Chemical Waves in B-Z Systems with Mixed Organic Substrates

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Spatio-temporal oscillations in systems (A) oxalic acid + acetone + BrO₃⁻ + Ce⁴⁺ / Mn²⁺ + ferroin + H₂SO₄ (B) mandelic acid + acetone + BrO₂⁻ + Ce⁴⁺ / Mn²⁺ + ferroin + H₂SO₄ (C) lactic acid + acetone + BrO₂⁻ + Ce⁴⁺ / Mn²⁺ + ferroin + H₂SO₄ have been investigated in detail both for the one-dimensional as well as the two dimensional wave propagation. The waves are found to be trigger waves for systems (A) and (C) which are both non-oscillatory. Phase waves are obtained in system (B) which is found to be oscillatory.

The wave velocity \( v \) is found to be given by

\[
v = k\cdot e^{-E_a/RT} [H^+]_0 \cdot [BrO₃⁻]^{1/2}
\]

where \( k \) depends on the nature of the system but is independent of temperature and concentration; \( E_a \) denotes the apparent energy of activation and the subscript 0 denotes the initial concentrations. \( E_a \) is the same for all the three systems both for one-dimensional and two-dimensional waves. The average value of \( E_a \) is found to be \( 44 \pm 2 \text{kJmol}^{-1} \).

For the three systems, it is found that the wave velocity of successive bands decreases in an ordered manner at a fixed temperature according to the relation.

\[
k = c' - a' n^2
\]

where \( c' \) and \( a' \) are constants and \( n \) is the number of successive bands. Temperature dependence of one-dimensional and two-dimensional wave velocities in other bromate-driven systems, viz., malonic acid + BrO₃⁻ + Ce⁴⁺ / Mn²⁺ + ferroin + H₂SO₄ have also been investigated and \( E_a \) is found to be similar to \( E_a \) of systems (A-C). Comparison of the results of ferroin + bromate + H₂SO₄ and tartaric acid + acetone + bromate + ferroin + H₂SO₄ systems for which \( E_a \) is identical shows that there is a common process which controls the wave propagation.

Chemical waves represent a typical far-from-equilibrium phenomenon in a system where the concentrations are not uniform not only in course of time but also vary in space and that too in periodic manner. Systems exhibiting chemical waves can display a variety of bifurcation phenomena. Such waves have been observed in the following type of systems: (i) BrO₃⁻ + Br⁻ + ferroin + malonic acid + H₂SO₄ (ref. 6); (ii) BrO₃⁻ + Ce⁴⁺ + ferroin + malonic acid + H₂SO₄ (ref. 7). In type (ii) malonic acid has been replaced by citric acid, malic acid and acetylacetone. Waves are also formed on thick porcelain membrane when it is soaked with type (ii) reagent. Possibility of formation of both phase and trigger waves has been indicated. Phase waves are reported to propagate independently of diffusion along a phase gradient in an oscillatory reagent. On the other hand, trigger waves propagate by the interaction of chemical reaction and diffusion of intermediate species in an excitable reagent. Recently, Rausser and Field have proposed a model of spatio-temporal oscillations in Type (i) reagent, based on reversible oregonator. Numerical solution of appropriate partial differential equation shows that the model yields solutions corresponding to both phase and trigger waves.

Clearer waves are formed in Type (ii) reagent as compared to those in Type (i) reagent. Still sharper wave fronts are obtained when Mn²⁺ is used as a catalyst in place of Ce⁴⁺ in Type (ii). In general, the leading edge of the wave front is sharper while the trailing end is diffuse. Experimental studies in such systems clearly show the relationship between temporal oscillations, chemical waves and space oscillations.

The propagation of a single band in Type (ii) reagent formally resembles the propagating fronts in the iodate oxidation of arsenous acid. Spatio-temporal oscillations are not as clearly understood as the temporal oscillations. Hence a detailed study of the properties of chemical waves is necessary. Both single and multiple propagating fronts have been observed and it is interesting to study whether their properties are the same. There are other related questions. How do wave velocities in one-dimensional and two-dimensional cases differ or how velocity differs when Ce⁴⁺ is replaced by Mn²⁺ (see refs 14, 15)? Why does the concentration dependence of wave velocity differ in Type (i) and Type (ii) reagents? Is there any evidence to show that in all BrO₃⁻ driven reactions, the same autocalytic subset controls the spatio-temporal oscillations? All the questions require careful study and this has been attempted in the present investigation. Results show that the sequence of events leading to propagation of multiple fronts...
particularly with respect to timing has very good reproducibility. Further, it is found that for all systems the wave velocity depends on $[\text{BrO}_3^-]^{1/2}$ and $[\text{H}^+]_0^{-1}$ and the apparent energy of activation is the same.

**Materials and Methods**

Analytical grade oxalic acid (Loba Chemicals), acetone (S.D.'s), ceric ammonium sulphate (B D H, England), Mn$^{2+}$ (Thomas Baker), sulphuric acid (B D H), potassium bromate (Sarabhai Chemicals), ferroin (C D H), mandelic acid (B D H), lactic acid (Sisco Chemical), and malonic acid (B D H), were used as such.

**Results**

**Study of spatio-temporal oscillations:**

(a) One-dimensional wave propagation

Fresh and filtered solutions of the reagents in 1.5 M $\text{H}_2\text{SO}_4$ were used. The reaction mixture containing organic acid, acetone, ceric ammonium sulphate and potassium bromate in sulphuric acid medium was homogenized in a beaker by vigorous stirring. Temporal oscillations were allowed to continue for sometime and an aliquot (5 ml) from the reaction mixture was taken in a tube (length, 40 cm; diam, 5 mm) and to this ferroin solution (0.5 ml) was added. The tube was cleaned before hand by steaming. The solution was rendered homogeneous by inverting the tube several times. The solution turned blue within 2 min. Experiments were performed at 25.0±0.1°C in an air-thermostat.

A red nucleus was formed in the reaction tube after some time ($t_1$/min) from the time of mixing at the top of the tube. The nucleus grew in size and moved downwards reaching the bottom within 10 min. As soon as the red colouration touched the bottom of the tube, a blue nucleus was formed at the bottom. This moved gradually upward with a fixed velocity and the entire solution turned blue within 10 min. The colour remained as such for 75 min. At this stage a red nucleus was again formed at the bottom and a red band started moving upwards, but this time it went only up to a distance of 5 cm and then it got submerged into blue region. After some time ($t_2$/min), a red nucleus was formed at the bottom and a red band started moving upwards. Again after a lapse of some time period ($t_3$/min) from the initial time a second red nucleus again appeared at the bottom and a second band started moving upwards. After $t_4$ minutes, the tube had three red bands and three blue bands. The number of bands ($n$) increased with time and consequently 26 red and 26 blue bands were produced in the tube after a lapse of a certain time period ($t_5$/min) from the initial time. The bands moved very slowly upwards with a fixed velocity. Similar results were obtained when Ce$^{4+}$ was replaced by Mn$^{2+}$ and the time intervals $t_1$ to $t_5$ had excellent reproducibility.

The plot of $x$, the position of wave front versus time $t$ was linear. The velocity of propagation of each red and blue band was measured as a function of time $t$. The dependence of the velocity of each band on concentration of the reactants was also studied. The results are plotted in Figs 1 and 2 for a typical case. The wave formation in all the systems has excellent reproducibility. The sequence, the time and velocity have very good reproducibility. The time of appearance of nuclei was reproducible to ±0.2 min while the velocity of band propagation was reproducible to ±0.01 cm/min. The measurements were repeated by replacing Ce$^{4+}$ by Mn$^{2+}$. The waves were formed in a narrow range of concentrations of reactant systems (A-C) (Table 1).
Density determination

In order to ascertain the absence of convection in the experimental setup, the density of red zone and blue zone in the reaction system was determined by pyknometer in the usual manner at 25°C. The values are recorded in Table 2. The data show that the density of two zones are almost identical, thereby showing the absence of convection. Hence the results can be analyzed from the viewpoint of irreversible thermodynamics and non-linear dynamics. Further, it follows that the usual reaction-diffusion equation can also be applied in the present case.

Nature of waves

In order to ascertain whether the waves are trigger or phase waves, experiment was repeated in a similar tube but having a stopcock in the middle for all the systems. Wave was generated and allowed to move upwards. When the stopcock was closed, cessation of wave propagation indicated that the waves were trigger waves in the systems (A) and (C) (Table I). On the other hand, the waves were not obstructed in system (B). Thus, in the case of system (B) the observed waves are phase waves.

Nature of excitability of the medium

Redox potential measurements with electronic recorder showed that in the presence of ferroin systems (A) and (C) were non-oscillatory while in its absence these were found to be oscillatory.

Influence of reagents on wave structure

Bromate (0.1 ml, 0.2994 M) was added when the waves and the banded structure died out. After about time $t_6$, the formation of waves again started following the process described above.

(b) Two-dimensional wave propagation

Prior to mixing, all solutions prepared in 1.5 M sulphuric acid medium were kept in an air-thermostat maintained at 25 ± 0.1°C. A mixture of the organic acid and sulphuric acid was taken in the lower part of the cell while solutions of $\text{Mn}^{2+}/\text{Ce}^{4+}$ and potassium bromate were taken in the upper part of the cell, which was similar to that used earlier. When the cell attained a constant temperature, the reactants were allowed to mix and the resulting solution stirred continuously electromagnetically at a fixed rate for a definite period and temporal oscillations were allowed to occur. A fixed volume of the solution (5 ml) was transferred to a specially constructed rectangular cell (7.5 x 7.5 x 2.0 cm$^3$) consisting of plain glass having a glass cover. This was specially fabricated so that the depth of the solution would remain constant at every place. Ferroin (0.5 ml) was added so that the depth of the solution was 1.5 mm. The rectangular cell was placed on the base of a travelling microscope which was kept horizontal.

A red nucleus was formed at the centre of the cell at a fixed time ($h$) after the addition of the indicator. It moved towards the wall with a fixed velocity. Again after time $t_9$ a blue ring was formed at the centre which also moved towards the wall with a fixed velocity. After time $t_9$ (sec) form initial time a second red ring was formed at the centre of the vessel which moved towards the wall with a fixed velocity. Again another blue ring was formed after time $t_10$. In this manner, ten blue and eleven red rings were formed.

The movement of the wave front was followed with the help of a travelling microscope and the time was noted with an electronic digital stop watch having least count equal to 0.01 sec. The experiment was repeated several times under identical conditions. Experiments were done in air-thermostat maintained at 25 ± 0.1°C.

Whereas in the one-dimensional case, velocities of the successive bands $v_1$, $v_2$, $v_3$ etc. decrease, this was not so for the two-dimensional case. It was found

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Table 1—Temperature and Concentration Ranges of Reactants in System Showing Waves

<table>
<thead>
<tr>
<th>System</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic acid</td>
<td>$1.8 \times 10^{-3} M$ to $4.3 \times 10^{-1} M$</td>
<td>$2.7 \times 10^{-2} M$ to $9.3 \times 10^{-2} M$</td>
<td>$2.7 \times 10^{-2} M$ to $9.4 \times 10^{-1} M$</td>
</tr>
<tr>
<td>Pot. bromate</td>
<td>$1.1 \times 10^{-2} M$ to $0.16 M$</td>
<td>$4.0 \times 10^{-2} M$ to $0.16 M$</td>
<td>$3.9 \times 10^{-2} M$ to $0.15 M$</td>
</tr>
<tr>
<td>Acetone</td>
<td>$3.4 \times 10^{-2} M$ to $3.6 \times 10^{-1} M$</td>
<td>$1.6 \times 10^{-1} M$ to $2.5 M$</td>
<td>$0.15 M$ to $2.6 M$</td>
</tr>
<tr>
<td>$\text{Ce}^{4+}/\text{Mn}^{2+}$</td>
<td>$1.3 \times 10^{-4} M$ to $1.8 \times 10^{-2} M$</td>
<td>$4.7 \times 10^{-4} M$ to $1.8 \times 10^{-2} M$</td>
<td>$4.2 \times 10^{-4} M$ to $1.9 \times 10^{-2} M$</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>$0.17 M$ to $5.1 M$</td>
<td>$0.17 M$ to $5.2 M$</td>
<td>$0.1 M$ to $5.0 M$</td>
</tr>
<tr>
<td>Temp</td>
<td>8°—40.3°C</td>
<td>11.5°—45.5°C</td>
<td>9°—44.5°C</td>
</tr>
</tbody>
</table>

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Table 2—Density (g/cc) of Red and Blue Zones in Reaction Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Red zone</th>
<th>Blue zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.2775 ± 0.0002</td>
<td>1.2866 ± 0.0002</td>
</tr>
<tr>
<td>B</td>
<td>1.3912 ± 0.0002</td>
<td>1.3980 ± 0.0002</td>
</tr>
<tr>
<td>C</td>
<td>1.3212 ± 0.0002</td>
<td>1.3232 ± 0.0002</td>
</tr>
</tbody>
</table>
that $V_1^* > V_2^* = V_3^*$ for blue bands while for corresponding red bands $V_2^* = V_3^* = V_4^*$. There was no red band corresponding to first blue band. (Prime b stands for blue while that for r stands for red; the subscript denotes the number of the band). Measurements for all the systems were repeated by replacing Ce$^{4+}$ by Mn$^{2+}$ and the results were similar.

**Comparison with previous work**

Previous detailed quantitative work on one-dimensional waves in B-Z systems was due to Rastogi et al.\(^8\)\(^-\)\(^1\)\(^4\). Accordingly one-dimensional wave velocities for malonic acid/citric acid + BrO$_3^-$ + Ce$^{4+}$/Mn$^{2+}$ + ferroin + H$_2$SO$_4$ systems were measured. These are compared in Table 3 for the first band. The agreement is satisfactory. Temperature dependence of velocity in one of the systems was also investigated and the results are recorded in Table 4.

The reliability of the technique followed for the determination of two-dimensional wave velocity was checked by making measurements on the B-Z system employed by Field and Noyes\(^1\)\(^1\). Here the procedure was slightly different to that described earlier. Ferroin was added to the reaction mixture and one temporal oscillation was allowed to occur so that the solution turned red. Now 5.5 ml of this solution were transferred to a petri-dish. After some time a blue nucleus was formed which propagated outwards followed by successive propagation of red and blue waves initiated by red and blue nuclei respectively. The results are given in Table 3 and the agreement is again gratifying. In agreement with Field and Noyes\(^1\)\(^1\) it was observed that wave velocity is given by the relation (1)

$$v = k [H^+]_{0}^{1/2} [BrO_3^-]_{0}^{1/2}$$  \(\ldots (1)\)

where $k$ is a constant (subscript 0 denotes the initial concentration). However, we obtained $k = 2.38$ cm/min/mol as compared to the value of 2.48 obtained from the data of Field and Noyes. The agreement is again reasonably good.

**Discussion**

There are certain specific features which are common to all the systems. The decay and formation of the waves always start from the top. It is found that there is a very narrow range concentration of reactants as well as a narrow range of temperature in which waves are formed (Table 1). The successive bands are formed at specific time intervals which are

<table>
<thead>
<tr>
<th>System</th>
<th>Temp $^\circ$C</th>
<th>Nature of wave</th>
<th>Velocity (cm min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Mn$^{2+}$ (0.0008 M) + malonic acid (0.128 M) + BrO$_3^-$ (0.044 M) + H$_2$SO$_4$ (1.5 M) + ferroin</td>
<td>35.0 ± 0.1</td>
<td>One-dimensional</td>
<td>0.31 ± 0.01</td>
</tr>
<tr>
<td>(ii) Mn$^{2+}$ (0.0032 M) + citric acid (0.128 M) + BrO$_3^-$ (0.044 M) + H$_2$SO$_4$ (1.5 M) + ferroin</td>
<td>35.0 ± 0.1</td>
<td>One-dimensional</td>
<td>0.32 ± 0.01</td>
</tr>
<tr>
<td>(iii) Bromomalonic acid (0.075 M) + BrO$_3^-$ (0.233 M) + H$_2$SO$_4$</td>
<td>25.0 ± 0.1</td>
<td>Two-dimensional</td>
<td>0.55 ± 0.01</td>
</tr>
</tbody>
</table>

Table 3—Test of Experimental Technique and Comparison with Earlier Work

Table 4—Apparent Energy of Activation for Wave Propagation in Different Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Metal ion</th>
<th>$k$ cm x min$^{-1}$ mol$^{-1/2}$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ce$^{4+}$</td>
<td>2.06(a)</td>
<td>42(a)</td>
</tr>
<tr>
<td>B</td>
<td>Ce$^{4+}$</td>
<td>5.13(b)</td>
<td>40(b)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>2.01(a)</td>
<td>45(a)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>5.07(b)</td>
<td>43(b)</td>
</tr>
<tr>
<td></td>
<td>Ce$^{4+}$</td>
<td>1.49(a)</td>
<td>47(a)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>3.24(a)</td>
<td>44(b)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>3.36(b)</td>
<td>47(b)</td>
</tr>
<tr>
<td></td>
<td>Ce$^{4+}$</td>
<td>1.07(a)</td>
<td>50(a)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>1.05(a)</td>
<td>44(a)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>2.30(b)</td>
<td>43(b)</td>
</tr>
<tr>
<td></td>
<td>Ce$^{4+}$</td>
<td>2.34(b)</td>
<td>45(b)</td>
</tr>
<tr>
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<td>Mn$^{2+}$</td>
<td>1.05(a)</td>
<td>44(a)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>2.30(b)</td>
<td>43(b)</td>
</tr>
<tr>
<td></td>
<td>Ce$^{4+}$</td>
<td>2.2(a)</td>
<td>43(a)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>3.18(b)</td>
<td>43(b)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>2.18(a)</td>
<td>46(a)</td>
</tr>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>3.14(b)</td>
<td>45(b)</td>
</tr>
</tbody>
</table>

Concentrations of the reactants in the system (D) are as follows:
Malonic acid (0.032 M), Ce$^{4+}$/Mn$^{2+}$ (0.0008 M), BrO$_3^-$ (0.044 M), H$_2$SO$_4$ (1.5 M) and ferroin (2.14 x 10$^{-3}$ M).

(a) Values for one-dimensional wave.
(b) Values for two-dimensional wave.
reproducible. These probably correspond to successive bifurcations. The number of ultimate propagating bands is also reproducible. It is found that \( v_1 > v_2 > v_3 \) where \( v_1 \), \( v_2 \) and \( v_3 \) are the velocities of first, second and third red bands, respectively. Two types of propagating bands are formed: one in the upper region and the other in the lower region. Although the velocities of red and blue bands are identical in each zone, the velocity in the lower region is always found to be higher. This is probably associated with convection. In the course of time, bands from the two zones adjust to yield a well-defined banded structure of definite number of blue and red bands.

Similar behaviour is observed in the case of two-dimensional waves. Here also circular bands are produced at definite time intervals which are reproducible. The number of circular rings is also reproducible. Further, except for the first band, velocities of red and blue bands are the same. In this respect the behaviour of two-dimensional waves differs from that of one-dimensional wave. The sequence of events in the case of system which \( \text{Mn}^{2+} \) or \( \text{Ce}^{4+} \) is identical. The velocities of the bands differ only slightly when \( \text{Ce}^{4+} \) is replaced by \( \text{Mn}^{2+} \).

The results further show that the velocity of two-dimensional wave propagation is always greater than that of one-dimensional wave propagation. Nevertheless, the ratio \( r \) between the two is approximately the same for all the systems. This indicates that \( r \) is a function of the geometry of the system.

Dependence of wave velocity on the initial concentrations of the reactants has been studied for each band in the case of one-dimensional propagation both for phase as well as trigger waves. In each case, the velocity is given by the reaction (2)

\[
v = k[H^+]^{-1}[\text{BrO}_3^-]^{1/2}
\]

where \( k \) is different for each band. It may be noted that \( k \) depends on the number of bands or the number of bifurcations as well as on temperature. The relationship (2) is similar to that found earlier. The values of \( v \) for different bands (system A) have been plotted against \( n \) in Fig. 3 which shows that \( k \) is related to \( n \) by the expression (3)

\[
k = c' - a'n^2
\]

where \( c' \) and \( a' \) are constants at a specific temperature. Here \( n \) denotes the number of successive waves. Further the plots of \( k \) against reciprocal of temperature are linear. A typical plot is given in Fig. 4 so that an Arrhenius type equation (4)

\[
k = A \cdot e^{-E_A/kT}
\]

satisfies the data. \( E_A \) may be called apparent energy of activation and \( A \) is a constant. Both the Eqs (2) and (4) are found valid for two-dimensional waves also for all the three systems. A comparison of the values of \( A \) and \( E_A \) (Table 4) shows that magnitude of \( E_A \) is the same for all the systems for both one-dimensional and two-dimensional waves. It would be interesting to compare the values of \( E_A \) for the above systems with the case when metal ions are absent. Incidentally, one-dimensional and two-dimensional wave propagation in tartaric acid + acetone + bromate + \( \text{H}_2\text{SO}_4 \) + ferroin and one-dimensional wave propagation in bromate + ferroin + \( \text{H}_2\text{SO}_4 \) systems have been investigated recently. It is found that in both the cases, although Eq. (1) and not Eq. (2) satisfies the data, \( E_A \) is found to be 44 ± 1 and 42 kcal mol\(^{-1}\) respectively. From these results it follows that there is a common process which controls the wave propagation in B-Z oscillators of different types.

Qualitatively, the observation that wave velocity primarily depends on the \([H^+]\) and \([\text{BrO}_3^-]\) is understandable, since former has a very high value of diffusion coefficient and \([\text{BrO}_3^-]\) is the principal reactant according to the above mechanism. However, it is little baffling that quantitative dependences of velocities in Type (i) and Type (ii) systems on \([H^+]\) are different. Differences are also evident in the time periods of temporal oscillations in the two types of
systems. For example, in the ferroin-catalyzed oscillations the period (T) is given by the relation (5)

\[ T(s) = C\left[[\text{BrO}_3]_0^{1.8}\left[\text{H}_2\text{SO}_4\right]_0^{2.7}\left[\text{MA}\right]_0^{0.27}\times s\text{mol dm}^{-3}\right]^{1/2} \quad ... \ (5) \]

where \( C \) is a constant. On the other hand, for manganese catalysed oscillations for the type (II), it is found that

\[ T(s) = C'\left[[\text{BrO}_3]_0^{1.2}\left[\text{MA}\right]_0^{1.2}\left[\text{H}_2\text{SO}_4\right]_0^{1.0}\times s\text{mol dm}^{-3}\right]^{-1/2} \quad ... \ (6) \]

where \( C' \) is some other constant. The difference in the reactivities of the two types of systems is perhaps due
to difference in the mechanism of autocatalytic oxidation of \([\text{Fe(Phen}_3]_2^+ \) by bromate\(^{22}\) and the corresponding cerous bromate reaction\(^3\). There is

It should be noted that amount of \( \text{Ce}^{4+} \) present at the

\[ \text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightleftharpoons \text{HOBr} + \text{HBrO}_2 \quad (\text{R}_1) \]

\[ \text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightleftharpoons 2\text{HOBr} \quad (\text{R}_2) \]

\[ \text{HOBr} + \text{Br}^- + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O} \quad (\text{R}_3) \]

\[ \text{Br}_2 + \text{CH}_3\text{COCH}_3 \rightleftharpoons \text{Br}^- + \text{H}^+ + \text{CH}_3\text{COCH}_2\text{Br} \quad (\text{R}_4) \]

\[ \text{Ce}^{4+} + \text{organic acid} \rightleftharpoons \text{Ce}^{3+} + \text{products} \quad (\text{R}_5) \]

\[ \text{Ce}^{4+} + \text{Br}^- \rightleftharpoons \text{Ce}^{3+} + [\text{Br}_2] \quad (\text{R}_6) \]

It should be noted that amount of \( \text{Ce}^{4+} \) present at the

On the other hand following reaction set \((\text{R}_7 \text{ to } \text{R}_9)\) occurs preferentially in the red zone,

\[ \text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightleftharpoons 2\text{Br}2\text{O}_2 + \text{H}_2\text{O} \quad (\text{R}_7) \]

\[ \text{BrO}_3^- + \text{Ce}^{3+} + \text{H}^+ \rightleftharpoons \text{Ce}^{4+} + \text{HBrO}_2 \quad (\text{R}_8) \]

\[ 2\text{HBrO}_2 \rightleftharpoons \text{H}^+ + \text{Br}_2 + \text{HBrO} \quad (\text{R}_9) \]

\[ \text{Ce}^{4+} \text{ is replaced by } \text{[Fe(Phen}_3]_2^+ \text{. ferroin, i.e. } \text{[Fe(Phen}_3]_2^{3+} \text{ is formed in step (R}_8\text{), reaction analogous to (R}_9\text{)} \text{ would not occur, but that corresponding to (R}_9\text{) would occur as follows.} \]

\[ \text{[Fe(Phen}_3]_2^{3+} + \text{Br}^- \rightleftharpoons [\text{Fe(Phen}_3]_2^{2+} + [\text{Br}_2] \]

However, in the case of \( \text{Ce}^{4+} \), probably the back reaction \((\text{R}_9)\) takes place while this is not so when ferroin is present.

It is not easy to find a quantitative explanation for Eqs (1)-(3). Field and Noyes obtained the reaction (7)

\[ v = 4\left[D_{\text{HBrO}_2}\right]^{1/2}\left[\text{H}^+\right]^{1/2}\left[\text{BrO}_3^-\right]^{1/2} \quad ... \ (7) \]

which is similar to Eq. (1) under drastic assumptions. Equation (7) predicts that wave velocity is proportional to \( [\text{H}^+]^{1/2}\) and \( [\text{BrO}_3^-]^{1/2}\) in agreement with experimental results. It suggests that autocatalytic subset is the controlling factor. Further the apparent energy of activation \( (E_A)\) is made up of the

activation energy of diffusion of \( \text{HBrO}_2 \) and the energy of activation of step \((\text{R}_8)\). However, it does not explain the dependence of wave velocity on \( [\text{H}^+]\) and \( [\text{BrO}_3^-]\). Further, it does not explain why the velocity decreases for subsequent waves and how the wave velocity can be zero under certain circumstances so that dissipative structure can be obtained. Decrease in wave velocity and emergence of dissipative structure can be qualitatively understood if \((\text{R}_9)\) and \((\text{R}_8)\) are simultaneously taken into consideration as suggested by Tilden\(^{23}\) and supported by Reusser and Field. However, if reactions \((\text{R}_5)\), \((\text{R}_9)\) and the back reaction \((\text{R}_9)\) are also taken into account as it should be, the reaction diffusion equation becomes unduly complicated and difficult to solve. Combining Eqs (2)(4), we may write

\[ v = (c'' - a'' n^2)\left[\text{H}^+\right]^{1/2}\left[\text{BrO}_3^-\right]^{1/2} A'e - R^1 \quad ... \ (8) \]

where \( c'', a'' \) and \( A' \) are constants so that

\[ (c'' - a'' n^2)A' = (c'' - a'' n^2) \quad ... \ (9) \]

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