A. I. CHERKESOV

1962

SovietRxiv

Abstract

Full Text

A. I. CHERKESOV

ON THE MECHANISM OF COMPLEX-FORMATION REACTIONS OF IONS OF CERTAIN DIVALENT METALS WITH AZO DERIVATIVES OF 8-HYDROXYQUINOLINE

(Presented by Academician A. A. Grinberg, October 5, 1961)

Azo derivatives of 8-hydroxyquinoline have found fairly broad analytical application; they are used as analytical reagents for the determination of small amounts of a number of elements. Some azo derivatives of 8-hydroxyquinoline are good mercurimetric indicators; recently reagents of this type have been used for the chromatographic separation of metal ions ([1]). Azo derivatives of 8-hydroxyquinoline were first studied by Gutzeit and Monnier ([2]), then by V. I. Kuznetsov ([3]) and a number of other authors, who, in studying the analytical properties of the series of reagents under consideration, assigned to them the structure corresponding to para-azo compounds (I). However, there are indications in the literature that, when diazo components are coupled with 8-hydroxyquinoline, ortho-azo-substituted structures (II) are obtained ([4]):

R—N=N—(8-hydroxyquinoline residue)
(I)

(ortho-azo-substituted 8-hydroxyquinoline residue)
(II)

Upon interaction of solutions of azo derivatives of 8-hydroxyquinoline with solutions of salts of a number of divalent metals ($Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}$, etc.) in a neutral medium, yellow or greenish-yellow solutions of reaction products are formed; in an acidic medium, with the same reaction components, the color deepens—products arise that have a red or red-violet color in solution, or brightly colored precipitates are formed.

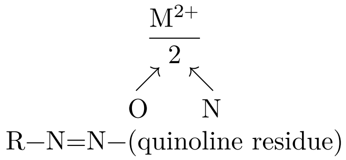
For the above structure (I) of azo derivatives of 8-hydroxyquinoline, only one type of complex formation is possible, namely formation of a product of structure (III):

$$\text{R—N=N—(quinoline residue)—O} \rightarrow \frac{M^{2+}}{2} \leftarrow \text{N}$$

(III)

For reagents of structure (II), twofold complex formation is possible:
a) with the occurrence of a coordination bond of the metal with the tertiary ni-

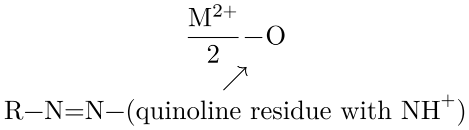
trogen atom of the quinoline ring IV, or b) with the occurrence of a coordination bond of the metal with the nitrogen atom of the azo group (V):



$$\begin{array}{c} \frac{M^{2+}}{2} \\ \nearrow \quad \nwarrow \\ O \qquad N \\ R{-}N{=}N{-}(\text{quinoline residue}) \end{array}$$

(IV)

in a neutral medium



$$\begin{array}{c} \frac{M^{2+}}{2}{-}O \\ \nearrow \\ R{-}N{=}N{-}(\text{quinoline residue with } NH^{+}) \end{array}$$

(V)

in an acidic medium

It is known that tertiary nitrogen is more basic than the nitrogen of an azo group; therefore, one should expect that complexes of structure (IV) should be more stable than complexes (V)^(5). We carried out a systematic study of the reactions of a series of azoderivatives of 8-hydroxyquinoline, both in neutral and in acidic media, with Cu^2+, Ni^2+, and Co^2+ ions. By the method of physicochemical analysis it was established that, under the adopted reaction conditions, in all cases complexes are formed in solution with a ratio of stoichiometric coefficients $M^{2+} : R = 1 : 2$, where R is an azoderivative of 8-hydroxyquinoline.

The instability constants of the complexes formed in neutral medium and the equilibrium constants of the reaction of the red-colored complexes with hydrogen ions at the corresponding pH values* were determined (see Table 1); comparison of them indicates the greater stability toward dilution of the yellow-colored complexes.

Table 1

Instability constants and equilibrium constants for some complexes

Complex	Metal ion	Metal ion	Metal ion	pH
Complex	Cu^2+	Ni^2+	Co^2+	pH

Complex	Metal ion	Metal ion	Metal ion	pH
$HO_3S—C_6H_4—N{=}N—$8-hydroxyquinoline complex with $M^{2+}/2$ coordinated through O and N	$6.9 \cdot 10^{-14}$	$4.0 \cdot 10^{-13}$	$3.78 \cdot 10^{-12}$	
$C_6H_4(COOH)—N{=}N—$8-hydroxyquinoline complex with $M^{2+}/2$ coordinated through O and N	$6.3 \cdot 10^{-13}$	$6.4 \cdot 10^{-11}$	$1.4 \cdot 10^{-10}$	
$HO_3S—C_6H_4—N{=}N—$protonated 8-hydroxyquinoline complex with $M^{2+}/2$ coordinated through O and azo N, +NH	$5.0 \cdot 10^{-5}$	$7.0 \cdot 10^{-3}$	$1.15 \cdot 10^{-2}$	4; 5; 5
$C_6H_4(COOH)—N{=}N—$protonated 8-hydroxyquinoline complex with $M^{2+}/2$ coordinated through O and azo N, +NH	$1.28 \cdot 10^{-5}$	$6.4 \cdot 10^{-3}$	$0.69 \cdot 10^{-2}$	3; 5; 5

structural formula VI

Figure 1: structural formula VI

structural formulas VII and VIII

Figure 2: structural formulas VII and VIII

From the structure V given above it is evident that the complex group in acidic medium for 7-azobenzol-8-hydroxyquinoline should be a positively charged group. We carried out electrolysis of an acetic-acid solution of this complex; the experiment confirmed the presence of a clearly expressed electrophoresis: the layer colored red (the color of the complex solution) moves toward the cathode.

To confirm the results obtained in studying the mechanism of complex formation of a series of azoderivatives of 8-hydroxyquinoline with ions of divalent metals, we also synthesized an azo dye from 7-bromo-8-hydroxyquinoline and diazotized aniline; this dye can have only the single possible structure represented by structure VI:

Formation of the ortho-azo-substituted product is excluded here. Dye VI in an acidic medium does not form with Cu^{2+} (and other ions of divalent metals) a complex compound which, in solution or as a precipitate, would give a product colored red. Moreover, this dye, like other azo derivatives of 8-hydroxyquinoline, has indicator properties and, not being bound to metal cations, in an acidic medium gives a red color, which is apparently a consequence of the formation of the quinonehydrazone structure VII:

After addition of a solution of a copper salt, the red color of the reagent VII solution disappears and a yellow color appears, characteristic of complexes formed in a neutral medium VIII; further acidification of the solution leads to destruction of the copper complex and to the reappearance of the red color of the dye solution.

Fig. 1. Absorption spectra of aqueous-methanolic solutions: 1 –5-azobenzol-7-bromo-8-hydroxyquinoline; 2 –the same in acidic medium, 3 –the same and methanolic solution of $CuSO_4$, 4 –7-azobenzol-8-hydroxyquinoline + $CuSO_4$ (neutral medium); 5 –the same + buffer solution (pH 4)

Fig. 1 absorption spectra

Figure 3: Fig. 1 absorption spectra

---

* The constants were calculated according to formulas proposed by N. P. Komar, ZhAKh, 5, 139 (1950).

The absorption spectra of aqueous-alcoholic solutions of the free dye VI, of this dye in an acidic medium, and of its copper complex (also in an acidic medium) are presented in Fig. 1; for comparison, the same Fig. 1 gives the absorption spectra of solutions of the copper complex of 7-azobenzol-8-hydroxyquinoline in a neutral medium and in an acidic medium at pH 4.

Thus, the experimental material presented confirms that, as a result of carrying out conventional syntheses of azo derivatives of 8-hydroxyquinoline, ortho(7)-azo-substituted compounds are formed, which, depending on the medium conditions (pH), are capable of forming two series of complex compounds with ions of divalent metals (Cu^{2+}, Ni^{2+}, Co^{2+}, etc.); whereas para(5)-azo-substituted 8-hydroxyquinolines do not form, with the same ions in an acidic medium, compounds more deeply colored than yellow-colored compounds.

It should be particularly emphasized that the main cause of the deepening of the color of the reaction products during complex formation in an acidic medium of divalent metal ions with azo derivatives of 8-hydroxyquinoline is coordination of the metal with the nitrogen of the azo group.

Saratov State Pedagogical Institute

Received
3 X 1961

CITED LITERATURE

1. Q. Fernando, M. de Silva, *Analyst*, **79**, 711 (1954).
2. G. Gutzeit, R. Monnier, *Helv. chim. acta*, **16**, 233 (1933).
3. V. I. Kuznetsov, ZhOKh **20**, 807, 816 (1950).
4. I. M. Kogan, *Chemistry of Dyes*, Moscow, 1956, p. 206.
5. Kh. Kh. Khakimov, Dissertation, Leningrad, 1960.
6. A. K. Babko, *Physicochemical Analysis of Complex Compounds in Solutions*, Publishing House of the Academy of Sciences of the Ukrainian SSR, Kiev, 1955.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.