Stability Constants of Palladium, Copper, Nickel, Zinc and Manganese Complexes of 3-Hydroxy-3-phenyl-1-p-chlorophenyltriazene

BY D. N. PUROHIT and N. C. SOGANI

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In recent years Sogani et al.[1-5] have reported hydroxytriazenes as a very useful class of chelating reagents. They possess common functional grouping -N(OH)-N=N-. The parent compoud of the series, 3-hydroxy-1,3-diphenyltriazene, is a highly selective reagent for palladium[1] and copper[2]. Substitution of different groups at different positions of the aryl nuclei of the present compound influenced the stabilities of resulting metal chelates. The present investigation deals with determination of stabilities of bivalent metal chelates of para chloro substituted hydroxytriazene, namely, 3-hydroxy-3-phenyl-1-*p*-chlorophenyltriazene, in 70% v/v dioxan-water mixture, by employing Bjerrum-Calvin pH titration technique.[6] Titrations were carried out in duplicate using 40 : 1 ratio of chelating agent to metal ion concentration.

Experimental

Chelating Agent Solution.—3-Hydroxy-3-phenyl-1-*p*-chlorophenyltriazene was prepared by employing the method given by Sogani et al.[3] Weighed amount of this compound was dissolved in 70% v/v dioxan-water mixture and diluted to give 0.04 M solution.

Standard Palladium, Copper, Nickel, Zinc, and Manganese Solutions.—Analytical grade reagents of palladium chloride, copper chloride, nickel sulphate, zinc oxide, and manganese sulphate were used for preparing standard solutions. After standardizing these solutions by usual classical methods, these were diluted to 0.002 M solution.

Sodium Hydroxide. — Approximately 0.1 M carbonate free sodium hydroxide was prepared and standardized with analytical grade potassium hydrogen phthalate. It was diluted to give 0.02 M solution.

Dioxan. — The B.D.H. dioxan was purified by Weissberger's method.[7]

Potentiometric Titrations.—The pH-titrations of the chelating agents with standard alkali solution in absence and in the presence of different metal ions were carried out by using Cambridge bench-type pH-meter which gave values accurate to 0.01 pH unit. The pH-meter was standardized before, and checked after, each titration with buffer solutions of pH 4.0 and 9.2. Electrode system consisted of glass electrode (pH range 1∼13) and saturated calomel-electrode as reference.

Ten milliliters of 0.04 M chelating agent solution in 70% v/v dioxan-water mixture was pipetted in a titration vessel. Sufficient amount of 0.02 M nitric acid was added to it to lower the pH to about

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[1] N. C. Sogani and S. C. Bhattacharya, *Anal. Chem.*, **28**, 81 (1956).

[2] N. C. Sogani and S. C. Bhattacharya, ibid., **28**, 1616 (1956).

[3] N. C. Sogani and S. C. Bhattacharya, *J. Indian Chem. Soc.*, **36**, 563 (1959).

[4] T. C. Jain, H. K. L. Gupta and N. C. Sogani, ibid., **37**, 531 (1960).

[5] H. K. L. Gupta and N. C. Sogani, ibid., **38**, 771 (1961).

[6] M. Calvin and N. C. Melchior, *J. Am. Chem. Soc.*, **70**, 3270 (1948).

[7] A. Weissberger and E. S. Proskauer, "Organic Solvents," Oxford (1935), p. 139.

2. Final ionic concentration was maintained at 0.1 M by adding 2.5 ml. of 2 M potassium chloride. When titrating in presence of metal ions, 5 ml. of 2×10^{-3} M metal solution were added at this stage. The total volume of the contents was made to 50 ml. by adding varying amounts of dioxan and distilled water in such proportions that it finally became 70% v/v dioxane-water mixture. It was titrated against 0.02 M sodium hydroxide. The temperature of the solution throughout the titration was maintained at 25±0.5°C. The pH-meter readings obtained at a given alkali addition in duplicate titrations were reproducible with a maximum variation of ±0.01 pH unit. The titration curves are given in Figs. 1 and 2.

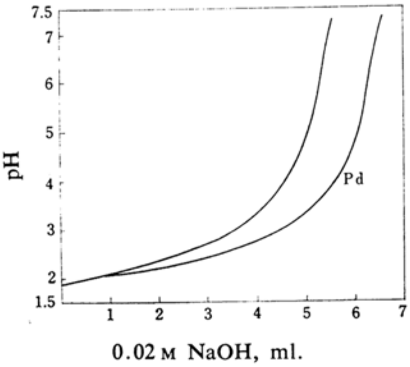
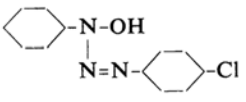


Fig. 1. Titration curve for



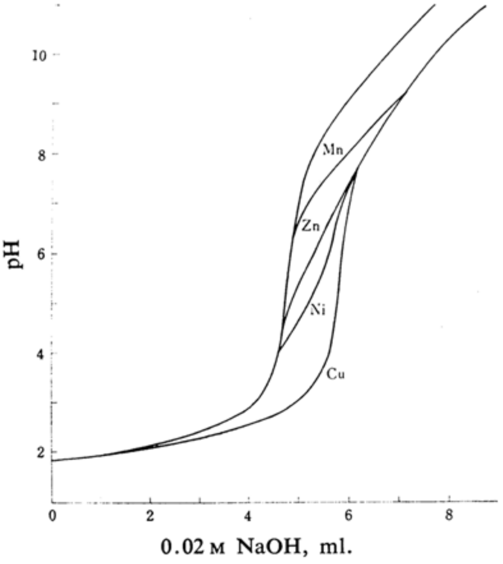
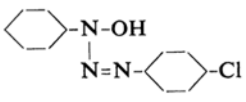


Fig. 2. Titration curve for



Calculations. — The horizontal distance between the reference titration curve and the curve obtained in presence of a metal ion gives the concentration of metal bound chelating agent. This value divided by the total concentration of metal ion gives the value for $\bar{n}$. In this way the values of $\bar{n}$ at different pH values were calculated.

At any pH, the value of free chelating ion concentration, $[T^-]$, was calculated from the total concentration of the chelation agent, and its dissociation quotient. This is based on the assumption that the amount of chelating agent over metal ion is so great that the removal of HT by chelation does not cause any significant change in the equilibrium: $HT \rightleftharpoons H^+ + T^-$. The pK_a value of 3-hydroxy-3-phenyl-1-*p*-chlorophenyltriazene has been determined spectrophotometricaly[8] as 10.72.

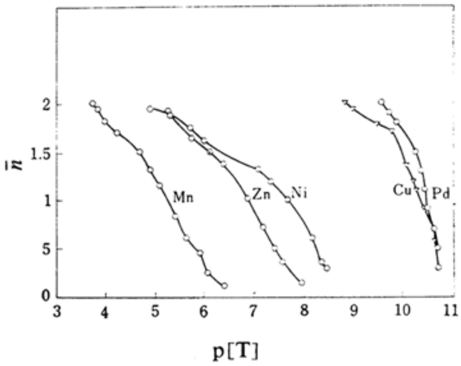
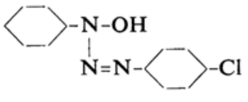


Fig. 3. Formation curves for metal chelates of



In calculating the values for $\bar{n}$ and $[T^-]$, the concentrations were corrected for changes in volume, produced by addition of alkali during titrations. In this way, a series of values for $\bar{n}$ and $[T^-]$, corresponding to different pH values, was obtained. The formation curves for metal chelates of 3-hydroxy-3-phenyl-1-*p*-chlorophenyltriazene are shown in Fig. 3. The values for stepwise stability constants and average stability constant i.e., $\log k_1$, $\log k_2$, and $\log K_{av}$ ($1/2\log K$) for different metal chelates were

TABLE I. STABILITY CONSTANTS OF METAL CHELATE OF 3-HYDROXY-3-PHENYL-1-*p*-CHLOROPHENYLTRIAZENE

Metal ion	$\log k_1$	$\log k_2$	$\log K_{av}$	$\log k_1k_2$
Palladium	10.70	10.25	10.47	20.95
Copper	10.67	9.98	10.35	20.65
Nickel	8.25	6.33	7.66	14.58
Zinc	7.41	6.12	6.84	13.53
Manganese	5.83	4.67	5.25	10.50

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[8] D. N. Purohit, Ph. D. Thesis, University of Rajasthan, Jaipur (India), 1963.

read directly from the formation curves and are given in Table I. K is the overall stability constant.

Discussion

The consumption of alkali during the course of titration may be due to the chelating agent, the hydrolysis of metal ion, and the protons of the chelating agent liberated in complex formation.

The chelating agent under study is a very weak acid ($pK_a=10.72$) Thus, the proton of the chelating agent as such is not in a titrable form. Hydrolyses of these metal ions have been studied in 70% v/v dioxan-water mixture.[8] The pH for $\bar{n}=1.5$ in all the cases is lower than the pH at which the hydrolysis of these metal ions start. Hence, hydrolyses of these metal ions do not interfere in the stability measurements. Moreover, there was no precipitation during chelation titrations, ruling out the possibility of appreciable hydrolyses of these metal ions in the presence of large excess of the chelating agent.

Thus, the consumption of an excess of alkali in chelation titration over the simple chelating agent titration is due to protons of the chelating agent liberated during the complex formation. This may be represented as:

$$M^{2+} + HT + OH^- \rightleftharpoons MT^+ + H_2O \qquad (1)$$

$$MT^+ + HT + OH^- \rightleftharpoons MT_2 + H_2O \qquad (2)$$

The order of stability of hydroxytriazene metal chelates has been found as palladium > copper > nickel > zinc > manganese.

Summary

Stabilities of palladium, copper, nickel, zinc, and manganese chelates of 3-hydroxy-3-phenyl-1-*p*-chlorophenyltriazene have been determined in 70% v/v dioxan-water mixturre by employing Bjerrum-Calvin pH titration technique. The titration medium was maintained at a constant ionic strength (0.1 M, potassium chloride) and at a temperature, 25±0.5°C. Log K, palladium 20.95, copper 20.65, nickel 14.58, zinc 13.53, and manganese 10.50.

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Chemistry Department
University of Rajasthan
Jaipur, India