

Kinetics of the iodate reduction by hydrogen peroxide and relation with the Briggs-Rauscher and Bray-Liebafsky oscillating reactions

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Electronic supplementary information

1. Table ES1. Initial rates (M s^{-1}) of the iodate reduction by hydrogen peroxide at low concentrations

$[\text{HClO}_4]_0$	$[\text{KIO}_3]_0$	$[\text{H}_2\text{O}_2]_0$	$[\text{H}^+]$	$[\text{IO}_3^-]$	$d[\text{I}_2]/dt \times 10^8$
25°					
0.0385	0.0962	0.385	0.029	0.087	1.12
0.0385	0.0962	0.385	0.029	0.087	0.89
0.040	0.099	0.099	0.030	0.089	0.24
0.040	0.100	0.050	0.030	0.090	0.13
0.078	0.098	0.220	0.061	0.080	0.87
0.098	0.098	0.196	0.077	0.077	1.00
39°					
0.0096	0.019	0.385	0.009	0.019	0.62
0.0096	0.096	0.385	0.007	0.093	2.1
0.0098	0.020	0.196	0.009	0.019	0.31
0.0098	0.098	0.039	0.007	0.095	0.29
0.0098	0.098	0.196	0.007	0.095	1.1
0.0099	0.099	0.099	0.007	0.096	0.66
0.038	0.019	0.385	0.036	0.017	1.0
0.038	0.096	0.385	0.028	0.086	3.7
0.039	0.020	0.039	0.037	0.017	0.093
0.039	0.020	0.196	0.037	0.017	0.49
0.039	0.098	0.039	0.029	0.088	0.47
0.039	0.098	0.196	0.029	0.088	1.8
0.040	0.020	0.099	0.037	0.017	0.26
0.040	0.099	0.099	0.029	0.088	0.96

0.083	0.083	0.167	0.066	0.066	2.7
0.091	0.091	0.091	0.070	0.070	1.54
0.098	0.049	0.196	0.085	0.036	2.1
0.099	0.099	0.099	0.075	0.075	2.2
0.190	0.048	0.476	0.171	0.028	7.5
0.192	0.096	0.385	0.155	0.059	12.4
0.196	0.049	0.196	0.175	0.028	3.3
0.196	0.098	0.196	0.157	0.059	6.1
0.196	0.098	0.196	0.157	0.059	6.2
0.198	0.099	0.099	0.159	0.060	3.0

60°

$[\text{HClO}_4]_0$	$[\text{NaIO}_3]_0$	$[\text{H}_2\text{O}_2]_0$	$[\text{H}^+]$	$[\text{IO}_3^-]$	$d[\text{I}_2]/dt \times 10^8$
0.038	0.101	0.051	0.026	0.090	6.8
0.038	0.097	0.052	0.027	0.086	7.2
0.044	0.050	0.091	0.036	0.043	7.4
0.044	0.100	0.041	0.031	0.087	5.9
0.047	0.118	0.029	0.031	0.102	5.1
0.050	0.063	0.024	0.040	0.052	2.4
0.050	0.189	0.026	0.028	0.167	6.9
0.052	0.050	0.050	0.043	0.041	4.2
0.057	0.057	0.043	0.047	0.047	4.5
0.062	0.047	0.053	0.053	0.038	4.8
0.062	0.049	0.090	0.052	0.039	8.1
0.062	0.099	0.095	0.044	0.082	17.0
0.062	0.189	0.053	0.035	0.162	15.4
0.062	0.200	0.091	0.034	0.171	30
0.063	0.100	0.023	0.045	0.082	3.8
0.063	0.095	0.026	0.045	0.078	4.2
0.063	0.100	0.048	0.045	0.082	7.9
0.063	0.100	0.058	0.045	0.082	10.1
0.074	0.198	0.042	0.041	0.165	12.7
0.074	0.200	0.050	0.041	0.167	15.9

0.075	0.047	0.026	0.064	0.036	2.6
0.075	0.047	0.053	0.064	0.036	5.4
0.075	0.095	0.027	0.055	0.075	4.9
0.075	0.095	0.053	0.055	0.075	9.5
0.075	0.189	0.053	0.042	0.157	17.5
0.075	0.200	0.054	0.041	0.166	17.5
0.087	0.200	0.050	0.049	0.162	17.0
0.094	0.100	0.056	0.069	0.075	11.7

2. Comparison with the rate law $r_{\text{ini}} = (k'_R + k''_R [\text{HClO}_4]_o) [\text{KIO}_3]_o [\text{H}_2\text{O}_2]_o$

Figures ES1 and ES2 show that the values of $r_{\text{ini}} / [\text{KIO}_3]_o [\text{H}_2\text{O}_2]_o$ depend on the $[\text{KIO}_3]_o$ values. Thus, the rate law $r_{\text{ini}} = (k'_R + k''_R [\text{HClO}_4]_o) [\text{KIO}_3]_o [\text{H}_2\text{O}_2]_o$ is not verified. On the contrary, the values of $r_{\text{ini}} / [\text{IO}_3^-] [\text{H}_2\text{O}_2]_o$ do not depend on $[\text{IO}_3^-]$.

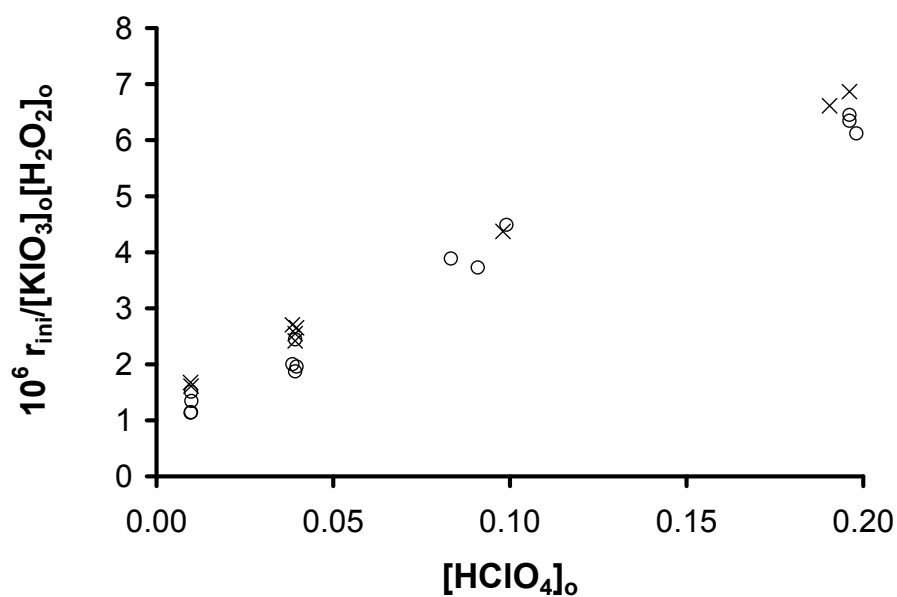


Fig.ES1. The values of $r_{\text{ini}} / [\text{KIO}_3]_o [\text{H}_2\text{O}_2]_o$ at 39° are higher when $[\text{KIO}_3]_o < 0.05$ M (×) than when $[\text{KIO}_3]_o > 0.08$ M (O).

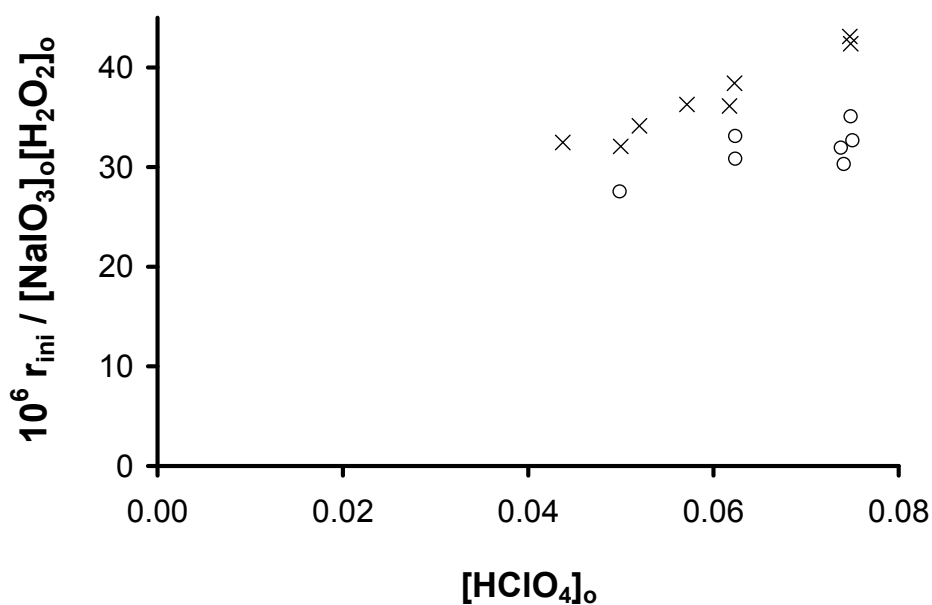


Fig.ES2. The values of $r_{\text{ini}} / [\text{NaIO}_3]_o [\text{H}_2\text{O}_2]_o$ at 60° are higher when $[\text{NaIO}_3]_o \sim 0.05 \text{ M}$ (x) than when $[\text{NaIO}_3]_o \sim 0.19 \text{ M}$ (O).

3. Initial rates of the iodate reduction by hydrogen peroxide at high concentrations

There is no simple rate law valid in the whole domain of concentrations. However, to see more clearly the effect of the concentrations on the radical pathway, we have looked for an empirical correlation between the rates and the concentrations. Table ES2 compares the experimental rates for $[\text{HClO}_4]_o = 0.10 \text{ M}$ and the values calculated by the following equation. r_1 is given by equation (1) in the main text and the best fit was obtained using $x = 2.35$, $k = 2.2 \times 10^{-4}$ and $K = 641$.

$$r_{\text{exp}} = r_1 + k \frac{[\text{H}_2\text{O}_2]^x [\text{IO}_3^-]}{1 + K[\text{IO}_3^-]}$$

Table ES2. Experimental and calculated initial rates (M s^{-1}) of the iodate reduction by hydrogen peroxide. $[\text{HClO}_4]_0 = 0.10 \text{ M}$.

$[\text{KIO}_3]_0$	$[\text{H}_2\text{O}_2]_0$	$[\text{H}^+]$	$[\text{IO}_3^-]$	$r_{\text{exp}} \times 10^6$	$r_{\text{calc}} \times 10^6$	$r_{\text{calc}}/r_{\text{exp}}$
0.001	1.0	0.0997	0.00074	0.099	0.112	1.10
0.001	1.0	0.0997	0.00074	0.115	0.112	0.97
0.002	1.0	0.0995	0.00147	0.20	0.17	0.87
0.005	1.0	0.0987	0.00369	0.23	0.25	1.07
0.005	1.0	0.0987	0.00369	0.26	0.25	0.94
0.01	1.0	0.0974	0.00740	0.26	0.30	1.16
0.01	1.0	0.0974	0.00740	0.30	0.30	1.00
0.01	1.0	0.0974	0.00740	0.27	0.30	1.10
0.002	1.5	0.0995	0.00147	0.48	0.44	0.91
0.0033	1.5	0.0991	0.00243	0.57	0.55	0.96
0.005	1.5	0.0987	0.00369	0.64	0.64	0.99
0.01	1.5	0.0974	0.00740	0.67	0.76	1.13
0.001	1.99	0.0997	0.00074	0.48	0.56	1.16
0.005	1.99	0.0987	0.00369	1.56	1.23	0.79
0.002	2.0	0.0995	0.00147	1.15	0.86	0.75
0.01	2.0	0.0974	0.00740	1.23	1.48	1.19
0.01	2.0	0.0974	0.00740	1.37	1.48	1.08
0.001	3.0	0.0997	0.00074	1.48	1.47	0.99
0.002	3.0	0.0995	0.00147	2.44	2.23	0.91
0.005	3.0	0.0987	0.00369	3.75	3.20	0.86
0.01	3.0	0.0974	0.00740	4.08	3.81	0.93
Intermediate region						
0.10	0.40	0.078	0.0780	0.094	0.079	0.84
0.10	0.35	0.078	0.0780	0.062	0.064	1.03
0.01	0.35	0.097	0.0074	0.026	0.028	1.09
0.10	0.30	0.078	0.0780	0.051	0.050	0.98
0.01	0.30	0.097	0.0074	0.020	0.020	1.01