

Hydrolytic reactions of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ and $\text{NO}(\text{H}_2\text{O})_4\text{Cr—NC—Hg}^{3+}$ catalyzed by acetate and its α -chloro derivatives

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The catalytic effect of acetate and its α -chloro derivatives as components of buffer solutions on the hydrolysis of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ was studied. The observed rate of aquation of the first CN ligand is the sum of the contributions of acid hydrolysis and catalytic terms. The magnitude of the catalytic term depends on the concentration of carboxylate anions and H^+ ions. Acetate anions also increase the rate of decomposition of the binuclear complex $\text{NO}(\text{H}_2\text{O})_4\text{Cr—NC—Hg}^{3+}$, where the reaction rate is independent of the concentration of H^+ ions. The reactions are of pseudo-first order with respect to the Cr complex. The equilibrium and rate constants of the hydrolytic reactions were found and compared with the kinetic parameters of the catalyzed aquation of $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$. A reaction scheme was proposed. The dependence of the kinetics of the hydrolysis of the CN ligand on the concentration of H^+ ions is attributed to the protonation of the dissociated CN group. The catalytic effect of the carboxylate is interpreted in terms of outer sphere effects, where the determining characteristic is the basicity, *i.e.* the electron donor properties of the carboxylate anion.

Было изучено каталитическое влияние ацетата и его α -хлорпроизводных в качестве компонентов буферных растворов на гидролиз $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$. Наблюдаемая скорость акватации первого лиганда CN состоит из вклада кислотного гидролиза и каталитического члена. Величина каталитического вклада гидролиза зависит от концентрации карбоксильного аниона и концентрации ионов H^+ . Ацетатные анионы ускоряют также разложение двухядерного комплекса $\text{NO}(\text{H}_2\text{O})_4\text{Cr—NC—Hg}^{3+}$, причем скорость реакции не зависит от концентрации ионов H^+ . Реакции являются реакциями псевдопервого порядка по отношению к комплексу хрома. Были определены константы равновесия и скорости реакций гидролиза и сравнены с кинетическими параметрами катализированной акватации $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$. Была постулирована схема реакции. Зависимость кинетики гидролиза лиганда CN от концентрации ионов H^+ была присуждена протонизации отделяющейся группы CN. Каталитическое

действие карбоксилатов интерпретировано внешнесферным взаимодействием, определяющей характеристикой которого является основность, т.е. электродонорные свойства карбоксильного аниона.

The effect of various ions present in solution on the behaviour of complex compounds and particularly on the rate of their substitution reactions is a constant source of interest in coordination chemistry.

The reactivity of the $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$ complex in buffer solutions of acetate and its α -chloro derivatives was described in our previous paper [1]. The catalytic effect of the components of these buffer solutions on the rate of hydrolysis of the CN ligand was evaluated quantitatively. A reaction scheme describing the fact that carboxylate-catalyzed reactions retain the character of acid hydrolysis (except for solutions with higher pH values, in which hydrolysis independent of the concentration of hydrogen ions is of greater importance) was proposed.

Study of further members of the series of complexes of the $\text{Cr}(\text{CN})_{5-x}(\text{H}_2\text{O})_x\text{NO}^{x-3}$ type and of complexes in which protonation of the cyanide group is not possible can give a more complete picture of the role of the proton in the overall mechanism of carboxylate catalysis. In the latter case the coordination bond is broken *via* a mechanism different from that found for acid hydrolysis.

In this paper, the electroneutral complex $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ and binuclear complex ion $\text{NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$ were chosen for study.

Experimental

Chemicals

The preparation and purification of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ has been described elsewhere [2]. The formation of the binuclear adduct $\text{NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$ has also been described [3]. In our experiments the binuclear complex was prepared *in situ* using a 10-fold excess of Hg^{2+} ions with respect to the concentration of $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$. The other chemicals employed were of anal. grade and were not purified further.

Kinetic measurements

The hydrolysis of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ was carried out in buffer solutions of acetate—acetic acid or their α -chloro derivatives with a constant ionic strength of 1 mol dm^{-3} (ClO_4^- , $\text{Cl}_x\text{CH}_{3-x}\text{COO}^-$ for $x=0$ to 2, Na^+ , H^+) at 20°C and the kinetics of the dissociation of the first cyanide ligand was monitored spectrophotometrically at a wavenumber of $17.1 \times 10^3 \text{ cm}^{-1}$, where the molar absorption coefficient of $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$ is equal to that of $\text{Cr}(\text{H}_2\text{O})_5\text{NO}^{2+}$.

The decomposition of the binuclear adduct $\text{NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$ was studied spectrophotometrically at $23.25 \times 10^3 \text{ cm}^{-1}$ in acetate buffer solutions with a constant ionic strength of 1 mol dm^{-3} (ClO_4^- , CH_3COO^- , Na^+ , H^+) at 20°C .

In all the measurements a recording Specord UV VIS spectrophotometer (Zeiss, Jena) was employed. The observed pseudo first-order rate constants k_{obs} were obtained from the time dependence of the absorbance, $\ln (A - A_\infty)$. The data treatment was the same as in [1].

Results

Hydrolysis of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$

The observed pseudo first-order rate constants for the first hydrolysis step of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ are given in Table 1. The pH dependence of the rate constant

Table 1

Observed pseudo first-order rate constants for the first step of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ hydrolysis in the presence of $\text{Cl}_x\text{CH}_{3-x}\text{COO}^-$
Ionic strength 1 mol dm^{-3} , 20°C , analytical concentration of $\text{Cl}_x\text{CH}_{3-x}\text{COOH}$ 1 mol dm^{-3}

Buffer systems	pH	$10^3 c_0$ complex mol dm^{-3}	$10^4 k_{\text{obs}}$ s^{-1}
CH_3COO^- CH_3COOH	5.66	1.0	3.57
	5.00	1.0	4.99
	4.67	1.0	6.33
	4.17	1.0	6.90
	4.08	1.0	6.71
	3.90	1.0	5.95
	3.56	1.0	5.03
	3.04	1.0	3.17
	2.54	1.0	1.70
	2.15	1.0	1.58
$\text{ClCH}_2\text{COO}^-$ ClCH_2COOH	3.39	4.5	1.72
	3.12	3.0	2.20
	3.00	4.5	2.80
	2.64	4.5	3.95
	2.30	4.5	2.29
	2.13	3.0	2.64
	1.56	4.5	3.94
$\text{Cl}_2\text{CHCOO}^-$ Cl_2CHCOOH	2.18	4.5	3.34
	1.72	4.5	4.89
	1.28	4.5	6.70
	0.89	4.5	8.15
	0.58	4.5	9.40

k_{obs} for each individual type of buffer solution has a complicated shape similar to that with $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$ [1]. The quantity k_{obs} must therefore be considered a sum of the contributions of an acid hydrolysis term k_{H} and a term corresponding to the catalytic effect of the carboxylate ions k_{Ac} . Since the data on the acid hydrolysis of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ published in [2] were obtained under different experimental conditions, we studied and evaluated the kinetics of loss of the first CN ligand from $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ in unbuffered solutions over a suitable pH range. Special care was taken to improve the precision of the k_{H} values to be subtracted from k_{obs} .

The course of the dependence of $k_{\text{Ac}} = k_{\text{obs}} - k_{\text{H}}$ on pH for buffer solutions of acetate—acetic acid and their α -mono and α -dichloro derivatives is shown in Fig. 1. In the pH region of the assumed catalytic effect of the $\text{Cl}_2\text{CHCOO}^- - \text{Cl}_2\text{CHCOOH}$ buffer system, the acid hydrolysis of the CN ligand is predominant. The shape of the pH dependence of the rate constant k_{Ac} indicates that the catalytic effect of the buffer solutions depends on the presence of the dissociated form of the carboxylic acid. The degree of catalytic effect decreases with an increasing number of Cl atoms on the α carbon of the carboxylate.

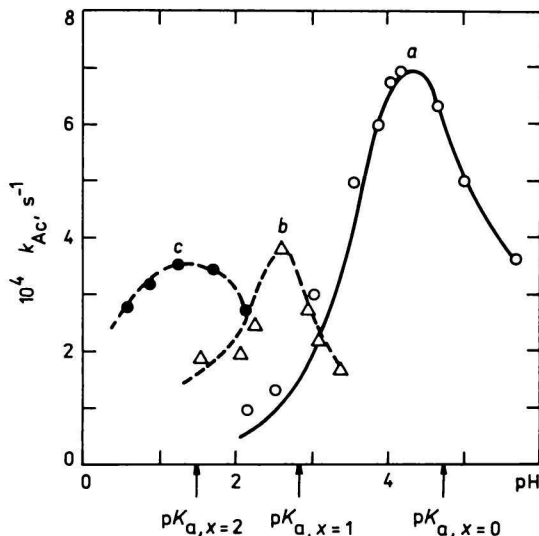


Fig. 1. pH Dependence of pseudo first-order rate constant $k_{\text{Ac}} = k_{\text{obs}} - k_{\text{H}}$ for the first step of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ hydrolysis in carboxylate buffer solutions.

Analytical concentration of $\text{Cl}_x\text{CH}_2-x\text{COOH}$ 1 mol dm^{-3} , ionic strength 1 mol dm^{-3} , 20°C , $x=0, 1, 2$ for curves *a, b, c*, respectively; $c_0 = 1 \times 10^{-3} \text{ mol dm}^{-3}$ (curve *a*), $c_0 = 4.5 \times 10^{-3} \text{ mol dm}^{-3}$ (curves *b, c*)



Curve *a* calculated according to eqn (4) for $k_0 = 6 \times 10^{-4} \text{ s}^{-1}$, $k_1 = 8 \times 10^{-3} \text{ s}^{-1}$, $K_{\text{Ac}} = 1.1 \text{ dm}^3 \text{ mol}^{-1}$, $K_{\text{Ac,H}} = 9 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$, $K_a = 1.8 \times 10^{-5} \text{ mol dm}^3$.

The dependence of the observed rate constant for the hydrolysis of the first CN ligand of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ on the concentration of CH_3COO^- in solutions with a constant pH value ($\text{pH}=4.0$, $k_{\text{obs}}=k_{\text{Ac}}$ in this pH region) (Fig. 2) indicates a mechanism with a rapid preceding chemical equilibrium. Attainment of the limiting state under the experimental conditions was prevented by the high analytical concentration of CH_3COOH . The course of the dependence shown in Fig. 2 can be described by the equation

$$k_{\text{Ac}} = \frac{k' K_{\text{Ac}} [\text{CH}_3\text{COO}^-]}{1 + K_{\text{Ac}} [\text{CH}_3\text{COO}^-]} \quad (1)$$

Treatment of experimental data for the dependence of k_{Ac} on $[\text{CH}_3\text{COO}^-]$ according to eqn (1) yielded the value of the equilibrium constant for the formation of the associate $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ with CH_3COO^- ions, $K_{\text{Ac}} = 1.1 \text{ dm}^3 \text{ mol}^{-1}$. The effect of the concentration of H^+ is included in the overall rate constant for the hydrolysis of the acetate associate, k' .

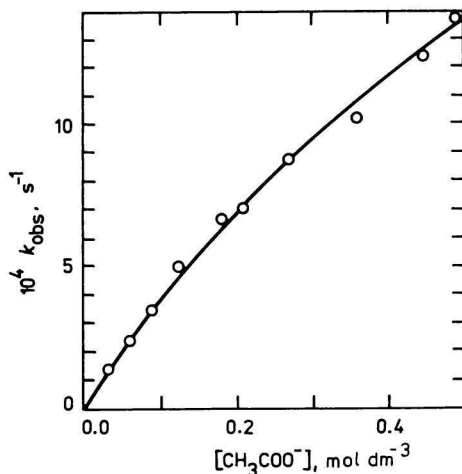


Fig. 2. Dependence of observed pseudo first-order rate constant for the first step of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ hydrolysis on CH_3COO^- concentration.

pH 4.0, ionic strength 1 mol dm^{-3} , 20°C , $c_0 = 5 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$. Curve calculated according to eqn (1) for $k' = 3.9 \times 10^{-3} \text{ s}^{-1}$, $K_{\text{Ac}} = 1.1 \text{ dm}^3 \text{ mol}^{-1}$.

After expressing $[\text{CH}_3\text{COO}^-]$ as a function of the analytical concentration of CH_3COOH , c , and the pH

$$[\text{CH}_3\text{COO}^-] = \frac{K_a c}{K_a + [\text{H}^+]} \quad (2)$$

where the dissociation constant of CH_3COOH , $K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$ ([4, 5] and the references therein), eqn (1) and the quantity $K_{\text{Ac}} = 1.1 \text{ dm}^3 \text{ mol}^{-1}$ could be employed to calculate the values of the overall rate constant k' for the hydrolysis in acetate buffer solutions from the data summarized in Table 1 or in Fig. 1. This rate

constant depends on the concentration of H^+ ions in solution, as expressed by the equation

$$k' = k_0 + \frac{k_1 K_{Ac,H} [H^+]}{1 + K_{Ac,H} [H^+]} \quad (3)$$

The parameters in eqn (3) have been calculated. The following values were found: $k_0 = 6 \times 10^{-4} \text{ s}^{-1}$, $k_1 = 8 \times 10^{-3} \text{ s}^{-1}$, and the protonation constant of the acetate associate $K_{Ac,H} = 9 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$. Corresponding dissociation constant $K_d = 1/K_{Ac,H}$ is given by the value $pK_d = 3.9$.

The dependence of the rate constant k_{Ac} for the first step in the hydrolysis of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ on the concentration of H^+ ions in solution under conditions of a constant concentration of CH_3COO^- ions was also studied. The data obtained are given in Table 2. The trend of the dependence of k' on $[H^+]$ expressed by eqn (3) was confirmed (k' approaches a limiting value). Quantitative treatment, however, yielded k_0 , k_1 , and $K_{Ac,H}$ values which were different from those given above. The reason for this difference was apparently very high analytical concentration of acetic acid required to maintain the constant CH_3COO^- ion concentration (0.45 mol dm^{-3}).

Table 2

Observed pseudo first-order rate constants k_{Ac} for the first step of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ hydrolysis in acetate buffers

$[\text{CH}_3\text{COO}^-] = 0.45 \text{ mol dm}^{-3}$, ionic strength 1 mol dm^{-3} , 20°C , $c_0 = 5 \times 10^{-3} \text{ mol dm}^{-3}$
 $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$

pH	Analytical concentration of CH_3COOH , mol dm^{-3}	$10^4 k_{Ac}$ s^{-1}
4.67	1.0	6.33
4.45	1.3	8.40
4.20	2.0	10.8
4.00	3.0	12.4
3.85	4.0	13.5
3.62	6.5	16.0
3.52	8.5	16.4

Combination of eqns (1–3) yields the general form of kinetic eqn (4) for the first step in the hydrolysis of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ catalyzed by CH_3COO^- ions

$$k_{Ac} = \frac{(k_0 + k_0 K_{Ac,H} [H^+] + k_1 K_{Ac,H} [H^+]) K_{Ac} K_a C}{(1 + K_{Ac,H} [H^+]) (K_a + [H^+] + K_{Ac} K_a C)} \quad (4)$$

The course of the dependence of rate constant k_{Ac} on the concentration of components of the acetate buffer solution at an analytical concentration of CH_3COOH , $c = 1 \text{ mol dm}^{-3}$, calculated according to eqn (4) is shown in Fig. 1, curve *a*.

The general eqn (4) is of the same type as the relationship for the catalyzed hydrolysis of $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$ [1].

Decomposition of $\text{NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$

The binuclear complex $\text{NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$ decomposes spontaneously in unbuffered solutions, with a pH independent rate [3]. In studying this reaction in acetate—acetic acid buffer solutions a marked catalytic effect on the rate of decomposition with formation of $\text{Cr}(\text{H}_2\text{O})_5\text{NO}^{2+}$ was observed.

The observed pseudo first-order rate constants obtained from the spectrophotometric study of the reaction in buffer solutions with a constant analytical concentration of CH_3COOH and varying pH, as well as with a constant pH value and varying analytical concentration of CH_3COOH , are given in Fig. 3. The dependence is the same for both types of experiment described. This confirms that the catalytically effective component of the buffer solution is the anionic form of

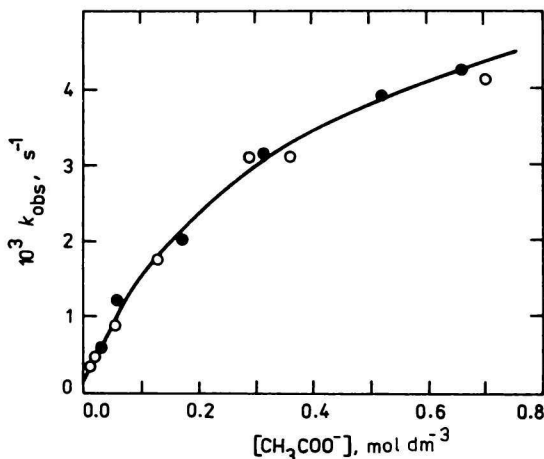


Fig. 3. Dependence of observed pseudo first-order rate constant for $\text{NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$ decomposition on CH_3COO^- concentration.

Ionic strength 1 mol dm^{-3} , 20°C , $c_0 = 1 \times 10^{-3} \text{ mol dm}^{-3} \text{ NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$.

○ Analytical concentration of CH_3COOH 1 mol dm^{-3} , pH was changed; ● pH 4.3, analytical concentration of CH_3COOH was changed.

Curve calculated according to eqn (5) for $\bar{k} = 2 \times 10^{-4} \text{ s}^{-1}$, $k_{\text{Hg-Ac}} = 6.5 \times 10^{-3} \text{ s}^{-1}$, $K_{\text{Hg-Ac}} = 2.5 \text{ dm}^3 \text{ mol}^{-1}$.

the carboxylic acid and the rate of decomposition of the complex is independent of the concentration of H^+ ions, as in the absence of acetate ions. The value of the positive intercept on the ordinate axis, $k_{\text{obs}} = 2 \times 10^{-4} \text{ s}^{-1}$ is in agreement with the literature data [3] for spontaneous decomposition of the binuclear complex.

The shape of the k_{obs} vs. $[CH_3COO^-]$ dependence indicates the existence of an equilibrium (equilibrium constant $K_{\text{Hg,Ac}}$) followed by rate-determining step of breaking of the coordination bond (rate constant $k_{\text{Hg,Ac}}$). This reaction sequence can be described by the rate equation

$$k_{\text{obs}} - \bar{k} = \frac{k_{\text{Hg,Ac}} K_{\text{Hg,Ac}} [CH_3COO^-]}{1 + K_{\text{Hg,Ac}} [CH_3COO^-]} \quad (5)$$

where \bar{k} is the rate constant of the spontaneous decomposition of the binuclear adduct. Transformation of eqn (5) to coordinates $1/(k_{\text{obs}} - \bar{k})$ vs. $1/[CH_3COO^-]$ results in a linear dependence. The values $k_{\text{Hg,Ac}} = 6.5 \times 10^{-3} \text{ s}^{-1}$ and $K_{\text{Hg,Ac}} = 2.5 \text{ dm}^3 \text{ mol}^{-1}$ were found from the intercept on the ordinate axis and from the slope, respectively.

Identification of reaction products

In an attempt to determine the location of the carboxylate anion in the chromium coordination sphere, the products of the hydrolytic decomposition of $Cr(CN)_2(H_2O)_3NO$ and $NO(H_2O)_4Cr-NC-Hg^{3+}$ were studied. The electronic absorption spectra in the visible region and ion exchange elution on cation exchange resin Dowex 50-W-X4 did not confirm permanent complexation of the carboxylate ions in the first coordination sphere. The main product of the hydrolysis of $Cr(CN)_2(H_2O)_3NO$ and $NO(H_2O)_4Cr-NC-Hg^{3+}$ in all the carboxylate buffer solutions employed is the $Cr(H_2O)_5NO^{2+}$ complex ion.

Discussion

The character of the changes in the kinetics of the aquation reactions of both complex species studied, $Cr(CN)_2(H_2O)_3NO$ and $NO(H_2O)_4Cr-NC-Hg^{3+}$, in carboxylate buffer solutions is analogous to that observed for the $Cr(CN)-(H_2O)_4NO^+$ ion [1]. In addition, comparison of the kinetic parameters for the first step in the hydrolysis of $Cr(CN)_2(H_2O)_3NO$ and $Cr(CN)(H_2O)_4NO^+$ measured in buffered and unbuffered solutions (Table 3) indicates that the way of breakage of the $Cr-CN$ bond is similar for catalyzed and uncatalyzed hydrolysis (the loss of the second last CN ligand is faster than the loss of the last ligand; the CN ligand is dissociated with participation of H^+ ions).

Table 3

Kinetic parameters for the first step of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ hydrolysis and $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$ hydrolysis in nonbuffered solutions and in buffered acetate solutions
Ionic strength 1 mol dm^{-3} , 20°C

Complex	Parameter						Ref.
	K_{H} $\text{dm}^3 \text{ mol}^{-1}$	k s^{-1}	$K_{\text{Ac,H}}$ $\text{dm}^3 \text{ mol}^{-1}$	k_1 s^{-1}	K_{Ac} $\text{dm}^3 \text{ mol}^{-1}$	k_0 s^{-1}	
$\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$	9	1×10^{-3}	9×10^3	8×10^{-3}	1.1	6×10^{-4}	This paper
$\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$	2	1×10^{-3}	5×10^3	6×10^{-3}	1.9	6×10^{-4}	[1]

The dependence of the rate of hydrolysis of the first CN ligand of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ on the concentration of the components of the buffer solution confirms the mechanism of stepwise association of $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ with carboxylate anion and proton, as proposed and discussed for $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$ [1]. The value of the association constant with the acetate anion indicates weak interaction. For the positively charged $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$ species $K_{\text{Ac}} = 1.9 \text{ dm}^3 \text{ mol}^{-1}$ and for the electroneutral complex $K_{\text{Ac}} = 1.1 \text{ dm}^3 \text{ mol}^{-1}$.

Evaluation of the experiments carried out in solutions with low concentrations of H^+ ions for the dicyano complex led to introduction of the concept of an acid-independent pathway for breakage of the Cr—CN bond, represented in the rate equation by the term k_0 . The magnitude of this kinetic parameter is approximately the same as that for $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$. Similarly, as with $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$, this pathway was not observed for $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ during hydrolysis in unbuffered solutions [2]. The dissociation of the coordination bond in the acid-independent pathway is thus apparently dependent on the presence of the carboxylate anion.

Confirmation of the reality of this pathway and information on the localization of the proton in the acid-dependent decomposition of the acetate associates should be obtained from experiments with the binuclear adduct $\text{NO}(\text{H}_2\text{O})_4\text{Cr}—\text{NC}—\text{Hg}^{3+}$ (Fig. 3). The dependence of rate constant on pH of acetate buffer in the case of this complex corresponds to the pH dependence of CH_3COO^- anion concentration. The abscissa of the inflection point of the $k_{\text{obs}}—\text{pH}$ dependence under the conditions of constant analytical concentration of CH_3COOH (Fig. 4) is identical with the $\text{p}K_{\text{a}}$ value of CH_3COOH .

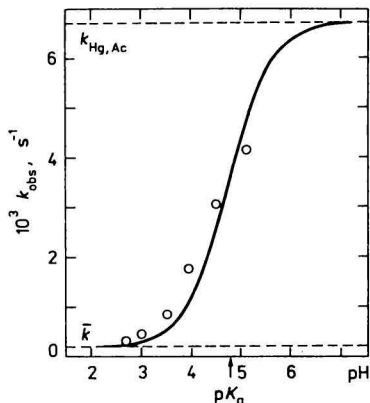
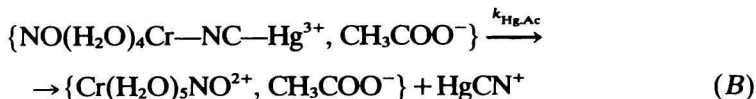
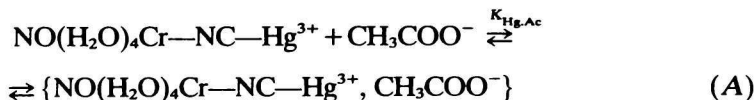


Fig. 4. Dependence of observed pseudo first-order rate constant for $\text{NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$ decomposition on pH of acetate buffer solution.

Analytical concentration of CH_3COOH 1 mol dm^{-3} , ionic strength 1 mol dm^{-3} , 20°C , $c_0 = 1 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$. Points are experimental, the curve is dissociation curve of CH_3COOH , $K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$.

For the decomposition of the binuclear complex $\text{NO}(\text{H}_2\text{O})_4\text{Cr}-\text{NC}-\text{Hg}^{3+}$ in acetate buffer solutions, a similar reaction scheme can be proposed as that for catalyzed aquation of the $\text{Cr}-\text{CN}$ bond [1]



The increase in the association constant $K_{\text{Hg,Ac}}$ compared with the values given for the mononuclear complexes is in agreement with the trend in the increase in the positive charge of the complex species.

In the decomposition of binuclear complex, involving breakage of the $\text{Cr}-\text{N}$ bond, experiments confirmed that the acetate anion alone has a specific labilizing effect. The acid-independent pathway for the dissociation of the CN ligand from the acetate associate of substances $\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_3\text{NO}$ and $\text{Cr}(\text{CN})(\text{H}_2\text{O})_4\text{NO}^+$ can be therefore considered a realistic parallel reaction to acid hydrolysis. It remains questionable to what extent the manifestation of such effect, *i.e.* the faster and easier aquation, is related to the complexation of cyanide with Hg in the binuclear adduct or with possible intramolecular protonation of the strongly basic CN ligand in the mononuclear complexes.

Examples of catalytic activity of the molecular form of CH_3COOH have been given in the literature [6]. In our case, however, the undissociated form of the carboxylic acid in solution is catalytically ineffective. The experiments with the

binuclear adduct further confirmed that acetate anions have a sufficient labilizing effect even without participation of protons. Therefore, there is no reason to assume that the effect of the H^+ ion concentration is related to the protonation of the carboxylic anion bound to the Cr complex. Moreover, the values of equilibrium protonation constants $K_{Ac,H}$ in the hydrolysis of the second last and last CN ligands in the studied type of complexes (Table 3) exhibit the same trend as those for uncatalyzed acid hydrolysis. The large basicity of the CN ligand evidently leads in both cases to localization of protonation to this ligand. This conclusion is in agreement with some published data concerning protonation of leaving basic groups [7, 8].

The basis of the catalytic effect of carboxylate anions in the hydrolysis of the CN ligand studied here depends on a shift of protonation of this basic group to a region of lower H^+ ion concentration in solution. Such a change in the ability of the CN ligand to bind a proton depends on the basicity of the given carboxylate anion (Fig. 1), or on its electron donor properties. These properties apparently also determine the magnitude of the catalytic effect (the values of the rate constants) and other specific features of this effect (acid-independent decomposition path).

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