

Kinetics & Mechanism of Oxidation of Coordinated Formate by Chlorine

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Received 13 November 1980; revised 9 July 1981; rerevised and
accepted 25 May 1982

The kinetics of chlorine oxidation of formatopentaamminecobalt(III) perchlorate has been investigated in the temperature range 45 to 60°C. The reaction is first order each in the reactants. The reaction rate is enhanced by increasing pH and increasing [chloride]. Assuming Cl_2 and OCl^- to be the active oxidising species a probable mechanism has been proposed.

Though kinetics of chlorine oxidation of a number of substrates have been studied, similar studies on coordinated substrate species are lacking. Presently we have investigated the kinetics and mechanism of oxidation of coordinated formate in a substitution-inert complex like formatopentaamminecobalt(III) perchlorate by chlorine.

Formatopentaamminecobalt(III) perchlorate was prepared by following published method¹. The compound was characterised by estimating cobalt² and formate³. All solutions were prepared from reagent grade chemicals. Sodium perchlorate and sodium chloride solutions, standardised by ion exchange method using Dowex 50 WX-8 cation exchange resin, were used to maintain ionic strength and chloride concentration respectively. Acetic acid-sodium acetate buffer was used for adjusting pH. A standard solution of chlorine in water was used as oxidant. It was standardised iodometrically.

The course of the reaction, which was conducted in dark-coloured bottles, was followed by estimating unreacted chlorine iodometrically. Iodine did not react with formate complex under these conditions. Blank experiments indicated that the loss of chlorine under the present experimental conditions was only 3% and hence was neglected. The results of stoichiometric runs with five-fold excess of chlorine indicated that one mol of substrate consumes one mol of oxidant.

The reaction between chlorine and formate complex was studied under second order conditions and the kinetic results fitted best the second order rate equation. The observed second order rate constant, k_{obs} was independent of both the [substrate] and [oxidant] (Table 1) indicating that the reaction is first order in each reactant. The second order rate constant did not vary with change in ionic strength. The reaction rate was enhanced by increasing [chloride] and increasing pH. For example, increasing [chloride] from 0.05 to 0.4 mol dm^{-3} at 45°C when [complex] = [chlorine] = $3 \times 10^{-3} \text{ mol dm}^{-3}$ and pH = 4.4 increased $10^2 k_{\text{obs}}$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) from 0.79 to 2.02 while the increase was from 0.87 to 7.71 when pH was increased from 4 to 5.6 at $[\text{Cl}^-] = 0.1 \text{ mol dm}^{-3}$ all other conditions remaining the same.

Chlorine in aqueous solution exists as Cl_2 , HOCl and OCl^- as per the following equilibria 1 and 2.



The values of K_1 and K_2 at 25°C have been reported⁴ to be 4.2×10^{-4} and 3.4×10^{-8} respectively. Since water is present in large excess its concentration is constant; the value of $K (= K_1 [\text{H}_2\text{O}])$ was calculated to be 2.34×10^{-2} .

Using Eqs 1 and 2 it is possible to deduce Eqs 3 and 4 under the conditions pH = 4 to 5.6 and $[\text{Cl}^-] = 0.05$ -0.4 mol dm^{-3} .

$$[\text{Cl}_2]_f = \frac{[\text{H}^+][\text{Cl}^-][\text{Cl}_2]_T}{K} \quad \dots(3)$$

$$\text{and } [\text{OCl}^-] = \frac{K_2 [\text{Cl}_2]_T}{[\text{H}^+]} \quad \dots(4)$$

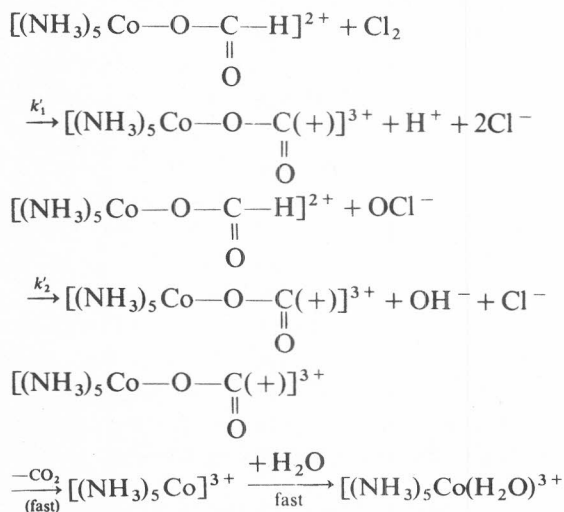
(where $[\text{Cl}_2]_f$ and $[\text{Cl}_2]_T$ are free and total chlorine concentrations respectively). The observed variation of the second order rate constant with $[\text{Cl}^-]$ and $[\text{H}^+]$ can be explained by assuming Cl_2 and OCl^- to be the oxidant species and the following mechanism (Scheme 1) for the reaction may be proposed:

Table 1—Effect of Varying Reactant Concentration on Rate

Temp. = $50 \pm 0.1^\circ \text{C}$, pH = 4.4, $[\text{Cl}^-] = 0.1 \text{ mol dm}^{-3}$							
$10^3 [\text{Complex}]$, mol dm^{-3}	3.0	4.0	6.0	8.0	10.0	3.0	3.0
$10^3 [\text{Chlorine}]$, mol dm^{-3}	3.0	3.0	3.0	3.0	3.0	4.0	6.0
$10^2 k_{\text{obs}}$, $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	1.94	1.76	1.74	1.89	1.88	2.04	2.06
	(± 0.02)	(± 0.24)	(± 0.20)	(± 0.30)	(± 0.31)	(± 0.28)	(± 0.06)

Table 2—Rate Constants and Activation Parameters

Temp. (°C) dm ³ mol ⁻³ s ⁻¹	$k_1 \times 10^{-2}$ s ⁻¹	$k_2 \times 10^7$ s ⁻¹	$\Delta H^\ddagger$ (kJ mol ⁻¹)		$\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	
			k_1 -path	k_2 -path	k_1 -path	k_2 -path
45 ± 0.1	8.57 ± 0.30	2.18 ± 0.12				
50 ± 0.1	21.88 ± 1.51	4.22 ± 0.68	120.1	159.6	131.9	51.7
55 ± 0.1	53.52 ± 4.52	10.95 ± 1.19				
60 ± 0.1	80.94 ± 1.32	16.15 ± 1.15				



Scheme 1

The rate of the reaction is given by Eq. (5),

$$\text{Rate} = k'_1 [\text{Cl}_2]_f [\text{S}] + k'_2 [\text{OCl}^-] [\text{S}] \quad \dots (5)$$

where [S] stands for the substrate concentration. Substituting the values of $[\text{Cl}_2]_f$ and $[\text{OCl}^-]$ from Eqs (3) and (4) in Eq. (5) one obtains Eq. (6).

$$\text{Rate} = [\text{S}] [\text{Cl}_2]_T \left(\frac{k'_1 [\text{H}^+] [\text{Cl}^-]}{K} + \frac{k'_2 K_2}{[\text{H}^+]} \right) \quad \dots (6)$$

The observed second order rate constant, k_{obs} is obviously given by

$$k_{\text{obs}} = k_1 [\text{H}^+] [\text{Cl}^-] + k_2 / [\text{H}^+] \quad \dots (7)$$

(where $k'_1/K = k_1$ and $k'_2 K_2 = k_2$)

Eq. (7) indicates that at constant pH, the plot of k_{obs} versus $[\text{Cl}^-]$ should be linear as has indeed been observed. Plot of k_{obs} versus $[\text{H}^+]$ or $1/[\text{H}^+]$ was non-linear as expected from the nature of Eq. (7). From the plot of k_{obs} versus $[\text{Cl}^-]$ at constant pH, the values of k_1 and k_2 were calculated (slope = $k_1 [\text{H}^+]$ and intercept = $k_2 / [\text{H}^+]$). k_1 , k_2 and the corresponding activation parameters calculated from Eyring equation are incorporated in Table 2.

Data presented in Table 2 indicate that k_1/k_2 is about 5×10^9 and the contribution of the k_2 path to the overall rate appears to be negligible. In this connection the following points may be considered. The values of k_1 and k_2 have been calculated from the k_{obs} versus

$[\text{Cl}^-]$ plot in $[\text{Cl}^-]$ range 0.05 to 0.4 mol dm⁻³ at pH = 4.4. Under such experimental conditions it is possible to show, using Eq. (7), that contribution of rate of the Cl_2 path to the overall rate ranges from about 30 to 75% and that of the OCl^- path from 70 to 25%. Thus the contributions of the Cl_2 and the OCl^- paths to the overall rate are comparable. But to decide the fate of the overall reaction, besides the rates, the activation parameters should also be considered. Table 2 indicates that the Cl_2 path (k_1 path) is associated with lower activation enthalpy which probably makes the reaction in the Cl_2 path much more favourable than that in OCl^- path. The greater reactivity of Cl_2 may be due to the fact that Cl_2 is a much stronger oxidant⁵ than OCl^- . The rate is almost unaffected by the variation in ionic strength. This further indicates that the major portion of the reaction proceeds via the Cl_2 path.

When carboxylatopentaamminecobalt(III) complexes are oxidised, the products formed are either $(\text{NH}_3)_5\text{Co}(\text{H}_2\text{O})^{3+}$ or Co^{2+} or both depending on the nature of the oxidant used and the life period of the reaction intermediate generated^{6,7}. In the present investigation $(\text{NH}_3)_5\text{Co}(\text{H}_2\text{O})^{3+}$ was shown to be the only reaction product³.

Compared to the k_1 path, the lower value of $\Delta S^\ddagger$ for the k_2 path implies that the transition complex is more ordered. The opposite charges associated with the substrate and the oxidant (OCl^-) are probably responsible for the formation of a more ordered transition complex for the k_2 path.

The authors are thankful to the UGC, New Delhi for financial assistance.

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