

Studies on the Kinetics of Mercuration of *o*-, *m*- and *p*-Hydroxy Benzoato-Pentaammine Cobalt (III) Complexes

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Abstract

The kinetics of mercuration of *o*-, *m*- and *p*-hydroxy benzoato pentaammine Co(III) perchlorate in aqueous perchloric acid have been studied using $\text{Hg}(\text{ClO}_4)_2$ as the mercurating agent. The second order rate constants are found to be independent of HClO_4 concentration within the range 0.10-0.25M. The average value of the rate constants at 40° for the *o*-, *m*- and *p*-hydroxy benzoato complexes and the activation energy (E_A) for the reaction are found to be $3.5 \times 10^{-2} \text{ sec}^{-1} \text{ M}^{-1}$ (13.4 K. cal/mole), $3.0 \times 10^{-3} \text{ sec}^{-1} \text{ M}^{-1}$ (12.3 K. cal/mole) and $2.0 \times 10^{-3} \text{ sec}^{-1} \text{ M}^{-1}$ (10.2 K. cal/mole) respectively.

Keywords: Aromatic, Kinetic, Diazo, Ligand, Nitration, Mercuration, Coupling, Stoichiometric, Estimated, Quantitatively, Thermostat, Neutralised, Complexes, Activation, Electrophilic, Dissociation, Chelate.

Introduction

AROMATIC ligands, with donor functions suitably situated in the aromatic system, on co-ordination to metal ions could, in principle, provide a number of systems in which the change in the reactivity of the aromatic ring towards electrophilic reagents on co-ordination to metal ions could be conveniently examined. The rates of iodination of 8-quinolinol and its derivatives^{1,2} have been reported to be significantly reduced, compared to free ligand anions, in presence of several metal ions. Similar observations have been made in the kinetic study of the diazo coupling of the Zn (II) chelate of 8-quinolinol-5-sulphonic acid³ and the mercuration of the Cu (II) chelate of 8-quinolinol⁴. With labile complexes of the type cited above it is rarely possible to interpret the rate data unequivocally in terms of the reactivity of the ligand which remains co-ordinated to the metal ion during the entire course of the reaction. Jones et.al⁵ have reported that rate of bromination of aniline in $[\text{Co}(\text{en})_2(\text{Aniline})\text{Cl}]^{2+}$ or $[\text{Co}(\text{en})_2(\text{Aniline})(\text{OH}_2)]^{3+}$ is retarded by a factor of 10^{10} as compared to free aniline. Gillard, Houghton and Tucker⁶ have also reported that 1,10-phenanthroline when co-ordinated to Rh(III) or Co(III) undergoes nitration at a faster rate as compared to the free ligand under comparable conditions. In the present paper the kinetics of the mercuration reaction of *o*-hydroxy-, *m*-hydroxy and *p*-hydroxy benzoatopentaammine cobalt(III) complexes in aqueous perchloric acid solution using Hg(II) perchlorate as the mercurating reagent are reported. These constitute a system of inter complexes from which the release of the phenolic acids⁷ are known to take place too slowly to complicate interpretation of the rate data in any way. Since Hg^{++} is known to be the attacking agent in aromatic mercuration⁸, mercuric perchlorate in aqueous perchloric acid, as used in the present investigation, would be expected to be a superior mercurating agent⁹. Hg(II) perchlorate in dilute aqueous solution may be assumed to be fully ionised and as such, its use as the mercurating agent would be expected to simplify the form of the rate expression.

Aim of the Study

The Kinetics of the mercuration reaction of *o*-hydroxy, *m*-hydroxy and *p*-hydroxy benzoatopentaammine cobalt (III) complexes in aqueous perchloric acid solution using Hg (II) perchlorate as the mercurating reagent are reported.



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Experimental

The hydroxy benzoatopentaammine cobalt(III) perchlorates were prepared by the method of Gould and Taube¹⁰. The purity of the complexes were checked by estimating their Co content¹¹. Anal Calc. for [(NH₃)₅Co (o-hydroxy benzoato)] (ClO₄)₂(I) : Co, 12.28. Found : Co. 12.40 ; [(NH₃)₅Co (m-hydroxy benzoato)] (ClO₄)₂ (II) : Co. 12.28. Found : Co. 12.07 ; [(NH₃)₅Co (p-hydroxy benzoato)] (ClO₄)₂(III) : Co, 12.28. Found : Co, 12.0.

Mercuric perchlorate solution was prepared by dissolving weighed amount of yellow mercuric oxide (G.R, E.M) in slightly more than the stoichiometric amount of 70% HClO₄(G.R, E.M). The mixture was warmed over a steam bath for 2 hours, allowed to cool to the room temperature and filtered. Hg content of the stock solution was estimated by E.D. T.A. titration using Erio-T indicator¹². In order to determine the free perchloric acid in the stock Hg (ClO₄)₂ solution, to a known volume of the solution was added excess of Dowex 50x8 cation exchange resin in the acid form. After allowing for the exchange to be complete, the solid particles were filtered on a bed of glass wool and washed quantitatively with distilled water. The total acid in the filtrate was estimated by titration against standard alkali. Hg⁺⁺ content of the solution being known. the free acid could be calculated.

All other reagents used were of B.D.H., A.R quality. Double distilled water was used for preparing all reagent solutions.

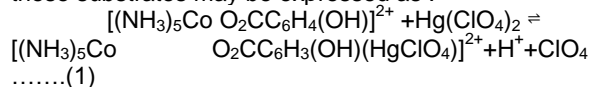
For measuring the rate of mercuration of the substrates a weighed amount of the complex was transferred in to 5 ml volumetric flask containing calculated amount of HClO₄ and NaClO₄ (to adjust the ionic strength). The contents were allowed to equilibrate inside a water thermostat maintained at a definite temperature. Hg(ClO₄)₂ solution of appropriate concentration was also allowed to equilibrate at the same temperature. After thermal equilibrium was attained, a definite volume of the Hg(ClO₄)₂ solution was quickly transferred into the reaction flask and the timer was started. The volume was made up with distilled water equilibrated at the same temperature, the contents were well-shaken and the reaction flask was quickly replaced inside the thermostat. 5.0 ml aliquots were withdrawn at preset time intervals and run into conical flasks containing 5.0 ml of 1M NaCl solution so as to quench the reaction. Excess HClO₄ in the mixture was neutralised with a few drops of 0.5M NaOH and then diluted with about 30 ml of

distilled water. Sufficient EDTA (0.01 M) solution so as to be in slight excess was run in, followed by 2.0 ml of a NH₄Cl – NH₄OH buffer (pH=10). Excess EDTA was back titrated with 0.01M ZnSO₄ solution using Erio-T indicator. EDTA is known to react¹³ only with the free HgCl₂. The concentration of the unreacted Hg(II) at different time Intervals, was, therefore, computed from the volume of ZnSO₄ consumed.

Results and Discussion

The kinetics of mercuration of all the three complexes has been carried out at 35, 40 and 45° and at an ionic strength of 0.3M. The concentration of the complex and Hg(ClO₄)₂ was kept fixed at 5.0 × 10⁻³M for all the runs. HClO₄ concentration in the reaction mixture was varied within 0.10-0.25M. Kinetic runs at lower acidities were not undertaken order to avoid the hydrolysis of Hg(ClO₄)₂. The concentration of free HClO₄ present in Hg (ClO₄)₂ was taken into account in calculating the total [H⁺] of the reaction mixtures. The rate constants (k_{obs}) for the mercuration reaction of the substrates were calculated from reasonably good second order plots. The k_{obs} values for the o, m and p-hydroxy benzoatopentaammine Co(III) complexes at different temperatures and [HClO₄] are collected in Table. The activation energies (E_A) for the mercuration reaction of the complexes were calculated from the slopes of the plot of log k_{obs} vs 1/T. The 'E_A' values for each of the complexes are collected in Table.

The overall reaction for the mercuration of these substrates may be expressed as :



Jones et. al⁴ obtained evidence for multiple mercuration (two-Hg Acetate in one ring and one-Hg Acetate in the other) of the bis-chelate of 8-hydroxy quinoline Cu(II) complex in the course of their preparative experiments. In the present experiments the mercuration kinetics was followed up to 50-60% reaction in each case. The second order rate constants were calculated on the assumption that the mercuration reaction of these substrates were first order with respect to the complex and first order with respect to Hg(ClO₄)₂. The fact that good straight line plots were obtained which yielded reasonably constant values of 'k_{obs}' leads us to believe that the reactions proceed in accordance Eq(1) and therefore, multiple mercuration does not take place under these experimental conditions.

Table
Kinetics of Mercuration of Hydroxy Benzoato⁻ Pentaammine Cobalt(III) Perchlorates

[Complex]= 5.0×10 ⁻³ M	[Hg(ClO ₄) ₂]= 5.0×10 ⁻³ M	Ionic strength= 5.0×10 ⁻³ M, 0.3M		
[HClO ₄],M	10 ³ k _{obs} Sec ⁻¹ M ¹	E _A , K.cal/mole		
	35°C	40°C	45°C	50°C
Complex : [(NH ₃) ₅ Co (o-hydroxy benzoato)] (ClO ₄) ₂				
0.10	2.8	3.5	5.9	—
0.15	3.1	3.5	5.3	—
0.20	2.8	3.5	5.7	13.4
0.25	2.7	—	—	—

Complex : [(NH ₃) ₅ Co (<i>m</i> -hydroxy benzoato)] (ClO ₄) ₂					
0.10	2.5	2.9	4.2	—	
0.15	2.2	3.1	4.5	—	
0.20	2.4	3.1	4.6	—	12.0
0.25	2.5	—	4.1	—	
Complex : [(NH ₃) ₅ Co (<i>p</i> -hydroxy benzoato)] (ClO ₄) ₂					
0.10	2.3	2.8	3.8	—	
0.15	2.3	2.6	3.8	—	10.2
0.20	2.3	2.6	3.8	—	

The second order rate constants for all the three substrates are seen to be practically independent of [H⁺] within range 0.10 to 0.25M. This indicates that the reverse reaction (Eq.I) is not kinetically significant under the present experimental conditions. The electrophilic substitution reactions of phenols have generally been interpreted in terms of the reactivity of the phenol and the phenate species. The dissociation constant of the phenolic group *o*-, *m*- and *p*-hydroxy benzoato pentaammine Co(III) complexes have been found to be 5.1×10^{-12} , 2.8×10^{-10} and 4.3×10^{-10} respectively at 30°¹⁴. In view of the very low dissociation constants of the phenolic group of these substrates, at the [H⁺] at which the present investigation has been carried out, the phenol form of the substrate would be expected to be the only reactive species. The independence of the 'k_{obs}' values of [H⁺] is in accordance with this assumption. Further, the acid independence of second order rate constants for the mercuration reaction of these substrates indicate that the ligands remain coordinated to the (NH₃)₅Co(III) centre during the course of the reaction.

The activation energy (E_A) for the mercuration reaction of the *o*-, *m*- and *p*-hydroxy benzoato complexes have been found to be 13.4, 12.0 and 10.2 K. cal/mole respectively. The activation energy for the mercuration of the bis-Cu(II) chelate of 8-hydroxy quinoline by mercuric acetate in glacial acetic acid has been reported to be 10 K.cal/mole⁴ and that for the mercuration of benzene and toluene under similar experimental conditions to be 21 K.cal/mole¹⁵. These values, though close to the results obtained in the present investigation, are not strictly comparable since different mercurating agents and different media have been used. Comparison of the activation energy data reported in this paper with those of corresponding free ligands would have been

more meaningful, but these could not be determined due to the low solubility of the Hg(II) salts of these hydroxy benzoic acids.

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References

1. C. BOSTIC, Q. FERNANDO and H. FREISER, *Inorg. Chem.*, 1963, 2, 232.
2. C. BOSTIC, Q. FERNANDO and H. FREISER, *Inorg. Chem.*, 1965, 4, 602.
3. K. D. MAGUIRE and M. M. JONES, *J. Amer. Chem. Soc.*, 1963, 85, 154.
4. N. K. CHAWLA and M. M. JONES, *Inorg. Chem.*, 1964, 3, 1549.
5. N. K. CHAWLA, D. G. LAMBERT and M. M. JONES. *J. Amer. Chem. Soc.*, 1969, 89, 557.
6. R.D. GILLARD, R. P.HOUGHTON and J. N. TUCKER, *Transition Met. Chem.*, 1976, 1, 67.
7. A. C. DASH and R. K. NANDA, *Inorg. Chem.*, 1973, 12, 2020.
8. C. K. INGOLD, 'Structure and Mechaism' in *Organic Chemistry*, G. Bell and Sons Ltd. London, 1963, p, 304.
9. W. J. KLAPPROTH and F. H. WESTHEIMER, *J. Amer. Chem. Soc.*, 1950, 72, 4461.
10. E. S. GOULD and H. TAUBE, *J. Amer., Chem., Soc.*, 1964, 86, 1318.
11. H. A. LAITINEN and L. W. BURDETT, *Anal., Chem.*, 1951, 23, 1268.
12. G. SCHWARZENBACH, 'Complexometric Titration', *Inter, Sci*, p. 87, 1957.
13. D. S. MATTESON and E. KRAINER, *J. Amer., Chem., Soc.*, 1968, 90, 7261.
14. H. C. BROWN and C. W. MCGARV, *J. Amer, Chem., Soc.*, 1955, 77, 2306.