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INDIVIDUAL QUANTUM YIELDS OF $Fe^{3+}(HCO_2^-)_n$ COMPLEXES ($n = 1 - 4$) IN AQUEOUS ACIDIC SOLUTIONS

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Summary

The following molar absorbancies and individual quantum yields (IQYs) of iron(III)–formate complexes were determined at a wavelength of 254 nm: $\epsilon(Fe^{3+}HCO_2^-) = 4080 \pm 320$ M^{-1} cm^{-1}; $\epsilon\{Fe^{3+}(HCO_2^-)_2\} = 3440 \pm 170$ M^{-1} cm^{-1}; $\epsilon\{Fe^{3+}(HCO_2)_3\} = (2 \times 10^3) \pm 10^3$ M^{-1} cm^{-1}; $\epsilon\{Fe^{3+}(HCO_2^-)_4\} = 5040 \pm 130$ M^{-1} cm^{-1}; $\Phi(Fe^{3+}HCO_2^-) = 0.9 \pm 0.1$; $\Phi\{Fe^{3+}(HCO_2^-)_2\} = 0.31 \pm 0.06$; $\Phi\{Fe^{3+}(HCO_2^-)_3\} = 0.15 \pm 0.1$; $\Phi\{Fe^{3+}(HCO_2^-)_4\} = 0.38 \pm 0.02$. A detailed computation procedure for the determination of the IQYs of kinetically labile complexes is discussed.

1. Introduction

A number of researchers have studied the photolysis [1 - 7] and radiolysis [8 - 14] of formic acid and formate anions in the presence of different transition metal ions, but investigations of individual quantum yields (IQYs) of metal–formate ion associates have not been included in these studies. Baxendale and Bridge [1] stated that in aqueous solutions of iron(III) formate it is the $Fe^{3+}HCO_2^-$ ion pair which is photosensitive, but they did not perform a photochemical study of higher complexes. Carey and Langford [2] chose a low pH, and thus the majority of formate anions were protonated and the Fe^{3+} ions could not be complexed. Our aim was to determine the IQYs of the iron(III)–formate complexes. Even though the IQYs must be determined by complicated computational processing of the measurements, the reliability of the IQY data can be ascertained from a comparison of measured and computed values. The IQYs of iron [15 - 17], copper [18, 19] and cobalt [20] complexes were determined by this method.

2. Experimental details

The irradiations were carried out by a low pressure mercury vapour lamp (Voltarc UV LUX TM OT5, Applied Photophysics) which gave more

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than 90% of its power at 254 nm. The radiation at other wavelengths was removed by a $CoSO_4$–$NiSO_4$ filter solution. The samples were contained in a quartz cuvette of optical path 0.5 cm and were bubbled with argon for 30 min before irradiation.

The $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$, HCO_2Na (Reanal) and H_2SO_4 (Carlo–Erba) were analytical grade and the argon was a commercial product. The traces of oxygen in the argon were removed by a BASF-R3-11 catalyst and other chemicals were used without further purification. All solutions were made up with doubly distilled water.

The Fe^{2+} ions formed in the photoreduction were estimated using *o*-phenanthroline [21]. UV–visible spectra were recorded using a Specord UV–visible spectrophotometer (Carl Zeiss Jena).

The following concentration ranges were employed. In each solution the initial concentrations of iron(III) and H_2SO_4 were 10^{-3} M and 5×10^{-3} M respectively. The concentrations of formic acid and sodium formate were varied between 0.02 - 1.0 M and 0.02 - 0.40 M respectively. To determine the molar absorbancies of HCO_2H and HCO_2^- the spectra of 0.1, 1 and 2.5 M formic acid solutions were recorded, in the presence of 0.025, 0.05 and 0.2 M sodium formate.

2.1. *Computation procedure*

The procedure consists of the computation of the following four quantities: (1) the concentration (*i.e.* mole ratio) distribution; (2) the molar absorbancies at the irradiation wavelength; (3) the experimental quantum yields; (4) the individual quantum yields.

The concentration distribution was computed by the program described in ref. 16, taking into account the dependence of the stability constants on the ionic strength. The stability constants were obtained via statistical analysis on all the available data regarding the complexes discussed in the present paper. The method of data processing has been described previously [22]. The composition matrix and the stability constants are given in Table 1. For the computation of the molar absorbancies of the ion associates the UV spectra of the solutions (with computed concentration distributions) were recorded; then, for the objective function given by the equation

$$U(\epsilon) = \sum_{i=1}^{m} \left(A_{i,\,\mathrm{md}} - d \sum_{j=1}^{n} \epsilon_j C_{i,j} \right)^2 \qquad (1)$$

the ϵ vector was determined which gave the minimum value of U. For the meaning of the symbols see Appendix A.

The iteration was carried out by the Newton–Raphson method. In the determination of the experimental quantum yields the reaction mechanism should be taken into account. The proposed mechanism is shown in Fig. 1. This is a partly extended part of an already published, more detailed mechanism [17]. In the present paper only the excitation of iron(III)

TABLE 1

Composition matrix of the iron(III)–formate system in sulphuric acid and the stability constants at zero ionic strength

Complex	*Components*				lg β_t
	Fe^{3+}	*HCO_2^-*	*SO_4^{2-}*	*H^+*	
$Fe^{3+}HCO_2^-$	1	1	0	0	2.60 ± 0.14
$Fe^{3+}(HCO_2^-)_2$	1	2	0	0	5.10 ± 0.12
$Fe^{3+}(HCO_2^-)_3$	1	3	0	0	5.78 ± 0.6
$Fe^{3+}(HCO_2^-)_4$	1	4	0	0	7.23 ± 0.6
$HCO_2^-H^+$	0	1	0	1	3.84 ± 0.09
$Fe^{3+}SO_4^{2-}$	1	0	1	0	4.05 ± 0.12
$Fe^{3+}(SO_4^{2-})_2$	1	0	2	0	5.57 ± 0.64
$Fe^{3+}SO_4^{2-}H^+$	1	0	1	1	2.83 ± 0.87
$Fe^{3+}(SO_4^{2-})_2H^+$	1	0	2	1	6.55 ± 0.6
$H^+SO_4^{2-}$	0	0	1	1	1.96 ± 0.10
$Fe^{3+}OH^-$	1	0	0	−1	−2.79 ± 0.13
$Fe^{3+}(OH^-)_2$	1	0	0	−2	−6.13 ± 0.32
$Fe_2^{3+}(OH^-)_2$	2	0	0	−2	−2.83 ± 0.27

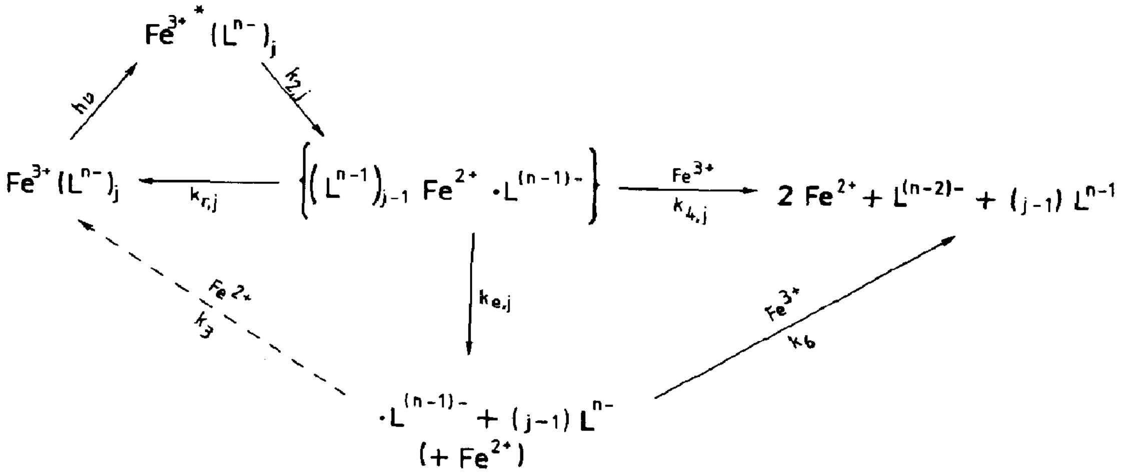

Fig. 1. Proposed reaction scheme for photoprocesses of the iron(III)–formate complexes.

species is considered. Because of the low absorbancies the excitation of iron(II) can be neglected.

As in the case of formate and oxalate anions, the L$^\bullet$ radical is a reducing agent, and the degree of conversion is not large (k_6[Fe(III)] ≫ k_3[Fe(II)]), so the reaction with the broken arrow in Fig. 1 can be neglected. Thus the IQY of iron(II) formed photochemically from $Fe^{3+}(L^{n-})_j$ is given by

$$\Phi_j = \frac{k_{2j}}{k_{1j} + k_{2j}}\ \frac{k_{ej} + k_{4j}[\mathrm{Fe(III)}]}{k_{rj} + k_{ej} + k_{4j}[\mathrm{Fe(III)}]} \qquad (2)$$

To each Fe^{2+} ion formed photochemically there belongs an Fe^{2+} ion formed thermally by the reducing radical. Consequently the kinetic equation is as follows:

$$\frac{d[Fe(II)]}{dt} = 2 \sum_{j=0}^{n} P_j \Phi_j \tag{3}$$

P_j can be expressed by P_{abs}, ϵ and α (see Appendix B), so the rate of iron(II) formation can be written as

$$\frac{d[Fe(II)]}{dt} = 2P_{abs} \frac{\sum_{j=0}^{n} \epsilon_j \alpha_j \Phi_j}{\sum_{j=0}^{n} \epsilon_j \alpha_j}$$

$$= 2P_{abs}\Phi_{exp} \tag{4}$$

where the term Φ_{exp} is the quantum yield which can be determined experimentally. Φ_{exp} depends on the molar absorbancies, the mole-ratio distribution and the IQYs; however, it is constant, since during the photoreduction the mole-ratio distribution of iron(III) species does not change significantly. Differential equation (4) was solved numerically by the fourth-order Runge–Kutta method, and the optimal Φ_{exp} was obtained for each system by fitting the calculated curve to the measurements. The IQYs can be computed by optimizing the objective function [17]

$$U(\Phi) = \sum_{i=1}^{m} \left(\Phi_{exp,i} - \frac{\sum_{j=0}^{n} \epsilon_j \alpha_{i,j} \Phi_j}{\sum_{j=0}^{n} \epsilon_j \alpha_{i,j}} \right)^2 \tag{5}$$

Φ_{exp}, ϵ and α are known from the previous steps, but the Φ_j ($j = 0 - n$) should be fitted.

3. Results and discussion

The calculated concentration distributions, the measured and calculated absorbancies and the molar absorbancies computed for the formic acid–formate ion system are given in Table 2. The molar absorbancies are in accordance with the results of Szyper and Zuman [23].

The mole-ratio distribution *vs.* $p_{HCO_2^-}$ for the case of the iron(III) species is shown in Fig. 2. The absorbancies and the free formate concentrations of solutions prepared for the computation of the molar absorbancies are collected in Table 3. The iteration was performed with the average molar absorbancies for the $Fe^{3+}(SO_4)_pH_q$ ($p = 0 - 2$; $q = 0, 1$) species. The

TABLE 2

Solutions made up for the computation of the molar absorbancies of HCO_2H and HCO_2^- at 254 nm

	Analytical concentration (M)		$[HCO_2^-]$ (M)	$[HCO_2H]$ (M)	*A/d*	
	HCO₂H	*HCO₂Na*			*Measured*	*Computed*
1	2.50	0.025	0.0355	2.484	0.187	0.181
2	2.50	0.05	0.0541	2.491	0.173	0.184
3	2.50	0.20	0.2109	2.493	0.183	0.183
4	1.00	0.025	0.0289	0.9948	0.073	0.073
5	1.00	0.05	0.0530	0.9955	0.077	0.073
6	1.00	0.20	0.2046	0.9970	0.080	0.074
7	0.10	0.025	0.0255	0.0994	0.015	0.0074
8	0.10	0.05	0.0508	0.0994	0.015	0.0075
9	0.10	0.20	0.2006	0.0997	0.027	0.0082

$\epsilon_{HCO_2} = 4.6 \times 10^{-3}\ M^{-1}\ cm^{-1}$; $\epsilon_{HCO_2H} = 7.3 \times 10^{-2}\ M^{-1}\ cm^{-1}$.

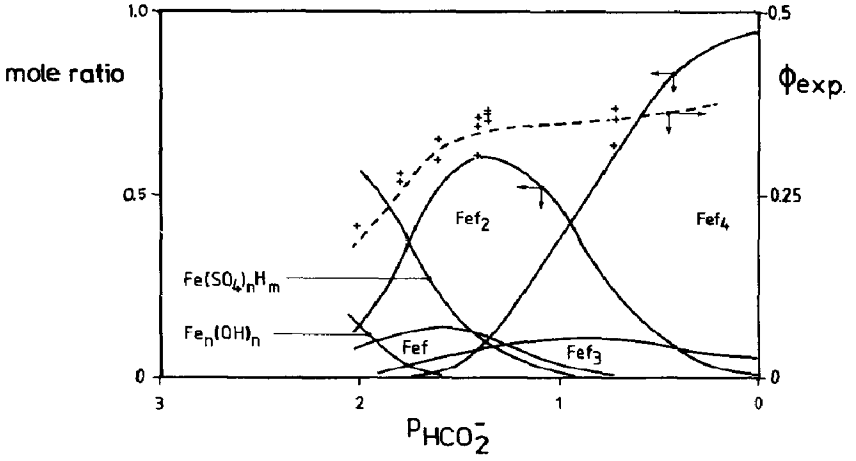

Fig. 2. Mole ratios and quantum yields (found and computed) for iron(III)–formate complexes in aqueous acidic solutions ($[Fe(III)] = 10^{-3}$ M; $[H_2SO_4] = 5 \times 10^{-3}$ M; +, measured quantum yields; — — —, computed curve according to IQYs).

computed molar absorbancies of iron(III) ion associates are given in Table 4. The reason for the deviations is the fact that the stability constants themselves are also probability variables. The experimental quantum yields for each solution are collected in Table 5 and the IQYs are given in Table 4. The experimental quantum yields and the curve derived from the summarized products of the IQYs and the mole ratios are also compared in Fig. 2. The fit is reasonable. It can be stated that the experimental quantum yield of the aqueous acidic iron(III)–formate system varies with the composition. The experimental results can be rationalized in terms of the IQY

TABLE 3

Solutions for the determination of the molar absorbancies of the iron(III)–formate species at 254 nm (C_{Fe} = 0.001 M and $C_{H_2SO_4}$ = 0.005 M in each solution)

	Analytical concentration (M)		$[HCO_2^-]$	*A/d*
	HCO_2H	*HCO_2Na*		
1	2.50	0.025	0.0312	3.28
2	2.50	0.05	0.0475	3.53
3	2.50	0.20	0.1952	4.27
4	1.00	0.025	0.0243	3.63
5	1.00	0.05	0.0434	3.81
6	1.00	0.20	0.1901	4.59
7	0.10	0.025	0.0157	3.19
8	0.10	0.05	0.0393	3.48
9	0.10	0.20	0.1871	4.18

TABLE 4

Molar absorbancies and individual quantum yields of the iron(III)–formate–sulphate system at 254 nm

Complex	$10^{-3}\epsilon$ (M^{-1} cm^{-1})	*Quantum yield*
$Fe^{3+}HCO_2^-$	4.08 ± 0.32	0.9 ± 0.1
$Fe^{3+}(HCO_2^-)_2$	3.44 ± 0.17	0.31 ± 0.06
$Fe^{3+}(HCO_2^-)_3$	2.0 ± 1.0	0.15 ± 0.10
$Fe^{3+}(HCO_2^-)_4$	5.04 ± 0.13	0.38 ± 0.02
$Fe^{3+}(SO_4^{2-})_nH_m^+$	3.04 ± 0.01	0.0
$Fe_n{}^{3+}(OH^-)_n$	0.80 ± 0.10[a]	(2 - 5) × 10^{-2}[b]

[a] See refs. 24 and 25.

[b] See ref. 26.

TABLE 5

Experimental quantum yields of iron(III)–formate systems (C_{Fe} = 0.001 M and $C_{H_2SO_4}$ = 0.005 M in each solution)

	Analytical concentration (M)		$p_{HCO_2^-}$	*Experimental quantum yield*
	HCO_2H	*HCO_2Na*		
1	0.02	0.0194	2.02	0.21
2	1.00	0.01	1.80	0.27
3	1.00	0.01	1.80	0.28
4	0.10	0.01	1.80	0.28
5	1.00	0.025	1.61	0.29

(continued)

TABLE 5 *(continued)*

	Analytical concentration (M)		$p_{HCO_2^-}$	*Experimental quantum yield*
	HCO_2H	HCO_2Na		
6	1.00	0.025	1.61	0.33
7	1.00	0.025	1.61	0.33
8	0.10	0.050	1.41	0.30
9	1.00	0.40	1.41	0.34
10	1.00	0.40	1.41	0.35
11	1.00	0.050	1.36	0.35
12	1.00	0.050	1.36	0.36
13	1.00	0.050	1.36	0.37
14	1.00	0.20	0.72	0.36
15	1.00	0.20	0.72	0.37
16	0.10	0.20	0.73	0.32

of the different complexes. Our results are in accordance with those obtained by Baxendale: the $Fe^{3+}HCO_2^-$ complex has the largest IQY.

4. Conclusion

According to the published literature, of the $Fe^{3+}(HCO_2^-)_n$ complexes only $Fe^{3+}HCO_2^-$ is photoactive. In this study the molar absorbancies and the IQYs of all $Fe^{3+}(HCO_2^-)_n$ complexes ($n = 1 - 4$) have been determined.

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Appendix A: Nomenclature

A	absorbance
C	molar concentration (M)
d	optical path (cm)
I	ionic strength (M)
k	reaction rate constant
L	ligand
m	number of measurements
n	number of iron(III) species in the solution
P	irradiation power per unit volume of the photoreactor (mol photon dm^{-3} s^{-1})
t	time
U	objective function

Greek symbols

α	mole ratio
β	complex stability constant
ϵ	molar absorbance (M^{-1} cm^{-1})
ϕ	individual quantum yield
Φ	experimentally determinable quantum yield

Indices

i	quantity referring to the *i*th measurement
j	quantity referring to the *j*th iron(III) species

Subscripts

abs	absorbed
calcd	calculated or computed
exp	experimental
md	measured

Appendix B: Calculation of some quantities

$$\alpha_j = \frac{[\mathrm{Fe}^{3+}L_j]}{C_{\mathrm{Fe(III)}}}$$

$$P_{\mathrm{abs}} = P_0\{1 - 10^{-d(C_{\mathrm{Fe(III)}}\Sigma\epsilon_j\alpha_j + C_{\mathrm{Fe(II)}}\epsilon_{\mathrm{Fe(II)}})}\}$$

$$P_j = P_{\mathrm{abs}} \frac{\epsilon_j\alpha_j}{\sum_{j=0}^{n} \epsilon_j\alpha_j + C_{\mathrm{Fe(II)}}\epsilon_{\mathrm{Fe(II)}}/C_{\mathrm{Fe(III)}}}$$