# Study of Spectrophotometric and Electrochemical Properties of Complexes of the Type $[Cr(CN)_{5-x}(H_2O)_xNO]^{x-3}$

# J. MOCÁK, D. BUSTIN and M. ŽIAKOVÁ

Department of Analytical Chemistry, Slovak Technical University, 880 37 Bratislava, Czechoslovakia Received August 20, 1976

Spectrophotometric (in UV, visible and IR region) and chemical properties of the complexes formed by stepwise hydrolysis of  $[Cr(CN)_5NO]^{3-}$  are described. The spectra of the intermediates and their electrochemical characteristics were obtained on the basis of the measurement of the kinetic parameters. A procedure for preparation of  $[Cr(CN)_2(H_2O)_3NO] \cdot H_2O$  by acid hydrolysis of  $[Cr(CN)_5NO]^{3-}$  using a cationexchanger in the hydrogen cycle is described. The spectral data are explained in terms of the character of the NO coordination and the charge on the complex. Complexes  $[Cr(CN)_{5-x}(H_2O)_xNO]^{x-3}$  (where x = 3-5) are oxidized on a carbon electrode with an overall exchange of four electrons. The existence of parallel chemical reactions in the electrochemical oxidation process is discussed. The shifts in the halfpeak potentials for the oxidation of the series of substances studied are explained by an increase in the irreversibility of the primary oxidation step.

# Introduction

During the study of complexes with the Cr-NO bond, especially in comparing the properties of [Cr- $(CN)_5NO$ <sup>3-</sup> and  $[Cr(H_2O)_5NO]^{2+}$ , the possibility of following changes in the properties and chemical and electrochemical reactivity during gradual substitution of the CN<sup>-</sup> ligands with water was found to be interesting. This gradual substitution represents a change in the ligand field strength, its symmetry and in the charge on the complex species. The results published in this field have been devoted to changes in the EPR and partially also in the electronic spectra of  $[Cr(CN)_5NO]^{3-}$  on addition of acid [1, 2] and to changes in the polarographic behaviour of [Cr(CN)5-NO]<sup>3-</sup> during acid hydrolysis [3]. The latter paper also studied the kinetics of the hydrolytic reaction pH-statically.

The present paper deals with a voltammetric and spectrophotometric study (in the visible and UV regions) of the kinetics of all steps in the acid hydrolysis of  $[Cr(CN)_5NO]^{3-}$  and describes the electrochemical and optical properties of the

individual members in the series  $[Cr(CN)_{5-x}(H_2O)_{x}NO]^{x-3}$ .

## Experimental

#### Reagents

 $K_3[Cr(CN)_5NO] \cdot H_2O$  and  $[Cr(H_2O)_5NO](ClO_4)_2$ were prepared and purified according to the published procedures [4, 5].  $[Cr(CN)_2(H_2O)_3NO]$  was obtained as a product of the hydrolysis of [Cr(CN)<sub>5</sub>-NO<sup>3-</sup> in a weakly acidic medium (pH 4) [6]; [Cr- $(CN)_4(H_2O)NO]^{2-}$  and  $[Cr(CN)(H_2O)_4NO]^+$  were formed in solution as hydrolytic intermediates [6, 7]. Stock solutions of the complexes were prepared immediately before use and were protected against light. The experiments were performed in the dark to prevent photolysis. Other chemicals were of analytical reagent grade purity and were not further purified. The chromium in the complexes was determined spectrophotometrically after oxidation of the substance with hydrogen peroxide in an alkaline medium to give chromate.

#### Instruments

The spectrophotometric measurements in the visible and UV region were carried out using a UV-VIS Specord spectrophotometer (Zeiss, Jena), in thermostatted cuvettes. The IR spectra were obtained on a UR-10 instrument (Zeiss, Jena) employing the nujol technique. The electrochemical data were obtained on an OH-102 polarograph (Radelkis, Budapest), using an unshielded carbon disk indicator electrode in a three-electrode circuit. The voltammetric and chronoamperometric measurements and the determination of the effective electrode surface area were carried out in the same manner as in ref. [8].

## Results

#### Electronic Absorption Spectra

So far, the absorption spectra of  $[Cr(CN)_5NO]^{3-}$ [9],  $[Cr(CN)_2H_2O)_3NO]$  [3] and  $[Cr(H_2O)_5NO]^{2+}$  [5, 9, 10] have been described in the literature. The literature data for the last substance are at variance to a certain extent. The results of our measurements are closest to the data from ref. [9]. For a band in the UV region which was not described in ref. [5, 9], we found  $\lambda_{max} = 240$  nm and  $\epsilon = 1207$ , in relatively good agreement with ref. [10]. The spectra for [Cr(CN)<sub>5</sub>-NO]<sup>3-</sup> and [Cr(CN)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>NO] obtained by us are identical with the cited literature data.

Substance  $[Cr(CN)_2(H_2O)_3NO]$  and the other studied ions in the series were obtained by acid hydrolysis of  $[Cr(CN)_5NO]^{3-}$ :

$$[Cr(CN)_{5-x}(H_2O)_xNO]^{x-3} + H^{+} \underbrace{\overset{xx+1}{\longleftarrow}}_{(Cr)} [Cr-(CN)_{5-x}(H_2O)_xNOH]^{x-2} \quad (1)$$
$$[Cr(CN)_{5-x}(H_2O)_xNOH]^{x-2} + H_2O \xrightarrow{k_{x+1}}_{(Cr)} [Cr-(CN)_{4-x}(H_2O)_{x+1}NO]^{x-2} + HCN \quad (2)$$

where x = 0 to 4.

The equilibrium and rate constants in this series have the following values for a solution ionic strength equal to 2M (NaClO<sub>4</sub>) [6, 7]:

$$K_{1} = (1.36 \pm 0.19) \times 10^{3} 1 \text{ mol}^{-1};$$

$$k_{1} = (14.3 \pm 2.0) \times 10^{-3} \text{ s}^{-1} (20 \text{ °C});$$

$$K_{2} = (1.25 \pm 0.18) \times 10^{2} 1 \text{ mol}^{-1};$$

$$k_{2} = (25 \pm 3) \times 10^{-3} \text{ s}^{-1} (20 \text{ °C});$$

$$K_{4} = (13.5 \pm 1.3) 1 \text{ mol}^{-1};$$

$$k_{4} = (2.50 \pm 0.24) \times 10^{-3} \text{ s}^{-1} (25 \text{ °C});$$

$$K_{5} = (5.8 \pm 0.6) 1 \text{ mol}^{-1};$$

$$k_{5} = (1.45 \pm 0.14) \times 10^{-3} \text{ s}^{-1} (25 \text{ °C}).$$

The procedure for obtaining the rate constants is described elsewhere [6].

The hydrolytic rate constant for the third step is very large compared with the first and second steps (k<sub>3</sub> cannot be determined) and consequently the concentration of  $[Cr(CN)_3(H_2O)_2NO]^-$  did not attain a sufficient value for determination of its properties during the hydrolysis. It follows from the given values of the equilibrium and rate constants that a high concentration of complex  $[Cr(CN)_2(H_2O)_3NO]$  is formed during acid hydrolysis. If the hydrolysis takes place in a weakly acidic solution (pH 3-5), this substance is the final product. Hence, the hydrolysis can be studied as a two-step reaction according to Eqs. (1) and (2) with intermediates  $[Cr(CN)_4(H_2O)NO]^2$ and  $[Cr(CN)(H_2O)_4NO]^+$  when the pH is chosen appropriately. The spectra of these intermediates were obtained from the spectrum of the reaction mixture and the calculated concentrations of the reactants. This balance was determined at a time when the concentration of the appropriate intermediate was maximal (32% [Cr(CN)<sub>4</sub>(H<sub>2</sub>O)-



Figure 1. Electronic spectra of complexes of the type [Cr-(CN)<sub>5-x</sub>(H<sub>2</sub>O)<sub>x</sub>NO]<sup>x-3</sup>. Ionic strength, 1*M* (ClO<sub>4</sub>). 1) [Cr-(CN)<sub>5</sub>NO]<sup>3-</sup>; Britton-Robinson buffer, pH 7. 2) [Cr(CN)<sub>4</sub>-(H<sub>2</sub>O)NO]<sup>2-</sup>; 0.02*M* HClO<sub>4</sub>-0.98*M* NaClO<sub>4</sub>. 3) [Cr(CN)<sub>2</sub>-(H<sub>2</sub>O)<sub>3</sub>NO]; HClO<sub>4</sub>-NaClO<sub>4</sub>, pH 4. 4) [Cr(CN)(H<sub>2</sub>O)<sub>4</sub>-NO]; 0.1*M* HClO<sub>4</sub>-0.9*M* NaClO<sub>4</sub>. 5) [Cr(H<sub>2</sub>O)<sub>5</sub>NO]<sup>22</sup>; 1*M* HClO<sub>4</sub>.



Figure 2. Electronic absorption spectra of complexes of the type  $[Cr(CN)_{5-x}(H_2O)_xNO]^{x-3}$  – detailed representation at longer wavelengths. For the caption see Fig. 1.

NO]<sup>2-</sup> in mixture with  $[Cr(CN)_5NO]^{3-}$  and  $[Cr-(CN)_2(H_2O)_3NO]$ , or 60%  $[Cr(CN)(H_2O)_4NO]^+$  in mixture with  $[Cr(CN)_2(H_2O)_3NO]$  and  $[Cr(H_2O)_5-NO]^{2^+}$ , depending on the reaction conditions).

Figs. 1 and 2 give the absorption spectra of the whole series of compounds  $[Cr(CN)_{5-x}(H_2O)_{x} NO]^{x-3}$  except for  $[Cr(CN)_3(H_2O)_2NO]^-$  (Fig. 2 represents the red part of the spectra in greater detail in order to point out the differences). The spectrum of  $[Cr(CN)_4(H_2O)NO]^{2-}$  contains three absorption bands with the following maxima and molar absorption coefficients: 678 nm (29.4), 455 nm (121) and 332 nm (560). The spectrum of  $[Cr(CN)(H_2O)_4NO]^+$  has four absorption bands with the following maxima and molar absorption coefficients: 610 nm (37), 450 nm, (120), 370 nm (211) and 303 nm (194).

#### Vibrational Spectra

Among the series of substances of the type [Cr- $(CN)_{5-x}(H_2O)_xNO]^{3-x}$ , only the IR spectra of [Cr-(CN)\_5NO]^{3-} and [Cr(H\_2O)\_5NO]^{2+} have so far been described [9]. Difficulties in the separation of [Cr- $(CN)_4(H_2O)NO]^{2-}$  and  $[Cr(CN)(H_2O)_4NO]^+$  as the solid substances (these intermediates are unstable and sensitive to changes in the medium) were such that the IR spectra of these substances could not be obtained. The spectra in aqueous solutions were obscured by the IR absorption of water in the region of interest. However, the preparation of solid [Cr(CN)2- $(H_2O)_3NO$ ]·H<sub>2</sub>O by evaporation of the hydrolysis product of  $K_3[Cr(CN)_5NO]$  to the third step in a weakly acidic medium was successful. The H<sup>+</sup> ions were added in the form of gradual addition of the Dowex 50W-X8 cation-exchanger in the hydrogen cycle so that the pH did not decrease below 3 and its amount only slightly exceeded the equivalent consumption of 3  $H^{+}$  per mol. The HCN liberated in the reaction was removed by passing air through the solution. An advantage of this procedure is that no salt is introduced into the solution as normally happens during hydrolysis. The potassium form of the cation-exchanger was filtered off from the solution. The yellow-brown evaporation residue obtained in vacuo at ambient temperature was dried over silica gel. The elemental analysis has shown that the substance composition corresponds to the formula  $[Cr(CN)_2(H_2O)_3NO] \cdot H_2O$  (found: C 11.94%, N 20.01%, H 2.28%, Cr 24.86%; calculated: C 11.66%, N 20.39%, H 3.91%, Cr 25.28%).

The relatively large discrepancy in the analysis for hydrogen is caused by a lack of a suitable method (the results for various methods of determining H were considerably scattered). The substance was poorly soluble in water and completely insoluble in common organic solvents (alcohols, dioxan, acetone, ether, *etc.*); it was readily soluble in 0.01*M* NaOH and 0.1*M* KCN. The former is connected with the formation of anionic hydroxocomplexes and the latter with the formation of anions on substitution of water by cyanide.

The IR spectrum of  $[Cr(CN)_2(H_2O)_3NO] \cdot H_2O$  obtained using the nujol technique is given in Table I.

TABLE I. Infrared Absorption Spectrum of  $[Cr(CN)_2-(H_2O)_3NO] \cdot H_2O$ .

Absorption Maxima [cm <sup>-1</sup> ]	Band Intensity <sup>a</sup>	Assignment	
2 162	S	ν(CN)	
2 1 2 3	w	ν(CN)	
1 720	vs	ν(NO)	
1 626	S	δ (HOH)	
764	w		
627	w	$\nu(CrN)$	
596	w	$\nu(CrC)$	
481	S	δ(CrCN)	

<sup>a</sup>vs = very strong, s = strong, w = weak.

# Electrochemical Oxidation

Voltammetry on a stationary carbon electrode indicated that all complexes in the series studied are anodically oxidized. The voltammetric characteristics of [Cr(CN)<sub>5</sub>NO]<sup>3-</sup>, [Cr(CN)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>NO] and  $[Cr(H_2O)_5NO]^{2+}$  were obtained in aqueous solutions, using base electrolytes in which the substances do not undergo chemical changes, namely [Cr(CN)<sub>5</sub>NO]<sup>3--</sup> in a solution with a pH of approximately 7,  $[Cr(CN)_2(H_2O)_3NO]$  in a solution with pH around 4 and  $Cr(H_2O)_5NO^{2+}$  in strong acidic solutions. Similar to the spectrophotometric study, information about the properties of [Cr(CN)<sub>4</sub>(H<sub>2</sub>O)NO]<sup>2-</sup> and [Cr(CN)- $(H_2O)_4NO$  was obtained from changes in the voltammetric i-E curves during the hydrolysis. The way in which the voltammogram for the first intermediate was reconstructed in depicted in Fig. 3.

The electrochemical properties of the complexes in the series studied are summarized in Table II. In all cases studied the peak current dependence on the square root of the potential scan rate was linear. No counterpeak was observed in cyclic voltammetry, although the cyclic experiments were carried out at various degrees of hydrolysis and with various scanreversal potentials.

On increasing the pH, the i-E curve for  $[Cr(CN)_2-(H_2O)_3NO]$  gradually decreased and a pre-peak appeared; moreover, the voltammogram changed with time. This can be explained by the formation of a hydroxocomplex undergoing a polymerization reaction leading eventually to the formation of a fine precipitate. Similar behaviour was also exhibited by  $[Cr-(H_2O)_5NO]^{2+}$  on increasing the pH. However, if excess cyanide ions were present in alkaline medium, both complexes were converted into  $[Cr(CN)_5NO]^{3-}$ , as was found from quantitative polarographic analysis and from the comparison of the electronic absorption spectra.



Figure 3. Reconstruction of the I-E curve for  $[Cr(CN)_4-(H_2O)NO]^{2-}$  in 1*M* NaClO<sub>4</sub>. pH maintained at a value of 5.3; stationary carbon electrode, potential scan rate, 1.25 ×  $10^{-2}$  Vs<sup>-1</sup>. 1) I-E curve of  $[Cr(CN)_5NO]^{3-}$ . 2) I-E curve of  $[Cr(CN)_2(H_2O)_3NO]$ . 3) Experimental I-E curve (corresponding to all three reactants). 4) Reconstructed I-E curve for  $[Cr(CN)_4(H_2O)NO]^{2-}$  obtained as the difference of curve 3 and the sum of curves 1 and 2. Initial concentration of  $[Cr(CN)_5NO]^{3-}$ , 8 ×  $10^{-4}$  *M*. The concentrations of the corresponding electroactive substances are after a hydrolysis time of 376 min for all I-E curves.

#### Discussion

It can be seen from Fig. 1 that all studied complexes have a band close to 450 nm. This band, as was pointed out in our earlier paper [3], is also exhibited by other nitrosyl complexes of chromium and is characteristic of electron transfer from the metal to the antibonding  $\pi$ -orbital of NO. The maximum of the lowest-energy band is gradually shifted from 724 nm (for  $[Cr(CN)_5NO]^{3-}$ ) to 567 nm (for  $[Cr(H_2O)_5-$ NO]<sup>2+</sup>), reflecting the replacement of cyanides in the coordination sphere by water. The opposite trend was observed with the third band (counting from the red end of the spectrum). A qualitative interpretation of this effect was given in ref. [2]. However, the shifts in the maxima were plotted in ref. [2] against equivalents of acid added to [Cr(CN)<sub>5</sub>NO]<sup>3-</sup>. It follows from the above values of the equilibrium and rate constants that equivalent additions of acid do not lead to the formation of the individual members of the series,  $[Cr(CN)_{5-x}(H_2O)_xNO]^{x-3}$  and hence the spectra thus obtained are spectra of mixtures. The above-given continuous shifts in  $\lambda_{max}$  (Figs. 1 and 2) with the spectrum type being preserved in spite of considerable changes in the complex symmetry during the hydrolysis, indicate that the Cr-NO unit exerts a predominant influence on the ordering of the molecular orbitals. The NO group is bound to the central atom similarly as in complexes [Cr(CN)<sub>2</sub>(H<sub>2</sub>- $O_{3}NO_{1}$ ,  $[Cr(CN)_{5}NO]^{3-}$  and  $[Cr(H_{2}O)_{5}NO]^{2+}$ . This follows from the comparison of the frequencies of the NO group valence vibration in these complexes: for  $[Cr(CN)_5NO]^{3-} \nu_{N-O} = 1645 \text{ cm}^{-1}$  [9], for [Cr $(CN)_2(H_2O)_3NO]$ ,  $\nu_{N-O} = 1720 \text{ cm}^{-1}$  and for [Cr- $(H_2O)_5NO]^{2+}$ ,  $\nu_{N-O} = 1747 \text{ cm}^{-1}$  [9].

The differences in the valence vibration frequencies are too small to represent a basic change in the oxidation state of the NO ligand ( $\Delta \nu_{N-O}$  for a change in the oxidation state ot the free ligand is *ca.* 400 or 500 cm<sup>-1</sup> in the series, NO<sup>+</sup>, NO, NO<sup>-</sup>). The decrease in the  $\nu_{N-O}$  in the series from  $[Cr(H_2O)_5NO]^{2+}$  to  $[Cr(CN)_5NO]^{3-}$  can be explained by a greater degree of back-donation  $Cr \rightarrow \pi^*$  NO and a consequent decrease in the N-O bond order. The increase in back-donation is caused by an increase in the negative charge on the complex moiety along the given series. With the weak  $\pi$ -acceptor ability of the cyanide ligands, the shift in the electron density is localized predominantly in the direction toward the NO ligand.

The electrochemical characteristics given in Table II indicate that the electrode oxidation mechanism is basically different for  $[Cr(CN)_5NO]^{3-}$  and for its hydrolytic products. While the product of the oneelectron oxidation of  $[Cr(CN)_5NO]^{3-}$  does not undergo further oxidation at the given potential [11] (this probably also holds for  $[Cr(CN)_4(H_2O)NO]^{2-}$ ), the other are oxidized with dissociation of the complex. The final products of these four-electron oxidations are Cr(III) and nitrate. From the electrochemical experiments it is impossible to determine in which oxidation stage the Cr–N or Cr–C bond is broken.

In the four-electron oxidation process, at least one chemical reaction must be involved, leading either to separation of NO or to its bonding isomerization (formation of the Cr–O–N group). Otherwise the N-nitratochromium(III) complex would have to be formed by the oxidation, which is very improbable from the point of view of the electronic structure of the nitrato ligand [12]. The rate of this parallel chemical reaction (and possibly of other reactions) must be high, as the current dependence on the potential scan rate indicates diffusion control. The non-existence of a counter-peak in the cyclic voltammetry indicates that none of the products formed in any oxidation step is electrochemically reversible.

The broadening of the oxidation peak for the fourelectron oxidation on gradual replacement of  $CN^-$  by water in the coordination sphere of the complex (Table II) is caused by a decrease in the rate constant of the electrode reaction in the primary oxidation step. An increase in the irreversibility is also manifested by a shift in the half-peak potentials (Table II). This fact can be explained by the increase in the positive charge on the complex, which is oxidized on the positively charged electrode surface.

Similar to the oxidation, replacement of  $CN^{-}$  by water in the coordination sphere of  $[Cr(CN)_5NO]^{3-}$ also causes changes in the reduction mechanism [13, 14], connected with a decrease in the redox stability of the product of the primary one-electron reduction step.

Electroactive Species	Medium	Ep	E <sub>p/2</sub>	$(E - E_{p/2})$	Ip/e	n <sup>a</sup>
		V vs. SCE		$10^{3} \mathrm{A \ mol}^{-1}$ 1		
[Cr(CN)5NO] <sup>3–</sup>	BR. buffer, pH 7.0 $\mu = 0.5M$ (NaClO <sub>4</sub> )	0.859	0.810	0.049	23	1 ch
	2M NaClO <sub>4</sub> , pH 7.0	0.934	0.886	0.048	24	
$[Cr(CN)_4(H_2O)NO]^{2-}$	0.1 <i>M</i> H <sub>3</sub> BO <sub>3</sub> , pH 5.3, $\mu = 2M$ (NaClO <sub>4</sub> )	1.040	0.975	0.065	29	(1?) v
[Cr(CN) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> NO]	0.5 <i>M</i> NaClO <sub>4</sub> , pH 3.4	1.135	1.065	0.070	69	4 ch
	$\frac{1}{\mu} = 2M \text{ (NaClO4)}$	I.120	1.055	0.065	67	
[Cr(CN)(H <sub>2</sub> O) <sub>4</sub> NO] <sup>+</sup>	0.5 <i>M</i> NaClO <sub>4</sub> , pH 3.4	1.125	1.050	0.075	72	4 v
	1M NaClO <sub>4</sub> , pH 2 to 4	1.120	1.045	0.075	74	
[Cr(H <sub>2</sub> O) <sub>5</sub> NO] <sup>2*</sup>	0.1 <i>M</i> HClO <sub>4</sub> -0.9 <i>M</i> NaClO <sub>4</sub>	1.235	1.140	0.095	66	4 ch
	0.5 <i>M</i> HClO <sub>4</sub> -0.5 <i>M</i> NaClO <sub>4</sub>	1.300	1.155	0.145	64	
	0.85M HClO <sub>4</sub> -0.15M NaClO <sub>4</sub>	1.360	1.180	0.180	62	

TABLE II. Voltammetric Properties of Complexes of the Type  $[Cr(CN)_{5-x}(H_2O)_xNO]^{x-3}$ ; scan rate  $12.5 \times 10^{-3}$  Vs<sup>-1</sup>

<sup>a</sup>Number of exchanged electrons n determined chronoamperometrically is designed ch; n determined by comparison of voltammetric peaks is designed v (the peak of  $[Cr(CN)_4(H_2O)NO]^{2^-}$  was compared with the peak of  $[Cr(CN)_5NO]^{3^-}$ ; the peak of  $[Cr(CN)(H_2O)_4NO]^+$  was compared with the peak of  $[Cr(H_2O)_5NO]^{2^+}$ ).

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