Mechanism of photochemical reduction of chromium(VI) by alcohols and its environmental aspects

Piotr Mytych, Andrzej Karocki, Zofia Stasicka*

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland

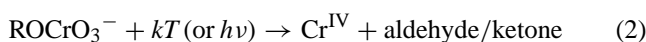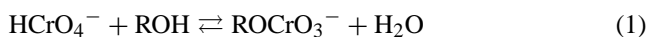Received 22 April 2003; accepted 6 May 2003

Abstract

The idea of photochemical abatement of the Cr(VI) pollution has been verified by investigating the photoreduction mediated by aliphatic alcohols under conditions mimicking the environmental ones. Effects of the alcohol nature, pH and presence of oxygen are analysed. The time-resolved spectra are used to follow the generation of the transient chromium Cr(V), Cr(IV) and Cr(II) species and the $R_1R_2CHOH^{\bullet+}$ radicals. A direct interaction between chromate(VI) and an electron donor is a precondition of the photoreduction via the photoinduced electron transfer (PET). Two pathways of the PET are identified: one-electron transfer for intermolecular and two-electron transfer for the intramolecular systems. In the case of the alcohol mediators the option is pH-controlled.
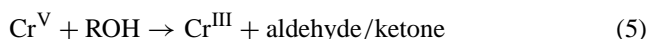© 2003 Elsevier B.V. All rights reserved.

Keywords: Hexavalent chromium; Photoreduction; Mediation by aliphatic alcohols; Photoinduced electron transfer (PET)

1. Introduction

The photochemical oxidation of alcohols by chromate(VI) has been known for more than 80 years. Initially, the interest in the reaction resulted from searching for an optimal procedure of alcohol oxidation by chromate(VI) in moderately acidic medium. As neat chromate(VI) is photochemically inactive in every of its forms existing in aqueous solution, its photoreduction by alcohols was interpreted in terms of the photochemical reactivity of the chromate(VI) esters [1–5]. The thermal reactions in the Cr(VI)—alcohol—acid systems were largely studied and several pathways were proposed. Similar conclusions were drawn for the photochemical mode. The most generally accepted mechanism comprises of the two-electron reduction of Cr(VI) giving rise to an aldehyde or ketone and a Cr(IV) species. The formation of the chromate(VI) ester is mostly assumed as condition sine qua non of the redox or photoredox reaction series [2,3,5–8].

$$HCrO_4^- + ROH \rightleftarrows ROCrO_3^- + H_2O \tag{1}$$

$$ROCrO_3^- + kT\,(\text{or}\,h\nu) \rightarrow Cr^{IV} + \text{aldehyde/ketone} \tag{2}$$

$$Cr^{IV} + Cr^{VI} \rightarrow 2Cr^V \tag{3}$$

$$3Cr^V \rightarrow 2Cr^{VI} + Cr^{III} \tag{4}$$

and/or

$$Cr^V + ROH \rightarrow Cr^{III} + \text{aldehyde/ketone} \tag{5}$$

The fate of the generated Cr(V) species depends strongly on its surrounding: in some solid or organic matrices [9,10] or at low temperatures [6] its formation could be easily observed. In other cases Cr(V) is reduced fast into a Cr(III) species and/or is re-oxidized to Cr(VI) (Eqs. (4) and (5)).

Recently, the chromate(VI) photoreduction has become again the centre of interest mainly because of its relevance to production of holographic optical elements [10], to the Cr-induced carcinogenesis [11–13] and to the environmental chemistry [14,15]. Moreover, at present time many systems are recognized, in which ester formation and/or two-electron transfer are not indispensable features of the photoreduction [8,10,16,17].

From the environmental point of view knowledge of chromium(VI), (photo)reduction mechanism is essential not only for tracing Cr(VI) fate in the environment but also for understanding its role in remediation of the pollution by the organic compounds. The behaviour of Cr-species depends strongly on its oxidation state: Cr(VI) is mobile and highly toxic, whereas Cr(III) is mostly immobile and environmentally friendly [18]. Reduction of Cr(VI) to Cr(III) thus leads to drastic decrease in the bioavailability and toxicity of this element. Known thermal pathways of Cr(VI) $\rightleftarrows$ Cr(III) interconversion cannot substantiate the amount concentrations

---

* Corresponding author. Tel./fax: +48-12-633-5392.
E-mail address: stasicka@chemia.uj.edu.pl (Z. Stasicka).

of the two forms found in specified regions. Especially, significant quantities of Cr(III) determined in oxygenated sunlit surface waters suggest strongly that the Cr(VI) reduction in environment proceeds not only via thermal but also via photochemical processes [14,15].

The Cr(VI) photoreduction initiated by sunlight in natural waters was interpreted in terms of photochemical generation of such reducers as copper(I), superoxide (O_2^-), or iron(II) [14,15,19–21]. More detailed studies showed, however, that reduction by H_2O_2 proceeds inefficiently [22,23], whereas Cu(I) photochemical generation in nature needs simultaneous presence of Cu(II) and H_2O_2 and the reaction rate is strongly reduced by ligating species (e.g. EDTA or its analogues, increased concentration of Cl$^-$) [14]. The mostly studied system consisted of Cr(VI) and Fe(II) added or generated photochemically [15,19,24–26]. In alkaline medium the reaction proceeds fast, whereas the results obtained at environmental pH values lead to acutely divergent conclusions, such as 'the reaction of Fe(II) with Cr(VI) is extremely rapid' or 'the reaction is too slow to explain seasonal changes in the Cr(VI) to Cr(III) ratio' (for a more detailed discussion see [20,21]). Moreover, under similar conditions, opposite reaction, i.e. oxidation of Cr(III) to Cr(VI) induced by light and Fe(III) was also reported [27,28].

The role of the environmental photoactivators may be played as well by semiconductors such as TiO_2 (both rutile and anatase), WO_3, Fe_2O_3, $SrTiO_3$, etc. which were found to drive the Cr(VI) to Cr(V) reduction [29–34].

All these effects stimulated us to reinvestigate the photochemical reduction of chromate(VI) by alcohols using fast photochemical techniques and continuous irradiation procedures under conditions mimicking the natural ones. We expected to find a better mechanistic interpretation and understanding the pathways of the Cr(VI) decay in the environmental self-cleaning and pollution remediation processes.

2. Results and discussion

The studied systems consist of chromate(VI) and an alcohol at constant pH, which under experimental condition are thermally stable within at least 24 h. The aliphatic alcohols (methanol, ethanol, propanol or butanol) are the basic photoreducers used in this study. The results are completed by single experiments with some other electron donors.

2.1. Continuous photolysis

The results of the continuous irradiation confirm previously reported behaviour: in neutral, moderately acidic or alkaline aqueous solutions the redox reaction between chromate(VI) and the alcohols does not proceed in the dark [34]. Under specific conditions, however, the process can be initiated by switching on the radiation mimicking sunlight ($\lambda >$ 300 nm) and interrupted by switching the light off.

The rate of Cr(VI) photoreduction depends not only on the irradiation conditions but also on the alcohol nature and the reaction medium. In the case of aliphatic alcohols the reaction rate depends on the alcohol structure and decreases in the series (see Table 1):

butan-1-ol > butan-2-ol $\gg$ propan-2-ol > ethanol

$\gg$ methanol > 2-methyl-propan-2-ol
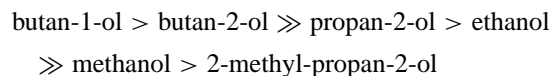
The behaviour resembles thus the relative rates of the thermal reduction recorded in strongly acidic solutions [35–37]. The length of the main chain and nature of the carbon atom bonded to the OH group is here of relevance: the oxidation of the primary alcohols is faster than that of secondary, whereas for tertiary it is much slower. The Cr(VI) photoreduction is faster when more than one OH group is present, as in glycerine (Table 1).

Beside the alcohol nature the reaction rate is sensitive to the solution pH value, presence of molecular oxygen and other medium components, but insensitive to temperature within 283–303 K. The pH effect was discussed in many papers and increasing reaction rate with an increase in acidity was interpreted in terms of higher susceptibility of $HCrO_4^-$ than CrO_4^{2-} to undergo reduction and the chromate(VI) ester formation [1,3–5]. The latter is difficult to prove, because the spectral changes reported earlier as characteristic for the ester formation [1] appeared to be confused with the pH effect on the spectrum related to the $CrO_4^{2-} \rightleftarrows HCrO_4^-$ interconversion. We observed, moreover, that the lower pH, the higher retardation effect of Mn(II), which is known to react selectively with Cr(IV) [38–40] (Fig. 1, Table 1). This means that besides the ester formation the increased acidity favours generation of Cr(IV), which must be accompanied with transformation of the chromium coordination sphere from tetrahedral to octahedral, e.g. in reaction [41]:

$$HCrO_4^- + 2e + 7H^+ + 2H_2O \rightarrow [Cr(H_2O)_6]^{4+} \qquad (6)$$
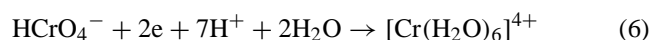
However, opposite to the thermal reaction, the photoreduction rate is not very sensitive to H^+ concentration within pH 2–4 (Table 1). It may point, as well, that at pH not low enough to favour the Cr(VI) $\rightleftarrows$ Cr(IV) photoreduction (Eq. (6)), the one-electron transfer competes effectively with the two-electron reduction pathway.

Under these pH values the more crucial factor is the presence of molecular oxygen: the reaction is the faster at lower concentration of O_2 (Fig. 1, Table 1). O_2 may be considered as oxidant converting generated tetrahedral Cr(V) back to Cr(VI) [42], example:

$$HCrO_4^{2-} + O_2 \rightarrow HCrO_4^- + O_2^- \qquad (7)$$
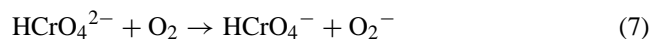
Furthermore, molecular oxygen may act here as radical scavenger. The hypothesis is verified by a somewhat higher sensitivity towards O_2 at higher pH values. The O_2 effect on the reduction rate depends as well on the alcohol nature: in particular, the primary alcohols are more susceptible to the O_2 suppression than with the secondary ones (Table 1). The

Table 1

Relative rates of Cr(VI) photoreduction mediated by alcohols (in deaerated solutions at pH 4, irradiated by $\lambda \geq 300$ nm, if not otherwise stated)

Compound	Concentration (mm)		Conditions	$k_{obs} \times 10^7$ (s^{-1})
	Cr(VI)	Alcohol		
Effect of the alcohol nature				
Methanol	0.7	140		2.70
Ethanol				11.20
Propan-2-ol				17.50
Butan-1-ol				38.70
Butan-2-ol				33.32
2-Methyl-propan-2-ol				2.55
Effect of the alcohol concentration				
Ethanol[a]	0.7	17.5		0.92
		35.0		2.17
		175.0		7.43
		350.0		14.70
pH effect				
Butan-2-ol	0.35	70	pH 2.0	13.30
			pH 3.0	11.20
			pH 4.0	10.85
			pH 7.0	1.01
			pH 9.0	0.34
Effect of O$_2$				
Propan-2-ol[b]	1.4	140	Deoxygenated	0.92
			Oxygenated	0.61
Butan-1-ol	0.2	20	pH 4.0, deoxygenated	0.38
			pH 4.0, aerated	0.16
Butan-2-ol[b]	1.4	140	Deoxygenated	2.73
			Oxygenated	1.45
1,2,3-propanetriol	0.7	35	Deoxygenated	3.83
			Oxygenated	2.87
Butan-2-ol	0.2	40	pH 4.0, oxygenated	0.99
			pH 4.0, deoxygenated	1.22
			pH 2.0, oxygenated	1.31
			pH 2.0, deoxygenated	1.35
Effect of added M^{n+}				
Butan-2-ol	0.2	40	pH 4.0, 0.2 mM MnSO$_4$, oxygenated	0.79
			pH 4.0, 0.2 mM MnSO$_4$, deoxygenated	1.10
			pH 2.0, 0.2 mM MnSO$_4$, oxygenated	0.82
			pH 2.0, 0.2 mM MnSO$_4$, deoxygenated	1.00
Butan-2-ol[a]	0.7	35	0.014 mM Fe$_2$(SO$_4$)$_3$ added	5.20
			Without any added M^{n+}	5.20

[a] Full light of mercury lamp.

[b] $\lambda_{irr} = 365$ nm.

latter influence can be interpreted in terms of the oxygen contribution to oxidation of an aldehyde [43].

The origin of the medium effects observed in continuous photolysis was elucidated by means of the flash photolysis technique.

2.2. Flash photolysis

The chromium(VI) aqueous solutions were exposed to laser pulses of 355 or 266 nm, i.e. radiation from its first or second CT-band. No spectral variations were recorded until any alcohol was added to the solution and pH was lower than

6. When these preconditions are satisfied, the time-resolved UV-Vis. spectra show the most interesting behaviour in two separated time intervals: within 60 ns–4 µs and within 1–45 ms. Qualitatively, the spectra recorded within nano- and milli-second resolution time are independent of the irradiation wavelength (355 or 266 nm). In both cases the laser pulse causes a significant decrease in the Cr(VI) concentration and, at pH $\geq$ 3, increase in the short-wave absorption with $\lambda_{max} \leq 230$ nm (Fig. 2). Within the next 4 µs upon pulse a decrease in absorption within the 420–240 nm range is continued, and at pH $\geq$ 3 it is accompanied by a faster decay of the short-wave absorption with $\lambda_{max} \leq 230$ nm
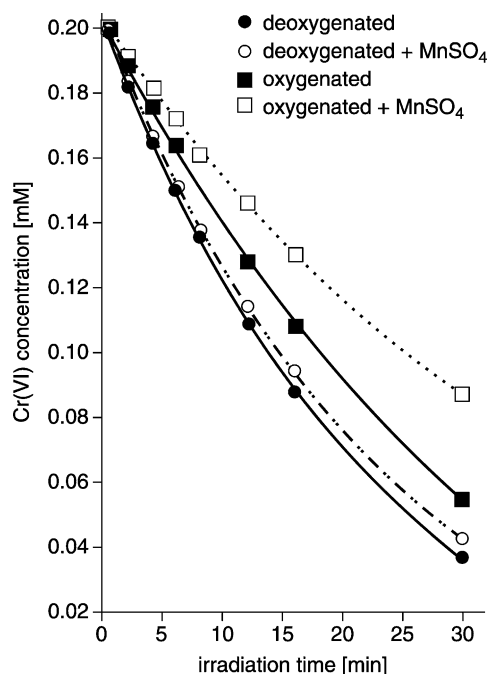
Fig. 1. Effect of pH, oxygen and Mn(II) on the Cr(VI) photoreduction rate during continuous irradiation ($\lambda \geq 300$ nm) of 1 mM $HCrO_4^-$ and 0.2 M butan-2-ol at pH 2.

Fig. 2. Transient absorption recorded 60 ns upon exposure to a 355 nm laser pulse of 1 mM $HCrO_4^-$ deoxygenated solution containing 200 mM butan-2-ol at pH 2, 3 and 4.

2.3. Reaction mechanism

The mechanism derived from both flash and continuous photolysis experiments presumes that the effective photoreduction of chromate(VI) proceeds upon excitation within its both CT-bands provided that the anion is in direct contact with an alcohol or other electron donor (Eq. (8)).

$$(HCrO_4^-)_{alc} + h\nu \rightarrow {}^*\{(HCrO_4^-)_{alc}\} \tag{8}$$

When the prerequisite is satisfied, the photoinduced electron transfer (PET) could be effective enough to initiate the redox process. If the contact between chromate(VI) and an electron donor is efficient in formation of a chemical bond,

(Fig. 3a and b). Within the 1–45 ms interval the opposite effect is observed: the absorption in the whole studied range, except that within 290–330 nm and at $\lambda < 250$ nm, increases and the spectral changes are characterized by three isosbestic points at about 330, 290 and 250 nm (Fig. 4). The spectral changes recorded within the nano- and microsecond time scales are sensitive to the presence of molecular oxygen (Fig. 5).
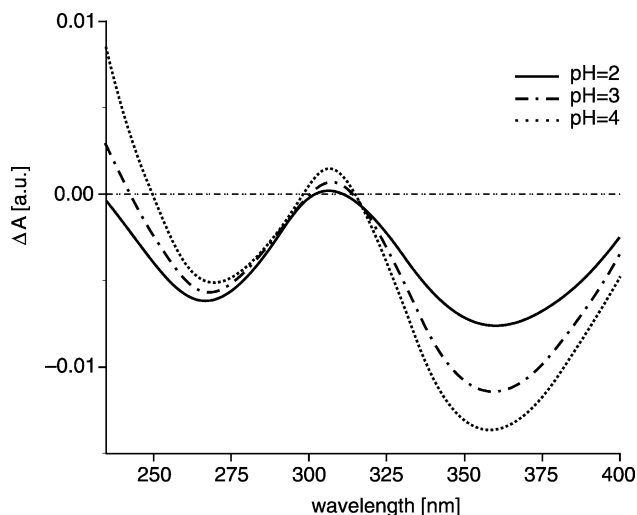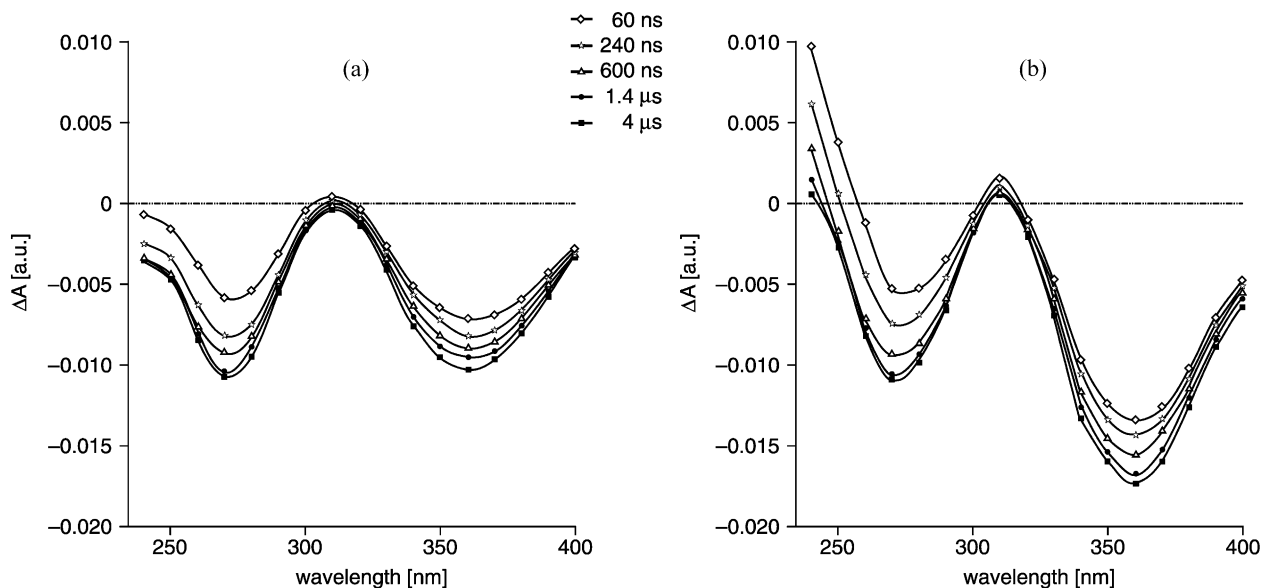

Fig. 3. Time-resolved spectra recorded within 60 ns to 4 µs interval upon flashing by a 355 nm pulse of 1 mM $HCrO_4^-$ deoxygenated solution containing 200 mM of butan-2-ol at pH 2 (a) and pH 4 (b).

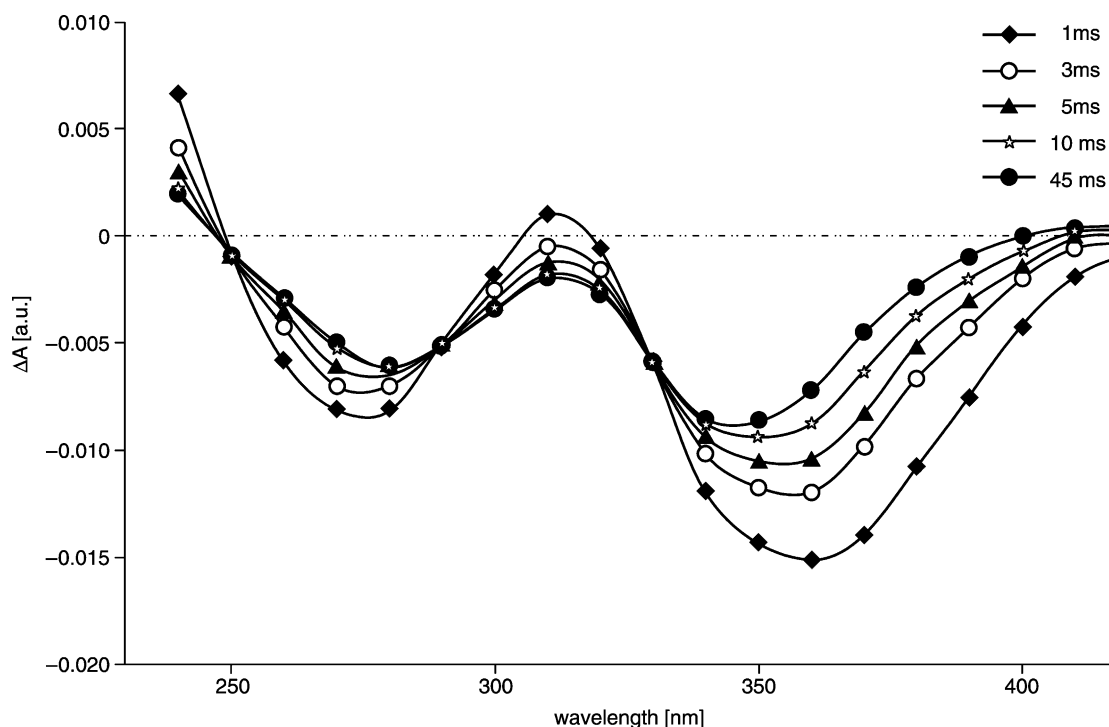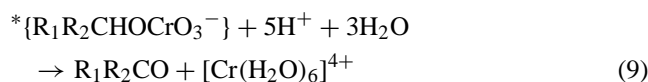Fig. 4. Time-resolved spectra recorded within 1 to 45 ms interval upon flashing by a 365 nm pulse of 1 mM $HCrO_4^-$ deoxygenated solution containing 200 mM of butan-2-ol at pH 4.

as in an ester, the innersphere electron transfer can comprise two-electrons, likewise in thermal reaction (Eq. (9)); when the interaction is weaker—the outersphere one-electron transfer is observed (Eq. (10)). For the secondary alcohols the PETs would thus proceed as follows:

$$^*\{R_1R_2CHOCrO_3^-\} + 5H^+ + 3H_2O$$
$$\rightarrow R_1R_2CO + [Cr(H_2O)_6]^{4+} \tag{9}$$

$$^*\{(HCrO_4^-)_{alc}\} + R_1R_2CHOH$$
$$\rightarrow H_2Cr^VO_4^- + R_1R_2CHO^\bullet \tag{10}$$

The choice of one of the two modes depends on pH, as the higher H^+ concentration favours not only esterification but also reduction to Cr(IV) (Eq. (6)), which is accompanied by reconstruction of the coordination sphere [44]. This is illustrated in Fig. 2, where the pH dependence of transient absorption recorded 60 ns upon pulse is shown: The short-wavelength increase in absorption ($\lambda_{max} \leq 230$ nm), recorded at pH ≥ 3 cannot be assigned to neither form of the reduced chromate, as all of them existing in deaerated aqueous medium are weaker absorbers than chromate(VI) [41,44]. The only exception is $H_2Cr^VO_4^-$, for which the

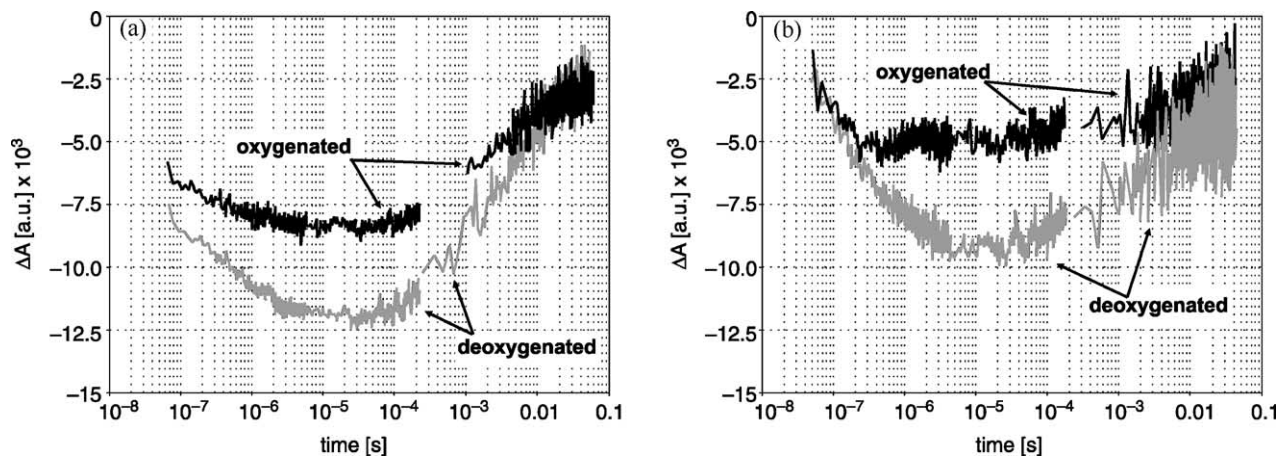
Fig. 5. Kinetic traces following a 355 nm laser pulse of 1 mM $HCrO_4^-$ and 200 mM butan-2-ol at pH 2 recorded within nano- and milli-second interval at 360 nm (a) and 260 nm (b).

absorption between 290 and 330 nm and at $\lambda < 250$ nm is only somewhat higher than that of $HCrO_4^-$ [44]. Moreover, the decay of absorption with $\lambda_{max} \leq 230$ nm is faster than that characteristic of chromate(VI). Thus, the significant short-wave absorption (with $\lambda_{max} \leq 230$ nm) can be assigned only to the $R_1R_2CHO^\bullet$ radical, especially as its appearance, according to the Eq. (10), is accompanied by a minute increase in absorption due to $H_2Cr^VO_4^-$ (noticeable at ~310 nm). The photoreduction of Cr(VI) to Cr(V) in one-electron transfer was found earlier for polyvinylalcohol solutions at similar pH range (4–5) [10]. Generation of Cr(V) in the chromate(VI)—alcohol—acid systems in thermal or photochemical reactions was documented by its EPR spectrum by many authors [5,16,45] but this spectroscopy is useless for the mechanistic considerations, unless the EPR detection is coupled with the flash photolysis.

The production of the $R_1R_2CHO^\bullet$ radicals is no longer observed at pH ≤ 2, although the decrease in $HCrO_4^-$ concentration upon the 355 nm pulse is comparable to those recorded at higher pH values (Fig. 2). Thus, the two-electron transfer (Eq. (9)) should be mostly responsible for the redox process at pH ≤ 2. The spectral evidence for generation of the Cr(IV) transient species is doubtful due to its weak absorption between 420 and 250 nm [41]. The argument of its formation is supported by the inhibiting effect of the Cr(IV)-trapping by Mn(II), which becomes more substantial at pH 2 (cf. Table 1). The two-electron transfer was reported earlier as the only pathway of chromate(VI) thermal reduction [2,3,6–8] and of its photoreduction by propan-2-ol and some other aliphatic alcohols in acidic medium [5].

The time-resolved spectra recorded within 60 ns and 4 μs (Fig. 3) show the secondary thermal decay of chromate(VI), which at pH 2 (Fig. 3a) can be interpreted simply by the comproportionation:

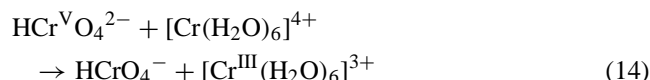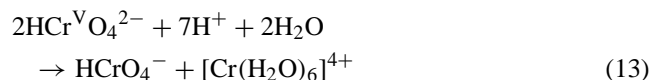$$[Cr(H_2O)_6]^{4+} + HCrO_4^- \rightarrow 2H_2Cr^VO_4^- + 5H^+ + 2H_2O \tag{11}$$
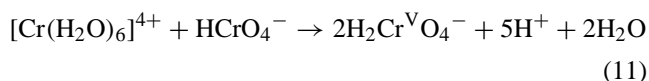
whereas at pH 3 and 4 the reaction is accompanied by the $R_1R_2CHO^\bullet$ radical decay, presumably in the reaction (Fig. 3b):

$$R_1R_2CHO^\bullet + HCrO_4^- \rightarrow R_1R_2CO + H_2Cr^VO_4^- \tag{12}$$

In accordance with the previous arguments the rate of the thermal Cr(VI) decay at pH 2 ($k_{obs} \approx 1 \times 10^7\,s^{-1}$) is somewhat higher than that at pH 4 ($k_{obs} \approx 3 \times 10^6\,s^{-1}$). The latter is accompanied by somewhat faster decay of the $R_1R_2CHO^\bullet$ radicals is ($k_{obs} \approx 1 \times 10^7\,s^{-1}$), presumably because of a concurrent recombination of the $R_1R_2CHO^\bullet$ radicals.

Next process recorded within 1–45 ms time scale consists in partial regeneration of the $HCrO_4^-$ ions from the Cr(V) transient species. At first sight it looks as should be very complex as the protonated Cr(V) form depends on pH: the main species are $H_3Cr^VO_4$, $HCr^VO_4^{2-}$ and a mixture of $H_2Cr^VO_4^-$ and $HCr^VO_4^{2-}$ at pH 2, 3 and 4, respectively.

Additionally, the Cr(V) species were reported to exist in fast equilibrium of their tetrahedral and octahedral forms [41,44]. Fortunately, the absorption spectra are not strongly sensitive to the Cr(V) form within pH 2–4 and thereby the recorded changes in absorption seem to illustrate simple transformation of a Cr(V) into Cr(VI) species qualitatively independent of pH within this range (Fig. 4). Kinetics of these changes, in accordance with the earlier reports on the Cr(V) disproportionation [41,44], points at two consecutive reactions:

$$2HCr^VO_4^{2-} + 7H^+ + 2H_2O$$
$$\rightarrow HCrO_4^- + [Cr(H_2O)_6]^{4+} \tag{13}$$

$$HCr^VO_4^{2-} + [Cr(H_2O)_6]^{4+}$$
$$\rightarrow HCrO_4^- + [Cr^{III}(H_2O)_6]^{3+} \tag{14}$$

The additional support of the photoinduced two-electron transfer comes from analysis of the O_2 effect. Investigation of time dependence of transient absorption at 360 and 260 nm (Fig. 5) shows that, in the presence of O_2 the initial decrease in absorption (due to Cr(VI) → Cr(V) reduction in reactions (11) and (12)) is arrested (Fig. 5a) or even followed by a small increase which reaches a maximum within microseconds (Fig. 5b). Then, within the μs/ms interval, the absorption is approximately constant and then increases again in consequence of the partial reproduction of chromate(VI) at the expense of Cr(V) (Eqs. (13) and (14)). This behaviour is mostly consistent with Cr(VI) regeneration by molecular oxygen (cf. Eq. (7)) but the transient absorption at $\lambda < 290$ nm must originate from a new species produced only in the presence of oxygen. Such features are characteristic of Cr^{2+} (aq) which was reported to be formed in the Cr(VI)—alcohol—acid systems in result of Cr(IV) thermal reduction [39,46,47]:
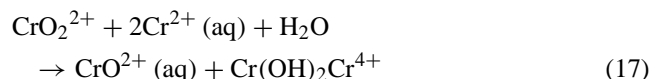
$$[Cr(H_2O)_6]^{4+} + R_1R_2CHOH \rightarrow Cr(II)\,(aq) + R_1R_2CO \tag{15}$$
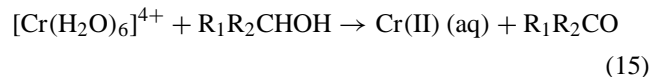
In the presence of molecular oxygen in excess, a transient peroxo-compound of Cr(III), CrO_2^{2+}, is generated:

$$Cr^{2+}\,(aq) + O_2 \rightarrow CrO_2^{2+} \tag{16}$$
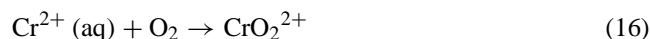
which is known to absorb strongly in the near UV, with maxima at 290 and 245 nm [46,47].

The species decays fast, mostly in reaction [46]:

$$CrO_2^{2+} + 2Cr^{2+}\,(aq) + H_2O$$
$$\rightarrow CrO^{2+}\,(aq) + Cr(OH)_2Cr^{4+} \tag{17}$$

The growing and decay of the transient absorption due to peroxochromium(III) intermediate observed in the presence of O_2 verifies the hypothesis of photoinduced two-electron transfer pathway in the Cr(VI)-alcohol systems.

3. Conclusions

Considering these results, one had to conclude that the environmental Cr(VI) to Cr(III) photoconversion proceeds via PET between the excited Cr(VI) ion and an alcohol or another electron donor. Depending on the mutual interaction between the two species, controlled by the medium acidity, the photoreaction may proceed by one or two-electron transfer. This phenomenon enables to abate the Cr(VI)-pollution within relatively wide environmental pH range.

The results certify the environmental relevance of photoreduction of hexavalent chromium, which can be accomplished in sunlit surface waters containing alcohols or other electron donors. This is an important task, as Cr(VI) is considered as priority pollutant and is rather resistant to chemical reduction and even to bioremediation [48].

Moreover, photoreduction of the Cr(VI) species is accompanied by oxidation of the electron donor, what creates a possibility of photodegradation by this way of many organic pollutants. The additional advantage is coming from sensitivity of the Cr(VI) photoreduction to the surface catalytic effects [20,49–51,53] or to the presence of an additional electron donors and/or acceptors: then a synergistic effect is observed in two- or multi-component systems [50–55].

4. Experimental

4.1. Chemicals

All reagents of highest available purity were used as purchased. Solutions of all reagents were freshly prepared for each experiment using demineralized and triply distilled water to prevent potential catalytic effect of iron and/or other metal ion [20,21]. The reagent concentrations used in experiments were 0.2–2 mM, in buffered solutions (pH 2–6), containing 0.04 M H_3PO_4, 0.04 M H_3BO_3, 0.04 M CH_3COOH, and NaOH. All chromium solutions were stored in the dark to avoid light-induced reactions. Oxygen-free and oxygenated solutions were made by 30 min saturation of samples with argon and oxygen, respectively. All measurements were performed at 293 ± 0.1 K, although rates of the Cr(VI) photoreduction were found unaffected by temperature changes within 183–303 K.

4.2. Instrumentation

UV-Vis. spectra were recorded in thermostated (1 cm) or tandem (0.874 cm) quartz cells using a Shimadzu UVPC 2100 or a Hewlett-Packard HP 8463 spectrophotometer. Continuous irradiations were carried out using a high-pressure mercury HBO-200 lamp equipped with cut-off glass filters transmitting $\lambda < 320$ nm or $\lambda < 300$ nm. pH values were measured using a CX-741 (Elmetron) pH-meter with a glass electrode. Pulse photolysis within nano- to milli-second was performed using a LKS 60 Spectrometer (Applied Photophysics) equipped with Nd:YAG laser pump source Surlite I-10 (Continuum), operating in third or four harmonic (355 or 266 nm, max 100 mJ pulses, 6 ns FWHM). Absorbance changes were monitored using a 150 W Xenon arc lamp supplied with a pulse unit, and a photomultiplier tube 1P28. Data were recorded on a digital storage oscilloscope HP 54522A with 0.5 ns time resolution and transferred to a computer for subsequent handling.

References

[1] U.K. Kläning, Acta Chem. Scand. 11 (1957) 1313–1316;
U.K. Kläning, Acta Chem. Scand. 12 (1958) 576–577, 807–813.
[2] U.K. Kläning, M.C.R. Symons, Proc. Chem. Soc. (1959) 95–96.
[3] U.K. Kläning, M.C.R. Symons, J. Chem. Soc. (1960) 977–982.
[4] K.B. Wiberg, H. Schäfer, J. Am. Chem. Soc. 89 (1967) 455–457;
K.B. Wiberg, H. Schäfer, J. Am. Chem. Soc. 91 (1969) 927–932.
[5] U.K. Kläning, J. Chem. Soc. Faraday Trans. 1 73 (1977) 434–455.
[6] M. Mitewa, A. Malinovski, P.R. Bontchev, K. Kabassanov, Inorg. Chim. Acta 8 (1974) 17–27.
[7] P.R. Bontchev, M. Mitewa, K. Kabassanov, A. Malinovski, Inorg. Nucl. Chem. Lett. 11 (1975) 799–806.
[8] G. Manivannan, R. Changkakoti, R.A. Lessard, G. Mailhot, M. Bolte, J. Phys. Chem. 97 (1993) 7228–7233.
[9] H.A. Headlam, P.A. Lay, Inorg. Chem. 40 (2001) 78–86.
[10] C. Pizzocaro, C. Lafond, M. Bolte, J. Photochem. Photobiol. A 151 (2002) 221–228.
[11] A. Nemes, A. Bakac, J.H. Espenson, Inorg. Chem. 40 (2001) 2720–2724.
[12] G. Barr-David, M. Charara, R. Codd, R.P. Farrell, J.A. Irwin, P.A. Lay, R. Bramley, S. Brumby, J.-Y. Ji, G.R. Hanson, J. Chem. Soc. Faraday Trans. 91 (1995) 1207–1216.
[13] M. Cieślak-Golonka, Coord. Chem. Rev. 109 (1991) 223–249.
[14] K.E. Abu-Saba, D.L. Sedlak, A.R. Flegal, Marine Chem. 69 (2000) 33–41.
[15] R.J. Kieber, G.R. Helz, Environ. Sci. Technol. 26 (1992) 307–312.
[16] M. Mitewa, P.R. Bontchev, Coord. Chem. Rev. 61 (1985) 241–272.
[17] S.N. Mahapatro, M. Krumpolc, J. Roček, J. Am. Chem. Soc. 102 (1980) 3799–3806.
[18] J. Kotaś, Z. Stasicka, Environ. Pollut. 107 (2000) 263–283.
[19] S.E. Kaczynski, R.J. Kieber, Environ. Sci. Technol. 27 (1993) 1572–1576.
[20] B. Deng, A. Stone, Environ. Sci. Technol. 30 (1996) 2484–2494.
[21] J. Kieber, J.D. Willey, S.D. Zvalaren, Environ. Sci. Technol. 36 (2002) 5321–5327.
[22] J.F. Perez-Benito, C. Arias, J. Phys. Chem. 101 (1997) 4726–4733.
[23] M. Pettine, L. Campanella, F.J. Millero, Environ. Sci. Technol. 36 (2002) 901–907.
[24] J.H. Espenson, J. Am. Chem. Soc. 92 (1970) 1183–1880.
[25] S.J. Hug, H.U. Laubscher, Environ. Sci. Technol. 31 (1997) 160–170.
[26] M. Pettine, L. D'Ottone, L. Campanella, F.J. Millero, R. Passino, Geochim. Cosmochim. Acta 62 (1998) 1509–1519.
[27] H. Zhang, R.J. Bartlett, Environ. Sci. Technol. 33 (1999) 588–594.
[28] H. Zhang, Atmos. Environ. 34 (2000) 1633–1640.
[29] G. Colón, M.C. Hidalgo, J.A. Navío, Appl. Catal. A 231 (2002) 185–199.

[30] G. Colón, M.C. Hidalgo, J.A. Navío, Langmuir 17 (2001) 7174–7177.

[31] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Water Res. 33 (1999) 1173–1180.

[32] Y. Ku, I.-L. Jung, Water Res. 35 (1) (2001) 135–142.

[33] S.G. Botta, J.A. Navío, M.C. Hidalgo, G.M. Restrepo, M.I. Litter, J. Photochem. Photobiol. A 129 (1999) 89–99.

[34] S. Zheng, Z. Xu, Y. Wang, Z. Wei, B. Wang, J. Photochem. Photobiol. A 137 (2000) 185–189.

[35] P. Mytych, P. Cieśla, Z. Stasicka, Int. J. Photoenergy 3 (2001) 181–186.

[36] F. Hasan, J. Roček, J. Am. Chem. Soc. 98 (1976) 6574–6577.

[37] M. Rahman, J. Roček, J. Am. Chem. Soc. 93 (1971) 5455–5462.

[38] C. Arias, J.F. Perez-Benito, Collect. Czech. Chem. Commun. 57 (1992) 1821–1835.

[39] J.F. Perez-Benito, C. Arias, D. Lamrhari, J. Chem Soc. Chem. Commun. (1992) 472–474.

[40] J.F. Perez-Benito, C. Arias, R.M. Rodriguez, J. Phys. Chem. A 105 (2001) 1150–1157.

[41] G.V. Buxton, F. Djouder, D.A. Lynch, T.N. Malone, J. Chem. Soc. Faraday Trans. 93 (1997) 4265–4268.

[42] N. Bailey, M.C.R. Symons, J. Chem. Soc. (1957) 203–207.

[43] K.B. Wiberg, G. Szeimies, J. Chem. Soc. 96 (1974) 1889–1890.

[44] G.V. Buxton, F. Djouder, J. Chem. Soc. Faraday Trans. 92 (1996) 4173–4176.

[45] J. Chappell, B. Chiswell, A. Canning, Talanta 46 (1998) 23–38.

[46] S.L. Scott, A. Bakac, J.H. Espenson, J. Am. Chem. Soc. 114 (1992) 4205–4213.

[47] C. Palopoli, S. Signorella, L.F. Sala, New J. Chem. 21 (1997) 343–348.

[48] E.J. Yurkow, Environ. Pollut. 117 (2002) 1–3.

[49] C.R. Chenthamarakshan, K. Rajeshwar, Langmuir 16 (2000) 2715–2721.

[50] F. Hasan, J. Roček, J. Org. Chem. 38 (1973) 3812–3814.

[51] S. Ramesh, S.N. Mahapatro, J.H. Liu, J. Roček, J. Am. Chem. Soc. 103 (1981) 5172–5175.

[52] S. Goeringer, C.R. Chenthamarakshan, K. Rajeshwar, Electrochem. Commun. 3 (2001) 290–292.

[53] I.J. Buerge, S.J. Hug, Environ. Sci. Technol. 33 (1999) 4285–4291.

[54] T. Kendelewicz, P. Liu, C.S. Doyle, G.E. Brown, Surf. Sci. 469 (2000) 144–163.

[55] G. Schrank, H.J. José, R.F.P.M. Moreira, J. Photochem. Photobiol. A 147 (2002) 71–76.