

A NOVEL APPROACH TO THE STUDY OF BRIGGS-RAUSCHER REACTION

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The Briggs-Rauscher reaction with substrates containing acidic hydrogen such as malonic acid, acetyl acetone has been studied. The employment of mixed media involving an organic solvent and water enabled the study of water-insoluble substrates. The present communication reports the oscillatory behaviour of malonic acid in the iodate system in different mixed media (5 vol.% of the organic solvent) as well as the oscillatory behaviour of seven substrates in acetonitrile-water mixed medium of which two are new substrates hitherto unreported in any of the oscillatory systems.

The oscillatory behaviour of different organic substrates in the uncatalyzed and catalyzed bromate systems has been extensively studied¹. The iodate-hydrogen peroxide (Briggs-Rauscher, B-R) system has been studied²⁻⁶ with substrates having acidic hydrogen, such as malonic acid, acetyl acetone and acetyl acetone. The mechanistic aspects of the Briggs-Rauscher reaction have also been discussed⁷⁻¹⁰. The low solubility of many substances in water is an impediment in employing them as substrates in the study of oscillatory reactions. Studies using mixed media involving an organic solvent and water have facilitated the water-insoluble substrate to be taken into solution. The use of mixed media has enabled the study of the oscillatory behaviour of large number of new substrates in the uncatalyzed as well as in the catalyzed bromate systems¹¹⁻¹⁴. The present communication deals with the oscillatory behaviour of malonic acid in the Briggs-Rauscher reaction in different mixed media as well as the behaviour of seven substrates in aqueous acetonitrile. Two of the compounds studied have hitherto been not employed as substrates in any oscillatory system owing to their poor solubility in water.

EXPERIMENTAL

Chemicals (a.g.) were used without further purification. Triply distilled water was used for preparing all the solutions. The addition of the last component, namely hydrogen peroxide, to the well-stirred and thermostatted (30 ± 0.1 °C) solution containing all other constituents triggered off the oscillations. The oscillations were followed potentiometrically by using a Kompensograph (Siemens) with a platinum indi-

cator electrode coupled to a saturated calomel electrode through a potassium nitrate salt bridge. The experiments were carried out in a polythene beaker in order to get good reproducibility.

RESULTS AND DISCUSSION

The oscillatory behaviour of malonic acid in different mixed media (5% by volume of organic solvent) is presented in Table I and Fig. 1. The system oscillates in all the mixed media employed, including methanol and dimethyl sulfoxide. The behaviour is found to be even better in 5% (by volume) acetonitrile and benzene when compared to pure aqueous medium. In most mixed solvents large number of oscillations (up to 22) of large amplitude (150 – 200 mV) were observed. However, in aqueous tetrahydrofuran, malonic acid gives a single oscillation of small amplitude (40 mV).

The behaviour of iodate system is found to be different from that of bromate system in different mixed solvents. For example, in the bromate–gallic acid system, there are no oscillations in media involving methanol and dimethyl sulfoxide (20 vol.%). But in the iodate system, malonic acid is found to oscillate even in 20% methanol (9 oscillations in 90 s with an amplitude of 150 mV).

Among the different mixed solvents used, acetonitrile is found to be highly suitable, even better than water giving a large number of oscillations (17 oscillations in 216 s) of

TABLE I
Oscillatory characteristics of 0.04M malonic acid–0.06M-KIO₃–0.4M-H₂O₂–0.02M-MnSO₄–0.04M-H₂SO₄ system in different solvents at 30 ± 0.1 °C

No.	Solvent ^a	$T_{ind.}$ s	T_{total} s	Oscil- lations number	Time/ oscil- lation, s	Amplitude mV	Potential range ^b , V
1	Water	1	102	11	9.3	140	0.54 – 0.68
2	Water–acetonitrile	1	216	17	12.7	190	0.50 – 0.69
3	Water–dimethylformamide	0.5	60	11	5.5	120	0.55 – 0.67
4	Water–tetrahydrofuran	–	3	1	3.0	40	0.46 – 0.50
5	Water–1,4-dioxan	1	78	10	7.7	150	0.55 – 0.70
6	Water–1-methyl-2-pyrrolidone	1	72	11	6.5	170	0.53 – 0.70
7	Water–benzene	1	204	22	9.2	210	0.49 – 0.70
8	Water–methanol	0.5	78	8	9.7	170	0.53 – 0.70
9	Water–dimethyl sulfoxide	8	126	8	14.8	250	0.51 – 0.76
10	Water–methanol ^c	–	90	9	10.0	150	0.47 – 0.63

^a Mixed solvents contained 5 vol.% of organic solvent; ^b vs SCE; ^c 20 vol.% of methanol.

large amplitude (190 mV). A medium containing 5% (by volume) benzene is also found to be very good, but due to the fact that it is not miscible with water, acetonitrile was chosen for the study of seven substrates including two new ones, namely, benzoyl acetone and dibenzoylmethane. It is observed that there are no oscillations in the malonic acid-iodate system in aqueous acetonitrile with larger than 10% (by volume) acetonitrile.

The concentration conditions and oscillatory characteristics of the five different substrates including ethyl acetoacetate, acetyl acetone, acetyl acetone, malonic acid and ethyl cyanoacetate are presented in Table II. All these substrates are water soluble. However, the experiments were carried out in 5% acetonitrile in order to establish that these substrates show oscillatory behaviour in mixed media as well. The number of oscillations is as large as 162 with acetyl acetone and 202 with ethyl cyanoacetate as substrates.

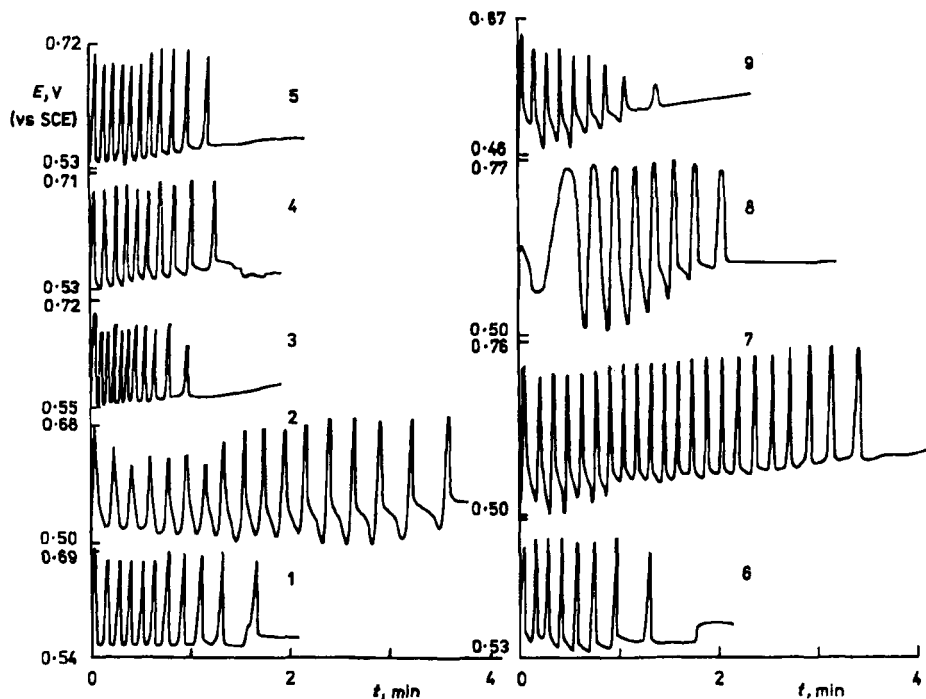


FIG. 1

Oscillatory profiles for malonic acid-iodate system in different mixed media. Conditions given in Table I: 1 water, 2 acetonitrile, 3 dimethylformamide, 4 1,4-dioxan, 5 1-methyl-2-pyrrolidone, 6 methanol, 7 benzene, 8 dimethyl sulfoxide, 9 methanol (20 vol.%)

The concentration range of the different constituents with benzoyl acetone and dibenzoylmethane as substrates are presented in Table III. The oscillatory characteristics for the two substrates are given in Table IV and Fig. 2. There are 28 oscillations in 36 min when dibenzoylmethane is employed as the substrate. The precipitated

TABLE II
Concentration of reagents (mol/l) and oscillatory characteristics of different substrates (S) in 5 vol.% acetonitrile at 30 ± 0.1 °C

Substrate	S	H ₂ SO ₄	KIO ₃	MnSO ₄	H ₂ O ₂	T _{ind.} s	T _{total} s	Oscillations number	Potential range ^a , V
EAA ^b	0.07	0.10	0.045	0.003	0.5	6	780	7	0.59 – 0.71
AcoAc ^c	1.4	0.16	0.05	0.02	1.0	60	5 400	162	0.60 – 0.71
Ac.Ac ^d	0.04	0.40	0.035	0.005	0.4	12	570	10	0.62 – 0.79
MA ^e	0.04	0.04	0.06	0.04	0.4	4	198	14	0.53 – 0.68
ECA ^f	1.0	0.1	0.05	0.003	1.5	138	1 260	202	0.6 – 0.67

^a vs SCE; ^b ethyl acetoacetate; ^c acetonylacetone; ^d acetylacetone; ^e malonic acid; ^f ethyl cyanoacetate.

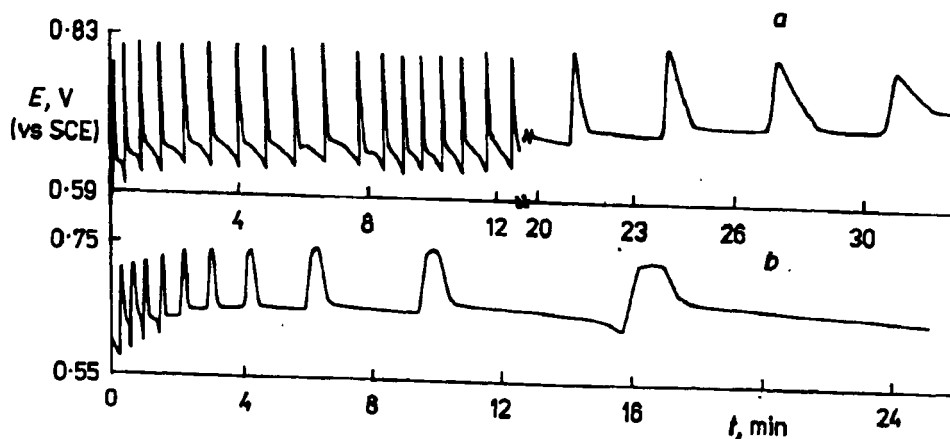


FIG. 2
Oscillatory profiles for dibenzoylmethane and benzoylacetone in the iodate system at 35 ± 0.1 °C. Concentration conditions (mol/l): **a** Dibenzoylmethane, 0.018 (in acetonitrile, 40 vol.%); H₂SO₄, 0.4; MnSO₄, 0.005; KIO₃, 0.015; H₂O₂, 0.6. **b** Benzoylacetone, 0.01 (in acetonitrile, 20 vol.%); H₂SO₄, 0.25; MnSO₄, 0.005; KIO₃, 0.015; H₂O₂, 1.0

product at the end of the oscillatory reaction when dibenzoylmethane was used as substrate has been isolated and the NMR spectra of both the starting compound (dibenzoylmethane) and the product were taken.

^1H NMR spectrum of parent compound shows signals at δ 7.99 – 7.52 corresponding to ten aromatic protons and at 6.8 corresponding to the methylene protons. It also showed a signal at δ 16.98 showing the enolic proton. The product, however, does not give the signal at δ 16.98. Instead, it gives a signal at δ 6.9 corresponding to the $\text{O}=\text{C}-\text{CHI}-\text{C}=\text{O}$ proton. The melting point of the product is 103 °C which agrees with the literature value¹⁵ for dibenzoyliodomethane.

The results obtained in the present study establish that different aqueous–organic mixed media can be successfully employed in the Briggs–Rauscher reaction. The oscillatory behaviour of the iodate–hydrogen peroxide system depends on the nature of the substrate employed as well as the nature of the organic solvent in the mixed medium. The study widens the scope of the Briggs–Rauscher oscillatory system as it permits the inclusion of water-insoluble substrates which could not so far be investigated.

TABLE III

The concentration range of reagents (mol/l) for benzoylacetone and dibenzoylmethane in aqueous acetonitrile at 35 ± 0.1 °C

Substrate	S	H_2SO_4	MnSO_4	KIO_3	H_2O_2
Benzoylacetone ^a	0.007 – 0.017	0.15 – 0.5	0.005 – 0.02	0.01 – 0.025	0.3 – 1.0
Dibenzoylmethane ^b	0.01 – 0.022	0.2 – 1.0	0.005 – 0.03	0.013 – 0.02	0.4 – 1.0

^a 20 vol.% acetonitrile; ^b 40 vol.% acetonitrile.

TABLE IV

The oscillatory characteristics under the concentration conditions given in Fig. 2

Substrate	T_{ind} min	T_{total} min	Oscillations number	Time/oscil- lation, min	Amplitude mV	Potential range ^a , V
Benzoylacetone	0.3	18	10	1.8	130	0.58 – 0.71
Dibenzoylmethane	0.1	33	27	1.2	210	0.60 – 0.81

^a vs SCE.

REFERENCES

1. Gurel O., Gurel D.: *Topics in Current Chemistry, Oscillations in Chemical Reactions*, p. 118. Springer-Verlag, Berlin 1983.
2. Furrow S. D.: *J. Phys. Chem.* **85**, 2026 (1981).
3. Furrow S. D.: *Int. J. Chem. Kinet.* **14**, 927 (1982).
4. Ramaswamy R., Mohan S.: *Curr. Sci.* **54**, 1063 (1985).
5. Ramaswamy R., Ramanathan S., Savithri I.: *Indian J. Technol.* **20**, 318 (1982).
6. Cooke D. O.: *React. Kinet. Catal. Lett.* **3**, 377 (1975).
7. Cooke D. O.: *J. Chem. Soc., Chem. Commun.* **1976**, 27.
8. Noyes R. M., Furrow S. D.: *J. Am. Chem. Soc.* **104**, 45 (1982).
9. DeKepper P., Epstein I. R.: *J. Am. Chem. Soc.* **104**, 49 (1982).
10. Roux J. C., Vidal C.: *Synergetics, Far from Equilibrium* (A. Pacault and C. Vidal, Eds), p.47. Springer-Verlag, Berlin 1979.
11. Lalitha P. V., Ramaswamy R.: *Proc. Indian Acad. Sci., Chem. Sci.*, in press.
12. Lalitha P. V., Ramaswamy R.: *React. Kinet. Catal. Lett.* **47**, 133 (1992).
13. Lalitha P. V., Ramaswamy R.: Unpublished results.
14. Lalitha P. V., Ramaswamy R., Geetha Ramakrishnan, Sambasiva Rao P.: *J. Phys. Chem.*, in press.
15. Urasaki I., Ogata Y.: *J. Chem. Soc., Perkin Trans. 1* **1975**, 1285.