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Study of Cyanoaquonitrosyl Complex of Chromium. II[a]. Acid Hydrolysis of $[Cr(CN)_2(H_2O)_3NO]$: an Example of a Solution of Two-Step Kinetics of Successive One-Directional First-Order Reactions with Unknown Intermediate Properties

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A procedure for evaluation and calculation of the rate constants for a direct two-step chemical reaction using the time-dependence of an analytical property proportional to the intermediate concentration is described. The method does not require that the intermediate properties be known. The calculation is demonstrated employing the absorbance as the analytical property. The method proposed is applied to the spectrophotometric study of the kinetics of hydrolysis of $[Cr(CN)_2(H_2O)_3NO]$ *in a strongly acid medium (0.025–2* M $HClO_4$*). The rate and the protonation equilibrium constants for the hydrolytic steps and the activation parameters are given and the hydrolytic scheme is postulated.*

Introduction

In agreement with ref. [2] it was found that the product of hydrolysis of $[Cr(CN)_5NO]^{3-}$ in a weakly acid medium, *i.e.* $[Cr(CN)_2(H_2O)_3NO]$, undergoes a further two-step reaction in a strongly acid medium, the Cr–NO bond remaining intact. The kinetics of the hydrolysis in a strongly acid medium were followed by monitoring the time changes of the EPR signal [2], which is not very common in quantitative study of reaction courses. The present paper is a study of the two-step acid hydrolysis of $[Cr(CN)_2(H_2O)_3NO]$ in a strongly acid medium, by measurements of the absorbance in the visible and UV regions. A method is proposed for the calculation of the rate constants for both steps in a two-step reaction using the time dependence of an analytical property proportional to the intermediate concentration (*e.g.* the absorbance), when the coefficient of this proportionality (*e.g.* the absorption coefficient) is unknown (the intermediate properties are unknown).

Calculation of the rate constants for a series first-order process based on the least squares method of analyzing spectrophotometric data with the unknown value of extinction coefficient has been described in [3]. The procedure proposed in this paper is a graphical one and only working curves used for matching with the experimental runs are calculated using a CDC 3300 computer.

Experimental

Reagents

The initial substance, $[Cr(CN)_2(H_2O)_3NO]$, can be prepared by one of the following procedures:

(i) By pH-static hydrolysis of $[Cr(CN)_5NO]^{3-}$ by a strong acid [4]; the product prepared is very pure and anionic and cationic complexes that might be present are completely separated on ion-exchangers.
(ii) By hydrolysis of $[Cr(CN)_5NO]^{3-}$ by a strongly acidic cation-exchanger in the H^+-cycle (Dowex 50W–X8) at a controlled pH [5]; this procedure, in contrast to the previous one, provides a solution of $[Cr(CN)_2(H_2O)_3NO]$ not containing a salt of the acid used, which permits preparation of the solid substance by evaporation of the aqueous solution under decreased pressure [5].
(iii) By hydrolysis of $[Cr(CN)_5NO]^{3-}$ in a pH 3–4 buffer. The use of a buffer makes it possible to work without maintenance of pH-static conditions, but the purity of the $[Cr(CN)_2(H_2O)_3NO]$ prepared *in situ* is rather poor, as $[Cr(CN)(H_2O)_4NO]^+$ is always present (the buffer components catalyze further hydrolysis of $[Cr(CN)_2(H_2O)_3NO]$).

From the point of view of the study of the hydrolysis, the first preparation procedure proved to be the most advantageous. The considerable difference between the rate constant values for hydrolysis of $[Cr(CN)_5NO]^{3-}$ and $[Cr(CN)_2(H_2O)_3NO]$ [5] and for further hydrolysis enabled the use of $[Cr(CN)_5NO]^{3-}$ as the initial substance, as $[Cr(CN)_2(H_2O)_3NO]$ is formed in a negligibly short time relative to the rate of further hydrolysis. The rate constants obtained with preparation of the initial substance were identical, within the experimental error, with the values measured during the

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[a] Part I of this series is considered to be the paper [1].

experimentally more demanding preparation of the $[Cr(CN)_2(H_2O)_3NO]$.

Stock solutions of the complexes were prepared immediately before use and were protected against the light. The experiments were carried out in the dark (except for the light from the monochromator of the measuring spectrophotometer), in order to prevent possible photolysis. The other chemicals were of *p.a.* purity and were not further purified. The chromium in the complexes was determined spectrophotometrically after oxidation of the substance by hydrogen peroxide in an alkaline medium with formation of chromate.

Instruments

The spectrophotometric measurements were performed on a UV–VIS Specord instrument (Zeiss, Jena) in thermostatted cuvettes.

The working curves for the evaluation of the kinetic parameters of the direct two-step reaction were calculated numerically on a GIER computer (GIER–AlGOL–IV programming language) and on a CDC 3300 computer (USASI FORTRAN language).

Results and Discussion

Calculation of the Rate Constants from the Time-Dependence of an Analytical Property Proportional to the Intermediate Concentration

The Evaluation of the Time-Dependence. The relationships for this calculation will be derived for the absorbance as the analytical property, as it is frequently employed for following substance concentrations. However, the relationships are applicable to any other quantity proportional to the concentration.

The time-change in the spectrum must be evaluated at a wavelength at which the initial substance X has a molar absorption coefficient identical with that of the final product, Z. Under these conditions, any change in the absorbance reflects a change in the intermediate Y concentration, provided that the intermediate absorption coefficient is different at this wavelength. The absorbance value varying in time can then be expressed in terms of the material balance, as the sum of the contributions from the reactants,

$$A = (c_X)_o a_X b + c_Y (a_Y - a_X) b \tag{1}$$

where b is the cuvette thickness, c is the molar concentration of the indicated component, a is the molar absorption coefficient of the component and $(c_X)_o$ is the initial concentration of the reactant.

Both the first term on the right-hand side of Eq. (1) and the product, $(a_Y - a_X)b$, are constant in time, so that the change in the absorbance reflects the change in the concentration of intermediate Y. If the value of the proportionality coefficient, $(a_Y - a_X)b$, is known, the solution described in the literature [7] can be applied. However, the intermediate molar absorption coefficient is mostly unknown. The following procedure enables simultaneous determination of the absorption coefficient value or of another intermediate property, which was used for the study of the kinetics and the determination of the rate constants for a direct two-step reaction:

$$X \xrightarrow{k_X} Y \xrightarrow{k_Y} Z \tag{2}$$

It is advantageous to introduce dimensionless parameters:

$$\rho = \frac{c_Y}{(c_Y)_m} \tag{3}$$

$$\kappa = \frac{k_Y}{k_X} \tag{4}$$

$$\tau = k_X \cdot t \tag{5}$$

where $(c_Y)_m$ is the maximum concentration of intermediate Y, which is attained during reaction (2) and t is time.

The concentration profile of intermediate Y can be expressed according to ref. [7], Eq. (12), as

$$c_Y = \frac{(c_X)_o}{\kappa - 1} (e^{-\tau} - e^{-\kappa\tau}) \tag{6}$$

and $(c_Y)_m$ from the condition $dc_Y/d\tau = 0$,

$$(c_Y)_m = (c_X)_o \kappa^{\frac{\kappa}{1-\kappa}} \tag{7}$$

The time function of dimensionless parameter ρ can then be expressed by

$$\rho = \frac{\kappa^{\frac{\kappa}{\kappa-1}}}{\kappa - 1} (e^{-\tau} - e^{-\kappa\tau}) \tag{8}$$

A set of calculated curves for the ρ *vs.* $\log\tau$ dependence can then be plotted for various values of κ. On comparison of the experimental $c_Y/(c_Y)_m$ *vs.* log t dependence with the calculated curves, the value of κ can be determined from the best matching curves and the value of $\log k_X$ from the shift of the log t axis with respect to $\log \tau$ (as $\log \tau = \log k_X + \log t$). The time change of quantity $c_Y/(c_Y)_m = \rho$ is experimentally accessible as the fraction,

$$\left| \frac{A - (c_X)_o a_X b}{A_{ex} - (c_X)_o a_X b} \right| \tag{9}$$

where A is the absorbance at an arbitrary time and A_{ex} is the extreme absorbance value attained during reaction (2) – a maximum or a minimum (see Fig. 1).

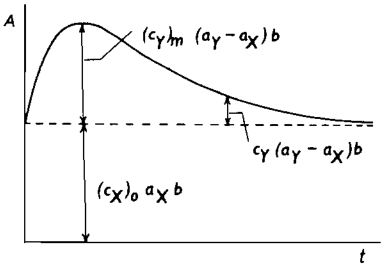

Figure 1. A scheme of the absorbance contributions for a direct two-step reaction at a wavelength where $a_X = a_Z$.

The absolute absorbance value has been introduced in relationship (9) in order that both the case when $a_Y > a_X$ (maximum absorbance) and $a_Y < a_X$ (minimum absorbance) could be discussed together.

If there are several wavelengths for which $a_X = a_Z$, then the wavelength for which the value,

$$Q = \left|\frac{A_{ex} - (c_X)_o a_X b}{(c_X)_o a_X b}\right| \qquad (10)$$

is maximal should be selected from the point of view of the precision of the rate constant determination, as the expression $|a_Y - a_X|/a_X$, also has a maximum value at this wavelength.

Eq. (8), expressing the implicit relationship among ρ, κ and τ, was solved numerically on a CDC 3300 computer for κ values from 0.05 to 20.00 with a step of 0.05 and in a range of values of log τ from –2 to +2 in 0.1 log unit steps; the range width and the number of values are sufficient. The computation results given (Table I) contain the dependence of ρ on log τ for $\kappa = 5.00$.

TABLE I. ρ *vs.* logτ Dependence for $\kappa = 5.00$.

logτ	ρ	logτ	ρ
–2.0	0.072563	–0.3	0.979849
–1.9	0.090648	–0.2	0.914844
–1.8	0.113015	–0.1	0.809436
–1.7	0.140550	+0.0	0.675041
–1.6	0.174248	+0.1	0.527321
–1.5	0.215180	+0.2	0.382450
–1.4	0.264425	+0.3	0.254081
–1.3	0.322954	+0.4	0.151613
–1.2	0.391434	+0.5	0.079121
–1.1	0.469944	+0.6	0.034890
–1.0	0.557591	+0.7	0.012446
–0.9	0.625031	+0.8	0.003400
–0.8	0.748976	+0.9	0.000664
–0.7	0.841819	+1.0	0.000085
–0.6	0.921637	+1.1	0.000006
–0.5	0.977870	+1.2	0.000000
–0.4	0.999954	+1.3	0.000000

The computer X–Y plotter constructed 50 curves of the ρ = f(log τ) dependence for selected values of parameter κ. Several of these curves are given in Fig. 2.

The value $\kappa = 1.05$ was selected in Fig. 2 instead of $\kappa = 1.00$, as function (8) is not defined for $\kappa = 1.00$.

The values of k_X and k_Y determined by this method make it possible to calculate the concentration of intermediate Y, as well as that of the other two components, X and Z, at any time. From these data and from the known values of the total absorbance at various wavelengths, the spectrum of the intermediate, $a_Y = f(\lambda)$, can be calculated, as $a_X = f(\lambda)$ and $a_Z = f(\lambda)$ are known from the measurement at the beginning and at the end of the two-step reaction.

However, an analysis of the method for the determination of k_Y and k_X has shown that the result is ambiguous. A similar ambiguity has been reported also in [3]; two curves for the ρ = f(logτ) dependence always have identical shapes, namely,

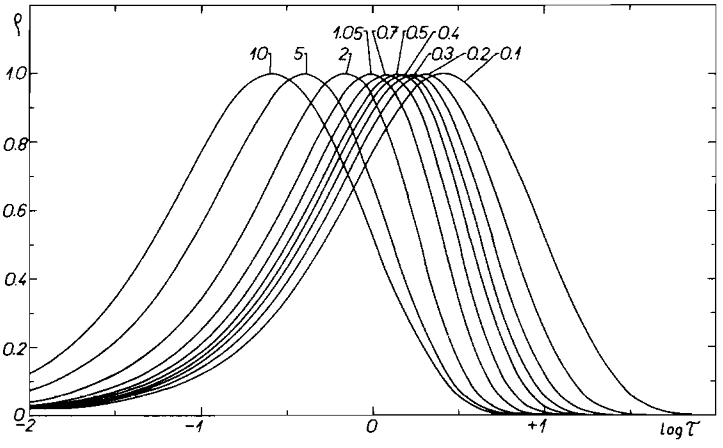

Figure 2. Curves for the ρ = f(logτ) dependence for various values of the rate constant ratio, κ (specified on the curves).

that for the given value, κ_A, and that for its reciprocal value, κ_B. This naturally leads to two different $a_Y = f(\lambda)$ dependences, only one being physically significant.

Procedure for Removing the Ambiguity of the Solution. The correct values of k_X and κ can be selected by changing the κ value by a change in the experimental conditions, a change in the pH, the temperature or other physical or chemical conditions[b].

A change in the κ value is related to the maximum concentration by Eq. (7), *i.e.* the $(c_Y)_m$ value is an unambiguous function of κ (Fig. 3). Variable β employed in Fig. 3 is defined as the ratio, $(c_Y)_m/(c_X)_o$. It follows from Fig. 3 that an increase in the maximum intermediate concentration, experimentally accessible as the Q value, is caused by a decrease in the κ value and *vice versa*.

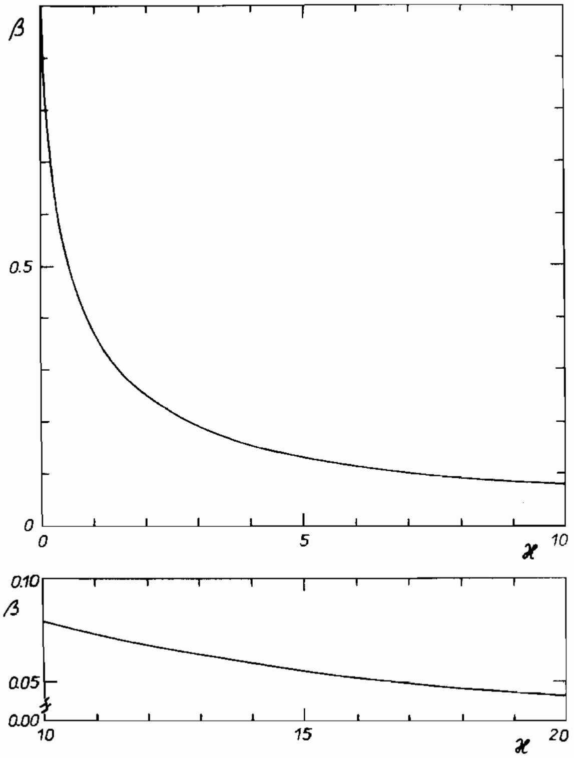

Figure 3. Dependence of β on κ.

In practical procedure it is recommended to order the values according to increasing Q,

$$Q_1 < Q_2: \quad \kappa_{A1} > \kappa_{A2}$$
$$\kappa_{B1} < \kappa_{B2}$$

wherein κ_{A1} and its reciprocal, κ_{B1}, correspond to Q_1, and κ_{A2} and its reciprocal, κ_{B2}, to Q_2.

From four possible transfers of κ from subscript 1 to subscript 2 (in the direction of increasing Q),

$$1)\ \kappa_{A1} \longrightarrow \kappa_{A2} \qquad 3)\ \kappa_{B1} \longrightarrow \kappa_{A2}$$
$$2)\ \kappa_{A1} \longrightarrow \kappa_{B2} \qquad 4)\ \kappa_{B1} \longrightarrow \kappa_{B2},$$

only two satisfy the condition of decreasing κ. Transfer 1 satisfies it by definition (and transfer 4 does not satisfy it by definition); for 2) and 3), the conditions for decrease,

$$2)\ \kappa_{A1} > \kappa_{B2} \quad \text{and} \quad 3)\ \kappa_{B1} > \kappa_{A2}$$

can be rearranged to:

$$2)\ \kappa_{A1} > \frac{1}{\kappa_{A2}} \quad \text{and} \quad 3)\ \kappa_{A1} < \frac{1}{\kappa_{A2}}$$

For no pair κ_{A1} and κ_{A2} can both these conditions be valid simultaneously, but one of them must be valid for any pair. Let us now assume that transfer 2) satisfies the condition of a decrease in κ. The selection between the two possibilities, 1) and 2), is then carried out by comparing the relative changes in β (determined from Fig. 3 according to the given κ values) with the experimental relative change in the Q value.

It follows from Eqs. (10) and (1) (written for A_{ex}) and from the definition of β that

$$\frac{Q_2 - Q_1}{Q_1} = \frac{\beta_{A2} - \beta_{A1}}{\beta_{A1}}; \tag{11}$$

analogously it holds for transfer 2) that

$$\frac{Q_2 - Q_1}{Q_1} = \frac{\beta_{B2} - \beta_{A1}}{\beta_{A1}} \tag{12}$$

For no pair $\kappa_{A1} > \kappa_{A2}$ can both equations, (11) and (12), be valid simultaneously; however, one of them is valid and determines the actual transfer. The solution thus becomes unambiguous after this determination of the correct pair of κ values.

The same procedure is employed when the condition of a decrease in κ is met by transfer 3); then it is necessary to find whether Eq. (11) or (13) is valid:

$$\frac{Q_2 - Q_1}{Q_1} = \frac{\beta_{A2} - \beta_{B1}}{\beta_{B1}} \tag{13}$$

Kinetics of Acid Hydrolysis of $[Cr(CN)_2(H_2O)_3NO]$

In order to follow the kinetics of the two-step acid hydrolysis of $[Cr(CN)_2(H_2O)_3NO]$ by monitoring the time-changes in the absorbance, wavelengths of λ = 431, 504, 559 and 606 nm are suitable; they were found as intercepts of the $[Cr(CN)_2(H_2O)_3NO]$ and $[Cr(H_2O)_5NO]^{2+}$ spectra, the latter substance being

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[b] Chemical and physical conditions for the reaction are usually varied in order to find the rate law, the activation parameters, *etc.* Of course, the procedure assumes that these changes do not lead to changes in the properties of components X, Y and Z.

TABLE II. Removing the Ambiguity of the Solution.

t (°C)	Q	κ_A	κ_B	β_A	β_B	$\frac{Q_2 - Q_3}{Q_1}$[a]	$\frac{\beta_{A2} - \beta_{A1}}{\beta_{A1}}$[a]	$\frac{\beta_{A2} - \beta_{B1}}{\beta_{B1}}$[a]
15	0.95	0.64	1.56	0.45	0.29	0.28	0.22	0.90
25	1.06	0.55	1.82	0.48	0.26	0.15	0.15	1.12
35	1.10	0.47	2.13	0.51	0.24	0.11	0.08	1.29
44.7	1.18	0.42	2.38	0.53	0.22	0.03	0.04	1.50
54.7	1.22	0.38	2.63	0.55	0.21	–	–	–

[a] Q value for 54.7 °C (maximum Q value) was used as Q_2. 0.55 corresponding to Q_2 was used for β_{A2}. This value obeys the rule about the decrease of κ in the direction of increasing Q (κ_{A2} = 0.38). *E.g.* comparing Q values for 54.7 and 44.7 °C one gets β_{A1} = 0.53 (κ_{A1} = 0.42) and β_{B1} = 0.22 (κ_{B1} = 2.38).

TABLE III. Temperature and pH Dependence of Observed Rate Constants (Initial Concentration $[Cr(CN)_5NO]^{3-}$ 0.004 *M*, ionic Strength 2*M* ClO_4^-, Na^+, H^+).

c_{H^+} (mol l^{-1})	t (°C)	$10^4 \times k'_4$ (s^{-1})	$10^4 \times k'_5$ (s^{-1})
0.025[a]	25.0	2.67	0.95
0.026[a]	25.0	6.20	2.20
0.028[a]	25.0	4.10	1.65
0.064	25.0	11.1	4.18
0.071	25.0	9.71	3.45
0.100	25.0	15.6	6.70
0.102	25.0	14.9	6.20
0.107	25.0	14.1	5.30
0.118	25.0	14.2	5.38
0.190	25.0	19.8	8.93
0.470	25.0	22.1	11.6
0.745	25.0	20.8	9.90
0.950	25.0	23.1	12.2
1.13	25.0	22.3	11.8
1.52	25.0	23.4	12.9
1.71	25.0	25.2	14.5
1.90	25.0	22.5	12.1
0.096	16.9	3.03	1.90
0.096	25.2	13.5	5.16
0.096	32.7	27.4	12.1
0.096	41.3	80.8	29.3
0.096	51.0	209	83.4
1.90	19.3	9.8	5.4
1.90	25.2	22.5	13.7
1.90	34.1	51.0	38.8
1.90	49.2	260	154
1.90	61.0	743	359

[a] First order reaction conditions were not fulfilled in kinetic experiments.

identified as the only final hydrolysis product. Considering the requirement of the maximum Q value (Eq. (10)), the wavelength, λ = 606 nm, was selected for further work.

The shape of the absorbance *vs.* time dependence indicated that only one intermediate with a non-negligible maximum concentration is formed. The temperature dependence was utilized to make the solution unambiguous (Table II).

It can be seen from the table that the relative change in Q is in good agreement with the calculated values of $(\beta_{A2} - \beta_{A1})/\beta_{A1}$ and in pronounced disagreement with the calculated values of $(\beta_{A2} - \beta_{B1})/\beta_{B1}$. Consequently, the κ_A values are the correct solution, leading to a single pair of values of k'_4 and k'_5.

The dependence of the rate constants on the temperature and the solution pH is given in Table III. A change in the concentration of $[Cr(CN)_2(H_2O)_3$-$NO]$ or $[Cr(CN)_5NO]^{3-}$ had no effect on the rate constants.

The dependence of the rate constants observed on the hydrogen ion concentration can be seen in Fig. 4. This dependence is described by the rate laws

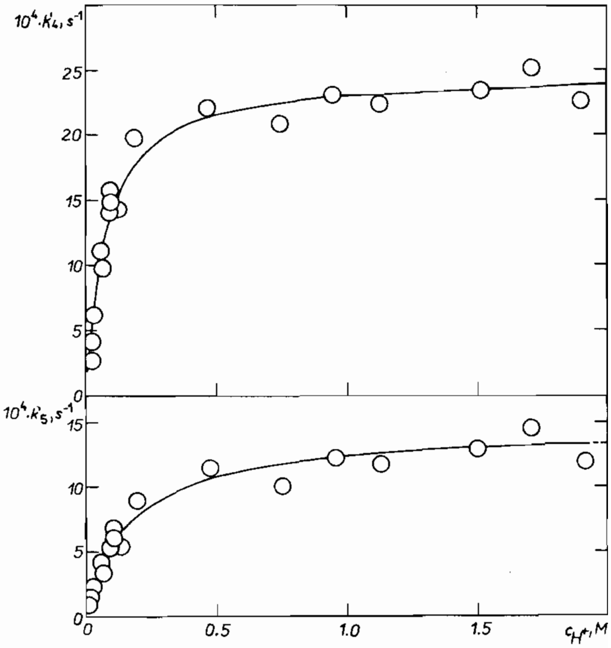

Figure 4. Dependence of rate constants k'_4 and k'_5 on the H^+ concentration; ionic strength 2*M* (ClO_4^-, Na^+, H^+), initial concentration of $[Cr(CN)_5NO]^{3-}$ 0.004*M*, temperature 25 °C.

$$k_4' = \frac{k_4K_4c_{H^+}}{1 + K_4c_{H^+}};\ k_5' = \frac{k_5K_5c_{H^+}}{1 + K_5c_{H^+}} \qquad (14)$$

The limiting values of k_4' and k_5', *i.e.* those of k_4 and k_5, were not attained even with the highest hydrogen ion concentrations used. Their values have been calculated, together with the equilibrium constant values, by the least squares method and the curves given in Fig. 4 have been constructed by substituting the calculated values into the rate laws, (14). The rate and equilibrium constants for a temperature of 25 °C and an ionic strength of 2*M* ClO_4^-, Na^+, H^+ equal[e]

$$k_4 = (25.0 \pm 2.4) \times 10^{-4}\ s^{-1}; k_5 = (14.5 \pm 1.4) \times 10^{-4}\ s^{-1};$$

$$K_4 = 13.5 \pm 1.3\ l\ mol^{-1}; K_5 = 5.8 \pm 0.6\ l\ mol^{-1}.$$

The following hydrolysis scheme thus satisfies rate laws (14):

$$[Cr(CN)_2(H_2O)_3NO] + H^+ \xrightleftharpoons{K_4} [Cr(CN)_2(H_2O)_3NO{\cdot}H]^+ \qquad (15)$$

$$[Cr(CN)_2(H_2O)_3NO{\cdot}H]^+ + H_2O \xrightarrow{k_4} [CrCN(H_2O)_4NO]^+ + HCN \qquad (16)$$

$$[CrCN(H_2O)_4NO]^+ + H^+ \xrightleftharpoons{K_5} [CrCN(H_2O)_4NO{\cdot}H]^{2+} \qquad (17)$$

$$[CrCN(H_2O)_4NO{\cdot}H]^{2+} + H_2O \xrightarrow{k_5} [Cr(H_2O)_5NO]^{2+} + HCN \qquad (18)$$

The values of the activation energy and entropy for both steps were determined from the temperature dependences of the rate constants observed at a hydrogen ion concentration of 0.1*M* and 1.9*M* (ionic strength, 2*M* ClO_4^-, Na^+, H^+):

		Loss of 4th Cyanide	Loss of 5th Cyanide
Activation Energy;	0.1*M* H^+	22.3 ± 1.2	20.5 ± 0.3
(kcal mol^{-1})	1.9*M* H^+	20.4 ± 0.8	18.7 ± 1.0
Activation Entropy; (e.u)	1.9*M* H^+	−3 ± 1	−9 ± 3

Considering the values of the equilibrium constants of the two steps (Eq. (14)), the values of the activation parameters at a hydrogen ion concentration of 1.9*M* can be considered as pure activation parameters. The activation energies corresponding to 0.1*M* H^+ also involve the heats of protonation reactions (15) and (17). The protonation reactions in both steps are slightly endothermic.

These rate and equilibrium constants and the activation parameters can be compared with the corresponding quantities in ref. [2], even though the results in paper [2] were obtained in perchlorate solutions of ionic strength 1.70*M* (k_4 = 25 × 10^{-4} s^{-1}; K_4 = 15.9 l mol^{-1}; k_5 = 5 × 10^{-4} s^{-1}; K_5 = 5.0 l mol^{-1}; $\Delta H_4^\ddagger$ = 19.2 ± 0.7 kcal mol^{-1}; $\Delta S_4^\ddagger$ = −6 ± 2 e.u.; $\Delta H_5^\ddagger$ = 13.3 ± 1.2 kcal mol^{-1}; $\Delta S_5^\ddagger$ = −24 ± 4 e.u.). The rate and equilibrium constants corresponding to the loss of the 4th cyanide are in good agreement. For the loss of the 5th cyanide (the second step in the hydrolysis of $[Cr(CN)_2(H_2O)_3NO]$) the value of rate constant k_5 determined by us is, however, about three-times larger than the value given in ref. [2], while equilibrium constants, K_5 are in good agreement. This disagreement can be explained by the circumstance that in ref. [2] the kinetics were followed using changes in the EPR signal of $[Cr(CN)(H_2O)_4NO]^+$, obtained as a property of the solution after addition of 4 acid equivalents to the parent ion $[Cr(CN)_5NO]^{3-}$. However, this procedure for the preparation of the intermediate necessarily leads to a mixture of $[Cr(CN)_2(H_2O)_3NO]$, $[Cr(CN)(H_2O)_4NO]^+$ and $[Cr(H_2O)_5NO]^{2+}$, which might influence the results of the kinetic measurements.

The difference in the activation parameters corresponding to the loss of the fifth cyanide is apparently connected with the disagreement in the values of rate constant k_5. The activation energy corresponding to the loss of the fourth cyanide is in a good agreement with ref. [2]. The fact that the activation parameters were determined for 1.6*M* H^+ in ref. [2] (in the present paper for 1.9*M* H^+) cannot explain the above differences, as the rate constant changes only a little within this H^+ concentration range.

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[e] The precision of the values was evaluated in terms of the confidence limits for 95% probability [6].