Formation of Carbon Dioxide in the Belousov-Zhabotinsky-Reaction

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The rate of formation of CO_2 in the BZ system is measured and compared to the predictions of the Field-Körös-Noyes (FKN)-theory. The experimental rate is found to be larger than the theoretical rate by a factor of about 100. This discrepancy cannot be easily explained without severe changes in the FKN model. Moreover, improved rate constants of the most important organic reactions in the BZ system are given.

1. Introduction

If Ce^{4+} is injected into a mixture of malonic acid (MA) and $HBrO_3$ in sulfuric acid solution, the reactions

$$2\,Ce^{4+} + MA + H_2O \rightarrow 2\,Ce^{3+} + TA + 2\,H^+\,, \qquad (R\,1)$$

$$4\,Ce^{3+} + HBrO_3 + 4\,H^+ \rightarrow 4\,Ce^{4+} + HOBr + 2\,H_2O \qquad (R\,2)$$

are started. In (R 1) MA is oxidized to tartronic acid (TA), and the Ce^{3+} produced in this reaction undergoes the overall reaction (R 2) with bromate. Consequently, a stationary state will be established in which a nearly constant Ce^{4+}-concentration is expected (Fig. 1; in reality, the Ce^{4+}-concentration decreases slightly due to consecutive reactions). As soon as HOBr is produced by (R 2), MA is brominated according to (R 3)

$$HOBr + MA \rightarrow BrMA + H_2O. \qquad (R\,3)$$

The bromomalonic acid (BrMA) will be oxydized by Ce^{4+}

$$2\,Ce^{4+} + BrMA + H_2O \rightarrow 2\,Ce^{3+} + GOA + Br^- + CO_2 + 3\,H^+ \qquad (R\,4)$$

and Br^- is formed besides glyoxylic acid (GOA) and CO_2. The overall reaction (R 2) is inhibited by Br^-; as soon as Br^- reaches a critical value c_{crit}, (R 2) is stopped, and a fast decrease of the Ce^{4+}-concentration is observed. With decreasing Ce^{4+},

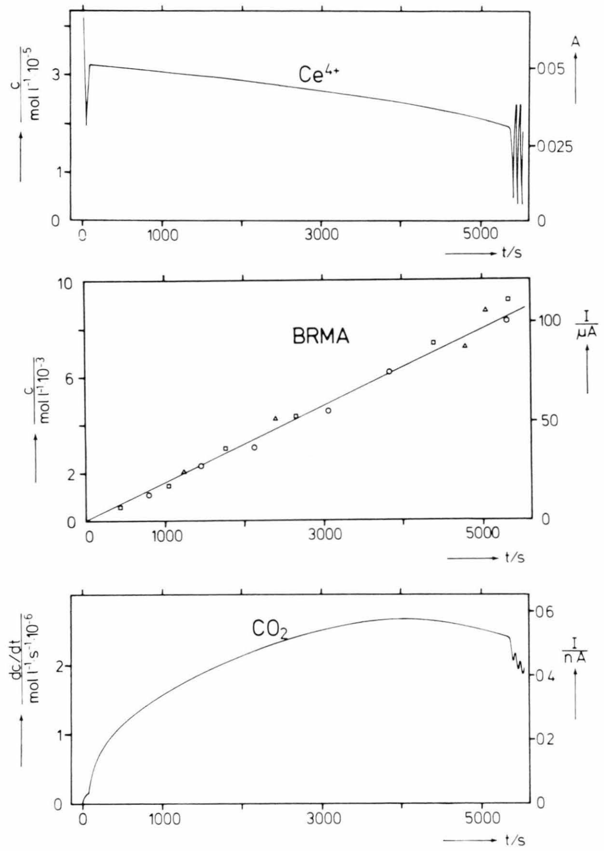

Fig. 1. Concentration c of Ce^{4+} and BrMA and rate of formation dc/dt of CO_2 during the induction period of the BZ-reaction (left hand scale). Initial concentrations: 0.1 m MA, 0.1 m $NaBrO_3$ and $1 \cdot 10^{-4}$ m $Ce(SO_4)_2$ in 1 m H_2SO_4; temperature 20 °C; oxygen was excluded by applying a stream of H_2 and N_2, respectively. Ce^{4+} was followed by the absorbance A at 400 nm, BrMA by the polarographic current I (polarographic voltage set on −0.35 V, reference saturated AgCl-electrode) and CO_2 by the FID current I (right hand scale).

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(R4) will be slowed down, and the remaining Br^- will disappear according to the overall reaction

$$2\,Br^- + HBrO_3 + 3\,MA + 2\,H^+ \rightarrow 3\,BrMA + 3\,H_2O\,. \qquad (R5)$$

If the Br^--concentration is lower than c_{crit}, (R2) will start again, and oscillations occur (Figure 1).

The reactions (R1) to (R5) have been proposed by Field, Körös and Noyes [1–4] (FKN-theory). In this paper the formation of CO_2, which is the final product in the organic subsystem, is studied in more detail.

Within the framework of the FKN-theory the main contributions to the formation of CO_2 are the oxidation of TA (which is formed in (R1))

$$2\,Ce^{4+} + TA \rightarrow 2\,Ce^{3+} + GOA + CO_2 + 2\,H^+ \qquad (R6)$$

and the oxidation of BrMA in (R4). In order to compare the rate of formation of CO_2 to the theoretical predictions, the concentrations of CO_2, BrMA and Ce^{4+} were measured simultaneously. In all experiments oxygen was excluded from the reaction mixture by applying a gas stream of H_2 or N_2.

2. Procedure

Experiments

To follow Ce^{4+} and CO_2, a sample cell (volume 10 ml) of optical path length 2 cm was used. The Ce^{4+} was monitored by the absorbance at 400 nm, measured by the dual wavelength technique [5]; the CO_2 was followed simultaneously by bubbling a stream of hydrogen through the solution and measuring the current in a flame ionization detector (FID) after reducing the CO_2 catalytically to CH_4 [6]. In a separate experiment, a reaction cell of 200 ml volume was used, Ce^{4+} was monitored as described above, samples of 10 ml were taken, neutralized and diluted by 10 ml of a buffer solution (acetic acid/acetate buffer, pH 4.6); the content of BrMA was determined polarographically [7, 8]. In this experiment O_2 was excluded by bubbling nitrogen through the reaction mixture.

Reagents: $Ce(SO_4)_2$, MA and conc. H_2SO_4 (p.a. Fluka) were taken without further purification. TA (p.a. Fluka) was purified by washing it with acetic acid ethyl ester. $NaBrO_3$ (p.a. Fluka) was recrystallized twice from hot water.

BrMA (in the form of its potassium salt) was synthesized according to a preparation suggested by Burger [9]. A solution of 0.1 mol MA in 50 ml diethylether is stirred and kept cool in an ice bath. 0.2 mol Br_2 (solved in 60 ml CCl_4) are added dropwise. At the end of the reaction the solvents are removed by a vacuum line. The yellowish residue is solved in 5 ml water and added to a saturated solution of 30 g potassium acetate in ethanol. The white precipitate is isolated by filtration and the product is further purified by solving it in an ethanol/H_2O-mixture (10:1) and adding the same volume of ethanol to the solution. The absorption spectrum of a solution of BrMA in 1 m H_2SO_4 is characterized by the following values of the extinction coefficient (measured in $1\,mol^{-1}\,cm^{-1}$, wavelength range from 280 to 200 nm, steps of 10 nm): 5, 16, 60, 127, 242, 360, 442, 494, 578.

FKN-model

Within the FKN-model the rate of CO_2-formation is given by the following rate equations based on the reactions (R1), (R4) and (R6):

$$\mathrm{d}c_{CO_2}/\mathrm{d}t = k_4\, c_{Ce^{4+}}\, c_{BrMA} + k_6\, c_{Ce^{4+}}\, c_{TA}\,, \qquad (1)$$

$$\mathrm{d}c_{TA}/\mathrm{d}t = k_1\, c_{Ce^{4+}}\, c_{MA} - k_6\, c_{Ce^{4+}}\, c_{TA}\,. \qquad (2)$$

As can be seen from Fig. 1, the concentration of Ce^{4+} decreases slowly during the induction period and may be replaced by its mean value; moreover, c_{MA} may be assumed to be nearly constant too, and c_{BrMA} is a linear function of time. Hence (1) and (2) reduce to

$$\mathrm{d}c_{CO_2}/\mathrm{d}t = k'_4\, a\, t + k'_6\, c_{TA}\,, \qquad (3)$$

$$\mathrm{d}c_{TA}/\mathrm{d}t = k'_1\, c_{MA,O} - k'_6\, c_{TA} \qquad (4)$$

($k'_4 = k_4 c_{Ce^{4+},m}$, $a = \mathrm{d}c_{BrMA}/\mathrm{d}t$, $k'_6 = k_6 c_{Ce^{4+},m}$, $k'_1 = k_1 c_{Ce^{4+},m}$; $c_{Ce^{4+},m}$ = mean value of the concentration of Ce^{4+}; $c_{MA,O}$ = initial concentration of MA).

From (4) we obtain by integration [10]

$$c_{TA} = c_{MA,O}\,\frac{k'_1}{k'_6}\,(1 - e^{-k'_6 t})\,. \qquad (5)$$

c_{TA} is inserted in (3):

$$\mathrm{d}c_{CO_2}/\mathrm{d}t = k'_4\, a\, t + c_{MA,O}\, k'_1\,(1 - e^{-k'_6 t})\,. \qquad (6)$$

In order to compare this theoretical prediction with experiment, the rate constants k_1, k_4 and k_6 have to be determined in separate experiments. In the case of (R1), 200 µl of a 0.1 m solution of $Ce(SO_4)_2$ in 1 m H_2SO_4 were injected into 200 ml of a 0.1 m solution of MA; the solution was bubbled with nitrogen and kept at 20 °C. The change in absorbance was measured spectroscopically. From a first order plot, the first order rate constant was obtained (Fig. 2, curve a) giving the value $k_1 = 0.10\ \mathrm{l\ mol^{-1}\ s^{-1}}$. In a similar way the constants $k_4 = 0.046\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and $k_6 = 0.33\ \mathrm{l\ mol^{-1}\ s^{-1}}$ were obtained (Fig. 2, curves c and b).

The mean concentration $c_{Ce^{4+},m} = 2.8 \cdot 10^{-5}\ \mathrm{mol\ l^{-1}}$ and the slope $a = 1.67 \cdot 10^{-6}\ \mathrm{mol\ l^{-1}}$ are taken from Fig. 1, and the first order rate constants k'_1, k'_4 and k'_6 are calculated ($k'_1 = 2.8 \cdot 10^{-6}\ \mathrm{s^{-1}}$, $k'_4 = 1.3 \cdot 10^{-6}\ \mathrm{s^{-1}}$ and $k'_6 = 9.2 \cdot 10^{-6}\ \mathrm{s^{-1}}$). The end of the induction period is reached at $t = 5420$ s; under this condition is $k'_6 t$ small compared to 1, and the exponential in (6) may be replaced by the first two terms of the power series. In this way, (6) may be further simplified:

$$dc_{CO_2}/dt = (k'_4 a + c_{MA,0}\, k'_1 k'_6)\, t\,. \qquad (7)$$

From this simple model the rate of CO_2 formation is expected to increase linearly with time. The situation is not essentially changed if the differential equations (1) and (2) are solved rigorously by numerical integration using the experimental curves for Ce^{4+} and BrMA in Fig. 1 (Fig. 3); the main difference is that the rate of CO_2-formation at the end of the induction period is lower by about 20% due to the decrease in Ce^{4+}-concentration. Anyway, the rate calculated from (7) may be considered as an upper limit.

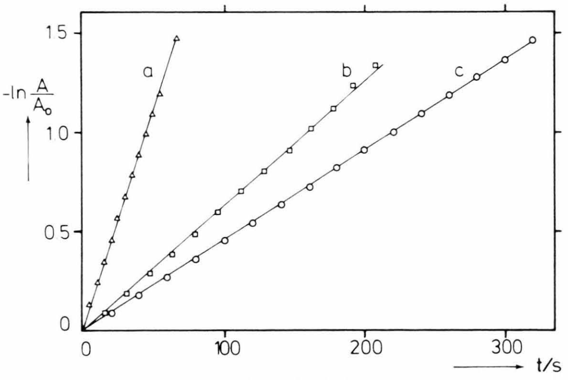

Fig. 2. First order plots ($-\ln(A/A_0)$ versus time t) for the reactions of MA (curve a), TA (curve b) and BrMA (curve c), initial concentrations 0.1 m, 0.01 m and 0.05 m, respectively, with Ce^{4+} in 1 m H_2SO_4 at 20 °C; A is the absorbance of Ce^{4+} at 400 nm ($A_0 = 0.8$), the optical path-length is 10 cm. In order to evaluate the second order rate constants k_1, k_4 and k_6 from these plots a factor of 0.5 must be applied according to Eqs. (1) and (2).

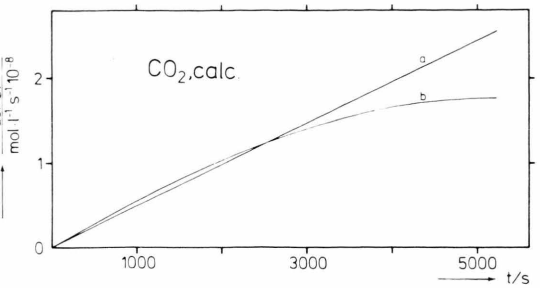

Fig. 3. Calculated rate of formation of CO_2 during the induction period. Curve a: calculated from (7); curve b: calculated by numerical solution of (1) and (2) using the experimental curve for Ce^{4+} and BrMA in Figure 1.

If we compare this upper limit value calculated at $t = 5420$ s, using the rate constants given above ($dc_{CO_2}/dt = 2.6 \cdot 10^{-8}\ \mathrm{mol\ l^{-1}\ s^{-1}}$), to the experimental value given in Fig. 1 ($dc_{CO_2}/dt = 2.5 \cdot 10^{-6}\ \mathrm{mol\ l^{-1}\ s^{-1}}$), we obtain the very striking result that the experimental value is larger than the theoretical one by two orders of magnitude. The situation is nearly the same if the initial concentration of Ce^{4+} is changed in the range from $1 \cdot 10^{-4}$ m to $10 \cdot 10^{-4}$ m (Table 1, rows 1–4). The discrepancy between experiment and theory would be even larger at shorter times t, since the theoretical values for dc/dt increase linearly with t whereas the experimental ones become nearly constant at large values of t (see Figure 1).

3. Discussion

In order to check our experimental values, further work in literature was included. First we examined our rate constants k_1, k_4 and k_6. The value $k_1 = 0.14\ \mathrm{l\ mol^{-1}\ s^{-1}}$ reported by Barkin et al. [11] for 25 °C (oxygen excluded from the reaction mixture) is in good agreement with our value $0.10\ \mathrm{l\ mol^{-1}\ s^{-1}}$, which is valid for 20 °C. The value $k_4 = 0.07\ \mathrm{l\ mol^{-1}\ s^{-1}}$ reported by Iwo and Noyes [2] for 25 °C is not far from our value $0.046\ \mathrm{l\ mol^{-1}\ s^{-1}}$ for 20 °C. The value $k_6 = 1.4\ \mathrm{l\ mol^{-1}\ s^{-1}}$ for 25 °C reported by Iwo and Noyes [2] is larger than our value $0.33\ \mathrm{l\ mol^{-1}\ s^{-1}}$ by a factor of 4; we found out, however, that the value of k_6 is strongly affected by oxygen and by small amounts of impurities.

Table 1. Rate of CO_2 formation at the end of the induction period (time t after mixing). $c_{Ce^{4+},O}$, $c_{MA,O}$ and $c_{HBrO_3,O}$ are the initial concentrations of Ce^{4+}, MA and $HBrO_3$; $c_{Ce^{4+},m}$ is the mean concentration of Ce^{4+} during the induction period, and a is the rate of formation of BrMA. All experiments are performed in 1 m H_2SO_4 at 20 °C. – *Rows 1–6:* this paper, *row 7:* experimental values by Noszticzius [12]; *rows 8–9:* experimental values by Bar-Eli [13]. Values in parantheses are estimated.

$\frac{c_{Ce^{4+},O}}{mol\ l^{-1}}$	$\frac{c_{MA,O}}{mol\ l^{-1}}$	$\frac{c_{HBrO_3,O}}{mol\ l^{-1}}$	$\frac{c_{Ce^{4+},m}}{mol\ l^{-1}}$	$\frac{a}{mol\ l^{-1}\ s^{-1}}$	$\frac{t}{s}$	$\frac{dc_{CO_2}/dt}{mol\ l^{-1}\ s^{-1}}$		$\frac{\text{Exp. rate}}{\text{Theor. rate}}$
						Experiment	Theory	
$1 \cdot 10^{-4}$	0.1	0.1	$2.8 \cdot 10^{-5}$	$1.7 \cdot 10^{-6}$	5420	$2.5 \cdot 10^{-6}$	$2.6 \cdot 10^{-8}$	99
$2 \cdot 10^{-4}$	0.1	0.1	$6.2 \cdot 10^{-5}$	$3.2 \cdot 10^{-6}$	2640	$5.3 \cdot 10^{-6}$	$5.8 \cdot 10^{-8}$	91
$5 \cdot 10^{-4}$	0.1	0.1	$14.0 \cdot 10^{-5}$	$7.8 \cdot 10^{-6}$	1200	$11.0 \cdot 10^{-6}$	$13.8 \cdot 10^{-8}$	80
$10 \cdot 10^{-4}$	0.1	0.1	$25.0 \cdot 10^{-5}$	$(16.0 \cdot 10^{-6})$	720	$19.0 \cdot 10^{-6}$	$2.8 \cdot 10^{-7}$	68
$3.45 \cdot 10^{-4}$	0.1	0.03	$6.2 \cdot 10^{-5}$	$3.3 \cdot 10^{-6}$	1400	$2.9 \cdot 10^{-6}$	$3.1 \cdot 10^{-8}$	93
$1.32 \cdot 10^{-4}$	0.1	0.3	$6.2 \cdot 10^{-5}$	$3.2 \cdot 10^{-6}$	6000	$5.0 \cdot 10^{-6}$	$1.3 \cdot 10^{-7}$	39
$20 \cdot 10^{-4}$	0.15	0.035	$(25.0 \cdot 10^{-5})$	$(25.0 \cdot 10^{-6})$	240	$3.4 \cdot 10^{-5}$	$1.4 \cdot 10^{-7}$	240
$1 \cdot 10^{-4}$	0.1	0.1	$2.8 \cdot 10^{-5}$	$1.7 \cdot 10^{-6}$	5420	$2.4 \cdot 10^{-6}$	$2.6 \cdot 10^{-8}$	92
$10 \cdot 10^{-4}$	0.1	0.1	$25.0 \cdot 10^{-5}$	$(16.0 \cdot 10^{-6})$	720	$12.0 \cdot 10^{-6}$	$2.8 \cdot 10^{-7}$	43

In our experiments, oxygen was excluded and the commercial p. a. grade TA was carefully purified. Our value is the limiting value after a series of purification procedures.

Secondly we examined experimental observations on the rate of CO_2-formation. Noszticzius [12] investigated a system containing 0.15 m MA, 0.035 m $HBrO_3$ and $2 \cdot 10^{-3}$ m Ce^{4+} in 3 m H_2SO_4. At the end of the induction period ($t = 240$ s) the rate of CO-formation was $2.4 \cdot 10^{-6}$ mol l^{-1} s^{-1}; from the ratio $CO/(CO_2 + CO) = 0.07$ the value $dc/dt = 3.4 \cdot 10^{-5}$ mol l^{-1} s^{-1} is obtained for CO_2. Since the Ce^{4+}-steady state concentration and the rate of BrMA-formation are not given in that paper, we made an estimation by extrapolating our values: $c_{Ce^{4+},m} = 2.5 \cdot 10^{-4}$ mol l^{-1}, $a = 25 \cdot 10^{-6}$ mol l^{-1} s^{-1}. Inserting these values into (7), we calculate $dc/dt = 1.4 \cdot 10^{-7}$ mol l^{-1} s^{-1} at $t = 240$ s. The ratio exp. rate/theor. rate = 240 is of the same order of magnitude as in our former experiments (Table 1, row 7). Bar-Eli and Haddad [13] studied the BZ-reaction at similar initial concentrations as ourselves. Their values for two different cerium concentrations are listed in rows 8 and 9 of Table 1 and compared to theory. The ratios exp. rate/theor. rate = 92 and 43, respectively, are also of the same order of magnitude as ours. Similar conclusions can be drawn from other data on CO_2 evolution available in literature, e.g. by Degn [14] and by Bornmann, Busse and Hess [15].

From these considerations it seems to be clear that the observed discrepancy in the rate of CO_2 formation cannot be due to experimental errors. To overcome these difficulties, Noszticzius [16] assumed that radicals which are formed in a first step of R1 [11] react directly with bromate as an oxidizing agent, and additional CO_2 is formed. In order to check this hypothesis, the rate of CO_2 formation was measured at different bromate concentrations, the initial concentration of MA and the mean Ce^{4+}-concentration being held constant in the experiments. The results are given in Fig. 4 and

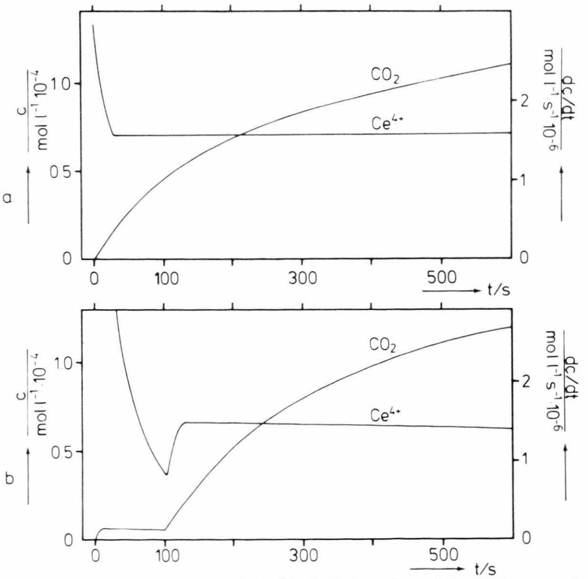

Fig. 4. Concentration c of Ce^{4+} (left hand scale) and rate of formation dc/dt of CO_2 (right hand scale) during the induction period. Initial concentrations a) $1.32 \cdot 10^{-4}$ m Ce^{4+}, 0.1 m MA, 0.3 m $HBrO_3$, b) $3.45 \cdot 10^{-4}$ m Ce^{4+}, 0.1 m MA, 0.03 m $HBrO_3$. Temperature 20 °C, oxygen excluded by applying a stream of H_2.

Table 1 (rows 5, 6). Using a bromate concentration of 0.03 m, the same ratio exp. rate/theor. rate is obtained as in the case 0.1 m; using a bromate concentration of 0.3 m, the ratio is not at all enlarged, as would be expected, but even reduced by a factor of 2. From this experiment we conclude that bromate does not react directly with radicals formed in (R1).

Further conclusions on the mechanism of CO_2-formation are obtained if Fig. 1 is discussed in more detail. The curve for the Ce^{4+} concentration passes a minimum at $t_{min} = 50$ s before reaching the steady state value. This feature, which has already been pointed out in an earlier paper [17], is more pronounced at lower bromate concentration (Fig. 4b, $t_{min} = 100$ s) and disappears at higher bromate concentrations (Fig. 4a). From Figs. 1 and 4b we conclude that (R2) does not start immediately after the injection of Ce^{4+}. Although the reason for this unexpected behaviour is not clear at all (e.g. this effect cannot be observed if oxygen is present in the solution), conclusions concerning the CO_2 evolution process may be drawn: from Fig. 1 and 4b it is to be seen that the rate of CO_2 evolution is very small in the beginning of the reaction, and a sudden increase is observed as soon as (R2) starts and the steady state value is reached.

A quantitative investigation reveals that the curves for Ce^{4+} are the same as calculated from (R1) if the time intervall from 0 to t_{min} is considered. The mean rate of CO_2 formation from $t = 0$ to t_{min}, however, is larger than calculated from theory by a factor of about 2. The reason for this additional discrepancy is not yet clear.

From our experiments it may be concluded that the process of formation of CO_2 in the BZ-system depends strongly on the presence of transient bromine species; this result cannot be understood within the framework of the FKN-theory and may also affect the understanding of the Br^--formation process, which is coupled with the set of organic reactions.

Acknowledgements

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$$\frac{dc_{TA}}{dt} = \frac{1}{2}\frac{dc_{Ce^{4+}}}{dt} \quad \text{and} \quad \frac{dc_{BrMA}}{dt} = \frac{1}{2}\frac{dc_{Ce^{4+}}}{dt}.$$

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