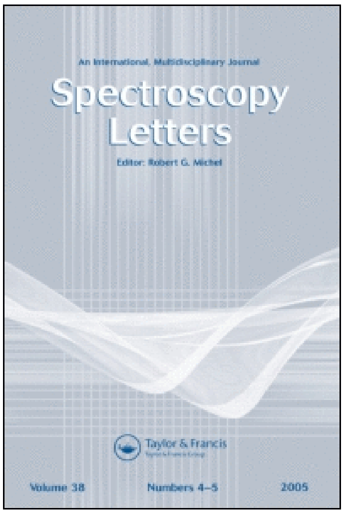

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Spectrophotometric Study of Hexanitrocobaltate(III) Ion Spontaneous Reduction in Water-Ethanol and Water-Acetone Mixtures

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SPECTROPHOTOMETRIC STUDY OF HEXANITROCOBALTATE(III) ION SPONTANEOUS REDUCTION IN WATER-ETHANOL AND WATER-ACETONE MIXTURES

Keywords: *Hexanitrocobaltate (III) ion, reduction, mixed solvents, kinetics.*

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ABSTRACT

The kinetics of the spontaneous reduction of hexanitrocobaltate(III) ion have been investigated spectrophotometrically (λ=360 nm at 298 K) in ethanol or acetone water mixtures containing 0, 10, 25 and 50 % of organic solvents. The mechanism of this process was expressed by means of two consecutive first-order reactions. Both of the first-order rate constants decrease with the increasing nonaqueous species content. The reduction of hexanitrocobaltate(III) ion in the mixtures was much slower than the corresponding reaction in water.

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INTRODUCTION

The structure of hexanitrocobaltate (III) ion in the solid form has been determined by X-ray crystallography[1]. It is a regular octahedron (T_h symmetry) with the N- bonded nitro groups. Its chemical and spectroscopic properties[2,3] are not in accordance with those predicted for complex ion with N-bonded nitro ligand as a strong ligand in spectrochemical series which is sited between NH_3 and CN^-. The high ligand field strength of the H-bonded nitro group to π donation from the metal ion[4] should stabilize the d^6 Co(III) configuration relative to the d^7 Co(II). The nitrite groups, however, are rapidly displaced by other ligands, including water, and in the dilute aqueous solutions spontaneous reduction to Co(II) occurs[5]. Analysis of ^{59}Co-, ^{14}N- and ^{17}O- NMR spectra [6] showed that the major species after dissolution of the complex salt are $[Co(NO_2)_6]^{3-}$ and $[Co(NO_2)_5(H_2O)]^{2-}$. The presence of nitrite complexes with O-bonded nitrito ions, such as $[Co(NO_2)_5(ONO)]^{3-}$, $[Co(NO_2)_4(ONO)_2]^{3-}$ and $[Co(NO_2)_4(ONO)(H_2O)]^{2-}$ was also established [6]. The kinetics of the spontaneous reduction of hexanitrocobaltate (III) ion in dilute aqueous solutions has been investigated in the earlier paper[7]. A mechanism, based on the intramolecular nitro-nitrito isomerization that facilitates ligand exchange and the electron transfer, was proposed.

The aim of this work was to investigate the spontaneous reduction of the hexanitrocobaltate(III) ion in ethanol or acetone water mixtures. It was expected for selected solvents (ethanol or acetone) to be important for the redox stability of this complex salt i.e., for stabilization of Co(III) in respect to Co(II) configuration.

EXPERIMENTAL

Dilute aqueous sodium hexanitrocobaltate(III) solutions (1.25×10^{-4} M) were prepared from reagent grade $Na_3[Co(NO_2)_6]$ (Merck). Other chemicals (ethanol, acetone) were p.a. (Alkaloid). The mixtures contained 0, 10%, 25% and 50% ethanol or acetone in water. The reduced solubility of the complex salt in the mixture with more than 50% of nonaqueous solvents have made them unsuitable for the investigation. A spectrophotometric analysis of the complex salts was performed using a Beckman DU-50 spectrophotometer in the wavelength range of 260-400 nm. The kinetic maesurements were followed by monitoring the increase of the optical absorbance at 360 nm. The quoted values are the average of at least five runs under identical experimental conditions. All measurements were carried out at 298K.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of sodium hexanitrocobaltate(III) solution in water and in water-ethanol and water-acetone mixtures were recorded immediately after dissolution and again two days later. The results obtained are shown in Fig. 1.

In those absorption spectra two absorption bands at 360 and 266 nm could be seen in water and in water-ethanol mixture. In the case of acetone the absorption band at 266 nm is missing.

The presence of those bands could be explained in accordance with literature data. The spectrum of sodium hexanitrocobaltate(III) solution in water has two charge transfer CT bands[8]. One of them at 360 nm is assigned to $Co(d_\pi) \rightarrow NO_2^- (\pi^*)$[8]

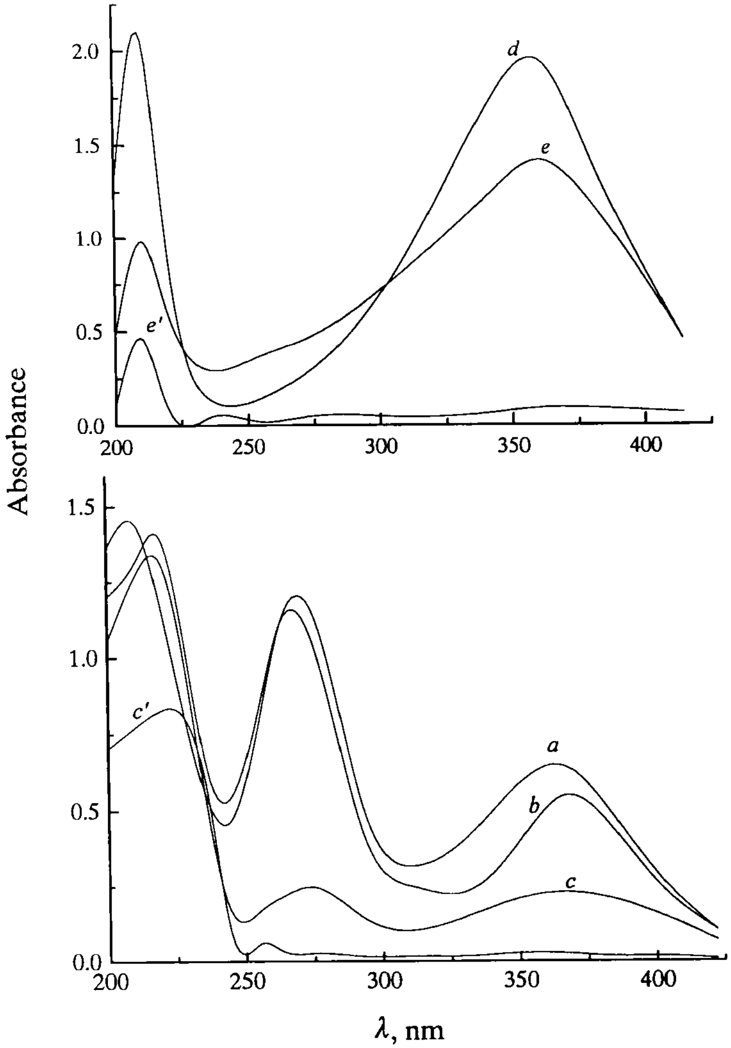

FIG. 1. Absorption spectra of 1.25x10^{-4} M $Na_3[Co(NO_2)_6]$, 298 K, in water mixtures contained (a) 0; (b) 10; (c) 50 % ethanol and (d) 10; (e) 25% acetone, immediately after dissolution (a, b, c, d, e) and two days latter (c', e').

a metal-to-ligand CT band, as a consequence of nitro ligand well pronounced π-acceptor behaviour. Since the σ-bonded nitrito ligand is rather π-donor, it does not absorb at 360 nm, but both ligands, nitro and nitrito, have a strong absorption band at about 266 nm[8]. This band is probably a ligand-to-metal CT band, $L(\pi) \to Co(\sigma^*)$. The intensities of these bands are also smaller since the orbitals of cobalt and nitro groups are orthogonal and the appearance of charge transfer bands could not be possible without vibration coupling[9].

Also, according to Tanabe-Sugano diagrams[10] two spin-allowed d-d transitions in the UV VIS region were expected: ${}^1A_{1g} \to {}^1T_{1g}$ and ${}^1A_{1g} \to {}^1T_{2g}$. The latter one is described as a shoulder[11]. Both of them should be weak bands whose wavelengths are uncertain, since they are covered by the strong charge transfer bands[8].

The presence of all those bands in the water and water-ethanol mixtures indicates their similar origin with those described above. In the case of water-acetone mixture, where the absorption band at 266 nm is missing, it seems that this band is moved to higher wavelengths and covered by the band at 360 nm.

It is well known from literature data[3] that the position of CT bands depends on solvent as it was confirmed here. So, only the position of CT bands in water solution (Fig. 1a) is analogous to report[8]. In two mixtures investigated in this work, there are some shifts of bands in respect to the same bands in water solution. The bands in aceton-water mixtures show hypsochromic and in ethanol-water mixtures batochromic shifts (Fig. 1, b,c,d,e). The obtained results are presented in Table 1.

TABLE 1

Effect of ethanol-water and acetone-water mixtures on the absorption spectra of 1.25 x 10^{-4} M $Na_3[Co(NO_2)_6]$.

Solvent	Ethanol (acetone) %	λ / nm	$\Delta\lambda$ / nm
water		360	
ethanol-water	10	364.1	+ 4.1
	50	365.5	+ 5.5
acetone-water	25	359.7	- 0.3
	10	355.7	- 4.3

As it can be seen the observed shifts in CT bands are in agreement with the order acetone ⟨ ethanol, and could be connected with the increase in the solvent polarity[12].

Kinetic measurements

The kinetic curves of hexanitrocobaltate(III) ion reduction in water and in different water-ethanol and water-acetone mixtures are shown in Figs. 2 and 3. The measured absorbancies at 360 nm in all the solvents were fitted by means of a computer program to the two-exponential expression, as shown bellow:

$$A_t - A_e = K_1 \exp(-k_1 t) + K_2 \exp(-k_2 t) \qquad [1]$$

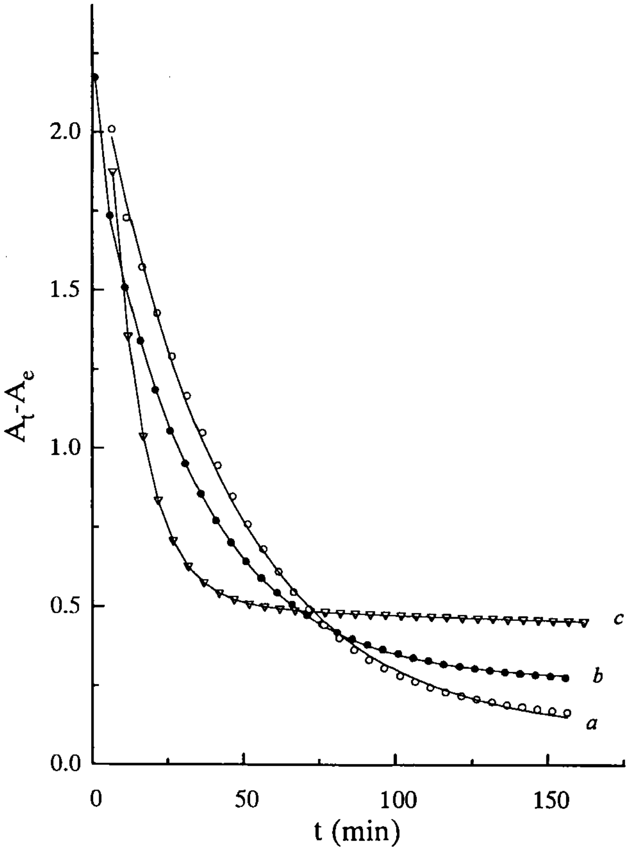

FIG.2. Plot of absorbance vs. time according to Eq.1 for the reduction of 1.25×10^{-4} M $Na_3[Co(NO_2)_6]$, 298 K, at 360 nm, in water mixtures contained (a) - 0; (b) - 25; (c)- 50% ethanol. The lines represent Eq.1, fitted to the experimental points by means of a computer program.

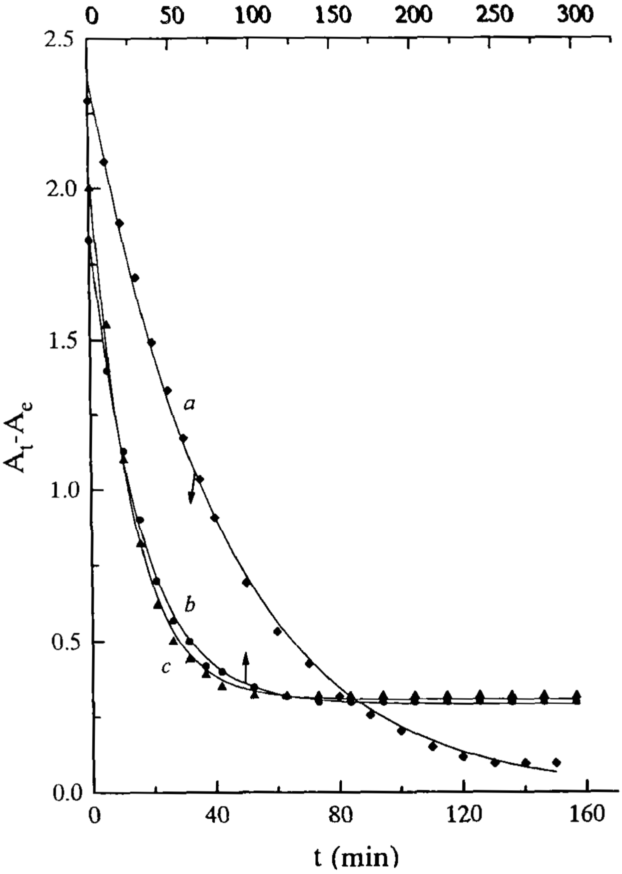

FIG.3. Plot of absorbance vs. time according to Eq.1 for the reduction of 1.25×10^{-4} M $Na_3[Co(NO_2)_6]$, 298 K, at 360 nm, in water mixtures contained (a) - 0; (b) - 25; (c) - 50% acetone. The lines represent Eq.1, fitted to the experimental points by means of a computer program.

The above expression is characteristic for two consecutive first-order reactions of the type

$$X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$$[4]

Here, k_1 and k_2 are first-order rate constants, where k_1 refers to a solvent dependent ligand substitution, and k_2 to the reduction of the Co(III), according to the model proposed in the next section. K_1 and K_2 are constants that must satisfy the equality:

$$K_1 + K_2 = A_0 - A_e$$

The absorbancies A_0, A_t, and A_e refer to zero time, time t and infinite time, respectively.

The results of kinetic measurements are collected in Table 2.

One can note much faster process of reduction of hexanitrocobaltate(III) ion in water than in mixtures, while in mixtures the reduction rate decreases with the decreasing water content.

Interpretation of results

The simplest interpretations of kinetic data suggest the same mechanism in water-ethanol and water-acetone mixtures as well as in dilute aqueous solutions[7].

The point model developed previously[7] predicts a fast nitro-nitrito intramolecular isomerization:

$$[Co(NO_2)_6]^{3-} \rightleftharpoons [Co(NO_2)_5(ONO)]^{3-} \rightleftharpoons [Co(NO_2)_4(ONO)_2]^{3-} \qquad (fast) \qquad [2]$$

TABLE 2

Rate constants according to the Eq. 1.; 1.25 x 10^{-4} M $[Na_3(Co(NO_2)_6]$ at 298 K in water-ethanol and water-acetone mixtures.

water v (%)	k_1 x 10^{-4} /s^{-1}	k_2 x 10^{-4} / s^{-1}	k_1/k_2	K_1	K_2	1/ε*
water-ethanol						
100.00	10.60	3.63	2.92	3.62	2.19	1.27
90.00	8.91	1.92	4.64	2.14	0.13	1.37 x 10^{-2}
75.00	8.15	0.51	15.98	1.98	0.03	1.56 x 10^{-2}
50.00	6.11	0.17	35.94	1.73	0.01	1.82 x 10^{-2}
water-acetone						
90.00	5.13	0.83	6.18	1.85	0.21	1.37 x 10^{-2}
75.00	0.61	1.13	0.53	1.58	0.34	1.56 x 10^{-2}
50.00	1.39	0.17	8.18	1.40	0.26	2.07 x 10^{-2}

Accurancy of the rate constants is about 15 %.; * from ref. 13

The next process involves the first-order substitution of one nitrito ion by the water molecule:

$$[Co(NO_2)_5(ONO)]^{3-} + H_2O \xrightarrow{k_1} [Co(NO_2)_5(H_2O)]^{2-} + NO_2^- \quad (fast) \qquad [3]$$

The intermediate $[Co(NO_2)_5(H_2O)]^{2-}$ is also subject to the rapid nitro-nitrito isomerization (Eq.4). A relatively slow spontaneous reduction of Co(III) to Co(II) that follows is associated with NO_2 release (Eq.5). In this reaction, the reducing agent is nitrito ligand which is simultaneously oxidized to gaseous NO_2 and replaced by water molecule. It is connected with hydrogen ions production (Eq. 7).

$$Co(NO_2)_5(H_2O)]^{2-} \rightleftharpoons [Co(NO_2)_4(ONO)(H_2O)]^{2-} \quad (fast) \qquad [4]$$

$$[Co^{III}(NO_2)_4(ONO)(H_2O)]^{2-} + H_2O \xrightarrow{k_2} [Co^{II}(NO_2)_4(H_2O)_2]^{2-} + NO_2(g) \quad (slow) \qquad [5]$$

$$[Co^{II}(NO_2)_4(H_2O)_2]^{2-} + 4\ H_2O \rightleftharpoons [Co(H_2O)_6]^{2+} + 4NO_2^- \quad (fast) \qquad [6]$$

$$2NO_2 + H_2O \rightarrow HNO_2 + NO_3^- + H^+ \qquad [7]$$

The resulting $[Co^{II}(NO_2)_4(H_2O)_2]^{2-}$ complex is labile regarding ligand exchange and nitro ligands are rapidly substituted by water producing $[Co(H_2O)_6]^{2+}$ ion . All the complex species and products of the reactions listed in Eqs. (2) - (7) have been identified after dissolution of the $Na_3[Co(NO_2)_6]$ complex salt in water: the nitrito complexes of Co(III) by NMR spectrometry[6] and the products $[Co(H_2O)_6]^{2+}$, nitrous and nitric acids by polarography[5,7].

The results given in Table 2 show that the first-order rate constants k_1 and k_2 for the fast and slow reaction step, respectively, decrease with water content decreasing in water-ethanol mixtures, but their ratio k_1 / k_2 increases, as the decreasing of reduction rate is less than substitution rate. This conclusion confirms stabilization of Co(III) configuration. The substitution of ONO^- ligand by a water molecule is much slower, since k_2 depends not only on ligand substitution, but also on Co(III) reduction. Hence, k_2 values are smaller in respect to k_1. The variation in K_1 and K_2 is ordinary (Table 2) and approximately those previously reported[7] as the process involves the two rate-limiting steps claimed.

The rate constants dependence on ethanol or acetone content could be explained by different outer-sphere mechanisms of intermediate complex formation in the investigated mixtures[14]. As a water content decrease in those mixtures, the substitution of ONO^- ligand by water (Eq. 3) becomes slower (Table 2, k_1 values). ONO^- ion is more efficient ligand than a NO_2^- ion[7] in the sence of Co(II) stabilization. The process of an intramolecular ligand isomerization explains facilitate nitrito ligand exchange. The nitrito ligand, ONO^-, is a weak π-donor that increases the electron density at the cobalt ion. It makes smaller ligand field splitting, and complex becomes labile towards substitution. At the other hand, as a π-donor the nitrito ligand should be a better reducing agent that favores the high spin $Co^{2+}[(t_{2g})^5(e_g)^2]$ complex. On the contrary, nitro ligand, as a π-acceptor, stabilize $Co^{3+}[(t_{2g})^6]$ complex.

Ethanol and acetone represent solvents with equal electron donor ability[15,16] and the corresponding mixtures with water have nearly the same dielectric constants[17]. Electron acceptor abilities that are relevant, are in the order: acetone < ethanol < water. Although the electron donor ability is of importance for associative ligand substitution at octahedral Co(III) complexes, the decreasing of both first order rate constants (k_1 and k_2) is observed. In those two mixtures water molecule would undergo to the coordination sphere rather than ethanol or aceton. On the basis of the literature data[18] it is in the case for 50 % content of many nonaqueous solvents.

The change of the k_1 and k_2 values with the change of solvent dielectric constants (ε) have been studied here as well. The dielectric constants are often related to the solvents bonding ability [16]. The obtained results are shown in Fig. 4. It

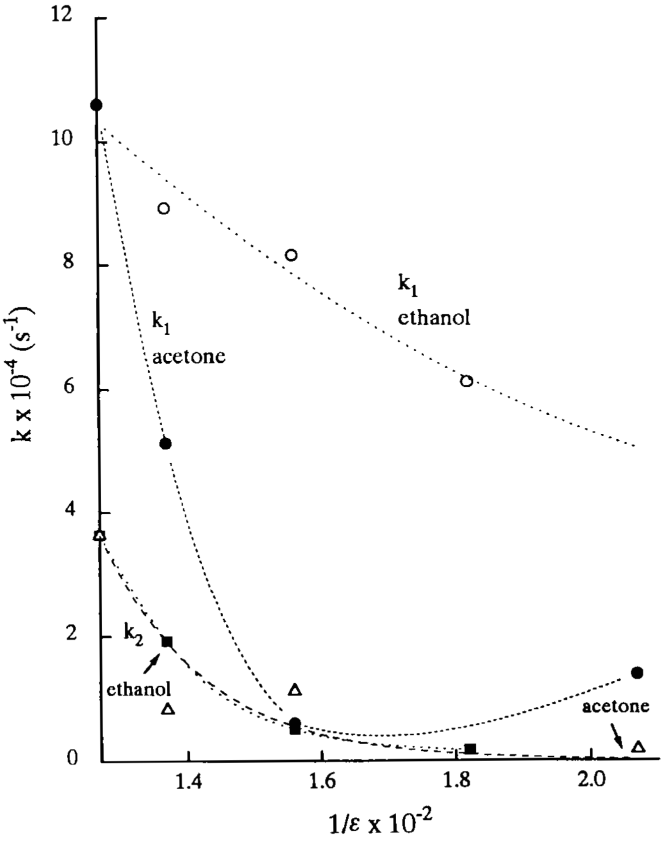

FIG.4. Plot of k_1 and k_2 vs. 1/ε. at 298 K for the reduction of $Na_3[Co(NO_2)_6]$.

can be observed that k_1 and k_2 values decrease with 1/ε. The interdependence of k_1 (k_2) and 1/ε shown in Fig. 4 suggests that the influence of ethanol and acetone might be of great importance on an outer-sphere complex. On the basis of an intramolecular nitro-nitrito isomerization a decreasing of $[Co(NO_2)_6]^{3-}$ concentration facilitates exchange of nitrito ligand and the electron transfer. It favors $[Co^{II}(H_2O)_6]^{2+}$ formation, which is due to a decreasing water content. The solvation effect of ethanol and acetone, however, is expected to imply a decrease of spontaneous reduction [Eq. 5].

According to the protolysis constants of water, ethanol and acetone[15] , it is evident that the effect of hydrogen bonding in general is not negligible. The increased strength of hydrogen bonding in ethanol probably relates to the field effect factor[6,19], resulting in an increased density of charge on the cobalt ion and ligand exchange becomes facile. This unables ONO^- ligand in the case of acetone to be exchanged by water more than in the case of ethanol-water mixtures. It could be good explanation for the variation of k_1 vs. $1/\varepsilon$.

On the basis of all aforesaid it can be concluded that the role of the selected solvents is decisive in the redox behaviour of the hexanitrocobaltate (III) ion and by changing in the redox properties are also changed.

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