The Oxidation of Hydroxylamine by Iodate or Periodate: an Oligo-oscillatory Reaction

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In the oxidation of hydroxylamine with either iodate or periodate three extrema on the iodide concentration *versus* time curves may be found. Perturbing the periodate oxidation with malonic acid increases the number of extrema to five. Taking into account the five rate equations of the component reactions, all except one of which can be independently obtained, and considering the inhibitory effect of iodate on the iodine–hydroxylamine reaction, good agreement has been found between the calculated and experimental change in concentrations of iodide, iodine, and nitrous acid. These reactions are the first oligo-oscillatory ones in which only one oxidant and one reductant is involved initially.

REACTIONS in which the concentration of one or more intermediates exhibit several extrema as a function of time are termed oligo-oscillatory reactions. We reported [1,2] recently that such a reaction can be designed by perturbing a ' clock ' reaction with a suitable reagent. We found, however, that even a simple reaction may take place in an oligo-oscillatory manner. Simple means here that only *one oxidant* and *one reductant* are initially involved, but the mechanism of an oligo-oscillatory reaction is inherently rather complex.

When hydroxylamine is oxidized by either iodate or periodate in an acidic medium the concentration of iodide shows three extrema as a function of time in certain concentration ranges of the reactants (Figure 1).

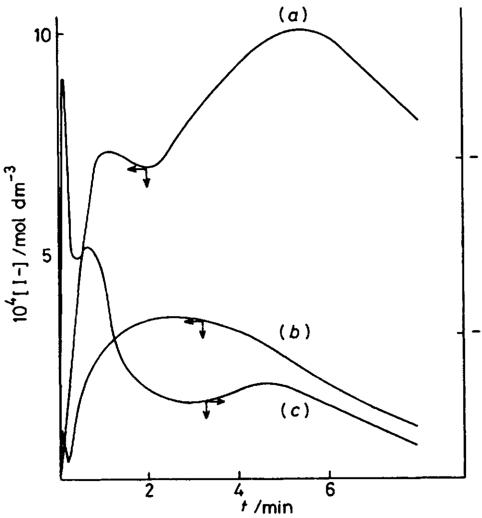

FIGURE 1 The concentration of iodide ion *vs.* time: (*a*) $[IO_3^-]_0$ = 0.005, $[NH_3OH^+]_0$ = 0.011; (*b*) $[IO_4^-]_0$ = 0.005, $[NH_3OH^+]_0$ = 0.011; and (*c*) $[IO_4^-]_0$ = 0.02, $[NH_3OH^+]_0$ = 0.03 mol dm^{-3}. [malonic acid] = 0.045 mol dm^{-3}, pH = 2.5 (adjusted with acetic acid), 25 °C

From the curves of Figure 2, the oligo-oscillatory character of the reaction is manifested in a rather narrow range of the ratio of the concentrations of the reactants. This range is highly dependent on the hydrogen-ion concentration but only slightly on the absolute concentration of iodate and hydroxylamine. In the case of oxidation with iodate in 0.5 mol dm^{-3} acetic acid solution, oligo-oscillatory behaviour was found when $2.4 > [NH_3OH^+]/[IO_3^-] > 2.0$. A small increase or decrease of the hydrogen-ion concentration leads to the disappearance of this peculiar phenomenon. In the case of oxidation with periodate, oligo-oscillatory behaviour is found in a much broader range of hydrogen-ion concentration. Thus, in 0.1 mol dm^{-3} perchloric acid solution three extrema were found when $4 > [NH_3OH^+]/[IO_4^-] > 1.5$. On decreasing the hydrogen-ion concentration this range narrows, *e.g.* in 0.5 mol dm^{-3} acetic acid solution the limits are 2.5 and 1.8, respectively.

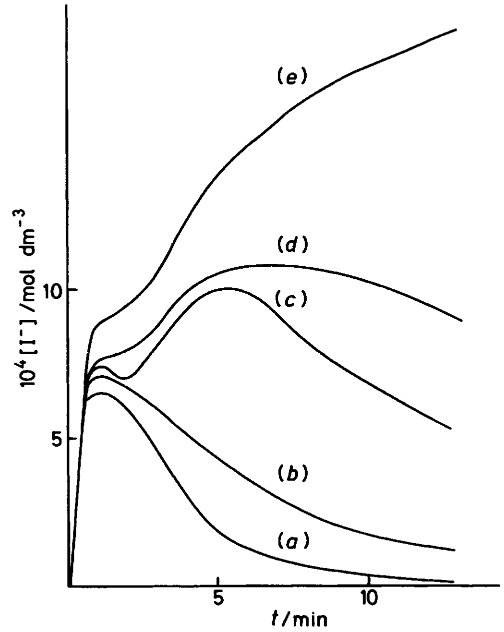

FIGURE 2 The concentration of iodide ion *vs.* time in the iodate–hydroxylamine reaction. $[IO_3^-]_0$ = 0.005; $[NH_3OH^+]_0$ = 0.008 (*a*), 0.010 (*b*), 0.011 (*c*), 0.012 (*d*), and 0.015 mol dm^{-3} (*e*); pH = 2.5, 25 °C

By perturbing the periodate oxidation of hydroxylamine with malonic acid, as many as *five* extrema are found in the concentration of iodide as a function of time [Figure 1, curve (*c*)].

The oxidation with iodate is obviously much simpler and (as will be shown) a quantitative description of this reaction is possible. The stoicheiometry of the reaction depends on the initial concentration of the reactants. In the concentration range of the oligo-oscillatory behaviour iodate is reduced to iodine (iodide being an intermediate only) and hydroxylamine is oxidized mainly to dinitrogen oxide and to nitrous acid, only trace amounts of NO being found.

Since the formation of iodine and iodide occurs in the initial period of the reaction when most of the unreacted hydroxylamine is still present, the oxidation of hydroxylamine with iodine should be considered as an essential part of the whole reaction. The kinetics of this reaction were recently elucidated by us.[3] In order to describe the whole reaction system the oxidation of hydroxylamine and iodide with iodate should also be taken into account. The increase of the nitrous acid and iodide concentration permits assumption of the stoicheiometry (1) for the initial reaction. The reaction between iodate

$$2IO_3^- + 3\,NH_3OH^+ \longrightarrow 3\,HNO_2 + 2I^- + 3\,H_2O + 3H^+ \quad (1)$$

and iodide is as (2). Based on the study of the oxidation

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3\,I_2 + 3H_2O \quad (2)$$

of hydroxylamine with iodine three more reactions (3)—(5) should be considered. Each of these reactions is

$$NH_3OH^+ + 2I_2 + H_2O \longrightarrow HNO_2 + 4I^- + 5H^+ \quad (3)$$

$$NH_3OH^+ + HNO_2 \longrightarrow N_2O + 2H_2O + H^+ \quad (4)$$

$$2HNO_2 + 2I^- + 2H^+ \longrightarrow 2NO + I_2 + 2H_2O \quad (5)$$

rather complex and the corresponding rate equations are known except for the first one. For this a simple second-rate law (1′) is assumed. The rate of oxidation of iodide with iodate under our experimental conditions is as in (2′), while the rate of the reaction between iodine and hydroxylamine is given by (3′).[3] The rate equation

$$v_1 = -d[IO_3^-]/dt = k_1[IO_3^-][NH_3OH^+] \quad (1')$$

$$v_2 = -d[IO_3^-]/dt = k_2[IO_3^-][I^-]^2[H^+]^2 \quad (2')$$

$$v_3 = -\frac{d[I_2]}{dt} = \left(k_3 + \frac{k_3'}{[H^+]}\right)\frac{[NH_3OH^+][I_2]}{1 + K[I^-] + Q[I^-]^2} \quad (3')$$

for the oxidation of hydroxylamine with nitrous acid has been determined by Hughes and Stedman [4] and has been

$$v_4 = -d[NH_3OH^+]/dt = k_4[HNO_2][NH_3OH^+][H^+] + k_4'[NH_3OH^+][HNO_2][I^-] \quad (4')$$

extended by us [3] by use of a second term which takes into account the iodide-catalysed path [equation (4′)].

The reaction between nitrous acid and iodide plays a minor role in the whole reaction system and its rate equation (5′) has been determined by Dózsa *et al.*[5]

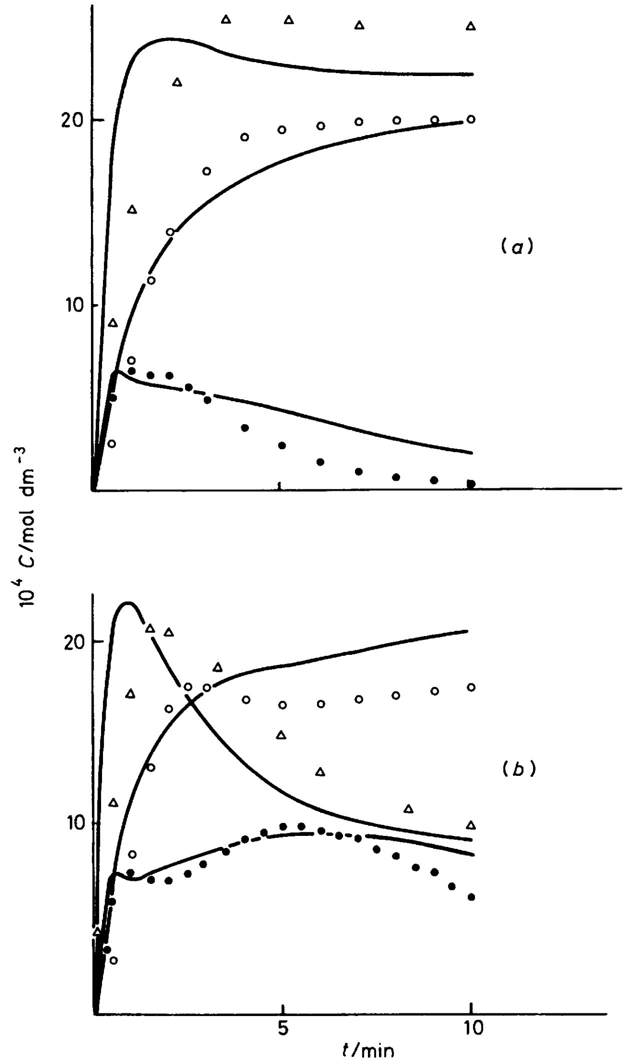

FIGURE 3 The kinetic curves of the iodate–hydroxylamine reaction. $[IO_3^-]_0 = 0.005$; $[NH_3OH^+]_0 = 0.015$ (*a*) and 0.011 mol dm^{-3} (*b*). The points (●, I^-; ○, I_2; △, HNO_2) indicate experimentally measured values; the full lines were calculated using the following set of rate constants: $k_1 = 0.85$ dm^3 mol^{-1} s^{-1}; $k_2 = 6 \times 10^8$ dm^{12} mol^{-4} s^{-1}; $k_3 = 2.3$ dm^3 mol^{-1} s^{-1}; $k_3' = 6.7 \times 10^{-2}$ s^{-1}; $K = 785$ dm^3 mol^{-1}; $Q = 4\,9 \times 10^4$ dm^6 mol^{-2}; $Q' = 5 \times 10^3$ dm^3 mol^{-1}; $Q'' = 4 \times 10^6$ dm^6 mol^{-2}; $k_4 = 2.5$ dm^6 mol^{-2} s^{-1}; $k_4' = 3.5 \times 10^3$ dm^6 mol^{-2} s^{-1}; $k_5 = 3.7 \times 10^3$ dm^9 mol^{-3} s^{-1}; $k_5' = 3.7 \times 10^{10}$ dm^{15} mol^{-5} s^{-1}

The solution of the differential equations (1′)—(5′) has been obtained by applying a fourth-order Runge–Kutta method. We found, however, that to obtain

$$v_5 = +d[I_2]/dt = k_5[HNO_2][H^+][I^-]^2 + k_5'[HNO_2]^2[H^+]^2[I^-]^2 \quad (5')$$

three extrema in the iodide concentration as a function

$$v_3 = \frac{-d[I_2]}{dt} = \left(k_3 + \frac{k_3'}{[H^+]}\right)\frac{[NH_3OH^+][I_2]}{1 + K[I^-] + Q[I^-]^2 + Q'[IO_3^-] + Q''[IO_3^-][I^-]} \quad (3'')$$

of time required a drastic change of the experimentally found rate constants of (3′). (Both k_3 and k_3' had to be taken as a tenth of the experimentally found values.) Figure 3 shows that a rather good agreement between the calculated and found curves is achieved if (3′) is replaced by rate equation (3″). We think that the difference in the denominators of (3′) and (3″) is a consequence of the reaction of iodate with NH_2OHI^+, an intermediate in the oxidation of hydroxylamine with

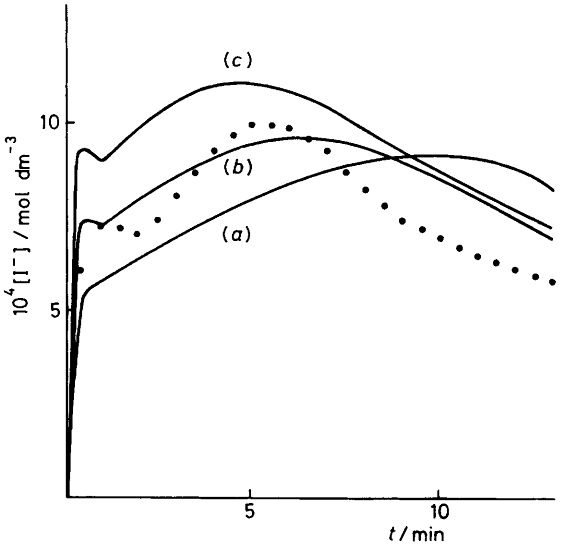

FIGURE 4 Influence of k_1 on the change in iodide concentration as a function of time in the first stage of the reaction. The numerical values of other constants are as in Figure 3. Points indicate measured values. k_1 = 0.425 (*a*), 0.85 (*b*), and 1.7 $dm^3\ mol^{-1}\ s^{-1}$ (*c*)

$$NH_2OH + I_2 \rightleftharpoons NH_2OHI^+ + I^- \quad (6)$$

$$NH_2OHI^+ \longrightarrow NOH + I^- + 2H^+ \quad (7)$$

iodine.[3] Assuming two-electron oxidation reactions, there are three possibilities: either the nitrogen or the iodine atom of NH_2OHI^+ or both are oxidized [equations (8)—(10)].

$$NH_2OHI^+ + IO_3^- \longrightarrow NOH + I^+ + IO_2^- + H_2O \quad (8)$$

$$NH_2OHI^+ + IO_3^- + H_2O \longrightarrow NH_2OH + 2HIO_2 \quad (9)$$

$$NH_2OHI^+ + IO_3^- \longrightarrow N + I^{2+} + IO_2^- + H_2O + OH^- \quad (10)$$

Reaction (10) is very unlikely because of the instability of I^{2+} and in fact no formation of elementary nitrogen was observed. The occurrence of reaction (8) cannot be excluded, but the inhibitory effect of iodate can only be explained by reaction (9). Applying a steady-state treatment to NH_2OHI^+ appearing in (6), (7), and (9) and considering the tri-iodide equilibrium and the protonation of hydroxylamine, results in the hydrogen-ion concentration dependent term of (3″). The pH-independent term can similarly be obtained by considering analogous reactions of NH_3OHI^{2+}. The contribution of this term is negligible in the pH range where the oligo-oscillatory behaviour is observed. The formation of HIO_2 slightly increases the rate of (2).

The form of the curves is influenced by k_4', too. [The first term of (4′) is always negligible.] Only an approximate value, $\approx 10^4\ dm^6\ mol^{-2}\ s^{-1}$, is available for k_4'. The calculated curves of Figure 3 were obtained using $k_4' = 3.5 \times 10^3\ dm^6\ mol^{-2}\ s^{-1}$. The positions of the first and second maxima sensibly depend on the value of k_1 (see Figure 4).

EXPERIMENTAL

The analytical procedures for the iodometric determination of hydroxylamine, potentiometric monitoring of iodide-ion concentration, and spectrophotometric determination of iodine and nitrous acid have been described previously.[3] The gaseous products were analysed by an ATOMKI NZ-850 type quadrupole mass spectrometer. The solutions were prepared with doubly distilled water and were deoxygenated by bubbling argon through the solution. The pH was adjusted with acetic acid. The ionic strength was constant due to the high concentration of acetic acid. To avoid a loss of iodine during the reaction the reaction vessel was closed.

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