A Kinetic Study of the Oxidation of Indigo Carmine with Acidic Bromate

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The oxidation kinetics of indigo carmine (disodium 3,3'-dioxobi-indolin-2,2'-ylidene-5,5'-disulphonate) with potassium bromate have been studied in aqueous sulphuric acid, by monitoring the absorbance of indigo carmine (IC) at 610 nm. The reaction involves competitive and consecutive reaction steps—an initial slow step followed by a rapid one for depletion of IC. For the initial stages the reaction order is four-first-order with respect to IC and bromate ion and second order with H^+ ion. For the fast reaction step the studies are limited to qualitative treatment due to the complex nature of the reaction. The rate of depletion of IC increased with time and with the increase in HOBr concentration. Hypobromous acid, the reaction intermediate, may possibly compete with bromate ion for IC to give an intermediate, which is further oxidised to yield the final product, isatin-5-monosulphonic acid. The stoicheiometric ratio of IC to bromate is 3:2. The dual role of bromine ion as an inhibitor and autocatalyst in the reaction mechanism is discussed. Computer simulations were performed using the proposed mechanism. The results of the computer simulations are similar to the experimental observations.

Considerable effort has been devoted towards the understanding of the chemistry of the bromate ion in aqueous sulphuric acid and to the elucidation of the mechanism of the oscillating closed chemical systems.[1] Numerous reactions involving different organic and inorganic substrates and acidic bromate are known.[2-5]

Indigo carmine (IC) is a well known dyestuff used as a microscopic stain in biology.[6] The organic chemistry of IC and indigotin compounds has been discussed in detail by Rodd.[7] Oxidation of IC by peroxydisulphate ion in aqueous sulphuric acid[8,9] and its application as an indicator for the determination of Ag^I concentration has been reported.[10] Mn^{II} catalysed oxidation of IC by hydrogen peroxide has also been reported.[11]

Different organic substrates have been scanned for suitable reductant properties to react with acidic bromate, and which can act as a selective catalytic indicator for the determination of trace concentrations of V^V. Indigo carmine was, among the number of substrates, chosen due to its sharp absorption peak in the visible region. Investigations showed that V^V and other cations have no significant effect on the oxidation rate of IC by acidic bromate. Interestingly the reaction has two distinct stages for depletion of IC, a slow initial step followed by a very rapid one, indicating the existence of a competitive or an autocatalytic step. We now report a kinetic study of the oxidation of indigo carmine by acidic bromate.

Experimental

Reagents.—All the reagents employed were of AnalaR grade or of high purity. All the standard solutions and dilutions were made in deionised distilled water following standard procedures.

Methods.—*Kinetic measurements.* The reaction mixtures were stirred magnetically and the solutions were maintained at constant temperature (25 ± 0.5 °C) by circulating water from a thermostat through a water jacket surrounding the reaction vessel.

The stock solutions were mixed in the following order: requisite volume of water to make up the total volume; aqueous sulphuric acid, IC, and then the other reagents as needed. The reaction was started by the separate addition of bromate solution (at 25 ± 0.5 °C)

The kinetic studies were followed by monitoring absorbance at 610 nm, an absorption maximum for IC in acidic solution (ε 6.31 × $10^3 M^{-1} cm^{-1}$) (Pye-Unicam SP-150 spectrophotometer). Interference from other reagents and products at this wavelength was negligible. All the kinetic data were collected in the presence of excessive concentrations of hydrogen and bromate ions, unless otherwise specified. In the concentration range of IC employed, Beer's law was valid.

Determination of $[BrO_3^- + HOBr]$.[12] Aliquots of the reaction mixture were added at intervals to a mixture of 0.1M-$HClO_4$ (10 ml) and 10% w/v potassium iodide solution (10 ml) with 10^{-6}M-molybdate catalyst. After incubation for about 30—40 min the liberated iodine was titrated with 0.002M-sodium thiosulphate solution using starch as indicator, and a correction for blanks was made. (6M-sodium thiosulphate ≡ 1M-bromate).

Determination of [HOBr].[12] For the determination of HOBr concentration alone, the same iodometric method was used, but with a slight modification. Aliquots of the reaction mixture were added to a fixed volume of aqueous NaOH in order to bring the mixture to neutral pH, this was followed by the addition of a mixture of 0.1M-acetate buffer (10 ml) and 10% KI (10 ml) solution (reaction of bromate ion with KI does not occur at the mixture pH 4.5). The solutions were incubated for 30—40 min, then the liberated iodine titrated with 0.002M-sodium thiosulphate solution and correction for the blank was made in the titre values. The concentration of HOBr was calculated using the equation 2M-sodium thiosulphate ≡ 1M-HOBr. Actual concentrations of bromate ion were determined by substracting [HOBr]/3 from the corresponding value of $[BrO_3^- + HOBr]$.

E.m.f. measurements. Electrochemical potential measurements (Pye-Unicam pH meter with expanded scale) were determined using a platinum electrode and a saturated calomel electrode, immersed in the reaction solution (25 ± 0.5 °C) and connected by an agar gel-KNO_3 salt bridge.

Stoicheiometry. The stoicheiometry of the reaction was determined using 1:1 and 1:2 molar ratios of IC and bromate ion in the presence of an excess of H^+ concentration. After 16 h and 40 h, the concentration of the reactants were determined and it was found that IC reacted with bromate ion in 3:2 ratio.

Product analysis. For the product analysis the following reactant concentrations were used H^+ 5.0M, bromate ion 0.05M, and IC 0.01M. After 24 h reaction at room temperature (about

Table 1. Effect of indigo carmine initial concentration on the initial depletion rate of IC[a]

[Bromate]$_0$ Curves in Figure 1	1.0 × 10^{-3}M (a)	(b)	[H$^+$]$_0$ 1.50M (c)	(d)
[IC]$_0$/10^{-5}M	3.55	7.10	9.20	11.0
k'_1/10^{-4} s^{-1}	1.382	1.384	1.326	1.391

[a] Entries are the average values of two duplicate experiments obtained by linear regression fitting and the values had 5% average deviation.

Table 2. Order with respect to bromate ion[a]

[IC]$_0$ 9.20 × 10^{-5}M Curves in Figure 1 and 2	(e)	[H$^+$] 1.50M (c)	(f)	(g)
[BrO$_3^-$]$_0$/10^{-3}M	0.5	1.0	2.0	3.0
k'_1/10^{-4} s^{-1}	0.642	1.326	2.643	4.104
k_1/10^{-2} M^{-3} s^{-1}	5.706	5.893	5.876	6.080

Mean k_1 (5.899 ± 0.19)10^{-2} M^{-3} s^{-1}

Overall reaction rate constant $k_1 = k'_1/[\text{H}^+]_0^2[\text{BrO}_3^-]_0$

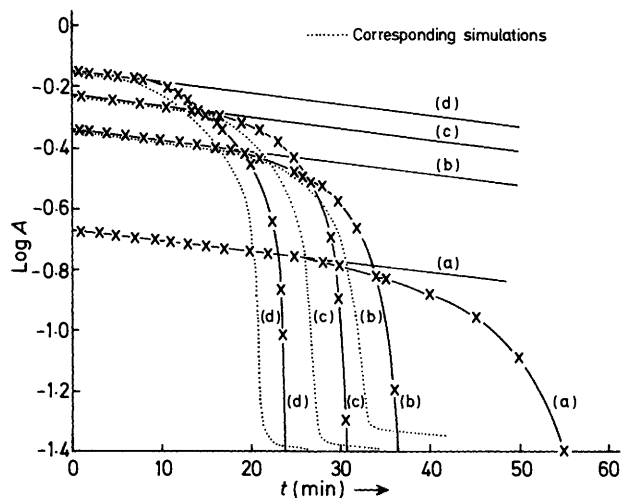[a] Entries are average values of two experiments and the values had 5% average deviation.

Figure 1. Effect of indigo carmine concentration on the reaction rate. The dotted lines indicate the computer simulation fit to traces (b), (c), and (d). Conditions: [bromate]$_0$ 1.0 × 10^{-3}M; [H$^+$]$_0$ 1.50M; [IC]$_0$ (a) 3.55 × 10^{-5}M; (b) 7.10 × 10^{-5}M; (c) 9.20 × 10^{-5}M; (d) 11.0 × 10^{-5}M
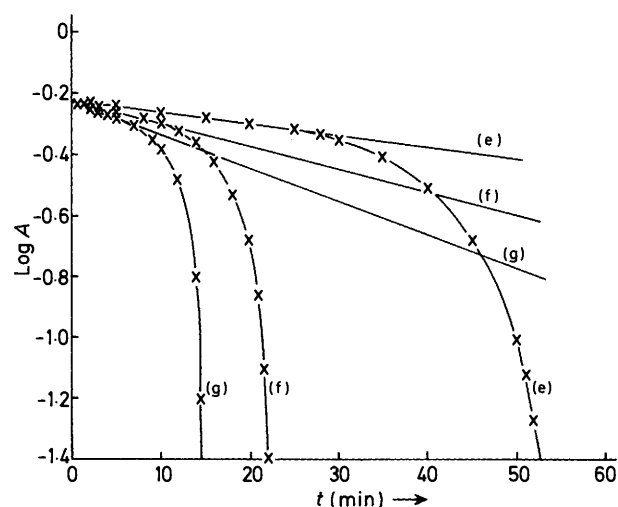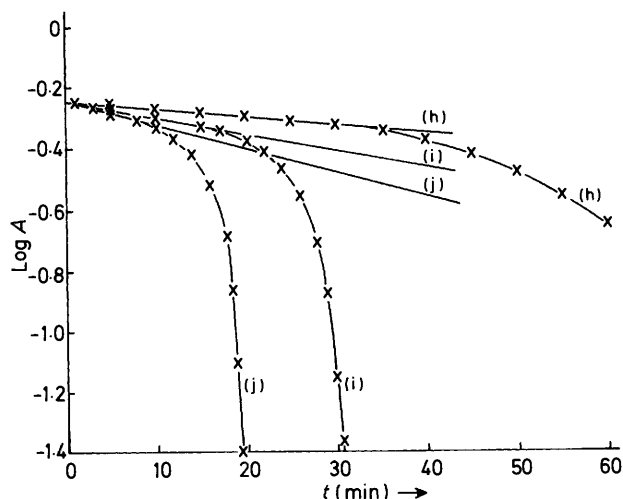

Figure 2. Effect of bromate ion concentration. Conditions: [IC]$_0$ 9.20 × 10^{-5}M; [H$^+$]$_0$ 1.50M; [bromate]$_0$ (e) 0.5 × 10^{-3}M; (f) 2.0 × 10^{-3}M; (g) 3.0 × 10^{-3}M

18 °C), the reaction mixture was separated with diethyl ether. The G.C.–M.S. analysis with VG-13-250 Quadrapole instrument of the ether extract showed the major compound m/z 227 (M^+, 8%) with other significant peaks at 212(16), 211(10), 183(80), 146(20), and 90(50) indicating that the major oxidation product is isatin-5-monosulphonic acid (2,3-dioxoindoline-5-sulphonic acid).

Results and Discussion

Preliminary investigations in which the IC concentration at 610 nm was monitored, taking into account the excessive concentrations of sulphuric acid and potassium bromate, revealed that depletion of IC occurred in two distinct steps—a slow step followed by a rapid one, indicating that the reaction follows complicated kinetics involving possibly competitive, consecutive, and autocatalytic reactions. Hence the kinetics of the reaction were studied by varying initial concentrations of the reactants whilst maintaining the excess concentrations of H$^+$ and bromate ions.

Order with Respect to Indigo Carmine.—Kinetic data were collected for initial reactant concentrations of H$^+$ 1.50M, bromate ion 1.00 × 10^{-3}M, and of IC in the range 3.55 × 10^{-5}M— 11.00 × 10^{-5}M. All experiments had identical characteristics, an initial slow reaction followed by a fast step. The transition to the rapid stage (induction time, I_t) was faster with increased initial concentration of IC. Figure 1 shows the log absorbance (A) *versus* time plots of the kinetic data for different [IC]$_0$ values. A

careful perusal of the curves (a), (b), (c), and (d) and analysis of the data show that the gradients of the tangents drawn for the initial stages of the curves have the same value. The fairly constant k'_1 values obtained for different initial concentrations of IC confirm that the slow depletion of IC follows pseudo-first-order kinetics (Table 1). Hence taking into consideration the complex nature of the reaction, the analysis of the kinetic data was restricted to the initial stages of the reaction, although this represents only a fraction of the total reaction, but we have extended a qualitative treatment to the latter stages of the reaction.

Dependence of Initial Rate on Bromate Concentration.—The kinetics of consumption of IC for different initial concentrations of bromate ion (0.5—3.0 × 10^{-3}M) were studied. The log A–time curves obtained from the data are shown in Figure 2. The k_1 values, calculated from the gradients of the curves, increased with an increase in [BrO$_3^-$]$_0$ (see Table 2). The log–log plot of k_1 *versus* [BrO$_3^-$]$_0$ gave a fairly straight line with a gradient 1.04 ± 2.0 × 10^{-2} (corr. coefft. 0.98), indicating a first-order dependence of the reaction rate on the bromate concentration.

Order with Respect to Hydrogen Ion Concentration.—The kinetic data obtained for different initial concentrations of H$^+$ (1.2—2.25M) are illustrated in Figure 3 in the form of log A *versus* time curves. The pseudo-first-order rate constants, k'_1, obtained for different [H$^+$]$_0$ are given in Table 3. The log–log plot of the k'_1 *versus* [H$^+$]$_0$ data gave a line with a gradient

Table 3. Order with respect to H^+ concentration[a]

[IC]$_0$ 9.20 × 10^{-5}M Curves in Figures 1 and 3	[BrO$_3^-$]$_0$ 1.0 × 10^{-3}M			
	(h)	(c)	(i)	(j)
[H$^+$]/M	1.25	1.50	1.87	2.25
$k_1'/10^{-4}$ s^{-1}	0.926	1.326	2.052	2.986
$k_1/10^{-2}$ M^{-3} s^{-1}	5.946	5.893	5.843	5.908

Mean $k_1 = 5.89 \pm 0.06) \times 10^{-2}$ M^{-3} s^{-1} where the overall reaction rate constant $k_1 = k_1'/[H^+]_0^2[BrO_3^-]_0$

[a] Entries are the average values of two experiments and the values had 5% average deviation.

Figure 3. Effect of hydrogen ion concentration. Conditions: [IC]$_0$ 9.20 × 10^{-5}M; (bromate)$_0$ 1.0 × 10^{-3}M; [H$^+$]$_0$ (h) 1.25M; (i) 1.8M; (j) 2.25M

Figure 4. Effect of bromide ion. Conditions: [IC]$_0$ 9.20 × 10^{-5}M; [bromate]$_0$ 1.0 × 10^{-3}M; [H$^+$]$_0$ 1.5M; [Br$^-$]$_0$ (l) 1 × 10^{-6}M; (m) 2.5 × 10^{-6}M; (n) 5.0 × 10^{-6}M

1.98 ± 2.1 × 10^{-2} (corr. coefft. 0.99) indicating that the order with respect to H$^+$ ion is two. Hence, the overall reaction rate constant, k_1, for the initial stage of the reaction is calculated, by dividing k_1 by the corresponding [BrO$_3^-$]$_0$ [H$^+$]$_0^2$ values and the results are summarised in Tables 2 and 3. The k_1 values obtained were fairly constant within the limits of experimental error.

Effect of Bromide Ion on the Reaction Rate.—The effect of the initial addition of bromide ion on the reaction is shown in Figure 4. Examination of the curves, with [bromide]$_0$ (l) 1.0 × 10^{-6}M, (m) 2.5 × 10^{-6}M, and (n) 5.0 × 10^{-6}M and curve (c) (from Figure 1) under identical conditions shows that the curves (l), (m), and (n) are distinctly different, with a marked increase in gradient in the initial stages of the reaction. Compared with curve (c), curves (l) and (m) have longer induction periods (I_t), *i.e.* time for transition to the rapid stage, whereas curve (n) has a shorter I_t. It was observed that depletion of IC was very fast for [Br$^-$]$_0$ > 5.0 × 10^{-5}M. The increased induction times at low [Br$^-$] and reduced I_ts for high [Br$^-$] point towards the dual role of the bromide ion as inhibitor and autocatalyst. The role of the bromide ion as a control intermediate is well known in Beleusov–Zhabotonisky chemical oscillatory systems.[1,13] The role of bromide ion as inhibitor and autocatalyst has also been observed by Hasty *et al.*, during their studies on the oxidation of Methyl Orange by acidic bromate.[14,15]

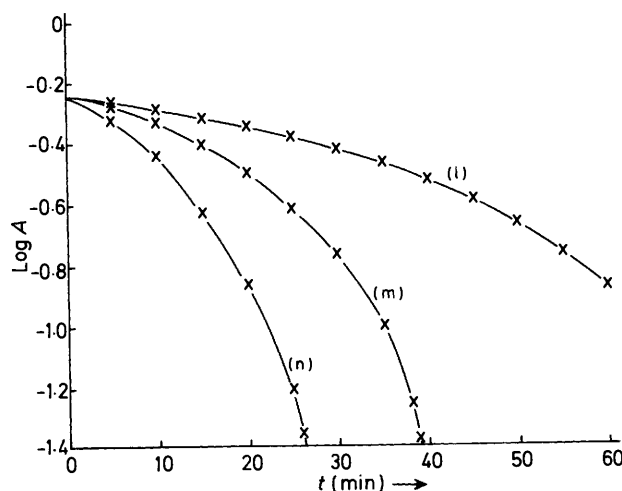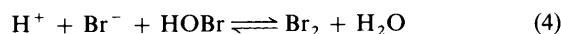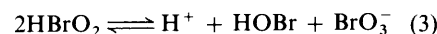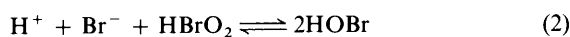The chemistry of the bromate ion in acidic solution can be represented by the following equations.[12]

$$2H^+ + Br^- + BrO_3^- \rightleftharpoons HOBr + HBrO_2 \qquad (1)$$

$$H^+ + Br^- + HBrO_2 \rightleftharpoons 2HOBr \qquad (2)$$

$$2HBrO_2 \rightleftharpoons H^+ + HOBr + BrO_3^- \qquad (3)$$

$$H^+ + Br^- + HOBr \rightleftharpoons Br_2 + H_2O \qquad (4)$$

With sufficient bromide ion present, a rapid equilibrium is established between the concentrations of bromate and HOBr through equations (1) and (2) which can be represented by equation (5).[3,16]

$$BrO_3^- + 3H^+ + 2Br^- \rightleftharpoons 3HOBr \qquad (5)$$
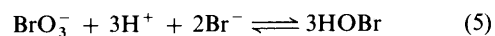
where the equilibrium constant $K_5 =$

$$\frac{[HOBr]^3}{[BrO_3^-][Br^-]^2[H^+]^3} \qquad (6)$$

Under the present experimental conditions, with no initial bromide ion added, the order of dependence of the initial reaction on IC(unity), bromate ion (unity), and H$^+$ (two) observed points, towards a possible direct reaction between IC and the bromate ion in the presence of H$^+$, analogous to equation (1). Replacement of the bromide ion by IC, and subsequent oxidation of the latter, yields an intermediate, I.

$$2H^+ + IC + BrO_3^- \xrightarrow{k_1} I + HBrO_2 \qquad (7)$$
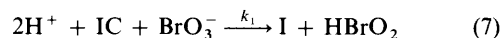
In the absence of bromide ion in the initial stages of the reaction, HBrO$_2$ disproportionates rapidly through equation (3) (4 × 10^7 M^{-1} s^{-1}) giving HOBr[12] which in turn competes with bromate ion for IC.

$$IC + HOBr \xrightarrow{k_2'} I + Br^- \qquad (8)$$
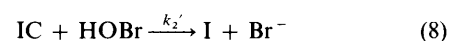
It is possible that HOBr further oxidises the intermediate, I, in a fast reaction step giving the final products isatin-5-mono-sulphonic acid (P), Br$^-$, and H$^+$ ions.

$$I + HOBr \xrightarrow{fast} P + Br^- + 2H^+ \qquad (9)$$
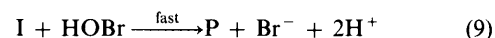
Isatin-5-monosulphonic acid has been reported as an oxidation product of the IC–acidic peroxydisulphate reaction.[9]
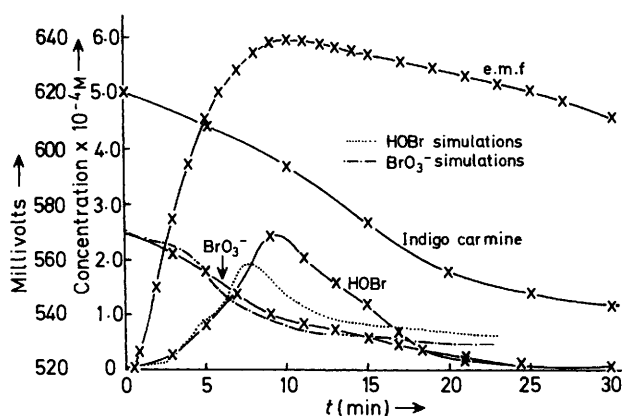
Figure 5. Pseudo-second-order kinetic curve of IC–acidic bromate reaction. Conditions: $[IC]_0$ 5×10^{-4}M; $[\text{bromate}]_0$ 2.5×10^{-4}M; $[H^+]_0$ 3.57M. The computer simulation fits are also shown for BrO_3^- and HOBr

The role of HOBr as a competitive reacting species was verified, by studying the reaction under different reactant concentrations. Using an excessive concentration of H^+ (3.57M) and the same range of concentrations of bromate ion (2.50×10^{-4}M) and IC (5.00×10^{-4}M), the kinetics were determined, e.m.f. profiles plotted, and the concentration changes of IC, residual bromate, and HOBr with time simultaneously monitored (see Figure 5). A perusal of the trends of the curves shows that, as anticipated, both IC and bromate deplete at a slow rate under the initial conditions, followed by a higher rate, although this does not predominate. The fact that the concentration of HOBr builds up to reach a maximum and then undergoes depletion indicates that HOBr is an intermediate. The overall potential also followed the same trend as the HOBr concentrations (redox potential BrO_3^-/HOBr 1.58 V). The observed increase in the depletion rate of IC with concomitant increase in the HOBr concentration further confirms the role of HOBr as a competitive intermediate of the reaction.

The dual role played by bromide ion can be explained taking into consideration the forward reaction rate constants for equations (1), (2), and (4), respectively 2.1 M^{-3} s^{-1}, 2.0×10^9 M^{-2} s^{-1}, and 8.0×10^9 M^{-2} s^{-1}. At low concentrations of Br^- a situation such as that of equation (4) may predominate, causing depletion of the HOBr concentration. Thus, the Br^- ion acts as inhibitor for transition from the slow reaction step to the fast one, thereby increasing I_t. In contrast, an increase in the concentration of Br^- beyond a critical limit through equations (8) and (9) allows the Br^- ion to play the role of an autocatalyst through equations (1) and (2), rapidly increasing the concentration of HOBr[17] and leading to an equilibrium between different oxybromo species. This results in rapid depletion of IC as witnessed in the fast step.

Rate Laws.—The rate of consumption of IC can be represented by the following equation:

$$\frac{-d[IC]}{dt} = k_1[H^+]^2[BrO_3^-][IC] + k_2'[HOBr][IC] \quad (10)$$

For initial conditions, when $[HOBr] = 0$, equation (10) reduces to:

$$\frac{-d[IC]}{dt} = k_1[H^+]^2[BrO_3^-][IC] \quad (11)$$

and when the concentration of H^+ and bromate ions are in excess, the rate expression can be written as a pseudo-first-order equation:

Table 4. Computer simulations of the rate constants of reactions (1)—(4), (5), and (7)—(9)

Kinetic constants

(1)	$k_1 = 2.1$ M^{-3} s^{-1}, $k_{-1} = 1 \times 10^4$ M^{-1} s^{-1}
(2)	$k_2 = 2 \times 10^9$ M^{-2} s^{-1}, $k_{-2} = 5 \times 10^{-5}$ M^{-1} s^{-1}
(3)	$k_3 = 4 \times 10^7$ M^{-1} s^{-1}, $k_{-3} = 2 \times 10^{-10}$ M^{-2} s^{-1}
(4)	$k_4 = 8 \times 10^9$ M^{-2} s^{-1}, $k_{-4} = 110$ s^{-1}
(5)	$k_5 = 1 \times 10^7$ M^{-5} s^{-1}, $k_{-5} = 500$ M^{-2} s^{-1}
(7)	$k_7 = 5.9 \times 10^{-2}$ M^{-3} s^{-1}, $k_{-7} = 1 \times 10^{-10}$ M^{-1} s^{-1}
(8)	$k_8 = 750$ M^{-1} s^{-1}, $k_{-8} = 1 \times 10^{-10}$ M^{-1} s^{-1}
(9)	$k_9 = 1 \times 10^6$ M^{-1} s^{-1}, $k_{-9} = 1 \times 10^{-10}$ M^{-4} s^{-1}

$$\frac{-d[IC]}{dt} = k_1'[IC] \quad (12)$$

where $k_2' = k_1[H^+]^2[BrO_3^-]$

In the latter stages, with the increase in concentration of HOBr, the rate law is represented by equation (10). Substituting the value of [HOBr] from equation (6), we obtain

$$\frac{-d[IC]}{dt} = k_1[H^+]^2[BrO_3^-][IC] +$$
$$k_2'K_5[H^+][BrO_3^-]^{\frac{1}{3}}[Br^-]^{\frac{1}{3}}[IC] \quad (13)$$

$$= \{k_1[H^+]^2[BrO_3^-] +$$
$$k_2[H^+][BrO_3^-]^{\frac{1}{3}}[Br^-]^{\frac{1}{3}}\}[IC] \quad (14)$$

where $k_2 = k_2'K_5$

Equation (14) explains the observed increase in the depletion rate of IC with progress of the reaction. With excessive concentrations of H^+ and bromate ions, in the absence of bromide ion, *i.e.* in the initial stages, the reaction rate is dependent only on IC concentration. But as the reaction proceeds, and formation of bromide ion increases, the consumption rate of IC is dependent on the concentrations of depleting IC and increasing bromide ion in the system.

Computer Simulations

Computer simulations were performed using our proposed mechanism. The Numerical Algorithms Group (NAG) version of the Gear algorithm was implemented. The reactions used in our computer simulations and their rate constants are shown in Table 4. Literature values of kinetic parameters were used for reactions (1)—(4).[12] Estimated values were used for reactions (5), (8), and (9). The rate constant evaluated in this work was used for reaction (7). The simulations were insensitive to values of k_8 and k_9 as long as both were larger than k_7. Both reactions (8) and (9) were essentially made irreversible. The simulations were most sensitive to the values of k_5 and k_{-5}. The kinetic parameters for reaction (5) determined the reaction duration and the sigmoidal shape of the disappearance of the indigo carmine. The simulations were thus very easy because after setting values for k_8 and k_9 (both greater than k_7), k_5 was next adjusted until the reaction duration equalled that experimentally observed.

The results of the computer simulations were very similar to the experimental observations. There was good agreement between experiments and simulations on the effects of bromate and acid. The effect of bromide was a little more difficult to simulate. We found the simulations to be insensitive to bromide concentrations as we increased the initial bromide concentra-

tions from 10^{-12}M—10^{-7}M. At a critical concentration of bromide of about 5×10^{-6}M, the bromide began to catalyse the reaction. This has also been experimentally observed. Although we could not obtain slower kinetics with added bromide, the insensitivity to $[Br^-]_0$ as the bromide concentration is increased by five orders of magnitude suggests that low quantities of bromide cannot catalyse the reaction because they are depleted by a reaction which is extraneous to the oxidation of indigo carmine. The most probable reaction is the formation of bromine from HOBr and bromide. Further simulations are still being carried out in which bromine also oxidises indigo carmine, but at a slower rate than oxidation by HOBr.

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