component reactions may be more easily characterized experimentally than the more reactive MA BZR.

Acknowledgement

The author wants to thank Prof. Dr. R. M. Noyes for a stimulating discussion on BZ systems.

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Zeitschrift für Physikalische Chemie Neue Folge, Bd. 135, S. 171 – 184 (1983)

Oscillations, Excitability and Stirring Effects in Closed Methylmalonic Acid Belousov-Zhabotinsky Systems

By

Peter Ruoff* and Bengt Schwitters

Department of Chemistry, University of Oslo, Oslo 3, Norway

(Received August 16, 1983)

Chemical oscillations / Belousov-Zhabotinsky reaction / Excitability / Induction period

The Belousov-Zhabotinsky reaction with methylmalonic acid exhibits oscillations and induction periods of considerably greater lengths than the corresponding malonic acid system. The enlarged induction periods are shown to be the result of the slower formation of bromomethylmalonic acid. The oscillating period is lengthened by decreasing the initial concentration of methylmalonic acid, and shortened by decreasing the initial concentration of Ce(IV). The total number of oscillations increases in a nitrogen atmosphere, whereas the number of oscillations is less when the reaction is performed under oxygen conditions. At the end of the oscillating domain, the system may be found in an excitable steady state. When excitable, continuous addition of $AgNO_3$ or a decrease in the stirring rate results in high frequency oscillations.

Die Oszillationen und Induktionsperioden der Belousov-Zhabotinsky-Reaktion mit Methylmalonsäure sind bedeutend länger als das entsprechende System mit Malonsäure. Es wird gezeigt, daß die größeren Induktionsperioden als Resultat der langsameren Bildung von Brommethylmalonsäure zustande kommen. Die Oszillationsperiode wird durch Verringerung der Ausgangskonzentration von Methylmalonsäure erhöht, während eine Verminderung der Ce(IV) Konzentration die Perioden verkürzt. Unter Stickstoffatmosphäre erhöht sich die Gesamtzahl der Oszillationen, während unter Sauerstoffatmosphäre die Gesamtzahl niedriger ist verglichen mit aeroben Bedingungen. Am Ende der Oszillationen ist das System in einem anregbaren stationären Zustand. Durch ständiges Zufügen von $AgNO_3$ oder durch Verminderung der Rührgeschwindigkeit werden höherfrequente Oszillationen hervorgerufen.

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* Author to whom correspondence should be addressed

Introduction

Since its discovery in 1958, the Belousov-Zhabotinsky reaction (BZR) has, like many other chemical oscillating systems, attracted much attention. In its original version [1] citric acid was used as the organic substrate together with a Ce(IV) salt and bromate. Today, in its general form, a BZR is a metal-ion catalyzed oxidation of easily-brominated organic material by bromate ions in aqueous acidic media [2]. Several oscillating BZRs having different organic substrates and catalysts have been described [3–8].

Field *et al.* [9] proposed a mechanism (the so-called FKN mechanism) which explains most of the observed phenomena. Although originally only addressed to the malonic acid (MA) BZR, it is believed that the basic features may also be valid in systems having different catalysts and organic substrates [2]. On the basis of the FKN mechanism, several mathematical models have been constructed [10–14]. One of the first and most investigated is the so-called Oregonator [10] which often serves as a basis for more sophisticated simulation models.

In the present paper experimental investigations of induction periods, oscillating regime and the non-oscillatory excitable steady state of methylmalonic acid (MeMA) BZR [15] finally obtained are reported. On the basis of the FKN mechanism an approximate relationship between induction period length, formed bromo-methylmalonic acid (BrMeMA) and initial MeMA concentration is deduced.

Materials and Method

In all experiments reported here, the BZR was performed in a thermostat-regulated glass container with magnetic stirring. The temperature of the reaction mixture was kept constant at 25° C. The oscillations were followed potentiométrically with uncalibrated platinum and silver electrodes. A standard calomel electrode was used as a reference. The potentials were measured and recorded by a two-channel x/t recorder. If not stated otherwise, the reaction mixture was exposed to air.

The reagents were of analytical grade, except for the MeMA, which was of *purum* quality (Fluka). All chemicals were used without further purification.

The reaction volume was 30 ml and the reactants were always mixed in the following order: 1 M H_2SO_4 – MeMA – $(NH_4)_2Ce(NO_3)_6$ – and finally $KBrO_3$. If not specified otherwise, the following initial concentrations were used: 0.28 M MeMA, 0.1 M $KBrO_3$, and $2.1 \cdot 10^{-3}$ M $(NH_4)_2Ce(NO_3)_6$.

At the end of the induction period the BrMeMA formed was determined by the following extraction/titration method. The reaction mixture was extracted three times with ice-cold diethylether. Thereafter the total ether fraction was treated with 50 ml 2 M NaOH. Then the aqueous phase was split into three and concentrated H_2SO_4 was added until the pH was about one. Finally an excess of KI was added. After 72 h the amount of I_2 released was titrated with 0.05 M $Na_2S_2O_3$ as described by Jander *et al.* [16]. The total amount of BrMeMA formed was determined according to the stoichiometry of the equation

$$H^+ + BrMeMA + 2I^- \rightarrow MeMA + I_2 + Br^- . \tag{1}$$

Excitability thresholds were estimated by the rapid addition of an $AgNO_3$ solution of known concentration into the reaction mixture until a single Ce(IV) pulse appears [17, 18].

Results

Induction period and oscillatory behaviour

A typical train of oscillations is shown in Fig. 1. Both induction period and oscillating period depend upon initial concentrations of the reagents (Table 1). A decrease of the initial MeMA or Ce(IV) concentrations results in increased induction periods, whereas low $KBrO_3$ concentrations shorten the induction period. Our observed induction periods lie in the range of 40 to 120 min. At several initial MeMA concentrations, the BrMeMA concentration was determined at the end of the induction period (X_{crit}) using the extraction/titration method described in the previous section (Fig. 2).

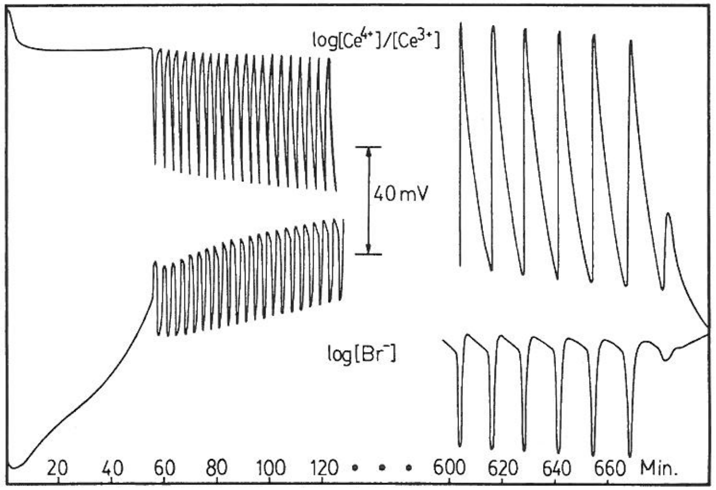

Fig. 1. Induction period and train of oscillations in the MeMA BZR. The reaction is performed in a nitrogen atmosphere. The platinum electrode indicates the change in the Ce(IV) concentration, while the silver electrode reflects changes in the Br^- concentration. Note the relative increase in both potentials and the sudden stop of the oscillations

Table 1. *Dependence of induction period length (in min), oscillation period length (in min) and excitation threshold on various initial reagent concentrations (in mol/dm^3)*

MeMA	$KBrO_3$	$(NH_4)_2Ce(NO_3)_6$	Ind. period length	Osc. period length[a]	Excitation threshold[b]
0.21	0.075	$2.1 \cdot 10^{-3}$	45	4.0	$9 \cdot 10^{-6}$
0.21	0.10	$2.1 \cdot 10^{-3}$	48	4.1	$2 \cdot 10^{-5}$
0.21	0.15	$2.1 \cdot 10^{-3}$	59	3.9	$8 \cdot 10^{-5}$
0.21	0.20	$2.1 \cdot 10^{-3}$	71	4.0	$5 \cdot 10^{-5}$
0.14	0.20	$2.1 \cdot 10^{-3}$	118	4.0	—[c]
0.175	0.20	$2.1 \cdot 10^{-3}$	80	4.5	—[c]
0.28	0.20	$2.1 \cdot 10^{-3}$	64	3.0	$3 \cdot 10^{-5}$
0.14	0.10	$1.0 \cdot 10^{-3}$	113	4.0	$3 \cdot 10^{-5}$
0.28	0.10	$1.0 \cdot 10^{-3}$	91	2.5	$6 \cdot 10^{-6}$
0.14	0.10	$4.2 \cdot 10^{-3}$	57	7.0	$4 \cdot 10^{-5}$
0.28	0.10	$4.2 \cdot 10^{-3}$	54	3.0	$1 \cdot 10^{-5}$
0.14	0.10	$2.1 \cdot 10^{-3}$	70	5.5	$3 \cdot 10^{-5}$
0.28	0.10	$2.1 \cdot 10^{-3}$	49	3.6	$3 \cdot 10^{-5}$

[a] The period of the second oscillation was measured

[b] Lowest estimated $AgNO_3$ concentration (in mol/dm^3) which gave a Ce(IV) pulse immediately after the oscillating regime

[c] Decreasing amplitude, no excitability observed

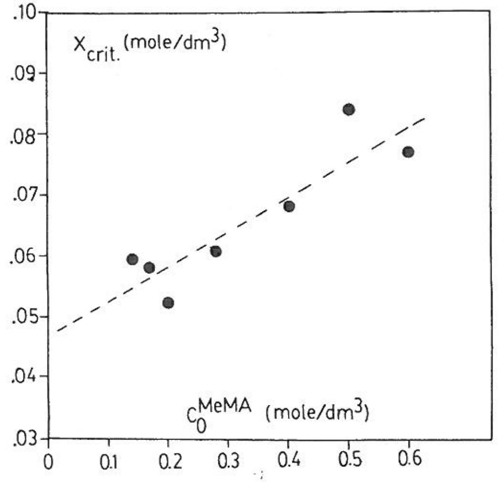

Fig. 2. Experimentally determined critical BrMeMA (X_{crit}) concentration at various initial MeMA concentrations. Dashed line indicates the least squares line $X_{crit} = 0.0565 \cdot C_0^{MeMA} + 0.0471$. Initial concentrations of Ce(IV) $= 2.1 \cdot 10^{-3}$ M and $KBrO_3 = 0.2$ M

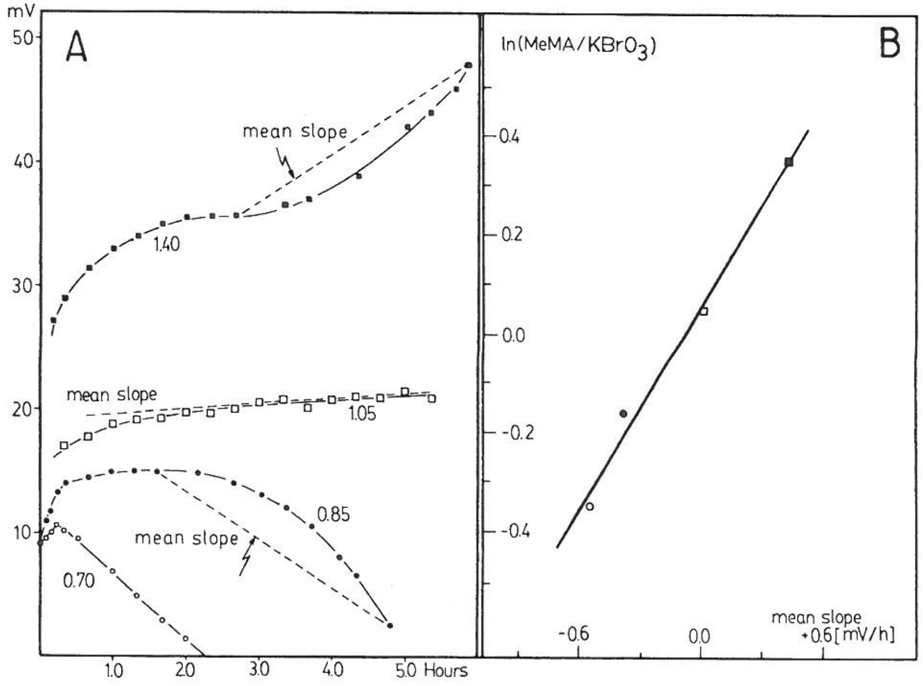

Fig. 3. (A) Increase and decrease of the silver electrode's potential amplitude. The numbers indicate the initial MeMA/$KBrO_3$ ratio. (B) Logarithmic dependence of the initial concentration ratio MeMA/$KBrO_3$ on the mean slope shown in Fig. 3A. The initial $KBrO_3$ and Ce(IV) concentrations were 0.1 M and $2.1 \cdot 10^{-3}$ M

At the beginning of the oscillating regime, period lengths (second period) were measured using different initial reagent concentrations. It was found that the period is lengthened when the MeMA concentration is decreased and shortened when the Ce(IV) concentration is decreased. Variations of $KBrO_3$ show only minor effects (Table 1).

When the $KBrO_3$ initial concentration is smaller than the MeMA concentration, the potential amplitudes of the platinum and silver electrodes increase during the oscillating regime. Finally, the oscillating domain ends with a sudden stop of the oscillations (Fig. 1). However, when the $KBrO_3$ initial concentration is greater than the MeMA concentration, the oscillations stop with a damping of the amplitudes. In Fig. 3A the situation is shown for several MeMA/$KBrO_3$ ratios. It is interesting to note, that when the MeMA/$KBrO_3$ is about one, the amplitude of the oscillations is nearly constant. This indicates a logarithmic dependency between the MeMA/$KBrO_3$ ratio and the change of the amplitude. Fig. 3B shows this relationship.

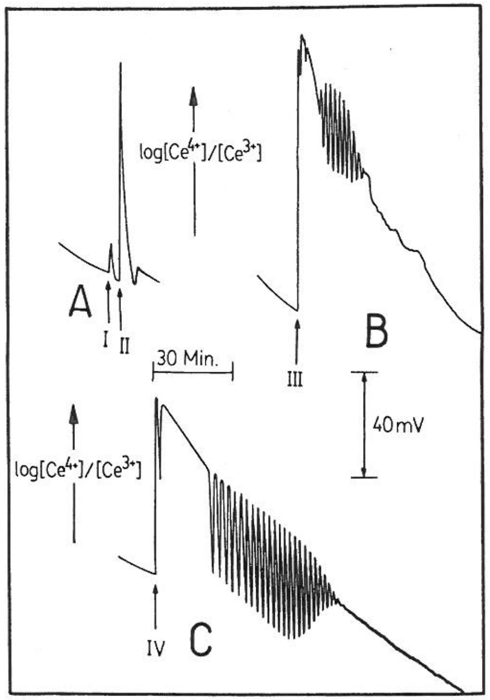

Fig. 4. (A) Excitable steady state in the MeMA BZR. Above a critical amount of added $AgNO_3$ a Ce(IV) spike is observed. I $= 2.5 \cdot 10^{-5}$ M $AgNO_3$, II $= 3.3 \cdot 10^{-5}$ M $AgNO_3$. (B) An excess of $AgNO_3$ above the excitation threshold causes several oscillations. III $= 5 \cdot 10^{-3}$ M $AgNO_3$. (C) In IV oscillations are induced by continuous addition (0.45 ml/min) of 0.01 M $AgNO_3$ into the quiescent excitable reaction mixture. Note the appearance of an induction period and the sudden onset of fully-developed oscillations

Excitability

When a sudden stop of the oscillations is observed, the quiescent region exhibits excitability, i.e. above a certain amount of added $AgNO_3$ a single Ce(IV) spike is induced, while under the threshold the perturbed system returns to a steady state (Fig. 4A).

The threshold was determined for various initial concentrations directly after the oscillations had stopped. At high initial Ce(IV) and $KBrO_3$ concentrations we obtain an increased threshold, whereas when the initial MeMA concentration is low the threshold increases. However, when the amplitude successively decreases, i.e. MeMA/$KBrO_3$ ratios less than one, excitability was not observed (Table 1).

The threshold of the excitable steady state was found to increase with time. Generally, in the first 2 h the threshold increases in magnitude about $10-10^2$ times (Fig. 5).

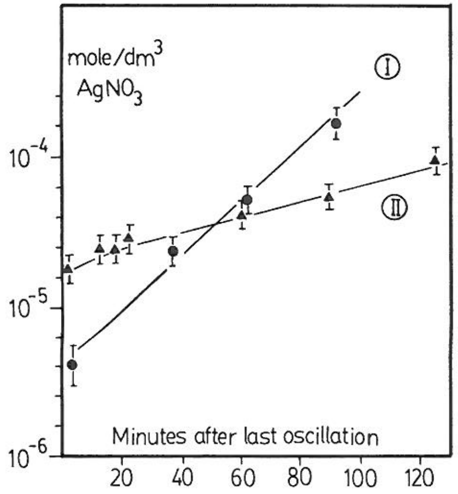

Fig. 5. Increase of threshold in the excitable regime. The threshold is defined as the smallest amount of $AgNO_3$ necessary to induce a single Ce(IV) pulse. The vertical bars indicate an error of ± 1 drop of $AgNO_3$ solution added. I: MeMA $= 0.28$ M, $KBrO_3 = 0.1$ M and Ce(IV) $= 1.0 \cdot 10^{-3}$ M. II: MeMA $= 0.28$ M, $KBrO_3 = 0.1$ M and Ce(IV) $= 2.1 \cdot 10^{-3}$ M

As in the MA BZR [17, 18], oscillations can be imposed when the excitable steady state is treated with an excess of $AgNO_3$ (Fig. 4B) or if $AgNO_3$ is added continuously to the medium (Fig. 4C).

Oxygen effects

Oxygen has a marked influence on the oscillation and induction periods. When oxygen is bubbled into the medium, we observe a lengthening of the induction period and a considerable decrease in the total number of oscillations compared with aerobic conditions. Relative to the increased induction period, oxygen acts as an inhibitor at the beginning of the oscillating domain. The oscillations stop at a high Ce(IV) state. This is different to MA systems, where the oscillations stop at a low Ce(IV) state (Fig. 6). Unlike MA systems [18], excitability is *not* observed in the oxygen-inhibited MeMA BZR. Later in the oscillating regime, oxygen only produces minor increase in oscillation period.

With a nitrogen atmosphere, the induction period is decreased, while the number of oscillations is increased (Table 2). Thus, nitrogen bubbled through the medium is able to initiate oscillations when they have stopped under oxygen or aerobic conditions. In Table 2 the trend of the excitability thresholds under nitrogen and oxygen atmospheres is shown. The threshold is much higher under nitrogen conditions than under an oxygen atmosphere.

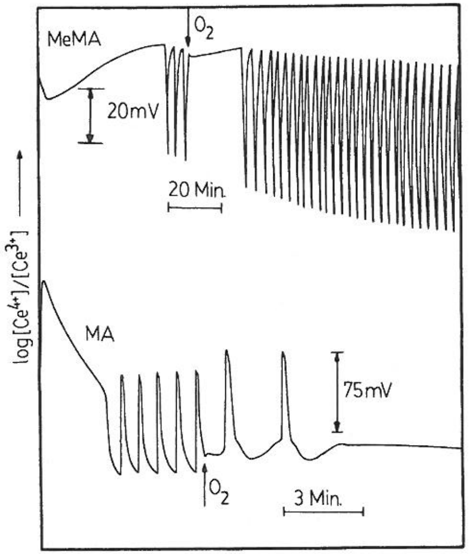

Fig. 6. At the beginning of the oscillating regime, oxygen may act as an inhibitor. The oscillations stop at a high Ce(IV) state (above). In MA systems the oscillations are completely inhibited at a low Ce(IV) state (below). Initial concentrations of reagents: MeMA and MA = 0.28 M, $KBrO_3$ = 0.1 M and Ce(IV) = $2.1 \cdot 10^{-3}$ M

Table 2. *Effect of oxygen and nitrogen atmosphere on induction period length, number of oscillations and excitation threshold with slow and rapid stirring in* MeMA BZR[a]

Stirring	Induction period length[b]		Number of oscillations		Excitation threshold[c]	
	oxygen	nitrogen	oxygen	nitrogen	oxygen	nitrogen
Rapid	61	55	56	97	$3 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
Slow	62	53	107	135	$4 \cdot 10^{-5}$	$1 \cdot 10^{-4}$

[a] MeMA = 0.28 M, $KBrO_3$ = 0.10 M and $(NH_4)_2Ce(NO_3)_6 = 2.1 \cdot 10^{-3}$ M

[b] In minutes

[c] Lowest estimated $AgNO_3$ concentration (in mol/dm^3) which gave a Ce(IV) pulse immediately after the oscillating regime

Stirring

Stirring influences the number and the shape of the oscillations. In Fig. 7, we see the effect of stirring under a nitrogen atmosphere. In the absence of a reasonable quantitative and reproducible measure of the influence of stirring, the qualitative terms *slow* and *rapid* stirring have been introduced. During rapid stirring, the amplitude and period is greater than during slow stirring. The same qualitative behaviour is observed under oxygen conditions.

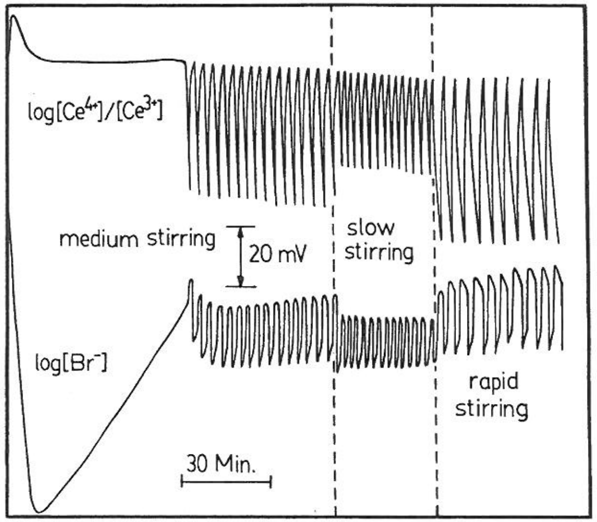

Fig. 7. Effect of stirring in a nitrogen atmosphere

It was also found that slow stirring, either under nitrogen or oxygen conditions leads to an increased number of oscillations (Table 2). Thus slow stirring combined with a nitrogen atmosphere leads to a drastic increase in the number of oscillations (ca. 130), while rapid stirring together with the bubbling of oxygen results in only a few oscillations (ca. 15). It was also observed that systems having many oscillations often have small period lengths in the beginning.

In the excitable state, high frequency oscillations may be induced by decreasing the stirring rate (Fig. 8). On the other hand, increasing the rate of stirring in the excitable regime, both under nitrogen and oxygen conditions, has only a minor influence on excitation thresholds (Table 3).

Discussion

Compared to the MA BZR, the most obvious difference is the longer induction period, oscillation period and the considerably longer oscillating regime (Table 4).

Although BZRs are generally expected to consist of easily-brominated organic substrates [2], MeMA reacts considerably more slowly with bromine than does MA [19, 20] and this may explain the longer induction period. The

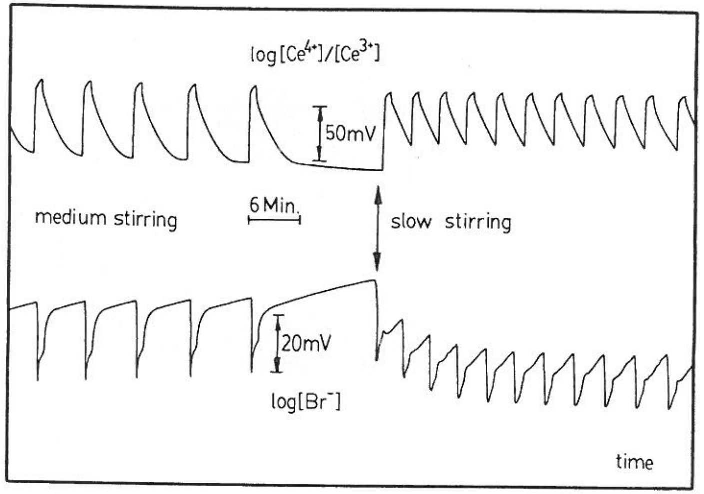

Fig. 8. In the quiescent excitable regime, oscillations may be initiated by decreasing the stirring rate

Table 3. *Effect of stirring on the excitation threshold in the non-oscillatory excitable regime*

Stirring	Threshold[a]	
	aerobic	anaerobic
Slow	$3 \cdot 10^{-5}$	$3 \cdot 10^{-4}$
Rapid	$4 \cdot 10^{-5}$	$4 \cdot 10^{-4}$

[a] Lowest estimated $AgNO_3$ concentration (in mol/dm³) which gave a Ce(IV) pulse

Table 4. *Comparison of a* MA BZR *and* MeMA BZR *in a nitrogen atmosphere*[a, b]

Induction period[c]		Oscillation period[c, d]		Oscillating regime length[c]		Number of oscillations	
MA	MeMA	MA	MeMA	MA	MeMA	MA	MeMA
3	53	0.5	2.5	235	601	170	135

[a] MeMA and MA = 0.28 M, $KBrO_3$ = 0.10 M and $(NH_4)_2Ce(NO_3)_6 = 2.1 \cdot 10^{-3}$ M
[b] Slow stirring
[c] In minutes
[d] The period of the second oscillation was measured

bromination of MeMA is assumed to occur, as in MA systems via an acid-catalyzed enolization mechanism [9, 21], with the enolization step as the rate-determining reaction. In the induction period, we consider the following simplified reaction scheme ("starred" species represent the intermediate enol-forms):

$$\mathrm{A} \xrightarrow{k_1} \mathrm{Br_2} \text{ (continuous formation of } \mathrm{Br_2}) \tag{2a}$$

$$\mathrm{MeMA} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{MeMA^*} \text{ (enolization of MeMA)} \tag{2b}$$

$$\mathrm{MeMA^*} + \mathrm{Br_2} \xrightarrow{k_3} \mathrm{BrMeMA} + \mathrm{HBr} \text{ (bromination of enol)} \tag{2c}$$

$$\mathrm{BrMeMA} \xrightarrow{k_4} Q \text{ (other products)}\,. \tag{2d}$$

Assuming that MeMA* is in a steady state, i.e.

$$\frac{\mathrm{d[MeMA^*]}}{\mathrm{d}t} = 0 \tag{3}$$

the rate of BrMeMA formed reads:

$$\frac{\mathrm{d[BrMeMA]}}{\mathrm{d}t} = k_2 \cdot \mathrm{[MeMA]} - k_{-2} \cdot \mathrm{[MeMA^*]_{SS}} - k_4 \cdot \mathrm{[BrMeMA]}\,. \tag{4}$$

We assume that

$$\mathrm{[MeMA]} = C_0^{\mathrm{MeMA}} - \mathrm{[BrMeMA]} \tag{5}$$

i.e. we only consider MeMA to react with bromine and $Q \ll \mathrm{[BrMeMA]}$ (C_0^{MeMA} is the initial MeMA concentration). With $X = \mathrm{[BrMeMA]}$ we may write

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_2\,(C_0^{\mathrm{MeMA}} - X) - k_{-2}\,\mathrm{[MeMA^*]_{SS}} - k_4 \cdot X \tag{6a}$$

or

$$\frac{\mathrm{d}X}{K - K' \cdot X} = \mathrm{d}t \tag{6b}$$

where

$$K = k_2 \cdot C_0^{\mathrm{MeMA}} - k_{-2} \cdot \mathrm{[MeMA^*]_{SS}}$$

and

$$K' = k_2 + k_4\,.$$

Integrating X from $X=0$ to $X=X_{\mathrm{crit}}$ and t from $t=0$ to $t=\tau_{\mathrm{ind}}$ (τ_{ind} is the length of the induction period) we find

$$\ln\left(1 - \frac{K' \cdot X_{\mathrm{crit}}}{K}\right) = -\tau_{\mathrm{ind}} \cdot K' \tag{7}$$

and set approximately

$$\ln\left(1-\frac{K'\cdot X_{\mathrm{crit}}}{K}\right) \approx -\frac{K'\cdot X_{\mathrm{crit}}}{K} \tag{8}$$

which implies

$$\frac{K'\cdot X_{\mathrm{crit}}}{K} \ll 1 \,.$$

Neglecting the $k_{-2}\cdot[\mathrm{MeMA}^*]_{\mathrm{SS}}$ term we finally write

$$\tau_{\mathrm{ind}} \approx \frac{X_{\mathrm{crit}}}{k_2\cdot C_0^{\mathrm{MeMA}}} \,. \tag{9}$$

We see that the slower rate-determining enolization step (expressed by k_2) has the effect of increased induction periods. Equation (9) may be checked by experiment. Using various initial MeMA concentrations we measured the induction period and X_{crit} and calculated k_2. Within our experimental error we conclude that k_2 may be regarded as a constant (Table 5). Inserting the least squares line of Fig. 2 and the mean k_2 value ($\bar{k}_2$ in Table 5), a curve is obtained which describes quantitatively the length of the induction period τ_{ind} as a function of initial MeMA concentration C_0^{MeMA} (Fig. 9). Field *et al.* have empirically described an analogous relationship for MA systems [9].

For MA systems, Burger and Körös [22, 23] have recently described an alternative approach to connect the critical bromo-malonic acid concentration and the induction period length.

Also the longer oscillation periods may be the result of the slower reaction of the less reactive MeMA in some rate-determining step. Sensitivity analysis of the Oregonator model [24] indicates that this may be the oxidation of BrMeMA by Ce(IV) ions. However this step seem to consist of several radical reactions still not fully understood.

Table 5. *k_2 determined from experimental τ_{ind}, X_{crit} and C_0^{MeMA} values*[a]

C_0^{MeMA} (mol/dm^3)	τ_{ind} (min)	X_{crit} (mole/dm^3)	$k_2 = \frac{X_{\mathrm{crit}}}{\tau_{\mathrm{ind}}\cdot C_0^{\mathrm{MeMA}}}$ (s^{-1})
0.14	130.0	0.0594	$5.54\cdot10^{-5}$[b]
0.17	96.0	0.0580	$5.92\cdot10^{-5}$[b]
0.20	82.0	0.0524	$5.33\cdot10^{-5}$[b]
0.28	59.4	0.0606	$6.07\cdot10^{-5}$[b]
0.40	51.3	0.0678	$5.51\cdot10^{-5}$[b]
0.50	49.0	0.0839	$5.71\cdot10^{-5}$[b]
0.60	44.0	0.0766	$4.84\cdot10^{-5}$[b]

[a] Initial $KBrO_3$ concentration 0.2 M and initial Ce(IV) concentration $2.1\cdot10^{-3}$ M
[b] $\bar{k}_2$ (mean k_2) $= 5.56\cdot10^{-5}\ s^{-1}$

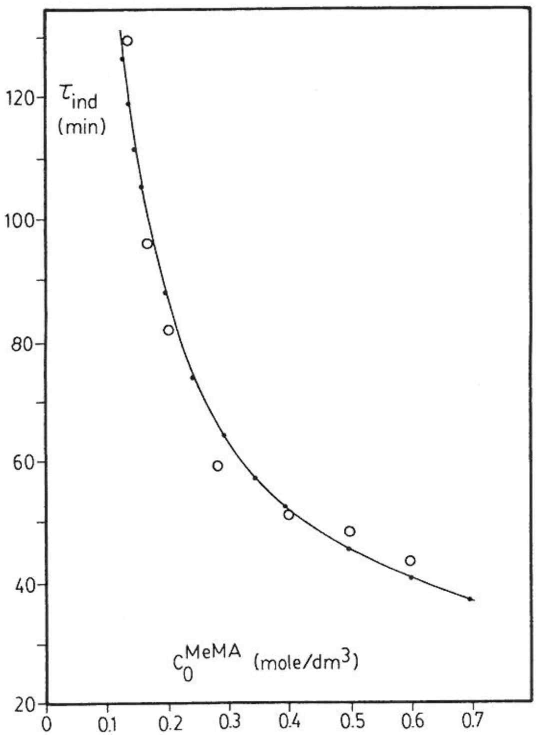

Fig. 9. Solid curve shows calculated relationship between initial MeMA concentration and induction period τ_{ind} using Eq. (9), $\bar{k}_2$ from Table 5, and the least squares line of Fig. 2. Open circles indicate experimental results

The most remarkable difference from MA systems is that oxygen makes the oscillations disappear at a high Ce(IV) concentration while excitability is not observed. This effect still waits an explanation. However, apart from this special oxygen effect, the MeMA BZR has similar qualitative dynamical behaviour as MA systems under various constraints such as stirring, N_2 or O_2 atmospheres. Together with the similar quantitative behaviour of the induction period and the ability of performing simulations of single $AgNO_3$-induced Ce(IV) spikes by the Oregonator [25], it seems that also for MeMA systems a FKN mechanism with modified rate constants describes the "core reactions" properly.

There are still aspects in BZRs not yet satisfactorily understood, such as stirring effects, the electrodes' response to various intermediates, the radical reaction subset, and the control of oscillations at low Br^- concentrations [26, 27]. In this respect, the slower reacting MeMA may have the advantage that component reactions may be more easily characterized experimentally than the more reactive MA BZR.

Acknowledgement

The author wants to thank Prof. Dr. R. M. Noyes for a stimulating discussion on BZ systems.

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