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Photooxidation of Iron(II) Evolving Hydrogen

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Introduction

Although some results are known in connection with the photooxidation of iron(II) in solution evolving hydrogen [1–3], a systematic investigation is missing on concentration and anion dependence of the phenomenon.

Experimental

The investigations were carried out under N_2 atmosphere at 30 ± 3 °C in a photoreactor, made at our department, having the lamp in a central position. The lamp used was a TUNGSRAM HgLI type high pressure one with 80 W power. Iron(III) traces in iron(II) sulphate solutions were reduced by iron powder before beginning the experiments. Fe(III) formed during photooxidation was measured spectrophotometrically at 304 nm and H_2 evolved was determined with a gas-chromatograph. We found a good agreement with Stein's data [2], that mole ratio of iron(III) and H_2 was 2:1. Sampling was made from

TABLE I. Concentration of Fe(III) in the $FeSO_4$–H_2SO_4 system; $C_{H_2SO_4}$ = 0.05 mol dm^{-3}.

Time (h)	$10^3 \times C_{Fe(III)}$ (mol dm^{-3})			
	C_{FeSO_4} (mol dm^{-3})			
	0.05	0.1	0.5	1.0
1	0.21	0.21	0.44	0.57
2	0.38	0.42	0.71	0.75
3	0.55	0.62	0.98	1.05
4	0.71	0.80	1.27	1.26
5	0.88	0.91	1.44	1.56
	$C_{H_2SO_4}$ = 0.1 mol dm^{-3}			
1	0.30	0.42	0.81	0.42
2	0.56	0.71	1.53	0.72
3	0.75	0.98	2.03	1.12
4	1.05	1.27	2.57	1.41
	$C_{H_2SO_4}$ = 0.5 mol dm^{-3}			
1	0.40	0.46	0.50	0.45
2	0.74	0.84	0.86	0.70
3	0.95	1.16	1.26	1.03
4	1.37	1.46	1.68	1.33
	$C_{H_2SO_4}$ = 1.0 mol dm^{-3}			
1	0.30	0.47	0.44	0.48
2	0.55	0.63	0.67	0.67
3	0.78	1.09	0.88	0.87
4	1.04	1.36	1.19	1.20
5	1.32	1.61	1.49	1.34

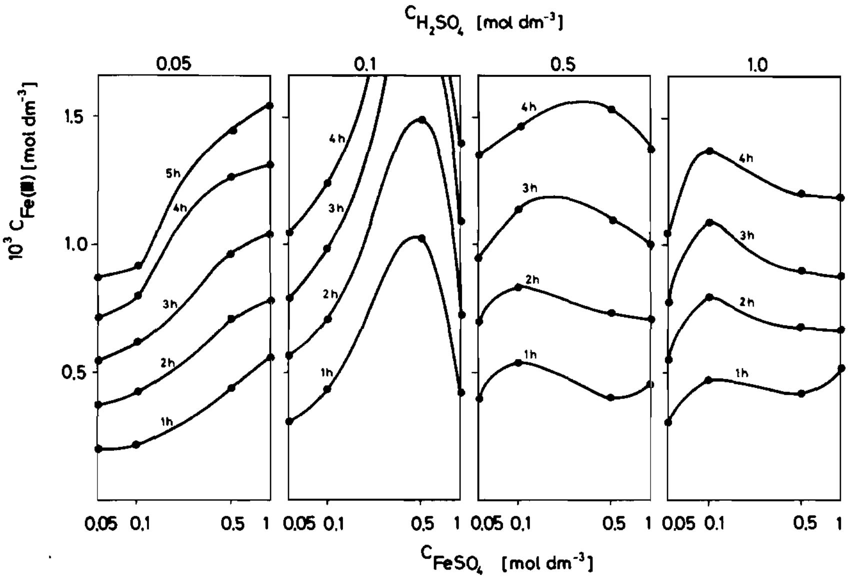

Fig. 1. Sections from the $C_{Fe(III)}$ *vs.* time diagrams.

TABLE II. Concentration of Fe(III) in the $FeSO_4$–$Na_2SO_4(H_2SO_4)$ system; $C_{H_2SO_4} = 0.05$ mol dm^{-3}.

Time (h)	$10^3 \times C_{Fe(III)}$ (mol dm^{-3})			
	C_{FeSO_4} (mol dm^{-3})			
	0.05	0.10	0.50	1.0
	$C_{Na_2SO_4} = 0.05$ mol dm^{-3}			
1	0.172	0.246	0.438	0.691
2	0.352	0.452	0.722	0.679
3	0.540	0.636	1.10	1.14
4	0.687	0.838	1.39	1.29
5	0.839	1.032	1.70	1.42
	$C_{Na_2SO_4} = 0.45$ mol dm^{-3}			
1	0.183	0.239	0.425	0.477
2	0.345	0.473	0.648	0.647
3	0.528	0.645	0.804	0.820
4	0.634	0.843	1.05	1.01
5	0.807	1.01	1.23	1.17
	$C_{Na_2SO_4} = 0.95$ mol dm^{-3}			
1	0.158	0.225	0.379	0.356
2	0.377	0.372	0.528	0.441
3	0.467	0.536	0.712	0.605
4	0.552	0.705	0.902	0.819
5	0.716	0.890	1.08	1.033

the properly constructed reactor with a syringe every 20 minutes.

Concentrations of iron(II) sulphate and H_2SO_4 were 0.05, 0.1, 0.5 and 1.0 mol dm^{-3}, respectively. Thus 16 systems were investigated. Generally irradiations were made for 5 hours. In another series iron(II) sulphate concentrations were the same but by 0.05 mol dm^{-3} H_2SO_4 concentration the 0.1, 0.5 and 1.0 mol dm^{-3} sulphate contents were adjusted by Na_2SO_4.

Results and Discussion

From the experimental data it can be stated that the concentration of iron(III) under irradiation depends on time approximately linearly and its maximum value could achieve 1.5–2.5 X 10^{-3} mol dm^{-3} at the given experimental conditions. In contrast the dependence of photooxidation rate on concentration of iron(II) and H_2SO_4 could not be already surveyed so easily at once. It can be seen, however, that in the case of more concentrated iron(II) and H_2SO_4 solutions the rate of photooxidation decreased again. To get a clear picture, sections were made from the iron(III) concentration *vs.* time diagrams at data for the first, second, third, fourth and fifth hours (Table I and Fig. 1). Thus it has unambiguously come to light that an iron(II) sulphate–sulphuric acid concentration pair exists where photooxidation rate has a maximum.

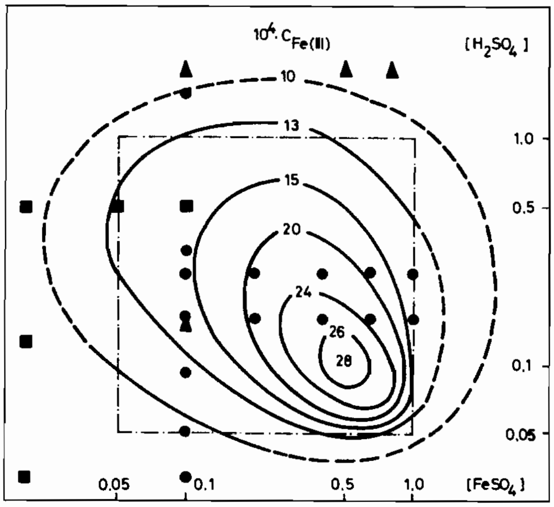

Fig. 2. The $FeSO_4$–H_2SO_4 system; investigated area: ▲ [1], ■ [2], ● [3], –.– this work.

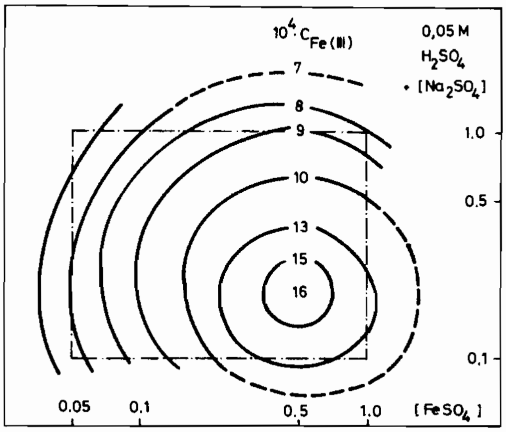

Fig. 3. The $FeSO_4$–$Na_2SO_4(H_2SO_4)$ system.

The level-line diagram of the fourth hour's sections for the $FeSO_4$–H_2SO_4 pair is shown in Fig. 2. From this diagram it is clear that in the system of 0.5 *M* $FeSO_4$–0.1 *M* H_2SO_4 the photooxidation rate has a maximum. In Fig. 2 are plotted other results which were published at this time [1–3], illustrating that even the most interesting area has been avoided by former investigations. The results of $FeSO_4$–$Na_2SO_4(H_2SO_4)$ systems are similar (Table II and Fig. 3), only their iron(III) contents produced are less.

In Table III the Mössbauer parameters of frozen solutions of $FeSO_4$–H_2SO_4–H_2O systems are shown at proper concentrations. It can be seen that by constant quadrupole splitting the lowest isomer shift (i.e. the lowest 3d-electron density at the iron nuclei) are obtained even at the marked concentration pair.

On the basis of these results ion-pair or sulphate-complex structures can be assumed in the solution, where the excitation process or escape for electrons are favoured.

Further investigations are in progress.

TABLE III. Mössbauer Parameters of the $FeSO_4$–H_2SO_4–H_2O Systems in Frozen Solutions[a] (77 K).

$FeSO_4$ (mol dm^{-3})	H_2SO_4 (mol dm^{-3})	δ (mm s^{-1})	ΔE (mm s^{-1})
0.25	0.05	1.15	3.44
1.00	0.05	1.15	3.45
0.10	0.10	1.18	3.49
0.50	0.10	1.06	3.49
0.316	0.158	1.12	3.48
1.00	0.20	1.12	3.49
1.00	1.00	1.19	3.48

[a] Radiation source: ^{57}Co–Pt. Error of measurements: ±0.03 mm/s. Reference: $Na_2[Fe(CN)_5NO] \cdot 2H_2O$.

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