plexes may lead to the blue cobalt(II)–thiocyanate complex.[21]

With respect to the autoxidation of cobalt–azide solutions it should be mentioned that it can be considerably accelerated by very small amounts of soluble sulfites. On the basis of this phenomenon spot tests for the detection of both cobalt and sulfites have been developed.[22] Studies on the nature of the cobalt–azide oxidized solutions are in course.

Acknowledgments.—The author is greatly indebted to the Rockefeller Foundation and Conselho Nacional de Pesquisas (Rio de Janeiro) for grants supporting this work.

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[21] W. A. C. Campen and H. Geerling, *Chem. Weekblad*, **48**, 193 (1952); *C. A.*, **46**, 7462 (1952).

[22] P. Senise, *Mikrochim. Acta*, 640 (1957).

SÃO PAULO, BRAZIL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FRANKLIN AND MARSHALL COLLEGE]

Metal Derivatives of Aryl Azo Pyrazolone Dyes. III. Molarity Quotients of *para*- and *meta*-Substituted Pyrazolone Dyes[1]

BY FRED A. SNAVELY AND BRUCE D. KRECKER

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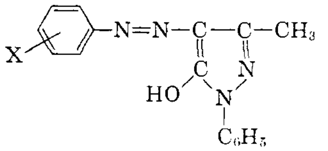
The relative stabilities of the metal derivatives of simple aryl azo pyrazolone compounds have been measured potentiometrically in 75 volume % dioxane. The order of decreasing stability, Cu > Ni > Co > Zn, agrees with previously reported pyrazolone dyes. The log Q_2 values are greater than the log Q_1 values. Stability of the copper derivatives of the *para*-substituted dyes increases in the order: NO_2 < (Cl,Br) < I < OCH_3 < CH_3 < H. Four new copper derivatives of the azo compounds were prepared.

Introduction

In order to continue the study of the effect of *ortho*-, *meta*- and *para*-substitution of various groups on the stability of the metal derivatives of aryl azo pyrazolone compounds, these dyes were prepared and studied



where X represents *p*-Br, *p*-I, *m*-CH_3, *m*-Br, *m*-Cl and *m*-NO_2

Experimental

Preparation of the Azo Compounds.—The azo compounds were prepared by senior honors students[2] by coupling the appropriate diazotized amines to 1-phenyl-3-methyl-5-pyrazolone. The dyes were recrystallized from hot dioxane.

(I) 1-phenyl-3-methyl-4-(3-methylphenylazo)-5-pyrazolone, orange-red needles, m.p. 119–120°.

(II) 1-phenyl-3-methyl-4-(4-iodophenylazo)-5-pyrazolone, orange needles, m.p. 155–156°.

(III) 1-phenyl-3-methyl-4-(3-bromophenylazo)-5-pyrazolone, tiny orange crystals, m.p. 157–158°.

(IV) 1-phenyl-3-methyl-4-(4-bromophenylazo)-5-pyrazolone, fibrous, orange crystals, m.p. 152–153.5°; reported[3] 152–153°.

(V) 1-phenyl-3-methyl-4-(3-chlorophenylazo)-5-pyrazolone, orange-red fibers, m.p. 134–135°.

(VI) 1-phenyl-3-methyl-4-(3-nitrophenylazo)-5-pyrazolone, orange needles, m.p. 183–184°.

Each of the azo compounds was tested for purity as previously reported.[4] Determination of neutral equivalents gave values within 0.5% of the calculated values.

Potentiometric Titrations.—The titrations were performed at 30.0 ± 0.1° in 75% dioxane as described previously.[4] The solutions were so adjusted that in 100 ml. of solution there was 1.00 mmole of dye, 0.913 mmole of nitric acid and 0.200 mmole of metal nitrate. A 0.9982 *N* solution of sodium hydroxide was used. The meter reading correction factor ($\log U_H$) equals 0.45.

TABLE I

MOLARITY QUOTIENTS OF THE METAL DERIVATIVES OF THE PYRAZOLONE DYES

Dye	pQ_D	Metal	Log Q_n			Log Q_{av} at $n = 1$
			$n = 1$	$n = 2$	$n = 3$	
I	11.54[a]	Cu	9.0	10.4		9.7
		Ni	7.3	7.5	4.6[b]	7.4
		Co	6.3	7.5	3.8[b]	6.9
II	10.88[a]	Cu	9.1	9.8		9.45
		Ni	6.6	7.7	4.9[b]	7.15
		Co	6.0	7.6	4.6[b]	6.8
		Zn	5.4	7.3		6.4
III	10.80[a]	Cu	9.2	9.6		9.4
		Ni	6.1	8.2	5.2[b]	7.15
		Co	6.1	7.4	4.7[b]	6.8
		Zn	5.3	7.4		6.35
IV	10.78[a]	Cu	8.9	9.9		9.4
		Ni	6.3	7.8	5.0[b]	7.1
		Co	6.4	6.9	4.4[b]	6.7
		Zn	5.8	6.8		6.35
V	10.81[a]	Cu	9.0	9.6		9.3
		Ni	6.5	7.7	5.3[b]	7.1
		Co	6.1	7.2	4.6[b]	6.6
		Zn	5.9	6.5		6.2
VI	10.23[a]	Cu	8.4	9.4		8.9
		Ni	6.9	7.3	5.7	7.2[c]
		Co	5.8	7.4	5.3	6.6[c]
		Zn	5.3	6.6	3.6	5.95[c]

[a] The color of the dyes in solution in either the dissociated or the undissociated form was the same, a light orange. (Exception dye VI. Acid form orange, base form red.) [b] Values taken from the formation curves at $\bar{n} = 2.5$. [c] Values taken from the formation curves at $\bar{n} = 1.5$.

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[1] From a portion of a thesis presented by Bruce D. Krecker in partial fulfillment of the requirements for the degree of Master of Science, June, 1957.

[2] M. M. Chamberlain and C. E. Glassick, Senior Honors Dissertations, Franklin and Marshall College, 1953.

[3] A. Lapworth, *J. Chem. Soc.*, 1124 (1903).

[4] F. A. Snavely, W. C. Fernelius and R. P. Block, THIS JOURNAL, **79**, 1028 (1957).

[5] B. P. Block and G. H. McIntyre, Jr., THIS JOURNAL, **75**, 667 (1953).

TABLE II

Dye	Color	M.p., °C.	Theoretical, % C	H	N	Cu	Found, % C	H	N	Cu
I	Dark brown crystals	225–227			17.34	9.83			17.5	9.7
III	Brown microcrystalline powder	238–239	49.52	3.12	14.45		49.88	3.34	13.90	
IV	Brown crystalline powder	258–259	49.52	3.12	14.45		49.88	2.84	15.96	
VI	Brown crystalline powder	242–244			19.78	8.97			19.6	8.9

Calculations.—The molarity quotients were calculated by the method of Block and McIntyre.[5] At least 4 sets of $\bar{n}$ and pCh^- values were used.

Discussion

The molarity quotients, Table I, show the same trend noted with other simple pyrazolone dyes. The strongest acid (the *meta*-nitro dye) forms quite stable 3:1, dye to metal, nickel(II), cobalt(II) and zinc derivatives. The other dyes form relatively weak 3:1 derivatives and their zinc 2:1 derivatives are poorly defined. Chloro and bromo substitution in both the *meta*- and the *para*-position have about the same inductive effect on the acidity of the dye molecule. Of course, with similar pQ_D values the molarity quotients for the metal derivatives of the chloro and the bromo dyes are about the same.

The decreasing order of acidity, Table I, of the *para*-substituted dyes as presented in a previous paper[4] is extended as follows: $NO_2 >> (Cl, Br) > I > OCH_3$[6] $> CH_3 > H$. With the exception of the methoxy derivative the order fairly well follows the electron attracting power of the substituent groups. It would seem that the inductive effect of the methoxy group is greater than the resonance effect. The pQ_{av} values of the metal derivatives increase in the same order; that is, the nitro dye forms the least stable 2:1 compounds. This stability order (exception methoxy dye) is in good agreement with that reported by Calvin and Bailes.[7] The more limited number of *meta*-substituted dyes and their metal derivatives follow the same order.

The *meta*-nitro dye is a slightly weaker acid than the *para*-nitro dye[4] and the tendency for 3:1 complex formation is decreased. The order of stability of the 3:1 derivatives appears to be the reverse of the 2:1 compounds. That is, the formation of the anion complex, $M(dye)_3^-$, occurs more readily with the stronger acids.

The *ortho* derivatives of this series of dyes (with the exception of o-OCH_3 and o-SCH_3)[6] are too insoluble to be studied at the concentrations used in this work, 1.00×10^{-2} M in azo compound. It is interesting to note that the only *ortho*-substituted dyes which were soluble enough to study were the two which contained relatively strong electron releasing groups.

Near the end of the potentiometric titrations the copper derivatives of four of the dyes precipitated as nicely crystalline compounds. They were suction filtered, washed with cold alcohol and dried in a vacuum desiccator (Table II).

Acknowledgment.—The authors are indebted to the Research Corporation for financial support in carrying out this investigation.

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(6) F. A. Snavely, B. D. Krecker and C. G. Clark, THIS JOURNAL, **81**, 2337 (1959).

(7) M. Calvin and R. H. Bailes, *ibid.*, **68**, 953 (1946).

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[CONTRIBUTION FROM THE BASIC RESEARCH DEPARTMENT, STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION AMERICAN CYANAMID CO.]

Bonding in Ni(0) Complexes. I. Phosphine Exchange Kinetics and Infrared Spectra of Nickel–Carbonyl–Phosphine Complexes[1]

BY LEWIS S. MERIWETHER AND MARILYN L. FIENE

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The kinetics of the phosphine exchange reaction between nickel–dicarbonyl–diphosphine complexes and tertiary phosphines have been determined. The reaction is first order in complex and independent of the added phosphine. An SN1 dissociative mechanism is proposed. Nickel–tricarbonyl–monophosphines usually exchange a CO for phosphine initially. The effect of varying the structure of the phosphine ligand on the exchange rates and the the infrared carbonyl frequencies of the complexes has been determined. The nature of the bonding between nickel and the phosphine and carbonyl ligands is discussed.

Introduction

The mechanisms of ligand exchange in transition metal complexes only recently have been explored.[2] In general, exchange reactions may occur either by (1) unimolecular, dissociative, SN1-type processes or by (2) bimolecular, displacement, SN2-type processes. In their extensive studies of substitutions in octahedral Co(III) complexes, Ingold, Nyholm and co-workers[3] have presented stereochemical and kinetic evidence for both SN1 and SN2 mechanisms, the mode of exchange depending upon the nature of the ligands on the metal, the nucleophilicity of the attacking species, and the solvent. As a result of their investigation of the base hydrolysis of Co(III) complexes, Pearson and Basolo[4] have developed a dissociative SN1CB (substitution, nucleophilic, unimolecular, conju-

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(1) Presented at the Gordon Research Conference on Inorganic Chemistry, New Hampton, N. H., August 18–22, 1958.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

(3) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674, 2680, 2696 (1953), and later papers in the series.

(4) R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956).