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Use of semiconductor oxides in the photocatalytic reaction of sodium hexanitrocobaltate(III)

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Abstract

The photocatalytic reaction of sodium hexanitrocobaltate(III) over semiconducting oxides has been investigated. The effect of different parameters, such as the pH, concentration of the complex, intensity of the light, amount and nature of the semiconductor, etc., on the rate of the photocatalytic reaction has been observed. A tentative mechanism for the photocatalytic decomposition of sodium hexanitrocobaltate(III) has been proposed. © 1997 Elsevier Science S.A. All rights reserved.

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1. Introduction

The photochemistry of cobalt(III) complexes has been extensively studied, and it has been observed that photoaquation and photoredox decomposition proceed simultaneously with photochemical reaction. The photochemistry of some NO_2-substituted Co complexes has been studied. Tsuneda and Oouchi [1], Watanabe [2] and Beck and Dozsa [3] reported studies on the photochemical behaviour of the $[Co(NH_3)_x(NO_2)_{6-x}]^{x-3}$ series. These complexes undergo an oxidation–reduction decomposition reaction with the formation of Co^{2+}.

$[Co(NH_3)_3(NO_2)_3]$ [4,5] and *trans*-$[Co(NH_3)_3(NO_2)(Ox)]$ [6], with ammine ligands, are remarkably stable with respect to thermal substitution reactions. The photochemical behaviour of $[Co(NH_3)_5(NO_2)]^{2+}$ is still obscure due to various conflicting results. According to most workers [2,7–9], irradiation causes the formation of Co^{2+} or Co(II) species depending on the pH of the reaction medium, while other researchers [1,10,11] are of the opinion that the photodecomposition does not involve a redox process, but simply yields $Co(OH)_3$, $5NH_3$ and NO_2^-.

The photochemistry of $[Co(NO_2)_6]^{3-}$ is not well established; however, some interesting observations are available on the photochemistry of mixed ligand complexes, such as $[Co(NH_3)_5(NO_2)]^{2+}$ [12] and $[Co(NH_3)_3(NO_2)_3]$ [5]. The photocatalytic reaction of such complexes in the presence of a photocatalyst still requires better understanding, and therefore the present work has been undertaken.

2. Experimental details

A solution of 15.0 g of $NaNO_2$ in 15.0 ml of water was cooled to 50–60 °C. Then, 5.0 g of $Co(NO_3)_2.6H_2O$ was added, followed by 50% of CH_3COOH in small portions with shaking. A fast stream of air was bubbled through this reaction mixture for 2 h. A brown precipitate was obtained, which was filtered off. The filtrate was stored. The brown precipitate was stirred with 5.0 ml of water at 70–80 °C. The solution was separated from undissolved $K_3[Co(NO_2)_6]$ and combined with the stored clear filtrate. This combined filtrate solution (about 30.0 ml) was treated with 25.0 ml of 96% alcohol. The resulting precipitate was allowed to settle for about 2 h. It was filtered under suction, dried and washed three to four times with alcohol. It was then washed with ether and dried in air.

The photocatalytic reaction of $[Co(NO_2)_6]^{3-}$ in the presence of ZnO was carried out. The progress of the reaction was followed colorimetrically at $\lambda_{max} = 490$ nm. The complex (0.091 g) was dissolved in 30.0 ml of doubly distilled water and 0.16 g of ZnO was added; the solution was then exposed to a 200 W tungsten lamp so that the intensity of light falling on the surface of the reaction mixture was 26.0 mW cm^{-2}. The light intensity was measured by Surya Mapi (solarimeter; CEL model 501) in milliwatts per square centimetre.

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Table 1
A typical run ([complex] = 1.0×10^{-3} M; intensity of light, 26.0 mW cm^{-2}; [ZnO] = 0.15 g; pH 4.5)

Time (min)	Optical density (OD)	1 + log(OD)
0.0	0.489	0.6893
15.0	0.442	0.6454
30.0	0.398	0.5998
45.0	0.363	0.5599
60.0	0.327	0.5145
75.0	0.316	0.4996
90.0	0.279	0.4456
105.0	0.251	0.3996
120.0	0.234	0.3692
135.0	0.209	0.3201
150.0	0.193	0.2655
165.0	0.178	0.2504
180.0	0.158	0.1986
195.0	0.146	0.1643
210.0	0.133	0.1238
225.0	0.122	0.0863

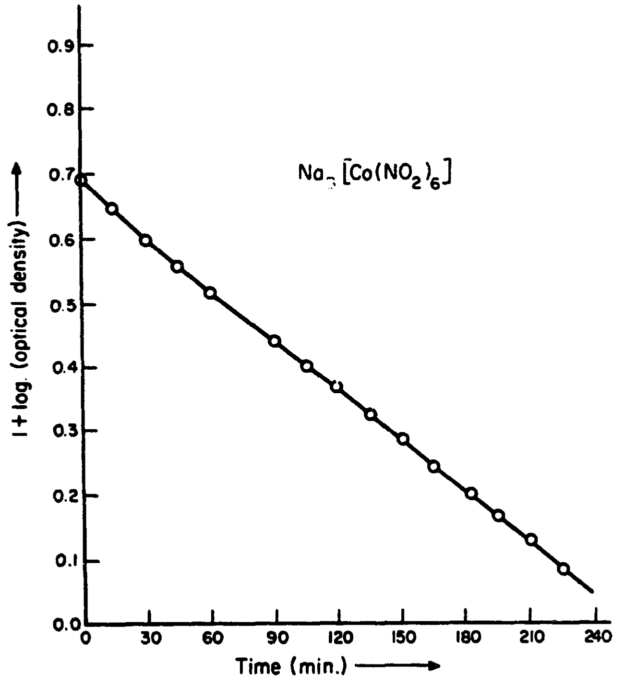

Fig. 1. A typical run.

An aliquot of 4.0 ml was taken at regular intervals and the optical density of the reaction mixture was measured. The solution was transferred back into the reaction vessel. A plot was drawn between log(optical density) and time, which was linear. It follows pseudo-first-order kinetics. The rate constant was calculated from the expression

$$K = 2.303 \times \text{slope} \qquad (1)$$

The results are given in Table 1 and are graphically represented in Fig. 1.

3. Results and discussion

The effect of different parameters on the rate of the photocatalytic reaction was studied.

Table 2
Effect of pH ([complex] = 1.0×10^{-3} M; intensity of light, 26.0 mW cm^{-2}; [ZnO] = 0.15 g)

pH	Rate constant $K\times10^2$ (min^{-1})
2.5	0.71
3.0	0.88
3.5	1.09
4.0	1.11
4.5	1.11
5.0	1.43
5.5	1.41
6.0	2.20
6.5	2.76

Table 3
Effect of the amount of semiconductor ([complex] = 1.0×10^{-3} M; intensity of light, 26.0 mW cm^{-2}; pH 4.5)

Amount of semiconductor (g)	Rate constant $K\times10^2$ (min^{-1})
0.05	0.69
0.08	0.75
0.12	0.82
0.15	1.15
0.20	1.15
0.25	1.16
0.30	1.15

3.1. *Effect of the pH*

The rate of the photocatalytic reaction of $[Co(NO_2)_6]^{3-}$ was observed at different pH values. The results are given in Table 2. It is clear from the data given in Table 2 that the rate of reaction increases with an increase in the pH of the medium under our experimental conditions (pH 2.5–6.5). This can be explained on the basis that the NO_2^- ligand is removed during the photocatalytic reduction of the complex $[Co(NO_2)_6]^{3-}$, and a higher pH facilitates the removal of NO_2^- ions.

3.2. *Effect of the amount of the semiconductor*

The effect of a variation in the amount of the semiconductor on the rate of the photocatalytic reaction was also studied. The results are summarized in Table 3. As the amount of semiconductor increases, the exposed surface area will also increase, thus causing a corresponding increase in the rate of reaction. After a particular limit (amount of semiconductor, 0.15 g), there is virtually no increase in the rate of reaction, as any additional amount of semiconductor above this limit will only increase the thickness of the layer of the semiconductor and not the surface area. This can be considered as a saturation point.

3.3. *Effect of the nature of the semiconductor*

The effect of the nature of the semiconductor on the photocatalytic reaction of $[Co(NO_2)_6]^{3-}$ was also investigated

Table 4
Effect of the nature of the semiconductor ([complex] = 1.0×10^{-3} M; intensity of light, 26.0 mW cm^{-2}; [ZnO] = 0.15 g; pH 4.5)

Semiconductor	Rate constant $K\times10^2$ (min^{-1})
ZnO	1.15
Fe_2O_3	1.09
WO_3	0.69
Al_2O_3	0.90

Table 5
Effect of the concentration of the complex ([ZnO] = 0.15 g; intensity of light, 26.0 mW cm^{-2}; pH 4.5)

[Complex] $\times10^3$ (M)	Rate constant $K\times10^2$ (min^{-1})
0.50	0.86
0.67	1.01
1.00	1.15
1.33	0.97
2.00	0.72

Table 6
Effect of the intensity of light ([complex] = 1.0×10^{-3} M; pH 4.0; [ZnO] = 0.15 g)

Intensity of light (mW cm^{-2})	Rate constant $K\times10^2$ (min^{-1})
12.0	0.53
18.0	0.84
26.0	1.15
36.0	1.38
51.0	1.57
65.0	1.86

using different photocatalysts, such as ZnO, Fe_2O_3, WO_3 and Al_2O_3. The results are reported in Table 4. The order of the efficiency of the semiconductors used was as follows: ZnO > Fe_2O_3 > Al_2O_3 > WO_3. The effectiveness of the photocatalyst depends on the nature of the semiconductor; however, this order does not follow the band gap order.

3.4. *Effect of the concentration of the complex*

To study the effect of the concentration of the complex $[Co(NO_2)_6]^{3-}$ on the rate of reaction, solutions of different concentration were taken in beakers and irradiated in the presence of the semiconductor ZnO. The results are presented in Table 5. It is clear that, with an increase in the concentration of the complex, the rate of reaction also increases. This may be attributed to the fact that a large number of $[Co(NO_2)_6]^{3-}$ molecules are available to accept the electrons and for consecutive degradation, thus giving rise to an increased rate of reaction.

As the concentration of the complex is increased, the rate of reaction is affected favourably but, at a certain concentration, there is an adverse effect of an increase in concentration of the complex. This may be explained on the basis that, as the concentration of the complex increases, more molecules are available for reaction. However, beyond a certain limit (1.0×10^{-3} M), the complex itself will start to act as a filter and will not permit the desired light intensity to reach the photocatalyst in the limited time, thus causing a corresponding decrease in the rate of reaction at larger concentrations.

3.5. *Effect of the light intensity*

A variation in light intensity was attained by using light sources of different wattage. It was observed that the rate of reaction increases with an increase in the light intensity. The results are given in Table 6. More intense light sources give a higher rate of decomposition. It may be concluded that the rate of reaction is affected favourably by an increase in the light intensity. This may be explained on the basis that a larger number of photons will generate more electrons and holes in the semiconductor and, therefore, more molecules of the complex will be utilized in a limited time, thus giving an increase in the reaction rate.

3.6. *Mechanism*

It is well known that Co(III) complexes are kinetically inert, whereas Co(II) complexes are very labile, because of the presence of electrons in the σ^* (e_g) antibonding orbitals [13].

The photocatalytic behaviour of $[Co(NO_2)_6]^{3-}$ can be explained on the basis of the following proposed steps

$$SC \xrightarrow{h\nu} SC^* \qquad (2)$$

$$SC^* \rightarrow SC^+(h^+) + e^- \qquad (3)$$

$$[Co(III)(NO_2)_6]^{3-} \overset{+e^-}{\rightleftharpoons} [Co(II)(NO_2)_6]^{4-} \qquad (4)$$

$$[Co(II)(NO_2)_6]^{4-} \rightarrow Co^{2+}(aq) + \text{other products} \qquad (5)$$

where SC and SC* denote the semiconductor in its ground and excited state respectively and h^+ denotes a hole.

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