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Manifestations of the peripheral group effects in photooxidation of 5-hydroxy-4H-pyran-4-ones coordinated to the iron(III) central atom

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Abstract

Anions of heterocyclic 5-hydroxy-4H-pyran-4-ones coordinate to the iron(III) central atom forming tris(*O,O*-chelate)iron(III) complexes. The complexes are redox stable in the dark, their irradiation leads to the photoreduction of Fe(III) to Fe(II) associated with oxidation of a ligand to its radical. The efficiency of the photoredox process is strongly wavelength dependent and influenced by the peripheral 2-CH_2R and 6-CH_3 groups of the ligands. The results on electrochemical properties of the free anions and the complexes are given also. Relations between the electronic properties of the peripheral groups R, redox potential values and quantum yields of the photoreduction are reviewed. © 1997 Elsevier Science S.A.

Keywords: Ferric complexes; Photoredox; Pyranones; Peripheral group effects; Electrochemistry

1. Introduction

The term "peripheral group effect" denotes an influence of the electronic properties of the atom or polyatomic moieties bonded on the periphery of ligands on the chemical processes of complexes involving their central atom [1]. The electronic properties of the peripheral groups are usually characterized by relevant (Hammett or Taft) substituent constants [2]. Observed trends in chemical behaviour can be attributed as being a consequence of the variation in the peripheral group properties only for homologous families of compounds having similar size and ligand skeleton, the same chromophore and charge. 5-hydroxy-4H-pyran-4-ones and their complexes fulfill such requirements.

It would be worth mentioning that for some ground state properties, e.g. electrochemical properties of complexes [3,4] or central atom substitution reactions [5] the peripheral group effects or, more generally, the influence of ligands, have clearly been observed and quantified. In the field of photochemistry of coordination compounds it has been documented that the electronic properties of remote ligand groups can be correlated with the rate constants of excited state quenching or the threshold energy of photoredox processes [6]. As for the efficiency of photoredox reactions, three different relationships between the ligands (their peripheral groups) characteristics and quantum yield values have been found: (a) for Fe(III) complexes with *meso*-substituted porphyrins irradiated in ethanol, no observable influence of the peripheral *meso*-groups on overall quantum yields has been found [7]; (b) for outer-sphere transfer of an electron from excited $*[Ru(NN)_3]^{2+}$ (NN denotes derivatives of 2,2′-bipyridine or 1,10-phenanthroline with various peripheral groups) to Fe^{3+} cation and other electron acceptors, there is a linear dependence of the cage escape quantum yield on the driving force of the electron transfer [8]; (c) for Co(III) complexes [9] and for Fe(III) complexes with open-chain tetradentate ligands [6], no correlation between the overall quantum yields of the central atom photoreduction and any relevant parameters of the ligand properties or the characteristics of ligand groups have been observed. Knowledge of such correlations is of a great practical importance since it allows to tune and optimize the photoredox reactivity of complexes.

In this contribution, the results on the spectral, photoredox and electrochemical properties of the complexes $[Fe(R\text{-}P)_3]$, where R-P are anions of 5-hydroxy-4H-pyran-4-ones with eight different peripheral groups -CH_2R localized in 2- or 6-position, are presented. The structure of the ligands and their abbreviations are shown in Fig. 1.

2. Experimental details

The ligands H(R-P) were synthesized, purified and characterized by elemental analysis, NMR and IR spectra in

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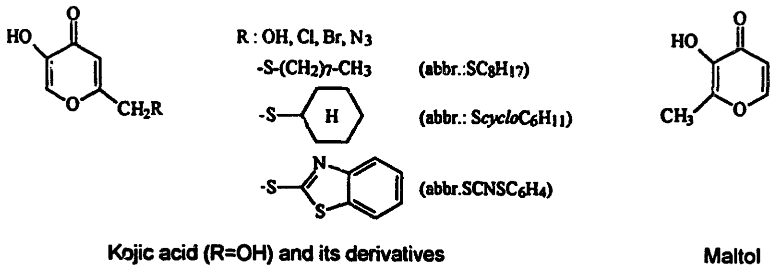

Fig. 1. Structure of the 5-hydroxy-4H-pyran-4-ones H(R-P).

our laboratory [10]. Methanol (Lachema, reagent grade) was distilled before use from $Mg(OCH_3)_2$. Potassium tris(oxalato)ferrate(III) (Oxford Organic Chemicals) and 1,10-phenanthroline (Aldrich) were of analytical grade and used without further purification. The other chemicals were of analytical grade (Lachema) and used as received.

The irradiated solutions were prepared in situ by dissolving solid $Fe(NO_3)_3.9H_2O$, ligand H(R-P) and $NaOCH_3$ in water-free methanol so as to obtain solutions with the initial concentrations $c(Fe^{III}) = 4.0 \times 10^{-4}$ M, $c(H(R\text{-}P)) = 3.2 \times 10^{-3}$ M, and $c(NaOCH_3) = 1.2 \times 10^{-3}$ M. Solutions for the measurement of potentials E_{ap} of anodic oxidation of R-P$^-$ to R-P$^\cdot$ were prepared in situ from 1.0×10^{-2} M H(R-P), 1.1×10^{-1} M $NaOCH_3$ and 1.0 M $NaClO_4$ in water-free methanol. Solutions for determination of electrode potentials $E_{1/2}([Fe(R\text{-}P)_3]^{0/-})$ were prepared by a similar manner, in addition they contain Fe^{3+} cations and the ratio of $c(H(R\text{-}P)):c(Fe^{III})$ was in the range of 10–14. Ferrocene (Fc) was used as an internal standard.

Steady state photolysis was performed in a three-chambered temperature-controlled (20 ± 2 °C) quartz photoreactor. As a radiation source, a medium pressure Hg lamp (Tesla RVK, 125 W, radiation monochromatized by solution filters [11]) and a low pressure Hg lamp (Germicidal Lamp G8T5) were used. The studied solutions were deoxygenated by bubbling with argon 30 min prior and during irradiation. The intensity of the incident radiation was determined by a ferrioxalate actinometer [11] to be of the order 10^{18} quanta $s^{-1} cm^{-2}$.

The course of photoredox changes was monitored as time evolution of $c(Fe^{II})$ by electronic absorption spectroscopy [12]. Formaldehyde was determined as 3,5-diacetyl-1,4-dihydrolutidine [13], pyranones were determined as $[Fe(R\text{-}P)(CH_3OH)_4]$ [14].

Electronic absorption spectra were scanned on a Specord M-40 spectrometer (Zeiss, Jena, Germany). Infrared spectra were measured by a FTIR spectrometer PU 9800 (Philips Analytical, Cambridge, UK). Electrochemical measurements were carried out under argon atmosphere with a PA3 polarographic analyser (Laboratory instruments, Prague, Czech Republik) using a three electrode (a Pt wire, a Pt foil, a SCE electrode) system. Cyclic voltammograms of the ligands and complexes were recorded with scan rates 20, 50, 100, and 200 mV s^{-1}.

3. Results and discussion

Electronic absorption spectra of all complexes $[Fe(R\text{-}P)_3]$ consist of three structured bands. The absorption of a photon in the visible region is associated with LMCT (O2p → Fe3d) transitions and depending on the peripheral group R, the corresponding split band exhibits a maximum at 405–435 nm and a shoulder at 460–495 nm. Two bands in the ultraviolet region are centered at 225–230 nm and 269–275 nm and in accordance with [15] they can be attributed to intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

Methanolic solutions of the prepared complexes are redox stable in the absence of visible or ultraviolet radiation. The presence of oxygen does not change the spectra or redox state of the central atom.

Irradiation of methanolic solutions of the complexes $[Fe(R\text{-}P)_3]$ leads to the photoreduction of Fe(III) to Fe(II). At 436 or 365 nm the incident light is absorbed by the complexes only. At 254 nm or 313 nm part of the photons is absorbed by noncoordinated H(R-P) and R-P$^-$ which, as was proved elsewhere [12], are photochemically inactive, the other portion of radiation is absorbed by the complexes. In these cases, the intensity of the radiation, absorbed by the complexes, I_C, was calculated from the total intensity of the absorbed radiation, I_T, according to relation (Eq. (1)):

$$I_C(\lambda) = I_T(\lambda) c_C \epsilon_C / (c_C \epsilon_C + c_L \epsilon_L) \qquad (1)$$

where c_C and c_L are the concentrations of the complex (4.0×10^{-4} M) and of noncoordinated ligand (2.0×10^{-3} M), respectively, ϵ_C and ϵ_L are the related molar absorption coefficients at a given wavelength λ. The values of ϵ_C and ϵ_L were calculated from the electronic absorption spectra of solutions in the absence (ϵ_L) and in the presence (ϵ_C) of Fe(III). The values of ϵ_C, ϵ_L and $I_C(\lambda)/I_T(\lambda)$ are listed in Table 1. The quantum yield values of Fe(II) formation, ϕ, based on experimental time evolutions of Fe(II) and the calculated values of $I_C(\lambda)/I_T(\lambda)$, are gathered in Table 2.

The final product of oxidation, formaldehyde, is related to the formed Fe(II) in a molar ratio of approximatively 1:2. Introduction of oxygen (air) into solutions after irradiation leads to a reappearing of the spectra of the parent Fe(III) complexes within a few min. The total contents of H(R-P) in solutions before and after their irradiation are identical.

Table 1
Molar absorption coefficients (in mol^{-1} dm^3 cm^{-1}) of the complexes [Fe(R P)$_3$] and their ligands, ϵ_C and ϵ_L, respectively, and values of $I_C(\lambda)/I_T(\lambda)$ at the wavelength of incident radiation λ

R/λ, nm	254			313			365 [a]	436 [a]
	ϵ_c	ϵ_L	I_c/I_T	ϵ_c	ϵ_L	I_c/I_T	ϵ_c	ϵ_c
OH	19 400	4700	0.48	2700	2100	0.22	3600	4000
Cl	19 500	4100	0.51	5400	2200	0.35	3700	4100
Br	26 300	3600	0.62	4700	2100	0.33	3950	4600
N_3	23 600	6800	0.44	8200	2300	0.44	3200	4200
$S_{cyclo}C_6H_{11}$	25 400	5800	0.57	9300	850	0.68	2000	3150
$SCNSC_6H_4$	34 300	9360	0.22	20000	2100	0.68	2060	3140
SC_8H_{17}	26 600	6200	0.37	9050	970	0.65	1870	3100
H (maltol)	19 900	2900	0.60	9300	2000	0.51	2900	3700

[a] The ligands do not absorb at these wavelengths.

Table 2
Quantum yield values of Fe(II) formation, ϕ, for the complexes [Fe(R-P)$_3$] irradiated in methanol, Hammett constants $\sigma(R)$ of the peripheral groups R, anodic potentials E_{pa} for oxidation of the ligands R-P$^-$, and half-wave potentials $E_{1/2}(Fe^{III/II})$ for the complexes [Fe(R-P)$_3$] (the potential values expressed versus the Fc$^+$/Fc couple)

R	$\sigma(R)$	E_{pa}	$E_{1/2}(Fe^{III/II})$	ϕ (254)	ϕ (313)	ϕ (365)	ϕ (436)
OH	−0.70	0.36	−0.70	0.16	0.10	0.029	0.018
Cl	−0.19	0.38	−0.66	0.17	0.14	0.061	0.038
Br	−0.22	[c]	[c]	0.13	0.11	0.043	0.026
N_3	−0.40	0.35	−0.69	[a]	[a]	0.27	0.16
$S_{cyclo}C_6H_{11}$	−0.25	0.35	−0.70	0.16	0.15	0.049	<0.0001
$SCNSC_6H_4$	[b]	0.37	−0.67	0.99	0.029	0.023	0.018
SC_8H_{17}	−0.23	0.40	−0.71	0.30	0.086	0.047	<0.0001
H (maltol)	0.00	0.37	−0.80	0.0030	0.0018	0.0016	0.0012

a = values non determined due to nonlinear time dependences of $c(Fe^{II})$.
b = unpublished value.
c = reliable values of the potentials undeterminable from experimental cyclic voltammograms.

Neither the investigated complexes nor the free ligands give luminescence using excitation wavelengths in the region of 220 nm–500 nm at room temperature.

The ability of the ligands themselves to undergo oxidation was characterized by their oxidation potentials, which are listed, along with Hammett constants [2] of the peripheral groups R, in Table 2. The influence of the peripheral groups R on the electrochemical properties, expressed in the form of electrode potential values $E_{1/2}([Fe(R\text{-}P)_3]^{0/-})$, is negligible, as follows of the data included in Table 2. A more negative value for the complex with maltol can be related to the presence of electron donating CH_3 group located in the vicinity of the central atom.

Anions of 5-hydroxy-4H-pyran-4-ones behave as bidentate ligands bonded to the central atom Fe(III) via the carbonyl and hydroxyl oxygen atoms [12]. Five-membered metallocyclic chelates are fairly stable, e.g. the stability constant $p\beta([Fe(OH\text{-}P)_3]) = -23.35$ in water [16]. At our experimental conditions, i.e. in the presence of strongly basic $NaOCH_3$ and at a given ratio of $c(R\text{-}P^-)$: $c(Fe^{III})$ the equilibrium between the kinetically labile complexes:

$$Fe^{3+}(solv) \overset{(R-P)^-}{\rightleftarrows} Fe(R-P)^{2+}(solv)$$
$$\overset{(R-P)^-}{\rightleftarrows} Fe(R-P)_2^+(solv) \overset{(R-P)^-}{\rightleftarrows} Fe(R-P)_3 \qquad (2)$$

is almost completely shifted to the neutral high-spin complexes [Fe(R-P)$_3$]. Photochemical and electrochemical properties of the investigated systems are, therefore, attributed to these complexes.

Excited sextet states of the complexes, populated by irradiation at 365 nm or 436 nm can be, in a simple but adequate mode, described as Fe(II) complexes with one coordinated radical (R-P$^·$) and two anionic R-P$^-$ ligands. Primary excitation at 313 nm or 254 nm apparently does not involve the central atom Fe(III); photons of the given wavelengths are absorbed both by free ligands and by the complexes, populating their intraligand sextet excited states. It is a generally accepted rule that the photoredox reactive state(s) should involve the central atom, i.e. to be of spin allowed short lived ^{6}LMCT or spin forbidden longer lived ^{4}LMCT nature. Such states can be populated either directly (using visible incident light) or from an energy richer intraligand sextet ^{6}IL both by the internal conversion (ic) leading to ^{6}LMCT and intersystem crossing (isc) yielding ^{4}LMCT. The wavelength dependence of ϕ can be understood as a consequence of two factors (which cannot be distinguishable for nonluminescent complexes in a simple way). The first one is the different ratio of the LMCT states which depends on the pathways of partial physical deactivation of the IL states. The second factor lies in the different content of vibrational energy in the photoreactive LMCT states which influences the efficiency of separation and/or recombination of the primary photoproducts.

Based on the present experimental results and a determination of the radicals OH-P$^\cdot$ in an aqueous solution and $^\cdot$CH$_2$OH in a methanolic solution of the complex [Fe(OH-P)$_3$] by spin trapping EPR method in our previous works [14,17], the following mechanism of the photochemical and photophysical processes occurring in irradiated solutions of the complexes [Fe(R-P)$_3$] can be suggested:

$$(GS^6)[Fe^{III}(R-P)_3] \xrightarrow{h\nu(VIS)} (LMCT^6)[Fe^{III}(R-P)_3] \quad (3)$$

$$(GS^6)[Fe^{III}(R-P)_3] \xrightarrow{h\nu(UV)} (IL^6)[Fe^{III}(R-P)_3] \quad (4)$$

$$(LMCT^6)[Fe^{III}(R-P)_3] \xrightarrow{isc} (LMCT^4)[Fe^{III}(R-P)_3] \quad (5)$$

$$(IL^6)[Fe^{III}(R-P)_3] \xrightarrow{isc} (LMCT^4)[Fe^{III}(R-P)_3] \quad (6)$$

$$(IL^6)[Fe^{III}(R-P)_3] \xrightarrow{ic} (LMCT^6)[Fe^{III}(R-P)_3] \quad (7)$$

$$(LMCT^6)[Fe^{III}(R-P)_3] \vee (LMCT^4)[Fe^{III}(R-P)_3] \rightarrow \text{nonredox and physical deactivations} \quad (8)$$

$$(LMCT^6)[Fe^{III}(R-P)_3] \vee (LMCT^4)[Fe^{III}(R-P)_3] \rightarrow [Fe^{II}(R-P)_2] + R-P^\cdot \quad (9)$$

$$[Fe^{II}(R-P)_2] + R-P^\cdot \rightarrow (GS^6)[Fe^{III}(R-P)_3] \quad (10)$$

$$R-P^\cdot + CH_3OH \rightarrow H(R-P) + {}^\cdot CH_2OH \quad (11)$$

$${}^\cdot CH_2OH + (GS^6)[Fe^{III}(R-P)_3] \rightarrow [Fe^{II}(R-P)_2] + H(R-P) + CH_2O \quad (12)$$

The electrochemical reversibility of the complexes (details on electrochemistry of the ligands and complexes will be published elsewhere [18]) suggests that anions R-P$^-$ remain coordinated to the Fe(II) central atom. It should be mentioned that the composition of highly labile Fe(II) complexes was not investigated in detail and is given in the above mode only for the sake of stoichiometry. The mechanism is consistent with all obtained experimenal data and the known reducing ability of the radical $^\cdot$CH$_2$OH for that $E_{1/2}(^\cdot CH_2OH/CH_2O) = -0.92$ V [19].

The results concerning the influence of the peripheral groups R on electrochemical and photochemical properties of the studied complexes can be evaluated as follows. The electronic properties of the groups R are reflected only very slightly in the anodic peak potentials E_{pa}. Due to the high rate of reaction (Eq. (11)) the electrode process is totally irreversible and no signal of an electrode reduction of the radicals R-P$^\cdot$ is observed even in the highest scan rates. Half-wave potentials $E_{1/2}$ are associated to reversible processes, they are more sensitive to the peripheral groups R, however, no correlation between the $E_{1/2}$ values and Hammett constants $\sigma(R)$ seems to exist.

Quantum yields of Fe(II) formation vary with the nature of the groups R. The highest quantum yield of Fe(II) formation is observed for the complex [Fe(N$_3$-P)$_3$], the lowest reactivity exhibits the complex containing maltol. This finding can be of practical importance as in applications it is often necessary to avoid using compounds, producing harmful radical products under the influence of light. Turning back to the three categories of complexes, based on correlation of their quantum yields with the properties of ligands or their peripheral substituents (see Section 1), the investigated complexes can be included into the category *c*. It means that at the current level of knowledge of their ligands, for Fe(III) complexes with 5-hydroxy-4H-pyran-4-ones there is, in general, no possibility to tune and optimize the efficiency of their photoredox decomposition.

References

[1] J. Šima, *Coord. Chem. Rev.*, in press.

[2] C. Hansch, A. Leo and R.W. Taft, *Chem. Rev.*, *91* (1991) 165.

[3] A.B.P. Lever, *Inorg. Chim. Acta*, *203* (1993) 171.

[4] J. Šima and J. Labuda, *Comments Inorg. Chem.*, *15* (1993) 93.

[5] J. Šima, P. Fodran, J. Hledík, A. Kotočová and D. Valigura, *Inorg. Chim. Acta*, *81* (1984) 143.

[6] J. Šima, *Comments Inorg. Chem.*, *13* (1992) 277.

[7] C. Bartocci, A. Maldotti, G. Varani, P. Battioni, V. Carassiti and D. Mansuy, *Inorg. Chem.*, *30* (1991) 1255.

[8] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, New York, 1992, p. 154.

[9] H. Hennig, D. Walter and P. Thomas, *Z. Chem.*, *23* (1983) 446.

[10] M. Veverka, *Chem. Papers*, *46* (1992) 206.

[11] S.L. Murov, *Handbook of Photochemistry*, M. Dekker, New York, 1973.

[12] J. Šima, B. Chochulová, M. Veverka, J. Makáňová, M. Hajšelová and A. Bradiaková, *Pol. J. Chem.*, *67* (1993) 1369.

[13] T. Nash, *Biochem. J.*, *55* (1953) 417.

[14] J. Šima, J. Makáňová and M. Veverka, *Monatsh. Chem.*, *126* (1995) 149.

[15] R. Petrola, *Finn. Chem. Lett.*, (1985) 207.

[16] W.A.E. McBryde and G.F. Atkinson, *Can. J. Chem.*, *39* (1961) 510.

[17] J. Šima, K. Havašová and T. Ducárová, *Z. Chem.*, *30* (1990) 446.

[18] A. Kotočová, J. Makáňová, J. Šima and M. Veverka, (submitted).

[19] J.F. Endicott, in A.W. Adamson and P.D. Fleischauer (eds.), *Concepts of Inorganic Photochemistry*, Wiley, New York, 1975.