The Stability Constants of the Palladium, Copper, Nickel, Zinc and Manganese Chelates of 3-Hydroxy-3-phenyl-1-o-tolyltriazene and -1-p-tolyltriazene

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(Received February 14, 1964)

In a previous communication,[1] the stabilities of the palladium, copper, nickel, zinc and manganese chelates of 3-hydroxy-3-phenyl-1-*p*-chlorophenyltriazene have been reported. The present investigation will deal with the influence of methyl groups at ortho and para positions of the parent compounds upon the stabilities of the metal chelates formed by them.

Experimental

Solutions of the Chelating Agents.—3-Hydroxy-3-phenyl-1-*o*-tolyltriazene and 3-hydroxy-3-phenyl-1-*p*-tolyltriazene were prepared by employing the method of Sogani et al.[2,3] Weighed amounts of these compounds were dissolved in a 70% v/v dioxane-water mixture, and the solution was diluted to give a 0.04 M solution. Solutions of 0.002 M palladium, copper, nickel, zinc and manganese ions and 0.02 M sodium hydroxide were prepared by usual, classical methods.

Potentiometric Titration. — Ten milliliters of a 0.04 M chelating agent solution in a 70% v/v dioxane-water mixture were pipetted in a titration vessel. A sufficient amount of 0.02 M nitric acid was added to it to lower the pH to about 2. The final ionic concentration was maintained at 0.1 M

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[1] D. N. Purohit and N. C. Sogani, This Bulletin, 37, 476 (1964).

[2] T. C. Jain, H. K. L. Gupta and N. C. Sogani, *J. Indian Chem. Soc.*, 37, 531 (1960).

[3] D. N. Purohit, Ph. D. Thesis, University of Rajasthan, Jaipur, India, 1963.

by adding 2.5 ml. of 2 M potassium chloride. When titrating in the presence of metal ions, 5 ml. of a 0.002 M metal solution were added at this stage. The total volume of the contents was increased to 50 ml. by adding varying amounts of dioxane and distilled water in such proportions that it finally became a 70% v/v dioxane-water mixture. It was then titrated against 0.02 M sodium hydroxide. The temperature of the solution throughout the titration was maintained at 25 ± 0.5°C. The titration curves are given in Figs. 1 and 2.

Calculations. — The pK_a values of 3-hydroxy-3-phenyl-1-*o*-tolyltriazene and 3-hydroxy-3-phenyl-1-*p*-tolyltriazene have been determined spectrophotometrically as 11.55 and 11.78 respectively. These values were used for calculating free chelating ion concentrations at different pH values. The values of $\bar{n}$ were calculated as has been described eariler.1) The formation curves for metal chelates are given in Figs. 3 and 4. The values of log k_1 and log k_2

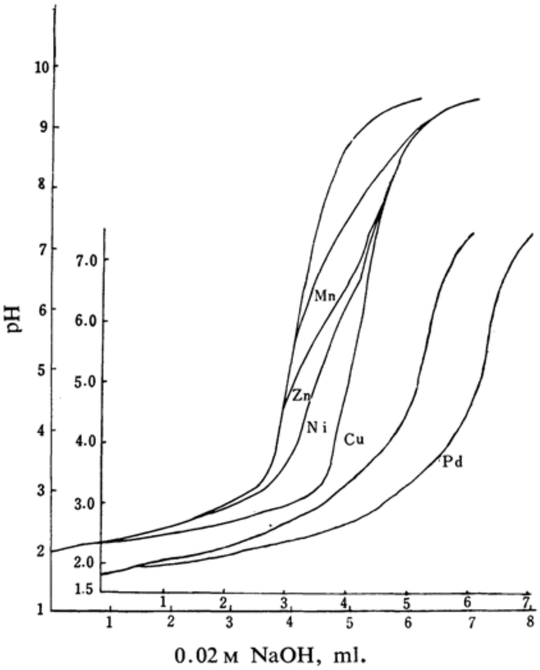
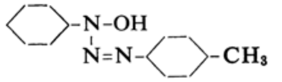


Fig. 1. Titration curves for



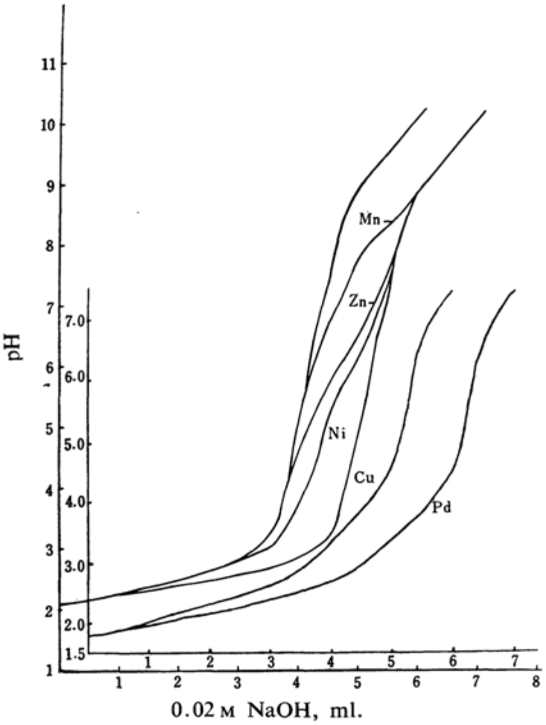
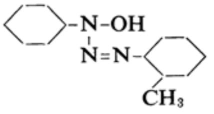


Fig. 2. Titration curves for



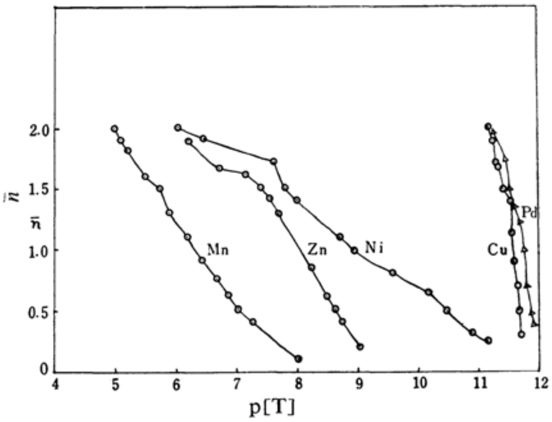
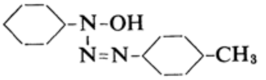


Fig. 3. Formation curves for metal chelates of



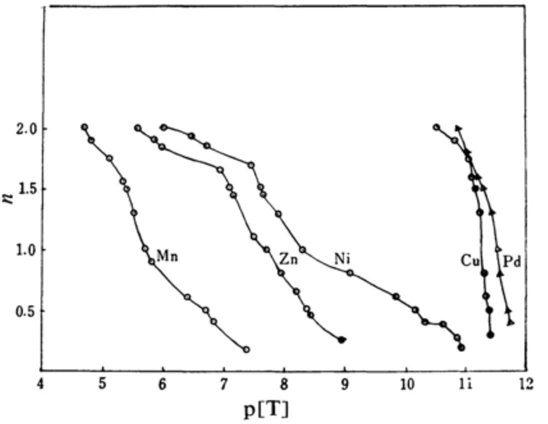


Fig. 4. Formation curves for metal chelates of

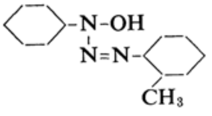


Table I. The stability constants of the metal chelates of 3-hydroxy-3-phenyl-1-*o*-tolyltriazene and 3-hydroxy-3-phenyl-1-*p*-tolyltriazene

Metal	3-Hydroxy-3-phenyl-l-*o*-tolyltriazene		3-Hydroxy-3-phenyl-1-*p*-tolyltriazene	
	$\log\beta_1$ ($\log k_1$) (first stability const.)	$\log\beta_2$ ($\log k_1k_2$) (over all stability const.)	$\log\beta_1$	$\log\beta_2$
Palladium	11.70	22.97	11.89	23.35
Copper	11.35	22.47	11.69	23.09
Nickel	10.17	17.76	10.46	81.23
Zinc	8.38	15.46	8.62	15.99
Manganese	6.68	12.07	7.02	12.74

for different metal chelates were read directly from the formation curves; they are given in Table I.

Discussion

An examination of the titration curves will show that curves for hydroxytriazenes in the presence of metal ions lie considerably below the simple chelating agent curves. This is due to the liberation of hydroxytriazene protons during complex formation. The chelate formation of palladium starts at pH 1.9; that of copper, at pH 2.0; that of nickel, at pH 2.6; that of zinc, at pH 4.5, and that of manganese, at pH 5.7. This corresponds to the order of stabilities of the hydroxytriazene chelates of these metals.

For the sake of simplicity, only the stabilities of palladium chelates with different hydroxytriazenes are discussed. A comparison of the values of the overall stability constants of the palladium chelates of para-chloro-substituted (reported earlier, $\log\beta_2=20.95$), ortho- and para-methyl-substituted ($\log\beta_2=22.97$ and 23.35 respectively) with the parent hydroxytriazene(3) ($\log\beta_2=22.66$) reveals that, while the chloro substitution lowers the stability of the resulting chelate, the methyl substitution increases it. The $-$I effect of the halogen lowers the pK_a value of the chloro-substituted hydroxytriazene (pK_a of parent compound$=11.41$, and chloro-substituted, $=10.72$) and hence the stability of its metal chelates.

The stabilities of the chelates given by methyl-substituted compounds are higher than those of the parent hydroxytriazene. This is due to the $+$I effect (electron pushing) of the methyl group. A hyperconjugation effect for the methyl group would have a similar effect. The hydroxytriazene with a methyl group at the ortho position should have been a weaker acid and formed more stable complexes than its para isomer because of the nearness of the $+$I effect of the group on –OH-bearing nitrogen atoms. However, the contrary is true. The greater acidity and lesser stability of the chelates of the ortho isomer compared to the para isomer are due to the ortho effect of the methyl group.

Summary

The stabilities of the palladium, copper, nickel, zinc and manganese chelates of 3-hydroxy-3-phenyl-1-*o*-tolyltriazene and 3-hydroxy-3-phenyl-1-*p*-tolyltriazene have been determined in a 70% v/v dioxane-water mixture and at an ionic strength of 0.1 M potassium chloride, by employing the Bjerrum-Calvin pH titration technique.

The authors wish to express their gratitude to Professor R. C. Mehrotra for providing facilities in the department. They are also grateful to the University Grants Commission for granting a research scholarship to one of them (D. N. Purohit).

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