PERTURBATIONS IN BROMATE OSCILLATORS BY GAMMA IRRADIATION

Mahalingam KRISHNARATNAM, Balasubramamian VISWANATHAN and Renganathan RAMASWAMY

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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The oscillatory characteristics of the catalyzed and uncatalyzed bromate oscillators are altered by gamma irradiation. These alterations could arise due to additional reactions to be included in the reaction scheme involving the species like $H^{\bullet}$, $OH^{\bullet}$, and $HO_2^{\bullet}$ generated as a result of gamma irradiation.

The chemical reaction in an oscillator can be perturbed without the addition of any external agent. This could be achieved by the generation of various species in situ by gamma irradiation[1]. Rama Rao and Prasad[2] first studied this mode of perturbation for the catalyzed bromate system ($KBrO_3$–H_2SO_4–Ce(IV)–malonic acid) and it was further examined by Koros et al.[3]. Both of them postulated that the quenching of oscillations by gamma irradiation is due to the radiolytic hydrogen atoms but they proposed two different pathways by which the radiolytic H-atoms quench the oscillations.

Rama Rao and Prasad[2] reported that the H-atom produced by gamma irradiation reacts with bromomalonic acid formed during the reaction thereby generating Br^-. The concentration of Br^- is thus built-up to a level higher than the critical concentration thereby quenching the oscillations. Koros et al.[3] on the other hand reported that the radiolytic H-atoms produced by gamma irradiation inhibit the oxidation of the metal complex thereby perturbing the oscillations.

The effect of gamma irradiation on the uncatalyzed bromate oscillator (UBO) has also been investigated by Koros et al.[4]. They have reported that the UBO has not been perturbed by gamma irradiation since the organic substrate acts as an effective hydrogen atom scavenger. In our earlier studies[5,6] we have reported the results obtained in the perturbation of the catalyzed and uncatalyzed bromate oscillator by gamma irradiation.

The aim of the present communication is to examine the reasons for the alterations in the oscillation characteristics as a result of gamma irradiation.

EXPERIMENTAL

All chemicals are of Analar purity and used without further purification. Oscillations were triggered off by the addition of potassium bromate to a solution containing all other constituents. The oscillations were followed potentiometrically with a platinum indicator electrode coupled to a saturated calomel electrode (SCE).

In the studies with gamma irradiation the reacting system, after the addition of the last constituent (potassium bromate) was irradiated from a ^{60}Co gamma radiation source (BARC, Bombay) at a dose rate of 0·24 M Rads/hour. The dose rate was measured by Fricke dosimetry.

RESULTS AND DISCUSSION

The results obtained in the catalyzed and uncatalyzed bromate systems are presented and discussed. The substrate employed in the catalyzed bromate system (CBS) is malonic acid together with Ce(III) as the metal ion. Gallic acid has been employed as the substrate in the UBO. The results obtained in the CBS employing metal ions like Ce(III) or Mn(II) and gallic acid as the substrate are also reported.

Catalyzed Bromate System

In the CBS, the oscillatory pattern obtained with and without gamma irradiation under varying concentration of potassium bromate (0·06 to 0·20 mol l^{-1}) are shown in Fig. 1. The results obtained on varying the concentration of malonic acid are given in Table I. The higher concentrations of potassium bromate (0·20 mol l^{-1}) or malonic acid (0·16 mol l^{-1}) employed are the conditions favourable for the build-up of higher concentration of Br^- under gamma irradiation. As per the conclusions of Rama Rao and Prasad[2] this situation would lead to the quenching of oscillations. The results obtained with and without irradiation show that the system is not quenched but only perturbed by gamma irradiation. In general, at various

TABLE I

Effect of malonic acid concentration on the oscillatory behaviour under irradiated and non-irradiated condition. Concentrations are: $[KBrO_3] = 0{\cdot}10$ mol l^{-1}, $[H_2SO_4] = 2{\cdot}00$ mol l^{-1}, $[Ce^{3+}] = 0{\cdot}005$ mol l^{-1}

Concentration of malonic acid mol l^{-1}	Without irradiation		With irradiation	
	induction time min	total time min	induction time min	total time min
0·16	0·80	24·00	0·77	18·00
0·10	1·37	36·00	1·20	24·00
0·06	1·83	17·00	1·57	11·50

concentrations of bromate and malonic acid under gamma irradiation, the time lag for the onset of oscillations (t_0), the potential amplitude of the oscillations and the total duration of oscillations (t_k) are decreased.

Even the variation of concentration of Ce(III) from 0·001 to 0·01 mol l^{-1} under gamma irradiation conditions in CBS does not result in quenching of oscillations. The alterations in the oscillation characteristics under irradiation conditions could result from the inhibition of the oxidation of the metal ions either by the radiolytic hydrogen atoms produced or other redox species generated.

It is observed that the presence of acetonitrile completely supresses the oscillations in the absence of gamma irradiation. This shows that acetonitrile completely inhibits the oscillating chemical reaction. It is noticed that under gamma irradiation conditions the system containing aqueous acetonitrile–nonaqueous medium with (12%) acetonitrile (for preparing malonic acid solution) oscillates for longer duration with enhanced amplitude and frequency compared to the corresponding nonirradiated system (Fig. 2.). Thus it is observed that gamma irradiation generates species either from water or acetonitrile itself which could cause and sustain the oscillations.

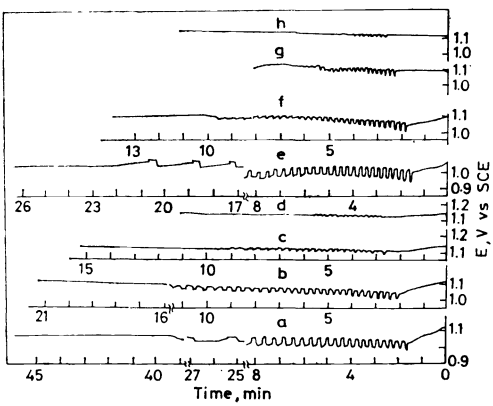

FIG. 1

Effect of potassium bromate concentration under irradiated and non-irradiated conditions. Concentrations are: $[H_2SO_4] =$ $= 2·00$ mol l^{-1}, [malonic acid] = 0·06 mol . . l^{-1}, $[Ce^{3+}] = 0·005$ mol l^{-1}, $[KBrO_3] =$ $= 0·06$ mol l^{-1} (a, e), 0·10 mol l^{-1} (b, f), 0·16 mol l^{-1} (c, g), 0·20 mol l^{-1} (d, h); a, b, c, d without irradiation, e, f, g, h under irradiation

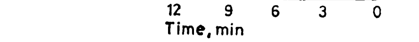

FIG. 2

Effect of malonic acid dissolved in acetonitrile under irradiated and non-irradiated conditions. Concentrations are: $[KBrO_3] =$ $= 0·10$ mol l^{-1}, $[H_2SO_4] = 2·00$ mol l^{-1}, [malonic acid] = 0·06 mol l^{-1}, $[Ce^{3+}] =$ $= 0·005$ mol l^{-1}; a without irradiation, b under irradiation

The oscillatory patterns in CBS involving the metal ion Ce(III) or Mn(II) as the catalyst and gallic acid as the substrate with and without gamma irradiation are shown in Fig. 3. Under normal experimental conditions (without gamma irradiation) the system oscillates in the potential range of 0·50 to 1·00 V (Fig. 3a and 3c) whereas under gamma irradiation conditions the system oscillates in the potential range of 0·82 to 0·90 V (Fig. 3b and 3d). It is noticed that the potential region of oscillations especially the base potential is shifted from 0·50 V under normal conditions to 0·82 V in the presence of gamma irradiation resulting in a considerable decrease in the amplitude.

In presence of gamma irradiation in air-saturated aqueous solutions one would generate various types of reactive species like $H^{\bullet}$, $HO_2^{\bullet}$, $OH^{\bullet}$ and H_2O_2. In addition to this, depending on the nature of organic substrate used one would have generated organic free radicals as well. The presence of the species ($H^{\bullet}$, $OH^{\bullet}$, $HO_2^{\bullet}$ and H_2O_2) could lead to the following reactions,

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \qquad (A)$$

$$HO_2^{\bullet} + Ce^{4+} \rightarrow Ce^{3+} + H^+ + O_2 \qquad (B)$$

$$H_2O_2 + Ce^{4+} \rightarrow Ce^{3+} + HO_2^{\bullet} + H^+ \qquad (C)$$

$$OH^{\bullet} + Ce^{3+} \rightarrow Ce^{4+} + OH^- \qquad (D)$$

while in the absence of oxygen i.e. hydrogen saturated solution the likely reaction is represented by Eq. (*E*).

$$H^{\bullet} + Ce^{4+} \rightarrow Ce^{3+} + H^+ \qquad (E)$$

In the experiments relating to the variation in the concentration of bromate, the

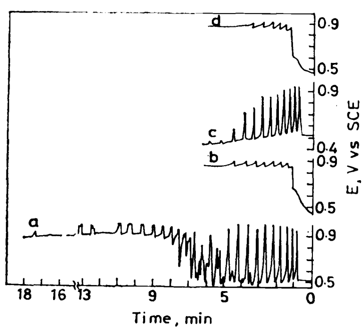

FIG. 3

Oscillatory characteristics of CBS under irradiated and non-irradiated conditions. Concentrations are: $[KBrO_3] = 0{\cdot}06$ mol . l^{-1}, $[H_2SO_4] = 1{\cdot}96$ mol l^{-1}, [gallic acid] = 0·026 mol l^{-1}, [metal ion] = = 0·001 mol l^{-1}; a, b Ce^{3+} metal ion added, c, d Mn^{2+} metal ion added; a, c without irradiation, b, d under irradiation alterations in the gamma irradiated system could have arisen from the additional reaction (*F*).

$$Br^- + OH^\bullet \rightarrow Br^\bullet + OH^- \qquad (F)$$

In the presence of acetonitrile the initiators of oscillations seem to be directly reacting with acetonitrile itself much faster than with the metal ions. However under gamma irradiation conditions the $H^\bullet$ and $OH^\bullet$ radicals produced can generate $_\bullet CH_2CN$ radicals from acetonitrile as follows,

$$H^\bullet + CH_3CN \rightarrow H_2 + {}^\bullet CH_2CN \qquad (G)$$

$$OH^\bullet + CH_3CN \rightarrow H_2O + {}^\bullet CH_2CN \qquad (H)$$

${}^\bullet CH_2CN$ radical can react with O_2 or H_2O_2 to give rise to the oxidized products. In view of this possibility, the normal inhibition of oscillations observed with acetonitrile under nonirradiation condition is eliminated. It is therefore necessary that one has to include these additional steps in the Belousov–Zhabotinsky (B–Z) oscillatory reaction scheme originally proposed by Field et al.[7]. It is interesting to note that in a recent communication, reactions of this type have been included in order to explain the effect of ultrasound on the oscillatory chemical reactions[8].

Uncatalyzed Bromate Oscillator

The oscillatory characteristics for different aromatics with and without gamma irradiation are given in Fig. 4. Under normal experimental conditions without gamma irradiation the system oscillates in the potential region of 0·50 to 0·95 V whereas under gamma irradiation condition the system oscillates with a decrease

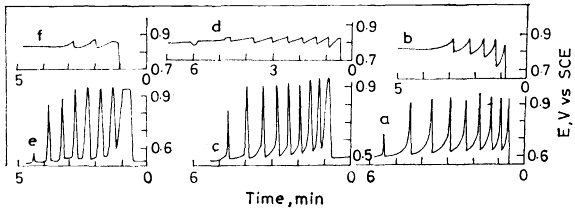

FIG. 4

Oscillatory characteristics under standard condition for different aromatic substrates under irradiated and non-irradiated conditions. Concentrations are: $[KBrO_3] = 0{\cdot}06\ mol\ l^{-1}$, $[H_2SO_4] = 1{\cdot}96\ mol\ l^{-1}$, $[substrate] = 0{\cdot}026\ mol\ l^{-1}$; a, b pyrogallol, c, d gallic acid, e, f methyl gallate; a, c, e without irradiation, b, d, f under irradiation in amplitude in the potential region of 0·70 to 0·85 V. There is also a decrease in the duration of oscillations under irradiation.

In order to examine the validity of the postulate that the aromatic substrates act as effective hydrogen atom scavenger under gamma irradiation conditions in UBO, experiments were carried out with solution purged with a stream of hydrogen gas. In presence of gamma irradiation, the hydrogen purged solution oscillates with smaller amplitude of nearly 40 mV at a higher potential region (0·84 to 0·90 V) whereas under identical conditions without gamma irradiation the system oscillates in the potential region of 0·50 to 0·90 V with an amplitude of nearly 300 mV. This shows that one of the radicals $H^{\bullet}$, $HO_2^{\bullet}$ and $OH^{\bullet}$ generated by gamma irradiation reacts directly with the organic substrate thus altering the characteristics of oscillations. The possible/preferrable reaction would be the addition of $OH^{\bullet}$ to the aromatic ring of pyrogallol or gallic acid or methyl gallate. The inclusion of these additional steps in the oscillatory reaction scheme of UBO could account for the changes in the characteristics of oscillations under gamma irradiation.

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