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Some Remarks on the Reaction Mechanism and Kinetic Rate Constants for the Pentacyanocobaltate(II)-catalyzed Hydrogenation of Olefins Using the Iterative Simulation Technique

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The reaction mechanism and kinetic-rate constants of the pentacyanocobaltate(II)-catalyzed hydrogenation of olefins were investigated. The present study with an iterative simulation technique supported the $Co(CN)_5^{3-}+H_2 \rightarrow Co(CN)_5H^{3-}+H\cdot$ and $Co(CN)_5^{3-}+H\cdot \rightarrow Co(CN)_5H^{3-}$ reactions for the uptake of H_2 by the cobaltate(II) during the initial stage of the reaction. An examination was also made of the stationary-state approximation used for the kinetic analysis of the reaction.

It is well known that pentacyanocobaltate(II) takes part in the reductive cleavage of covalent molecules:

$$2Co(CN)_5^{3-} + X\text{–}Y \rightarrow Co(CN)_5X^{3-} + Co(CN)_5Y^{3-} \quad (1)$$

where X–Y means such molecules as H_2,[1-5] H_2O,[2] Br,[6] I_2[6] H_2O_2,[7] $HONH_2$[8] ICN,[8] and organic halides.[9-11]

In the hydrogenation of olefins (denoted as A) with $Co(CN)_5^{3-}$, the molecular hydrogen has been considered, on the basis of the kinetic investigations,[4,12] to participate in the formation of hydropentacyanocobaltate(III), $Co(CN)_5H^{3-}$, through Reaction (2):

$$2Co(CN)_5^{3-} + H_2 \xrightarrow{k_1} 2Co(CN)_5H^{3-} \quad (2)$$

Reaction (2) is followed by:

$$Co(CN)_5H^{3-} + A \xrightarrow{k_2} Co(CN)_5^{3-} + AH\cdot \quad (3)$$

$$Co(CN)_5H^{3-} + AH\cdot \xrightarrow{k_3} Co(CN)_5^{3-} + HAH \quad (4)$$

where AH· and HAH denote a momentarily living radical intermediate and a saturated hydrocarbon respectively.

Although the mechanism expressed by Reactions (2—4) (named Mechanism I) has hitherto been accepted as the most plausible one for the $Co(CN)_5^{3-}$-catalyzed hydrogenation of olefins, the following mechanism (named Mechanism II) can also be considered in view of the fact that the uptake of H_2 by $Co(CN)_5^{3-}$ is between first- and second-order in cobalt from 0 to 25 °C[13] and that $Co(CN)_5^{3-}$ takes part in the reductive cleavage of such X–Y as organic halides by the two-step reaction ($Co(CN)_5^{3-}+X\text{–}Y \rightarrow Co(CN)_5X^{3-}+Y\cdot$ and $Co(CN)_5^{3-}+Y\cdot \rightarrow Co(CN)_5Y^{3-}$):

$$Co(CN)_5^{3-} + H_2 \xrightarrow{k_1} Co(CN)_5H^{3-} + H\cdot \quad (5)$$

$$Co(CN)_5^{3-} + H\cdot \xrightarrow{k_2} Co(CN)_5H^{3-} \quad (6)$$

$$Co(CN)_5H^{3-} + A \xrightarrow{k_3} Co(CN)_5^{3-} + AH\cdot \quad (7)$$

$$Co(CN)_5H^{3-} + AH\cdot \xrightarrow{k_4} Co(CN)_5^{3-} + HAH \quad (8)$$

Reactions (5, 6) indicate a first-order dependence on cobalt for the formation of $Co(CN)_5H^{3-}$, which corresponds to $[Co^{II}(CN)_5(\cdot H)]^{3-}$ rather than $[Co^{III}(CN)_5(:H)]^{3-}$.[14]

In Reaction (6), the highest singly-occupied d_{z^2} Co-orbital (at −11.01 eV)[15] of $Co(CN)_5^{3-}$ seems to play an important role in the reaction with the H radical.

In this paper, we will discuss the reaction mechanism and rate constants for the $Co(CN)_5^{3-}$-catalyzed hydrogenation of olefins on the basis of Mechanisms I and II, using an iterative simulation technique involving least-squares error analysis.

Computation Method

The rate constants in systems of nonlinear differential equations such as those derived from Reactions (2—4) or (5—8) can be estimated by means of such numerical integration methods as the Runge-Kutta integration,[16] the Marquardt method,[17] and Taylor's series expansions.[18] These methods, however, require very dense data, much computation time, and highly developed mathematical techniques to estimate the rate constants directly. Therefore, we will use an iterative simulation technique combined with the least-squares error analysis in the present paper. Here, we will briefly describe the present technique.

The differential equations (rate equations) can be simply expressed on the basis of the law of mass action as:

$$d(C_s)/dt = f(k_i,\ (C_r))$$

where (C_s) and (C_r) denote the concentrations of C_s (s=species number) and C_r (r=species number) respectively, and where $f(k_i,\ (C_r))$ means a function made by the rate constants, k_i (i=1—3 or 1—4 for Mechanism I or II respectively) and (C_r). The reaction increments of (C_s), $D(C_s)$, are shown with a very short time interval, Δt[19]:

$$D(C_s) = f(k_i,\ (C_r))\Delta t \quad (10)$$

The concentrations of C_s at the reaction time of t, $(C_s)_{t,\text{calcd}}$, are evaluated by means of the trapezoidal average method:[20]

$$(C_s)_{t,\text{calcd}} = (C_s)_0 + \sum^{n} D(C_s)_{\text{av}}\Delta t \quad (n\Delta t = t) \quad (11)$$

where $(C_s)_0$ and $D(C_s)_{\text{av}}$ indicate the initial concentrations and the average increments of C_s respectively.

In the evaluation of the $(C_s)_{t,\text{calcd}}$ values, the rate constants, k_i, are inserted into Eq. (11) in accordance with our previous technique:[17,19]

$$k_i = \min k_i + \sum^{m} 10^{(\gamma-\beta)} \min k_i,\ \gamma = \text{gauss}\left[\frac{m-1}{9\alpha}\right] \quad (12)$$

$$(m=1,2,\cdots\cdots;\ \beta=0,1,2,\cdots\cdots;\ \alpha=10)$$

where the notations have the same meanings as those in previous papers.[19,21]

The best set of k_i values are, then, selected from the set, minimizing the least-squares error between the experimentally observed concentrations of C_s, $(C_s)_{t,\text{given}}$, and the $(C_s)_{t,\text{calcd}}$ values by means of the iterative search technique:[21]

$$F = \text{minimize} \sum_{s=1}^{s-1} \sum_{p=1}^{p} \varepsilon_{p,s} \tag{13a}$$

$$\varepsilon_{p,s} = |(C_s)_{t,\text{given}} - (C_s)_{t,\text{calcd}}|^2 \tag{13b}$$

where the notations have the same meanings as in Ref. 21. The above equations were used because the F function has only one suitable $(C_s)_{t,\text{calcd}}$ value when $(C_s)_{t,\text{given}} = (C_s)_{t,\text{calcd}}$. The reliability of the rate constants estimated by the present method and some practical techniques for the accurate estimation of rate constants during a short computation time have already been described in detail in a previous paper.[21]

Computation Results and Discussion

We will first estimate the rate constants in Mechanisms I and II, using the time-dependence of the H_2 absorption in the hydrogenation of sodium cinnamate (0.20 M) by $Co(CN)_5^{3-}$ (0.010 M) at 25 °C.[22] The almost constant rate (4.86×10^{-7} M/s) or H_2 absorption up to 100 min is one of the characteristic features of this reaction. In order to apply the present technique to the estimation of the rate constants in Mechanisms I and II, we will use the F function as defined by Eqs. (15a, b) instead of by Eqs. (13a, b), because the time dependence of the concentration of each species can be evaluated on only the basis of the amount of H_2 absorbed, $(H_2)_{t,\text{absd}}$:

$$F = \text{minimize} \sum_{p=1}^{p} \varepsilon_p \tag{15a}$$

$$\varepsilon_p = |(H_2)_{t,\text{absd}} \text{ obtained experimentally} - (H_2)_{t,\text{absd}} \text{ obtained theoretically}|^2 \tag{15b}$$

where ε_p (p=checking point number) stands for the least-squares error at every checking point; the values for $(H_2)_{t,\text{absd}}$ obtained theoretically are calculated by means of the following kinetic relationships, given by the material balance of the hydrogen atom:

$$(H_2)_{t,\text{absd}} = (Co(CN)_5H^{3-})_{t,\text{calcd}}/2 + (AH\cdot)_{t,\text{calcd}}/2 + (HAH)_{t,\text{calcd}} \tag{16a}$$

for Mechanism I

$$(H_2)_{t,\text{absd}} = (Co(CN)_5H^{3-})_{t,\text{calcd}}/2 + (H\cdot)_{t,\text{calcd}}/2 + (AH\cdot)_{t,\text{calcd}}/2 + (HAH)_{t,\text{calcd}} \tag{16b}$$

for Mechanism II

The best sets of the rate constants in Mechanisms I and II will now be estimated under the conditions of Δt=1.0 s, n=6000, α=10 (β=1), m=1081, δ=−5,[21] and p=20 (every 5 min up to 100 min). The best sets of the k_i values, which take about 18 min to be obtained by means of the FACOM 230-60 computer, are shown in Table 1, together with the F and ε_p values. It may be seen from the F and ε_p values that Mechanism II seems to be better. This may coincide with the fact that the k_3 value of 2.4×10^{-3} M^{-1} s^{-1} for Mechanism II, as compared with the k_2 value of 9.0×10^{-4} M^{-1} s^{-1} for Mechanism I, is a better analytic fit for the rate constant of $1.5 \pm 0.5 \times 10^{-3}$ M^{-1} s^{-1} [22] for the $Co(CN)_5H^{3-} + CH_2{=}CHCOO^- \rightarrow Co(CN)_5^{3-} + CH_3\dot{C}HCOO^-$ reaction, although the best rate constant value of 1.0×10^2 M^{-1} s^{-1} for the $Co(CN)_5H^{3-} + AH\cdot \rightarrow Co(CN)_5^{3-} + HAH$ reaction is identical in both the mechanisms.

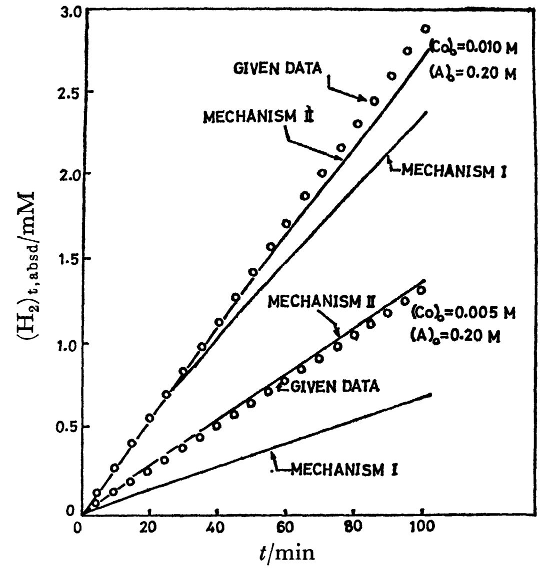

Fig. 1. Plots of $(H_2)_{t,\text{absd}}$ vs. t.
(The rate constants are listed in Table 2.)

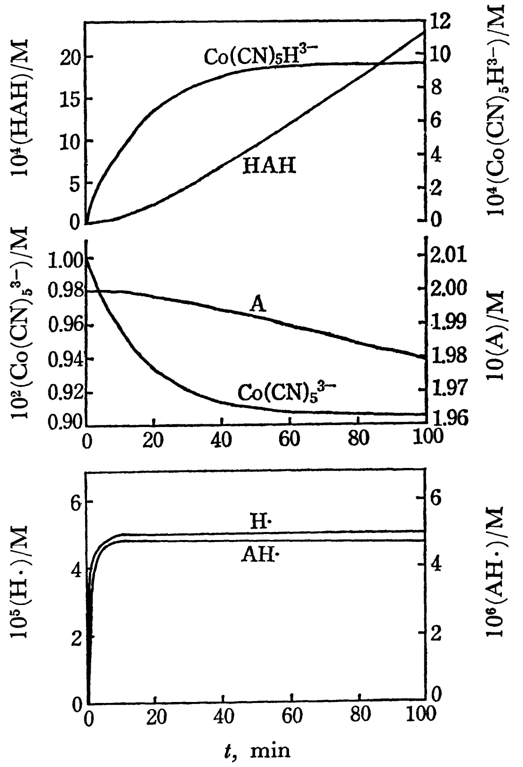

Fig. 2. Time conversions of $(Co(CN)_5^{3-})$, $(Co(CN)_5H^{3-})$, (H·), (AH·), and (HAH).

However, the present parameter-estimation procedure with Eqs. (15a, b) requires further computations of the F function with more than two different initial specifications (the so-called initial conditions) in order to check the reliability of the selected best set of k_i. We will simulate the time-dependence of the hydrogen absorption in both the mechanisms with the following different initial specifications: $(Co(CN)_5^{3-})_0=0.005$ M and $(A)_0=0.20$ M. The simulation results are shown in Fig. 1. As can be seen from Fig. 1, the predicted $(H_2)_{t,\mathrm{absd}}$ curves for Mechanism II accord more satisfactorily with the observed $(H_2)_{t,\mathrm{absd}}$ curves than those for Mechanism I.

It is of interest here to notice the time conversions of the concentrations of species participating in Mechanism II. From the time conversions of the species shown in Fig. 2, we can observe that the concentrations of the H and AH radicals ($(H\cdot)/(AH\cdot)\simeq 10$) seem to be relatively high despite their momentary lives, in comparison with those of $Co(CN)_5H^{3-}$ and HAH; the $(H\cdot)$ and $(AH\cdot)$ values are almost constant at $t \gtrsim 10$ min. Under these conditions, it seems that the stationary-state approximation can be used for the concentrations of both the intermediates. Then, we will test the stationary-state approximation in order to estimate the rate constants in Mechanism II. From the rate equations (differential equations) derived from Eqs. (5—8) and (16a, b), the rate of H_2 absorption, $R_{t,\mathrm{calcd}}$, can be expressed by the following kinetic relationships:

$$R_{t,\mathrm{calcd}} = d(H_2)_{t,\mathrm{absd}}/dt = a e^{-2at}((Co(CN)_5^{3-})_0-b/a) \\ -k_1(H_2)be^{-2at}/a+k_1(H_2)(A)(Co(CN)_5^{3-})_0/a \tag{17}$$

$$(H_2)_{t,\mathrm{absd}} = (1-e^{-2at})((Co(CN)_5^{3-})_0-b/a)/2 \\ +k_1k_3(H_2)(A)(Co(CN)_5^{3-})_0 t/a \\ +k_1(H_2)b(e^{-2at}-1)/2a^2 \\ +k_1(H_2)/2k_2+k_3(A)/2k_4 \tag{18}$$

where $a=k_1(H_2)+k_3(A)$ and $b=k_3(A)(Co(CN)_5^{3-})_0$.

Let us estimate the k_1 and k_3 values in Eq. (17) by means of the present technique under the following condition:

$$F' = \mathrm{minimize}\sum_{p=1}^{p}\varepsilon_p' = \mathrm{minimize}|R_{t,\mathrm{calad}}-R_{t,\mathrm{given}}|^2 \tag{19}$$

where $R_{t,\mathrm{calcd}}$ and $R_{t,\mathrm{given}}$ indicate the calculated and observed rates of H_2 absorption respectively.

The above procedure gave $k_1=1.0\times10^{-3}$ and $k_3=1.0\times10^{-1}$ $M^{-1}s^{-1}$ as the best set of rate constants, appreciably different from those ($k_1=1.2\times10^{-3}$ and $k_3=2.4\times10^{-3}$ $M^{-1}s^{-1}$) shown in Table 1. The computer simulations with the sets of both k_1 and k_3 values obtained by means of Eq. (17) indicate that the former set of rate constants gives a more precise fit to the $R_{t,\mathrm{given}}$ values than the latter one. However this is not a surprising phenomenon for the following reasons: (a) strictly speaking, the concentration of neither radical intermediate is constant; (b) the stationary-state approximation which neglects the rate constants of k_2 and k_4 (not extremely large rate constants) may bring about the apparent difference between the k_3 values mentioned above, and (c) the $R_{t,\mathrm{calcd}}$-value evaluation by means of Eq. (17), derived from the stationary-state approximation with only the set of k_1 and k_3 values for Mechanism II (see Table 1), cannot give an accurate time-conversion of the H_2 absorption rate. This discussion is reasonable if we notice that the $(H_2)_{t,\mathrm{absd}}$ values obtained from the present simulation with $k_1=1.0\times10^{-3}$, $k_2=1.0$, $k_3=1.0\times10^{-1}$, and $k_4=1.0\times10^{2}$ $M^{-1}s^{-1}$ are very small compared with the observed values. Furthermore, Eq. (18) brings about somewhat large $(H_2)_{t,\mathrm{absd}}$ values under $k_1=1.0\times10^{-3}$, $k_3=1.0\times10^{-1}$, and $k_4=1.0\times10^{2}$ $M^{-1}s^{-1}$ (Eq. (18) excludes k_2), while the simulation with the best set of k_i ($i=1$—4) values for Mechanism II indicates satisfactorily precise fits to the experimental results. It may be deduced, therefore, that the kinetic analysis by means of the present iterative simulation technique, which does not include any stationary-state approximation, gives more reliable information about the unknown rate constants in elementary reactions.

TABLE 1. THE BEST SETS OF RATE CONSTANTS AND THE LEAST-SQUARES ERROR FOR MECHANISMS I AND II

Mechanism I	Mechanism II
$k_1=1.3\times10^{-1}$ $M^{-1}s^{-1}$	$k_1=1.2\times10^{-3}$ $M^{-1}s^{-1}$
$k_2=9.0\times10^{-4}$	$k_2=1.0$
$k_3=1.0\times10^{2}$	$k_3=2.4\times10^{-3}$
	$k_4=1.0\times10^{2}$
$\varepsilon_p=7.121\times10^{-11}-2.837\times10^{-7}$ M^2	$\varepsilon_p=6.713\times10^{-12}-2.360\times10^{-8}$ M^2
$F=1.466\times10^{-6}$ M^2	$F=1.345\times10^{-7}$ M^2

In conclusion, we have demonstrated that, in the $Co(CN)_5^{3-}$-catalyzed hydrogenation of olefins, the two-step reaction of the complex and molecular hydrogen may play an important role in the formation of hydropentacyanocobaltate(III), especially during the initial reaction state.

The calculations were carried out on a FACOM 230—60 computer at the Data Processing Center of Kyushu University.

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