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Observation of a New UV Absorption Band of some $(H_2O)_5Cr^{III}–CR_1R_2R_3$ Complexes in Aqueous Solutions

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Abstract

The spectra of a series of Cr(III)–alkyl complexes, $(H_2O)_5Cr^{III}–CR_1R_2R_3$, were reinvestigated. In addition to the reported three typical absorption bands a new strong band in the 210–260 nm region is detected for most of the complexes studied. The proposed assignments for the two LMCT transitions give a satisfactory explanation to the effect of the substituents R_i.

Introduction

A variety of complexes of the family $(H_2O)_5$-$Cr^{III}–CR_1R_2R_3$ which contain a metal–carbon σ-bond have been studied in the past. Their properties, especially kinetics of formation and decomposition and UV–Vis spectra were reported [1].

Whereas short lived species were mainly observed using the pulse radiolysis technique, long lived members could be studied using conventional chemical methods [1–3]. However due to the experimental techniques employed, only spectra for $\lambda \geqslant$ 250 nm were obtained. These consist of three typical absorption bands:

(1) A weak band at 510–560 nm attributed to a d–d transition [3].

(2) A stronger band at 380–410 nm attributed to a d–d transition mixed with some charge-transfer character [3].

(3) A strong band at 250–310 nm attributed to a LMCT transition [3].

The location of the maximum of the LMCT transition is strongly affected by the nature of the substituents R_i. The available results seem to suggest that both electron withdrawing and electron donating substituents cause a red shift, thus the results point out that the optical electronegativities of all $–CR_1R_2R_3$ groups are lower than that of $–CH_3$ [3–5].

The aim of the present study was to obtain additional spectroscopic data, concerning the LMCT transitions, in order to find a satisfactory explanation to the effect of substituents. Thus the spectra of several complexes of the above series, which are stable enough to study them using a diode array spectrophotometer, were reinvestigated. Spectral changes were followed as far to the UV as the transparency of the appropriate organic solute allows (190–230 nm). A new strong band in the region 210–260 nm could be detected for most of the complexes studied.

Experimental

Materials

All solutions were prepared from AR grade chemicals and from distilled water (further purified by passing through a milli Q Millipore setup, final resistivity >10 Mohm/cm). $Cr(H_2O)_6^{2+}$ solutions were prepared as described elsewhere [6]. He or Ar was used to deaerate the solutions.

Techniques

pH determinations were carried out by immersing the glass electrode into the syringe, while Ar or He was bubbled through the solutions. For solutions below pH 2.5 the pH was calculated from the amount of added $HClO_4$.

Preparations of the Alkyl–Chromium(III) Complexes Using the Modified Fenton Reagent

A deaerated solution containing $Cr(H_2O)_6^{2+}$ and the organic solute at the required pH (adjusted by addition of $HClO_4$) is mixed in a syringe with a deaerated solution containing H_2O_2. Upon mixing the following reactions occur [7]

$$Cr(H_2O)_6^{2+} + H_2O_2 \longrightarrow Cr_{aq}^{3+} + \cdot OH + OH^- \quad (1)$$

$$\cdot OH + HCR_1R_2R_3 \longrightarrow H_2O + \cdot CR_1R_2R_3 \quad (2)$$

$$Cr_{aq}^{2+} + \cdot CR_1R_2R_3 \longrightarrow (H_2O)_5Cr^{III}–CR_1R_2R_3^{2+} \quad (3)$$

Methyl radicals are obtained in the reaction of OH radicals with $(CH_3)_2SO$ [8]

$$\cdot OH + (CH_3)_2SO \longrightarrow (CH_3)_2SOOH \quad (4)$$

followed by

$$(CH_3)_2SOOH \longrightarrow CH_3SOOH + \cdot CH_3 \qquad (5)$$

Under the conditions of excess Cr^{2+} the alkylchromium(III) complexes of α radicals decompose via a heterolytic pathway [1–3]

$$(H_2O)_5Cr^{III}\text{–}CR_1R_2R_3^{2+} \longrightarrow Cr_{aq}^{3+} + HCR_1R_2R_3 \qquad (6)$$

where the observed rate constant depends in the following way on the H_3O^+ concentration:

$$k_{6\,obs} = k_{6,1} + k_{6,2}[H_3O^+]$$

In the ethanol, 2-propanol and diethylether systems about 10% of the radicals are formed by hydrogen abstraction from the carbon β to the substituent. Under our experimental conditions the fast β-elimination reaction of the reaction products of the β radicals [3, 9] could not be observed.

Spectrophotometric measurements were carried out with a HP 8452 A Diode Array Spectrophotometer. Successive spectra (190–820 nm, accumulation time 0.1 s/spectrum) were taken every 30 or 60 s, depending on the rate of decomposition of the Cr–alkyl complexes.

The spectra of the intermediates, $(H_2O)_5Cr^{III}\text{–}CR_1R_2R_3$ were obtained by substracting successive spectra. It was always checked that their characteristics did not change during the decomposition by taking several different time intervals.

The extinction coefficients of the maxima were calculated by normalizing the spectra at the maximum in the region 250–310 nm using the reported molar extinction coefficients [1–3]. Where needed a correction due to the absorbance of $Cr(H_2O)_6^{3+}$, which is formed in the decomposition reaction of $(H_2O)_5Cr^{III}\text{–}CR_1R_2R_3$, was introduced. The results are also in good agreement with those, obtained by assuming that the initial H_2O_2 concentration equals the amount of products formed and extrapolating the optical densities to the time of mixing.

Results and Discussion

He or argon saturated solutions containing $(0.4–1.2) \times 10^{-3}$ M $Cr(H_2O)_6^{2+}$, 0.1 or 1 M of the required organic solute at pH 1–3 were mixed with H_2O_2, $(0.5–2.3) \times 10^{-4}$ M, and the spectra of the mixtures were studied as a function of time.

The spectra of the short lived transients were recorded, the results are summed up in Table 1, a typical spectrum is plotted in Fig. 1. The resulting spectra of all the compounds studied are in good agreement with literature data for the spectral regions earlier reported [1–3]. (Due to its low extinction coefficient the weak absorption band around 500 nm was usually not observed under our experimental conditions.) The kinetics of decomposition of the short lived intermediates were followed at the observed absorption maxima, and were found to be in accord with literature data for their acid promoted heterolytic decomposition [1–3].

For $CR_1R_2R_3 = CH_2OH$, $CH(CH_3)OH$, $C(CH_3)_2OH$, $CH(CH_3)OC_2H_5$, $\underbrace{CHCH_2OC_2H_4O}$ an additional strong band in the 210–260 nm region is observed as the solutes allow measurements until 190–200

TABLE 1. Spectral Data of $(H_2O)_5Cr^{III}\text{–}CR_1R_2R_3$ Complexes

$CR_1R_2R_3$	Lower detection limit (nm)	k_{obs} (at pH 1) (s^{-1})	λ_{max} (ϵ) (nm (M^{-1} cm^{-1}))			
			λ^1	λ^2	λ^3	λ^4
$C(CH_3)_2$[a]			290 (2330)		400 (488)	
CH_3[b]	230		260 (2500)		392 (230)	530 (~20)
CH_2OH	190	1.0×10^{-4}	216 (5600)	280 (2400)	388 (430)	
$CH(CH_3)OH$	200	4.9×10^{-4}	224 (7500)	292 (2800)	390 (570)	
$C(CH_3)_2OH$	200	3.1×10^{-3}	232 (7600)	308 (2500)	394 (620)	
			(6800)[c]	(2200)	(550)	
$CH(CH_3)OC_2H_5$	190	?	222 (6200)	292 (2200)	388 (450)	
			(5900)[c]	(1850)	(320)	
CH_2COOH	225	2.1×10^{-5}	$\leqslant$220 (>2200)[c]	270 (1500)	392 (85)	
$\underbrace{CHCH_2OC_2H_4O}$[d]	200	1.2×10^{-2}	210 (7000)[c]	268 (4300)	392 (300)	
CH_2CN[e]			209 (6500)	262 (4400)	409 (102)	527 (40)

[a] Data taken from ref. 9. [b] $k(Cr_{aq}^{2+} + CH_3) = 2.4 \times 10^8$ M^{-1} s^{-1} was determined by the pulse radiolytic technique. [c] ϵ calculated by extrapolating to mixing time and taking $c \sim c(H_2O_2)$. [d] $k_{6,1} \leqslant 1 \times 10^{-4}$ s^{-1} was measured for the heterolysis of $(H_2O)_5Cr^{III}\text{–}\underbrace{CHOCH_2CH_2OC}H_2^{2+}$. [e] Data taken from ref. 10.

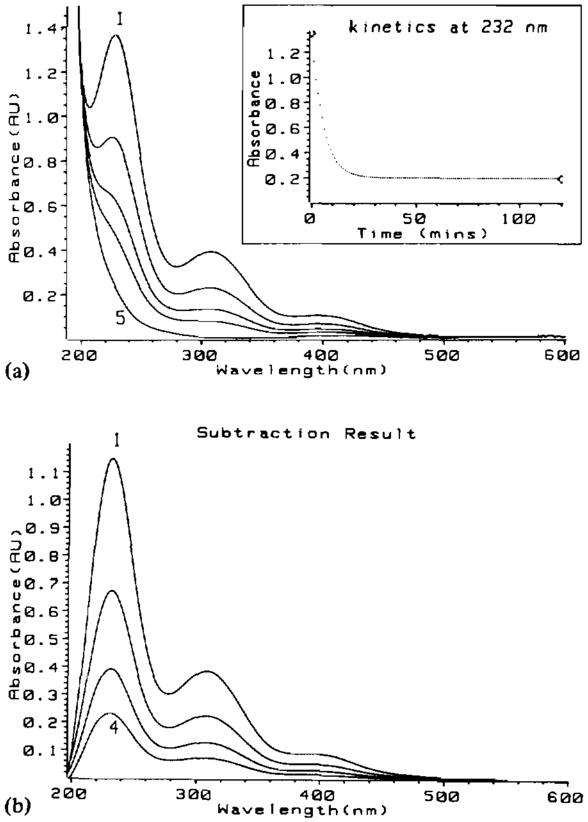

Fig. 1. (a) Spectral changes in the system Cr(II)/i-propanol (1–5: 1, 4, 7, 10, 120 min after mixing) and kinetics observed at 232 nm (insert) (starting concentrations [M]: Cr(II), 1×10^{-3}; H_2O_2, 2×10^{-4}; i-propanol, 1; H_3O^+, 0.1). (b) Substraction results of spectra in (a) minus final reaction spectrum (120 min).

nm. This band has to be attributed to the alkylchromium(III) complexes as the kinetics of its disappearance are identical to those of the known bands. The location of the maximum of this absorption band is affected by the nature of the substituents R_i in a similar fashion to that of the reported LMCT transition in the 250–310 nm region.

For acetic acid and $(CH_3)_2SO$ the lower detection limits are around 230 nm in 0.1 M solutions. No indication for a further band could be observed for $(H_2O)_5Cr^{III}–CH_3^{2+}$ whereas for $(H_2O)_5Cr^{III}–CH_2COOH^{2+}$ the rise of another band indicates a further maximum expected to be around 220 nm with an extinction coefficient ≥ 2200 M^{-1} cm^{-1}.

Thus the spectra of the $(H_2O)_5Cr^{III}–CR_1R_2R_3$ complexes are composed of 2–3 maxima in the region 190–450 nm. The dominant band in the far UV shows a maximum between 210–260 nm with absorption coefficients 2500–7000 M^{-1} cm^{-1}. The second band appears in the region 260–310 nm ($\epsilon \sim 1500–3300$ M^{-1} cm^{-1}). The maximum of the third, much weaker band, is hardly affected by the nature of the organic σ-donor ($\lambda_{max} = 385–410$ nm, $\epsilon = 50–560$ M^{-1} cm^{-1}) in accord with its assignment to a d–d transition mixed with some charge-transfer character. The calculated extinction coefficients for the latter absorption band are for most complexes studied somewhat smaller than those reported in the literature. We have no explanation for the origin of this discrepancy.

It is suggested that the second absorption band, the band in the region 260–310 nm, originates from a transition from a non-bonding electron pair on a substituent R_i, or from a π bond in R_i, to the central chromium cation. The new absorption band, which was observed in the present study, is then assigned to the $\sigma–t_{2g}$ LMCT transition. The absorption bands of the complexes with $CR_1R_2R_3 = CH_3$, C_2H_5, $C(CH_3)_2$ are assigned to the latter transition as they have no non-bonding electron pairs on the substituents. These assignments explain well the effect of substituents on the location of the maxima of the absorption bands. Electron withdrawing substituents cause a blue shift of the two absorption bands whereas electron donating substituents cause a red shift of them.

It is of interest to note that the difference in energy between these two transitions is 10 500 ± 300 cm^{-1} for all the complexes studied, which all have an :OR α-substituent. If the above suggested assignment is correct this means that the energy of the σ orbital is linearly correlated to that of the non-bonding electron pairs on the substituents. Kupferschmidt and Jordan [10] reported an electronic spectrum consisting of four absorption bands for $(H_2O)_5Cr–CH_2CN^{2+}$. The difference between the high energy transitions (209, 262 nm) is ~9700 cm^{-1}. Compared to our results this indicates a dependence of ΔE on the nature of the lone pair or π donor.

The alternative explanations seem less reasonable. Thus one could suggest that the two bands observed are due to a $\sigma–t_{2g}$ and a $\sigma–e_g$ transition. However the energy difference between these two transitions, 10 500 cm^{-1}, is considerably smaller than that corresponding to the lowest d–d transition which is *ca.* 20 000 cm^{-1}. Alternatively one could argue that the two bands observed are due to two $\sigma–t_{2g}$ transitions, from two different σ orbitals. In the latter case one has to assume that the energy of both these orbitals is affected in an identical way by the substituents R_i, an assumption which seems unreasonable.

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