Kinetics and Catalysis, Vol. 41, No. 1, 2000, pp. 48–51. Translated from Kinetika i Kataliz, Vol. 41, No. 1, 2000, pp. 57–60.
Original Russian Text Copyright © 2000 by Smirnova, Ermakov, Rozenkevich.

Photocatalytic Formation of Hydrogen in Aqueous–Alcohol Solutions of Cobalt Cyanide Complexes

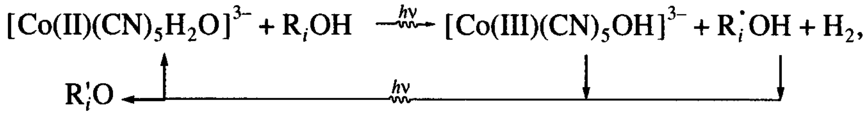
E. V. Smirnova, V. I. Ermakov, and M. B. Rozenkevich
Mendeleev University of Chemical Technology, Moscow, 125190 Russia

Received July 30, 1998

Abstract—The dependence of the parameters of the photocatalytic hydrogen formation in aqueous–alcohol (ethanol or isopropanol) solutions of cobalt cyanide on the compositions of binary and ternary solvents is studied. Experimental data are interpreted using ^1H NMR spectra of the solvents. The experimental observations are explained by possible solvation equilibria in the solutions. This photocatalytic system is a hypothetical model for the determination of relative solvation abilities of various organic compounds.

INTRODUCTION

When aqueous–organic solutions of cobalt cyanide complexes are exposed to light with a wavelength of 400 nm, molecular hydrogen is known to be formed [1–5] in a photocatalytic process. This process can be described as follows:



$$[Co(II)(CN)_5H_2O]^{3-} + R_iOH \xrightarrow{h\nu} [Co(III)(CN)_5OH]^{3-} + R_i^{\bullet}OH + H_2, \qquad (I)$$

$$R_i'O \xleftarrow{h\nu}$$

where $R_i^{\bullet}OH$ and $R_i'O$ are the radical and oxidized forms of the organic component (R_iOH) of the solution. For various R_iOH, the correlation between the rate of hydrogen formation and the reaction rate exists [6, 7].

$$H^{\bullet} + R_iOH \xrightarrow{k_H} H_2 + R_i^{\bullet}OH. \qquad (II)$$

The isotopic labeling method was used to show that the process of molecular hydrogen formation in this system occurs via the step of the formation of a complex in which hydrogen is close to atomic [8, 9]. These studies enabled the authors of the cited papers to conjecture that molecular hydrogen is formed inside the solvate shell of the starting Co(II) complex, and the rate of this process is determined by the composition of this shell at a constant composition of the solvent.

We use this conjecture to discuss the results of the comparative study of process (I) in binary and ternary aqueous–alcohol solvents together with the ^1H NMR data for these solvents.

EXPERIMENTAL

A photochemical experiment was carried out in a setup for stationary photolysis with the continuous registration of the amount of hydrogen formed. A DRSh-500 mercury lamp was used as a light source [10]. The IR part of a molecular beam was filtered with a 10-cm thick water filter. The intensity of spectral irradiation bands ($\lambda = 240–500$ nm) was determined using ferrioxalate actinometry [11] and a set of glass light filters. The value of light intensity for various lamps was within $(3–4) \times 10^{-5}$ einstein/min.

The starting solutions of $Na_3[Co(CN)_5H_2O]$ ($[Co(II)]_0 = 0.01$ mol/l) were prepared by mixing the preliminary deaerated solutions of $CoCl_2 \cdot 6H_2O$ (reagent grade) and NaCN (reagent grade) without air. The components of the solvent were doubly distilled water, ethanol, and isopropanol. The choice of these alcohols was due to the fact that they have different values of k_H (see reaction (II)): 2.8×10^7 and 8.2×10^7 l mol^{-1} s^{-1}, respectively [12]. The solutions were exposed to light in a quartz cell with an absorbing layer of 0.54 cm that maintained complete light absorption at $\lambda < 405$ nm (the region of light active in the photocatalytic process). In each run, the volume of irradiated solution was 2.2–2.4 cm^3, and the value of absorbed light intensity was (I_{ads}) – 18 ± 2% of the total intensity of light from the lamp.

During photolysis of the solutions, after 1.5–2.5 h after the start of irradiation, the photocatalytic system reached the stationary state, which was characterized by a certain ratio between the concentrations of the cyanide complexes of Co(II) and Co(III) ($[Co(II)]_0 = [Co(II)]_{st} + [Co(III)]_{st}$ according to scheme (I)) and by the

0023-1584/00/4101-0048$25.00 © 2000 MAIK “Nauka/Interperiodica”

stationary rate of molecular hydrogen formation $w^{st}_{H_2}$. For comparison of the photocatalytic system behavior at various compositions of the solvent, we used the stationary values of $[Co(II)]_{st}$, and $w^{st}_{H_2}$. $[Co(II)]_{st}$ was determined with an SF-26 instrument by the electron absorption spectra of $[Co(CN)_5H_2O]^{3-}$ using the values of light absorbance at $\lambda = 967$ nm ($\varepsilon = 297$ l mol^{-1} cm^{-1} [13]). The experimental value $w^{exp}_{H_2}$ was normalized taking into account the difference in light fluxes from the light sources used in our study ($w^{st}_{H_2} = w^{exp}_{H_2}/I_{ads}$). Therefore, the dimensionality of $w^{st}_{H_2}$ was (mmol H_2) per einstein of adsorbed light.

^1H NMR spectra of the solvents, which were free of $[Co(CN)_5H_2O]^{3-}$, were recorded on a BS-467 instrument (60 MHz) because the presence of this paramagnetic complex results in a substantial broadening of spectral lines and makes the interpretation of spectra difficult. The values of chemical shifts corresponding to the functional groups were determined relatively to tetramethylsilane (an internal standard) with an accuracy of 0.02 ppm.

RESULTS AND DISCUSSION

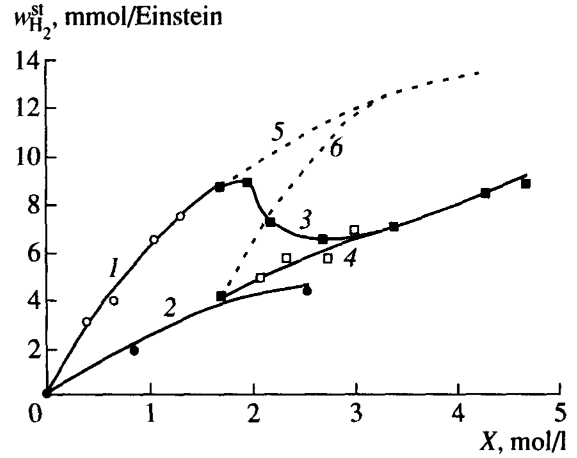
Table 1 and the figure show the results of a photochemical experiment. The characteristic changes in the parameters depending on the composition of the solution are discussed below.

Stationary Concentration of $[Co(CN)_5H_2O]^{3-}$

1. When passing from aqueous to aqueous–organic solutions, the value of $[Co(II)]_{st}$ increases (see Table 1). Using the data reported earlier [4–7], this can be explained by a change in the mechanism of the reductive semicycle of the photocatalytic process (I). In aqueous solutions, the CN^- ion is the electron donor for Co(III) reduction. In aqueous–organic solutions, the donor is a R_iOH radical. Note that, according to [14, 15], the reductive ability of the *iso*-$\dot{C}_3H_6OH$ radical is higher than that of $\dot{C}_2H_4OH$, whereas the value of $[Co(II)]_{st}$ is higher for the aqueous–ethanol solutions.

2. In the case of ternary solvents, the appearance of ethanol in the solution containing isopropanol results in an increase in $[Co(II)]_{st}$ and its absolute value becomes equal (within the experimental error) to the analogous value for the binary water–ethanol solutions. Conversely, the appearance of isopropanol in the solution containing ethanol does not change the $[Co(II)]_{st}$ value.

Note that these changes in the $[Co(II)]_{st}$ value are observed in both cases even when the amount of R_iOH is small (2–3 vol %). This value further remains constant within the experimental error.



The dependence of $w^{st}_{H_2}$ on the concentration X of the organic component of the solvent in 0.01 M solutions of $[Co(CN)_5H_2O]^{3-}$: (*1*) water–isopropanol; (2) water–ethanol; (*3*) water–1.7 mol/l isopropanol–X mol/l ethanol; (*4*) water–1.7 mol/l ethanol–X mol/l isopropanol; (*5*) water–1.7 mol/l isopropanol–X mol/l ethanol (additive); and (*6*) water–1.7 mol/l ethanol–X mol/l isopropanol (additive).

Rate of Hydrogen Formation in the Stationary State

1. In binary solvents, a monotonic increase in the $w^{st}_{H_2}$ value with an increase in $[R_iOH]$ (for the aqueous solution, $w^{st}_{H_2} = 0.1$ mmol/einstein) is observed. According to the values of k_H, the $w^{st}_{H_2}$ value is higher for isopropanol than for ethanol (see the figure, curves *1*, *2*). This completely agrees with the data reported earlier [5–9].

Table 1. The $[Co(II)]_{st}$ values in the aqueous solutions in binary and ternary solvents

Solvent composition	$[Co(II)]_{st} \times 10^3$, mol/l
H_2O	4.6 ± 0.4
Binary solvents:	
$H_2O + C_2H_5OH$, $[C_2H_5OH] = 0.4$–2.6 mol/l	6.8 ± 0.5
H_2O + *iso*-C_3H_7OH, [*iso*-C_3H_7OH] = 0.4–1.7 mol/l	5.7 ± 0.5
Ternary solvents:	
H_2O + 1.7 mol/l *iso*-C_3H_7OH + C_2H_5OH, $[C_2H_5OH] = 0.3$–3 mol/l	7.0 ± 0.4
H_2O + 1.7 mol/l C_2H_5OH + *iso*-C_3H_7OH, [*iso*-C_3H_7OH] = 0.4–1.7 mol/l	6.5 ± 0.3

Table 2. The values of chemical shifts (δ_i) in ^{1}H NMR solvents

Solvent*	Chemical shift, ppm			
	δ_{OH}	δ_{CH}	δ_{CH_2}	δ_{CH_3}
C_2H_5OH	5.34	–	3.61	1.10
iso-C_3H_7OH	5.36	3.85	–	1.12
$H_2O + C_2H_5OH$	5.08	–	3.87	1.39
$H_2O +$ *iso*-C_3H_7OH	5.12	4.33	–	1.40
$H_2O + C_2H_5OH +$ *iso*-C_3H_7OH	5.10	4.33	3.87	1.37

* The concentration of R_iOH in aqueous–organic mixtures is 1.7 mol/l.

2. In the ternary solvent, a change in the $w^{st}_{H_2}$ value with the appearance of the third component is more complex. The addition of ethanol to the water–isopropanol solution (curve *3*) results in a substantial decrease in the $w^{st}_{H_2}$ value. At high ethanol concentrations, the value of $w^{st}_{H_2}$ approaches the values characteristic of the binary water–ethanol solvents. Conversely, the addition of isopropanol to the water–ethanol solutions (curve *4*) results in an increase in $w^{st}_{H_2}$. However, when its concentration is equal to 1.7 mol/l, the $w^{st}_{H_2}$ value remains ~1.5 times lower than for the binary water–isopropanol solvent with the same isopropanol concentration (compare curves *1* and *4*).

Before discussing the reasons for the apparent behavior of the system, let us consider the results of ^{1}H NMR study of the solutions (Table 2). The data reported in this table suggest that, when R_iOH is mixed with water, all the values of δ_i are changed. This points to a substantial difference in the structure of alcohol in the solution from its structure in pure R_iOH. However, we did not observed mutual influence of R_iOH in ternary solvents over the studied ranges of alcohol concentrations (the last row in Table 2).

If the molecular hydrogen formation in the photocatalytic process were completed in the bulk of the solution, then the apparent dependence of $w^{st}_{H_2}$ on the composition of the solution in ternary mixtures would be additive with respect to the corresponding dependences in binary solvents (dashed lines in the figure). The experimental dependence is different. Therefore, we conclude that the data agree with the earlier hypothesis that the process is completed in the solvate shell of the Co(II) complex and that the composition of the shell determines the value of $w^{st}_{H_2}$.

The above data can be described by the following scheme of solvation equilibria in the solution.

$$\{[Co(CN)_5H_2O]^{3-}\}, nH_2O \underset{-R_1OH}{\overset{+R_1OH}{\rightleftarrows}} \{[Co(CN)_5H_2O]^{3-}\}, (n-x)H_2O, xR_1OH, \qquad \text{(III)}$$

$$\begin{tikzcd}[column sep=small] & \{[Co(CN)_5H_2O]^{3-}\}, (n-x-y)H_2O, xR_1OH, yR_2OH \quad \text{(IVa)} \\ \{[Co(CN)_5H_2O]^{3-}\}, (n-x)H_2O, xR_1OH, \arrow[ur, "+R_2OH"] \arrow[dr, "+R_2OH"'] & \\ & \{[Co(CN)_5H_2O]^{3-}\}, (n-x)H_2O, (x-y)R_1OH, yR_2OH. \text{(IVb)} \end{tikzcd}$$

Equilibrium (III) takes place in binary solvents; equilibria (IVa) and (IVb) exist in ternary solvents.

Within the framework of the proposed scheme, the apparent changes in $w^{st}_{H_2}$ in ternary solvents are explained as follows. When ethanol is added into a water–isopropanol solution, the solvation equilibrium is attained according to scheme (IVb), that is, by the substitution of isopropanol for ethanol in the solvate shell. As the concentration of ethanol increases, the characteristics of the system approach those that are typical of the binary water–ethanol solution. When isopropanol appears in the water–ethanol solution, the solvation equilibrium is attained according to the scheme (IVa) and the values $w^{st}_{H_2}$ are intermediate between those characteristic of two binary solvents.

The data enable us to conjecture that opposing trends in changing the reductive ability of R_iOH radicals and the value of $[Co(II)]_{st}$ in binary solvents suggest that, in the photocatalytic process, the rate-limiting steps responsible for attaining the stationary state of the systems are the reactions of the oxidative semicycle. In this case, despite the high reductive ability of *iso*-$\dot{C}_3H_6OH$, the values of $[Co(II)]_{st}$ in the water–isopropanol solution are lower because isopropanol has a much higher value of the k_H parameter, which determines the rate of hydrogen formation in the oxidative semicycle.

To summarize, we note that our findings agree with the earlier hypothesis on the crucial role of solvation in the photocatalytic process of hydrogen isolation from the solutions of cobalt cyanide complexes. Therefore, the experimental determination of the parameters of this process ($[Co(II)]_{st}$ and $w^{st}_{H_2}$) in aqueous–organic solutions of various compositions may be usable as a method for the determination of the relative solvation ability of various organic components of the solvent

REFERENCES

1. Gogolev, A.V., Potapov, I.A., Rozenkevich, M.B., and Sakharovskii, Yu.A., *Kinet. Katal.*, 1979, vol. 20, no. 3, p. 807.
2. Potapov, I.A., Rozenkevich, M.B., and Sakharovskii, Yu.A., *Koord. Khim.*, 1979, vol. 5, no. 2, p. 294.
3. Gogolev, A.V., Potapov, I.A., Rozenkevich, M.B., and Sakharovskii, Yu.A., *Kinet. Katal.*, 1980, vol. 21, no. 2, p. 384.
4. Gogolev, A.V., Potapov, M.B., Rozenkevich, M.B., and Sakharovskii, Yu.A., *Kinet. Katal.*, 1981, vol. 22, no. 2, p. 327.
5. Rozenkevich, M.B. and Sakharovskii, Yu.A., *Kinet. Katal.*, 1986, vol. 27, no. 1, p. 29.
6. Rozenkevich, M.B. and Sakharovsky, Yu.A., *Proc. VI World Hydrogen Energy Conf.*, 1986, vol. 2, p. 626.
7. Rozenkevich, M.B. and Sakharovsky, Yu.A., *Int. J. Hydr. Energy*, 1989, vol. 14, no. 7, p. 431.
8. Myakon'kii, A.G., Marchenko, T.A., Rozenkevich, M.B., and Sakharovskii, Yu.A., *Kinet. Katal.*, 1986, vol. 27, no. 4, p. 813.
9. Myakon'kii, A.G., Rozenkevich, M.B., and Sakharovskii, Yu.A., *Trudy MKhTI im D.I. Mendeleeva* (Collected Works of Mendeleev Institute of Chemical Engineering), Moscow: Mendeleev Institute of Chemical Engineering, 1987, vol. 148, p. 103.
10. Potapov, I.A. and Rozenkevich, M.B., *Zh. Fiz. Khim.*, 1985, vol. 59, no. 3, p. 785.
11. Bowman, W.D. and Demas, J.N., *J. Phys. Chem.*, 1976, vol. 80, no. 10, p. 2434.
12. Pikaev, A.K. and Kabakchi, S.A., *Reaktsionnaya sposobnost' pervichnykh produktov radioliza vody* (Reactivity of Primary Products of Water Radiolysis), Moscow: Energoizdat, 1982, p. 160.
13. King, N.K. and Winfield, M.E., *J. Am. Chem. Soc.*, 1961, vol. 83, p. 3366.
14. Belevskii, V.N., *Khim. Vys. Energ.*, 1981, vol. 15, no. 1, p. 1.
15. Ershov, V.G., *Usp. Khim.*, 1981, vol. 10, p. 2137.