Conductimetric and amperometric study of the bromate-phenol-sulphuric acid oscillating reaction

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The bromate-phenol-sulphuric acid chemical reaction that exhibits sequential oscillations has been studied by conductivity measurements and ultrasonically enhanced chronoamperometric methods. Oscillatory behaviour is observed in conductivity and current on a working electrode at different potentials. The experimental results have been qualitatively analyzed and compared to a computer simulation using the GVKFR mechanism for uncatalyzed chemical reactions.

It is well known that the Belousov-Zhabotinsky reaction (BZ reaction) is the most characterized chemical oscillator as both chemical reaction and as a nonlinear chemical dynamic system\(^1\)\(^-\)\(^3\). A variety of organic mixed substrates give rise to sequential oscillations in the BZ reaction and chemical explanations to its kinetics with nonlinear dynamics analysis had been reported\(^9\).

Uncatalyzed bromate oscillators (UBO reactions) do not require any metal ion catalyst, and the organic substrate performs some of the functions of the metal ion as well\(^9\)\(^-\)\(^11\). The uncatalyzed bromate-phenol-sulphuric acid system exhibits an astonishing variety of dynamic behaviour including three stationary and two sequential oscillatory states, dual-frequency and dual-amplitude oscillations, and non-periodic oscillations in a closed and stirred batch reactor\(^11\)\(^-\)\(^14\). The most accepted model for the mechanism of the UBO reaction, proposed by Gyorgyi, Varga, Köros, Field and Ruoff (GVKFR model)\(^15\), closely simulates experimental results like the induction period and the first set of oscillations. However, it is unable to reproduce the second set of oscillations observed in the bromate-phenol-sulphuric acid system.

As compared to potentiometry, ultrasonically enhanced chronoamperometry has some advantages as an experimental tool for monitoring the bromate-phenol-sulphuric acid reaction\(^16\). Herein, we first explore the use of a conductimetric probe for monitoring the UBO reaction and also qualitatively compare the experimental results obtained by ultrasonically enhanced chronoamperometric and conductimetric techniques with numerical simulations based on the GVKFR model.

Materials and Methods

Potentiometric measurements were carried out using a Fluke 189 digital multimeter connected to a computer by an IR RS-232C port and controlled by FlukeView FORMS software. The indicator and reference electrodes were platinum and SCE, respectively. Conductivity was measured as a function of time using a conductivity meter connected to a computer universal interface ULI (Vernier) and controlled by LOGGER software. The solution was magnetically stirred with a teflon-coated stirrer. The reactants were introduced into the reaction vessel in the following order: 10 mL of aqueous 1.0 \(M\) \(H_2SO_4\), then 10 mL of 0.041 \(M\) phenol, and finally 10 mL of 0.18 \(M\) \(KBrO_3\). The phenol and bromate solutions were prepared in 1.0 \(M\) \(H_2SO_4\). When the conductance was measured in the presence of ultrasound, the reactor was placed inside a 30 kHz ultrasonic bath (ELMA) without a temperature control.

For the ultrasound experiments, an ultrasonic processor UP50H (dr. Hielscher) of 30 kHz with a MS7 sonotrode was used. The sonoelectrochemical experiments were conducted in a 100 cm\(^3\) thermostatted sonochemical cell, and the temperature was monitored by a stainless steel temperature probe (Vernier LabPro\(^6\)) connected to a computer universal interface (ULI Vernier) and controlled by LOGGER.
software. The sonoelectrochemical cell consisted of a conventional three-electrode cell with a saturated calomel reference electrode (SCE), a 3 mm diameter platinum working electrode mounted on the bottom of the reactor, and a Pt-sheet counter electrode. The ultrasonic horn was placed at a fixed distance from the top to the working electrode. The ultrasonic power used was either 3 W cm\(^{-2}\) or 1.5 W cm\(^{-2}\). All electrochemical experiments were performed using an \(\mu\)AUTOLAB II (Ecochemie, Netherlands) potentiostat.

The numerical simulation was carried out by integration of the set of differential equations resulting from the application of the mass action law to the GVKFR model. Since appropriate rate equations, rate constants, and activation energy values for the bromate-phenol oscillator are not available, the rate equations, rate constants and the initial values given in Ref. 15 were used. Hence, the analysis between the simulation and the experimental results is only qualitative. It is proposed in the GVKFR model\(^\text{15}\) that the \(H^+\) concentration should be kept constant, but in order to see the changes of this species we did not maintain this restriction. The numerical integration was carried out using the subroutine DLSODE that uses the Hindmarsh implementation of the Gear method\(^\text{17,18}\). The Fourier transforms were calculated using the Excel (Microsoft) routine FOURIER ANALYSIS.

Results and Discussion

Even though it is true that oscillations in \(pH\) have been observed when phenol is added to the bromite-hydroxylamine\(^\text{19}\) or bromite-thiosulfate\(^\text{20}\) systems, they have not been previously observed for UBO or Belousov-Zhabotinsky type reactions. Our attempts to measure the \(pH\) changes during the UBO reaction with solid and glass \(pH\) sensors failed due to experimental problems, such as the deactivation of the \(pH\) sensor by the formation of a passivating layer on the electrode surface (mainly due to the formation of polymeric insoluble products of reaction), and the sensor \(pH\) range. However, changes in \(H^+\) concentration could be detected with more accuracy in the highly passivating and corrosive medium by a conductimetric probe in spite of its lack of selectivity. The changes in solution conductivity that were observed during the present study of the UBO reaction can be explained in terms of the consumption and formation of some conducting species like \(H^+\) and \(BrO_3^-\), \(Br^-\), \(BrO_2^-\), or other inorganic and organic ions. The experimental conductivity during the course of the UBO reaction decreases constantly and a middle zone of tenuous oscillating variations is observed. However, the rapid decrease in the solution conductivity and the signal noise due to the presence of solids in suspension make the observation of the oscillating pattern very difficult.

In order to analyze the oscillating behaviour in more detail the drift line was subtracted from the experimental data and a noise filtration was done using Fourier transform. For the numerical simulations based on the GVKFR mechanistic model, the total conductivity of the system (\(\lambda_T\)) was directly calculated from Eq. 1,

\[
\lambda_T = \lambda_{H^+} + \lambda_{Br^-} + \lambda_{BrO_3^-} + \lambda_{BrO_2^-} + \lambda_{H^+} + \lambda_{SO_4^{2-}} \quad \ldots (1)
\]

For simplicity, the conductivity of each ion is calculated using Eq. 2,

\[
\lambda_i = \lambda_{m,i} C_i \quad \ldots (2)
\]

where \(\lambda_{m,i}\) is the molar conductivity of the \(i^{th}\) ion, and \(C_i\) is its concentration.

Figure 1a shows the result of deconvoluted solution conductivity. It is clear that the conductivity profile matches well the electric potential trace that was simultaneously measured. It can be seen that the Fourier transform analysis is an invaluable tool for the analysis and deconvolution of complex experimental data such as those obtained in the course of an oscillating reaction.

In order to test the hypothesis for the variations in the experimental conductivity, the UBO solution was perturbed with bromate and bromide ions. No significant variations were observed in the electrical conductivity signal. However, when the UBO solution was perturbed with \(H^+\) ions (1.0 \(M\) \(H_2SO_4\)) a significant increase in the signal was observed.

Extensive numerical simulations based on the GVKFR mechanism and Eq. 1 indicate that the \(H^+\) ion contributes the most to the total conductivity and to the amplitude of the conductivity oscillations. The simulations indicate that the electrical conductivity signal in the oscillatory zone can be accounted for by 76% contribution of the change in proton conductivity and by 18% due to change in the bromate conductivity. The other ions do not contribute significantly to the amplitude of the conductivity oscillations.
In order to test the hypothesis that the major contribution to the conductivity oscillations comes from the variation in proton concentration, an ultrasonically enhanced chronoamperometric register at -0.5 V vs SCE was obtained during the course of the UBO reaction. At this potential, $H_2^+$ is reduced to $H_2$, and therefore any change in the limiting current has to be mainly related to an $H^+$ concentration change. This shows a decrease in its absolute value; very similar to that of the conductimetric record. The oscillatory behaviour can be clearly observed after a deconvolution procedure like the one performed on the conductivity data. Figure 1b shows the results of the deconvoluted sonocurrent during the course of the reaction, and also the relationship between the solution electric potential trace and the observed sonocurrent on the working electrode. The difference in the time scale between Figs. 1a and 1b is due to the difference in temperature in the two experiments.

At –0.5 V versus SCE, bromine can also be reduced and its contribution to the total signal in curve B of Fig. 1b ranges from 20 - 40%. Taking into account the results shown in Fig. 1, we suggest that the electric potential oscillations observed during the first set of oscillations of the bromate-phenol-sulphuric acid oscillating reaction are coupled to oscillations in $H^+$ concentration when solid products are present in the suspension. Cataldo\textsuperscript{21} has shown that ultrasound increases the conductance of electrolytic solutions. In order to observe the effect of ultrasound on conductivity, the reactor with the conductivity probe was placed inside an ultrasonic bath, without temperature control during the course of the oscillating reaction (Fig. 2). Figure 2 shows that ultrasound makes the conductivity record of the first set of oscillations unclear during the UBO reaction due to increases in the signal noise. On the other hand, it has been reported that the potentiometric record is much better in the presence of ultrasound\textsuperscript{16}. However, it is noteworthy that after the first set of oscillations there is an intermediate non-oscillatory period during which the solid products were not already present. Subsequently, a second train of oscillations emerges accompanied by a well defined conductivity oscillating profile. During the intermediate non-oscillatory period, the turbidity disappeared and ultrasound cleaned up the conductivity probe, which may be the reason for the noise depletion observed in the signal after this point.

Dynamic processes that exhibit sequential oscillations are usually observed in nature, and the modelling of these phenomena is challenging in nonlinear dynamics. To the best of our knowledge, the sequential oscillations shown in Fig. 2 do not yet have a mechanistic explanation. The GVKFR model fails to predict the second oscillatory behaviour and in order to improve it or to develop a new reaction scheme, it is necessary to put together the major
experimental evidence available. It may be noted that this is the first time that the sequential oscillations of the UBO reaction have been followed with a technique other than potentiometry.

In the absence of ultrasound and at 20°C, the second set of oscillations in electrical potential appeared after 6 hours of reaction. However, the conductivity probe was not able to resolve the oscillatory behaviour and a noisy monotonic signal of the electrical conductivity was recorded, which may be due to the presence of a polymeric film on the surface of the conductivity probe. The fact that the second set of oscillations can be detected only in the presence of ultrasound during the course of the oscillating reaction indicates that the latter has a positive effect on the conductimetric register.

We have earlier reported some of the advantages of ultrasonically enhanced chronoamperometry as compared to potentiometry for studying the complex kinetic behaviour of the bromate-phenol-sulphuric acid reaction\(^{16}\). Now it is important to qualitatively analyze the correlation between the theoretical simulation of the oscillating reaction based on the GVKFR model and the experimental results from the ultrasonically enhanced chronoamperometric experiments.

Figure 3 shows the electric current trace on a platinum working electrode at 1.2 V (Fig. 3a) for the oxidation of Br\(^-\) to Br\(_2\) when the current is proportional to Br\(^-\) concentration, and at 0.6 V (Fig. 3c) for the reduction of Br\(_2\) to Br\(^-\) when the current is proportional to Br\(_2\) concentration. Figure 3a shows only anodic currents while Fig. 3c shows only cathodic currents; for simplicity the absolute values of the current have been plotted in Fig. 3. Figure 3 (b & d) shows the concentration profiles of bromide and bromine respectively, simulated by the GVKFR model at 25°C according to the kinetic data available for the model.

The experimental conditions in which the chronoamperometric data shown in Fig. 3 were recorded are: distance between the ultrasonic horn and working electrode, 10 mm; ultrasonic power, 1.5 W cm\(^{-2}\); temp., 41°C. At this temperature it was observed that the electrode is only slightly passivated. It appears that in the presence of ultrasound a thinner polymeric film is formed on the electrode during the phenol electrooxidation at this temperature\(^{16}\). This observation can be explained in terms of the shorter time of the experiment because phenol reacts in solution and its concentration rapidly decreases as it produces the insoluble organic compounds that accompany the oscillating reaction. Therefore, the oxidation current of phenol on the working platinum electrode has to be negligible in comparison to the Br\(^-\) oxidation current.

Although the simulations and experiments were carried out at different temperatures, a qualitative analysis between both results can be made. It can be seen that the profiles of Figs 3c and 3d are very similar and there is a significant correlation between Figs 3a and 3b. However, it is important to notice that in Fig. 3c, after the first oscillating period the current decreases more slowly than the simulated concentration of bromine (Fig. 3d). This means that a significant concentration of this species remains for a longer time in the reaction medium. Maybe this fact partially explains why the GVKFR model cannot simulate the second set of oscillations. It predicts that the bromine concentration falls very quickly to zero, while a significant bromine concentration in solution may be necessary for the induction of the second set of oscillations.

The source of the redox potential oscillations during the UBO reaction is not as clear as in catalyzed systems\(^{22}\). If the above analysis is correct, Figs 3a and
3c should be similar to the Br\(^{-}\) and Br\(_2\) concentration profiles, respectively. Also, if the electrical potential profile recorded using a platinum indicator electrode is due to the redox couple Br\(^{-}\) / Br\(_2\), taking Eqs 3 and 4 into account a reconstruction of the potential trace can be done from the data shown in Figs 3a and 3c.

\[ C_i = k_i I_i \quad \ldots (3) \]

\[ E = E^{\circ}_{(Br_2/Br^-)} + \frac{RT}{2F} \ln \frac{I_{ref}}{I_{br^-}} + \frac{RT}{2F} \ln \frac{k_{br^2}}{k_{br^-}} \quad \ldots (4) \]

Equation 3 is the Nernst equation as a function of limiting currents, where \( I_i \) is the limiting current of the \( i^{th} \) species, \( C_i \) is its concentration and \( k_i \) is a constant. For simplicity, the last term of Eq. 4 was ignored. In any case it has to be a constant and is not important for the following analysis.

The similarity between the reconstructed and the experimental potential traces [Fig. 4(a & b)] recorded at the same time with the current trace is noteworthy. However, there is a significant difference between the oscillation amplitudes in [Fig. 4(a & b)]. Sridevi and Ramaswany\(^{23}\) have reported that the large amplitude oscillations obtained with a Pt electrode are due to the sequential response of the indicator electrode to the varying concentration ratios of many redox couples present in the reaction mixture. The results of Fig. 4 seem to support this last hypothesis.

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