

strength of 0.1 *N*. This value and those obtained in the present investigation are in qualitative agreement with values found for other uni-bivalent exchanges.¹⁰

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[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Molarity Quotients of Some Metal Complexes of Pyrazolone Dyes¹

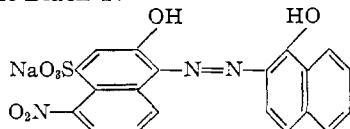
BY FRED A. SNAVELY,² W. CONARD FERNELIUS AND B. P. BLOCK

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The relative stabilities of the metal derivatives of simple azo pyrazolone compounds have been measured potentiometrically in 75 volume % dioxane. The order of decreasing stability of the metal derivatives, Cu > Ni > Co > Zn, agrees with the orders already reported for other bidentate groups. The log *Q* values for the compounds of a given metal ion are proportional to the *p*_{QD} values for the chelating agents. Three new metal derivatives of the azo compounds were prepared.

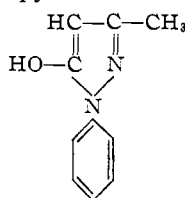
Introduction

Aryl azo compounds which contain an acidic or basic group *ortho* to the azo linkage are well known for their ability to form coordination compounds with metal ions. In spite of the many applications of these compounds in the dyeing of fabrics³ and in the preparation of organic pigments,⁴ almost no measurements have been made on the inherent stability of these metal derivatives toward dissociation into their constituent ions. The only measurements of this type recorded are those of Schwarzenbach and Biederman⁵ for the magnesium and calcium derivatives of dyes of the type of Eriochrome Black T.⁶



The work reported here was part of a general study undertaken to determine (1) the adaptability of the Bjerrum⁷-Calvin⁸ techniques to the study of the metal derivatives and (2) the order of stability among a series of metals with a given azo compound and among a series of azo compounds with a given metal ion.

The study of the simple azo derivatives of 1-phenyl-3-methyl-5-pyrazolone is reported here.



(1) From a portion of a thesis presented by Fred A. Snavely in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1952.

(2) Franklin and Marshall College, Lancaster, Pa.

(3) For reviews see H. Pfitzner, *Angew. Chem.*, **62**, 242 (1950); W. Wittenberg, *Meiliand Textilberichte*, **32**, 454 (1951).

(4) L. S. Pratt, "Chemistry and Physics of Organic Pigments," John Wiley and Sons, New York, N. Y., 1947, pp. 75-153.

(5) G. Schwarzenbach and W. Biederman, *Helv. Chim. Acta.*, **31**, 678 (1948).

(6) No. 203 in Rowe, "Colour Index," Society of Dyers and Colourists, Bradford, 1924.

(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

(8) M. Calvin and K. W. Wilson, *THIS JOURNAL*, **67**, 2003 (1945).

Experimental

Preparation of Materials.—The azo compounds were prepared by coupling the appropriate diazotized amines to 1-phenyl-3-methyl-5-pyrazolone. They were recrystallized from hot dioxane.

I. 1-Phenyl-3-methyl-4-(phenylazo)-5-pyrazolone: orange needles, m.p. 155°, reported⁹ 155°.

II. 1-Phenyl-3-methyl-4-(4-methylphenylazo)-5-pyrazolone: orange needles, m.p. 138-140°, reported¹⁰ 136-37°.

III. 1-Phenyl-3-methyl-4-(4-chlorophenylazo)-5-pyrazolone: long, bright orange needles (like colored glass wool), m.p. 141-142°, reported¹⁰ 141-142°.

IV. 1-Phenyl-3-methyl-4-(4-nitrophenylazo)-5-pyrazolone: red-orange platelets, m.p. 198-200°, reported¹¹ 198-99°.

Each of the azo compounds was tested for purity by use of a chromatographic column packed with 100/200 mesh Florisil.¹² Development of the chromatogram using dioxane showed only one band in each case. Determination of the neutral equivalents by potentiometric titration gave the values in Table I.

TABLE I

Dye	Wt. of	Milliequiv. NaOH	Exptl. neut. equiv.	Theor. neut. equiv.
I	0.2781	1.00	278	278.3
II	.2923	1.00	292	292.3
III	.3137	1.00	314	312.8
IV	.3234	1.00	323	323.3

Potentiometric Titrations.—The titrations were performed at 30.0 ± 0.1° in 75% dioxane as described previously.¹³

Titrations with iron(II) and cobalt(II) were carried out under a nitrogen atmosphere; all other titrations at *pH* values above 9 were made under a nitrogen atmosphere. The solutions were so adjusted that in 100 ml. of solution there was 1.00 mmole of dye, 1.482 mmoles of nitric acid and 0.210 mmole of metal nitrate. In general, no more electrolyte could be added without salting out the azo compounds or their metal derivatives. A 0.9983 *N* solution of sodium hydroxide was added in increments of about 0.05 to 0.10 ml., and readings were taken on the *pH* meter after each addition until a constant value was obtained. With this procedure, results were found to be reproducible. The average time per titration was about 2 to 2.5 hr.

In 75 volume % dioxane it was necessary to calibrate the *pH* meter. Van Uitert and Haas¹⁴ have shown that a cell containing a glass electrode measures hydrogen ion activity in dioxane-water solutions as defined by the hydrogen electrode and that at a given salt concentration an empirical

(9) M. Bockmuhl, *Med. u. Chem. Abhandl. med.-chem. Forschungsstätten. Farberind.*, **3**, 294 (1936); *C. A.*, **31**, 5797 (1937).

(10) A. Lapworth, *J. Chem. Soc.*, 1114 (1903).

(11) P. Karrer and E. B. Hershberg, *Helv. Chim. Acta*, **17**, 1014 (1934).

(12) Obtainable from the Floridon Co., Warren, Pa.

(13) B. E. Bryant, W. C. Fernelius and B. E. Douglas, *THIS JOURNAL*, **75**, 3784 (1953).

(14) L. G. Van Uitert and C. G. Haas, Jr., *ibid.*, **75**, 451 (1953).

calibration $-\log [H^+] = B + \log U_H$ holds over a range of meter readings from 2 to 11 ($[H^+]$ is the stoichiometric concentration of hydrogen ion in solution, B is the meter reading and $\log U_H$ is the correction factor).

The pH meter was calibrated by titrating an aqueous solution of known nitric acid content with dioxane. The values obtained in this fashion were checked against a titration of dioxane with a 0.10 N nitric acid solution.

The small change in the composition of the solution caused by titrating with aqueous sodium hydroxide can produce an error of ± 0.03 in the empirical calibration. The addition of 0.40 ± 0.03 to the reading of the pH meter gives a value which is equal to the negative logarithm of the hydrogen ion concentration.

Calculations.—The molarity quotients¹⁵ were calculated by the method of Block and McIntyre.¹⁶

Discussion

Representative titration curves with the azo compounds I and IV are given in Figs. 1 and 2. It is to be noted that the titration buffer zones with copper(II) ion present show that 2 hydrogen ions

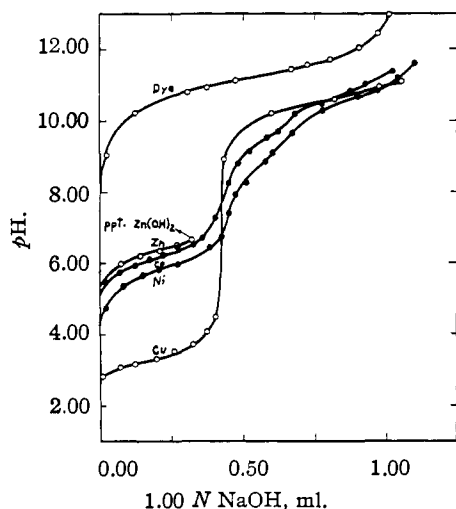


Fig. 1.—Titration curves of 1-phenyl-3-methyl-4-(phenylazo)-5-pyrazolone with metal nitrates.

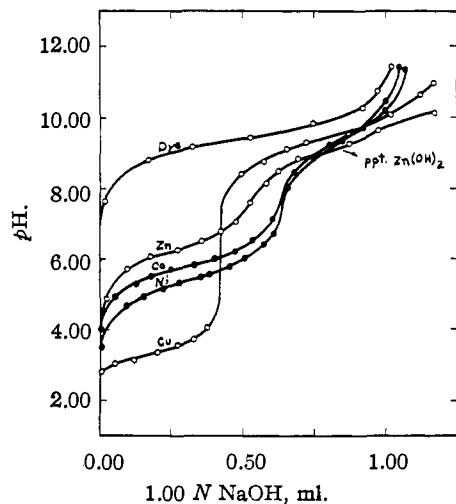


Fig. 2.—Titration curves of 1-phenyl-3-methyl-4-(4-nitrobenzeneazo)-5-pyrazolone with metal nitrates.

are liberated per metal ion or that a 2:1, dye to metal, compound is formed. The same type of compound forms with nickel(II) and cobalt(II). However, the latter ions, as well as Zn^{++} with dye IV also form 3:1 metal derivatives. This tendency is so great that with compound IV there is only one buffer zone of coordination. With the azo compounds other than IV the zinc derivatives are poorly defined and their formation buffer zones lie just below that of the formation of zinc hydroxide. In fact, in all cases a precipitate is obtained before the completion of the zinc titrations. Thus, any $\log Q$ values reported for the zinc derivatives are approximations.

The formation curves,⁷ \bar{n} plotted against pCH^- , are shown in Figs. 3, 4, 5 and 6. The successive formation quotients listed in Table II are an average of those evaluated by using various sets of \bar{n} and pCh^- values. The values for $\log Q_{av(1,2)}$ are taken from the formation curves where $\bar{n} = 1.00$. The values for $\log Q_{av(1,2,3)}$ are taken from the formation curve at $\bar{n} = 1.50$. In all but one case \log

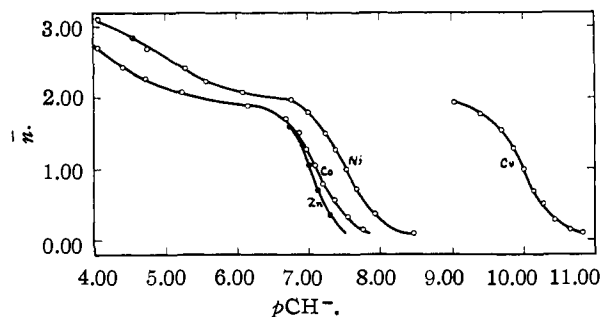


Fig. 3.—Formation curves with 1-phenyl-3-methyl-4-(benzeneazo)-5-pyrazolone with metal nitrates.

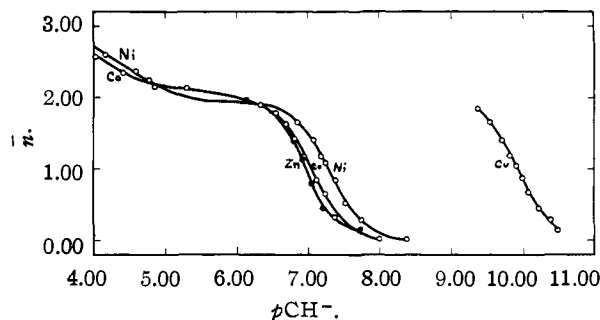


Fig. 4.—Formation curves with 1-phenyl-3-methyl-4-(4-methylbenzeneazo)-5-pyrazolone and metal nitrates.

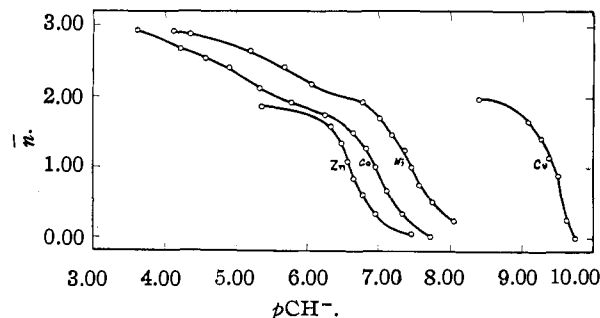


Fig. 5.—Formation curves with 1-phenyl-3-methyl-4-(4-chlorobenzeneazo)-5-pyrazolone and metal nitrates.

(15) R. M. Izatt, C. G. Haas, Jr., B. P. Block and W. C. Fernelius, *J. Phys. Chem.*, **58**, 1133 (1954).

(16) B. P. Block and G. H. McIntyre, Jr., *THIS JOURNAL*, **75**, 5667 (1953).

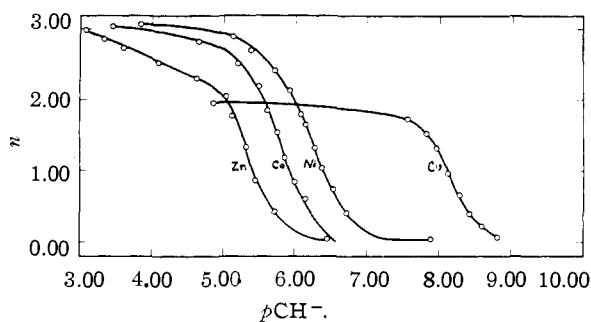


Fig. 6.—Formation curves with 1-phenyl-3-methyl-4-(4-nitrobenzeneazo)-5-pyrazolone and metal nitrates.

Q_2 is distinctly greater than $\log Q_1$. Note that in cases where N is equal to 3 for compound IV the three constants in two instances are found to be quite close together. The fact that $\log Q_2$ exceeds $\log Q_1$ can probably be explained on the basis that MCh_2 is a neutral entity and that MCh_2 has more symmetry than MCh^+ .

Dye	Metal	$n = 1$	$\log Q_n$ $n = 2$	$n = 3$	$\log Q_{av}$	$\log Q_{av}$ at $n = 1$
I	Cu	9.8	10.2		10.0	10.0
	Ni	7.3	7.7		7.5	7.5
	Co	6.7	7.55		7.1	7.1
II	Cu	9.4	10.4		9.9	9.9
	Ni	6.9	7.6		7.25	7.3
	Co	6.5	7.6		7.15	7.05
III	Cu	7.8	10.5		9.15	9.15
	Ni	6.6	7.7		7.15	7.15
	Co	6	ca. 7			6.65
IV	Cu	7.9	8.4		8.15	8.1
	Ni	6.3	6.35	5.8	6.15	6.2 ^a
	Co	5.3	6.5	5.3	5.7	5.8 ^a
	Zn	5.1	5.6	4.4	5.0	5.3 ^a

^a $\log Q_{av}$ at $n = 1.5$.

Dye	Color in acid soln.	pQ_D	Color in basic soln.
I	Yellow orange	11.64	Darker orange
II	Yellow orange	11.50	Darker orange
III	Light orange	10.80	Darker orange
IV	Light orange	9.80	Dark red

Dye	Metal	Color	M.p., °C.	Reptd. M.p., °C.	C	Theoretical H	N	C	Found H	N
I	Cu	Brown microcrystalline powder	226-228	228 ¹⁸	62.17	4.28	18.13	62.49	4.51	18.1
	Zn	Yell. crystalline powder	267-270		61.99	4.23	18.08	61.87	3.94	17.8
II	Ni	Red crystalline powder	269-272		63.44	4.70	17.42	62.76	4.72	17.2
IV	Cu	Red purple needles	268-270		54.27	3.42	19.78	54.51	3.56	20.0

The order of acidity for the azo compounds studied is as follows: IV > III > II > I (see Table III). The pQ_D of the azo compounds I and II are about the same. As one would predict, the nitro-substituted azo compound yields the strongest acid. In fact, the electrophilic character of the chloro

and nitro group are well demonstrated by the significant increase in the acidity of compounds III and IV as compared with I and II.

A plot of the negative logarithm of the acid dissociation constant, pQ_D against the logarithm of the average formation quotient, $\log Q_{av}$, for these compounds shows a direct relationship, in that the stronger the acid the weaker its power of coordination (see Fig. 7). These results agree with those

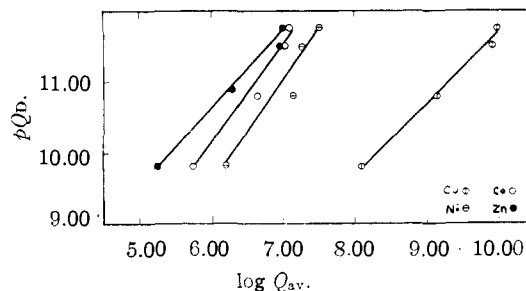


Fig. 7.—Pyrazolone dyes.

of other investigators using different chelating agents. That is, there is a direct relationship between the tightness with which a proton is held by a chelating agent and the tightness with which a metal ion is held.

The decreasing order of stability for the metal derivatives of any one azo compound is Cu > Ni > Co > Zn. This is in complete harmony with previously reported stability series.¹⁷

The solutions, after titration, were slowly evaporated over a steam-bath until a solid phase was obtained. The four derivatives reported (Table IV) were the only crystalline compounds of constant composition obtained by this method. In all cases only 2:1 compounds were isolated. Attempts to isolate the 3:1 metal derivatives yielded only the 2:1 compounds.

Cadmium, manganese(II) and iron(II) ions were tried without success. A color change was observed in the titrations with iron(II) but in each case a green flocculent precipitate was obtained which probably was iron(II) hydroxide.

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Chemical Company for financial support in carrying out this investigation.

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(17) See F. A. Snavely and W. C. Fernelius, *Science*, **117**, 15 (1953), for a partial listing of other investigators.

(18) G. B. Crippa and M. Long, *Gazz. chim. ital.*, **61**, 99 (1931).