[CONTRIBUTION FROM DEPARTAMENTO DE QUÍMICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO]

On the Reaction between Cobalt(II) and Azide Ions in Aqueous and Aqueous-organic Solutions[1]

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Pink-violet solutions of cobalt(II) and azide ions change to blue by the addition of water miscible alcohols, dioxane or acetone. Spectrophotometric studies have indicated the presence in aqueous solution of the cation CoN_3^+ and the possible formation of complexes with a higher content of azide. In blue water–acetone solutions evidence has been obtained of the existence of complexes up to a ratio of 1:4 of cobalt to azide. From aqueous solutions containing a large excess of azide ions the complex $[Co(N_3)_4]^{2-}$ has been isolated in the form of its tetraphenylphosphonium and tetraphenylarsonium salts. The spectra of acetone solutions of these salts have provided the confirmation that the blue color of water–acetone solutions referred to above is to be ascribed to the complex $[Co(N_3)_4]^{2-}$.

Introduction

The pseudo halogenoid character of hydrazoic acid and metal azides is well known. The analogy between azide and thiocyanate ions is rather remarkable in the reaction with ferric ions. The red coloration of solutions containing azide and ferric ions has found analytical application[2-5] and the presence of the cation $Fe(N_3)^{2+}$ has been recognized in such solutions.[6,7]

The behavior of azide ions in aqueous solution toward uranyl ions is apparently similar to that of thiocyanate and its importance as a means of determination of uranium has been pointed out.[8] Work in this line is being carried out in this Laboratory.

The analogies between thiocyanate and azide ions in their reactions with cobaltous ions, however, seem not to have been studied.[9]

Pink to violet aqueous solutions of cobalt(II) and thiocyanate ions change to blue by addition of suitable organic solvents, this property being the basis of the well known and extensively studied[10-15] Vogel reaction.[16]

A similar phenomenon, observed in solutions containing cobalt(II) and azide ions, has led to the present study.

Experimental

Apparatus and Materials.—A Beckman DU spectrophotometer and 1 cm. Corex cells were used throughout the spectrophotometric study. *p*H determinations were performed with a Beckman model G *p*H meter.

Cobaltous perchlorate stock solutions were prepared from C.P. cobaltous carbonate and C.P. 20% perchloric acid, a slight excess of the former being employed. Standardization was carried out gravimetrically by precipitation with α-nitroso-β-naphthol.[17]

Sodium azide (Baker) was purified by dissolving in water, filtering and precipitating with ethyl alcohol. Solutions were controlled by iodimetric titrations in the presence of CS_2.[18]

The ionic strength of solutions was always adjusted by the addition of anhydrous sodium perchlorate which was prepared from C.P. sodium carbonate and C.P. perchloric acid. This acid was used for the adjustment of *p*H. Organic solvents employed were commercial products properly purified, distilled and dried. All other materials occasionally used were reagent grade.

Tetrazidocobaltate(II) of Tetraphenylphosphonium and Tetrazidocobaltate(II) of Tetraphenylarsonium.—These compounds were obtained from aqueous cobaltous sulfate solutions containing an excess of about fifteen times of sodium azide and *p*H adjusted around 5, to which aqueous saturated solutions of tetraphenylphosphonium bromide and tetraphenylarsonium chloride, respectively, were added. In both cases blue crystalline precipitates were obtained which showed identical solubility properties in several organic solvents, being soluble in acetone, methyl ethyl ketone, chloroform and insoluble in benzene, ethyl alcohol, ethyl acetate and carbon tetrachloride. Recrystallization was performed in both cases by dissolving the product in acetone and precipitating by addition of carbon tetrachloride. Bright blue crystals with prismatic habit were formed which showed birefringence at the microscope. Both compounds melted at definite temperatures forming blue transparent liquids with no sign of decomposition. Melting points, determined in capillaries, were 164–165° and 153–154° for the phosphorus and arsenic containing compounds, respectively.

Anal. Calcd. for $C_{48}H_{40}N_{12}P_2Co$: N, 18.56; P, 6.68. Found: N, 18.48; P, 6.71. Calcd. for $C_{48}H_{40}N_{12}As_2Co$: N, 16.90; As, 15.05. Found: N, 17.01; As, 15.18.

Results and Discussion

General Characteristics of Aqueous Solutions.—Addition of increasing amounts of sodium azide to solutions of cobaltous perchlorate increases the absorption band and slowly shifts its maximum from 510 mμ to longer wave lengths. Variation of *p*H affects only the absorbance intensity, no change in spectral characteristics being observed. The decrease of absorbance values by decreasing the *p*H thus is due obviously to the decreasing of free azide ion concentration by the formation of undissociated hydrazoic acid.

It should be noted that in order to keep the solutions clear the *p*H must be adjusted below 7,

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preferably below 6.3, otherwise turbidity may appear due to basic salt formation. Solutions with a high ratio of azide to cobalt ions may remain clear for longer periods even at higher values of *p*H but slowly change their color from pink-violet to yellow-brown. Exposure to light accelerates this transformation which was found to be due to the oxidation of cobalt from the divalent to the trivalent state. To prevent oxidation of such solutions small amounts of ascorbic acid were used since in the conditions of the experiments no side reaction was observed in the presence of this substance.

Continuous Variation Study Applied to Aqueous Solutions.—The method of continuous variation[19,20] was applied to several series of solutions in different experimental conditions.

Data were secured at *p*H 4.5, 5.0 and 6.1; the total concentration of cobalt and azide ions was varied from 0.05 to 0.30 molar; ionic strength was adjusted at either 0.5 or 1.0. From all sets of experiments the species CoN_3^+ was clearly evidenced. Moreover, from the study made with the solutions of higher molarity, additional indications can be derived. Thus in the case of solutions 0.30 molar as shown in Fig. 1, the curves corresponding to the range of 480 to 520 mμ not only account for the formation of the cation CoN_3^+ but, being slightly tilted to the right, may also indicate the existence of compounds richer in azide. Results obtained at longer wave lengths indicate the formation of a 1:2 cobalt–azide species and compounds with a higher proportion of azide, though not definitely indicated, are still suggested by the shape of the curves.

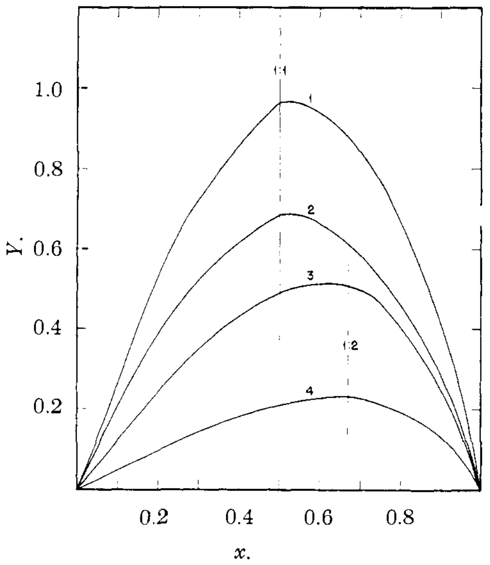

Fig. 1.—Continuous variation study of aqueous solutions. Absorbance differences *vs.* mole fraction of sodium azide (x): cobaltous perchlorate and sodium azide mixtures at total concentration of 0.3 M; *p*H 6.1; I = 1.0; (1) 512 mμ; (2) 480 mμ; (3) 560 mμ; (4) 580 mμ.

Slight indications of the possible formation of 1:4 cobalt azide complexes were obtained by the molar-ratio method, but results were not found satisfactory to be reported.

General Characteristics of Aqueous–Organic Solutions.—The pink-violet color of aqueous solutions of cobalt(II) salts containing a large excess of azide ions, change to blue by the addition of water miscible alcohols, dioxane or acetone. In order to obtain stable solutions autoxidation must again be prevented and *p*H preferably adjusted below 6.

In Fig. 2 absorption spectra of blue solutions obtained with different solvents are compared. Data relative to experiments with methyl and propyl alcohols are not reported, for the sake of clarity, since both curves, if plotted, would be almost coincident with the one corresponding to *t*-butyl alcohol.

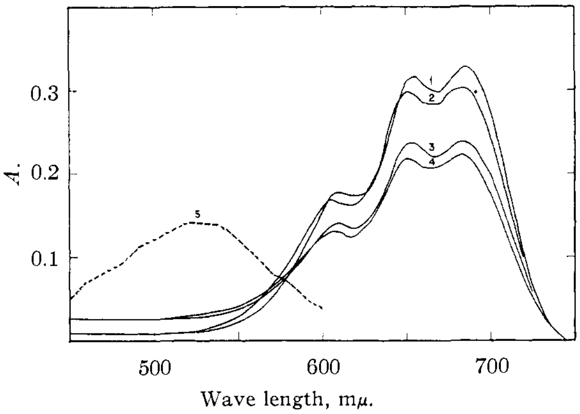

Fig. 2.—Absorption spectra of aqueous–organic solutions. 0.0004 M cobaltous perchlorate; 0.6 M sodium azide; 0.5 mg./ml. ascorbic acid; initial[a] *p*H 5.7. Solvent added to aqueous solution: (1) acetone; (2) ethyl alcohol; (3) dioxane; (4) *t*-butyl alcohol. Volume ratio water/organic solvent: 1/4.0. Curve (5) shows the spectrum of the same reaction mixture in aqueous solution, absorbance values being multiplied by a factor of 10.

[a] For initial *p*H in this and in other legends it is meant the *p*H determined before the addition of the organic solvent.

Spectral characteristics of all solutions being essentially the same, it may be inferred that all contain the same absorbing species and that the change of solvent affects only absorbance intensities. A number of experiments performed under different conditions confirmed that the highest absorbance values are obtained with acetone. In this connection it can be added that solutions containing only a moderate excess of azide with respect to cobaltous ions concentration, which show little or no change by the addition of alcohols and dioxane, still may develop a pronounced blue color with acetone. The volume ratio of water to organic solvent is also important. A high proportion of the latter is always desirable but the amount usually is limited by the solubility of the materials present in solution.

It is to be noted that addition of water-non-miscible, or partially miscible, solvents to aqueous solutions of cobalt and azide ions is of no effect. These solvents were tested: amyl, isoamyl,

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isobutyl alcohols, methylisobutylcarbinol, methyl isobutyl ketone, methyl isopropyl ketone, methyl ethyl ketone, ethyl acetate, butyl acetate and isoamyl acetate.

Continuous Variation Study Applied to Water–Acetone Solutions.—The method of continuous variation applied to water–acetone solutions provided strong evidence of the formation of a complex in the ratio 1:4 of cobalt to azide. In Fig. 3 results of a set of experiments are reported, and it can be seen from its inspection that although cobalt and azide ions can combine in the 1:1 to 1:4 ratio in such media, the 1:4 complex is the only species existing in solutions containing a high proportion of azide ions.

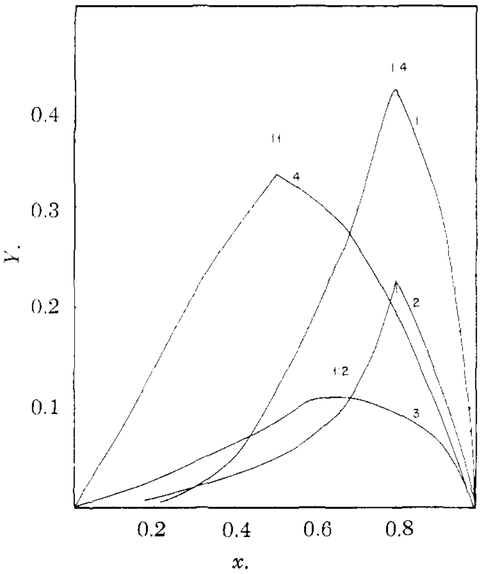

Fig. 3.—Continuous variation study of water–acetone solutions. Absorbance difference *vs.* mole fraction of sodium azide (x): cobaltous perchlorate and sodium azide mixtures at total concentration of 0.022 M; 2 mg./ml. ascorbic acid; initial pH 5.0. Volume ratio water/acetone: 1/4.2. Curve (1) 680 mμ; curve (2) 600 mμ; curve (3) 560 mμ; curve (4) 510 mμ (for this curve the values of Y are multiplied by a factor of 4).

Isolation of Complexes from Aqueous Solutions.—From solutions with a high concentration of azide ions blue crystalline compounds were isolated with the help of tetraphenylphosphonium and tetraphenylarsonium halides. Analyses of these compounds agree with the formulas of the salts $[(C_6H_5)_4P]_2[Co(N_3)_4]$ and $[(C_6H_5)_4As]_2[Co(N_3)_4]$, respectively.

Equimolar anhydrous acetone solutions of both salts show exactly the same absorption spectrum and, as can be seen from Fig. 4, spectral characteristics are identical with those of water–acetone solutions containing a very high ratio of azide to cobalt ions. This finding proves conclusively that the blue color of aqueous organic solutions is to be ascribed to the complex ion $[Co(N_3)_4]^{2-}$.

Remarks

Results reported provide sufficient evidence to assume that consecutive formation of complexes from CoN_3^+ to $[Co(N_3)_4]^{2-}$ tend to occur in aqueous cobaltous solutions by the addition of azide ions. The 1:4 complex, however, being very unstable would not be formed in significant amounts unless conditions which decrease the dissociation are established as, for instance, by the addition of a miscible solvent capable of retaining water or by the shift of the over-all equilibrium through the addition of a precipitant.

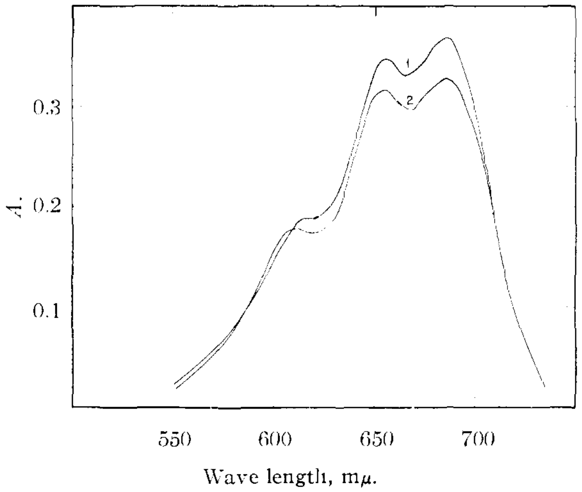

Fig. 4.—Absorption spectra of phosphonium and arsonium complexes. Curve (1) 0.0004 M acetone solution of $[(C_6H_5)_4X]_2[Co(N_3)_4]$, X = P,As: Curve (2) water–acetone solution of 0.0004 M cobaltous perchlorate, 0.6 M sodium azide, 0.5 mg./ml. ascorbic acid; initial pH 5.7; volume ratio water/acetone: 1/4.0.

It should be mentioned that during the spectrophotometric study of aqueous solutions a well defined absorption band in the near ultraviolet with a maximum at 290 mμ was observed when cobalt(II) solutions were treated with small amounts of azide ions. This band was found particularly suited for the study of the CoN_3^+ ion and for the determination of its formation constant. Results will be reported later.

The reaction between cobaltous and azide ions in solution being similar in many respects to that of cobaltous and thiocyanate ions, it seems interesting to point out some differences which arise from the present study. The absorption spectra of blue cobalt–thiocyanate aqueous–organic solutions as well as those of cobalt–selenocyanate solutions show a characteristic peak at 620 mμ[14] and are considerably different from those of the corresponding cobalt–azide solutions. In addition the blue thiocyanate complex is extracted by a number of non-miscible solvents like amyl and isoamyl alcohols, this property being of particular importance in the analytical application of the Vogel reaction while cobalt–azide solutions are not affected by non-miscible solvents.

Furthermore the blue solutions obtained with thiocyanate are very stable and no oxidation to corresponding trivalent cobalt compounds is possible. On the contrary addition of thiocyanate ions to solutions containing trivalent cobalt complexes 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.

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[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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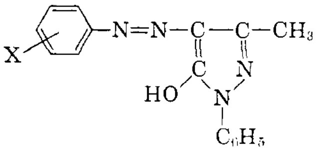
The relative stabilities of the metal derivatives of simple aryl azo pyrazolone compounds have been measured potentiometrically in 75 volume % dioxane. The order of decreasing stability, Cu > Ni > Co > Zn, agrees with previously reported pyrazolone dyes. The log Q_2 values are greater than the log Q_1 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 $n = 1$	$n = 2$	$n = 3$	Log Q_{av} at $n = 1$
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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