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Effect of Methyl Ketones in the Belousov−Zhabotinskii Reaction

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When a methyl ketone is added to the Belousov−Zhabotinskii (BZ) reaction, an increase of the induction period and in the number of oscillations is observed. This behavior can be explained by the competition of malonic acid and the methyl ketone for molecular bromine. We studied the effect of four methyl ketones in the BZ reaction and found a direct relationship between the induction period, the concentration, and the enolization constant of the ketone. A discussion of the results with regard to the crucial concentration of bromomalonic acid is given. The experimental results are supported by simulations based upon the GTF mechanism of the reaction.

1. Introduction

The great interest for oscillating chemical reactions is because they show a large variety of nonmonotonic behaviors,[1−3] The classic BZ reaction is the oscillatory bromination and further oxidation of malonic acid by bromate ions in the presence of cerium ions. The oscillatory behavior can be easily described with the following three global processes taken from the FKN[1,4] mechanism:

$$\text{(A) } BrO_3^- + 5Br^- + 6H^+ \rightleftharpoons 3Br_2 + 3H_2O$$

$$CH_2(COOH)_2 \rightleftharpoons HOOCCH{=}C(OH)_2$$

$$3HOOCCH{=}C(OH)_2 + 3Br_2 \rightarrow 3BrCH(COOH)_2 + 3Br^- + 3H^+$$

$$\text{(B) } 2Ce^{3+} + BrO_3^- + HBrO_2 + 3H^+ \rightarrow 2HBrO_2 + 2Ce^{4+} + H_2O$$

$$2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$$

$$\text{(C) } 2Ce^{4+} + BrCH(COOH)_2 + CH_2(COOH)_2 \rightarrow \Gamma Br^- + 2Ce^{3+}$$

It is accepted that the evolution in time for the BZ reaction is controlled by Br^-, and the magnitude of the bromide concentration says which of the processes A or B takes control of the reaction. The control of reaction from process B to process A is given when the concentration of Br^- is high enough and when it consumes $HBrO_2$ of the reaction.

When process A is dominant, the Br^- concentration is reduced, letting $HBrO_2$ accumulate. In a general way, the kinetic control of the BZ reaction between process A or B is given depending whether it is bromide ion or bromous acid that reacts with bromate. Process C generates Br^- so that the control of the reaction can switch between processes A and B.

One of the main characteristics of oscillating reactions of the BZ type is that, under some initial conditions, an induction period appears before oscillations take place. This induction period appears because one of the processes A or B takes kinetic control of the reaction for a long time while the reaction reaches certain conditions.[5] For the classic BZ reaction it has been experimentally demonstrated that the induction period occurs until a crucial concentration of bromomalonic acid is reached.[6] From the global processes that describe the BZ reaction it is seen clearly that the time to reach the crucial concentration of bromomalonic acid depends on its rate of formation during process A and of consumption in process C.

In this paper it is shown how the methyl ketones affect the global dynamics of the BZ reaction, through its direct participation in process A.

2. Materials and Methods

The BZ oscillator was studied under batch conditions in a cylindrical double-walled glass cell, 80 cm^3 capacity, thermostated to 25.00 ± 0.01 °C by circulating water through the internal wall of the cell. The solution was continuously magnetically stirred from the bottom, at a frequency of about 250 rpm, taking care not to form a vortex. The reaction was followed with a platinum electrode with an internal reference, Cole-Parmer 27006-21, connected to a multimeter Hewlett-Packard 3478A with sensitivity of 0.1 μV. Data acquisition was made through a GPIB IEEE-488 interface.[7]

The reagents used were sulfuric acid (AnalytiCals Carlo Erba 96%), malonic acid (Merck fa), cerium(III) nitrate hexahydrate (Merck ultrapure), potassium bromate (Mallinckrodt chemical works, recrystallized from sulfuric acid), acetone (Merck fs), methyl ethyl ketone (Merck fs), methyl propyl ketone (Merck fs), and methyl isobutyl ketone (Merck fs). All solutions were prepared in 0.8 M sulfuric acid. The reaction started after the addition of 10 cm^3 of 0.182 M $KBrO_3$ to a solution containing 40 cm^3 of 2.17×10^{-3} M $CH_2(COOH)_2$, 27 cm^3 of 0.8 M H_2SO_4, 1 cm^3 of 0.029 M $Ce(NO_3)_3$, and 0.2 cm^3 of ketone.

3. Results and Discussion

Figure 1shows the independent effect of acetone, methyl ethyl ketone, methyl propyl ketone, and methyl isobutyl ketone, in the global dynamics of the BZ reaction.

The initial concentrations of bromate, malonic acid, sulfuric acid, cerium(III), and ketone are the same in Figure 1. The only

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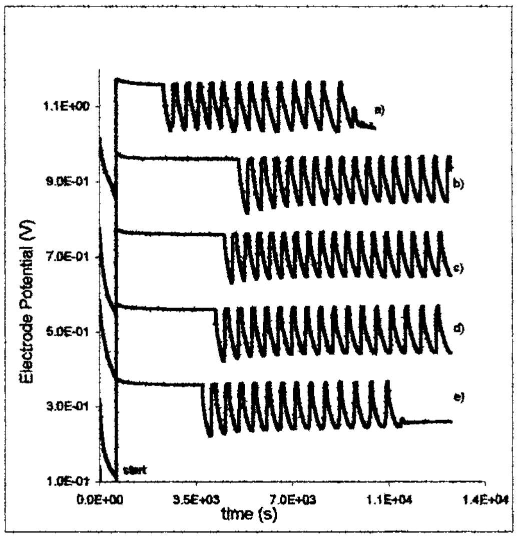

Figure 1. BZ reaction with ketones: (a) without; (b) acetone; (c) methyl ethyl ketone; (d) methyl propyl ketone; (e) methyl isobutyl ketone.

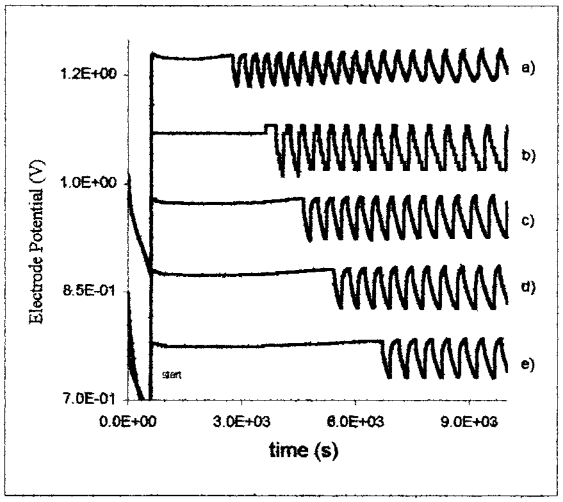

Figure 2. BZ reaction with acetone. The initial concentrations of acetone are (a) 0 M, (b) 0.02 M, (c) 0.035 M, (d) 0.047 M, and (e) 0.059 M.

change is the ketone that is used. In the BZ reaction the acetone (Figure 1a) makes a larger increase of the induction period, because it is of higher enolization constant. This increase in the induction period falls for methyl ethyl ketone, methyl propyl ketone, and methyl isobutyl ketone, in the order in which the value for the enolization constant goes down.

With acetone, methyl ethyl ketone, and methyl propyl ketone the BZ reaction continues oscillating for some hours with a minimal change in period and amplitude of oscillations. But with methyl isobutyl ketone the number of oscillations is 13, the same as when there is no ketone in the reaction.

We do not know values for the enolization constant for methyl ethyl ketone, methyl propyl ketone, and methyl isobutyl ketone, but their influence in the behavior of the BZ reaction permits us to establish an idea of their magnitude. In the following section it is shown how with simulations of experimental results we can estimate the values of those constants, but experimental values are required.

The effect of the acetone's concentration in the BZ reaction is shown in Figure 2 , where it is seen that by an increase in the concentration of acetone, the induction period grows and the number of oscillations increases. Experimentally, we found that with a very high concentration of acetone the BZ reaction does not oscillate. In the following section it is shown this results from simulations from the GTF mechanism. The way in which the acetone acts in oscillating chemical reactions is well-known by the reaction $BrO_3^-{-}Ce(IV){-}H_2SO_4{-}(COOH)_2{-}CH_3COCH_3$, for which there is a detailed mechanism.[8] Field and Boyd studied the role of acetone in this reaction and demonstrated experimentally that it does not react with bromate, cerium, or any oxybrominated compound. The formed enol of acetone reacts with bromine, as in the following reactions (numbers from Field and Boyd are preserved[8]):

$$CH_3COR + H^+ \rightleftharpoons CH_2{=}CHOHR + H^+ \qquad (R20)$$

For acetone $k_{20} = 8.3 \times 10^{-5}$ M^{-1} s^{-1}, $k_{-20} = 21.3$ M^{-1} s^{-1}.

$$CH_2{=}CHOHR + Br_2 \rightarrow BrCH_2COR + Br^- + H^+ \quad (R21)$$

$k_{21} = 1.03 \times 10^7$ M^{-1} s^{-1}.

As the reaction studied by Field and Boyd is of the same family as the BZ reaction, the effect of the acetone, and in general, the methyl ketones, is well described with reactions R20 and R21,[9] through a direct participation in process A. The increase of the induction period is explained by an increase in the time that it takes to achieve the crucial concentration of bromomalonic acid, due to the kinetic competition between the enol of the malonic acid and the enol of the ketone for Br_2. The rate of formation of bromomalonic acid is not only affected by its oxidation in process C but also by the rate in which the acetone's enol reacts with molecular bromine. This can be described by the following equations (the integrals are evaluated in the induction period interval):

$$[BrCH(COOH)_2]_{crucial} = -\int_0^T (d[Br_2]/dt)\,dt - \int_0^T (d[BrCH_2COR]/dt)\,dt$$

Regarding the oscillation period, we do not expect changes in the presence of ketones because the initial concentration of malonic acid is the same for all experiments. The increase in the number of oscillations is also explained for the competition between malonic acid and the ketone for Br_2. In a general way, for each cycle of oscillation an amount of malonic acid is consumed, mainly by oxidation in process C and by bromination in process A, but with ketones the amount of malonic acid consumed by process A is less than when there is no ketone, and so, the duration of the reaction is favored.

This can be seen by comparing the BZ reaction without ketones between Figure 1a and Figure 2a: when the concentration of malonic acid is 0.0150 M, 13 oscillations occur, but when it is 0.0250 M, a larger number of oscillations happen.

4. Simulations

We made simulations[10] with all of the reduced models that are frequently used to describe the BZ reaction, adding both reactions that include ketones, but none of them reproduced oscillations under these conditions. We also used the most complete versions of the FKN mechanism, but not one of them worked accurately. Thus, it was necessary to use the most detailed mechanism for the reaction, the GTF mechanism.[11,12] Both versions of the GTF mechanism, with 42 and with 80 reaction steps reproduced the experimental results obtained for the BZ reaction in the presence of methyl ketones, with a

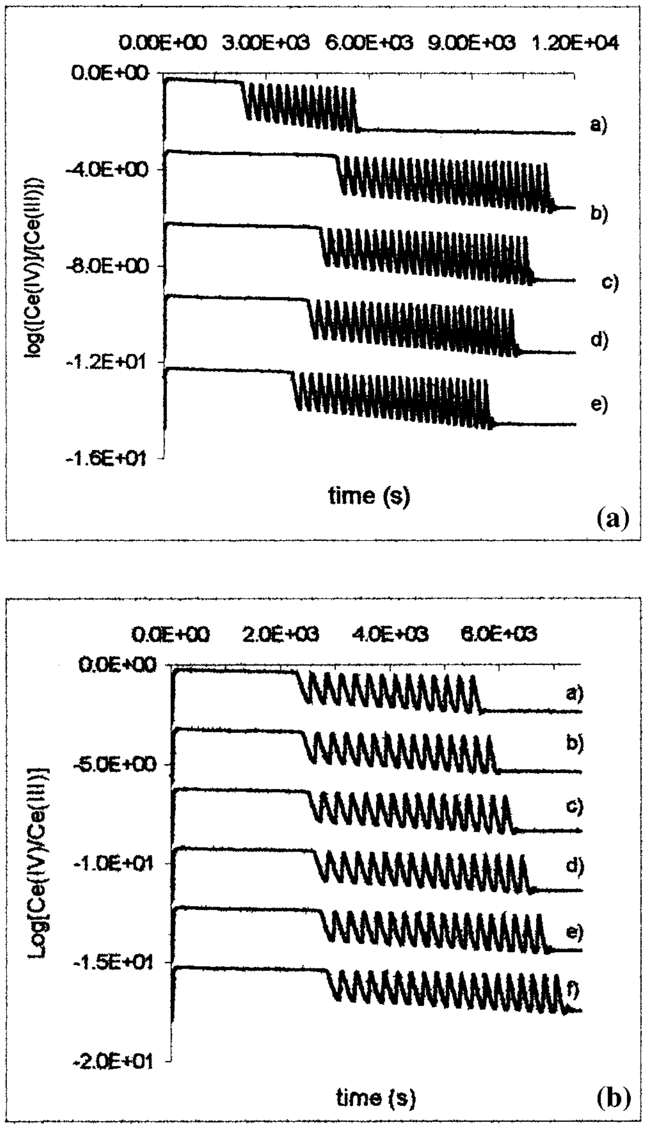

Figure 3. [a] Effect of different ketones (enolization constant) in the BZ reaction. Simulations based upon the GTF mechanism: (a) without; (b) acetone; (c) methyl ethyl ketone; (d) methyl propyl ketone; (e) methyl isobutyl ketone. [b] Effect of the concentration of acetone in the BZ reaction. Simulations based upon the GTF mechanism: (a) 0; (b) 0.01 M; (c) 0.02 M; (d) 0.03 M; (e) 0.04 M; (f) 0.05 M.

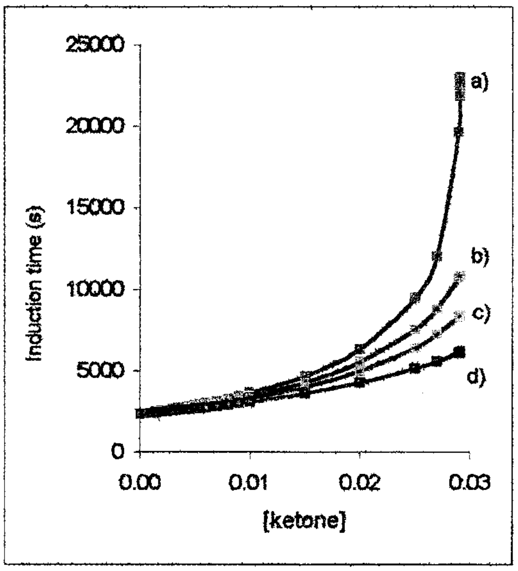

Figure 4. Correlation between the induction period and concentration of acetone: (a) acetone; (b) methyl ethyl ketone; (c) methyl propyl ketone; (d) methyl isobutyl ketone. Complete interval until oscillations are inhibited. Simulations based on the GTF mechanism.

minimal change in two constants (k_{14} changed from 7.0×10^3 to 5.0×10^3 M^{-1} s^{-1}, and k_{71}, from 1.0×10^7 to 6.0×10^5 M^{-1} s^{-1}).

From parts a and b of Figure 3, it is seen how the GTF mechanism can reproduce the experimental behaviors of Figures 1 and 2. As we do not know reported values of the enolization constant for methyl ethyl ketone, methyl propyl ketone, and methyl isobutyl ketone, they were estimated by modifying the constant for (R20), looking for a good agreement between simulations and experiments in the length of the induction period observed in the BZ reaction in the presence of each one of the ketones. The values used for the enolization constant for Figure 3a were 8.3×10^{-5} M^{-1} s^{-1} for acetone, 7.3×10^{-5} M^{-1} s^{-1} for methyl ethyl ketone, 6.5×10^{-5} M^{-1} s^{-1} for methyl propyl ketone, and 5.3×10^{-5} M^{-1} s^{-1} for methyl isobutyl ketone.

Figure 4 shows a clear correlation between the length of the induction period, especially in low concentrations of ketone where the correlation is linear. Figure 4 also shows that the behavior of the BZ reaction as a function of the concentrations of each of the methyl ketones approaches asymptotically the limit where the oscillations are inhibited, because the crucial concentration of bromomalonic acid is not reached.

These results show that the interpretation of the effect of the ketones in the BZ reaction is satisfactory.

5. Conclusions

The global dynamic of the BZ reaction can be altered by a selective kinetic control of process A with the addition of a methyl ketone. The methyl ketones consume molecular bromine, enlarging the time in which the crucial concentration of bromomalonic acid is reached and diminishing the consumption of malonic acid during each cycle of oscillations. Thus, the effect of the methyl ketones in the BZ reaction is an enlargement of the induction period and an increase in the number of oscillations. The behavior of the induction period as a function of the concentration of the ketone, or as a function of the enolization constant, is explained correctly under the hypothesis of a crucial concentration of bromomalonic acid.

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