

Kinetics of the reversible uptake of carbon dioxide and sulphur dioxide by the *cis*-(hydroxo)(imidazole)*bis*(ethylenediamine)cobalt(III) ion in aqueous medium. A comparative study

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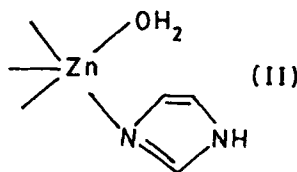
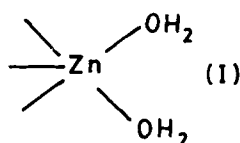
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Abstract. The addition of SO_2 to *cis*-(hydroxo)(imidazole)*bis*(ethylenediamine)cobalt(III) ion-generated-oxygen-bonded sulphito complex, the kinetics of which have been studied by the stopped-flow technique. The rate and activation parameters for the formation of *cis*- $[(\text{en})_2(\text{imH})\text{CoOSO}_2]^+$, the elimination of SO_2 from this O-bonded sulphito species which is H^+ -catalysed and of second order, and formation of the corresponding carbonato complex *cis*- $[(\text{en})_2(\text{imH})\text{CoOCO}_2]^+$, by the reaction of CO_2 with *cis*- $[(\text{en})_2(\text{imH})\text{CoOH}]$ have been determined. The bicarbonato complex, *cis*- $[(\text{en})_2(\text{imH})\text{CoCO}_2\text{H}]^{2+}$, undergoes spontaneous CO_2 elimination. The relatively low ΔH^\ddagger and large negative values of ΔS^\ddagger for CO_2 uptake by *cis*- $[(\text{en})_2(\text{imH})\text{CoOH}]^{2+}$ are in contrast to the values for other analogous complexes of cobalt(III) reported in the literature. Some specific effects of cobalt(III)-bound imidazole on CO_2 -addition processes have been inferred.

Keywords. Kinetics; *cis*-(hydroxo)(imidazole)*bis*(ethylenediamine)cobalt(III); sulphur dioxide; carbon dioxide.

1. Introduction

In recent years evidence has accumulated on the reversible uptake of SO_2 by octahedral hydroxo metal complexes in the stopped-flow time scale leading to the formation of oxygen-bonded sulphito complexes without metal–oxygen bond cleavage (Harris and Van Eldik 1980; Harris *et al* 1981; Harris and El-Awady 1981; Van Eldik *et al* 1982; Van Eldik 1984). Extensive studies have also been devoted to understanding the reversible uptake of CO_2 by hydroxo metal amine complexes of Co(III), Rh(III), Ir(III) and related complexes (Van Eldik and Palmer 1983; Van Eldik 1984). These are typical model reactions simulating the hydration of CO_2 by the enzyme carbonic anhydrase in a biological domain (Lindskog *et al* 1971; Buckingham 1977; Lindskog and Silverman 1988). Khalifah (1971) has reported the competitive inhibitory action



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of imidazole on the hydration of CO_2 by human carbonic anhydrase B. The carbonic anhydrase B (I) and its imidazole complex (II) are believed to exist in solution (Hay 1980).

The purpose of this study was to investigate the effect of the presence of imidazole, a biologically important ubiquitous ligand, on the rate of the reversible formation of the O-bonded sulphito and carbonato complexes of *cis*- $[(\text{en})_2(\text{imH})\text{CoOH}]^{2+}$. Relevant data for the corresponding (aqua)-(hydroxo) complexes, $[\text{N}_4\text{Co}(\text{OH}_2)\text{OH}]^{2+}$ ($\text{N}_4 = 2\text{en}$ or a tetradentate amine ligand) are available for comparison.

2. Experimental

Cis-(aqua)(imidazole)*bis*(ethylenediamine)cobalt(III)trinitrate was prepared by meta-thetic reaction of *cis*-(chloro) (imidazole)*bis*(ethylenediamine) cobalt(III) chloride with AgNO_3 at 60°C ; AgCl was filtered off and the solution was concentrated to a small bulk which deposited orange-red crystals on cooling in an ice-bath. The crude product collected by filtration was recrystallized repeatedly from warm water acidified with HNO_3 , washed successively with absolute alcohol, diethyl ether and stored over fused calcium chloride. Calculated for $[\text{Co}(\text{en})_2(\text{imH})(\text{OH}_2)](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$: Co, 12.6; C, 17.9; H, 4.9; N, 26.9%. Found: Co, 12.4; C, 17.7; H, 4.4; N, 26.4%. The aqua cation exhibits λ_{max} , nm (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) at 480 (80) and 330 (84) in $0.1 \text{ mol dm}^{-3} \text{HClO}_4$ medium in agreement with the previously reported values (Dash and Mohapatra 1977).

Analar grade chemicals were used. $\text{Na}_2\text{S}_2\text{O}_5$ was used as the source of S(IV) which rapidly hydrates on dissolution in water. Self-buffered sulphite, mixture of sodium acetate and acetic acid, imidazole and *tris*(hydroxy methyl)aminomethane buffers were used to control *pH*. The solutions were prepared in double-distilled water, the second distillation being made from alkaline KMnO_4 in an all-glass apparatus. Ionic strength was adjusted with NaClO_4 .

The *pH* measurements were made with an Elico digital *pH*-meter, model LI 120, equipped with a combination electrode glass- Ag/AgCl , NaCl (2.0 mol dm^{-3}) (Model CI 51). Standard NBS buffers (Perrin and Dempsey 1974) (*pH* = 4.01, 6.86 and 9.2) were used to calibrate the *pH*-meter. A Jasco 7800 recording spectrophotometer was used for UV-visible spectral measurements using 1-centimetre matched quartz cells.

2.1 Kinetics

The SO_2 uptake by *cis*- $[\text{Co}(\text{en})_2(\text{imH})\text{OH}]^{2+}$ and the acid-catalysed decomposition of the O-bonded sulphito complex were followed using a fully automated SF-51 stopped-flow spectrophotometer equipped with C85D thermostat and FC 200 cooler (Hi-Tech, UK). The reaction was monitored at 340 nm, where large increase/decrease in absorbance occurred due to formation/decomposition of O-bonded sulphito complex (Harris and Van Eldik 1980; Harris *et al* 1981).

For CO_2 uptake reaction, the acidification method (Harris *et al* 1973) which involved generating CO_2 by acidifying NaHCO_3 to *pH* ~ 3 was employed. The reaction was monitored at 300 nm, where large increase in absorbance occurred due to formation of the carbonato complex. For decarboxylation reaction, the carbonato complex, *cis*- $[(\text{en})_2(\text{imH})\text{CoOCO}_2]^+$, was prepared *in situ* by dissolving *cis*-

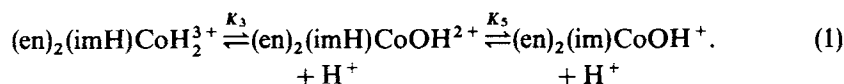
[(en)₂(imH)CoOH₂](NO₃)₃ in NaHCO₃ solution (Co(III)_T:NaHCO₃ = 1:50) adjusting the pH to ≈ 8.2. One of the reservoir syringes of the stopped-flow assembly was filled with the carbonato complex and the second syringe was filled with HClO₄. The ionic strength of each of these solutions was adjusted to 0.5 mol dm⁻³ with required amounts of NaClO₄. The reactants were mixed in the stopped-flow assembly and the decay of the carbonato complex was monitored at 290 nm.

All runs were made under pseudo-first-order conditions and rate constants were calculated by an on-line Apple IIGS PC using an ADS2 software suite available from M/s Hi-Tech Scientific Ltd (UK). Seven to eight replicate measurements were made for each run from which the mean value of the pseudo-first-order rate constants and its standard deviation was calculated.

3. Results and discussion

3.1 *pK*'s of *cis*-[(en)₂(imH)CoOH₂]³⁺

The molar extinction coefficient of the aqua-complex around 285 nm increased with pH with two inflexion points at pH 6.5 and 10.0 in conformity with the acid-base equilibria given by



The measurement of the dissociation constant (*K*₃) was attempted in imidazole buffer (pH = 6.10 – 7.40) at 290 nm. The dissociation constant calculated from the relationship

$$\frac{a}{(D_{\text{obs}} - D_1)} = \frac{1}{(\epsilon_2 - \epsilon_1)l} + \frac{[\text{H}^+]}{K_3} \cdot \frac{1}{(\epsilon_2 - \epsilon_1)l} \quad (2)$$

where *a* = [complex]_{total}, *D*_{obs} = optical density due to the complex at a given pH, *D*₁ = *ε*₁ *al*, *ε*₁ and *ε*₂ are the extinction coefficients of the (aqua)(imidazole) and (hydroxo)(imidazole) complexes respectively, *l* is the cell path length, and *K*₃ is the dissociation constant of the aqua-complex. The data were fitted to (2) by a least-squares computer program and the values of *pK*₃ = 6.22 ± 0.03, 6.17 ± 0.06, and 6.10 ± 0.03 at 20.0, 25.0 and 29.0°C respectively (*I* = 1.0 mol dm⁻³) and 6.34 ± 0.08, 6.25 ± 0.07 and 6.20 ± 0.04 at 25.0, 30.0 and 35.0°C, respectively (*I* = 0.50 mol dm⁻³), were obtained. These data compare well with the value of *pK*₃ = 6.40 at 50°C (*I* = 2.0 mol dm⁻³) reported in the literature (House and Fenemor 1976). The absorbance data of the aqua-complex at 285 nm in the range of pH 9.30–11.60 were used to calculate the dissociation constant of the N–H group of the coordinated imidazole by a method similar to that used for evaluation of *pK*₅ (Dash and Dash 1976). We obtained *pK*₅ = 10.3 ± 0.1 at 25°C (*I* = 0.50 mol dm⁻³) which compare satisfactorily with the analogous data for *cis*-[Co(en)₂(imH)X]²⁺ (X = Cl⁻, N₃⁻, NCS⁻, C₆H₄(O)(OH)CO₂⁻) (Hay *et al* 1979; Dash and Mohanty 1980; Dash *et al* 1984).

3.2 SO₂-uptake reaction

Formation of O-bonded sulphito complex, *cis*-[(en)₂(imH)CoOSO₂]⁺ was indicated by the instantaneous colour change from orange-yellow to orange-red when the aqua

complex was mixed with the sulphite solution (Harris and Van Eldik 1980; Harris and El-Awady 1981; Harris *et al* 1981). The time variation of the absorbance data observed in the stopped flow traces fitted well to a single exponential curve indicating that any other side reactions were insignificant during the life time of the reversible SO_2 addition reaction (Dash and Padhy 1989).

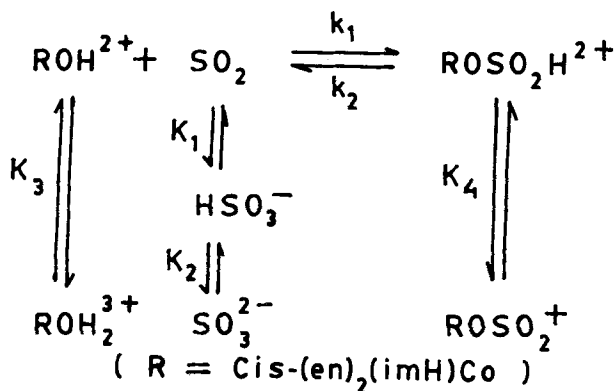
The rate data for the SO_2 -uptake process studied over the range $5.80 \leq \text{pH} \leq 7.30$ and $0.01 \leq [\text{S(IV)}]_T (\text{mol dm}^{-3}) \leq 0.08$ ($10.0 \leq \text{temperature } (^\circ\text{C}) \leq 25.0$) are summarized in table 1. At constant $\text{pH} (= 6.0 \pm 0.05)$ the plot of k_{obsd} against $[\text{S(IV)}]_T$ was linear, passing through the origin and indicating that the reverse (i.e. the SO_2 elimination) reaction is not significant at this pH . When the reaction was carried out in acetate buffer media ($3.60 \leq \text{pH} \leq 5.30$) at constant $[\text{S(IV)}]_T (= 0.0015 \text{ mol dm}^{-3})$, the value

Table 1. Rate data for SO_2 uptake by $\text{cis}-(\text{en})_2(\text{imH})\text{CoOH}]^{2+}$.

[S(IV) _T] (mol dm ⁻³)	Temperature (°C)							
	10.0 ± 0.1		15.0 ± 0.1		20.0 ± 0.1		25.0 ± 0.1	
	pH	k _{obsd} (s ⁻¹)	pH	k _{obsd} (s ⁻¹)	pH	k _{obsd} (s ⁻¹)	pH	k _{obsd} (s ⁻¹)
0.01	6.06	3.00 ± 0.12	6.04	5.23 ± 0.20	6.04	8.45 ± 0.20	5.93	14.5 ± 1.2
0.02	5.94	7.0 ± 0.23	5.92	11.4 ± 1.0	5.92	19.3 ± 0.1	5.92	28.7 ± 1.1
0.03	5.84	11.0 ± 0.50	5.80	17.4 ± 0.5	5.94	26.5 ± 0.1	5.90	40.5 ± 1.8
0.04	6.0	13.1 ± 0.6	5.98	21.7 ± 1.0	6.02	32.0 ± 1.0	6.06	53.0 ± 1.6
0.05	6.07	14.6 ± 0.1	6.05	26.6 ± 1.0	6.05	39.5 ± 1.0	6.05	63.0 ± 1.2
0.06	6.08	18.0 ± 0.6	6.06	30.3 ± 0.5	6.10	46.1 ± 0.5	6.10	72.5 ± 4.2
0.07	6.07	20.2 ± 0.8	6.08	34.4 ± 0.6	6.12	49.2 ± 1.0	6.12	83.2 ± 3.0
0.08	6.09	23.0 ± 0.6	6.08	38.0 ± 1.0	6.08	54.9 ± 1.0	6.08	95.5 ± 4.0
0.05	6.38	7.91 ± 0.32	6.36	11.5 ± 0.5	6.35	19.3 ± 0.2	6.30	37.5 ± 3.0
0.05	6.65	4.50 ± 0.12	6.64	5.62 ± 0.21	6.61	10.1 ± 0.1	6.59	18.2 ± 1.3
0.05	7.20	0.68 ± 0.04	7.19	0.85 ± 0.05	7.15	1.44 ± 0.10	7.14	2.51 ± 0.10
$10^{-7} k_1 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^b$	3.71 ± 0.21		4.64 ± 0.37		5.88 ± 0.04		7.71 ± 0.30	

^a $\lambda = 340 \text{ nm}$, $[\text{aqua complex}]_T = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$.

^b Values of $\text{p}K_1$ and $\text{p}K_3$ are 1.74, 1.79, 1.85, 1.92, and 6.36, 6.29, 6.22, 6.17, at 10, 15, 20 and 25°C, respectively; a constant value of $\text{p}K_2 = 6.30$ was used in the range of temperature 10–25°C (Harris and Van Eldik 1980)



Scheme 1

of k_{obsd} steadily increased as the pH was lowered. A mechanism for SO₂ uptake/elimination reaction consistent with the observation is delineated in scheme I for which the pseudo-first-order rate constant is given by

$$k_{\text{obsd}} = k_1 \left\{ \frac{K_3}{K_3 + [\text{H}^+]} \right\} f_1 [\text{S(IV)}]_T + k_r, \quad (3)$$

where,

$$k_r = k_2 [\text{H}^+] / ([\text{H}^+] + K_4),$$

$$f_1 = [\text{H}^+]^2 / ([\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2),$$

and K_1 , K_2 , K_3 and K_4 denote the acid dissociation constants as shown in scheme 1. The values of k_1 at different temperatures were calculated using the rate data in table 1 and the values of K_1 , K_2 (Harris and Van Eldik 1980) and K_3 neglecting the term k_r , as it did not contribute significantly under this condition. The values of k_1 at different temperatures are collected in table 1. A comparative listing of the values of k_1 and associated activation parameters for a number of sulphito complexes are presented in table 2.

At lower pH (i.e. $3.60 \leq \text{pH} \leq 5.30$), the rate data collected in table 3 were used to calculate k_r from (3) from the knowledge of k_1 and equilibrium constants. k_r varied linearly with $[\text{H}^+]$, thereby suggesting that $K_4 \gg [\text{H}^+]$ was valid ((3) reduced to the form $k_r = (k_2/K_4)[\text{H}^+]$). The values of $k'_2 = (k_2/K_4) = k_r/[\text{H}^+]$ are shown in table 3.

The SO₂-uptake rate constant for *cis*-[Co(en)₂(imH)OH]²⁺ is comparable to that of *cis/trans*-[Co(en)₂(OH)OH₂]²⁺ cations under comparable conditions. However, the variation of activation enthalpy and entropy, the former in particular, with the nature of the hydroxocobalt(III) species are quite appreciable. This must arise due to differential solvation effects of the substrates in initial state and transition state. The value of $k'_2 (= k_2/K_4)$ also compare with those for other similar oxygen-bonded sulphito complexes (see table 2) when correction is made for the temperature effect. Lack of evidence for specific effects of the coordinated imidazole on SO₂-addition and elimination reaction of the *cis*-[Co(en)₂(imH)OH]²⁺ and *cis*-[Co(en)₂(imH)OSO₂H]²⁺, respectively, are worth mentioning.

3.3 CO₂-uptake reaction

Formation of a carbonato complex, *cis*-[(en)₂(imH)CoOCO₂]⁺, is indicated from the comparison of UV-visible spectra of *cis*-[(en)₂(imH)CoOH]²⁺ and (*cis*-[(en)₂(imH)CoOH]²⁺ + NaHCO₃) mixture at pH ~ 8.20.

Rate data for the CO₂-uptake reaction in the range $6.70 \leq \text{pH} \leq 7.30$ by the acidification method (see § 2) are collected in table 4. The observed rate constant is given by the expression as (Harris *et al* 1973)

$$k_{\text{obsd}} = k_2 b \{ K_3 / ([\text{H}^+] + K_3) \} \quad (4)$$

where $b = [\text{CO}_2]_T$, k_2 is for the CO₂-uptake reaction and K_3 is as defined in (1). The values of k_2 are collected in table 4.

The decarboxylation reaction (see (5) below) of *cis*-[(en)₂(imH)CoOCO₂]⁺ was studied over the acidity range $0.010 \leq [\text{H}^+]$, mol dm⁻³ ≤ 0.10 and temperature range $15.0 \leq t$ (°C) ≤ 35.0 . The decarboxylation rate constant was independent of $[\text{H}^+]$

Table 2. Comparison of rate parameters for SO_2 -uptake and elimination reactions of various cobalt(III) amine complexes at 25°C and $I = 1.0 \text{ mol dm}^{-3}$.

Complex	$10^{-8} k_1$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{JK}^{-1} \text{ mol}^{-1}$)	$10^{-6} k_2^a$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{JK}^{-1} \text{ mol}^{-1}$)	Reference
$[(\text{NH}_3)_5\text{CoOH}]^{2+}$	4.7	39.8 ± 1.2	59 ± 2	2.2^b			Van Eldik and Harris (1980)
$[\text{Co}(\text{tren})(\text{OH})\text{OH}_2]^{2+}$	0.53	18.8 ± 0.4	-33 ± 1	30.2			Harris and El-Awady (1981)
$\text{cis-}[\text{Co}(\text{en})_2(\text{OH})\text{OH}_2]^{2+}$	1.0	25.1 ± 0.4	-6.7 ± 0.8	0.75 ^c			Harris and Dasgupta (1984)
$\text{cis-}[\text{Co}(\text{en})_2(\text{fmH})\text{OH}]^{2+}$	0.77	32.0 ± 1.2	13 ± 4	2.66	57.7 ± 2.6	72 ± 9	This work

^a $k_2 = (k_2/K_4)$; ^b 10.0°C ; ^c 10.1°C

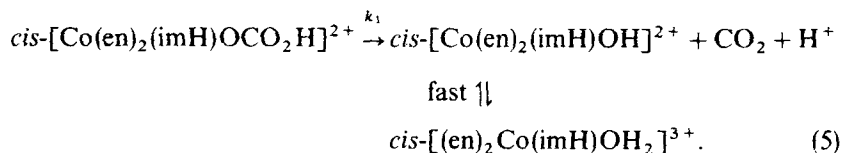
Table 3. Rate data for acid-catalysed elimination reaction of $\text{cis-}[\text{Co}(\text{en})_2(\text{fmH})\text{OSO}_2]^{2+}$ (acetic acid–sodium acetate buffer).

pH	Temperature ($^\circ\text{C}$)						
	10.0 ± 0.1	15.0 ± 0.1	20.0 ± 0.1	25.0 ± 0.1			
	$k_{\text{obsd}} (\text{s}^{-1})$	pH	$k_{\text{obsd}} (\text{s}^{-1})$	pH	$k_{\text{obsd}} (\text{s}^{-1})$	pH	$k_{\text{obsd}} (\text{s}^{-1})$
5.22	6.51 ± 0.51	5.21	7.95 ± 0.50	5.20	13.6 ± 0.6	5.19	17.8 ± 0.8
4.94	8.35 ± 0.10	4.93	14.5 ± 0.5	4.91	22.5 ± 1.0	4.92	38.3 ± 1.0
4.65	17.7 ± 0.6	4.62	30.5 ± 0.5	4.62	48.5 ± 1.0	4.61	74.5 ± 1.0
4.37	34.5 ± 0.8	4.36	60.5 ± 1.0	4.35	91.0 ± 2.0	4.34	130 ± 5
4.11	59.5 ± 1.0	4.10	106 ± 5	4.08	169 ± 5	4.08	223 ± 3
3.99	77.2 ± 2.0	4.0	135 ± 6	—	—	—	—
3.70	115 ± 5	3.70	278 ± 10	—	—	—	—
$10^{-6} k_2^b$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)							
	0.76 ± 0.08		1.26 ± 0.12		1.84 ± 0.12		2.66 ± 0.26

^a $[\text{S}(\text{IV})_T] = 1.5 \times 10^{-3}$, $[\text{aqua complex}]_T = 1.5 \times 10^{-4}$, (mol dm^{-3}) ; $I = 1.0$, $\lambda = 340 \text{ nm}$;

^b $k_2 = (k_2/K_4)$

and turned out to be 0.49 ± 0.01 , 1.43 ± 0.04 , 2.40 ± 0.05 , and $3.95 \pm 0.10 \text{ s}^{-1}$ at 15.0, 25.0, 30.0 and 35.0°C, respectively.



It is also worth noting that the CO_2 -uptake rate constant for $\text{cis-}[\text{Co}(\text{en})_2(\text{imH})\text{OH}]^{2+}$ is comparable with that of $\text{cis-}[\text{Co}(\text{en})_2(\text{OH}_2)\text{OH}]^{2+}$ (see table 5). However, relatively low values of ΔH^\ddagger and ΔS^\ddagger for imidazole complex is observed. Thus the effects of both ΔH^\ddagger and ΔS^\ddagger appear to be mutually compensatory. The large negative value of ΔS^\ddagger for the CO_2 -uptake reaction of the imidazole complex may evidently suggest that this process demands a relatively more ordered transition state. Del Bene and Cohen (1978) reported that imidazole is hydrated by water via hydrogen bonding interaction. Similar situation might prevail for the coordinated imidazole. If this hydrogen bonding effect results in a relatively more rigid transition state then this would lead to a negative value of ΔS^\ddagger . The decarboxylation rate constant for the imidazole complex is higher than those for $\text{cis/trans-}[(\text{en})_2(\text{NH}_3)\text{CoOCO}_2\text{H}]^{2+}$ and $\text{cis-}[(\text{en})_2\text{Co}(\text{OH}_2)\text{OCO}_2\text{H}]^{2+}$. The small rate-accelerating effect of imidazole despite the relatively large value of ΔH^\ddagger for the imidazole complex (see table 5) is worth noting. It is the magnitude of ΔS^\ddagger which evidently takes care of the rate-influencing effect of ΔH^\ddagger . It thus appears logical to think that the intimate mechanism remaining the same, the relative solvational changes in the initial state and transition state as perturbed by the nature of the ligand frame of the cobalt(III) centre largely mediate the activation parameters.

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