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SIMULTANEOUS DETERMINATION OF RATE CONSTANTS FOR FIRST ORDER CONSECUTIVE IRREVERSIBLE REACTIONS

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ABSTRACT. A method for simultaneous experimental determination of rate constants for a first-order, two stage, irreversible process is proposed. It is based on the monitoring of a commun product.The first and second rate coefficient are determined at small and high reaction degrees, respectively. The obtained values are independent from each other.

The method is ilustrated for the acvation of trans-dibromo-bis-dymethylglyoximato-cobalt (III) acid. Its evolution was monitored by potentiometrical means. Kinetic parameters are reported for a variety of experimental conditions. Activation parameters have been calculated and a dissociative monomolecular substitution mechanism is proposed for both the stages.

INTRODUCTION

Numerous reactions of industrial importance occur consecutively or competitively, by combining at least two independent reactions. Therefore, the individual rate coefficients are important in chemical reactor design. Their simultaneous experimental determination has to take into account the individual features of each studied process. However, some general "recipes" can be developed.

When experiments provide a product distribution, ratios of rate constants can be obtained for a variety of complex reactions by superposing the experimental and calculated plots [1]. A method to determine k_1 and k_2 (when $k_1 >> k_2$) is reported for two first-order consecutive reactions, when an additive propriety of the reaction mixture is monitored [2,3] (for example the absorbance). This method is similar to the one applied for first-order parallel processes which yield the same product [4]. Determination of individual rate coefficients for competitive reactions of different orders (first and second) [5] follows the same principle as for catalyzed and uncatalyzed competitive ones [6].

This paper presents a method to determine the individual rate constants k_1 and k_2 for a sequence of two first-order consecutive irreversible reactions. One of

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the products is yield in each of them. The method is based on monitoring its concentration versus reaction time.

A chemical system with these features is the acvation process of trans-dibromo-bis-dymethylglyoximato-cobalt (III) acid:

$$[Co(DH)_2Br_2]^- + H_2O \rightarrow [Co(DH)_2Br(H_2O)] + Br^- \qquad (k_1) \quad (1)$$

$$[Co(DH)_2Br(H_2O)] + H_2O \rightarrow [Co(DH)_2(H_2O)_2]^+ + Br^- \qquad (k_2) \quad (2)$$

where the commun product is bromide.

Sychev [7] and Zsako [8,11] studied the kinetics of these processes in water-dimethylformamide mixtures, at the pH of the reactant acid. They determined both k_1 and k_2: Sychev by studying reactions (1) and (2) separately and Zsako by monitoring the whole sequence. He first obtained the value of k_1 and than the one of k_2 by constantly adjusting it, till the experimental concentration plots superposed the theoretical ones. This way, value of k_2 is affected by the experimental determination of k_1.

Although Sychev and Zsako used both a potentiometric method, the ionic strength of the reaction mixture was not controlled. Neither was the pH, although experiments were carried out in acid media and it was recognized that acidity affects reaction rates.

By reconsidering these measurements, we tried not only to avoid, but also to complement the results Sychev and Zsako have arrived at [7,8,11].

EXPERIMENTAL

Analytical grade reagents, provided by "Reactivul-Bucuresti", were used without further purification. The reactant $H[Co(DH)_2Br_2]$ was syntetized by a known method [7]. HNO_3 and a CH_3COOH / CH_3COONa buffer were used to ensure a known acidity of medium. The ionic strength was adjusted to j = 1 mole.l^{-1} with KNO_3. All aqueous solutions were prepared in twice distilled water.

Two solutions were prepared for each kinetic experiment, so that after mixing the total volume became 8 ml. One solution contained the acid or the buffer and KNO_3. The other contained 70 mg of $H[Co(DH)_2Br_2]$ dissolved in N,N – dimethylformamide (DMFA) and was freshly prepared before each experiment. Both solutions were kept at controlled temperature, the first one in a double wall glass vessel connected to a precision circulation bath. It was placed on a magnetic stirrer. The second solution was added to the first one under stirring and a stop-watch was started.

A selective bromide electrode was introduced in the reaction mixture and connected together with a reference electrode to a digital RADELKIS multimeter. The salt bridge contained saturated aqueous solution of KNO_3. The electromotive force of the cell was recorded versus reaction time. Three to seven replicate runs were carried out for the same experimental conditions.

The value of acidity was verified with a glass pH electrode. Both the electrodes (bromide and pH) were calibrated at j = 1 mole.l^{-1} for each working temperature. After each experiment the bromide electrode was washed and dried.

RESULTS AND DISCUSSIONS

Determination of individual rate coefficients

For simplicity, reactions (1) and (2) are written schematically as follows:

$A \rightarrow B + D \qquad (k_1) \qquad (3)$

$B \rightarrow C + D \qquad (k_2) \qquad (4)$

where A stans for $[Co(DH)_2Br_2]^-$, B for $[Co(DH)_2Br(H_2O)]$, C for $[Co(DH)_2(H_2O)_2]^+$ and D for Br^-.

In order to study the kinetics of processes (1) and (2), the electromotive force *E* of the cell below was recorded versus reaction time *t*.

(-) Hg / Hg_2Cl_2 / Cl^- (sat) // Br^- (C_D) / EMIS – Br (+) (5)

C_D stands for the total molar concentration of released Br^- ions. Its values can be calculated by using equation (7) from the calibration lines (6):

$$E = A + B \lg C_D \qquad (mV) \qquad (6)$$

$$\lg C_D = \frac{E - A}{B} \qquad (7)$$

Relationship (6) is valid only for $10^{-3} \leq C_D \leq 10^{-1}$ mole.l^{-1}. The constants *A* and *B* were determined experimentally at j = 1 mole.l^{-1} and various temperatures. Their values, as well as the correlation coefficients of the corresponding calibration lines, are given in table 1.

Table 1.

Values of constants *A* and *B* at j = 1 mole.l^{-1}.

T (K)	298	308	320
A (mV)	- 128.71	- 121.76	-113.63
B (mV)	- 62.18	- 62.76	-65.60
r	0.9994	0.9991	0.9989

The kinetic model for two first-order consecutive irreversible reactions, provides the expressions of concentrations C_A and C_B [10]:

$$C_A = C_{Ao} \exp\left(-k_1 t\right) = C_{Ao} - C_D \qquad (8)$$

$$C_B = \frac{k_1 C_{Ao}}{k_2 - k_1}\left[\exp\left(-k_1 t\right) - \exp\left(-k_2 t\right)\right] \qquad (9)$$

Mass balances for Co(III) and Br^- written as:

$$C_{Ao} - C_A = C_B + C_C \qquad (10)$$

and $C_D = C_B + 2C_C$ (11)

will lead to the expressions of C_C and C_D. C_{A0} stands for the initial molar concentration of species A.

The linear form of equation (8) is:

$$\ln \frac{C_{Ao}}{C_{Ao} - C_D} = k_1 t \quad (12)$$

If $k_1 > k_2$, at low overall conversion (less than 8 ÷ 10 %), only reaction (3) occurs at a significant rate. Thus, k_1 can be obtained from the slope of the plot *ln* $[C_{Ao}/(C_{Ao} - C_D)]$ versus reaction time (see equation 12), as ilustrated in figure 1.

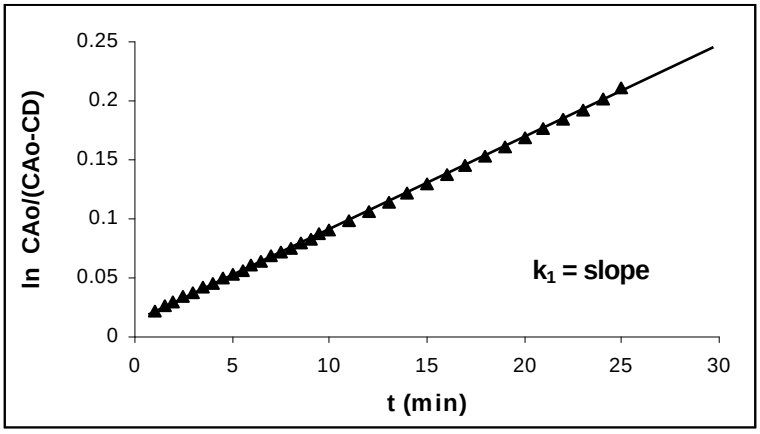

Figure 1. The plot of *ln* $[C_{Ao}/(C_{Ao} - C_D)]$ versus reaction time at T = 298 K, j = 1 mole.l^{-1}, $C_{Ao} = 1.95 \bullet 10^{-2}$ mole.l^{-1}, $[H^+] = 9.30 \bullet 10^{-3}$ mole.l^{-1} in water – 25 % vol DMFA mixture.

From equations (10) and (11), by introducing expressions (8) and (9), the result becomes:

$$C_D - C_{Ao}\left[1 - \exp\left(-k_1 t\right)\right] = C_{Ao}\left\{\frac{k_1}{k_1 - k_2}\left[\exp\left(-k_2 t\right)\right] - \frac{k_2}{k_2 - k_1}\left[\exp\left(-k_1 t\right)\right]\right\} \quad (13)$$

At high overall conversion (over70 ÷ 80 %), if $k_1 > k_2$, reaction (3) is already accomplished and variation of C_D is due only to reaction (4). Thus, at high *t*, values of *exp* $(-k_1 t)$ become negligible and equation (13) will be simplified at:

$$2C_{Ao} - C_D = C_{Ao}\frac{k_1}{k_1 - k_2}\exp\left(-k_2 t\right) \quad (14)$$

Its linear form is:

$$\ln\left(2C_{Ao} - C_D\right) = \ln\left(C_{Ao}\frac{k_1}{k_1 - k_2}\right) - k_2 t \quad (15)$$

Values of k_2 can be obtaind directly from experimental data, by using the plot of *ln* $(2C_{Ao} - C_D)$ versus reaction time (see equation 15), as ilustrated in figure 2.

Hence, individual rate coefficients k_1 and k_2 of reactions (1) and (2) respectively, can be determined ***directly*** from the experimental data:

- k_1 is calculated by using the plot of equation (12) and data collected at the beginning of the overall process
- k_2 is calculated by using the plot of equation (15) and data towards the end of the overall process.

Values of k_2 are independent of those obtained for k_1. For all experimental conditions, we found that.

- correlation coefficients of lines ilustrated in figures 1 and 2 were very good, between 0.9990 and 0.9994.
- $k_1 / k_2 \cong 2$, meaning that reaction (2) occurs aproximately twice as slow as reaction (1).

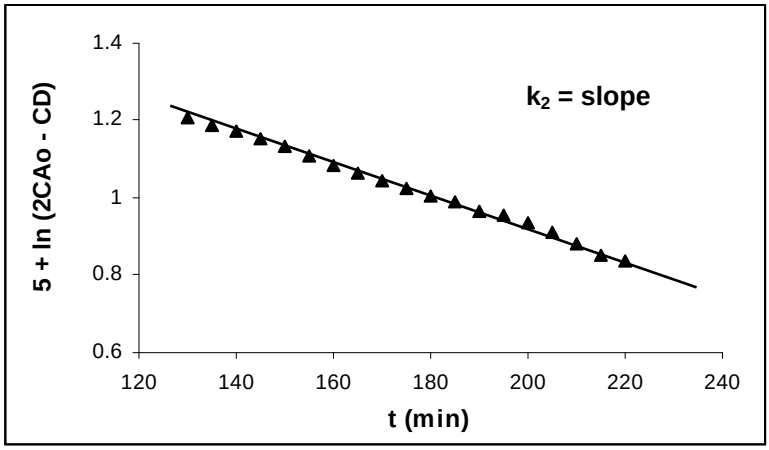

Figure 2. The plot of *ln* $(2C_{Ao} - C_D)$ versus reaction time at T = 298 K, j = 1 mole.l^{-1}, $C_{A0} = 1.95 \bullet 10^{-2}$ mole.l^{-1}, $[H^+] = 9.30 \bullet 10^{-3}$ mole.l^{-1} in water – 25 % vol DMFA mixture.

Validation of the method

Values of k_1 and k_2 obtained from experiments were used to calculate both the evolution of the electromotive force *E* of cell (5) and of the concentrations C_A, C_B, C_C and C_D during reaction time.

Figure 3 showes that the calculated plot $E = f(t)$ (see equation 6) superposes very closely the experimental one. The continuous line stands for calculated values, the circles for experimental values.

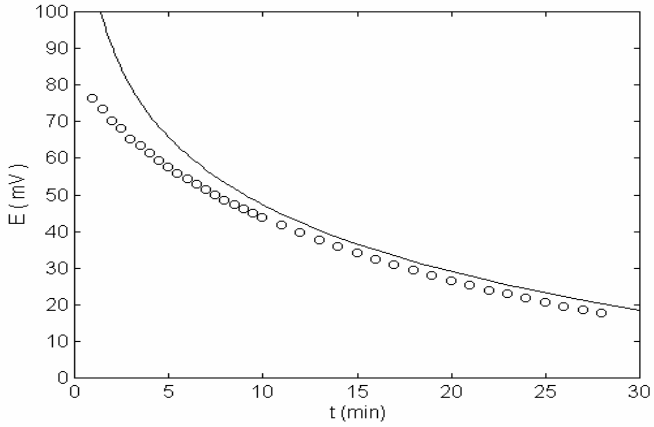

Figure 3. The calculated and experimental plots $E = f(t)$ at T = 298 K, j =1 mole.l^{-1}, $C_{A_0} = 1.95 \bullet 10^{-2}$ mole.l^{-1}, $[H^+] = 9.30 \bullet 10^{-3}$ mole.l^{-1} in water – 25 % vol DMFA mixture.

The slight difference at the beginning is due to the validity of relationship (6) only for $10^{-3} << C_D << 10^{-1}$ mole.l^{-1}, condition which is not respected during the first moments of processes (1) and (2).

The plots of equations (8) ÷ (11) are presented in figure 4. The concentration curves have tipical shapes for consecutive processes [10].

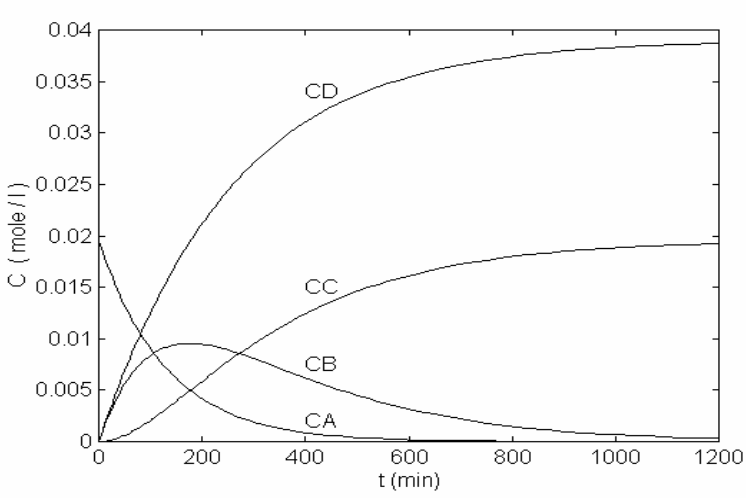

Figure 4. Calculated concentration curves at T = 298 K, j = 1 mole.l^{-1}, $C_{A_0} = 1.95 \bullet 10^{-2}$ mole.l^{-1}, $[H^+] = 9.30 \bullet 10^{-3}$ mole.l^{-1} in water – 25 % vol DMFA mixture.

Effect of acidity

The effect of hydrogen ion concentration on the reaction rate was studied at controlled temperature and ionic strength, in a water – 25 % vol DMFA mixture. Rate constants k_1 and k_2 obtained for a wide range of H^+ ion concentrations, are given in table 2 bellow.

Table 2.

Effect of hydrogen ion concentration on k_1 and k_2 at T=298 K, j =1 mole.l^{-1}, $C_{Ao} = 1.95 \bullet 10^{-2}$ mole.l^{-1} in water – 25 % vol DMFA mixture.

$[H^+]$ (mole.l^{-1})	10^4 k_1 (s^{-1})	10^5 k_2 (s^{-1})
$3.05 \bullet 10^{-5}$	62.40	51.00
$1.77 \bullet 10^{-4}$	15.50	21.80
$2.96 \bullet 10^{-3}$	3.60	9.40
$9.30 \bullet 10^{-3}$	2.36	6.75
$2.48 \bullet 10^{-2}$	1.20	5.37
$4.31 \bullet 10^{-2}$	1.34	5.15
$6.22 \bullet 10^{-2}$	1.26	4.85

The value of $[H^+] = 9.30 \bullet 10^{-3}$ mole.l^{-1} was obtained only by dissociation of the reactant acid $H[Co(DH)_2Br_2]$ itself. It was both measured as such and obtained from the dissociaton constant $K_a = 8 \bullet 10^{-3}$ mole.l^{-1} previously reported [9].

A differential method to determine reaction orders with respect to hydrogen ions, was employed. Figure 5 showes the plots of *ln* k_1 and *ln* k_2 versus *ln* $[H^+]$. Points lie on lines for both cases, with correlation coefficients of 0.9875 and 0.9888 respectively. The orders are negative and fractional (less than unity): 0.51 and 0.30 for process (1) and (2), respectively.

Rate coefficient k_1 decreases strongly when $[H^+]$ is increased and a trend to level off at $[H^+] > 10^{-2}$ mole.l^{-1} is observed. This value is an order of magnitude greater than that found previously by Zsako [8]. The dependence of k_1 on he acidity can be described by equation (16) with a corelation coefficient of 0.9980:

$$k_1 = A' + B' / [H^+] \qquad (16)$$

where A' = (2.22 ± 0.65)$\bullet 10^{-4}$ s^{-1} and B' = (1.85 ± 0.05)$\bullet 10^{-7}$ mole.l^{-1}.s^{-1} are constants.

Rate coefficient k_2 decreases strongly with increasing $[H^+]$ until aproximately $[H^+] = 10^{-2}$ mole.l^{-1}. Afterwards, its decrease slows down, but showes no trend to level off. No mathematical relationship having kinetic relevance and a good corelation coefficient, could be found with the available data, to expres the dependence of k_2 on acidity.

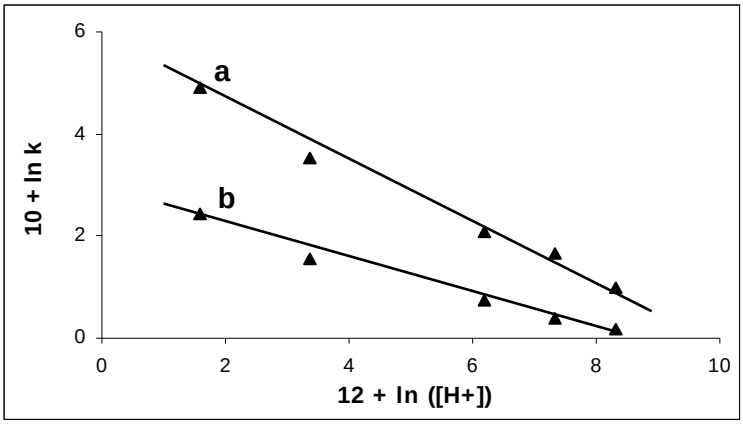

Figure 5. The plots of a.) *ln* k_1 and b.) *ln* k_2 versus *ln* $[H^+]$ at T =298 K, j =1 mole.l^{-1}, $C_{Ao} = 1.95 \bullet 10^{-2}$ mole.l^{-1} in water – 25 % vol DMFA mixture.

These findings may be explained by the existence of the following equlibria, even at the acidity of the reactant itself. Both the reactant $[Co(DH)_2Br_2]^-$ and the intermediate $[Co(DH)_2Br(H_2O)]$ are involved:

$$[Co(DH)_2Br_2]^- + H^+ \Leftrightarrow [Co(DH)(DH_2)Br_2] \quad (17)$$

$$[Co(DH)(DH_2)Br_2] + H^+ \Leftrightarrow [Co(DH_2)_2Br_2]^+ \quad (18)$$

$$[Co(DH)_2Br(H_2O)] \Leftrightarrow H^+ + [Co(DH)_2Br(OH)]^- \quad (19)$$

$$[Co(DH)_2Br(OH)]^- \Leftrightarrow H^+ \quad [Co(DH)_2Br(OH)_2]^{-2} \quad (20)$$

Equlibria (19) and (20) explain the slight decrease of k_2 for $[H^+] > 10^{-2}$ mole.l^{-1}.

The shift of equlilibria (17) and (18) towards the protonated forms is determined by te increasing hydrogen ion concentration of the mixture. The species $[Co(DH)(DH_2)Br_2]$ and $[Co(DH_2)_2Br_2]^+$ are most probably obtained by binding a hydrogen ion to the nitrogen atom of the nitrogen-oxygen groups within the dimethylglyoxime (DH). The hydrogen bridges in the DH will break and N-Co bonds will become weaker, while Co-Br bonds grow stronger. As a result, the substitution of bromide is more difficult.

The acvation process involves unprotonated as well as protonated forms. In strong acid media, the concentration of protonated forms is higher and the experimentally observed rate constants k_1 and k_2 will decrease.

Effect of solvent

The effect of solvent on reaction rates was studied by varying its dielectric constant. Experiments were performed at controlled temperature, ionic strength and hydrogen ion concentration, by adding N,N'-dimethylformamide (DMFA) to the reaction mixture. The values of rate constants k_1 and k_2 at different dielectric constants *D* of the medium are given in table 3.

Table 3 showes that k_2 is independent of *D*. Instead, k_1 slightly increases and reaction (1) becomes faster when the dielectric constant of the solvent decreases strongly. A possible explanation is based on the fact that at low *D*, hydrogen bridges within the dimethylglyoxime groups become more rigid and the Co-Br bonds are hydrolizable at an increased rate. Hence, acvation occurs easier. However, the available data are not enough to draw a doubtless conclusion.

Table 3.

Effect of solvent on k_1 and k_2 at T = 298 K, j = 1 mole.l^{-1}, C_{Ao} = 1.95•10^{-2} mole.l^{-1}, [H$^+$] = 9.30•10^{-3} mole.l^{-1}.

DMFA (% vol)	D	10^4 k_1 (s^{-1})	10^5 k_2 (s^{-1})
15	75.19	1.40	9.82
25	68.89	2.34	9.42
50	54.85	2.36	9.94

Effect of temperature

Temperature was varied within the range of 298 – 320 K, in order to study its effect on the reaction rates of processes (1) ad (2). Table 4 presents the values of k_1 and k_2 for various temperatures.

Table 4.

Effect of temperature on k_1 and k_2 at j = 1 mole.l^{-1}, C_{Ao} =1.95•10^{-2} mole.l^{-1}, [H$^+$] = 9.30•10^{-3} mole.l^{-1} in water – 25 % vol DMFA mixture.

T (K)	10^4 k_1 (s^{-1})	10^5 k_2 (s^{-1})
298	2.36	6.75
308	4.55	25.70
320	23.70	138.00

The plots of *ln k* versus *1/T* are linear for both processes, with very good corelation coefficients (0.9998 and 0.9999). The slope and the intercept provided the Arrhenius activation energy E_a and the preexponential factor *lnZ*, respectively. The activation enthalpy ΔH^* and entropy ΔS^* were obtained similary by plotting *ln (k/T)* versus *1/T*. Lines with corelation coefficients of 0.9858 and 0.9935 were found. Table 5 gives the activation parameters for reactions (1) and (2). The presented values are in good agreement with those reported previously [7,8,11].

Table 5.

Activation parameters at j = 1 mole.l^{-1}, C_{A_0} = 1.95•10^{-2} mole.l^{-1}, [H^+] = 9.30•10^{-3} mole.l^{-1} in water – 25 % vol DMFA mixture.

Reaction	E_a (KJ.mole^{-1})	ln Z	ΔH^* (KJ.mole^{-1})	ΔS^* (KJ.mole^{-1}.s^{-1})
(1)	107.9	34.5	105.3	33.4
(2)	113.8	37.0	111.2	53.5

Reaction mechanism

Because acvation of $H[Co(DH)_2Br_2]$ involves a ion-molecule interaction in both stages, the ionic strength of the medium will not affect reaction rates. Therefore, the sign and the magnitude of activation entropy ΔS^* were interpreted in order to propose a possible mechanism. Table 5 showes that for both processes, ΔS^* is positive and fairly small. This proves that solvatation of the activated complex in the rate determinig step is not different from that of the "parent" complex. Instead, the Co-Br bond is longer. This is possible only with a dissociative monomolecular substitution mechanism.

Hence, processes (1) and (2) occur as follows:

$$[Co(DH)_2Br_2]^- \Leftrightarrow [Co(DH)_2Br] + Br^- \quad \text{(Slow, } k_1\text{)} \quad (21)$$

$$[Co(DH)_2Br] + H_2O \rightarrow [Co(DH)_2Br(H_2O)] \quad \text{(Rapid)} \quad (22)$$

and

$$[Co(DH)_2Br(H_2O)] \Leftrightarrow [Co(DH)_2(H_2O)]^+ + Br^- \quad \text{(Slow, } k_2\text{)} \quad (23)$$

$$[Co(DH)_2(H_2O)] + H_2O \rightarrow [Co(DH)_2(H_2O)_2]^+ \quad \text{(Rapid)} \quad (24)$$

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