn. 5* may be reduced to *4* by cancellation of a factor common to numerator and denominator (see *Footnote 25* in [4]). For this reason, identical *R* values are expected for the rate laws *4* and *5*, and the reported, small differences (*Table 1, Footnotes b* and *c*) are due to rounding errors.

A preliminary set of kinetic data on the *acid-induced cleavage* in $\mathrm{NO_3^-/ClO_4^-}$ media clearly showed that rate law *5* was not adequate to describe the anion dependence of the rate in this case. While in the acid-induced cleavage in $\mathrm{Cl^-/ClO_4^-}$ media, the anion dependent numerator and denominator terms balance out to give a virtually linear function $f_1 = f([\mathrm{Cl^-}])$ up to $[\mathrm{Cl^-}] = 0.9$M, the analogous function $f_1 = f([\mathrm{NO_3^-}])$ was clearly parabolic over the whole range of concentrations. This suggested the inclusion of one further, anion dependent numerator term without change in the denominator terms. Thus, the best fit parameters to rate laws *6* and *7* were determined (*Table 2*). Rate law *6* differs from *4* only by a numerator term third order in [Y]. This accounts for a reactive, protonated ion quartet $\mathrm{MH\cdot Y_3^{3+}}$ as rate law *5*, but there is no provision made for a reactive ion pair $\mathrm{M\cdot Y^{4+}}$ of the unprotonated mono-ol cation.

By analogy, rate law *7* contains a numerator term fourth order in [Y], corresponding to a reactive ion quintet $\mathrm{MH\cdot Y_4^{2+}}$ of the protonated mono-ol. The best parameters for the rate laws *6* and *7* differed particularly in the values of the stability constants K_{Y} as in the case of the $\mathrm{Cl^-/ClO_4^-}$ media. Again, the *R* values were almost the same for the two rate laws, and they cannot be distinguished with certainty on the basis of this analysis alone. Once more, however, rate law *7* is preferred because it accounts for the independently proven, reactive $\mathrm{M\cdot Y^{4+}}$ and unreactive $\mathrm{M\cdot Y_2^{3+}}$ species, respectively.

Table 2. *Kinetics of Cleavage of* $[(NH_3)_5CoOHCo(NH_3)_5]^{5+}$ *in* NO_3^-/ClO_4^- *Media at* $\mu = 1.0$ M $(Na^+, NO_3^-/ClO_4^-)$ *and 25°*

$[NO_3^-]$ [M]	$[H^+]$ [M]	$10^3 \cdot k_{obs}$ a) $[s^{-1}]$	$10^3 \cdot k_{calc}$ $[s^{-1}]$	
			Eqn. 6 b)	*Eqn. 7* c)
0.0	$10^{-3.3}$	4.26 ± 0.06 (4)	4.42	4.26
0.02	$10^{-3.3}$	4.31 ± 0.05 (3)	4.30	4.26
0.039	$10^{-3.3}$	4.22 ± 0.02 (3)	4.20	4.23
0.091	$10^{-3.3}$	4.02 ± 0.24 (3)	3.93	4.06
0.167	$10^{-3.3}$	3.87 (1)	3.60	3.75
0.2	$10^{-3.3}$	3.65 (1)	3.47	3.62
0.25	0.125	6.38 ± 0.58 (4)	5.98	6.15
	0.25	8.20 ± 0.32 (5)	8.67	8.88
	0.5	13.2 ± 0.3 (5)	14.1	14.3
	0.75	18.4 ± 0.5 (4)	19.4	19.8
	1.0	24.0 ± 2.0 (3)	24.8	25.3
0.286	$10^{-3.3}$	3.54 (1)	3.18	3.29
0.334	$10^{-3.3}$	3.07 ± 0.17 (4)	3.04	3.13
0.445	$10^{-3.3}$	2.78 ± 0.28 (2)	2.76	2.80
0.5	$10^{-3.3}$	2.42 ± 0.13 (3)	2.64	2.66
	0.1	7.19 ± 0.68 (3)	6.80	6.88
	0.25	12.2 ± 0.5 (4)	13.1	13.2
	0.5	22.8 ± 1.1 (5)	23.5	23.8
	0.75	37.1 ± 0.9 (5)	33.9	34.4
	1.0	47.4 ± 1.2 (4)	44.4	45.0
0.556	$10^{-3.3}$	2.69 ± 0.00 (2)	2.52	2.53
0.667	$10^{-3.3}$	2.40 ± 0.41 (2)	2.33	2.31
0.715	$10^{-3.3}$	2.12 ± 1.20 (2)	2.25	2.22
0.75	0.125	10.7 ± 0.6 (2)	10.5	10.6
	0.25	17.5 ± 2.7 (3)	18.9	19.1
	0.5	35.6 ± 0.3 (3)	35.6	36.0
	0.75	43.9 ± 1.1 (3)	52.3	52.9
	1.0	70.3 ± 7.9 (2)	69.0	69.8
0.8	$10^{-3.3}$	2.21 ± 0.44 (2)	2.13	2.09
0.834	$10^{-3.3}$	2.10 ± 0.06 (4)	2.09	2.04
0.91	$10^{-3.3}$	1.88 ± 0.19 (3)	1.99	1.94
1.0	$10^{-3.3}$	1.72 ± 0.03 (5)	1.89	1.83
	0.167	16.6 ± 0.8 (5)	18.0	18.2
	0.334	35.6 ± 3.6 (3)	34.2	34.5
	0.5	56.7 ± 1.6 (2)	50.2	50.8
	0.715	69.1 ± 0.8 (3)	71.0	71.9
	1.0	101 (1)	98.6	99.8

a) Confidence limits for 95% probability; number of determinations in parentheses.

b) Calculated using $k_O = 4.42 \cdot 10^{-3} s^{-1}$, $K_{NO_3} = 1.4 M^{-1}$, $k_H = 6.2 \cdot 10^{-3} M^{-1} s^{-1}$, $k_{HNO_3} K_{HNO_3} K_{NO_3} = 0.060 M^{-2} s^{-1}$, $k_{H(NO_3)_2} K_{H(NO_3)_2} K_{(NO_3)_2} K_{NO_3} = 0.11 M^{-3} s^{-1}$, $k_{H(NO_3)_3} K_{H(NO_3)_3} K_{(NO_3)_3} K_{(NO_3)_2} K_{NO_3} = 0.053 M^{-4} s^{-1}$, and $R = 0.055$.

c) Calculated using $k_O = 4.26 \cdot 10^{-3} s^{-1}$, $k_{NO_3} = 4.4 \cdot 10^{-3} s^{-1}$, $K_{NO_3} = 8.9 M^{-1}$, $K_{(NO_3)_2} = 1.6 M^{-1}$, $k_H = 6.2 \cdot 10^{-3} M^{-1} s^{-1}$, $k_{HNO_3} K_{HNO_3} K_{NO_3} = 0.11 M^{-2} s^{-1}$, $k_{H(NO_3)_2} K_{H(NO_3)_2} K_{(NO_3)_2} K_{NO_3} = 0.59 M^{-3} s^{-1}$, $k_{H(NO_3)_3} K_{H(NO_3)_3} K_{(NO_3)_3} K_{(NO_3)_2} K_{NO_3} = 1.1 M^{-4} s^{-1}$, $k_{H(NO_3)_4} K_{H(NO_3)_4} K_{(NO_3)_4} K_{(NO_3)_3} K_{(NO_3)_2} K_{NO_3} = 0.56 M^{-5} s^{-1}$, and $R = 0.054$.

The values derived for the parameters for each rate law with $Y = Cl^-$, NO_3^- may be compared to each other. If the anion influence on the rate is due to ion pairing, then similar values of the ion-aggregation constants K_Y, K_{Y_2}... are expected. This is indeed found: $K_{Cl} = 17.1 M^{-1}$, $K_{Cl_2} = 2.37 M^{-1}$ and $K_{NO_3} = 8.9 M^{-1}$, $K_{(NO_3)_2} = 1.6 M^{-1}$. The order of magnitude of these values is consistent with those found for similar cations [4] [8]. On the other hand, the best parameters K_{Y}, K_{Y_2} derived for rate laws *4* and *6* are at variance with these reference values.

It has been argued [3] that ion pairing in the *acid-induced* pathways rendered attack of H^+ on the OH^- bridge more facile to the extent that electrostatic repulsion of the proton by the (5+)-charged complex was reduced. The efficiency of the ion aggregates in facilitating protonation depends appreciably on the size of the singly charged anions involved. The gross catalytic effect of this ion aggregation is a composite quantity. It depends on both the reactivity of each ion aggregate (as measured by the rate constant k_{HY_n}) and the stability of the aggregates (as determined by the value of the preequilibrium constants K_{HY_n}, K_{Y_n}). For Y = Cl^-, NO_3^-, their combined effect leads to an increase in rate by a factor of up to 11. A regular increase in the gross rate is observed from the ion pair ($\mathrm{MH} \cdot \mathrm{Y}^{5+}$) to the ion quartet ($\mathrm{MH} \cdot \mathrm{Y}_3^{3+}$), and still higher aggregates were found to be less reactive ($\mathrm{Y} = \mathrm{NO}_3^-$) or unreactive ($\mathrm{Y} = \mathrm{Cl}^-$) as is seen from the following values: $k_{\mathrm{HCl}} \cdot K_{\mathrm{HCl}} \cdot K_{\mathrm{Cl}} = 0.41\,\mathrm{M}^{-2}\mathrm{s}^{-1}$, $k_{\mathrm{HCl}_2} \cdot K_{\mathrm{HCl}_2} \cdot K_{\mathrm{Cl}_2} \cdot K_{\mathrm{Cl}} = 5.42\,\mathrm{M}^{-3}\mathrm{s}^{-1}$, $k_{\mathrm{HCl}_3} \cdot K_{\mathrm{HCl}_3} \cdot K_{\mathrm{Cl}_3} \cdot K_{\mathrm{Cl}_2} \cdot K_{\mathrm{Cl}} = 12.3\,\mathrm{M}^{-4}\mathrm{s}^{-1}$, and $k_{\mathrm{HNO}_3} \cdot K_{\mathrm{HNO}_3} \cdot K_{\mathrm{NO}_3} = 0.11\,\mathrm{M}^{-2}\mathrm{s}^{-1}$, $k_{\mathrm{H(NO_3)_2}} \cdot K_{\mathrm{H(NO_3)_2}} \cdot K_{\mathrm{(NO_3)_2}} \cdot K_{\mathrm{NO}_3} = 0.59\,\mathrm{M}^{-3}\mathrm{s}^{-1}$, $k_{\mathrm{H(NO_3)_3}} \cdot K_{\mathrm{H(NO_3)_3}} \cdot K_{\mathrm{(NO_3)_3}} \cdot K_{\mathrm{(NO_3)_2}} \cdot K_{\mathrm{NO}_3} = 1.1\,\mathrm{M}^{-4}\mathrm{s}^{-1}$, and $k_{\mathrm{H(NO_3)_4}} \cdot K_{\mathrm{H(NO_3)_4}} \cdot K_{\mathrm{(NO_3)_4}} \cdot K_{\mathrm{(NO_3)_3}} \cdot K_{\mathrm{(NO_3)_2}} \cdot K_{\mathrm{NO}_3} = 0.56\,\mathrm{M}^{-5}\mathrm{s}^{-1}$.

The ion aggregate stability constants derived in this and previous work [3] [4] require some interpretation. A constant ionic strength ($\mu = 1$, $NaClO_4$) was maintained in each experiment. Substitution of ClO_4^- by anions Y^- in the $[Y^-]$-dependent kinetics maintains this ionic strength, but at $\mu = 1$, the *Debye-Hückel* approximation is no longer adequate and appreciable differences in the total ion activity at different $[Y^-]$ are to be expected. However, it is common practice to neglect these activity differences and to calculate the parameters of the rate law on this basis. Only by continuing this practice it is possible to relate the results of this work to previous studies on this [3] [4] and similar [5–10] systems. The same remarks also apply to the treatment of possible ion aggregation with ClO_4^-. This certainly occurs to some extent and some of its consequences on rate law and rate parameters have been discussed [4], and the earlier approximations [4] have been maintained for the sake of comparison. The ion aggregates postulated in this and previous [3] [4] work are certainly very labile and should exchange anions at nearly diffusion-controlled rates. It remains presently unknown whether they should be considered as 'intimate' or solvent-separated species [11]. Furthermore, each anion in an aggregate of given (average) composition may occupy one of many non-equivalent sites in the proximity of the cation. Thus, the postulated anion aggregation is not easily distinguished from a *Debye-Hückel* ionic atmosphere [12]. However, the interpretation of the kinetic effect of anions Y^- in terms of n observable ion aggregate stability constants K_{Y_n} again facilitates the comparison with previously studied systems.

Anions Y^- in the surroundings of the cation have been shown to participate in product formation, both in spontaneous and acid-induced cleavage [3] [4]. A concerted (I_d) mechanism requires that the coordinated anions in the end product are scavenged from the second coordination sphere, and thus only intimate ion pairs could be product-forming species. However, a stepwise (D) mechanism has been postulated for these two pathways [3] [4]. This mechanism implies the existence of an intermediate that may scavenge anions penetrating from outside the second coordination sphere within its (very short) lifetime.

Finally, a remark is appropriate on the reactivity of the supposed ion aggregates in the spontaneous cleavage pathway. Reactive $M \cdot Y^{4+}$ and unreactive $M \cdot Y_2^{3+}$ have been identified [4], but the interpretation of the reactivity effects cannot be the same as in the acid-induced pathways, since protonation occurs only after the rate-determining step. In the absence of a protonation preequilibrium, anion aggregation may reduce the electrostatic repulsion between the Co(III) centres and thereby reduce the rate of cleavage. For further interpretation of the differences in reactivity of the different species in spontaneous cleavage, the activation parameters of the individual pathways are required. However, the present and previous [3] [4] results on this very complex multispecies system involving many parallel reaction pathways foreshadow great difficulties in obtaining these, since the reactivity and stability differences are rather small.

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Experimental Part. The materials and kinetic and computational procedures used were the same as in [4]. We reiterate that the kinetics in mixed NO_3^-/ClO_4^- media were run in supersaturated soln. [4]. However, the acid-induced reactions in these media were sufficiently fast to prevent inhomogeneity of the solns. Thus, in the majority of cases, linear plots of $\log(D_t - D_\infty)$ *vs.* time were obtained for > 3 half-lives (D_t, D_∞ are the optical densities of the reaction mixtures at time t and $t \rightarrow \infty$).

REFERENCES

[1] J. D. Ellis, K. L. Scott, R. K. Wharton, A. G. Sykes, *Inorg. Chem.* **1972,** *11,* 2562.

[2] R. K. Wharton, A. G. Sykes, *J. Chem. Soc., Dalton Trans.* **1973,** 439.

[3] D. A. Buckingham, W. Marty, A. M. Sargeson, *Inorg. Chem.* **1974,** *13,* 2165; in this ref. *Figs. 1* and *2* have to be interchanged.

[4] F. P. Rotzinger, W. Marty, *Inorg. Chem.* **1985,** *24,* 1617.

[5] A. M. Sargeson, *Pure Appl. Chem.* **1973,** *33,* 527, and ref. cit. therein.

[6] W. G. Jackson, G. A. Lawrance, A. M. Sargeson, *Inorg. Chem.* **1980,** *19,* 1001.

[7] W. L. Reynolds, S. Hafezi, A. Kessler, S. Holly, *Inorg. Chem.* **1979,** *18,* 2860.

[8] F. P. Rotzinger, W. Marty, *Inorg. Chem.* **1983,** *22,* 3593.

[9] W. L. Reynolds, E. R. Alton, *Inorg. Chem.* **1978,** *17,* 3355.

[10] D. A. Buckingham, C. R. Clark, W. S. Webley, *Inorg. Chem.* **1982,** *21,* 3353.

[11] J. M. Harris, *Progr. Phys. Org. Chem.* **1974,** *11,* 89.

[12] P. W. Atkins, 'Physical Chemistry', 2nd edn., Oxford University Press, Oxford, 1982, pp. 316–328.