

PHOTOCHEMICAL BEHAVIOUR OF Fe²⁺ AND Fe³⁺ IONS IN THE PRESENCE OF (C₄H₉)₄P⁺ IONS

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Summary

The photochemical behaviour of Fe²⁺ and Fe³⁺ ions in aqueous sulphuric acid has been studied in the presence of (C₄H₉)₄P⁺ (I) ions. Although the primary photochemical step was not influenced by I, the iron species and I competed for hydrogen and OH radicals formed in the primary photochemical processes, and thus the secondary thermal reactions were modified. A reaction mechanism is proposed, and the following reaction rate constants were estimated: $k(\text{H} + \text{I}) = 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; $k(\text{OH} + \text{I}) = 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

1. Introduction

Several researchers have investigated the photochemical interaction between transition metal ions and organic ligands such as triphenylphosphine [1, 2], triethylamine [3, 4] and the tetrabutylammonium ion [5, 6], but the alkylphosphonium ion has not yet been incorporated into these studies. The photo-oxidation of aqueous acidic solutions of Fe²⁺ ions has recently been studied in our department [7 - 9], and the interaction of transition metal ions with organic phosphonium ions was also investigated [10, 11]. Thus it occurred to us that it would be interesting to investigate by photochemical means aqueous solutions of the ion pairs formed between (C₄H₉)₄P⁺ cations and iron(II) and iron(III) species.

2. Experimental details

2.1. Analytical methods

An aqueous solution of [(C₄H₉)₄P]₂SO₄ was prepared by precipitation of iodide ions from (C₄H₉)₄PI solution using the stoichiometric amount of Ag₂SO₄. The pure [(C₄H₉)₄P]₂SO₄ solution was obtained when the AgI precipitate was filtered off. The (C₄H₉)₄PI was prepared from tributylphosphine and butyl iodide by quaternization [12]. An FeSO₄ solution was

prepared by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in appropriately diluted sulphuric acid. Traces of iron(III) were reduced by stirring the solution with pure iron wire. Equal volumes of $[(\text{C}_4\text{H}_9)_4\text{P}]_2\text{SO}_4$ and FeSO_4 solutions were mixed under nitrogen.

The properties of the $[(\text{C}_4\text{H}_9)_4\text{P}]_2\text{SO}_4\text{-FeSO}_4$ mixture enabled the purity of the $[(\text{C}_4\text{H}_9)_4\text{P}]_2\text{SO}_4$ solutions to be checked: in the presence of silver ions colloidal silver was formed because of reduction by iron(II) ions, but in the presence of iodide ions iodine was formed from the traces of iron(III).

The Fe^{3+} ions formed photochemically were determined spectrophotometrically [13]; thus the spectra of $\text{Fe}_2(\text{SO}_4)_3$ were recorded at all $(\text{C}_4\text{H}_9)_4\text{P}^+$ and H_2SO_4 concentrations studied. The calculated molar absorbances are given in Table 1.

TABLE 1

Molar absorbances of $\text{Fe}_2(\text{SO}_4)_3$ at different concentrations of $(\text{C}_4\text{H}_9)_4\text{P}^+$ and H_2SO_4

Concentration (M)		Wavelength (nm)	
Bu_4P^+	H_2SO_4	254	304
0.02	0.2	3050	2300
0.02	0.5	3050	2300
0.05	0.2	3450	2840
0.05	0.5	3450	2840

Before performing photoredox studies we confirmed that in the dark the aqueous solutions of Fe^{2+} and Fe^{3+} ions containing $(\text{C}_4\text{H}_9)_4\text{P}^+$ and H_2SO_4 respectively were neither thermally oxidized nor thermally reduced.

The compositions of the studied solutions were as follows: FeSO_4 0.1, 0.2 or 0.4 M; $(\text{C}_4\text{H}_9)_4\text{P}^+$ 0.02 or 0.05 M; H_2SO_4 0.2 or 0.5 M. The initial concentration of iron(III) was $(2 - 5) \times 10^{-4}$ M.

In addition, we studied the photoreduction of iron(III). The compositions used for this system were as follows: iron(III) 10^{-3} M; $(\text{C}_4\text{H}_9)_4\text{P}^+$ 0.02 or 0.05 M; H_2SO_4 0.5 M.

2.2. Chemicals

We used analytical grade chemicals without further purification: $(\text{C}_4\text{H}_9)_3\text{P}$, $\text{C}_4\text{H}_9\text{I}$ and Ag_2SO_4 (all Merck-Schuchardt), H_2SO_4 (Carlo Erba), iron wire (Riedel-de Haen AG), and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (Reanal). Traces of oxygen were removed from industrial nitrogen by using a BASF R3-11 catalyst.

2.3. Photochemical methods

The solutions were prepared under a nitrogen atmosphere, and the irradiations were carried out in a nitrogen-purged quartz cuvette of optical

path 0.5 cm. The light source was a low pressure mercury lamp of power 17 W (VOLTARC UV LUX TM OT5, Applied Photophysics). The incident irradiation power per unit volume of the reactor was 1.536×10^{18} photons $\text{dm}^{-3} \text{s}^{-1}$. The apparatus has been described in more detail previously [8, 9].

3. Calculations

3.1. Calculation of quantum yields according to the product (ϕ_p)

The mechanism described in ref. 9, with some modification, is shown in Fig. 1. Energy transfer is not included, since its effects are negligible compared with those of the secondary thermal reactions. Furthermore, according to the UV spectrum of $[(\text{C}_4\text{H}_9)_4\text{P}]_2\text{SO}_4$ ($\epsilon = 0$ at $\lambda > 230$ nm) its photochemical activity at the wavelength used can be ignored. Thus, introducing

$$\phi_2 = \frac{k_2}{k_1 + k_2} \frac{k_3[\text{H}^+]}{k_3[\text{H}^+] + k_{r2}}$$

and

$$\phi_3 = \frac{k_7}{k_6 + k_7} \frac{k_9}{k_9 + k_{r3}}$$

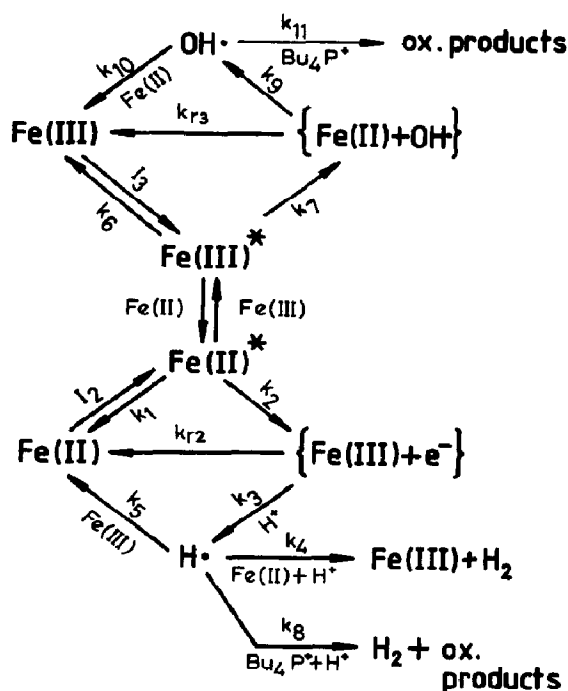


Fig. 1. Proposed reaction scheme for photoprocesses of $(\text{C}_4\text{H}_9)_4\text{P}^+$ ions and iron species.

the kinetic equation of the photoredox process can be written

$$\frac{d[\text{Fe(III)}]}{dt} = I_2\phi_2 + k_4[\text{H}\cdot][\text{H}^+][\text{Fe(II)}] - k_5[\text{H}\cdot][\text{Fe(III)}] - I_3\phi_3 + k_{10}[\text{OH}\cdot][\text{Fe(II)}] \quad (1)$$

According to the steady state treatment, $[\text{H}\cdot]$ and $[\text{OH}\cdot]$ can be expressed as

$$[\text{H}\cdot] = \frac{I_2\phi_2}{k_4[\text{H}^+][\text{Fe(II)}] + k_5[\text{Fe(III)}] + k_8[\text{H}^+][(\text{C}_4\text{H}_9)_4\text{P}^+]} \quad (2)$$

$$[\text{OH}\cdot] = \frac{I_3\phi_3}{k_{10}[\text{Fe(II)}] + k_{11}[(\text{C}_4\text{H}_9)_4\text{P}^+]} \quad (3)$$

Substituting these expressions into eqn. (1) we obtain:

$$\frac{d[\text{Fe(III)}]}{dt} = I_2\phi_2 \left(1 + \frac{k_4[\text{H}^+][\text{Fe(II)}] - k_5[\text{Fe(III)}]}{k_4[\text{H}^+][\text{Fe(II)}] + k_5[\text{Fe(III)}] + k_8[\text{H}^+][(\text{C}_4\text{H}_9)_4\text{P}^+]} \right) - I_3\phi_3 \left(1 - \frac{k_{10}[\text{Fe(II)}]}{k_{10}[\text{Fe(II)}] + k_{11}[(\text{C}_4\text{H}_9)_4\text{P}^+]} \right) \quad (4)$$

Since $k_5/k_4 < 0.1$ [16] and $[\text{Fe(III)}]/[\text{Fe(II)}] < 10^{-2}$, the product $k_5[\text{Fe(III)}]$ is negligible, so eqn. (4) can be rearranged:

$$\begin{aligned} \frac{d[\text{Fe(III)}]}{dt} &= I_2\phi_2 \frac{2k_4[\text{Fe(II)}] + k_8[(\text{C}_4\text{H}_9)_4\text{P}^+]}{k_4[\text{Fe(II)}] + k_8[(\text{C}_4\text{H}_9)_4\text{P}^+]} \\ &\quad - I_3\phi_3 \frac{k_{11}[(\text{C}_4\text{H}_9)_4\text{P}^+]}{k_{10}[\text{Fe(II)}] + k_{11}[(\text{C}_4\text{H}_9)_4\text{P}^+]} \\ &\equiv I_2\phi_2 S_2 - I_3\phi_3 S_3 \end{aligned} \quad (5)$$

Since the conversion was low, S_2 and S_3 were different for different solutions but remained constant during irradiation of a given solution. Thus it is advisable to treat the expressions $\phi_2 S_2$ and $\phi_3 S_3$ together, as the quantum yields referring to their products (ϕ_{2p} and ϕ_{3p}) and combinations of these should be analysed later. Solving the differential equation by the fourth-order Runge-Kutta method, the function

$$[\text{Fe(III)}] = f(t, [\text{Fe(III)}]_0, \phi_{2p}, \phi_{3p}, [\text{Fe(II)}], \epsilon_2, \epsilon_3)$$

can be calculated. Treating $[\text{Fe(III)}]_0$, ϕ_{2p} and ϕ_{3p} as independent variables, their best values can be obtained by the method of least squares. The optimum fit was determined by the Newton-Raphson method.

TABLE 2

Composition matrix of the $\text{Fe}^{2+} - (\text{C}_4\text{H}_9)_4\text{P}^+$ system in aqueous sulphuric acid

Complex	Components				lg β	Ionic strength	lg β_t
	Fe^{2+}	$(\text{C}_4\text{H}_9)_4\text{P}^+$	SO_4^{2-}	H^+			
$\text{Fe}^{2+}\text{SO}_4^{2-}$	1	0	1	0	1.0 [14]	1	2.22
$\text{Fe}^{2+}\text{H}^+\text{SO}_4^{2-}$	1	0	1	1	0, 29 ^a [14]	4	{ 0.02 2.27 ^b
$\text{H}^+\text{SO}_4^{2-}$	0	0	1	1	1.8 [15]	0.1	2.25
$\text{Fe}^{2+}(\text{C}_4\text{H}_9)_4\text{P}^+\text{SO}_4^{2-}$	1	1	1	0			2.0 ^c
$(\text{C}_4\text{H}_9)_4\text{P}^+\text{SO}_4^{2-}$	0	1	1	0			2.0 ^c

^alg β ($\text{Fe}^{2+}\text{HSO}_4^-$).^blg β_t ($\text{Fe}^{2+}\text{H}^+\text{SO}_4^{2-}$).^cSupposed values, discussed in the text.

3.2. Estimation of the rate of reaction of $(\text{C}_4\text{H}_9)_4\text{P}^+$ and H^+

The mole-ratio distribution of the species in the aqueous $\text{FeSO}_4 - [(\text{C}_4\text{H}_9)_4\text{P}]_2\text{SO}_4 - \text{H}_2\text{SO}_4$ solutions were computed using the program described in ref. 8. The composition matrix and stability constants of the complexes thought to be present are collected in Table 2; the mole-ratio distribution is given in Table 3. Since the stability constants of the $(\text{C}_4\text{H}_9)_4\text{P}^+\text{SO}_4^{2-}$ and $\text{Fe}^{2+}(\text{C}_4\text{H}_9)_4\text{P}^+\text{SO}_4^{2-}$ species were not available, their upper limits were estimated from the stability constants of $\text{H}^+\text{SO}_4^{2-}$ and $\text{Fe}^{2+}\text{H}^+\text{SO}_4^{2-}$ respectively. This is reasonable, because the $(\text{C}_4\text{H}_9)_4\text{P}^+$ ion is a larger cation than H^+ , with a lower charge density, and the mole ratio of $\text{Fe}^{2+}(\text{C}_4\text{H}_9)_4\text{P}^+\text{SO}_4^{2-}$ remains negligible.

Since the individual quantum yields of the species Fe^{2+} , $\text{Fe}^{2+}\text{SO}_4^{2-}$ and $\text{Fe}^{2+}\text{H}^+\text{SO}_4^{2-}$ are known [9], the ϕ_{2p} to be expected with no $(\text{C}_4\text{H}_9)_4\text{P}^+$ ions present could be calculated for each solution. After this the effect of the $(\text{C}_4\text{H}_9)_4\text{P}^+$ cation was considered by including the S_2 term, and the optimal k_8 was determined for the objective function Z :

$$Z = \sum_{j=1}^n \left(\phi_{2p,j} - \phi_{2,j} \frac{2k_4[\text{Fe(II)}]_j + k_8[(\text{C}_4\text{H}_9)_4\text{P}^+]_j}{k_4[\text{Fe(II)}]_j + k_8[(\text{C}_4\text{H}_9)_4\text{P}^+]_j} \right)^2 \quad (6)$$

According to Anbar and Neta [16], $k_4 = 1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

3.3. Estimation of ϕ_3 and the reaction rate of $(\text{C}_4\text{H}_9)_4\text{P}^+$ and OH^-

When k_8 was obtained, it was substituted into eqn. (4), and this equation was used to evaluate the photoreduction of the solutions containing mainly Fe^{3+} ions. The differential equations were solved, and the best ϕ_3 and k_{11} were determined for the objective function:

$$Z = \sum_{k=1}^m \{ [\text{Fe(III)}]_{\text{md}, k} - [\text{Fe(III)}]_{\text{calcd}, k}(t, \phi_3, k_{10}, k_{11}, [\text{Fe(II)}], [\text{Fe(III)}], \epsilon_2, \epsilon_3) \}^2 \quad (7)$$

TABLE 3

Mole ratios of iron(II) species calculated at various initial concentrations of FeSO_4 , $(\text{C}_4\text{H}_9)_4\text{P}^+$ and H_2SO_4

Species	$[(\text{C}_4\text{H}_9)_4\text{P}^+] = 0.02 M$		$[(\text{C}_4\text{H}_9)_4\text{P}^+] = 0.05 M$	
	$[\text{FeSO}_4] = 0.2 M$	$[\text{FeSO}_4] = 0.5 M$	$[\text{FeSO}_4] = 0.2 M$	$[\text{FeSO}_4] = 0.5 M$
$[\text{H}_2\text{SO}_4] = 0.1 M$				
$[\text{Fe}^{2+}]$ (mol.%)	69.7	69.4	69.7	69.1
$[\text{Fe}^{2+}\text{SO}_4^{2-}]$ (mol.%)	26.2	21.5	26.1	21.6
$[\text{Fe}^{2+}\text{H}^+\text{SO}_4^{2-}]$ (mol.%)	3.91	8.96	3.90	8.94
$[\text{Fe}^{2+}(\text{C}_4\text{H}_9)_4\text{P}^+\text{SO}_4^{2-}]$ (mol.%)	0.14	0.11	0.34	0.29
$[\text{H}_2\text{SO}_4] = 0.2 M$				
$[\text{Fe}^{2+}]$ (mol.%)	58.6	64.1	58.5	62.9
$[\text{Fe}^{2+}\text{SO}_4^{2-}]$ (mol.%)	37.3	26.5	37.2	27.3
$[\text{Fe}^{2+}\text{H}^+\text{SO}_4^{2-}]$ (mol.%)	3.91	9.39	3.91	9.40
$[\text{Fe}^{2+}(\text{C}_4\text{H}_9)_4\text{P}^+\text{SO}_4^{2-}]$ (mol.%)	0.15	0.12	0.37	0.30
$[\text{H}_2\text{SO}_4] = 0.4 M$				
$[\text{Fe}^{2+}]$ (mol.%)	46.7	54.5	46.6	53.3
$[\text{Fe}^{2+}\text{SO}_4^{2-}]$ (mol.%)	49.5	35.8	49.5	36.6
$[\text{Fe}^{2+}\text{H}^+\text{SO}_4^{2-}]$ (mol.%)	3.55	9.58	3.53	9.58
$[\text{Fe}^{2+}(\text{C}_4\text{H}_9)_4\text{P}^+\text{SO}_4^{2-}]$ (mol.%)	0.14	0.13	0.36	0.32

4. Results and discussion

The fitting of the kinetic curve for iron(II) photo-oxidation to the measurements for one solution is given in Table 4. The quantum yields ϕ_{2p} and ϕ_{3p} for all the experiments are given in Table 5; it can be seen that the ϕ_{2p} increase when the concentration of iron(II) or sulphuric acid increases or the $(C_4H_9)_4P^+$ content decreases. This finding is in agreement with the idea that the mole ratio of $Fe^{2+}SO_4^{2-}$ and $Fe^{2+}H^+SO_4^{2-}$ species increases on increasing the concentration of SO_4^{2-} or H^+ ions, and these ion pairs have higher individual quantum yields (0.30 and 0.67 respectively) than Fe_{aq}^{2+} ions (0.16) [9]. On the contrary, the $(C_4H_9)_4P^+$ cations compete with the iron(II) species for $H\cdot$ radicals.

As for the role of $Fe^{2+}(C_4H_9)_4P^+SO_4^{2-}$ ion associates, in Table 3 it can be seen that their ratio is below 1% in all cases. Thus, over the concentration range studied, contrary to our initial assumption, the quantum yield of photo-oxidation cannot be significantly influenced by $Fe^{2+}(C_4H_9)_4P^+SO_4^{2-}$ ion associates. It is worth noting that the UV spectra of $FeSO_4$ solutions were also not modified by the presence of $(C_4H_9)_4P^+$ ions.

The rate constant for the reaction of $(C_4H_9)_4P^+$ ions with $H\cdot$ radicals is approximately $3 \times 10^7 M^{-1} s^{-1}$.

The calculated mole ratios and quantum yields are compiled in Table 6, and the fitting of the measurements and the calculated curves is presented in Figs. 2 and 3.

Since the photoreduction of Fe^{3+} ions cannot be measured and evaluated accurately when the iron(II) concentration is dominant (Table 5),

TABLE 4

Measured and calculated data for the photo-oxidation of Fe^{2+} ions

t (s)	$10^4 \times [Fe^{3+}]$ (<i>measured</i>)	$10^4 \times [Fe^{3+}]$ (<i>calculated</i> , $\phi_{exp} = 0.413$)
0	0.013	0.035
40	0.318	0.348
80	0.720	0.680
120	0.950	0.999
160	1.353	1.304
200	1.669	1.598
240	1.899	1.882
280	2.129	2.156
320	2.445	2.422
360	2.692	2.679
400	2.948	2.929
440	3.134	3.173
480	3.364	3.409

$[Fe^{2+}] = 0.0862 M$; $[H_2SO_4] = 0.464 M$; $[(C_4H_9)_4P^+] = 0.02 M$.

TABLE 5

Quantum yields (ϕ_{2p} and ϕ_{3p}) referring to products of photo-oxidation and photo-reduction of aqueous acidic $Fe^{2+}-Fe^{3+}$ systems in the presence of $(C_4H_9)_4P^+$ ions

Initial concentration (M)		ϕ_{2p}	$10^3\phi_{3p}$
H_2SO_4	$FeSO_4$		
[[$(C_4H_9)_4P^+$] _{initial} = 0.02 M			
0.167	0.0823	0.38	3.2
0.163	0.115	0.41	1.8
0.178	0.194	0.41	3.0
0.155	0.209	0.41	2.7
0.159	0.406	0.48	0.9
0.172	0.413	0.45	0.7
0.464	0.0862	0.41	3.1
0.471	0.124	0.44	3.0
0.474	0.190	0.43	3.7
0.446	0.221	0.43	4.2
0.458	0.373	0.45	2.3
0.436	0.399	0.43	0
[[$(C_4H_9)_4P^+$] _{initial} = 0.05 M			
0.170	0.0735	0.31	1.4
0.162	0.138	0.36	0.3
0.153	0.210	0.36	0.4
0.150	0.380	0.45	0.7
0.456	0.094	0.41	5.0
0.467	0.119	0.39	3.5
0.466	0.120	0.39	3.0
0.468	0.132	0.39	0.9
0.467	0.1345	0.38	0
0.457	0.2085	0.37	3.1
0.448	0.218	0.42	1.0
0.438	0.387	0.47	29.8
0.430	0.3985	0.43	1.0

we studied the photoreduction of mainly iron(III)-containing solutions as well. The evaluated results are shown in Fig. 4. In aqueous sulphuric acid solution ϕ_3 (i.e. the likelihood of $OH\cdot$ radicals escaping from the solvent cage) can be estimated as 0.07, and the reaction rate constant of $(C_4H_9)_4P^+$ ions with $OH\cdot$ radicals is approximately $10^7 M^{-1} s^{-1}$, because the best value of k_{11}/k_{10} is 3×10^{-2} , and $k_{10} = 3.2 \times 10^8 M^{-1} s^{-1}$ [16].

5. Conclusion

The photoredox process of Fe^{2+} and Fe^{3+} ions in aqueous sulphuric acid solutions are significantly influenced by the $(C_4H_9)_4P^+$ cations, although

TABLE 6

Measured and calculated quantum yields referring to products of iron(II), with the best k_8 ($3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)

[Fe ²⁺] (M)	Mole ratios			ϕ_{2p}		
	Fe ²⁺	Fe ²⁺ SO ₄ ²⁻	Fe ²⁺ H ⁺ SO ₄ ²⁻	Measured	Calculated	Without (C ₄ H ₉) ₄ P ⁺
[(C₄H₉)₄P⁺] = 0.02 M						
0.0823	0.689	0.274	0.0344	0.38	0.369	0.431
0.115	0.671	0.294	0.0333	0.41	0.387	0.436
0.194	0.614	0.349	0.0353	0.41	0.420	0.453
0.209	0.594	0.375	0.0306	0.41	0.425	0.456
0.406	0.473	0.499	0.028	0.48	0.470	0.488
0.413	0.475	0.494	0.0304	0.45	0.471	0.489
0.0862	0.706	0.210	0.0832	0.41	0.399	0.463
0.124	0.686	0.227	0.0861	0.44	0.421	0.471
0.190	0.651	0.259	0.0887	0.43	0.446	0.483
0.221	0.638	0.278	0.0847	0.43	0.453	0.484
0.373	0.560	0.350	0.0878	0.45	0.486	0.507
0.399	0.548	0.368	0.0836	0.43	0.488	0.508
[(C₄H₉)₄P⁺] = 0.05 M						
0.0735	0.705	0.257	0.0344	0.31	0.312	0.426
0.139	0.653	0.310	0.0326	0.36	0.356	0.439
0.210	0.594	0.372	0.0301	0.36	0.389	0.454
0.380	0.486	0.485	0.0268	0.45	0.439	0.482
0.094	0.699	0.216	0.0822	0.41	0.354	0.463
0.119	0.686	0.226	0.0851	0.39	0.372	0.469
0.132	0.680	0.232	0.0858	0.39	0.380	0.472
0.1345	0.679	0.233	0.0857	0.38	0.381	0.472
0.2085	0.640	0.270	0.0861	0.37	0.413	0.482
0.218	0.637	0.276	0.0848	0.42	0.416	0.483
0.387	0.551	0.362	0.0837	0.47	0.461	0.506
0.3985	0.547	0.369	0.0823	0.43	0.463	0.507

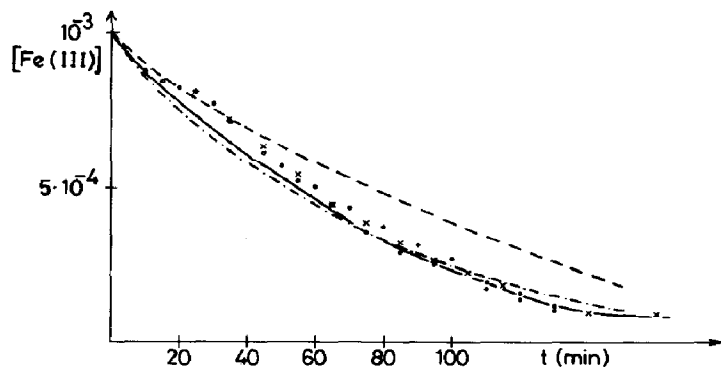


Fig. 4. Fitting of ϕ_3 to the measurements on the photoreduction of iron(III). Compositions of irradiated solutions: initial [Fe(III)] = 10^{-3} M, [H₂SO₄] = 0.5 M, [(C₄H₉)₄P⁺] = 0.05 M (○) or [(C₄H₉)₄P⁺] = 0.02 M (● and ×). Fitted ϕ_3 values: ---, 0.04; —, 0.07; - · -, 0.1.

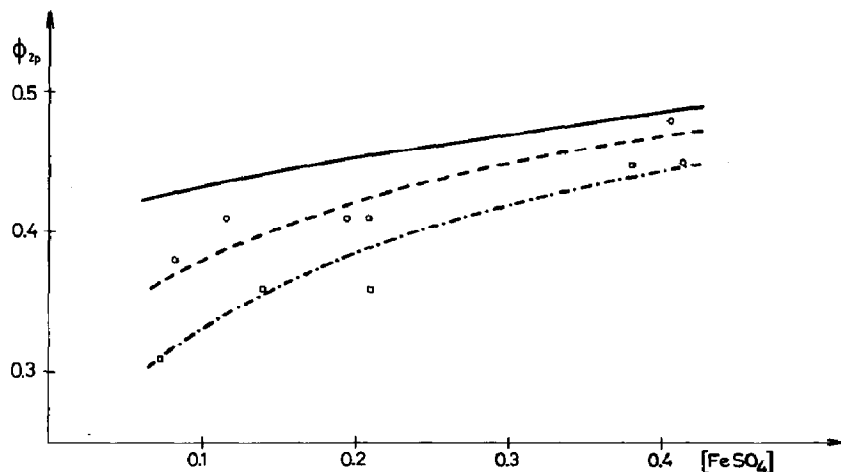


Fig. 2. Dependence of ϕ_{2p} on the concentration of FeSO_4 and $(\text{C}_4\text{H}_9)_4\text{P}^+$ in the presence of $0.16 \text{ M H}_2\text{SO}_4$. $(\text{C}_4\text{H}_9)_4\text{P}^+$ concentrations: 0.02 M (\circ , measurements; ---, calculated curve); 0.05 M (\square , measurements; - · -, calculated curve); —, calculated with no $(\text{C}_4\text{H}_9)_4\text{P}^+$ present.

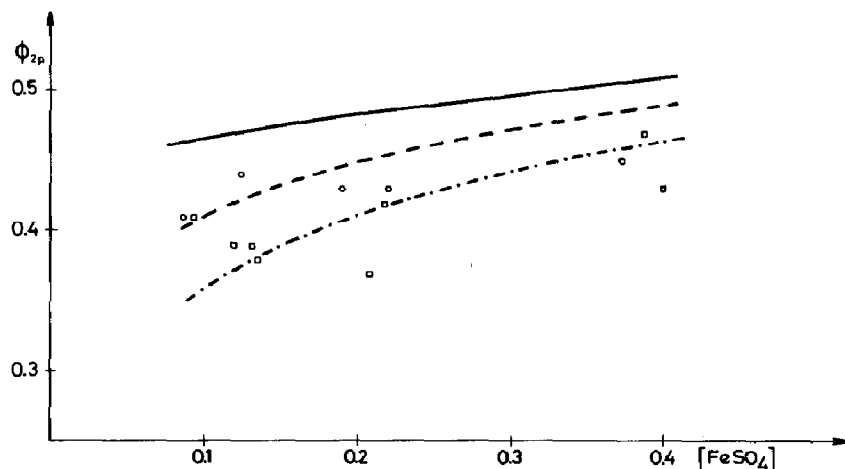


Fig. 3. Dependence of ϕ_{2p} on the concentration of FeSO_4 and $(\text{C}_4\text{H}_9)_4\text{P}^+$ in the presence of $0.45 \text{ M H}_2\text{SO}_4$. The symbols are as in Fig. 2.

ion associates are not formed by these ions. The proposed mechanism and the individual quantum yields are in very good accord with the experimental data recorded over a wide range.

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