# On the Kinetics of the Periodate + Iodide Reaction

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The reaction between periodate and iodide has been re-examined. The hydrogen-ion-dependent path is confirmed.

The rate of the reaction between periodate and iodide was measured by us in 1966 [1] using a microtitration method which is capable of great accuracy.[2] We found at least two reaction paths, one zero order and the other first order with respect to the hydrogen-ion concentration, both being first order with respect to the periodate-ion and iodide-ion concentrations. More recently, using a different method, Marques and Hasty [3] did not find any dependence of the rate upon $[H^+]$. They attributed this to an artefact of our results, namely to the reaction of periodate with thiosulphate. In reality, during our experiments thiosulphate was present only for a very small fraction of the reaction time, so that their explanation does not appear convincing. However, the discrepancy is important because it throws doubt on the validity of the microtitration method which has been used by us in a number of cases.[4]

We considered it useful therefore to re-examine this reaction using a different method, namely spectrophotometric determination of the iodine formed during the reaction. Other conditions, in particular the concentrations of $IO_4^-$ and $I^-$, were approximately the same as in our previous study [1] and the hydrogen-ion concentration was maintained not by using buffers (as done by Marques and Hasty [3]) but by adding perchloric acid.

It was important to measure the initial rate of reaction so as to avoid where possible complications due to the reaction of $IO_3^-$ with $I^-$ and in general to be sure of the composition of the reacting solution. Therefore, it was not possible to use the conventional method of reading the optical density at the end of reaction, and it was necessary to measure the small amount of $I_2$ and $I_3^-$ at the beginning of the reaction using the relevant absorption coefficient determined independently.

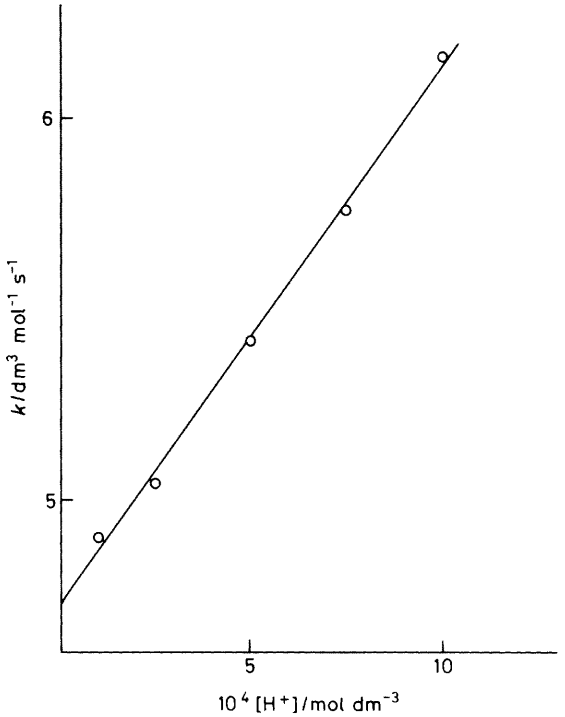

**Figure.** Dependence of the second-order rate constant on the hydrogen-ion concentration at $[KIO_4] = 1 \times 10^{-4}$, $[KI] = 2 \times 10^{-4}$, $I = 0.002$ mol dm$^{-3}$ ($KClO_4$), and 25 °C

## Experimental

The salts were commercial products of high purity used without further purification. A Perkin-Elmer 552 spectrophotometer and 100-mm cells were used to determine the optical density at 468 nm corresponding to the isosbestic point of the system $I_2$–$I_3^-$. The reacting solutions were protected from oxygen by means of $N_2$. We have tested that under our experimental conditions iodide ions are not oxidized by perchloric acid.

## Results

The Figure shows a plot of the second-order rate constant as a function of the hydrogen-ion concentration. Clearly there is a linear dependence of $k$ upon $[H^+]$, as found in our earlier study. Extrapolation to $[H^+] = 0$ yields an intercept of 4.72 ± 0.03 dm$^3$ mol$^{-1}$ s$^{-1}$ and a slope of (1.42 ± 0.04) × 10$^3$ dm$^6$ mol$^{-2}$ s$^{-1}$ respectively in fair agreement with the previous values of 4.78 ± 0.06 dm$^3$ mol$^{-1}$ s$^{-1}$ and (2.73 ± 0.24) × 10$^3$ dm$^6$ mol$^{-2}$ s$^{-1}$. The discrepancy in slope may be due to the fact that in this work the ionic strength was kept constant at 0.002 mol dm$^{-3}$ whereas in the previous study it changed from 0.000 31 to 0.000 81 mol dm$^{-3}$.

The validity of the microtitration method for measuring the reaction rates of this and similar reactions [4] is therefore confirmed and the dependence upon $[H^+]$ is by no means an artefact since no $Na_2S_2O_3$ was present under the present conditions. On the other hand, the fact that periodate exists in acidic solution in several forms ($IO_4^-$, $H_4IO_6^-$, $H_5IO_6$, or $H_3IO_6^{2-}$) [5] whose concentrations depend upon $[H^+]$ makes it very unlikely that there would be no dependence upon $[H^+]$. The reason for the difference from the results of Marques and

Hasty is probably due to the small range of hydrogen-ion concentration investigated by these authors and to the fact that the path dependent upon $H^+$ is much less important than the $H^+$-independent path under the conditions used by them. The minimum pH used by them was 3.51 which corresponds, more or less, to the second point in the present Figure. Moreover, they used a buffer system and it is possible that the presence of undissociated acetic acid has some influence on the rate.

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