

Iodine oxidation by hydrogen peroxide in acidic solutions, Bray-Liebhafsky reaction and other related reactions

Electronic supplementary information : Rate constant of reaction (R5)

Guy Schmitz

Faculty of Applied Sciences, Université Libre de Bruxelles, CP165/63, Av. F. Roosevelt 50, 1050 Brussels, Belgium. E-mail: gschmitz@ulb.ac.be

The value of the rate constant k_5 has been measured by Liebhafsky¹ and by Furrow². Furrow's value being ten times smaller than Liebhafsky's value, we have analysed the data published by these two authors trying to find the origin of such a discrepancy.

Furrow has calculated k_5 assuming that the rates of reactions (R5) and (R10) are nearly equal during the induction period of the iodine - hydrogen peroxide reaction without iodate (see main text). He has calculated the concentrations $[I_2]$ and $[I_3^-]$ from the absorbances at 462 nm and 353 nm, $[I^-]$ from the equilibrium $I_2 + I^- \rightleftharpoons I_3^-$, $[IOH]$ assuming the equilibrium of the hydrolysis (R4) and finally $k_5 = k_{10} [I^-]/[IOH]$ where k_{10} is known³. He has obtained $k_5 = 3 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ with a considerable scatter imputed to the low measurement precision of the low absorbances at 354 nm. Furrow has also mentioned that a true steady state is never reached, the absorbances showing a continuous downward drift. Moreover, we have found a strong correlation between his k_5 values and the iodide ions concentrations. Figure ES1 shows the k_5 values obtained by Furrow (table IV of ref.2) plotted versus the $[I^-]$ values calculated from the absorbances reported in the same table. The observed correlation and the large difference between the values of k_5 obtained by Furrow and by Liebhafsky suggest that the assumption $r_5 = r_{10}$ is not valid during the induction period. Numerical simulations using the proposed model support this explanation. As mentioned in the main text, the iodide ions produced during the induction period by reaction (R5) are not oxidized mainly by reaction (R10) but by reaction (R11) and by the pathway (R2) + (R6) (the sum of these two reactions gives $I^- + H^+ + H_2O_2 \rightarrow IOH + H_2O$). Thus, $r_5 = r_{10} + r_{11} + r_2$ with $r_{10} < r_{11} + r_2$ and the assumption $r_5 = r_{10}$ gives a too low value of r_5 .

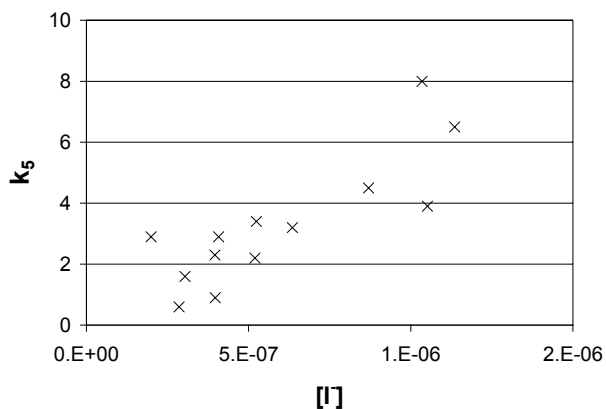


Figure ES1. k_5 values obtained by Furrow² versus the iodide ions concentrations.

Liebhafsky¹ has measured the rate of oxygen production in solutions saturated with iodine and containing hydrogen peroxide and perchloric acid. The iodide ions concentrations were fixed by thalious nitrate in equilibrium with solid thalious iodide. The experimental conditions were such that H_2O_2 did not oxidise IOH and that oxygen was produced only by reaction (R5). The value of k_5 are related to the experimental rate constant k reported in his table II by the expression

$$k = (d[\text{O}_2]/dt)/[\text{H}_2\text{O}_2] = k_5 [\text{IOH}]$$

The iodide ions concentrations are calculated from the solubility product of thalious iodide, $K_{s,\text{TII}} = [\text{I}^-][\text{TI}^+]$, and the hypoiodous acid concentrations are calculated assuming the equilibrium of the hydrolysis (R4).

$$[\text{IOH}] = \frac{[\text{I}_2][\text{TI}^+]}{K_{s,\text{TII}}K_4[\text{H}^+]} = \frac{\gamma_{\text{TII}}^2}{\gamma_{\text{HI}}^2} \frac{[\text{I}_2][\text{TI}^+]}{K_{s,\text{TII}}^\circ K_4^\circ[\text{H}^+]}$$

The values of the equilibrium constant K_4 used by Liebhafsky being slightly different from the more recent value⁴, we have recalculated his results using $K_4^\circ = 1.9 \times 10^{12}$. We have assumed, as done by Liebhafsky, that $\gamma_{\text{TII}} = \gamma_{\text{HI}}$. The values in figure ES2 showing no effect

of $[I^-]$, and thus no effect of $[TI^+]$, we conclude that they are more reliable than the values of Furrow and accept the mean value $k_5 = 23 \text{ M}^{-2} \text{ s}^{-1}$.

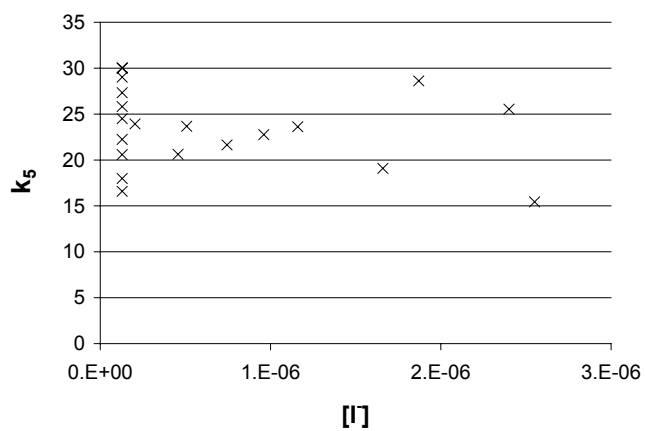


Figure ES2. k_5 values recalculated from the measurements of Liebhafsky¹ versus the iodide ions concentration.

References

- 1 H.A. Liebhafsky, *J. Am. Chem. Soc.*, 1932, **54**, 3504.
- 2 S. Furrow, *J. Phys. Chem.*, 1987, **91**, 2129.
- 3 H.A. Liebhafsky and A. Moammad, *J. Am. Chem. Soc.*, 1933, **55**, 3977.
- 4 G. Schmitz, *Int. J. Chem. Kinet.* 2004, **36**, 480.