Inorganica Chimica Acta, 44 (1980) L197–L199
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Nitrate Ion Catalysis of Co(III) Substitution Reactions

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Received November 26, 1979

In a recent study [1] it was shown that the anation reactions of *cis*-$Co(en)_2(OH_2)_2^{3+}$ (en = ethylenediamine) by $H_2C_2O_4$ and $HC_2O_4^-$ are strongly catalyzed by the presence of nitrate ion in solution. This effect resulted in abnormally high ion-pair formation constants [2] for the species *cis*-$Co(en)_2(OH_2)_2^{3+}\cdot H_2C_2O_4$ and *cis*-$Co(en)_2(OH_2)_2^{3+}\cdot HC_2O_4^-$ in nitrate medium. A detailed study [1] of the effect suggested that the anation process proceeds via the formation of a five-coordinate intermediate, *viz.* $Co(en)_2(OH_2)^{3+}$, in the presence of nitrate ions. It was further emphasized that since this nitrate-promoted process was not observed [3–5] in the case of the anation reactions of $Co(NH_3)_5OH_2^{3+}$ by a range of carboxylic acids and carboxylate ions, it must result because of an interaction of nitrate ion with the two water ligands in the *cis* position.

The above-mentioned study was not the first to report such an effect. Water exchange reactions of $Cr(OH_2)_6^{3+}$ are in general catalyzed by anions [6, 7], for which NO_3^- is more effective than ClO_4^-. Furthermore, the nitrate ion was shown [8, 9] to have some unusual labilization properties when it forms part of the ligand grouping of Cr(III) complexes. The anation of *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ by oxalate was also reported [10] to exhibit a significant nitrate-induced enhancement of the reaction. A similar effect was recently reported [11] for the oxalate substitution of (glycinato-N,O)bis(oxalato)Cr(III).

Weyh and co-workers [12, 13] studied the anation of α-*cis*-$Co(EDDA)(OH_2)_2^+$ (EDDA = ethylenediamine-N,N′-diacetate) by $H_2C_2O_4$ and $HC_2O_4^-$ in nitrate medium. They reported [13] ion-pair formation constants for the species α-*cis*-$Co(EDDA)(OH_2)_2^+\cdot H_2C_2O_4$ and α-*cis*-$Co(EDDA)(OH_2)_2^+\cdot HC_2O_4^-$ of 2.9 and 16 M^{-1}, respectively, at 69 °C. These values are of the order of magnitude of the ion-pair formation constants originally reported [2] for the species *cis*-$Co(en)_2(OH_2)_2^{3+}\cdot H_2C_2O_4$ and *cis*-$Co(en)_2(OH_2)_2^{3+}\cdot HC_2O_4^-$ in nitrate medium, if the difference in charge on the Co(III) species is taken into account. However, they are significantly higher than the ion-pair formation constants reported [3–5] for the anation reactions of $Co(NH_3)_5OH_2^{3+}$ by carboxylic acids and carboxylate ions, and for the anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by $H_2C_2O_4$ and $HC_2O_4^-$ in perchlorate medium [1]. This suggested that a nitrate catalyzed anation reaction may also be responsible for the rather high ion-pair formation constants reported [13] for the species α-*cis*-$Co(EDDA)(OH_2)_2^+\cdot H_2C_2O_4$ and α-*cis*-$Co(DDA)(OH_2)_2^+\cdot HC_2O_4^-$, which forms the basis of the present investigation.

Experimental

α-*cis*-$[Co(EDDA)(OH_2)_2]ClO_4$ was prepared by acidifying α-*cis*-$K[Co(EDDA)CO_3]\cdot 4H_2O$, which was synthesized as described previously [14]. Chemical analyses and UV-visible absorption spectra were in agreement with the theoretically expected values and those reported elsewhere [12, 14, 15], respectively. Chemicals of analytical grade and deionized distilled water were used throughout the investigation.

Repetitive scan spectra of 2.5 × 10^{-3} *M* α-*cis*-$Co(EDDA)(OH_2)_2^+$ in 0.4 *M* $H_2C_2O_4$ and 2 *M* $HClO_4$ or 2 *M* HNO_3, were recorded at 60 °C on a Unicam SP1800 spectrophotometer. Clean isosbestic points were observed at 438, 508 and 570 nm for the reaction in both perchlorate and nitrate medium. The reaction product was established [13] to be geometrically pure α-*cis*-$Co(EDDA)(C_2O_4)^-$ in both cases under these experimental conditions.

Rate measurements were performed at 386 nm in the thermostated cell compartment of a Zeiss PMQII spectrophotometer. Pseudo-first-order rate constants were estimated in the usual way, and the semi-logarithmic plots were linear for at least two half lives of the reaction.

Results and Discussion

Rate data for the anation of α-*cis*-$Co(EDDA)(OH_2)_2^+$ by $H_2C_2O_4$ in ClO_4^- and NO_3^- medium are summarized in Table I. It is obvious from this data that k_{obs} increases significantly in going from a perchlorate to a nitrate reaction medium. Furthermore, plots of k_{obs} *versus* [total oxalate] exhibit stronger curvature in the case of a nitrate medium than in a perchlorate medium.

Under the present experimental conditions the only reagent species in solution are α-*cis*-$Co(EDA)(OH_2)_2^+$ and $H_2C_2O_4$ [13, 16]. The suggested reaction mechanism [2, 12, 13], therefore, consists of the reactions

TABLE I. Rate Data for the Anation of α-*cis*-Co(EDDA)$(OH_2)_2^+$ by $H_2C_2O_4$. Temp = 70.0 °C, ionic strength = 2.0 *M*, [Co(III)] = 2.5×10^{-3} *M*, wavelength = 386 nm.

Reaction Medium	$[H^+]$ *M*	[total oxalate] *M*	k_{obs}[a] $\times 10^4$ sec^{-1}	k $\times 10^4$ sec^{-1}	Q M^{-1}
NO_3^-	2.0	0.1	1.51 ± 0.12	7.2 ± 0.2	2.64 ± 0.09
		0.2	2.52 ± 0.20		
		0.3	3.23 ± 0.25		
		0.4	3.67 ± 0.22		
	1.0	0.1	1.56 ± 0.10	6.8 ± 0.2	3.01 ± 0.15
		0.2	2.58 ± 0.21		
		0.3	3.19 ± 0.22		
		0.4	3.66 ± 0.25		
ClO_4^-	2.0	0.1	0.54 ± 0.05	6.6 ± 0.9	0.89 ± 0.15
		0.2	0.97 ± 0.03		
		0.3	1.42 ± 0.14		
		0.4	1.74 ± 0.21		
	1.0	0.1	0.55 ± 0.01	8.8 ± 0.3	0.66 ± 0.03
		0.2	1.04 ± 0.10		
		0.3	1.47 ± 0.11		
		0.4	1.84 ± 0.15		

[a] Mean value of between two and four kinetic runs.

$$\alpha\text{-}cis\text{-}Co(EDDA)(OH_2)_2^+ + H_2C_2O_4 \overset{Q}{\rightleftharpoons} \{Co(EDDA)(OH_2)_2^+ \cdot H_2C_2O_4\}$$

$$\Big\downarrow k$$

$$\alpha\text{-}cis\text{-}Co(EDDA)(C_2O_4)^- + 2H_3O^+$$

where Q is the ion-pair formation constant and k the interchange rate constant. No evidence for the presence of the intermediate species α-*cis*-Co(EDDA)$(OH_2)(C_2O_4H)$ was observed under the present experimental conditions, and the latter species probably undergoes a rapid (non-rate-determining) ring-closing reaction in acidic medium [1, 2, 17].

The rate law [3] for the suggested mechanism is

$$k_{obs} = \frac{kQ[H_2C_2O_4]}{1 + Q[H_2C_2O_4]}$$

which can be written in the double reciprocal form

$$(k_{obs})^{-1} = \{kQ[H_2C_2O_4]\}^{-1} + k^{-1}$$

The values of k_{obs} as a function of [total oxalate], *i.e.* $[H_2C_2O_4]$, in Table I were fitted to the above equation to estimate k and Q. Weyh and co-workers [13] reported that k = 4.3×10^{-4} sec^{-1} and Q = 2.9 M^{-1} at 69 °C, which is in close agreement with the values reported for k and Q in nitrate medium in Table I. Furthermore, the values of k are within experimental error limits not influenced by a change in reaction medium. The values of Q, however, decrease significantly in going from a nitrate to a perchlorate reaction medium. A similar tendency was observed [1] for the anation of *cis*-Co(en)$_2$$(OH_2)_2^{3+}$ by $H_2C_2O_4$, where the ion-pair formation constant decreases from 11 to 1.0 M^{-1} at 50 °C on going from a nitrate to a perchlorate reaction medium.

The average value of Q in perchlorate medium at 70 °C, *viz.* 0.8 ± 0.2 M^{-1}, indicates that very weak ion-pair formation occurs between α-*cis*-Co(EDDA)$(OH_2)_2^+$ and $H_2C_2O_4$, which is within expectation for such charged species. This value is indeed in close agreement with the value of 0.7 ± 0.2 M^{-1} reported [1] for the formation of the ion-pair *cis*-Co(en)$_2$$(OH_2)_2^{3+}\cdot H_2C_2O_4$ in perchlorate medium at 70 °C. The value of Q in nitrate medium, *viz.* 2.8 ± 0.3 M^{-1} (Table I), is significantly higher and partially represents the nitrate-catalytic effect as discussed in detail before [1]. The possible formation of a reactive five-coordinate intermediate under influence of nitrate ion, is not ruled out.

Acknowledgement

The author gratefully acknowledges financial support from the S.A. Council for Scientific and Industrial Research.

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16 See footnote 17 in ref. 1, from which it follows that [total oxalate] = $[H_2C_2O_4]$ under these conditions.

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