Kinetics of the Bromate–Iodide–Ascorbic Acid Clock Reaction: Different Mechanism of the Molybdenum and Vanadium Catalysis

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The kinetics of the molybdenum(VI)- and vanadium(V)-catalysed bromate–iodide–ascorbic acid clock reaction has been studied by means of spectrophotometry and pH-metric measurements. Two different types of catalysis were detected in this clock reaction. It was shown that Mo^{VI} catalyses the component process bromate + iodide of the clock system, while V^{V} catalyses the direct reaction between bromate and ascorbic acid. The rate equation $r = k_2[BrO_3^-][I^-][H^+]^2 + k_2'[BrO_3^-][I^-][H^+]^2[Mo^{VI}]$ describes the kinetics of the Mo-catalysed system, where $k_2 = 44 \pm 2$ dm^9 mol^{-3} s^{-1} and $k_2' = (4.3 \pm 1) \times 10^6$ dm^{12} mol^{-4} s^{-1}. In the vanadium-catalysed clock reaction the equation $r = k_1'[BrO_3^-][V^V] + k_2[BrO_3^-][I^-][H^+]^2$ was found, where $k_1' = 9.6 \pm 1$ dm^3 mol^{-1} s^{-1} and $k_2 = 42.6 \pm 2$ dm^9 mol^{-3} s^{-1}. At lower acidities (pH > 3) more complex kinetics appeared and further study was abandoned.

Owing to their spectacular behaviour, 'clock' (or Landolt) reactions are often used as lecture demonstration experiments in teaching reaction kinetics. The first clock reactions were studied a hundred years ago by Landolt,[1] and today many similar systems are known.[2–7] They have applications in analytical chemistry because numerous compounds exhibit catalytic effects on the different systems and selective and very sensitive analytical methods have been elaborated.[3,4,7–10] The very simple visual detection of the end-point (sometimes called 'chronometry') enables inexpensive determinations to be made with reasonable accuracy, but some instrumentation increases precision and automation.[9–11] Recently, clock reactions have constituted the basis of the design of systems exhibiting the overshoot–undershoot phenomenon[12] and other non-linear behaviour, *e.g.* bistability in a continuous stirred tank reactor (c.s.t.r.).[13]

The kinetics of many clock reactions have been investigated. The largest set of clock systems has the general form in equations (1)—(3). This set of equations summarises the

$$XO_3^- + 3\,A_{red} \xrightarrow{\text{very slow}} X^- + 3\,A_{ox} \quad (1)$$

$$XO_3^- + 5\,X^- + 6\,H^+ \xrightarrow{\text{slow}} 3\,X_2 + 3\,H_2O \quad (2)$$

$$X_2 + A_{red} + H_2O \xrightarrow{\text{fast}} 2\,X^- + A_{ox} + 2\,H^+ \quad (3)$$

common characteristics of the halogen-based systems;[1] X = halogen, A = reductant, *e.g.* sulphite, thiosulphate, ascorbate, arsenite, hexacyanoferrate(II) *etc.* The thermodynamic and stoicheiometric requirements are obvious and the kinetic condition for the three rates ($r_1, r_2 \ll r_3$) is also plausible.

The common effect of all the catalysts is the shortening of the Landolt-time, sometimes called the 'induction period'. In this study we investigated two different types of mechanism for catalytic effects found in the bromate–iodide–ascorbic acid clock reaction. Our study was initiated when we noticed that both molybdenum(VI)[4c,7,8,10,14] and vanadium(V)[14,15] catalyse this clock reaction, but the bromate–iodide reaction[16] is catalysed by molybdenum(VI)[17–19] only, while vanadium(V) does not have any accelerating effect.

Experimental

Ascorbic acid, $KBrO_3$, KI, $HClO_4$, NH_4VO_3, and $Na_2MoO_4 \cdot 2H_2O$ were of the highest available purity (Reanal, Hungary). Solutions were made from reagents without further purification. Dehydroascorbic acid solutions were prepared *in situ* by oxidising ascorbic acid with one equivalent of KIO_3. Ionic strength was held constant at 1.0 mol dm^{-3} using KNO_3, and thermostatted (25 °C) reaction vessels or spectrophotometer cells were used. Kinetic runs were started by rapid mixing of two solutions, one of which contained the reductants (iodide, ascorbic acid), the other the oxidants (bromate, catalyst), and both had the same pH. Reactions were followed spectrophotometrically at 467 nm (isosbestic point for the $I_2 + I^- \rightleftharpoons I_3^-$ system, $\varepsilon = 720$ dm^3 mol^{-1} cm^{-1}) using a Beckman ACTA-III instrument, or by pH measurements using a Radiometer PHM51 pH-meter with glass/calomel electrodes. The calomel electrode was connected through a KNO_3 salt bridge.

Results

Uncatalysed Reaction.—For completeness we carried out some experiments on the uncatalysed clock system in which we chose initial concentrations with excesses of bromate and iodide over that of ascorbic acid. This allowed us to measure the length of the induction period, the rate of iodine production, and the hydrogen-ion consumption after the clock phenomenon. The evaluation of the chronometric measurements is based on the relationship (4), where r_1 and r_2 are rates of bromate consumption in equations (1) and (2). Equation (4) assumes zero order kinetics for ascorbic acid (H_2A) and a negligible change in bromate concentration; $[I^-]$ and $[H^+]$ are constant during the clock period, t_L.

$$t_L = \frac{[H_2A]_0}{3(r_1 + r_2)} \quad (4)$$

For the uncatalysed reaction (5) we observed the commonly accepted rate equation (6), a result which suggests that $r_1 \sim 0$ in our uncatalysed clock reaction system, *i.e.* the direct reaction between bromate and ascorbic acid has no kinetic importance. On the other hand, it follows also that the bromate–bromide reaction[20] can be neglected under the conditions used. It was

$$BrO_3^- + 6\,I^- + 6\,H^+ \longrightarrow 3\,I_2 + Br^- + 3\,H_2O \quad (5)$$

$$r_2 = -\frac{d[BrO_3^-]}{dt} = k_2[BrO_3^-][I^-][H^+]^2 \quad (6)$$

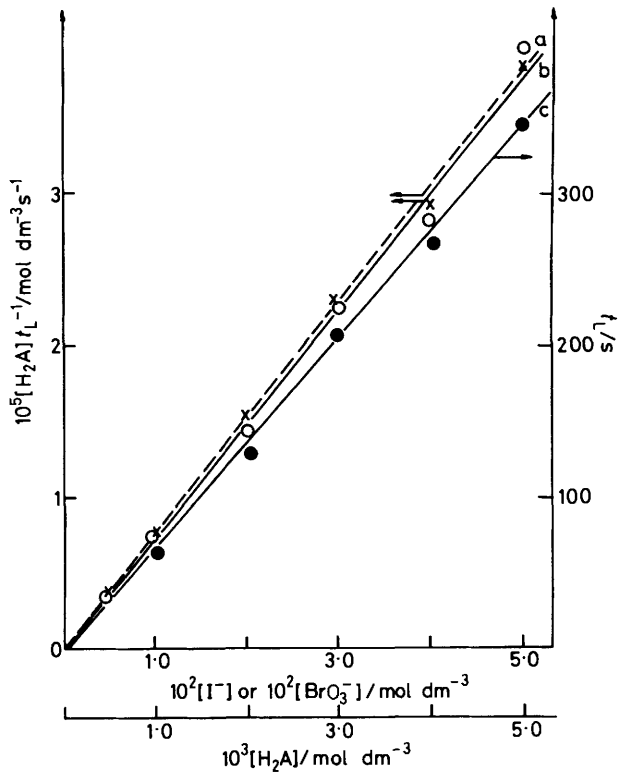

Figure 1. Effect of (*a*) initial bromate (×), (*b*) iodide (○), and (*c*) ascorbic acid (●) concentrations on the rate of the clock reaction. Initial conditions: (*a*) $[H_2A]_0 = 0.002$, $[BrO_3^-]_0 = 0.02$; (*b*) $[H_2A]_0 = 0.002$, $[I^-]_0 = 0.02$; (*c*) $[BrO_3^-]_0 = [I^-]_0 = 0.02$ mol dm^{-3}. In all cases $[H^+]_0 = 0.01$ and $[Mo]_0 = 2 \times 10^{-5}$ mol dm^{-3}

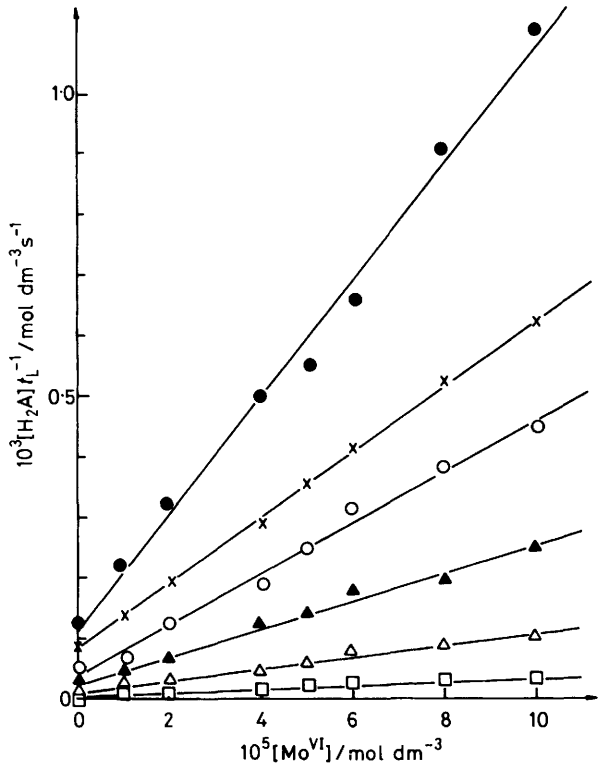

Figure 2. Effect of molybdenum(VI) concentration on the rate of the clock reaction at pH 1.4—2.5. Initial conditions: $[BrO_3^-]_0 = 0.04$, $[I^-]_0 = 0.02$, $[H_2A]_0 = 0.002$ (short Landolt times) or 0.01 mol dm^{-3} (long Landolt times); $[H^+]_0 = 0.030$ (●), 0.025 (×), 0.020 (○), 0.015 (▲), 0.010 (△), or 0.005 mol dm^{-3} (□)

found that the chronometric results are as reliable as the spectrophotometric measurements in the second (after-clock) stage of the reaction.

Molybdenum(VI) *Catalysis.*—In the molybdenum-catalysed clock reaction system, plots of $[H_2A]_0/t_L$ *vs.* $[BrO_3^-]$, $[H_2A]_0/t_L$ *vs.* $[I^-]$, and t_L *vs.* $[H_2A]_0$ were linear with zero intercepts (Figure 1); [Mo] and $[H^+]$ are constants during the clock period. These results are also consistent with a rate law which is first order in bromate and iodide and zero order in ascorbic acid for reaction (2). The negligible extent of reaction (1) under such conditions is also indicated. The effect of Mo as catalyst is shown in Figure 2 at different $[H^+]$ values. The *intercepts* represent the contribution of the uncatalysed path in reaction (2), and the *slopes* reflect the Mo-catalysed bromate–iodide reaction, which is first order with respect to molybdenum. If the series of these slopes and intercepts is plotted against $[H^+]$, information is obtained about the order of $[H^+]$ in the two reaction paths. Figure 3 shows that H^+ is second order in both the catalysed and uncatalysed reactions. This gives the rate equation (7) for the clock reaction system. Using this equation,

$$[H_2A]_0/t_L = 3k_2[BrO_3^-][I^-][H^+]^2 + 3k_2'[BrO_3^-][I^-][H^+]^2[Mo^{VI}] \quad (7)$$

the rate constants for the two reaction paths were calculated as $k_2 = 44 \pm 2$ dm^9 mol^{-3} s^{-1}, $k_2' = (4.3 \pm 1) \times 10^6$ dm^{12} mol^{-4} s^{-1}.

This simple situation becomes more complex at other concentration ranges. If $[BrO_3^-]_0$ and $[I^-]_0$ are increased and $[H^+]_0$ lowered, deviations from the rate equation (7) were found. With increasing $[Mo]_0$ and $[H_2A]_0$ the order for Mo became greater than one and $[H_2A]_0$ influenced the induction period of the catalysed reaction: the rate decreased with increasing H_2A concentration (Figures 4 and 5).

To explain these effects we assumed a kinetically important interaction between Mo^{VI} and dehydroascorbic acid (A), and therefore we studied the effect of A on the Mo-catalysed bromate–iodide reaction. Figure 6 shows the rate of this reaction as a function of [A]/[Mo]. Assuming 1:1 complex formation ($Mo + A \rightleftharpoons MoA$) the equilibrium constant, $K_1 = [MoA]/[Mo][A]$ was calculated from the curves of Figure 6 giving a value of $(7 \pm 1) \times 10^4$ dm^3 mol^{-1}. We did not consider the protonation of A and further steps of complex formation, although there is a slight indication of MoA_2 complex formation.

Incubation of a mixture of Mo^{VI} and A solutions was necessary to get reproducible results in the aforementioned experiments. This indicates a relatively slow interaction between Mo and A, its rate being comparable to r_2. All these effects make the catalysed clock reaction under these conditions too complicated for detailed explanation at present, and further study of this reaction was abandoned.

Vanadium(V) *Catalysis.*—It was found earlier,[15] and confirmed by us, that vanadium does not catalyse the bromate–iodide reaction (2). In these experiments the following ranges of initial concentration were applied: $[BrO_3^-]_0 = 0.01$—0.05, $[I^-]_0 = 0.01$—0.05, $[H^+]_0 = 0.01$—0.03, and $[V^V]_0 = (2$—$20) \times 10^{-5}$ mol dm^{-3}. Rate equation (6) was fulfilled and we found that $k_2 = 42.6$ dm^9 mol^{-3} s^{-1}, in excellent agreement both with vanadium-free and Mo-catalysed experiments. This

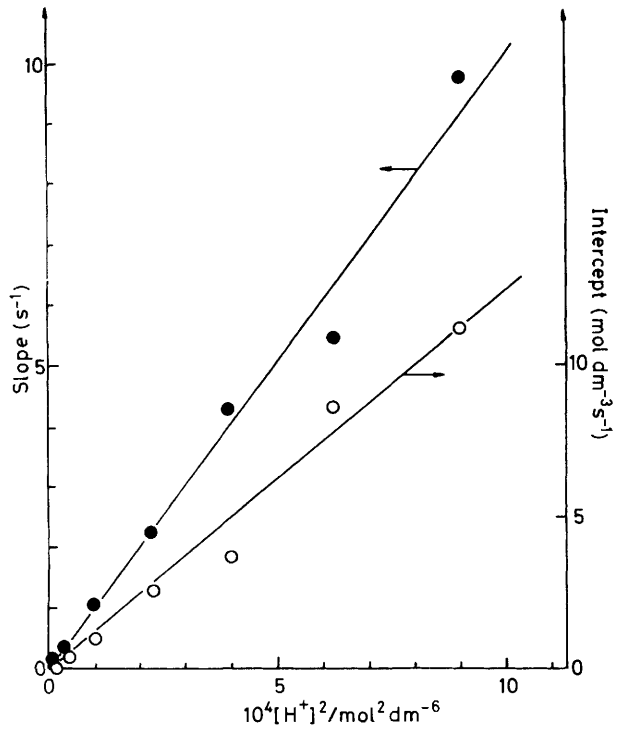

Figure 3. Plot of the slope and intercept values of the curves of Figure 2 *vs.* $[H^+]_0^2$ for the determination of the order of hydrogen ion in the Mo-catalysed clock reaction

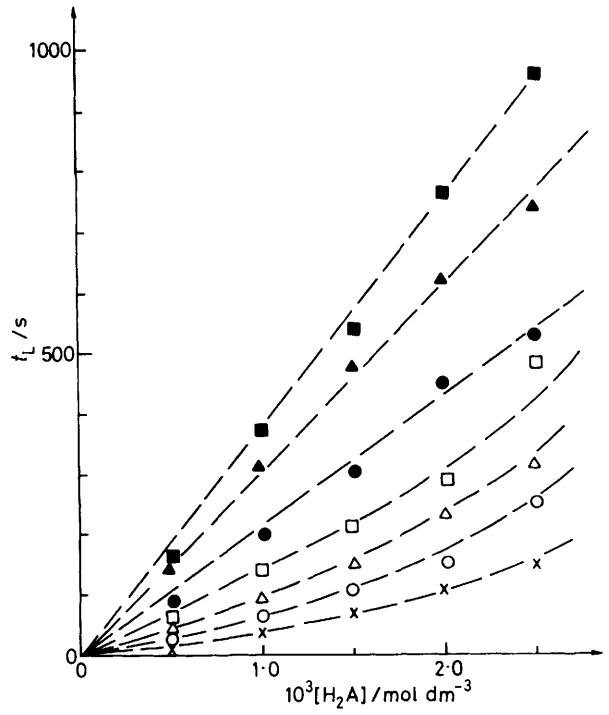

Figure 5. Effect of higher initial ascorbic acid concentration on the rate of the clock reaction. Initial conditions: $[BrO_3^-]_0 = [I^-]_0 = 0.05$, $[H^+]_0 = 0.002$ mol dm^{-3}; $[Mo^{VI}]_0 = 5 \times 10^{-6}$ (■), 1×10^{-5} (▲), 2.5×10^{-5} (●), 4×10^{-5} (□), 5×10^{-5} (△), 7×10^{-5} (○), or 1×10^{-4} mol dm^{-3} (×)

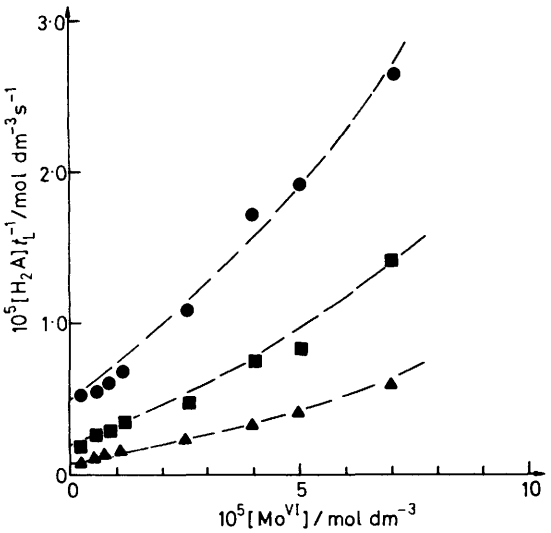

Figure 4. Effect of molybdenum(VI) concentration on the rate of the reaction at pH 2.46—2.94. Initial conditions: $[BrO_3^-]_0 = [I^-]_0 = 0.05$, $[H_2A]_0 = 0.002$ mol dm^{-3}; $[H^+]_0 = 3.45 \times 10^{-3}$ (●), 2.30×10^{-3} (■), or 1.15×10^{-3} mol dm^{-3} (▲)

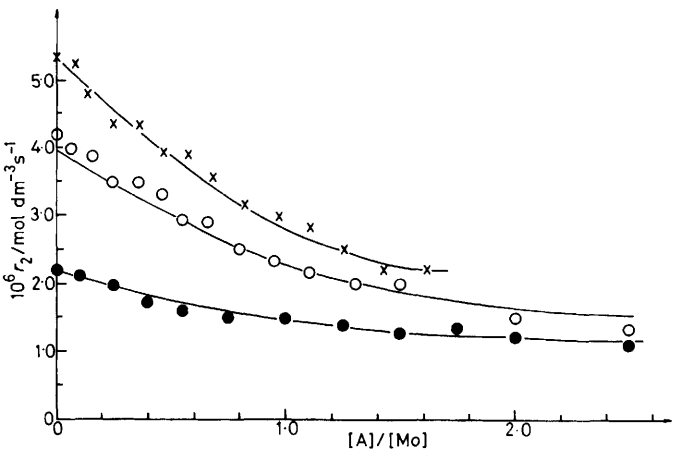

Figure 6. Effect of the ratio of dehydroascorbic acid to molybdenum(VI) on the rate of the bromate–iodide reaction. Initial concentrations: $[BrO_3^-]_0 = [I^-]_0 = 0.05$, $[H^+] = 2 \times 10^{-3}$ mol dm^{-3}; [Mo] = 7×10^{-5} (×), 5×10^{-5} (○), or 2.5×10^{-5} mol dm^{-3} (●)

result is supported by the fact that in the vanadium-catalysed systems the iodine production in the second stage of the reaction was independent of the catalyst concentration. To explain the catalytic activity of V^V in the clock reaction system, the direct reaction between bromate and ascorbic acid has to be considered. The rate of reaction (1) cannot be measured directly, but important information can be collected from the Landolt-time measurements: by proper plotting we can separate the r_1 and r_2 values and determine the form of rate equation. Similarly to the Mo catalysis, we found simple kinetic features under certain conditions but deviations appeared at higher pH.

Investigations in the Range pH 1.7—2.6.—The results of systematic variation of the initial reactant concentrations are shown in Figures 7—9. The curves in Figure 7 display the zero-order behaviour of H_2A. The straight line passes through the origin on the $[H_2A]_0/t_L$ *vs.* $[BrO_3^-]$ graph, Figure 8(*a*), which means first-order behaviour for bromate in both r_1 and r_2. From

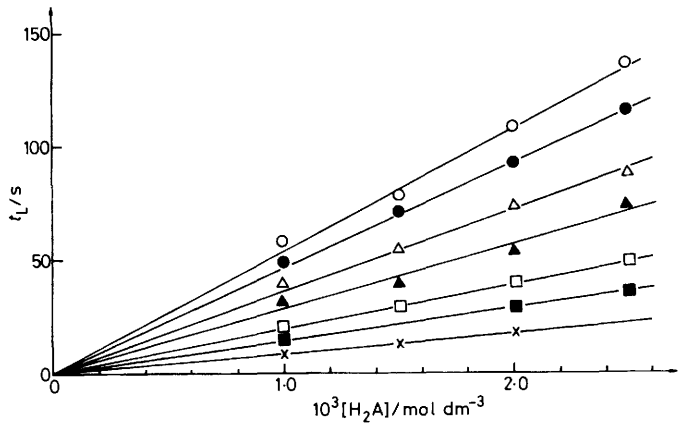

Figure 7. Plot of t_L values *vs.* $[H_2A]_0$ in the vanadium(V)-catalysed clock reaction at pH 1.7—2.6. Initial conditions: $[BrO_3^-]_0 = 0.05$ mol dm^{-3}; $[H^+]_0 = 2.95 \times 10^{-3}$ (○), 4.41×10^{-3} (●), 6.17×10^{-3} (△), 8.13×10^{-3} (▲), 1×10^{-2} (□), 1.26×10^{-2} (■), or 1.68×10^{-3} mol dm^{-3} (×)

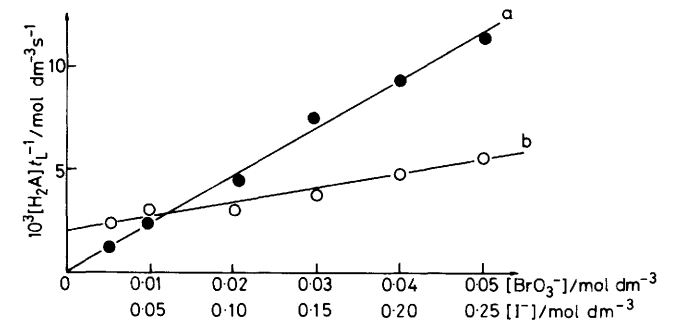

Figure 8. Effect of initial bromate (●) and iodide (○) concentration on the rate of the vanadium(V)-catalysed clock reaction. (*a*) $[H_2A]_0 = 0.001$, $[I^-]_0 = 0.05$, $[H^+]_0 = 0.003$, $[V^V] = 1 \times 10^{-5}$ mol dm^{-3}; (*b*) $[H_2A] = 0.001$, $[BrO_3^-] = 0.01$, $[H^+] = 0.003$, $[V^V] = 1 \times 10^{-5}$ mol dm^{-3}

the plot of $[H_2A]_0/t_L$ *vs.* $[I^-]$, Figure 8(*b*), first-order kinetics follows for iodine in r_2 and there is an iodide-independent reaction path, obviously r_1. We observed second-order kinetics for H^+ in r_2 (Figure 9). The lines are parallel at different V^V concentrations, which means that V^V does not appear in r_2, and $[H^+]$ has no effect on r_1. The same conclusion follows from Figure 10 and additionally it shows first-order kinetics for V^V in r_1. All these results lead to the formal rate equation (8). The

$$\frac{[H_2A]_0}{t_L} = k_1'[BrO_3^-][V^V] + k_2[BrO_3^-][I^-][H^+]^2 \quad (8)$$

direct bromate–ascorbic acid reaction can be neglected again, but the absence of H_2A in the first term of equation (8) needs explanation, which is given in the Discussion section.

Investigation in the Range pH 2.8—4.0.—Different types of pH *vs.* time curves were found under these conditions: the pH of the reaction mixture was not constant during the induction period although it was at higher $[H^+]$ values. This observation can be explained using the ascorbic acid protonation equilibrium (9), while assuming that a similar process for dehydroascorbic

$$H^+ + HA^- \rightleftharpoons H_2A \quad (9)$$

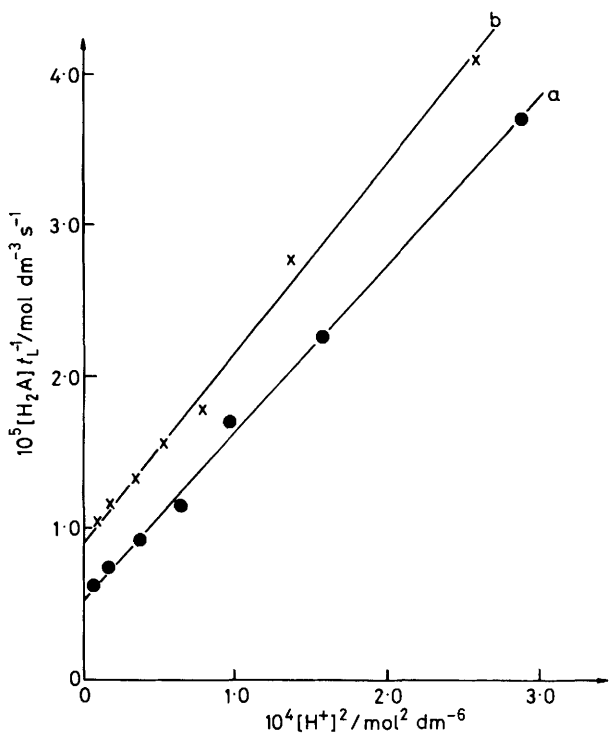

Figure 9. Plot of $[H_2A]_0/t_L$ *vs.* $[H^+]_0^2$. Initial conditions: $[BrO_3^-]_0 = [I^-]_0 = 0.05$ mol dm^{-3}; (*a*) $[V^V]_0 = 1 \times 10^{-5}$, $[H_2A]_0 = 0.001$ mol dm^{-3}; (*b*) $[V^V]_0 = 1.8 \times 10^{-5}$, $[H_2A]_0 = 0.002$ mol dm^{-3}

acid does not occur. While the oxidation takes place, equation (10), $[H^+]$ decreases. From a comparison of the measured

$$HA^- + H^+ + Ox \rightleftharpoons A + Red + H_2O \quad (10)$$

changes in $[H^+]$ and $[HA^-]$ the protonation equilibrium constant K_p for equilibrium (9) was calculated. Our value of 4.2 ± 0.05 for log K_p (in 1.0 mol dm^{-3} KNO_3) is in good agreement with the literature data (log $K_p = 4.04$ in 0.1 mol dm^{-3} KNO_3[21]).

The effect of V^V on the clock reaction is shown in Figure 11. The linearity of this graph indicates first-order kinetics for V^V and the very small (*ca.* 10^{-7} mol dm^{-3} s^{-1}) intercept expresses the minor contribution of reaction (2) to the overall reaction (calculated value is 1×10^{-7} mol dm^{-3} s^{-1}). From the slope of the curve in Figure 11 we calculate $k_1' = 16.4$ dm^3 mol^{-1} s^{-1} based on rate equation (8).

It is important to note that after the induction period there are two separate stages in the spectrophotometric absorbance *vs.* time curves. The first relatively rapid stage clearly corresponds to the oxidation of iodide by vanadium, the second one to the bromate–iodide reaction. These reactions do not influence the kinetics of the first part of the clock reaction.

Discussion

It is generally agreed in the literature that the bromate–iodide reaction has the rate equation (6), although values for the rate constant k_2 are different, depending partly on the circumstances of their determination. The values are summarised in the Table. Our results agree fairly well with those of Clark,[18] and Barton and co-workers.[19,22] The only quantitative study on the molybdenum(VI)-catalysed bromate–iodide reaction was

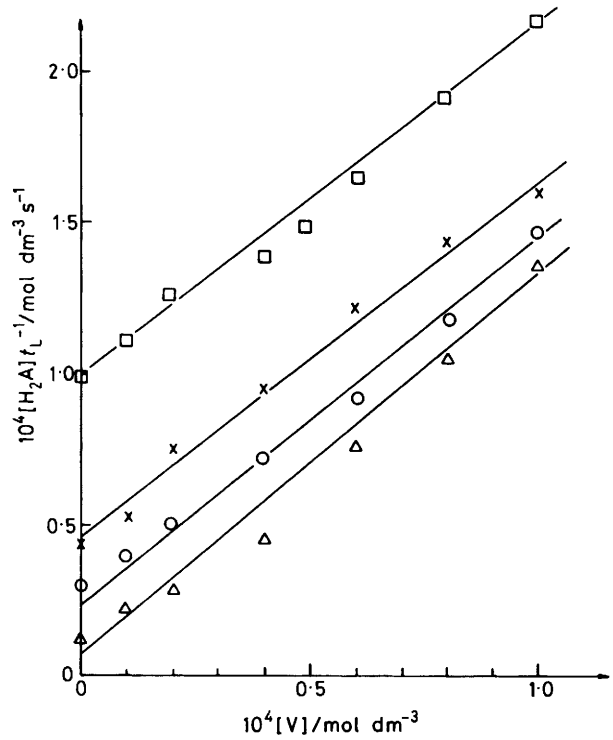

Figure 10. Effect of vanadium(v) concentration on the rate of the clock reaction at pH 1.6—2.0. Initial conditions: $[BrO_3^-]_0 = 0.04$, $[I^-]_0 = 0.02$, $[H_2A]_0 = 0.002$ mol dm^{-3}; $[H^+]_0 = 0.025$ (□), 0.020 (×), 0.015 (○), or 0.010 mol dm^{-3} (△)

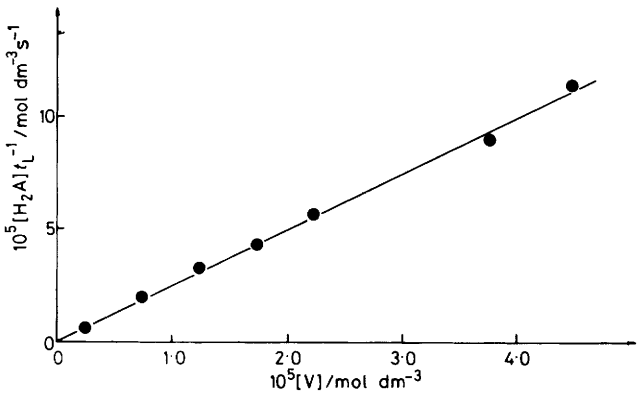

Figure 11. Effect of vanadium(v) concentration on the rate of the clock reaction at pH_0 3.26. Initial conditions: $[BrO_3^-]_0 = [I^-]_0 = 0.05$, $[H_2A]_0 = 0.0025$ mol dm^{-3}

carried out by Barton and Loo,[19] who found first-order kinetics for H^+ in the catalysed reaction. However, in our studies we obtained a second-order kinetics for H^+ in both terms of the rate equation (7) with a rate constant $k'_2 = (4.3 \pm 1) \times 10^6$ dm^{12} mol^{-4} s^{-1}. This difference may be attributed to different bromate and iodide concentrations used by these authors; both were lower by an order of magnitude than ours. The H^+ and Mo^{VI} concentrations were similar in the two studies [0.001—0.005 and (1—40) × 10^{-6} mol dm^{-3}, respectively]. The present study does not allow further speculation about detailed mechanism of the catalysed reaction. (In this respect we agree with the discussion of Barton and Loo.[19]) Our results clearly

Table. Rate constants of the bromate–iodide reaction (6)

k_2/dm^9 mol^{-3} s^{-1}	Conditions	Ref.
82	$[Br^-]_0 = 0$, 25 °C	4*f*
59	$[Br^-]_0 = 0.05$—0.3 mol dm^{-3}, 25 °C	4*f*
90	25 °C	14
84	25 °C	15
44, 5		18
50	1 mol dm^{-3} KNO_3, 25 °C	19
42 ± 3	1 mol dm^{-3} KNO_3, 25 °C	22
44 ± 2 42.6 ± 2	1 mol dm^{-3} KNO_3, 25 °C	This work

show that molybdenum catalyses only the bromate–iodide reaction in the clock reaction system and it has no catalytic effect on the bromate–ascorbic acid process, which is negligible under these experimental conditions. The effect of the product found here is considered as a result of the complex formation between dehydroascorbic acid and molybdenum(VI).

Our results and the data of Bognár and Jellinek[15] clearly demonstrate that V^V has no accelerating effect on the bromate–iodide reaction. Yatsimirskii and Kalinina[23] describe the catalytic determination of V^V based on its catalytic effect in this reaction. An attempt to reproduce this finding was unsuccessful in our laboratory.

It was possible to specify the reaction which is catalysed by V^V in the Landolt system. This is clearly reaction (1), *i.e.* the oxidation of ascorbic acid by bromate in a vanadium-catalysed cycle, and in this case it is not the bromate–iodide reaction. The formal rate equation (8) found in the systematic investigations corresponds to that published earlier.[15] The rate constants we obtained from two series of measurements are $k'_1 = 9.6 \pm 1$ dm^3 mol^{-1} s^{-1} and $k_2 = 42.6 \pm 2$ dm^9 mol^{-3} s^{-1}. At higher pH the value $k'_1 = 17 \pm 2$ dm^3 mol^{-1} s^{-1} was found, which is similar to $k'_1 = 18.2$ dm^3 mol^{-1} s^{-1} obtained in ref. 15. Although H_2A is zero-order in reaction (1), it is obvious that this reaction term should decrease to zero as H_2A is consumed.

To explain the first term in rate equation (8) an obvious approximation suggests a rapid step between ascorbic acid and vanadium(v) [see equation (12) below]. Stopped-flow experiments proved that this reaction is fast enough for this assumption. This is followed by the bromate oxidation of vanadium(IV). The kinetics of the latter was studied by Fuller and Ottoway.[24] They found the rate law (11) and proposed

$$r = \frac{k_{14}K_{13}[BrO_3^-][V^V]}{1 + K_{13}[BrO_3^-]} \qquad (11)$$

steps (13) and (14) to explain the kinetic results. From these considerations the first kinetically important steps of the catalytic mechanism are equations (12)—(14).

$$H_2A + V^V \xrightarrow{\text{rapid}} V^{IV} + \ldots \qquad (12)$$

$$BrO_3^- + V^{IV} \underset{K_{13}}{\overset{\text{rapid}}{\rightleftharpoons}} V^{IV}\text{–}BrO_3^- \qquad (13)$$

$$V^{IV}\text{–}BrO_3^- \xrightarrow{\text{slow}} V^V + \ldots \qquad (14)$$

Although this appears to be a reasonable supposition, our kinetic results did not show such a bromate dependence, and consequently another mechanism may be valid. The most probably explanation is the sequence of reactions (12), (15), and (16).

$$H_2A + V^V \xrightarrow{\text{rapid}} V^{IV} + \ldots \qquad (12)$$

$$V^{IV} + H_2A \overset{\text{rapid}}{\rightleftharpoons} H_2A\text{-}V^{IV} \quad (15)$$

$$H_2A\text{-}V^{IV} + BrO_3^- \xrightarrow{\text{slow}} V^V + \ldots \quad (16)$$

The first step is the same as previously proposed, *i.e.* rapid reaction between ascorbic acid and vanadium(V). An alternative proposal for the next step, instead of (13), is a rapid complex formation between vanadium(IV) and ascorbic acid, equation (15), and as the rate-determining step, equation (16) is proposed for the bromate oxidation of this complex. These assumptions lead to the rate equation (17) (taking into account $[H_2A] > [V^V]$).

$$v = \frac{k_{16}K_{15}[H_2A][V^V][BrO_3^-]}{1 + K_{15}[H_2A]} \quad (17)$$

If $K_{15}[H_2A] > 1$, which is reasonable, equation (17) leads to the experimentally found results [the first term in equation (8)]. In this case $k_{16} = k'_1$.

It is certainly true that most of the equations used in describing the kinetic behaviour of the catalysed clock-reaction systems represent reactions which are more complex than elementary steps. The experimental results do not give information about such fine details. However, they are suitable to distinguish between the two types of catalytic mechanism involving different metal ions in the same system. Molybdenum(VI) catalyses the oxidation of iodide, while V^V catalyses that of ascorbic acid. The difference found here does not detract from the possibility of application of this clock reaction to the analytical determination of molybdenum and vanadium.

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