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Oxidation of 3-Hydroxy-6-methyl-2-pyridinemethanol by Chromium(VI) in Acidic Aqueous Media; Kinetic and EPR Studies

by E. Kita and G. Wrzeszcz

Department of Chemistry, N. Copernicus University, 87-100 Toruń, Poland

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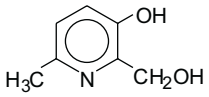
Kinetics of oxidation of 3-hydroxy-6-methyl-2-pyridinemethanol (hmpol) by Cr^{VI} at $HClO_4$ was studied under the pseudo-first-order conditions. The hmpol oxidation products were the appropriate aldehyde (hmpal) and acid (hmpac) coordinated to the chromium(III). The linear dependence of the pseudo-first-order rate constant (k_{obs}) on [hmpol] at 1.0 and 2.0 M $HClO_4$ and a parabolic dependence of k_{obs} on $[H^+]$ were established. The apparent activation parameters were determined from the second-order rate constants at 1.0 M $HClO_4$. The presence of the Cr^{II} and Cr^{IV} intermediates was deduced, based on rate retardation effect caused by O_2 and Mn^{II} respectively, whereas the presence of Cr^{V} was established by EPR. Some correlations between the structure and stability of intermediate chromium(V) complexes have been discussed from EPR spectra, recorded during the redox process.

Key words: kinetics, oxidation of 3-hydroxy-6-methyl-2-pyridinemethanol, reduction of chromium(VI), EPR of chromium(V)

Our previous studies on kinetics and mechanism on the oxidation of pyridine alcohols by chromium(VI) in aqueous acidic media [1–3] have given some correlations between structure and reactivity of the reductants. Two conclusions have been drawn: (i) the position of hydroxymethyl group slightly influences the reductant reactivity, (ii) chelating ability of the reductant increases its reactivity. The extremely low reactivity of 2-pyridinemethanol was attributed to the intramolecular hydrogen bond formation, which retards the reaction rate [3]. Mechanism of chromium(VI) reduction *via* two 2-electron transfers has been proposed, based on the products distribution and kinetic results. Chromium at unstable oxidation states, II, IV and V, was detected by kinetic tests and EPR spectrometry.

In this work oxidation of 3-hydroxy-6-methyl-2-pyridinemethanol (Scheme 1) was studied. The alcohol is an analogue of 2-pyridinemethanol, but its phenolic group gives an opportunity for an additional chelate ring formation *via* phenolato- and carboxylato oxygen atoms. This structural difference is expected to increase the reactivity of hmpol in comparison to a low reactivity of 2-pyol. Moreover, chromium(III) should exist as chelate complexes with organic ligands formed *via* their O,O′-atom donors.

Scheme 1



The alcohol is a white solid, easily dissolved in water. It is stable during storage and does not decompose in solution at 2 M $HClO_4$. Its UV spectrum in acidic and alkaline solution is like that described in [4] for 3-hydroxy-2-pyridinemethanol, however, the positions of λ_{max} are shifted 8–10 nm towards the longer wavelengths.

EPR is a fundamental method in studies on chromium(V) species, formed during chromate(VI) reduction. In former works on pyridine alcohols oxidation by chromium(VI), EPR studies were used only for chromium(V) detection [2,3]. In this work, more details on EPR data are given and an attempt of correlation between EPR signal persistence and the reductant structure is undertaken.

EXPERIMENTAL

Materials: The 3-hydroxy-2-hydroxymethyl-6-methylpyridine (98%), 70% $HClO_4$ and $NaClO_4 \cdot 2H_2O$ were purchased from Aldrich and were used without further purification. All solutions were prepared using redistilled H_2O. In some experiments Ar and O_2 of high purity were used. Sephadex SP C-25 (Pharmacia) was applied for chromatographic separations.

Reaction products: Oxidation of hmpol by chromium(VI) was performed in 2.0 M $HClO_4$, at 323 K, at molar ratio of reductant:chromium(VI) = 3. Total volume of the solution was 10 cm^3 and the chromium(VI) amount was 1 mmole. Conversion of chromium(VI) into chromium(III) was completed within 10 min and a colour of the reaction mixture turned from orange to green. The solution was diluted with H_2O (100 cm^3) and was passed through a column of Sephadex SP C-25. Three bands – gray-green, yellow-green and green – were eluted with 0.2 and 0.5 M $HClO_4$ (the last, orange band of a very high affinity to the Sepxadex was not eluted). Because the second and the third bands overlapped, their rechromatography was necessary. The UV-Vis spectra of collected fractions were recorded and the decomposition of the complexes in 0.1 M NaOH was done in order to characterize the liberated ligands.

Determination of the chromium(III)-complexes composition: Liberation of the coordinated organic ligands was done by heating the complex solution in 0.1 M NaOH at 363 K during 30 minutes. Then the alkaline solution was acidified with 1 M $HClO_4$ down to pH = 1 and the UV spectrum was recorded. Positions of λ_{max} in the spectra of liberated ligands are as follows: I fraction; 210.0, 310.0 (pH = 1) and 220.6, 242.6, 312.6 (pH = 13) nm, II fraction; 222.6, 296.6, 327.0 (pH = 1) and 257.4, 378.8 (pH = 13) nm, III fraction; 225.6, 295.5 (pH = 1) and 240.8, 310.6 (pH = 13) nm.

Tests for free aldehyde: Tests with 2,4-dinitrophenylhydrazine for free aldehyde in reaction mixture were performed at 1 M $HClO_4$. Because no positive results were obtained, additional test with glycine for Schiff base formation was done. The analysed solutions were mixed with an excess of glycine, alkalized to pH 11–13 and heated at 333 K for a few minutes. In the aldehyde presence the colour of alkaline solution became light yellow and was intensified during heating with glycine.

EPR measurements: EPR spectra were recorded with an ESR Bruker Physik 418S reflection type spectrometer in X-band (*ca.* 9.5 GHz) with a 100 kHz modulation of a steady magnetic field. The microwave frequency was monitored with a 18 GHz microwave counter (Marconi Instrument). The magnetic field was measured with an automatic MJ-110 R NMR-type magnetometer (Radiopan). All measurements were done for reaction mixture of 0.5 M chromium(VI) and 1.0 M reductant, at 0.01 M $HClO_4$, at 295 K. A flat quartz cell was used. WinSim EPR simulation software [5] was applied to estimate the spectral parameters. Satisfactory agreement between experimental and calculated spectra was

possible on the basis of Lorentzian line-shapes. The simulations do not include contributions from the minor peaks, that arise from the ^{53}Cr hyperfine coupling.

Kinetic measurements: The reaction rate was followed spectrophotometrically, using a Shimadzu UV-1601 PC instrument equipped with a Shimadzu CPS-Temperature Controller operated by a Dell computer. The decrease of absorbance at 450 nm was recorded (Figure 1).

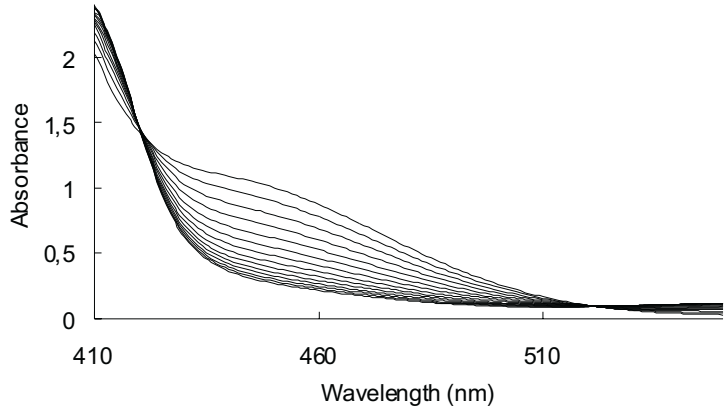


Figure 1. Absorbance changes during oxidation of 0.2 M hmpol by chromium(VI), $[Cr^{VI}] = 3.5 \times 10^{-3}$ M, $[H^+] = 1.0$ M, $I = 1.2$ M, T = 313 K; scans every 100 s.

All measurements were done under a pseudo-first-order conditions, keeping a large excess of the reductant and $HClO_4$ concentrations over concentration of chromium(VI) at constant ionic strength 1.2 or 2.1 M (H^+, Na^+, ClO_4^-). The time scale was 550–2800 s (3 $t_{1/2}$). The reactions were carried out at three different temperatures within the 293–313 K range. The concentration of the reductant was varied within the 0.03–0.15 M, the chromium(VI) concentration was usually 2.5×10^{-3} M, the concentration of $HClO_4$ was 1.00 or 2.00 M. Some measurements were done at different $[HClO_4]$ (0.5–2.0 M) at [reductor] = 0.05 at $I = 2.1$ M. Correction of H_3O^+ concentration was necessary, due to a partial neutralization of the acid by the pyridine nitrogen protonation. The reaction was started by addition of 0.02 cm^3 of 0.125 M $Na_2Cr_2O_7$ into 2 cm^3 of the thermostated solution containing all other components. The stock solutions of the reductant in 1.00 or 2.00 M $HClO_4$ were protected against light. Each kinetic run was repeated three times. The relative standard errors of the pseudo-first-order rate constant for a single run were *ca.* 0.2% and the relative standard errors of the mean k_{obs} were usually about 0.5–1%.

RESULTS AND DISCUSSION

The chromatographic properties, spectral characteristics of the three complexes eluted (Table 1) and the spectra of liberated ligands are consistent with following chromium(III)-complexes compositon: $[Cr(hmpac)(H_2O)_4]^{2+}$ (I fraction), $[Cr(hmpal)(H_2O)_4]^{3+}$ (II fraction) and $[Cr(hmpol)(H_2O)_4]^{3+}$ (III fraction) (where: hmpac = 3-hydroxy-6-methyl-2-pyridinecarboxylic acid and hmpal = 3-hydroxy-6-methyl-2-pyridinecarboxaldehyde). The all liberated ligands could be identified because their spectra are analogous to those described by Nakamoto and Martell [4,6] for 3-hydroxy-2-pyridinemethanol and its oxidation products (the aldehyde and the acid).

Table 1. Spectral characteristics of reaction products obtained during oxidation of hmpol by chromium(VI) in $HClO_4$ solutions.

Fraction	Compound	λ_{max}, nm (ε_{max}, $M^{-1}cm^{-1}$)
I	$[Cr(hmpac)(H_2O)_4]^{2+}$	261.0 (8450), 334.4 (5900), 425.5 (58), 559.5 (30)
II	$[Cr(hmpal)(H_2O)_4]^{3+}$	250.0 (9940), 310.6 (5500), 365.4 (2860), 578.5 (34)
III	$[Cr(hmpol)(H_2O)_4]^{3+}$	255.2 (4490), 307.0 (4290), 584.5 (32)

Negative tests with 2,4-dinitrophenylhydrazine and glycine for reaction mixture indicate that practically no free aldehyde is formed. On the other hand, the positive test with glycine for the second fraction after ligand liberation (in the presence of glycine the position of λ_{max}, characteristic for the alkaline solution of the pyridine aldehyde was shifted towards the longer wavelength 375.2 → 395.8 nm) indicates that hmpal is coordinated to chromium(III). Not eluted, the orange-brownish band of a high positive electric charge, probably also contains hmpal in the form of polynuclear chromium(III) complexes.

Formation of the chromium(III) complexes with hmpac and hmpal is consistent with generally accepted mechanism of chromium(VI) reduction by the two-electron reductors (eq. 1, 2), described previously [1–3, 7–9]:

$$Cr^{VI} + \text{hmpol} \overset{\text{fast eq.}}{\rightleftharpoons} Cr^{VI}\text{-(hmpol)} \xrightarrow{\text{slow}} Cr^{IV}\text{-(hmpal)} \overset{\text{fast eq.}}{\rightleftharpoons} Cr^{IV} + \text{hmpal} \quad (1)$$

$$Cr^{IV}\text{-(hmpal)} \xrightarrow{\text{fast}} Cr^{II}\text{-(hmpac)} \overset{\text{rapid eq.}}{\rightleftharpoons} Cr^{II} + \text{hmpac} \quad (2)$$

Presence of the $[Cr(hmpac)(H_2O)_4]^{2+}$ as well as lack of the free aldehyde in the reaction mixture indicate that Cr^{IV}-(hmpal) intermediate undergoes a fast intramolecular two-electron reduction to Cr^{II}-(hmpac) (2), which is next oxidized to Cr^{III}-(hmpac) by chromate(VI) (3). Chromium(V), formed during the later redox process (3), reacts with another alcohol molecule giving very inert $[Cr(hmpal)(H_2O)_4]^{3+}$ species (4):

$$Cr^{II}\text{-(hmpac)} + Cr^{VI} \xrightarrow{\text{fast}} Cr^{III}\text{-(hmpac)} + Cr^{V} \quad (3)$$

$$Cr^{V} + \text{hmpol} \overset{\text{fast eq.}}{\rightleftharpoons} Cr^{V}\text{-(hmpol)} \xrightarrow{\text{fast}} Cr^{III}\text{-(hmpal)} \quad (4)$$

Formation of Cr^{III}-(hmpol) can be explained assuming a consecutive reaction between the very labile Cr^{II} and the alcohol, being in a large excess. Analogous chromium(III) complexes were obtained during pyridoxine (vitamin B_6) oxidation [1], which is the 3-hydroxopyridine derivative. Presence of chromium(II) and chromium(IV) species was confirmed by kinetic tests with O_2 and manganese(II), respectively [2,3,7–12]. The rate retardation in O_2 with comparison to Ar atmosphere, as well as the rate retardation in the manganese(II) presence are consistent with formation of chromium(II) and chromium(IV) species during the reaction (Table 2).

Table 2. Influence of Mn^{II} and gas atmospheres on k_{obs}; [hmpol] = 0.15 M, [$HClO_4$] = 1.0 M, I = 1.2 M, [Cr^{VI}] = 2.6×10^{-3} M, T = 298 K.

0.02 M Mn(II), air	$10^4 k_{obs}$, s^{-1} Argon	Air	Oxygen
7.26 ± 0.07	10.0 ± 0.07	8.98 ± 0.08	8.37 ± 0.07

Chromium(V) was detected by EPR spectrometry. Electronic configuration of chromium(V) (d^1) makes convenient the EPR detection, specially if the ligand is able fo form a chelate ring with chromium(V) centre, what stabilizes this oxidation state [13]. EPR spectrum of hmpol-chromium(VI) reaction mixture (2:1) at pH = 2 exhibits two signals at g = 1.9775 and 1.9754 (Figure 2), which initially grow and then decay.

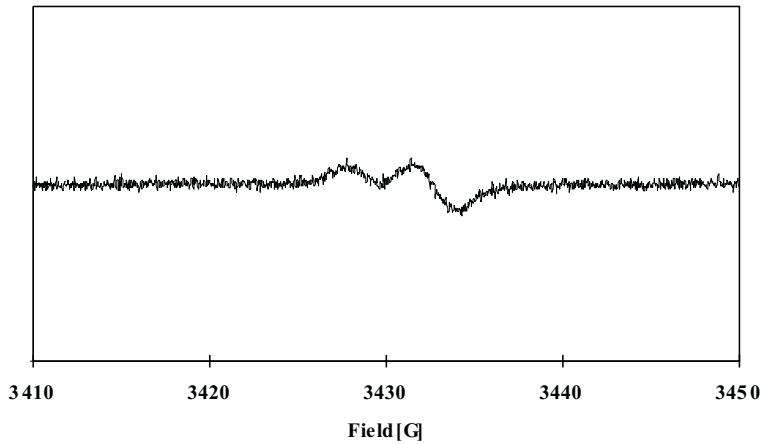


Figure 2. EPR spectrum for the hmpol–chromium(VI) system; [Cr^{VI}] = 0.5 M, [hmpol] = 1.0 M, pH = 2, T = 295 ± 1 K; reaction time – *ca.* 23 min.

As EPR signal of chromium(III) consists of a very broad singlet and Cr(IV) produces an EPR signal only at very low temperatures [14], the observed signals have to be assigned to chromium(V) intermediates. Maximum intensity of the signals was after *ca.* 25 minutes. No coupling with ^{53}Cr (*ca.* 9.5% abundance, I = 3/2) was observed, because of a weak signal intensity. Within *ca.* 100 minutes the chromium(V) signals disappear and a very broad signal of chromium(III) at $g \sim 2$ with ΔH_{pp} = 350 G appears. The both chromium(V) EPR signals are probably due to two different chromium(V)-hmpol complexes. Two chromium(V) species have been frequently observed [15–17], even in a relatively simple system, such as Cr(VI)-methanol [18]. As many as five chromium(V) intermediates have been reported during the oxalic acid oxidation by chromium(VI) [19]. Using an additive method developed by Barr-David *et al.* [20], two, the most probable chromium(V) intermediates in the 2,6-pydol–chromium(VI) system, in which chromium(V) is a five coordinated species, have been postulated. It is likely that the first signal can be assigned to the $[Cr(O)_2(hmpol\text{-}1H)(H_2O)]^0$ complex (where bidentate hmpol-1H is the monoanion

with protonated pyridine nitrogen and deprotonated phenolic and methanolic oxygen atoms), because experimental and calculated *g*-values, 1.9775 and 1.9779 respectively, are very close. The second, of higher intensity, can be assigned to the $[Cr(O)(hmpol)(H_2O)_3]^{3+}$ complex (where monodentate hmpol is the zwitterion with protonated pyridine nitrogen and deprotonated hydroxymethyl oxygen atoms); the experimental and calculated *g* values are 1.9754 and 1.9750, respectively. This proposal is rather unexpected, because one would assume that monodentate O-bonded hmpol coordinates *via* phenolate oxygen atom. However, much better convergence between the calculated and the experimental *g* values was obtained assuming bonding *via* the deprotonated methanolic oxygen atom. The expected proton superhyperfine coupling is unresolved and may result in broadening the signals. Typical simulated parameters show that individual line widths are higher than proton hyperfine coupling constants, ΔH_{pp} = 1–2.5 G and a_H = 0.8–1.5 G, respectively. In addition, as the reaction proceeded, a substantial broadening of the EPR signals occurred, due to the increase of viscosity of the reaction mixture.

Kinetic measurements were based on chromium(VI) disapperance at 450 nm, the lower energy CT transition in chromate(VI) (Figure 1). Usually, a decrease in absorbance at 350–370 nm region (the higher energy CT transition) is registered, but in the system studied this spectral region was disturbed by the reaction products absorption (Table 1). The pseudo-first-order conditions were maintained by applying at least 10-fold [hmpol] over $[Cr^{VI}]$ and a large excess of $[H^+]$. The pseudo-first-order dependence was obeyed very well. Pseudo-first-order rate constants (k_{obs}) as a function of [hmpol] determined at 1 M and 2 M $HClO_4$ are presented in Table 3.

Table 3. Dependence of k_{obs} on [hmpol]; $[Cr^{VI}] = 2.6 \times 10^{-3}$ M, (A) $[H^+] = 1.0$ M, $I = 1.2$ M, (B) $[H^+] = 1.0$ M, $I = 2.1$ M, (C) $[H^+] = 2.0$ M, $I = 2.1$ M.

[hmpol], M	$10^4 k_{obs}$, s^{-1}				
	293.7 K	303.2 K	312.7 K	293.7 K	293.7 K
	(A)			(B)	(C)
0.03	1.42 ± 0.01	2.47 ±0.03	4.39 ± 0.05	1.74 ± 0.01	8.50 ± 0.1
0.04	1.98 ± 0.02	3.35 ± 0.03	5.40 ± 0.06	2.34 ± 0.03	10.8 ± 0.1
0.06	2.97 ± 0.02	4.70 ± 0.04	8.20 ± 0.1	3.47 ± 0.05	16.8 ± 0.2
0.08	3.90 ± 0.03	6.37 ± 0.04	10.6 ± 0.1	4.63 ± 0.06	22.2 ± 0.2
0.10	4.82 ± 0.03	7.70 ± 0.1	13.2 ± 0.1	5.76 ± 0.06	27.9 ± 0.2
0.12	5.79 ± 0.04	9.80 ± 0.1	16.7 ± 0.1	–	33.0 ± 0.3
0.15	7.20 ± 0.04	11.9 ± 0.1	–	–	–

A linear dependence of k_{obs} on [hmpol] was established:

$$k_{obs} = a + b[\text{hmpol}] \quad (5)$$

Values of the *a* and *b* parameters, calculated by the linear least squares method, are given in Table 4. The slopes are the pseudo-second-order rate constants (k_1), which characterize reactivity of hmpol at given $[H^+]$. According to the ester mechanism [2,3,11,12, 21–23] $b = k_1 Q_1$, where Q_1 is the preequilibrium constant for chromate(VI)

ester formation. Intercepts (a), as in the most systems studied, are equal to zero within the errors limit.

Table 4. Linear parameters for k_{obs} on [hmpol]; (A) $[H^+] = 1.0$ M, $I = 1.2$ M, (B) $[H^+] = 1.0$ M, $I = 2.1$ M, (C) $[H^+] = 2.0$ M, $I = 2.1$ M.

Temp, K	$10^5 a$, s^{-1}	$10^3 b$, $M^{-1}s^{-1}$
(A)		
293.7	0.51 ± 0.35	4.78 ± 0.04
303.2	0.73 ± 1.56	7.89 ± 0.16
312.7	0.89 ± 3.46	13.5 ± 0.4
(B)		
293.7	0.32 ± 0.15	5.74 ± 0.02
(C)		
293.7	0.94 ± 2.45	27.6 ± 0.3

Comparison of the k_1 values determined at 1.0 and 2.0 M $HClO_4$ at $I = 2.1$ M indicates that the reaction rate strongly depends on acidity of the medium; the rate increases *ca.* 5-times, whereas the increase of the ionic strength from 1.2 to 2.1 only slightly affects the rate (Table 3).

Kinetic measurements at different $[H^+]$ at [hmpol] = 0.05 M and $I = 2.1$ M let to deduce, which chromium(VI) species are the most important for the redox process. The k_{obs}–$[H^+]$ dependence at constant ionic strength 2.1 M is shown in Figure 3.

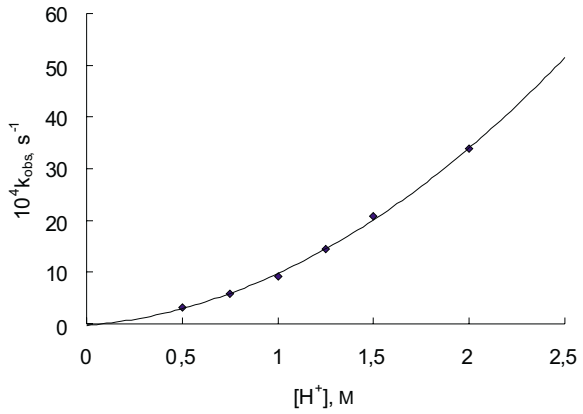


Figure 3. Dependence of the pseudo-first order rate constant (k_{obs}) on $[H^+]$; [hmpol] = 0.05 M, $I = 2.1$ M, temp. = 303 K.

The data were fitted to the parabolic function (6):

$$k_{obs} = b'[H^+] + c'[H^+]^2 \tag{6}$$

The b', c' parameters are composite quantities, which can be rationalized as before [2,3]:

$$b' = k_1' Q_{p1} \quad c' = k_2' Q_{p1} Q_{p2} \tag{7}$$

where: k_1', k_2' are the rate constants for H_2CrO_4 and $H_3CrO_4^+$ and Q_{p1}, Q_{p2} are successive apparent protonation constants for chromate(VI) in the free and ester form, provided that the extend of chromate(VI) protonation is small. The calculated b', c' parameters are as follows: $b' = (2.43 \pm 0.56) \times 10^{-4}\ M^{-1}s^{-1}$ and $c' = (7.30 \pm 0.35) \times 10^{-4}\ M^{-2}s^{-1}$. These results indicate that oxidation of hmpol by $H_3CrO_4^+$ is the main reaction path at $[H^+] > 1$ M, but at lower $[H^+]$ also H_2CrO_4 plays an important role. As in (6) there is no term independent on $[H^+]$, one can conclude that $HCrO_4^-$ species practically are not reactive towards hmpol under applied conditions. Values of the apparent activation parameters (at 1 M $HClO_4$), calculated from k_1 determined at three temperatures (Table 4, A), are collected in Table 5.

Table 5. The second-order rate constant at 298 K and the apparent activation parameters calculated from k_1 for oxidation of hmpol by Cr^{VI} at $[H^+] = 1.0$ M, $I = 1.2$ M.

$10^3\ k_1$, $M^{-1}s^{-1}$	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J K^{-1} mol^{-1}
5.98	40.2 ± 1.7	−153 ± 5

The reaction is characterized by small $\Delta H^{\neq}$ and high negative $\Delta S^{\neq}$ values, like other reactions in similar systems [1–3], what confirms the same type of redox mechnism. The comparison of $k_{1(298)}$ for oxidation of hmpol by chromate(VI) at 1.0 M $HClO_4$ (Table 5) with those determined for other pyridinemethanols [1–3] leads to the following reactivity order: 62 (PN) : 8 (hmpol) : 6.2 (3-pyol ≈ 4-pyol ≈ 2,6-pydol) : 1 (2-pyol), where pyol is pyridinemethanol, pydol – pyridinedimethanol, and PN – pyridoxine (vitamin B_6). This result is consistent with the postulated correlations between the structure and reactivity of the reductant (*vide* Introduction). The alcohol studied can form the chelate ring *via* the hydroxylic and phenolic oxygen atoms like pyridoxine, what facilitates the ester formation, but the presence of intramolecular hydrogen bond between the nitrogen proton and the hydroxymethyl oxygen makes ester formation difficult. Therefore, the hmpol reactivity is lower than that for PN and higher than that for 2-pyol. The position of hmpol in the reactivity order clearly demonstrates that chelating abilities of the reductant and formation of intramolecular hydrogen bond act in the opposite direction.

Some correlations between the structure and stability of intermediate chromium(V) complexes can be drawn from EPR spectra, recorded during the redox process. In all systems studied [2,3], one or two signals at g values within the 1.962–1.980 range were observed, what is characteristic to chromium(V) species. The signals intensities are low, except those for 2,6-pydol–chromium(VI) system, and are comparable to the hmpol–chromium(VI) system presented here. However, under the same reaction conditions, the signal magnitudes vary in a different way during the reaction time. The following results have been found: (i) the intensity of the chromium(V) EPR signal for 2-pyol decreases quickly and disappears after 40 min; (ii) the intensity of the chromium(V) EPR signals for 3- and 4-pyridinemethanols decreases very slowly during several hours. In both cases the maximal intensity was detected at the "beginning", typically within 3–5 min, after preparation

of the reaction mixture; (iii) the intensity of the chromium(V) EPR signals for 2,6-pydol and hmpol increases during 40 and 25 min respectively, and then slowly decreases during 200 and 100 min.

The content of the chromium(V) in the chromium(VI)-reductant systems depends on the relation between the rate of the chromium(V) formation and the rate of its decay [13]. Assuming that the rate of the chromium(V) formation is proportional to the $k_{1(298)}$, the above observations (i–iii) are in agreement with the presented reactivity order. Because 2-pyol reacts very slowly, so initially formed chromium(V) species quickly reaches an undetective level [the (i) case]. Higher reactivity of 3- and 4-pyridinemethanols causes a faster establishing of a quasistationary state and, therefore, the chromium(V) signal is observed for a longer time [the (ii) case]. The further increase of hmpol reactivity leads to typical first-order consecutive reactions of chromium(V) intermediate [the (iii) case].

Although 2,6-pydol–chromium(VI) system belongs to the (iii) case, changes of chromium(V) concentration do not correlate with the $k_{1(298)}$ value. This system shows exceptionally strong EPR signals (Figure 4), which allow to evaluate the maximum chromium(V) concentration as two orders of magnitude higher than for the other systems studied. We assume that it is probably due to a higher stability constant for 2,6-pydol–chromium(V) complex, than for the other chromium(V) intermediates. Additionally, contrary to other systems studied, 2,6-pydol is coordinated to chromium(V) *via* pyridine nitrogen atom, what is evident from the resolved hyperfine structure of the main EPR signal (Figure 4).

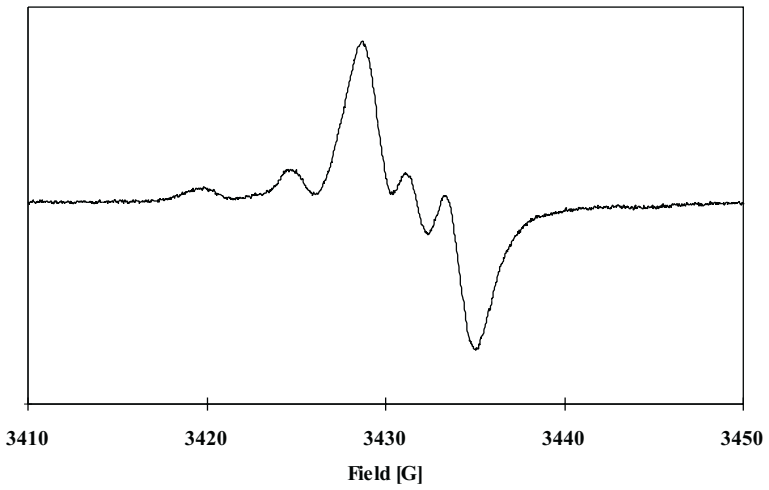


Figure 4. EPR spectrum for the 2,6-pydol–chromium(VI) system; [Cr^{VI}] = 0.5 M, [2,6-pydol] = 1.0 M, pH = 2, T = 295 ± 1 K; reaction time – *ca.* 40 min.

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