Inorganica Chimica Acta, 54 (1981) L159–L160
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Charge Transfer Photochemistry of Hydroxopentacyanocobaltate(III) Ion

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Received May 9, 1981

Introduction

According to early work [1], acidopentacyanocobaltate(III) ions exhibited anomalous photochemical behavior with respect to the other Co(III) complexes, in giving photosubstitution reactions upon ligand to metal charge transfer (LMCT) irradiation. Ferraudi and Endicott [2] showed that this anomaly is more apparent than real since they detected transient redox products (oxidized acido ligand) in the flash photolysis of $Co(CN)_5N_3^{3-}$ and the presence of $Co(CN)_5^{3-}$ in the continuous photolysis of the same complex.

A study of the continuous photolysis of $Co(CN)_5NO_2^{3-}$ [3] also reveals the occurrence of a primary ligand–metal homolytic bond splitting and gives some insight into the secondary thermal processes leading to the overall photosubstitution products.

In a previous communication Viaene and D'Olieslager [4] reported that LMCT irradiation of alakline solution of $Co(CN)_5H_2O^{2-}$ gave rise to small yields of $Co(CN)_5^{3-}$. The lack of photoreactivity in acidic medium was attributed to the instability of the reduced product. We report here the results of a quantitative and more detailed study on the redox photodecomposition of hydroxopentacyanocobaltate(III).

Experimental

Solutions of $Co(CN)_5H_2O^{2-}$ were prepared by exhaustive photolysis of acidic solutions of $K_3Co(CN)_6$ using a pyrex-filtered medium pressure Hg vapor lamp [5]. During the irradiation, HCN was eliminated from the solution by nitrogen gas purging.

Solutions of $Co(CN)_5OH^{3-}$ were prepared by alkalinization (pH $\geqslant$ 12) of solutions of $Co(CN)_5(H_2O)^{2-}$. This method was preferred to direct irradiation of $Co(CN)_6^{3-}$ in alkaline solution in order to avoid the formation of secondary photosubstitution products [6].

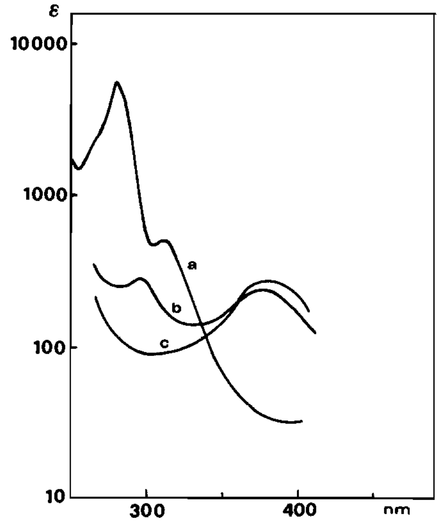

Fig. 1. Absorption spectra of a) $Co(CN)_5^{3-}$, b) $Co(CN)_5OH^{3-}$, c) $Co(CN)_5H_2O^{2-}$.

Apparatus

Quantitative measurements were performed using 254 nm radiations from a low pressure mercury vapor lamp. Spectra were recorded with a Perkin-Elmer UV, vis. Mod. 323 Spectrophotometer. Flash photolysis experiments were performed using an Applied Photophysics Model KR-10 apparatus.

Procedures

Quantum yields (see Results) were obtained spectrophotometrically from kinetic plots under zero-order conditions. The pH was adjusted before irradiation with NaOH and did not change appreciably during the kinetic runs.

Results

The absorption spectra of $Co(CN)_5H_2O^{2-}$, $Co(CN)_5OH^{3-}$, and $Co(CN)_5^{3-}$ in aqueous solution are reported in Fig. 1.

When alkaline (pH = 12), deaerated solutions of $Co(CN)_5OH$ were irradiated with 254 nm light, the initial spectral variations indicated that the reactant was converted into $Co(CN)_5^{3-}$. In the same conditions, aerated solutions gave rise to a peroxopentacyanocobaltate product (λ_{max} = 320 nm (7)), which could be converted into $Co(CN)_5H_2O^{2-}$ by subsequent acidification.

When acidic solutions of $Co(CN)_5H_2O^{2-}$ were irradiated with 254 nm light, no permanent changes were observed to occur either in aerated or in deaerated conditions.

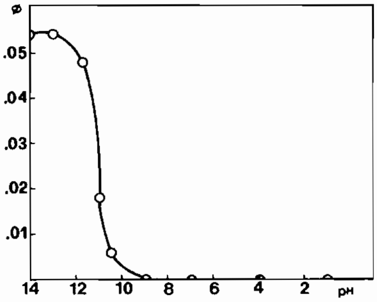

Fig. 2. Dependence of quantum yield of formation of Co(CN)$_5^{3-}$ in deaerated solution on pH.

The quantum yield of formation of Co(CN)$_5^{3-}$ in deaerated solutions changed as a function of pH, as shown in Fig. 2.

The quantum yield of formation Co(CN)$_5^{3-}$ was found to increase upon addition of alcohols. At pH = 12, the quantum yield changed from 0.045 to 0.09 upon addition of 0.03 *M* 2-propanol. No further increase in quantum yield was observed by increasing the 2-propanol concentration up to 0.4 *M*.

Flash photolysis (time resolution 20 μs) did not reveal any transient product preceding the formation of Co(CN)$_5^{3-}$ in deaerated alkaline solutions. Acidic solutions did not exhibit any transient spectral change under the same conditions.

Discussion

The results obtained point towards the following photoreaction mechanism:

$$\mathrm{Co(CN)_5H_2O^{2-} \rightleftarrows Co(CN)_5OH^{3-} + H^+} \qquad (1)$$

$$\mathrm{Co(CN)_5OH^{3-} \xrightarrow[254\,nm]{h\nu} Co(CN)_5^{3-} + \cdot OH} \qquad (2)$$

$$\mathrm{\cdot OH + Co(CN)_5^{3-} \rightarrow Co(CN)_5OH^{3-}} \qquad (3)$$

$$\mathrm{\cdot OH \rightarrow products} \qquad (4)$$

$$\mathrm{\cdot OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2\dot{C}OH} \qquad (5)$$

$$\mathrm{(CH_3)_2\dot{C}OH + Co(CN)_5^{3-} + H_2O \rightarrow (CH_3)_2CHOH + Co(CN)_5OH^{3-}} \qquad (6)$$

$$\mathrm{(CH_3)_2\dot{C}OH + Co(CN)_5OH^{3-} \rightarrow (CH_3)_2CO + Co(CN)_5^{3-} + H_2O} \qquad (7)$$

$$\mathrm{(CH_3)_2\dot{C}OH \rightarrow products} \qquad (8)$$

$$\mathrm{2Co(CN)_5^{3-} + O_2 \rightarrow Co(CN)_5O_2Co(CN)_5} \qquad (9)$$

According to this mechanism, Co(CN)$_5$H$_2$O^{2-} is practically unreactive, while Co(CN)$_5$OH^{3-} undergoes homolytic Co–OH bond splitting as a consequence of LMCT irradiation (reaction 2).

This point is born out by the pH dependence of the redox quantum yields which closely matches the change in concentration of the hydroxo species (the pK$_a$ value for equilibrium 1 is known to be 10.5 ± 0.5 [6]). The negative results obtained in flash photolysis of acidic solutions confirm this conclusion. Thus the previous suggestion [4] that the inefficiency of product formation in acidic solution could be due to the instability of Co(CN)$_5^{3-}$ in this medium is incorrect.

Reaction 3 represents secondary bulk recombination, reaction 4 indicates consumption of ·OH radicals either by radical coupling or by reaction with adventitious impurities, and reaction 5 describes the scavenging of OH radicals by 2-propanol. Equations 6, 7 and 8 describe the fate of the ketyl radicals which may either oxidize Co(CN)$_5^{3-}$ back to the reactant (eqn. 6), reduce a second reactant molecule to Co(CN)$_5^{3-}$ (eqn. 7), or disappear *via* coupling or hydrogen abstraction reactions (eqn. 8). The fact that the quantum yield of Co(CN)$_5^{3-}$ formation increases upon addition of 2-propanol and is constant in the 0.42–0.26 *M* 2-propanol range indicates that complete scavenging of bulk·OH radicals occurs in this concentration range. It is interesting to note that the quantum yield very nearly doubles upon scavenging. This can be straightforwardly accounted for if: (*i*) the quantum yield in the absence of 2-propanol is the primary 'out-of-cage' quantum yield (*i.e.* reaction 4 dominates over reaction 3), and (*ii*) the ketyl radicals produced in the scavenging step quantitatively reduce the reactant in a secondary reaction (*i.e.* reaction 7 dominates over reactions 6 and 8). Point (*ii*) is entirely plausible in view of the reactant concentration and the short irradiation times used.

Finally, the photochemical behavior observed in aerated alkaline solutions is the consequence of the well known (8) oxidation reaction of the Co(CN)$_5^{3-}$ primary product to μ-peroxocomplex.

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