STUDY OF BRIGGS–RAUSCHER OSCILLATORY REACTION IN AQUEOUS–ACETONITRILE MIXED MEDIUM

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The oscillatory behaviour of two new substrates namely, 2-thenoyltrifluoroacetone and cyanoacetic acid in the Briggs–Rauscher (B–R) system was studied in detail employing a mixed medium: aqueous–acetonitrile. The effect of acetonitrile concentration on the oscillatory behaviour is investigated. It is found that employing the aqueous–organic mixed media is highly beneficial in the oscillatory study, enabling the study of water-insoluble substances.

The oscillatory behaviour of different organic substrates in the uncatalyzed and catalyzed bromate systems has been studied in detail[1 – 3]. The iodate–hydrogen peroxide system (B–R reaction) has been studied with substrates having acidic hydrogen such as malonic acid, ethyl acetoacetate, acetylacetone and diethyl malonate[4]. Due to the poor solubility of many substances in water, their oscillatory study could not be done so far. The effect of organic solvents on the oscillatory characteristics has been studied for the catalyzed bromate systems[5 – 7]. Studies have recently been made employing aqueous organic media. The use of mixed solvent media has enabled the study of the oscillatory behaviour of a large number of new substrates in the iodate system[8] as well as the uncatalyzed and catalyzed bromate systems[9 – 12]. The present communication relates to the oscillatory behaviour of two new substrates, namely, 2-thenoyltrifluoroacetone and cyanoacetic acid in the Briggs–Rauscher system in 5 vol.% acetonitrile–water mixed medium.

EXPERIMENTAL

A. R. chemicals were used as received. Triply distilled water was used to prepare the solutions. Experiments were carried out under batch reaction conditions. Here all the constituents except the last one are taken in a polyethene beaker, kept well stirred and thermostatted (35 ± 0.1 °C). The

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addition of the last constituent (H_2O_2) into the reaction mixture triggered off oscillations (total volume of the oscillating solution was 25 ml). Potentiometric oscillations were recorded by a Siemens Kompensograph with a platinum indicator electrode (or iodide selective electrode) coupled to a saturated calomel electrode (SCE) through a potassium nitrate salt bridge. In the spectrophotometric follow up, a Zeiss PMQZ spectrophotometer was used and the reaction vessel was a 4 cm cell. Oscillations were recorded as a function of time at a wavelength of 480 nm.

RESULTS AND DISCUSSION

The oscillations obtained with 2-thenoyltrifluoroacetone or cyanoacetic acid as substrate in the B–R system were quite reproducible at 35 °C. Experiments were carried out in 5 vol.% acetonitrile–water mixed medium. The colour changed in both the cases from blue to colourless when 1% starch solution was included in the systems. The effect of changing the concentration of various constituents in turn has been studied.

2-Thenoyltrifluoroacetone

The oscillatory profiles for 2-thenoyltrifluoroacetone as substrate are given in Fig. 1. The oscillatory characteristics under different concentration conditions are presented in Table I. The oscillations recorded using three different techniques (using platinum electrode, iodide selective electrode and spectrophotometry) match well with respect to the number of oscillations and duration.

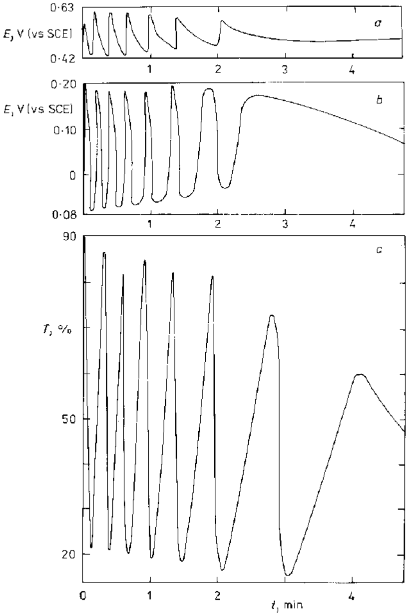

FIG. 1
Oscillatory profiles for 2-thenoyltrifluoroacetone–H_2SO_4–$MnSO_4$–KIO_3–H_2O_2 system (in 5 vol.% of acetonitrile). Concentration conditions: 0.013 M substrate, 0.187 M H_2SO_4, 0.035 M KIO_3, 0.064 M $MnSO_4$, 1.9 M H_2O_2; temperature 35 ± 0.5 °C. *a* Platinum electrode; *b* iodide selective electrode; *c* spectrophotometric profile at 480 nm

TABLE I
Oscillatory characteristics[a] of 2-thenoyltrifluoroacetone–H_2SO_4–$MnSO_4$–KIO_3–H_2O_2 system. Standard concentration conditions: 0.013 M substrate; 0.187 M H_2SO_4; 0.035 M KIO_3; 0.064 M $MnSO_4$; 1.9 M H_2O_2; 5 vol.% acetonitrile

Constituent varied mol l^{-1}	T_i	T_t	n	t	A	Potential range V (vs SCE)
Substrate						
0.003	0	0.6	2	0.30	70	0.59 – 0.66
0.007	0	2.3	4	0.56	200	0.40 – 0.60
0.010	0	2.0	6	0.33	200	0.45 – 0.65
0.013	0	2.0	8	0.25	200	0.40 – 0.60
0.017	0	2.0	11	0.18	170	0.38 – 0.55
H_2SO_4						
0.06	0	0.1	1	0.10	90	0.30 – 0.39
0.094	0	1.1	10	0.11	150	0.40 – 0.55
0.187	0	2.0	7	0.29	180	0.42 – 0.60
0.250	0	3.3	6	0.55	220	0.47 – 0.69
0.350	0	2.0	5	0.40	190	0.48 – 0.66
KIO_3						
0.02	0	1.3	10	0.13	120	0.38 – 0.50
0.03	0	1.7	8	0.21	150	0.42 – 0.57
0.04	0	2.0	6	0.33	170	0.47 – 0.64
0.05	0	2.0	5	0.40	180	0.49 – 0.67
0.06	0	2.3	5	0.46	180	0.48 – 0.66
$MnSO_4$						
0.016	1.7	2.7	3	0.33	30	0.44 – 0.47
0.032	0	2.7	6	0.45	190	0.42 – 0.61
0.064	0	2.7	6	0.45	220	0.40 – 0.62
0.10	0	2.7	7	0.39	190	0.36 – 0.55
0.20	chaotic oscillations only (for 2 min)					
H_2O_2						
0.3	1.0	1.7	1	0.70	170	0.44 – 0.61
0.6	0.7	3.7	4	0.75	170	0.43 – 0.60
1.0	0	3.0	7	0.43	190	0.43 – 0.62
1.5	0	2.0	7	0.29	180	0.45 – 0.63
1.9	0	2.3	7	0.33	180	0.42 – 0.60

[a] T_i Induction time (min), T_t total time (min), n number of oscillations, t time per oscillation (min), A the highest amplitude of oscillation (mV).

On increasing the substrate concentration from 0.003 to 0.017 mol l^{-1}, the number and frequency of oscillations increase. The induction time, total duration and amplitude of oscillations are almost constant (Table I). A higher concentration of the substrate accelerates the reduction of Mn(III) as well as the consumption of iodine.

The change in the acid concentration is found to have little effect on the induction time. But the total duration as well as the amplitude increases on increasing the acid concentration. There is also an increase in time per oscillation on increasing sulfuric acid concentration in the range 0.06 – 0.25 mol l^{-1}. There is a shift in the base as well as peak potential to a higher range on increasing sulfuric acid concentration. The peaks are also blunt presumably due to the stabilisation of Mn(III) at higher concentrations of acid.

The concentration of potassium iodate was varied over the range 0.02 to 0.06 mol l^{-1}. There is a decrease in the number of oscillations and increase in the time per oscillation with increase in iodate concentration. The base and peak potentials are shifted to higher values and flattening of the peak potentials are noticed at higher concentrations of potassium iodate. These observations suggest that there is stabilisation of Mn(III) at higher concentrations of potassium iodate. The concentration of hydrogen peroxide was varied over the range 0.3 to 1.9 mol l^{-1}. The system exhibits dynamic behaviour over a wide range of concentrations. With increase in the concentration of hydrogen peroxide, the peaks become sharper with a decrease in time per oscillation. This shows that Mn(III) ions are better stabilised at lower concentrations of hydrogen peroxide.

The variation of the concentration of Mn(II) in the range 0.016 to 0.2 mol l^{-1} indicates that both the upper and lower concentrations employed are not suitable to obtain sustained oscillations. The time per oscillation decreases with an increase in $MnSO_4$ concentration in the range 0.032 to 0.10 mol l^{-1}.

The iodate–hydrogen peroxide system with 2-thenoyltrifluoroacetone is characterized by an induction time of almost zero and small time per oscillation showing that it is a highly reactive substrate in this system. On increasing the substrate concentration, an increase in the number of oscillations is observed due to the availability of the substrate for the reaction to occur for a longer time. Further it enhances the rate of Mn(III)/Mn(II) redox reaction as well as the formation and consumption of iodine. At low sulfuric acid concentrations, the oscillatory peaks are very sharp compared to that at higher concentrations where the peaks are blunt. This is due to the stabilisation of Mn(III) at high sulfuric acid concentration. At low hydrogen peroxide concentration, the peaks are blunt due to the stabilisation of Mn(III). At higher concentrations, the frequency of oscillations is higher due to an acceleration of the redox reactions involving Mn(III)/Mn(II).

Cyanoacetic Acid

The oscillatory characteristics with cyanoacetic acid as the substrate are given in Table II. The effect of variation of the concentration of different constituents has been studied. In order to see the effect of the percentage of acetonitrile on the oscillatory behaviour, experiments were carried out using different concentrations of acetonitrile (Fig. 2, Table III). It is seen that the presence of small percentages of acetonitrile considerably improves the oscillatory behaviour. In the absence of acetonitrile (i.e. in pure aqueous

TABLE II
Oscillatory characteristics[a] of cyanoacetic acid–H_2SO_4–$MnSO_4$–KIO_3–H_2O_2 system. Standard concentration conditions: 0.04 M substrate; 0.1 M H_2SO_4; 0.02 M KIO_3; 0.08 M $MnSO_4$; 0.75 M H_2O_2

Constituent varied mol l^{-1}	T_i	T_t	n	t	A	Potential range V (vs SCE)
Substrate						
0.02	0.3	35.0	72	0.48	40	0.55 – 0.59
0.04	0.3	26.0	75	0.34	50	0.45 – 0.50
0.06	0.3	17.0	55	0.30	70	0.44 – 0.51
0.08	1.5	10.5	31	0.29	50	0.44 – 0.49
H_2SO_4						
0.07				no oscillations		
0.20	1.6	9	13	0.60	120	0.57 – 0.69
0.30	0.7	7	11	0.57	100	0.59 – 0.69
0.50	0.6	6	7	0.77	100	0.61 – 0.71
1.00	0.8	4	7	0.46	100	0.60 – 0.70
KIO_3						
0.014				no oscillations		
0.017	0.5	19	47	0.39	40	0.44 – 0.48
0.03	0.5	4.5	11	0.36	130	0.56 – 0.69
0.05	0.2	1.5	5	0.26	90	0.59 – 0.68
$MnSO_4$						
0.005				no oscillations		
0.02	0.5	23	75	0.3	100	0.57 – 0.67
0.04	0.5	13	24	0.52	110	0.58 – 0.69
0.12	0.5	13.5	23	0.57	120	0.57 – 0.69
H_2O_2						
0.3	8	19.5	15	0.77	160	0.51 – 0.67
0.5	0.4	30	71	0.42	60	0.53 – 0.59
1.0	0.2	8	26	0.30	30	0.53 – 0.56

[a] See note under Table I.

TABLE III

Effect of acetonitrile concentration on the oscillatory behaviour[a] of cyanoacetic acid–H_2O_2–KIO_3–$MnSO_4$ system. Concentration conditions: 0.04 M substrate; 0.1 M H_2SO_4; 0.02 M KIO_3; 0.04 M $MnSO_4$; 0.75 M H_2O_2; temperature 35 ± 0.1 °C

Acetonitrile vol.%	T_i	T_t	n	t	A	Potential range V (vs SCE)
0 (Pure aqueous)	0.1	1.0	6	0.15	50	0.60 – 0.65
5	0.5	13.5	23	0.57	120	0.57 – 0.69
10	2.3	35.0	91	0.36	60	0.45 – 0.51
20	14.5	30.0	47	0.33	40	0.46 – 0.50
40	0.3	3	3	0.9	190	0.48 – 0.67
		(after 3 min chaotic oscillations)				

[a] See note under Table I.

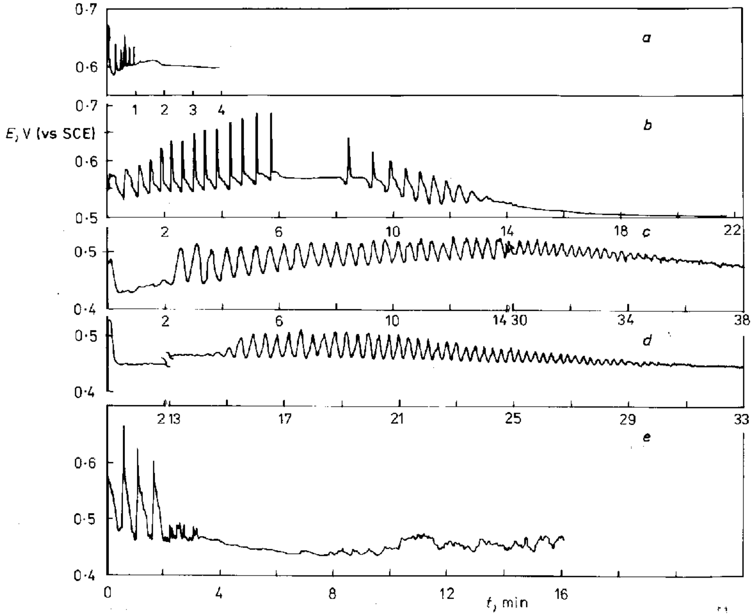

FIG. 2

Effect of variation of acetonitrile concentration on the oscillatory behaviour of cyanoacetic acid–H_2SO_4–$MnSO_4$–KIO_3–H_2O_2 system. Concentration conditions same as in Table III. *a* Pure aqueous medium; *b* 5 vol.% acetonitrile; *c* 10 vol.% acetonitrile; *d* 20 vol.% acetonitrile; *e* 40 vol.% acetonitrile medium) the system oscillates for a very small duration (ca 2 min) giving very few oscillations[7] of a small amplitude (50 mV). In the case of catalyzed and uncatalyzed bromate systems, the presence of acetonitrile is found to reduce the induction time and total duration and increase the frequency of oscillations[9,11]. But with cyanoacetic acid in iodate system, in presence of acetonitrile there is an increase in the induction time and total duration and a decrease in the frequency of oscillations. However, at higher percentages of acetonitrile (i.e. at 40%) the system shows poor oscillatory behaviour giving 3 oscillations in 3 min with an amplitude of 190 mV.

An interesting observation is that at certain concentration conditions, the system exhibits double oscillations with a second induction time in between. Cyanoacetic acid is characterized by a good oscillatory behaviour over a wide range of constituent concentrations. Over a large range of sulfuric acid concentration, the system is characterized by double oscillations. Double oscillations are also observed when the Mn(II) concentration is high (0.04 mol l^{-1}). Similarly, in 5 vol.% acetonitrile medium, it shows double oscillations, but under the same concentration conditions, on increasing the acetonitrile percentage normal oscillations are observed. The two types of wave trains may be due to cyanoacetic acid and iodocyanoacetic acid. For the monoiodination, the induction time is almost zero, and when the substrate gets monoiodinated, the second type of oscillations starts with an induction time. For the second train, the substrate is monoiodocyanoacetic acid undergoing diiodination. However, this has not been confirmed by product analysis.

On increasing the substrate concentration from 0.02 to 0.08 mol l^{-1}, the total duration and number of oscillations decrease. Thus at 0.02 mol l^{-1} concentration the system gave 72 oscillations in 35 min whereas at 0.8 mol l^{-1}, there are 31 oscillations in 10.5 min. The frequency of oscillations increased with increase in the concentration of the substrate. Similar is the effect of concentration of sulfuric acid and potassium iodate. On increasing the hydrogen peroxide concentration from 0.3 to 1.0 mol l^{-1}, the amplitude of oscillations decreases from 160 mV to 30 mV and the induction time decreases from 8 min to 0.2 min. But the total duration and number of oscillations are maximum at 0.5 M H_2O_2, above and below which the values decrease. A decrease in the concentration of H_2O_2 leads to an increase in the time per oscillation due to better stabilisation of Mn(III) at lower H_2O_2 concentration. This is obvious from the bluntness of the peak potential region.

In the iodate system in pure aqueous medium, cyanoacetic acid always gave very few, small amplitude oscillations over a small duration of time. The results show that acetonitrile in small concentrations is conducive for a sustained oscillatory behaviour characterized by a large number of oscillations over large duration.

The effect of variation of the concentration of substrate, H_2SO_4, KIO_3, H_2O_2 and Mn(II) in mixed medium is similar to that observed in pure aqueous medium when studied using different substrates[13]. In Fig. 1*a*, the points A and D, C and F and B and

E are equivalent. At A, Mn(II) is maximum and the iodine concentration is minimum (colourless solution). The potential then increases to B due to the formation of Mn(III) (red-brown colour). The fall of potential from B to C is fairly rapid sinchronising with the fading of red brown colour and intensification of blue colour of the experimental solution. At C, iodine concentration is maximum. Then it gradually decreases due to the iodination of organic substrate until it becomes minimum at D (colourless solution). These observations are similar to those observed in pure aqueous medium[14]. However, in presence of organic solvent, the base and peak potentials are lowered as compared to those in pure aqueous medium. The simultaneous recording of the spectrophotometric profile also enables in fixing points of maximum and minimum colour intensity of the experimental solution. This is in agreement with the conclusions drawn from the potentiometric profiles.

Ethyl acetoacetate when employed as substrate in the iodate system in the spectrophotometric follow up, it is found that oscillations last for a longer time on increasing acetonitrile concentration in the medium. In pure aqueous medium, after a small duration (ca 5 min) oscillations cease due to the formation of turbidity (iodo compound), whereas in presence of acetonitrile, the precipitate dissolves in it and the oscillatory profile is no longer affected by turbidity. Thus when ethyl acetoacetate gave only 3 – 4 oscillations in pure aqueous medium, there are 27 oscillations in 20% acetonitrile and 41 oscillations in 30% acetonitrile (Table IV).

Thus acetonitrile in small concentrations improves the oscillatory behaviour by increasing the solubility of the substrate as well as the product formed in the reaction mixture. In general, the time per oscillations and the induction time are larger in the mixed medium (i.e. in presence of an organic solvent), compared to that in pure aqueous medium. Further, with ethyl acetoacetate as the substrate, the time per oscillation increases on increasing the concentration of organic solvent in the medium. It has been reported that the preoscillatory period of pH oscillations (as well as the time per

TABLE IV

Effect of acetonitrile on the oscillatory characteristics of EAA–KIO_3–$MnSO_4$–H_2O_2 system. 0.1 M EAA; 0.1 M H_2SO_4; 0.058 M KIO_3; 0.003 $MnSO_4$; 0.5 M H_2O_2; temperature = 30 °C

Medium	Total duration, min	n^a	t^b
Pure aqueous	2.0	7	0.29
10 vol.% Acetonitrile	6.5	17	0.38
20 vol.% Acetonitrile	9.5	27	0.35
30 vol.% Acetonitrile	16.0	41	0.39

[a] Number of oscillations; [b] time per oscillation.

oscillation) increases with increase in H_2O_2 concentration in the H_2O_2–$[Fe(CN)_6]^{4-}$–acetonitrile–water system[15]. This is attributed to the fact that the excess of H_2O_2 is to be removed by a nonoscillatory catalytic decomposition before the start of oscillations. In this system acetonitrile acts as a reactant itself and oscillations are not possible in the absence of acetonitrile. H_2O_2 in water–acetonitrile mixture on addition of OH^- leads to a moderate base catalyzed decomposition of H_2O_2 to water and oxygen[16]. The oxidizing property of H_2O_2 depends on the pH of the system. The oxidizing property is more in lower pH than in higher values of pH. For the reaction (*A*)

$$2\ IO_3^- + 5\ H_2O_2 + 2\ H^+ \xrightarrow{Mn(II)} I_2 + 5\ O_2 + 6\ H_2O \qquad (A)$$

the induction period required to attain maximum rate is shorter at larger $[H_2O_2]$. The iodine produced is completely reoxidized to iodate at long times, which would leave reaction (*B*) as the net reaction.

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2 \qquad (B)$$

In the iodate–hydrogen peroxide system, the extent of reaction (*B*) can be greatly reduced if iodine is continuously removed from the solution by shaking with CCl_4 (ref.[17]) or by the addition of crotonic acid, which would quickly react with HOI, a precursor of I_2 in the iodine producing subsystem[18].

In the present system, iodine can be considered as being continuously removed from the system by the presence of acetonitrile. This would lead to a slower decomposition of H_2O_2 in presence of acetonitrile in acidic medium.

Thus, in presence of acetonitrile, the oxidation of Mn(II) to Mn(III) would be slower due to the slow decomposition of H_2O_2. It is observed in independent experiments that in the absence of the organic substrate, the rate of oxidation of Mn(II) to Mn(III) is slower in the presence of acetonitrile, for a system containing acetonitrile, H_2SO_4, KIO_3, Mn(II) and H_2O_2. Moreover, for the system with H_2SO_4, KIO_3 and H_2O_2, the rate of gas evolution (O_2 formation) was found to be less in presence of acetonitrile compared to that in pure aqueous medium. These explain the alterations observed in a B–R system in presence of an organic solvent.

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REFERENCES

1. Gurel O., Gurel D: *Topics in Current Chemistry, Oscillations in Chemical Reactions*. Springer, Berlin 1983.
2. Orban M., Koros E.: J. Phys. Chem. *82*, 1672 (1978).
3. Ramanathan S., Ramaswamy R.: Trans. SAEST *18*, 39 (1983).
4. Ramaswamy R., Mohan S.: Curr. Sci. *54*, 1063 (1985).
5. Bartetski A., Tlachala T.: Kinet. Katal. *20*, 841 (1979).
6. Dutt A. K., Banerjee R. S.: J. Indian Chem. Soc. *64*, 185 (1987).
7. Jha P. N., Prasad B. N., Prasad R. K.: J. Indian Chem. Soc. *65*, 177 (1988).
8. Lalitha P. V., Ramaswamy R.: Collect. Czech. Chem. Commun. *57*, 2235 (1992).
9. Lalitha P. V., Ramaswamy R.: Proc. Indian Acad. Sci., Chem. Sci. *104*, 619 (1992).
10. Lalitha P. V., Ramaswamy R.: React. Kinet. Catal. Lett. *47*, 133 (1992).
11. Lalitha P. V., Ramaswamy R.: Int. J. Chem. Kinet., in press.
12. Lalitha P. V., Ramaswamy R., Geetha Ramakrishnan, Sambasiva Rao P.: J. Phys. Chem. *96*, 7679 (1992).
13. Mohan S.: *Ph.D. Thesis*. Indian Institute of Technology, Madras 1986.
14. Ramaswamy R., Mohan S.: Curr. Sci. *54*, 1063 (1985).
15. Gyula Rabai: J. Chem. Soc., Chem. Commun. *1991*, 1083.
16. Roberts J. L., jr., Sugimoto H., jr., Barette W. C., Sawyer D. T.: J. Am. Chem. Soc. *107*, 4556 (1985).
17. Furrow S. D., Noyes R. M.: J. Am. Chem. Soc. *104*, 38 (1982).
18. Furrow S. D.: J. Phys. Chem. *86*, 3089 (1982).