

A Proposal for the Mechanism of the Photooxidation of Kinetically-Labile Transition Metal Complexes. Interpretation of Photoprocesses of FeSO_4 , $\text{Fe}(\text{ClO}_4)_2$ and FeCl_2 in Aqueous Acidic Solutions

LÁSZLÓ VINCZE, BÉLA KRAUT and SÁNDOR PAPP*

Department of General and Inorganic Chemistry, Veszprém University of Chemical Engineering, H-8201 Veszprém, Pf. 158 Hungary

Received July 18, 1983

A comprehensive mechanism is proposed for the photolysis of transition metal complexes in equilibrium solutions. This involves the photo-oxidation, a possibility of energy transfer and several secondary thermal reactions, e.g. forward and back reactions with photochemically-formed $\text{H}\cdot$ radicals. The scheme includes the individual quantum yield (IQY) of each species. The photo-oxidations of FeSO_4 , FeClO_4 , FeCl_2 in aqueous acidic solutions were studied by continuous irradiation. The IQY of $\text{Fe}_{\text{aq}}^{2+}$ (0.2), FeSO_4 (0.3), FeHSO_4^+ (0.67), FeClO_4^+ (0.06–0.2), FeCl^+ (0.8), FeCl_2 (0.3) were determined. The IQY was found to be dependent on H^+ concentration, due to competition with geminal recombination within the solvent cage. This dependence, and the efficiency of energy transfer between excited iron(III) species and iron(II) in ground state, are discussed.

Introduction

Until the end of the 70 s photochemical systems were generally supposed to contain only one photochemically active species, considered stable both thermodynamically and kinetically [1,2]. In the case of equilibrium systems in solution, the composition was chosen so that a single complex was dominant [3], or only one complex was supposed to be photoactive [4], or the overall changes were followed only, without any discussion of the individual process of each complex [5–8].

Beck [9] and Sykora [10] have proposed independently—mainly in solutions containing transition metal complexes—that several photoactive species should be taken into consideration, and that by combining the methods of photochemistry and equilibrium calculations these systems could be characterized more exactly. However, the actual systems can be more complicated than the men-

tioned ones, since i) some species absorb light without any photochemical change; ii) some absorbed energy can be transferred by these photochemically stable species to the photochemically active complexes; iii) photochemical processes are followed by thermal reactions.

Our aim was to extend the application of this method [9, 10, 12], and to propose a comprehensive mechanism of the photooxidation of transition metal complexes with low stability, since the mechanism was discussed in details only [5, 10, 12].

In the photochemical studies of acidic aqueous solutions of inorganic iron(II) compounds, the photochemistry of FeSO_4 [5, 7, 12] was thoroughly investigated, but about $\text{Fe}(\text{ClO}_4)_2$ fewer data are available [13]. In the photochemistry of FeCl_2 there are reported results in non-aqueous solvents only [14], but FeCl_3 was studied both in non-aqueous [3, 15] and aqueous [16] solutions, and also in the gas phase [17].

Experimental

Analytical Methods

$\text{Fe}(\text{ClO}_4)_2\text{--HClO}_4$ aqueous systems were made by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in aqueous perchloric acid of proper concentration, and the sulphate ions were precipitated by stoichiometric amounts of $\text{Ba}(\text{ClO}_4)_2$. The solution was centrifuged, then the traces of iron(III) were reduced by agitation with pure iron wire. The concentration of iron(III) formed photochemically was determined by a SPECORD-UV-VIS spectrophotometer. With $\text{pH} < 2$ the optical spectrum of iron(III) has an isobestic point at 272 nm ($\epsilon_{\text{Fe(III)}} = 1440 \text{ M}^{-1} \text{ cm}^{-1}$), i.e. the absorbance is independent of the pH [19]. When calculating the concentration of iron(III) the measured absorbance should be corrected, due to the absorbance of iron(II) ($\epsilon_{\text{Fe(II)}} = 1.8 \text{ M}^{-1} \text{ cm}^{-1}$).

In the $\text{FeCl}_2\text{--HCl}$ aqueous solution the concentration of iron(III) was also determined by spectro-

* Author to whom correspondence should be addressed.

metric analysis, since there is a joint band of iron(III) chloro complexes over 340–360 nm. The calibration curves were made so that at each experimental point the free concentration of chloride ions, and the ionic strength due to the given FeCl₂ and HCl content, were both computed; thus the spectrum of iron(III) ions was recorded in model solutions of NaClO₄–NaCl–HCl, having identical ionic strength, pH and free concentration of chloride ions. The composition matrix and stability constants of supposed complexes are collected in Table I; the mol-ratio distributions, the free concentrations of chloride ions and ionic strengths of iron(II) chloro complexes are given in Table II.

The iron content was controlled by complexometric titration, and the concentration of free chloride ions was determined with a chloride-selective electrode (Radelkis OP-Cl-7113-D).

Chemicals

HCl, HClO₄ were analytical grade (Carlo Erba); FeSO₄·7H₂O, FeCl₂·4H₂O, FeCl₃·9H₂O, NaCl, NaClO₄ were also analytical grade (Reanal). The iron wire was analytical grade (Riedel-de Haen AG). All chemicals were used without further purification. From the industrial argon the traces of oxygen were removed with a BASF R3-11 catalyst.

Photochemical Methods

The solutions were made under argon atmosphere, and the irradiation was also carried out in an argon-purged quartz cuvette of 0.5 cm optical path. The light source was a low-pressure mercury lamp of 17 W power (VOLTARC UV LUX TM OT5, Applied Photophysics), which produces more than 90 per cent of its power at 253.7 nm. The radiation at other wavelengths was cut by a CoSO₄–NiSO₄ filter solution [20]. The irradiation was continuous. Further details have been described elsewhere [12].

Procedure of Calculations

Calculation of experimental quantum yields

The proposed photophysical and photochemical processes for complexes ML_i (i = 0, 1, ... n) and ML_j (j = 0, 1, ... m) are shown in Fig. 1. The kinetic equation for the generation of the oxidized form (P product) is:

$$\begin{aligned} \frac{d[P]}{dt} = & \sum_{i=0}^n I_i \frac{k_{2,i}}{k_{1,i} + k_{2,i} + \sum_{j=0}^m k_{i,j}[ML_j]} \cdot \\ & \cdot \frac{k_{3,i}[H^+]}{k_{3,i}[H^+] + k_{r,i}} + [H\cdot][H^+] \sum_{i=0}^n k_{4,i}[ML_i] - \\ & - [H\cdot] \sum_{j=0}^m k_{5,j}[ML_j] + \\ & + \sum_{i=0}^n \frac{k_{2,i}}{k_{1,i} + k_{2,i} + \sum_{j=0}^m k_{i,j}[ML_j]} \cdot \frac{k_{3,i}[H^+]}{k_{3,i}[H^+] + k_{r,i}} \cdot \\ & \cdot \sum_{j=0}^m I_j \frac{k_{j,i}[ML_j]}{k_{6,j} + k_{7,j} \sum_{i=0}^n k_{j,i}[ML_i]} \end{aligned} \quad (1)$$

Substituting Φ_i , $\Phi_{j,i}$ and x into eqn. 1 we obtain;

$$\begin{aligned} C_M \frac{dx}{dt} = & \sum_{i=0}^n I_i \Phi_i + [H\cdot] C_M [[H^+](1-x)\sum k_{4,i}\alpha_i - \\ & - x\sum k_{5,j}\alpha_j] + \sum_{i=0}^n \Phi_i \sum_{j=0}^m I_j \Phi_{j,i} \end{aligned} \quad (2)$$

TABLE I. Composition Matrix of the Iron(II)–Iron(III) System in Hydrochloric Acid.

Complex	Components				lg β	Ionic strength
	Fe ²⁺	Fe ³⁺	Cl [−]	H ⁺		
Fe ²⁺ Cl [−]	1	0	1	0	0.36 [22]	2
Fe ²⁺ (Cl [−]) ₂	1	0	2	0	0.40 [23]	2
Fe ²⁺ OH [−]	1	0	0	−1	4.5 [24]	1
Fe ²⁺ (OH [−]) ₂	1	0	0	−2	16.5 [24]	1
Fe ³⁺ Cl [−]	0	1	1	0	1.48 [25]	0
Fe ³⁺ (Cl [−]) ₂	0	1	2	0	0.65 [25]	0
Fe ³⁺ (Cl [−]) ₃	0	1	3	0	−1.0 [25]	0
Fe ³⁺ (Cl [−]) ₄	0	1	4	0	−1.98 [26]	0
Fe ³⁺ OH [−]	0	1	0	−1	11.0 [27]	3
Fe ³⁺ (OH [−]) ₂	0	1	0	−2	21.7 [27]	3
(Fe ³⁺) ₂ (OH [−]) ₂	0	2	0	−2	25.1 [27]	3

TABLE II. Mol Ratios of Iron(II) Species and Ionic Strengths Calculated at Various Initial Concentrations of FeCl₂ and HCl.

Arrangement of data:	(Fe ²⁺) per cent	(Fe ²⁺ Cl ⁻) per cent	(Fe ³⁺ Cl ₂ ⁻) per cent	Free chloride, <i>M</i>	Ionic strength
[FeCl ₂] [HCl]	0.1			0.4	
	69.63			46.17	
		0.264		0.614	
0.06	24.73			35.87	
		0.33		0.80	
	5.50			17.98	
	51.04			34.85	
		0.537		0.831	
0.4	34.00			38.45	
		0.59		0.97	
	14.76			26.74	
	32.59			22.95	
		0.903		1.14	
0.8	38.63			38.44	
		0.94		1.23	
	29.02			38.52	
	25.31			18.32	
		1.09		1.30	
1	38.62			37.46	
		1.12		1.37	
	36.16			44.30	
				51.39	
				25.90	
				39.07	0.901
				30.45	1.15
				23.62	1.09
				38.75	1.28
				37.61	1.28
				16.19	1.36
				36.81	1.48
				46.93	1.48
				13.20	1.50
				35.35	1.60
				51.39	1.60
				25.90	1.69
				39.12	1.58
				35.04	1.27
				20.23	1.19
				38.24	1.39
				41.57	1.39
				14.09	1.44
				35.93	1.58
				50.00	1.58
				11.58	1.57
				34.41	1.57
				54.05	1.69

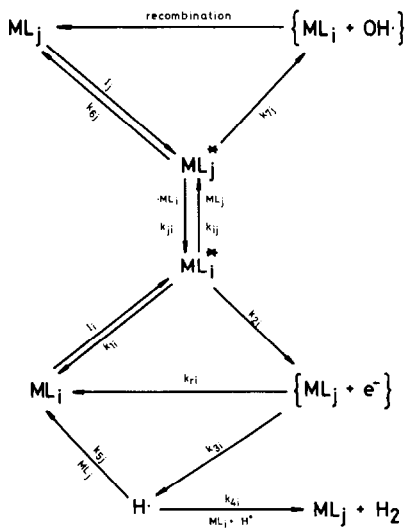


Fig. 1. Proposed reaction scheme for photoprocesses of kinetically labile transition metal complexes.

According to the steady-state treatment, [H•] can be expressed as:

$$[H^\bullet] = \frac{\sum I_i \Phi_i + \sum \Phi_i \sum I_j \Phi_{j,i}}{C_M [[H^+](1-x)\sum k_{4,i}\alpha_i + x\sum k_{5,j}\alpha_j]} \quad (3)$$

Substituting this expression into eqn. 2:

$$C_M \frac{dx}{dt} = \left[\sum_i I_i \Phi_i + \sum_i \Phi_i \sum_j I_j \Phi_{j,i} \right] \cdot \left[1 + \frac{[H^+](1-x)\sum k_{4,i}\alpha_i - x\sum k_{5,j}\alpha_j}{[H^+](1-x)\sum k_{4,i}\alpha_i + x\sum k_{5,j}\alpha_j} \right] \quad (4)$$

It is evident that the proper Φ_{exp} and Φ_t can be found for the following equations:

$$I_1 \Phi_{exp} = \sum_i I_i \Phi_i \quad (5)$$

$$\Phi_{exp} I_h \Phi_t = \sum_i \Phi_i \sum_j I_j \Phi_{j,i} \quad (6)$$

Φ_{exp} is the experimentally measured quantum yield of photooxidation. Φ_t reflects the average efficiency of sensitization of ML_i complexes by ML_j* complexes. When $\Phi_t = 0$, then sensitization cannot be detected.

Introducing the symbol

$$S = \frac{x \sum_{j=0}^m k_{5,j} \alpha_j}{[H^+](1-x) \sum_{i=0}^n k_{4,i} \alpha_i} \quad (7)$$

we obtain

$$C_M \frac{dx}{dt} = \underbrace{I_1 \Phi_{\text{exp}}}_A \left(1 + \underbrace{\frac{I_h}{I_1} \Phi_t}_B \right) \underbrace{\frac{2}{1+S}}_C \quad (8)$$

where the term A represents the photo-oxidation rate involving the inner filter effect [5, 12] of products, terms B and C are related to the energy transfer and thermal reactions of the $H\cdot$ radical respectively. Since in several cases $S \ll 1$, the term C can be merged with Φ_r , and $2\Phi_r$ can be considered as being the experimental quantum yield referring to product [12]. Solving the differential equation numerically, the $x(t, \Phi_{\text{exp}}, \Phi_t, C_M, S)$ function can be obtained. Treating Φ_{exp} and Φ_t as free parameters their best values can be obtained by the least-squares method.

Calculation of individual quantum yields

The principles of the method have already been reported [9, 10, 12], but the individual quantum yields have been assumed to be independent of the composition. However, according to eqn. 1, the dependence of individual quantum yields on $[H^+]$ can be expressed as:

$$\Phi_i = \frac{k_{2,i}}{k_{1,i} + k_{2,i} + \sum_{j=0}^m k_{i,j} [ML_j]} \cdot \frac{k_{3,i} [H^+]}{k_{3,i} [H^+] + k_{r,i}} \quad (9)$$

It is the consequence of the very fast scavenging of e_{aq}^- by H^+ ($k = 2-3 \times 10^{10} M^{-1} s^{-1}$ [18]), since the protons can compete with the geminal recombination [21] between ML_j and e_{aq}^- . Thus Φ_i can be defined by two parameters:

$$\Phi_i = a_i \frac{[H^+]}{[H^+] + b_i}, \quad (10)$$

and the objective function has $2n$ parameters in the case of n photoactive species:

$$Z = \sum_{k=1}^w \left(\Phi_{\text{exp},k} - \frac{\sum_{i=0}^n \epsilon_i \alpha_{i,k} a_i \frac{[H^+]}{[H^+] + b_i}}{\sum_{i=0}^n \epsilon_i \alpha_{i,k}} \right)^2 \quad (11)$$

Results and Discussion

Results on the photooxidation of iron(II) sulphate have been published elsewhere [12]. Data of one experimental point on aqueous acidic iron(II)-perchlorate system are collected in Table III; the quantum yields of all experimental points are shown in Table IV. In Table III it can be seen that the kinetic model fits better to the measurements when $\Phi_t > 0$, the differences being rather small however. The significance was checked with a random variation of measured absorbancies [11], the deviation of Φ_t remained within 20 per cent.

TABLE III. Measured and Calculated Data for the Photochemical Oxidation of Iron(II) Ions. $[Fe(II)]_0 = 0.1 M$, $[HClO_4] = 0.8 M$, $S = 0$.

t (s)	$10^4 [Fe(III)]$ measured	$10^4 [Fe(III)]$ calculated $\Phi_{\text{exp}} = 0.315$ $\Phi_t = 0$	$10^4 [Fe(III)]$ calculated $\Phi_{\text{exp}} = 0.303$ $\Phi_t = 0.08$
0	1.514	1.514	1.514
25	1.745	1.780	1.777
50	2.021	2.038	2.033
75	2.264	2.288	2.282
100	2.530	2.532	2.525
125	2.765	2.768	2.763
150	2.958	2.999	2.995
175	3.218	3.224	3.223
200	3.442	3.444	3.446
225	3.677	3.658	3.664
250	3.907	3.868	3.878

TABLE IV. Quantum Yields of Photo-oxidation and Energy Transfer.

$[Fe(ClO_4)_2]$ $[HClO_4]$	0.1	0.4	0.8	1
0.1	0.147 0	0.121 0.32	0.120 0	0.117 0
0.4	0.150 0.08	0.196 0	0.184 0	0.122 0.8
0.8	0.159 0.08	0.228 0	0.213 0	0.163 0
1	0.189 0	0.231 0	0.240 0	0.206 0

In Table IV it can be seen that the Φ_{exp} always increases with increasing acid concentration, but has a maximum as a function of iron(II) perchlorate concentration. The increase of Φ_{exp} can be interpreted by the individual quantum yields (by increasing the

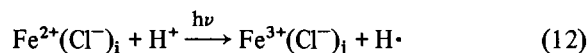
mol-ratio of species having high individual quantum yields) but the decrease of Φ_{exp} cannot be explained.

For computation of individual quantum yields two photoactive species were supposed to be the aquated iron(II) ion and the solvent separated $\text{Fe}^{2+}\text{ClO}_4^-$ ion pair (the concentration of iron hydroxides can be neglected at the acid concentration used). The composition matrix and the stability constants of the system are summarized in Table V. The mol-ratios of iron complexes are constant during the photooxidation [12], and they are collected in Table VI, where the ionic strengths are also given. The individual quantum yields depend on $[\text{H}^+]$, since the presence of protons diminishes the probability of geminal recombination in the solvent cage. The best fit parameters are shown in Table VIII, and the fit is demonstrated in Fig. 2.

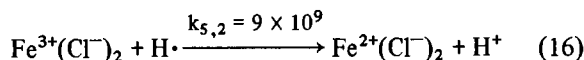
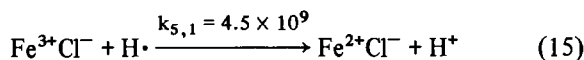
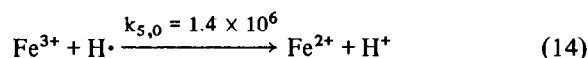
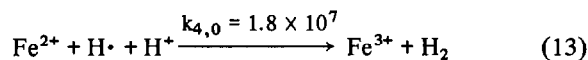
Since a value of zero was obtained for Φ_t in the three-fourths of the experiments, for Φ_t —in spite of Φ_{exp} —no tendency can be given and it is doubtful whether in iron(II)—perchlorate systems any energy transfer exists.

In the case of iron(II) chloride, the results of one experiment are shown in Fig. 3. It is obvious that the thermal reduction of iron(III) species has to be considered. According to our experiences the $\text{Fe}^{3+*} \rightarrow \text{Fe}^{2+}$ energy transfer is not a strong effect, so in this system it can be neglected in comparison with the other photochemical and thermal processes.

Beside the overall photochemical reaction



the following thermal reactions, having known rate constants, have been assumed [18]:



Rate constants are not available for the thermal reaction of iron(II) chloro complexes and the $\text{H}\cdot$ radical, thus these reactions were approximated by the rate constant of Fe^{2+} ion and $\text{H}\cdot$. The experimental quantum yields are collected in Table VII.

TABLE VI. Mol Ratios of Iron(II) Species and Ionic Strengths calculated at Various Initial Concentrations of $\text{Fe}(\text{ClO}_4)_2$ and HClO_4 . Arrangement of data: (Fe^{2+}) per cent; ($\text{Fe}^{2+}\text{ClO}_4^-$) per cent; ionic strength.

$\text{Fe}(\text{ClO}_4)_2$ HClO_4	0.1	0.4	0.8	1.0
0.1	99.1 0.88 0.40	97.0 2.39 1.28	90.2 9.71 2.34	84.8 15.2 2.80
0.4	98.3 1.68 0.70	95.6 4.52 1.56	97.1 12.9 2.58	81.0 19.0 3.00
0.8	97.0 3.05 1.09	92.8 7.21 1.92	82.2 17.8 2.88	75.4 24.6 3.26
1.0	96.1 3.93 1.28	91.1 8.89 2.10	79.5 20.5 3.02	72.5 27.5 3.37

For the computation of the individual quantum yields the existence of three photoactive iron(II) species was supposed. These are: aquated Fe^{2+} ion, $\text{Fe}^{2+}\text{Cl}^-$ and $\text{Fe}^{2+}(\text{Cl}^-)_2$ ion associations. The individual quantum yields also depend on $[\text{H}^+]$; an acceptable fit between experimental results and calcula-

TABLE V. Composition Matrix of the Iron(II)—Iron(III) System in Aqueous Perchloric Acid.

Complex	Components				lg β	Ionic strength
	Fe^{2+}	Fe^{3+}	ClO_4^-	H^+		
$\text{Fe}^{2+}\text{ClO}_4^-$	1	0	1	0	-0.9 [28]	0
$\text{Fe}^{2+}\text{OH}^-$	1	0	0	-1	4.5 [24]	1
$\text{Fe}^{2+}(\text{OH}^-)_2$	1	0	0	-2	16.5 [24]	1
$\text{Fe}^{3+}\text{ClO}_4^-$	0	1	1	0	-0.32 [29]	0
$\text{Fe}^{3+}\text{OH}^-$	0	1	0	-1	11.0 [27]	3
$\text{Fe}^{3+}(\text{OH}^-)_2$	0	1	0	-2	21.7 [27]	3
$(\text{Fe}^{3+})_2(\text{OH}^-)_2$	0	2	0	-2	25.1 [27]	3
H^+ClO_4^-	0	0	1	1	-1.54 [30]	0

TABLE VII. Experimental and Calculated Quantum Yields (Deviation of $\Phi_{\text{exp}} \pm 0.04$).

[FeCl ₂] (M)	[HCl] (M)	Φ_{exp}	Φ_{calcd}
0.120	0.060	0.36	0.37
0.420	0.060	0.42	0.42
0.821	0.058	0.41	0.43
1.036	0.028	0.42	0.40
0.083	0.323	0.64	0.44
0.400	0.330	0.47	0.46
0.790	0.340	0.54	0.46
0.990	0.340	0.43	0.45
0.087	0.810	0.69	0.46
0.389	0.808	0.43	0.46
0.820	0.745	0.40	0.45
1.000	0.785	0.44	0.44
0.108	1.16	0.52	0.46
0.389	1.18	0.45	0.45
0.820	1.18	0.44	0.44
1.000	1.18	0.47	0.43

TABLE VIII. Individual Quantum Yields, $\Phi_i = a_i \frac{[H^+]}{[H^+] + b_i}$.

Species	Acid	a_i	b_i	Φ_i
Fe ²⁺		0.16	7×10^{-3}	0.15–0.16
FeSO ₄	H ₂ SO ₄	0.30	5×10^{-4}	0.30
FeHSO ₄ ⁺		0.67	0.0	0.67
Fe ²⁺		0.21	6.3×10^{-2}	0.13–0.20
FeClO ₄ ⁺	HClO ₄	0.27	0.32	0.06–0.20
Fe ²⁺		0.24	6×10^{-3}	0.19–0.24
FeCl ⁺	HCl	0.80	2×10^{-4}	0.80
FeCl ₂		0.27	4×10^{-3}	0.24–0.27

tions was obtained, and values are shown in Table VIII. The relation between measured and calculated data is demonstrated in Fig. 4. The fit is not close, indicating that the individual quantum yields only give a correct model for the photochemical processes if the rates of thermal back reactions are smaller than those of the photochemical forward reactions.

The results obtained in Fe(ClO₄)₂–HClO₄ and FeCl₂–HCl aqueous systems suggested the re-investigation of the FeSO₄–H₂SO₄ system. From the results the dependence of individual quantum yields on [H⁺] has been proven negligible over the studied concentration range (Table VIII). There was an interesting but expected result, namely that $\Phi_{\text{FeHSO}_4^+}$ is not dependent on acid concentration since the electron released can form a H• radical within the solvent cage.

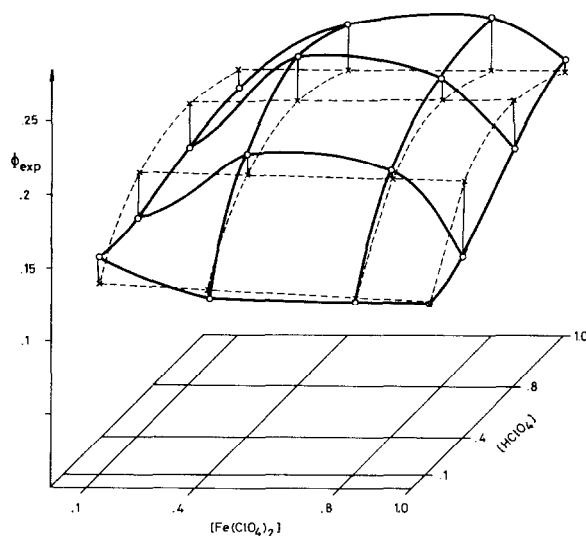


Fig. 2. Net quantum yields found and calculated for iron(II) species as a function of concentration.

In Table VIII it can be seen that the higher ion associates generally have higher individual quantum yields. This can be interpreted by the decrease of the effective positive charge of photochemically formed Fe³⁺L_j associates, thus the electron can escape easier from the solvent cage.

Conclusion

The experimental and calculation procedures used are suitable for the characterization of complex photochemical systems in equilibrium, including several photoactive species (and only thermally active ones) in the presence of the inner filter effect. The variation in ionic strength can also be taken into consideration.

The $\Phi_{\text{Fe}^{2+}}$ obtained was almost the same in the presence of different anions. This supports the assumption that the individual quantum yields have a real physical meaning.

Acknowledgments

We thank Dr. István Nagypál, Department of Inorganic and Analytical Chemistry, Kossuth Lajos University, and his colleagues for help in the adaption of the computer program to this work.

Appendix

Symbols

a factor of quantum yield, independent of [H⁺]

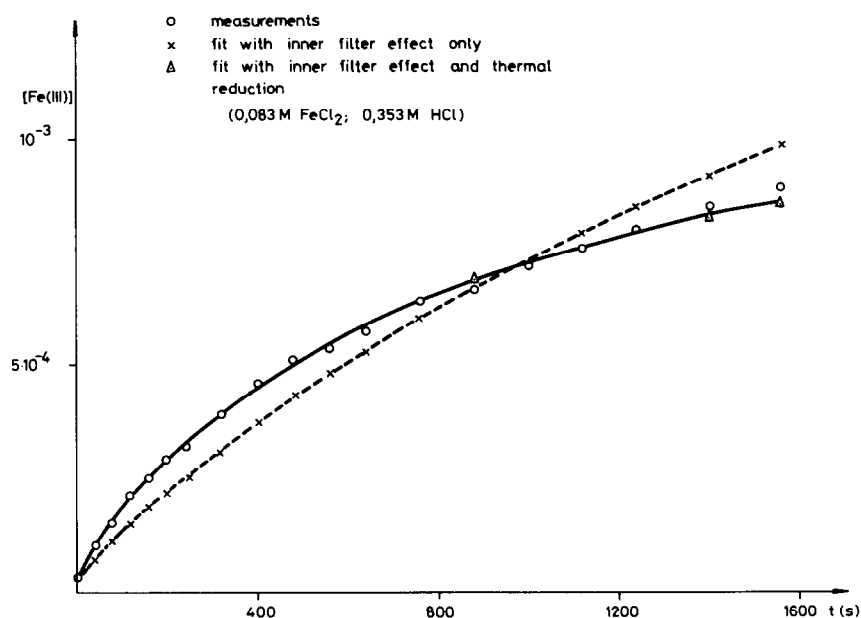


Fig. 3. Photo-oxidation of iron(II) chloride in aqueous hydrochloric acid solution.

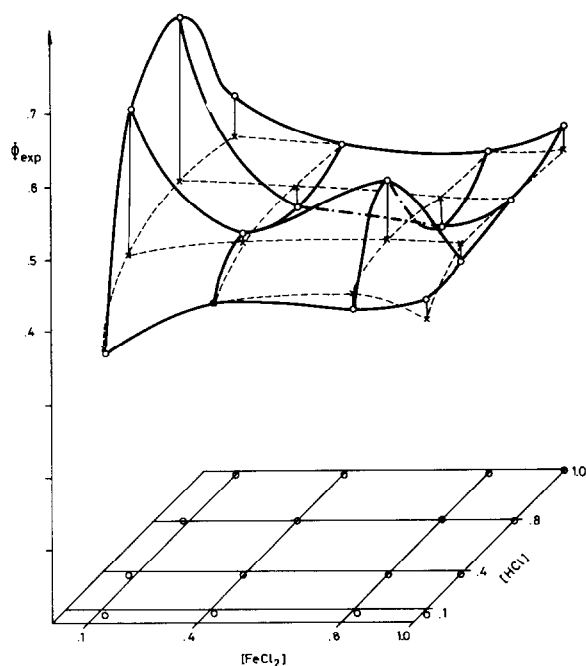


Fig. 4. Net quantum yields found and calculated for iron(II) species as a function of concentration.

- b factor of quantum yield in term dependent on $[H^+]$
- C_M total concentration of transition metal (mol dm^{-3})
- d optical path (cm)
- $[H^+]$ equilibrium proton concentration (mol dm^{-3})
- $H\cdot$ hydrogen radical

- I specific irradiation intensity ($\text{mol dm}^{-3} \text{s}^{-1}$)
- k rate constant
- $[P]$ concentration of product P (transition metal species in higher oxidation state) (mol dm^{-3})
- S ratio between rate of thermal reduction and oxidation of transition metal species due to $H\cdot$ radicals
- t time (s)
- x conversion of transition metal into the oxidized form
- α mol-ratio
- ϵ molar absorptancy ($\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$)
- Φ quantum yield
- *

Subscripts

- a absorbed
- i of species in lower oxidation state
- j of species in higher oxidation state
- ij according to energy transfer from ML_i to ML_j
- l overall quantity, according to lower oxidation state
- h overall quantity, according to higher oxidation state
- o incident light intensity
- exp experimental quantum yield
- t quantum yield referring to energy transfer

Calculation of some terms

$$\alpha_i = \frac{[ML_i]}{C_M(1-x)}$$

$$\alpha_j = \frac{[ML_j]}{C_M x}$$

$$I_a = I_o(1 - 10^{-C_M d((1-x)\sum \epsilon_i \alpha_i + x\sum \epsilon_j \alpha_j)})$$

$$I_l = I_a \frac{(1-x)\sum \epsilon_i \alpha_i}{(1-x)\sum \epsilon_i \alpha_i + x\sum \epsilon_j \alpha_j}$$

$$I_h = I_a \frac{x\sum \epsilon_j \alpha_j}{(1-x)\sum \epsilon_i \alpha_i + x\sum \epsilon_j \alpha_j}$$

$$I_i = I_l \frac{\epsilon_i \alpha_i}{\sum \epsilon_i \alpha_i}$$

$$I_j = I_h \frac{\epsilon_j \alpha_j}{\sum \epsilon_j \alpha_j}$$

References

- 1 J. F. Endicott, *Surv. Progr. Chem.*, **7**, 41 (1976).
- 2 A. W. Adamson and P. D. Fleischauer, 'Concepts of Inorganic Photochemistry', Wiley, New York, (1975).
- 3 J. Sima, E. Horvath and J. Gazo, *Anorg. Allg. Chem.*, **451**, 151 (1979).
- 4 C. H. Langford and J. H. Carey, *Can. J. Chem.*, **53**, 2430 (1975).
- 5 G. Stein and J. Jortner, *J. Phys. Chem.*, **66**, 1258 (1962).
- 6 E. Hayon and J. J. Weiss, *J. Chem. Soc.*, 3866 (1960).
- 7 L. J. Heidt *et al.*, *J. Phys. Chem.*, **66**, 336 (1962).
- 8 S. Papp and L. Vincze, *Inorg. Chim. Acta*, **44**, L241 (1980).
- 9 V. Gáspár and M. T. Beck, *Polyhedron*, **2**, 387 (1983).
- 10 J. Sykora, J. Sima and D. Valigura, *Chem. Zvesti.*, **35**, 345 (1981).
- 11 L. Vincze, B. Kraut and S. Papp, *Proc. ICCO.*, 119 (1982).
- 12 L. Vincze, B. Kraut and S. Papp, *Acta Chim. Hung.*, **112**, 183 (1983).
- 13 G. A. Korsunov and Y. S. Lebedev, *Russ. J. Phys. Khim.*, **42**, 915 (1968).
- 14 J. Sima and J. Gazo, *Proc. ICCO.*, 239 (1978).
- 15 D. Rehorek, *Z. Chem.*, **19**, 262 (1979).
- 16 F. David, *J. Phys. Chem.*, **80**, 579 (1976).
- 17 D. S. Rustad and N. W. Gregory, *Inorg. Nucl. Chem. Letters*, **16**, 521 (1980).
- 18 M. Anbar and P. Neta, *Int. J. Appl. Rad. Isotopes*, **18**, 493 (1976).
- 19 K. V. Buxton, *J. Chem. Soc.*, 4957 (1962).
- 20 C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, **63**, 22 (1959).
- 21 R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).
- 22 H. Olerup, *Diss. Lund.*, 1944, p. 78.
- 23 B. O. A. Hedström, *Arkiv. Kemi*, **5**, 457 (1953).
- 24 C. F. Wells and M. A. Salam, *J. Chem. Soc. (A)*, 308 (1968).
- 25 R. A. Robinson and J. M. Wilson, *J. Am. Chem. Soc.*, **64**, 1469 (1942).
- 26 G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).
- 27 B. O. A. Hedström, *Arkiv. Kemi*, **6**, 1 (1954).
- 28 J. Beuenkamp and K. D. Herrington, *J. Am. Chem. Soc.*, **82**, 3022 (1960).
- 29 J. Sutton, *Nature*, **169**, 71 (1952).
- 30 K. H. Dücker, *Dissertation*, Technische Hochschule, Aachen, 1964.