Kinetics of the Oxidation of Hydrazine by Periodate

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Hydrazine is quantitatively oxidized to nitrogen by periodate in a weakly acidic solution. The kinetics of the reaction were followed by measuring the volume of nitrogen evolved, and by determination of iodine and iodide concentration. The experimental curves were quantitatively described by taking into account five component reactions: periodate–hydrazine, iodate–hydrazine, iodine–hydrazine, periodate–iodide, and iodate–iodide. The kinetics of these component reactions are known in the literature. To improve the agreement between measured and calculated curves the calculation was corrected for the loss of iodine due to nitrogen evolution.

We have discovered recently that the oxidation of hydroxylamine by iodate or periodate is an oligo-oscillatory reaction:[1] the concentration of iodide exhibits several extrema with time in a relatively narrow range of the initial concentration of reactants. It is known that hydrazine reacts with iodine[2] with kinetics that are fairly similar to those of the hydroxylamine–iodine reaction.[3] Considering this and other similarities the question arises whether the oxidation of hydrazine with iodate or periodate represents this unusual type of kinetic behaviour.

Hasty[4] studied the reaction of hydrazine with iodate applying an iodide-selective electrode. He found that, in the presence of a small amount of iodide, the direct reaction between hydrazine and iodate is faster than the oxidation by iodine formed in the iodide–iodate reaction. Hasty applied an excess of hydrazine and found a monotonous increase of iodide concentration with time, with no unusual feature. According to our investigations oligo-oscillation cannot be observed even in the presence of excess of iodate: the concentration of iodide exhibits one maximum with time.

The oxidation of hydrazine by periodate has been studied by Verma and Grover,[5] mainly from the point of view of its analytical application. In an excess of periodate they found that periodate is quantitatively reduced to iodate and dinitrogen is formed. According to their kinetic studies the reaction is first order both for periodate and hydrazine. Plausibly, when hydrazine is in excess the system is much more complicated, several reactions take place and several intermediates should be considered. Theoretically there are therefore better chances for the appearance of oligo-oscillatory kinetics for either iodine or iodide, the species of detectable concentration. Though such oligo-oscillatory behaviour was not found, the results allow us to establish a mechanism; moreover, the comparison with the oxidation of hydroxylamine may throw light on the prerequisite of oligo-oscillations.

Experimental

Stock solutions of sodium periodate were prepared daily and stored in the dark. Hydrazinium hydrogensulphate was recrystallized before use. The pH was adjusted and kept constant using potassium dihydrogenphosphate–phosphoric acid buffer solutions. Prior to the measurements the solutions were deaerated with nitrogen and the reactions were carried out in a closed system with the exclusion of air. The reactions were initiated by injecting an appropriate amount of hydrazine stock solution and were followed by continuous monitoring of iodide and iodine concentrations and by measuring the volume of gaseous products. The iodide ion concentration was monitored using a Radelkis OP-1712D iodide-selective electrode with a saturated calomel electrode (s.c.e.) as reference and a Radiometer PHM 64 pH-meter, equipped with a Radelkis OH-814/1 recorder. To avoid disturbing effects of chloride a sodium nitrate salt bridge was used. The working electrode was calibrated using iodide solutions containing all the components of the reaction system except iodate. It was established that the KH_2PO_4–H_3PO_4 buffer does not affect the potential of this iodide-selective electrode at concentrations below 0.1 mol dm^{-3}, which is sufficient for maintaining pH and ionic strength constant. At concentrations of iodide below 10^{-5} mol dm^{-3} an increase of the hydrazine concentration results in a small increase of the potential. Longer contact of the electrode with hydrazine solutions leads to a decrease of its iodide sensitivity. (During the early measurements we observed three maxima in the potential of the iodide-selective electrode, under certain initial conditions. Initially we considered the reaction to be oligo-oscillatory. Later it became clear that hydrazine effects the potential of the electrode and during longer contacts with hydrazine solutions the electrode undergoes irreversible changes. Superposition of these factors on the factual changes of iodide concentration resulted in an apparent oligo-oscillatory behaviour.)

Iodine concentration was determined spectrophotometrically, at the isosbestic point of iodine and tri-iodide ion (λ = 468 nm, ε = 740 $dm^3 mol^{-1} cm^{-1}$). Bubbles of the evolved gas did not attach to the wall of carefully cleaned cells so they did not interfere significantly with the measurements. Gaseous products were analyzed on a mass spectrometer (ATOMKI NZ-850); the amounts of gases were measured volumetrically. When the solutions were presaturated with nitrogen and the rate of stirring was high enough (>700 r.p.m.) the rate of the evolution of N_2 was controlled by the kinetics of the chemical reaction.

Kinetic measurements were carried out at a constant temperature of 25 °C.

Results and Discussion

Stoicheiometry.—The behaviour of hydrazine towards one- and two-electron oxidizing agents is different. In the case of one-electron oxidations ammonia and nitrogen are formed in amounts depending on the initial concentrations. Reagents capable of transfer of two electrons in one step usually oxidize hydrazine to nitrogen. In applying an excess of periodate the nitrogen formation is stoicheiometric (Table 1), and according to the mass spectrometric analysis no other gaseous product is formed in the reaction.

No ammonia or nitrous acid could be detected among the products in solution. Periodate gives rise to the formation of iodate, iodine, or iodide, or a mixture of the three species, depending on the initial concentrations. When the hydrazine concentration exceeds twice the initial concentration of

Table 1. Volume of N_2 evolved in the hydrazine–periodate reaction: $T = 20$ °C, at pH 2.0 (at the end of the reaction), volume of reaction mixture = 40 cm^3

$[N_2H_5^+]$/ mol dm^{-3}	$[IO_4^-]$/ mol dm^{-3}	Volume of N_2 (cm^3) Calc.	Exptl.
0.001	0.005	0.96	1.01
0.002	0.005	1.92	2.01
0.003	0.005	2.88	2.93
0.004	0.005	3.84	3.80
0.001	0.010	0.96	1.02
0.002	0.010	1.92	1.80
0.003	0.010	2.88	2.95
0.004	0.010	3.84	3.95

Table 2. Concentrations of iodide, iodine, and iodate formed in the hydrazine–periodate reaction at different initial concentrations of reactants: * at pH 2.0, $[IO_4^-]_0 = 0.005$ mol dm^{-3}

$10^3[N_2H_5^+]_0$	$10^3[IO_3^-]$	$10^3[I_2]$	$[I^-]$
mol dm^{-3}			
12.5	0	0	5.1×10^{-3}
10.0	0	0	5.0×10^{-3}
9.0	0	1.96	1.1×10^{-3}
7.5	0.6	2.20	1.0×10^{-5}
7.0	1.5	1.75	$<5 \times 10^{-6}$
6.0	2.0	1.50	$<5 \times 10^{-6}$
5.0	3.1	0.95	$<5 \times 10^{-6}$
4.0	5.1	0.45	$<5 \times 10^{-6}$
3.0	4.6	0.20	$<5 \times 10^{-6}$
2.0	5.0	0	$<5 \times 10^{-6}$

* Concentrations of I_2 and I^- were determined experimentally; that of IO_3^- was calculated from the mass balance with $[IO_4^-]_0$ known.

periodate, all of the latter reduces to iodide according to the stoicheiometry of equation (1). Below this concentration of

$$IO_4^- + 2N_2H_5^+ \longrightarrow I^- + 2N_2 + 4H_2O + 2H^+ \quad (1)$$

hydrazine, periodate is reduced only to iodine and iodate (Table 2). Applying periodate in more than two-fold excess, the reaction takes place according to the stoicheiometry of equation (2).

$$2IO_4^- + N_2H_5^+ \longrightarrow 2IO_3^- + N_2 + 2H_2O + H^+ \quad (2)$$

Kinetics.—The kinetics of the reaction are very complex but, fortunately, the amount of three species, iodide ion, iodine, and evolved nitrogen can be followed as a function of time.

Kinetics of nitrogen evolution. Kinetic curves of nitrogen evolution under different initial conditions are shown in Figure 1. An obvious feature of these curves of unusual shape is their point of inflection which is not observed at small concentrations of hydrazine. The appearance of this inflection point leads to the conclusion that nitrogen is formed at least in two reaction pathways, one of them dominating in nitrogen evolution before the inflection point, the other being dominant after it. The amount of nitrogen up to the point of inflection is 2—2.5 cm^3, which corresponds under our experimental conditions to the hydrazine necessary for the reduction of all the initial periodate to iodate. If the initial amount of hydrazine is not more than that required for the periodate to iodate reduction, no inflection point occurs on the kinetic curves. Based on these findings it can be assumed that the first component reaction in the periodate–hydrazine system is the one described by equation (2), the contribution of which to the rate of the overall reaction being dominant during the initial phase. Therefore, determining the initial rate of nitrogen evolution gives a possibility for determining the rate equation of reaction (2). According to our results the rate of reaction (2), v_2, at a given pH is proportional to the initial concentrations both of periodate and hydrazine, equation (2a).

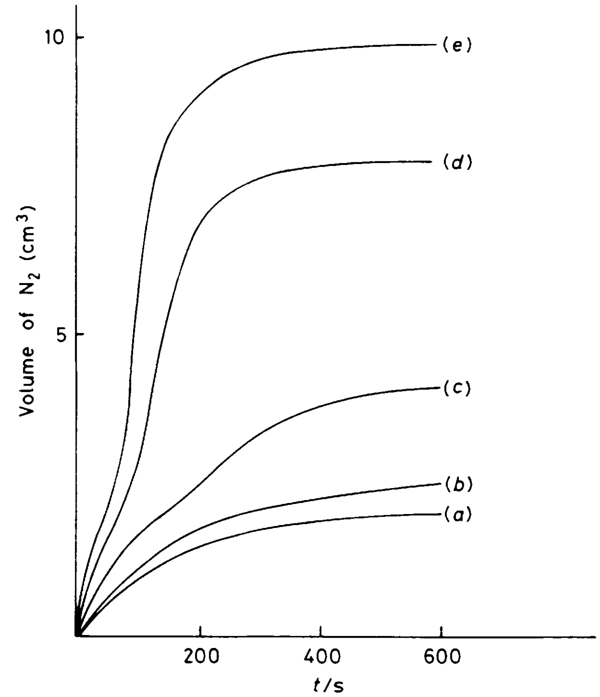

Figure 1. Kinetics of nitrogen evolution: volume of the reaction mixture = 30 cm^3; $[IO_4^-]_0 = 0.005$ mol dm^{-3}; at pH 2.0; $[N_2H_5^+]_0$ = 0.002 (a), 0.0025 (b), 0.004 (c), 0.008 (d), and 0.010 mol dm^{-3} (e); $T = 25$ °C

$$v_2 = \frac{d[N_2]}{dt} = \frac{-d[N_2H_5^+]}{dt} = k_2[N_2H_5^+][IO_4^-] \quad (2a)$$

$$k_2 = 1.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

In the case of an excess of periodate ($[IO_4^-]_0 > 2[N_2H_5^+]_0$) both the initial rate and the kinetic curve of nitrogen evolution can be calculated correctly by equation (2a). This means that under such circumstances the reaction is relatively simple because reactions (3)—(6) have no great significance.

Changes in the concentration of iodide ion during the reaction. When periodate is in a large excess over hydrazine, iodide as intermediate can be detected only in trace amounts. Significant iodide concentrations arise when $[IO_4^-]_0 < 2[N_2H_5^+]_0$ and this passes through a maximum with time, characteristic for an intermediate. A greater excess of hydrazine makes iodide an end-product, the concentration of which increases monotonously with time, with a shoulder on the kinetic curve. At an approximate ten-fold excess of hydrazine even this shoulder disappears and periodate is reduced fairly fast to iodide (Figure 2).

Formation of iodide ion starts in the reaction of hydrazine and the iodate formed in reaction (2): see reaction (3). In his

$$2IO_3^- + 3N_2H_5^+ \longrightarrow 2I^- + 6H_2O + 3H^+ + 3N_2 \quad (3)$$

paper mentioned earlier Hasty[4] gives the rate equation (3a) for this reaction.

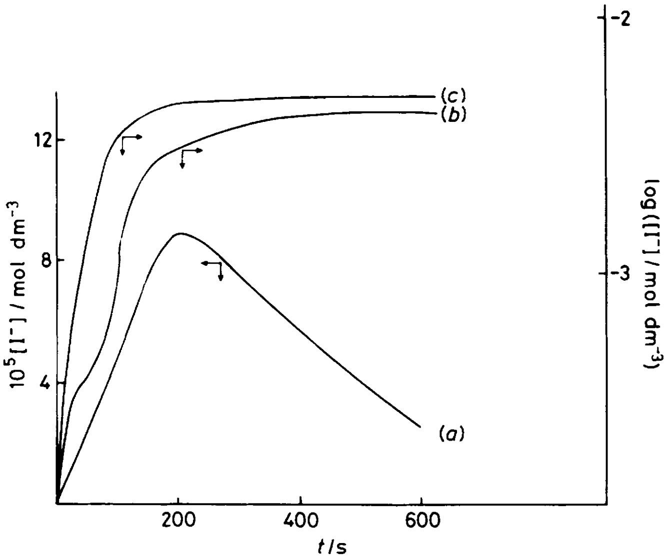

Figure 2. Change of iodide ion concentration with time in the hydrazine-periodate reaction: $[IO_4^-]_0 = 0.005$ mol dm^{-3}; at pH 2.0; $[N_2H_5^+]_0 = 0.004$ (*a*), 0.010 (*b*), and 0.05 mol dm^{-3} (*c*); $T = 25$ °C

$$v_3 = -\tfrac{1}{2}\frac{d[IO_3^-]}{dt} = k_3[N_2H_5^+][IO_3^-][H^+]^2 \qquad (3a)$$

$$k_3 = 1.5 \times 10^{-3}\ \text{dm}^9\ \text{mol}^{-3}\ \text{s}^{-1}$$

Changes of iodine concentration with time. The shape of the iodine concentration *vs.* time curves depends largely on the concentrations of reactants. Figure 3 shows the changes in the concentration of iodine with time at a fixed concentration of periodate and several different concentrations of hydrazine. When the initial concentration of hydrazine is less than half of that of the periodate, iodine does not appear in significant quantity. Above this concentration the kinetic curve of iodine formation shows an induction period and a stoicheiometric excess of hydrazine ($[N_2H_5^+]_0 > 2[IO_4^-]_0$) makes iodine an intermediate, characterized by a maximum on its kinetic curve. Figure 3 shows the sum of the concentrations of iodine and tri-iodide ion.

Iodine may be formed in this system by two plausible processes, reactions (4) and (5). On the other hand, consumption of iodine is the result of its reaction with hydrazine present: reaction (6).

$$IO_4^- + 2I^- + 2H^+ \longrightarrow IO_3^- + I_2 + H_2O \qquad (4)$$

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

$$N_2H_5^+ + 2I_2 \longrightarrow N_2 + 4I^- + 5H^+ \qquad (6)$$

The steep rise after the inflection point in the curves of Figure 1 is presumably due to reaction (6), the rate of which is evidently higher at higher iodine concentrations.

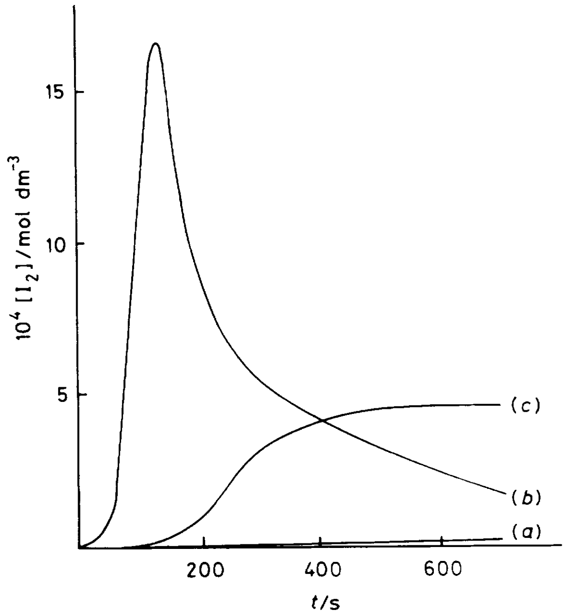

Figure 3. Change of the iodine concentration with time in the hydrazine–periodate reaction: $[IO_4^-]_0 = 0.005$ mol dm^{-3}; at pH 2.0; $[N_2H_5^+]_0 = 0.0025$ (*a*), 0.004 (*b*), and 0.010 mol dm^{-3} (*c*); $T = 25$ °C

It can be seen that the changes with time of all the three measured concentrations can be qualitatively explained on the basis of reactions (2)—(6). These processes are complex themselves. Several results are known in the literature concerning the kinetics of reactions (4), (5), and (6) which can be studied separately. According to Indelli *et al.*[6] the rate of reaction (4) depends on hydrogen ion concentration. Earlier work [7,8] and the recent results of Marques and Hasty [9] do not support this finding. However, there is a general agreement in the literature that the reaction is first order with respect both to periodate and iodide. Since in our experiments the hydrogen ion concentration was kept constant the controversy has no relevance to our results and equation (4a) gives the rate of reaction (4). The value of k_4 slightly increases with increasing

$$v_4 = -\frac{d[IO_4^-]}{dt} = k_4[IO_4^-][I^-] \qquad (4a)$$

ionic strength.[9] At the ionic strength of 0.1 mol dm^{-3} applied in our experiments and at 25 °C, $k_4 = 9.8$ dm^3 mol^{-1} s^{-1}.

The rate equation of the well known iodate–iodide reaction under our experimental conditions takes the form of equation (5a). In fact, $[I^-]$ in equation (5a) represents the sum of $[I^-]$

$$v_5 = -\frac{d[IO_3^-]}{dt} = k_5[IO_3^-][I^-]^2[H^+]^2 \qquad (5a)$$

$$k_5 = 6 \times 10^8\ \text{dm}^{12}\ \text{mol}^{-4}\ \text{s}^{-1}$$

and $[I_3^-]$. Since the tri-iodide ion concentration never exceeds 10% of the iodide ion concentration and because of the comparable reactivity of these two ions with iodate,[10] this simplification results in a negligible error.

The oxidation of hydrazine by iodine, reaction (6), was studied by King *et al.*,[2] who arrived at the rate equation (6a).

$$v_6 = -\tfrac{1}{2}\frac{d[I_2]}{dt} = k_6\frac{[I_2][N_2H_5^+]}{[H^+](1 + K[I^-])(1 + Q[I^-])} \qquad (6a)$$

$$k_6 = 0.145\ \text{s}^{-1},\ K = 725\ \text{dm}^3\ \text{mol}^{-1},\ Q = 12\ \text{dm}^3\ \text{mol}^{-1}$$

Making use of the stoicheiometric reactions (2)—(6) and the rate equations (2a)—(6a) the system of differential equations can be set up.

The system of equations (7)—(11) was solved numerically by the Runge–Kutta method. Consumption of hydrazine was considered equal to the evolved nitrogen. The calculated con-

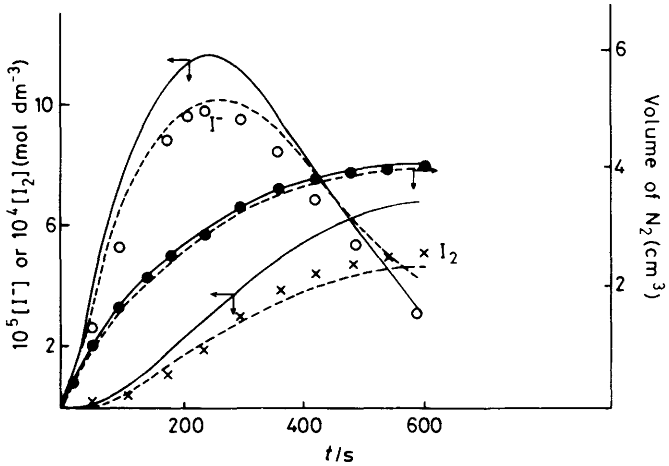

Figure 4. Kinetic curves of the hydrazine–periodate reaction. Points represent measured data; the lines were calculated with (— — —) and without (——) taking iodine loss into account: $[IO_4^-]_0 = 0.005$ mol dm^{-3}; at pH 2.0; $[N_2H_5^+]_0 = 0.004$ mol dm^{-3}; $T = 25$ °C

$$\frac{d[N_2H_5^+]}{dt} = -v_2 - 3v_3 - v_6 \qquad (7)$$

$$\frac{d[IO_4^-]}{dt} = -2v_2 - v_4 \qquad (8)$$

$$\frac{d[IO_3^-]}{dt} = 2v_2 - 2v_3 + v_4 - v_5 \qquad (9)$$

$$\frac{d[I^-]}{dt} = 2v_3 - 2v_4 - 5v_5 + 4v_6 \qquad (10)$$

$$\frac{d[I_2]}{dt} = v_4 + 3v_5 - 2v_6 \qquad (11)$$

centration *vs.* time curves agree well with the experimental ones in the case of nitrogen, but in the case of iodine and iodide they run above the experimental ones. Our explanation is that nitrogen removes some of the iodine from the solution. The efflux of iodine can be regarded as proportional to the concentration of iodine in the solution and to the rate of nitrogen evolution, the latter being proportional to the unreacted hydrazine present. Therefore the loss of iodine can be taken into consideration by using equation (12) instead of (11) for the integration, k_v being a factor of rate constant character.

$$\frac{d[I_2]}{dt} = v_4 + 3v_5 - 2v_6 - k_v[I_2][N_2H_5^+] \qquad (12)$$

$$k_v = 2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

With this correction the calculated curves agree fairly well with the experimental ones (Figure 4).

We wish to emphasize that we did not aim to construct a mechanism of elementary steps but considered complex reactions as building blocks of the mechanism. Under the given circumstances these component reactions do proceed, and in this particular case the results justify their use as a necessary and sufficient basis for a mechanism.

Contrary to the oxidation of hydroxylamine by periodate the oxidation of hydrazine with periodate is not an oligo-oscillatory reaction. Periodate, iodate, and iodine, capable of two-electron oxidations, oxidize the nitrogen of hydrazine from −2 to 0, so it leaves the system as molecular nitrogen. Therefore, on the nitrogen side, there are no stable intermediates; *i.e.* one of the likely prerequisites of oligo-oscillation, which could be found in the hydroxylamine–periodate system, is not provided.

Acknowledgements

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