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# Chemical chaos in novel iodate-driven oscillator–thiophenol–iodate–$H_2SO_4$ system

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**Abstract.** Chaotic oscillations in redox potential have been observed in thiophenol–$KIO_3$–$H_2SO_4$ system in batch reactors. These occur in a concentration and temperature range. Bifurcation from a stable regime to a chaotic regime occurs in a straight way in the entire concentration and temperature range. Oscillations were also studied in continuously stirred tank reactors. These oscillations are deterministic chaos. It is tentatively suggested that chaos in the system is due to a time delay caused by a large number of intermediates.

**Keywords.** Chaotic oscillations; chemical chaos; iodate-driven oscillator; thiophenol–$KIO_3$–$H_2SO_4$ system.

## 1. Introduction

Chemical turbulence, chaos or aperiodic oscillations, both temporal and spatial have aroused considerable current interest ever since it was recognised that chaos is not a necessarily random but a deterministic phenomenon (Ruelle and Takens 1971). Kruel and others distinguished between deterministic chaos and amplification of experimental noise (Freunel *et al* 1986). The view was reinforced by May (1976) who suggested a set of differential equations which could generate non-periodicity. Rössler (1977) showed that complex chemical kinetics involving three or more variables can generate chaos. The first example of chaos in an enzyme reaction was reported by Olsen and Degn (1977). Evidence of the chaotic state in the B–Z reaction in a CSTR was reported by Schmitz *et al* (1977). Chaos has been reported in similar systems by Heilweil and Epstein (1979). In a certain range of concentration and conditions, chaos has been reported in the $BrO_3^-$–$ClO_3^-$–$I^-$ system (De-Kepper *et al* 1981) and the $ClO_2^-$–$S_2O_3^{-2}$ system (Orbon and Epstein 1982). For a certain range of flow rates, chaotic oscillations have been observed in $BrO_3^-$–thiocyanate reaction (Simoyi 1987). In the system reported above, chaos could be generated by the control of the flow rate. In this manner aperiodicity involving one large amplitude followed by $n$ small amplitude oscillations ($n = 2, 3, 4\ldots$) has been achieved. These are examples of period doubling and period multiplicity bifurcation, which lead to quasi-periodic oscillations. In some systems, bifurcation from a periodic regime to an aperiodic regime has been reported (Orbon and Epstein 1982; Maselko and Epstein 1984). The example of bifurcation from a stable regime to a chaotic one and vice-versa has not been reported so far. In this communication a novel system is being introduced which is the first example of its kind from this angle.

## 2. Experimental

Thiophenol (CDH), Potassium iodate (BDH) and $H_2SO_4$ (BDH) of analytical grade were used as oscillatory reactants. Solutions of thiophenol and potassium iodate were prepared in 1·0 M $H_2SO_4$. The experimental procedure in the batch reactor was similar to that described by Rastogi and Srivastava (1987). Oscillations were studied in the reaction mixture containing thiophenol (0·018–0·006 M). $IO_3^-$ (0·011–0·0008 M) and $H_2SO_4$ (1·0 M). In the beginning, on mixing the reagents, the solution was clear. However, within a small time interval it became slightly turbid. Subsequently, turbidity disappeared and chaotic oscillations were produced. The oscillations were also studied in a continuously stirred tank reactor; the experimental procedure was similar to that described earlier (Rastogi and Srivastava 1987). All experiments were performed in a thermostat-regulated glass container maintained at 30°C $\pm$ 0·1°C, and the solution was continuously stirred by a magnetic stirrer at 1000 r.p.m.: the reaction was followed by recording the redox potential as a function of time, using a bright platinum electrode coupled with a reference calomel electrode, with an electronic recorder.

## 3. Results and discussion

Chaotic oscillations in redox potential have been observed in the thiophenol (0·018–0·006 M), $IO_3^-$ (0·011–0·0008 M) and $H_2SO_4$ (1·0 M). Typical results on thiophenol (0·012 M), $IO_3^-$ (0·0042 M) and $H_2SO_4$ (1·0 M) are shown in figure 1. The chaotic oscillations were also obtained when temperature was varied from 15 to 40°C. No Hopf

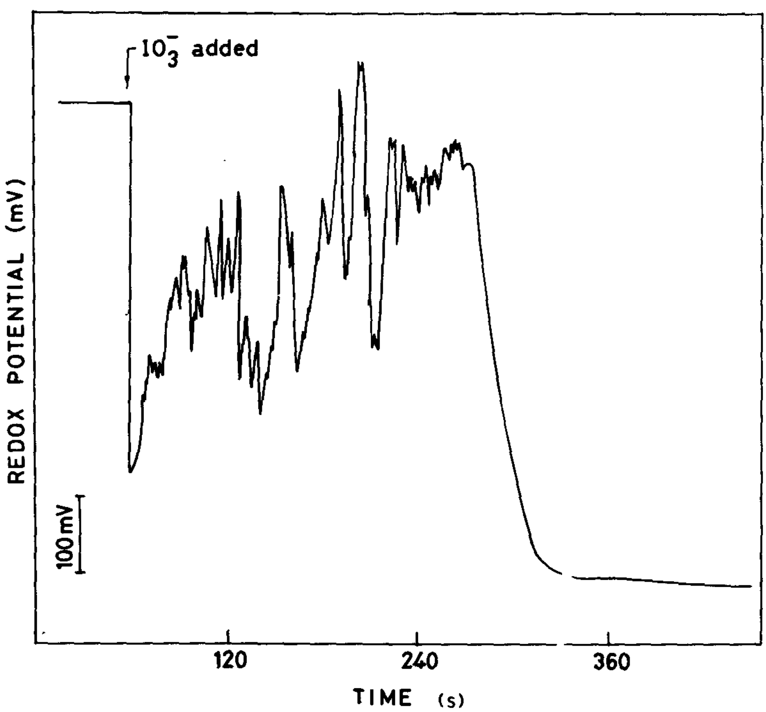


**Figure 1.** Chaotic oscillations in batch reactor, thiophenol (0·012 M), $IO_3^-$ (0·0042 M) and $H_2SO_4$ (1·0 M) at temperature 30°C.

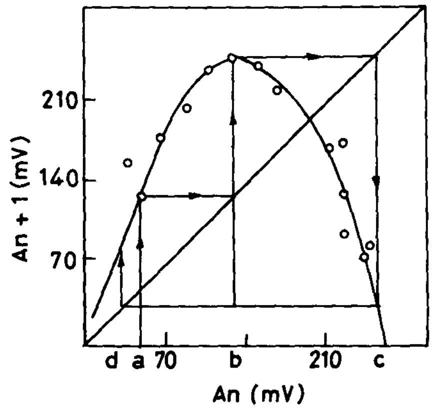


**Figure 2.** A plot of A$(n+1)$th oscillations amplitude against A $n$th oscillations amplitude, thiophenol (0·012 M), $IO_3^-$ (0·0042 M), $H_2SO_4$ (1·0 M) at temperature 30°C.

bifurcation was marked. On the other hand, the system was found to bifurcate directly into a chaotic regime from the stable branch. On the termination of aperiodic oscillations, the system bifurcates to a stable branch once again, period doubling was not observed beyond the bifurcation point. Between the two bifurcation points, there were chaotic oscillations all along. For the batch reactor, the amplitude of the $(n+1)$th oscillations has been plotted against the amplitude of $n$th oscillation as shown in figure 2, using thiophenol (0·012 M), $IO_3^-$ (0·0042 M), $H_2SO_4$ (1·0 M) and temperature 30°C $\pm$ 0·1°C, which shows that the Lyapunov exponent is greater than unity. Existence of aperiodic behaviour may be established by utilising the Li and Yorke (1975) theorem. This procedure was used experimentally by Olsen and Degn (1977) to show that chaotic behaviour existed in oscillation of $O_2$ concentration in a peroxidase catalysed oxidation reaction of NADH. Starting at the critical point b, as shown in figure 2, on tracing the next two iterates of the map, $c = f(b)$, and $d = f(c)$, as well as the preimage $a$, $b = f(a)$, since $a > d$ (i.e. if $d$ is to the left of $a$), there exist an infinite number of periodic points and the function can generate aperiodic motions. The Fourier transform of experimental data was performed by the computer and the power spectrum so obtained is shown in figure 3. The power spectrum consists of many significant frequencies. From the figures 2 and 3, it may be conjectured that the observed chaos is deterministic in natute.


**Figure 3.** Power spectrum of the experimental data containing thiophenol (0·012 M), $IO_3^-$ (0·0042 M) and $H_2SO_4$ (1·0 M) at temperature 30°C.

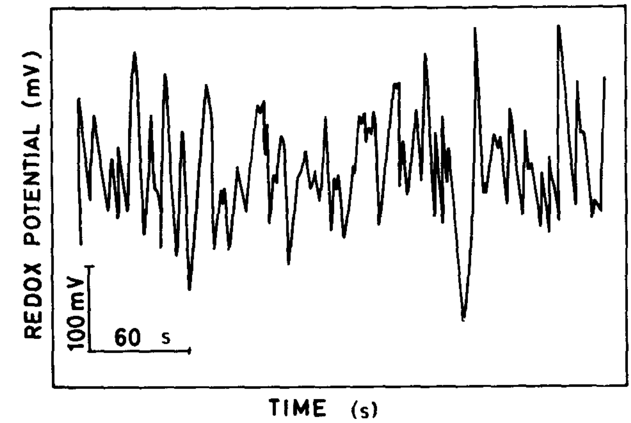


**Figure 4.** Chaotic oscillations in a continuously stirred tank reactor, thiophenol (0·012 M), $IO_3^-$ (0·004 M), $H_2SO_4$ (1·0 M) and $k_0 = 0{\cdot}035\,min^{-1}$ at temperature 30°C.

The oscillations were also observed in continuously stirred tank-reactors with change in flow rate. A typical potentiometric record with the reactant concentrations, thiophenol (0·012 M), $IO_3^-$ (0·004 M), $H_2SO_4$ (1·0 M) and flow rate $= 0{\cdot}035\,min^{-1}$ at temperature 30°C ± 0·1°C, led to a similar conclusion exhibiting chaotic oscillations as depicted in figure 4.

It has been pointed out that delay leading to chaos can be obtained in the system where we have more of the intermediates in the reaction chain (Szamosi and Lasky 1986; Rapp 1980) which is a precondition for the existence of chaos. It appears that in the studied system a number of intermediates are involved which are responsible for the generation of the chaos.

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## References

De-Kepper P, Epstein I R and Kustin K 1981 *J. Am. Chem. Soc.* **103** 2133
Freunel A, Kruel T and Schneider F W 1986 *Ber. Bunsenges. Phys. Chem.* **90** 1079
Heilweil E J and Epstein I R 1979 *J. Phys. Chem.* **83** 1359
Li T-Y and Yorke J A 1975 *Am. Math. Monthly* **82** 985
Maselko J and Epstein I R 1984 *J. Chem. Phys.* **8** 3175
May R M 1976 *Nature (London)* **261** 459
Olsen L F and Degn H 1977 *Nature (London)* **267** 177
Orbon M and Epstein I R 1982 *J. Phys. Chem.* **86** 3907
Rapp P E 1980 In *Mathematical models in molecular and cellular biology*, (ed.) L A Segel (Cambridge: University Press)
Rastogi R P and Srivastava P K 1987 *J. Non-Equilib. Thermodyn.* **12** 123
Rössler O E 1977 *Bull. Math. Biol.* **39** 275
Ruelle D and Takens F 1971 *Commun. Math. Phys.* **20** 167
Schmitz R A, Graniano K L and Hudson J L 1977 *J. Phys. Chem.* **67** 3040
Simoyi R H 1987 *J. Phys. Chem.* **91** 1557
Szamosi J and Lasky S J 1986 *J. Phys. Chem.* **90** 1995