

Effect of Trace Impurities on a Bifurcation Structure in the Belousov-Zhabotinskii Reaction and Preparation of High-Purity Malonic Acid

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We have found that impurities on the ppm level in malonic acid are sufficient to alter dramatically a sequence of bifurcations in the Belousov-Zhabotinskii (BZ) reaction. Samples of malonic acid from 15 vendors were tested, and each was found to contain one or more of the following impurities that affect the reaction dynamics: iron, paraformaldehyde, ethanol, methanol, ethyl ester, and methyl ester. We describe a straightforward procedure for purifying malonic acid. Reproducible bifurcation structures can only be observed with the highly purified malonic acid. Measurements with varying amounts of the above-mentioned impurities added to purified malonic acid show the striking effect of impurities on the dynamics of the BZ reaction.

I. Introduction

In recent years much attention has been focused on oscillating chemical reactions, and the most studied of such systems must certainly be the Belousov-Zhabotinsky (BZ) reaction¹⁻⁵ in a continuously fed stirred tank reactor (CSTR).⁶⁻¹⁶ When the input concentrations or residence time t_r (reactor volume/total flow rate) is changed, various nonequilibrium states can be observed in this reaction, and a variety of nonlinear phenomena such as multiple steady states, limit cycles, quasiperiodic and chaotic oscillations, and intermittency have been identified. Hence the BZ reaction is an excellent system for studying nonlinear dynamics in chemistry. There are several different versions of the BZ reaction that employ different organic substrates. In the studies specifically investigating the nonlinear dynamics, however, for historical and technical reasons nearly all experiments have been made with malonic acid as the organic substrate.⁶⁻¹⁶

Recent experiments in our laboratory have revealed that trace impurities in the malonic acid can substantially alter the dynamics and even the whole bifurcation structure of the BZ reaction.¹⁴ This paper examines the following questions:

- (1) What are the most important impurities affecting the dynamics, and how can commercial malonic acid samples be tested for these impurities? (See sections IIIA and IIC.)
- (2) What methods can be applied to produce high-purity malonic acid? (See section IIIB.)
- (3) What is the effect of the most common impurities on the bifurcation structure? (See section IIIC.)

II. Experimental Section

A. Materials. Potassium monomethyl malonate ($\text{KOCC-H}_2\text{COOCH}_3$) was produced from dimethyl malonate by combining the methods of Grakauskas and Guest¹⁷ and Breslow et al.¹⁸ A solution of 65 g (1.0 mol) of potassium hydroxide (Fisher reagent grade, ~87%) in 150 mL of methanol was added dropwise (in ~15 min) to a stirred solution of 132 g (1.0 mol) of dimethyl malonate (Sigma, ~99% purity) in 250 mL of methanol at room temperature. A white crystalline precipitate was formed. After another 15 min of continuous stirring, the precipitate was filtered and dried at laboratory temperature. The silky crystalline product readily dissolves in water. Yield: 126 g (~80%).

Potassium malonate ($\text{CH}_2(\text{COOK})_2$) was produced from dimethyl malonate via alkaline hydrolysis. First 130 g (2.0 mol) of potassium hydroxide (~87%) was dissolved in 50 mL of water; then 120 mL of dimethyl malonate (132 g, 1.0 mol) was added dropwise to the hot stirred solution. The temperature was kept between 60 and 80 °C with a hot plate. In this way most of the methanol produced in the hydrolysis was boiled away. At the end some droplets of unreacted ester remained on the surface of the

solution and the pH dropped to ~9. A few more KOH pellets (~5 g) were added until the ester phase disappeared and the pH had risen above 12. Then the solution was cooled to about 40 °C and 200 mL of methanol was added to it with continuous stirring. To start the crystallization, the solution was cooled further to room temperature (about 20 °C), and then 1 mL of the solution was removed and diluted with 1-2 mL of methanol; seed crystals then appeared after 1 to 2 min. The crystals formed in this way were added to the bulk, thereby starting a rapid crystallization. Yield: 196 g (~90%). The product contains water according to the formula $\text{CH}_2(\text{COOK})_2 \cdot 2\text{H}_2\text{O}$.

Barium Malonate. $\text{CH}_2(\text{COO})_2\text{Ba}$ was produced from potassium malonate. First 216 g (1.0 mol) of potassium malonate was dissolved in 2000 mL of hot water (about 70 °C) in a 4000-mL beaker. Then 316 g (1.0 mol) of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was dissolved in 1000 mL of hot water (about 70 °C) and was added to the potassium malonate solution with constant stirring. The barium malonate was filtered and washed with distilled water. So that the precipitate was washed effectively and all soluble contaminants were removed, the precipitate was mixed with 3000 mL of water and filtered again. The washing procedure was repeated three times. The barium malonate precipitate can take up a considerable amount of water; a large funnel is recommended for the filtration. The precipitate was dried at room temperature for several days.

Potassium Bromate. Reagent grade potassium bromate was recrystallized twice from water and dried at laboratory temperature for several days. During the first recrystallization the hot solution was filtered. For the filtration of this and other prepa-

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rations we always used glass fiber filter paper.

B. Methods for Purification of Malonic Acid. Recrystallization from Acetone–Chloroform Mixture. First 100 g of malonic acid was dissolved in 115 mL of acetone on a hot plate, and the hot solution was filtered and cooled to 20–25 °C in an ice bath. Then 175 mL of chloroform was added with continuous stirring and cooling. When the temperature dropped again to 20–25 °C, the crystals were filtered and dried at laboratory temperature. Yield: 85 g.

Recrystallization from Ethyl Acetate. This procedure is recommended as a second intermediate step only for malonic acid samples already purified by the acetone–chloroform method. Also, after a recrystallization from ethyl acetate, its traces have to be removed by a final recrystallization from acetone–chloroform. First 100 g of malonic acid was dissolved in 300 mL of ethyl acetate on a hot plate. Then the hot solution was filtered and cooled in an ice bath to 20–25 °C, and the resulting crystals were filtered and dried at laboratory temperature. Yield: 65 g.

Recrystallization from Acetone–Nitric Acid Mixture. This procedure is recommended as an alternative second step only after recrystallization from an acetone–chloroform mixture. Unpurified malonic acid samples may contain contaminants which can react with nitric acid. First 20 g of malonic acid was dissolved in 40 mL of concentrated HNO_3 at 40 °C. Then another 80 g of malonic acid was dissolved in 95 mL of acetone on a hot plate. Both solutions were filtered. The acetone solution was cooled to 60 °C and 10 mL of the nitric acid solution was added with continuous stirring and cooling in an ice bath. When the temperature dropped to 40 °C, another 20-mL portion of the nitric acid solution was added, and at 25 °C all the remaining amount was added. By adding NaCl to the ice bath the solution was cooled further to about –15 °C. Then the crystals were filtered and dried under the hood at laboratory temperature. Yield: 85 g.

C. Methods of Analysis. All methods described here were developed to make quick tests of the purity of untreated and recrystallized malonic acid samples. References are made to the sources where the original methods are discussed in detail.

Test for Iron.¹⁹ First 1 g of malonic acid was dissolved in 2 mL of water in a small test tube. Then 5 drops of concentrated HNO_3 and 10 drops of an NH_4SCN solution (20 g/100 cm^3) were added. The color was compared to a standard series of calibrating solutions containing 1, 2, 5, 10, and 20 μg of Fe^{3+} , respectively, and 1 g of iron-free malonic acid dissolved in 2 mL water; these calibrating solutions of 1–20 ppm of Fe^{3+} in malonic acid were treated with the same reagents as the test solution.

Test for Paraformaldehyde. First 2 g of malonic acid was dissolved in 2 mL of water in a 25-mL distilling flask equipped with a small Liebig condenser, and then the solution was evaporated to near dryness with a heat gun. (The heating was stopped when one drop of yellow material remained on the bottom of the flask. In the last stage of the distillation, acetic acid appears in the distillate as a decomposition product of the malonic acid. Also, a small fraction of malonic acid distills without decomposition.) The distillate was collected in a flask of known weight cooled in an ice bath during the distillation. At the end of the procedure the condenser was washed with some drops of water. The washing water (~0.5 mL) was united with the distillate and was weighed with the collecting flask. A 1-mL aliquot was transferred to a test tube. (A mixing of the collected distillate is necessary before removing the 1-mL sample.) Then the flask with the remaining distillate was weighed again to determine the relative amount of the 1-mL sample to the total distillate. The chromotropic acid method²⁰ was used to determine the formaldehyde content of the sample. To the 1-mL aliquot 4 mL of concentrated sulfuric acid was added with constant stirring and cooling. Then four drops of chromotropic acid reagent (a freshly prepared 2% aqueous solution of 4,5-dihydroxynaphthalene-2,7-disulfonic acid; Sigma)

was added, and the test tube was placed into a water bath at 60 °C for 10 min. The color that developed was compared to a standard series containing 5, 10, 20, and 40 μg of CH_2O , respectively, in 1 mL of water and treated in the same way as the sample.

The distillation is necessary for several reasons. First, large amounts of malonic acid interfere with the chromotropic acid reaction. Our experiments indicate that formaldehyde and malonic acid can react with each other in the sulfuric acid medium, most probably in a Knoevenagel²¹ type of reaction. Second, the distillation is necessary to produce free formaldehyde from paraformaldehyde in order to get a strong and reproducible reaction with chromotropic acid. Without distillation we were not able to detect the low level of paraformaldehyde in our samples using the chromotropic acid method. At the same time, our experiments show that no detectable traces of formaldehyde were produced due to the thermal decomposition of malonic acid. Thus the distillation is a necessary and safe method to separate the formaldehyde from malonic acid samples before making the analysis with chromotropic acid.

Test for Esters and Alcohols. First 2 g of malonic acid and 2 g of solid NaOH were weighed into a 25-mL distilling flask. The flask was equipped with a Liebig condenser attached to a collecting flask which was cooled in an ice bath. Then 2 mL of water was added to the distilling flask. The resulting acid–base reaction generates enough heat to start a boiling of the mixture. The boiling was maintained with a heat gun. After 1.0–1.2 mL of distillate was collected, the collected liquid was washed into a 2-mL volumetric flask, and the flask was filled with distilled water. To a 1-mL aliquot of that sample in a test tube was added 1 mL of concentrated sulfuric acid and 5 drops of $\text{K}_2\text{Cr}_2\text{O}_7$ solution (100 mg of $\text{K}_2\text{Cr}_2\text{O}_7$ in 10 mL of concentrated sulfuric acid). The solutions were mixed and the test tube was kept at about 60 °C for 5 min before cooling it to room temperature. The developed color was compared to a standard series that contained 0, 5, 100, and 200 mg of ethanol or methanol, respectively, in 1 mL of water and had been treated with sulfuric acid and potassium bichromate in the same way as the sample.

If the presence of an alcohol was indicated by a green or blue color, then the remaining half of the sample was used for a qualitative test²² to decide whether the alcohol present was methanol or ethanol. Then 5 drops of 5% KMnO_4 solution and 3 drops of 5% phosphoric acid solution were added to a 1-mL sample. After a 10-min waiting period the permanganate was reduced with 2 drops of saturated NaHSO_3 solution and the sample was tested for formaldehyde with the chromotropic acid method as before. If the alcohol in question is methanol, the formaldehyde test is positive. Otherwise, the alcohol is most probably ethanol since in industry only the methyl and ethyl esters are used to produce malonic acid.

Remarks: Naturally other volatile organic materials beside alcohols can give a reaction with the acidic chromate. For example, if malonic acid were distilled without NaOH, some of it could sublime to the distillate and react with the chromate. Therefore, the distillation was performed in the presence of NaOH to avoid an interference due to malonic acid and paraformaldehyde. At the same time any ester present will hydrolyze quickly in the alkaline medium to give a free alcohol. Acetone, however, produces an interference, reacting slowly with acidic chromate; thus samples already recrystallized from acetone always give a positive test result. The same is true for samples recrystallized from ethyl acetate; here ethanol coming from the hydrolysis of the contaminating ethyl acetate produces the interference.

D. Apparatus. We used the experimental setup already described by Coffmann et al.¹⁴ The only difference was that we applied a calomel reference electrode connected to the reactor via a “salt bridge” filled with 0.2 M H_2SO_4 . The feedstream con-

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centrations were as follows: (A) $[\text{Ce}^{3+}] = 2.5 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.3 \text{ M}$; (B) $[\text{KBrO}_3] = 0.3 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.3 \text{ M}$; (C) $[\text{CH}_2(\text{COOH})_2] = 0.75 \text{ M}$. Solutions A, B, and C were always pumped into the reactor at equal rates; thus without reaction the reactor concentrations would have had the following values: $[\text{Ce}^{3+}]_0 = 8.33 \times 10^{-4} \text{ M}$, $[\text{BrO}_3^-]_0 = 0.1 \text{ M}$, $[\text{CH}_2(\text{COOH})_2]_0 = 0.25 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$. In some experiments, solution C instead of solution B contained the sulfuric acid (with the same concentration, $[\text{H}_2\text{SO}_4] = 0.3 \text{ M}$). With purified chemicals the experimental results were the same, independently of whether the sulfuric acid was in solution B or C. The solutions were freshly prepared every 3–4 days and were filtered through a membrane filter (Millipore Cellulose Nitrate, pore size: $0.45 \mu\text{m}$). The temperature was $28.0 \pm 0.1^\circ\text{C}$.

III. Results and Discussion

A. Identification and Source of the Impurities Affecting the Dynamics. Commercial malonic acid is produced from its ethyl or methyl ester or from cyanoacetic acid via hydrolysis in aqueous sulfuric acid solutions.^{23,24} In the first case the esters (especially monoesters) and methyl or ethyl alcohol can be expected as trace organic impurities. The esters are purified by distillation in industry. Therefore, the occurrence of other organic impurities coming from the previous steps of the synthesis is less likely when an ester is used as a starting material than when the malonic acid is produced from cyanoacetic acid directly.²⁴

In some samples we could detect paraformaldehyde, which is a characteristic impurity of the acetic acid when it is produced from acetaldehyde.²⁵ Since we were not able to get information from our vendors about the way in which the different commercial malonic acid samples were produced, we cannot be absolutely sure that the paraformaldehyde contamination is a signature of the cyanoacetic acid hydrolysis process. Nonetheless, it is worthwhile remarking that we found no samples that contained both alcohols and paraformaldehyde simultaneously. If an alcohol was present, we could not detect any formaldehyde, and vice versa.

Significant levels of iron were found in 14 of the 15 samples we tested. The iron probably comes from adsorbents (especially activated charcoal) used in removing colored byproducts after hydrolysis. [Colored byproducts are formed during the high temperature ($\sim 70^\circ\text{C}$) industrial hydrolysis process, which can take several days.²³] Malonic acid is easily contaminated with iron since it can form a complex with it.²⁶ Most of the 15 malonic acid samples we tested contained 3–15 ppm of iron, but some contained 30–50 ppm; only one contained less than 1 ppm. When paraformaldehyde was present, its concentration was 30–50 ppm. The concentration of alcohols (and esters—our analytical procedure cannot distinguish between the ester and the free alcohol; see section IIC) and other organic impurities that could be oxidized with acidic chromate was in the range 100–500 ppm.

We could not find any commercial malonic acid sample which was free of all of the three characteristic impurities (iron, paraformaldehyde, alcohols). Moreover, most of the samples also contained insoluble impurities such as activated charcoal and calcium or barium sulfate, which are precipitates formed when the hydrolyzing sulfuric acid is removed from the product during the industrial procedure.

We conclude this discussion of impurities by emphasizing that, in spite of the presence of various impurities, our samples were relatively pure by the standards of organic research chemicals. Acid–base titrations showed that all samples contained 99.7% or more malonic acid.

B. Production of Pure Malonic Acid and Tests of Purity. As we will show in the following section, the bifurcation structure of the BZ reaction is extremely sensitive to some of the trace contaminants that are present in commercially available malonic

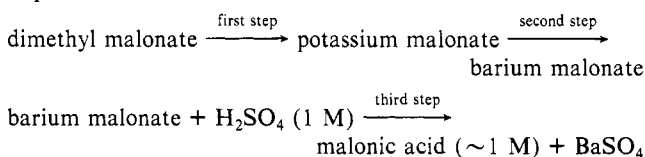
acid; hence it is important to develop a procedure for producing malonic acid that is sufficiently pure so that the remaining impurities have no measurable effect on the dynamics of the system. A classical method of purification is recrystallization. Unfortunately, water is not an appropriate medium for recrystallization because malonic acid is highly soluble in that solvent. However, we have found that ethyl acetate and two different solvent systems (the acetone–chloroform and acetone–nitric acid systems) are suitable. Details of the recrystallization procedures were given in section IIB.

A problem with the recrystallization methods is that trace amounts of the solvent itself or even its contaminants can play the role of a new contaminant. We examined this possibility by adding the above-mentioned solvents to the BZ reaction to observe their effects. Acetone, chloroform, and nitric acid produced no measurable change in the bifurcation structure, even when applied in concentrations corresponding to contamination levels of several thousand ppm w/w in the malonic acid. Ethyl acetate, however, had an effect; the active ingredient was probably not the ester itself but, instead, its decomposition product, ethanol.

Repeated recrystallizations from either the acetone–chloroform or the acetone–nitric acid systems yielded malonic acid samples producing identical bifurcation structures in the BZ reaction. This usually occurred after two or three recrystallizations, but sometimes four and even five recrystallizations were required if the original sample was badly contaminated. Further recrystallizations were without any measurable effect. Thus it seemed reasonable to assume that both the acetone–chloroform and the acetone–nitric acid methods gave a pure product, at least after four or five consecutive recrystallizations. In contrast, the samples recrystallized from ethyl acetate gave different and scattered results even after as many as seven recrystallizations.

By combining the acetone–chloroform and acetone–nitric acid purification methods, we found that only three recrystallizations were needed to obtain reproducible bifurcation sequences from even the most contaminated commercial malonic acid. The two methods were combined in the following order: first step, acetone–chloroform; second step, acetone–nitric acid; third step, acetone–chloroform. The acetone–chloroform method removes mainly the organic contaminants, while the acetone–nitric acid method is most effective in removing traces of iron.

While it was reasonable to assume that the acetone–chloroform and the acetone–nitric acid methods (or their combination) gave a pure product, we could not be absolutely sure. Since both methods started by dissolving large amounts of malonic acid in acetone at an elevated temperature, there was a slight chance that the end product would contain some reproducible contamination due somehow to the acetone or due to some minute organic reaction during the whole procedure. To eliminate any doubts, we produced malonic acid in an entirely different way by the following sequence:



The first two steps are described in section IIA. In the third step an excess of barium malonate was stirred with 1 M sulfuric acid for 15 min, and then the solution was filtered. The filtrate contained some dissolved barium malonate, so 1 M H_2SO_4 was added dropwise and the solution was filtered again. This was repeated several times until 1 drop of 1 M H_2SO_4 gave no more BaSO_4 precipitate. Then an aliquot of the malonic acid solution was titrated with NaOH to determine its concentration precisely. Finally, the malonic acid solution was diluted to 0.75 M and was used in the BZ experiment.

The malonic acid prepared in this way gave the same bifurcation structure as the samples purified with the acetone–chloroform or the acetone–nitric acid methods. It is important to note that in this preparation we started from a different chemical substance—the methyl ester—which has a spectrum of contam-

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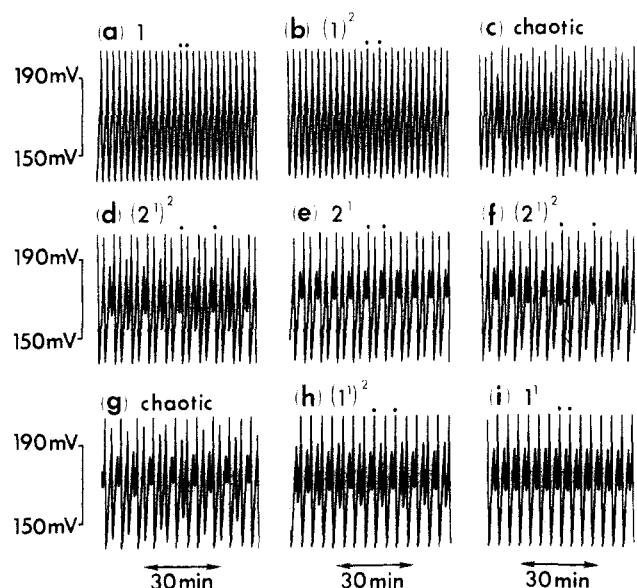


Figure 1. Time series for the bromide electrode potential (with respect to a calomel electrode) observed for some of the states in a bifurcation sequence in the BZ reaction with purified malonic acid. For the periodic states the duration of a single period is the time between the dots above the time series. The values of the residence time t_r for the different states are shown on the abscissa in Figure 2a. The notation $(L^S)^R$, as in ref 29, indicates the number L (S) of large (small) amplitude oscillations per period and the number of times R that the L^S motif repeats in each period with only small variations in the amplitudes. Thus, for example, the $(2^1)^2$ state in Figure 1f has in each period six oscillations, which occur in the following order: two large, one small, two large, one small; this is a period-doubled period-3 state—the waveforms for successive period-3 motifs are slightly different, as can be seen from the figure.

inants different from that of the malonic acid. (For example, we could not detect any iron impurity in the commercial ester.) Also, in this method we used no acetone and no elevated temperature. In spite of all these differences, the result was the same, proving that at least insofar as the BZ bifurcation structure is concerned, the acetone–chloroform and the acetone–nitric acid methods produce pure malonic acid.

Recommendations: If the commercial malonic acid contains less than 1 ppm iron, then one or two recrystallizations from acetone–chloroform gives a sufficiently pure product. On the other hand, if there is a considerable amount of iron (more than 5 ppm) in the sample, then the following sequence of recrystallization steps is recommended: (1) from acetone–chloroform, (2) from ethyl acetate, and (3) from acetone–chloroform again. (Although acetone–nitric acid can be used for the second step, it is more convenient to remove the iron with ethyl acetate rather than the acetone–nitric acid mixture, and the ethyl acetate residue is eliminated in the third step.) In the first two steps filtration is necessary (using warm funnels prewetted with the pure solvent to avoid any clogging of the filter), but in the third step it can be omitted. In the second step it is recommended that the wet crystals be washed with chloroform to reduce the ethyl acetate contamination before the final recrystallization.

The overall yield can be increased by evaporating the used acetone–chloroform mixtures under a hood. The residual malonic acid crystals can be used again as a raw material. Also, the ethyl acetate solution, saturated with malonic acid at room temperature after the recrystallization, can be reused several times; in this way most of the loss due to the second step can be avoided. Following these procedures, we achieved an overall yield of about 80% in the three-step recrystallization process. (The yield is limited by the decomposition of malonic acid into acetic acid at high temperatures.) After four or five recrystallizations some iron accumulates in the ethyl acetate. The ethyl acetate can then be discarded or it can be purified by first shaking with a small amount of water (2 mL/1000 mL), then mixing and shaking it with water-free CaSO_4 (50 g/1000 mL), and subsequently filtering it.

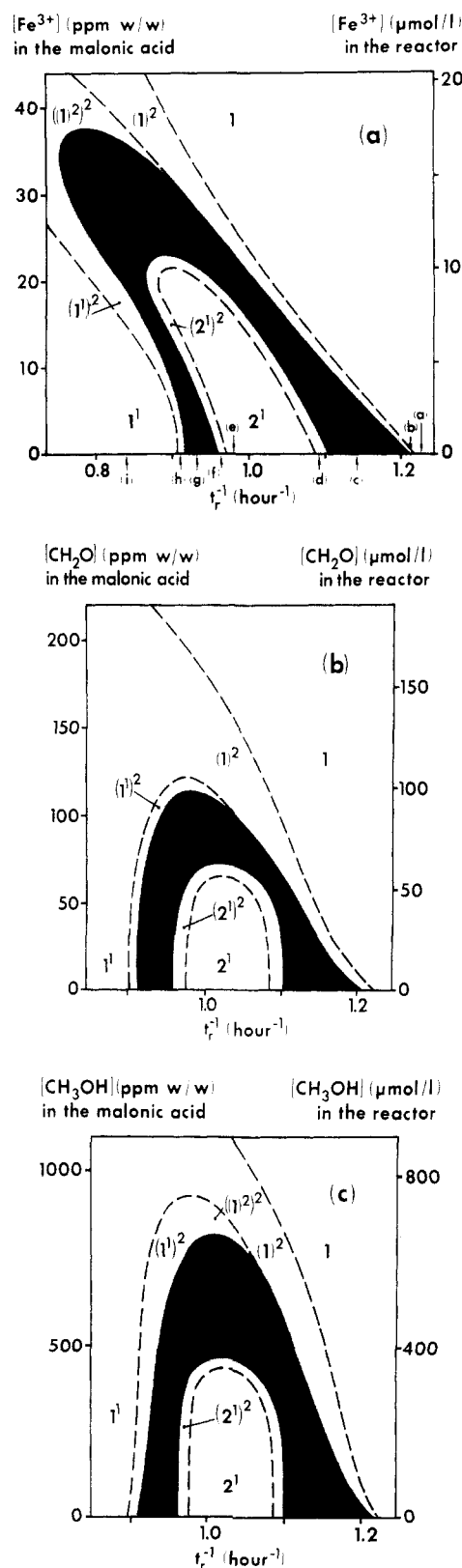
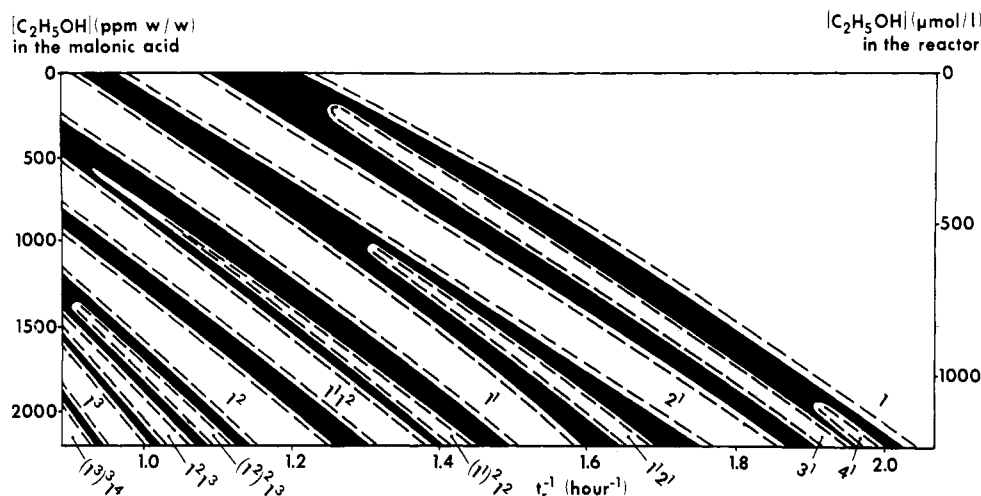


Figure 2. The effect of (a) iron, (b) formaldehyde, and (c) methanol on a bifurcation sequence in the BZ reaction. The figure should be viewed as schematic since the measurements were made with a fairly coarse mesh in concentration (steps of 20–30%) and t_r (steps of 2–5%). Only a few of the many periodic states are explicitly indicated; the notation is described in the caption for Figure 1. The white areas correspond to periodic states, while the black areas contain both chaotic and narrow periodic states; see text. Dashed lines mark the beginning of period doubling sequences. The letters a–i on the abscissa in (a) correspond to the time series in Figure 1. (The feed concentrations are given in section IID.)



indicate that methanol reacts with acidic bromate to form HBrO_2 and then BrO_2 . Thus the effect of methanol can probably also be explained by a reaction which is a source of the autocatalytic intermediate.

Monomethyl Malonate. To study the effect of ester impurities we used small amounts of the potassium salt of the monomethyl ester. (In the acidic medium the free acid was formed.) We used the monoester because any ester contamination is probably present in this form, and also the monoester readily dissolves in water, while this is not true for the dimethyl malonate. Surprisingly, even relatively high concentrations of the monoester produced no observable effect on the dynamics of the BZ reaction. Even with a methanol content of the contaminating ester equivalent to several thousand ppm of methanol in the malonic acid, we could not see any measurable change in the bifurcation structure. It is known^{34,35} that the esters of malonic acid hydrolyze rather slowly in acidic medium; nevertheless, we found it surprising that the ester is able to survive the harsh chemical environment of the BZ reaction without any reaction or any significant release of methanol.

Naturally, if a contaminated sample were used to prepare stock solutions which contain sulfuric acid as well, then the slow hydrolysis of the monoester would cause a shift in the bifurcation structure due to the appearance of methanol. To avoid such effects, in most of our experiments no sulfuric acid was added to the malonic acid stock solution.

Ethanol. The effect of all the impurities we have discussed thus far is to suppress the complex dynamics. In marked contrast, ethanol *increases* the region of complex behavior, as can be seen in Figure 3. Our convention in graphing the effect of impurities on the bifurcation structure is that the complexity decreases in the upward direction and increases in the downward direction; therefore, in Figure 3 the impurity concentration increases in the downward direction, while in Figure 2 the impurity concentration increases in the upward direction.

With increasing ethanol concentration several new states appear, including, for example, the 3^1 state (with three large oscillations and one small oscillation per period) and the 4^1 state (with four large oscillations and one small oscillation per period). In addition, daughter states of the form $L_1^{S1}L_2^{S2}$ are found between parent states L_1^{S1} and L_2^{S2} . For example, in Figure 3 the 1^11^2 state lies between the 1^1 and 1^2 states. When the ethanol concentration

is increased from zero, the chaotic sea between states 1^1 and 2^1 broadens, and then the new state 1^12^1 appears as a peninsula that parts that chaotic sea. Daughter states of the type 1^12^1 and even much more complex daughter states were studied by Maselko and Swinney,²⁹ but in their experiments there was no observable chaos between the periodic states.

It is surprising that analogous compounds like methanol and ethanol can have opposite effects. Perhaps both alcohols can react with acidic bromate and with bromous acid as well, but with different rates. Thus, the net effect of reactions with methanol could be the *production* of bromous acid, while the net effect of reactions with ethanol could be the *consumption* of bromous acid. Experiments are under way to test this hypothesis.

IV. Conclusions

Commercial malonic acid samples contain contaminants that can markedly change the bifurcation structure of the BZ reaction, as Figures 2 and 3 illustrate. In addition to the periodic states explicitly indicated in these figures, in the "chaotic" (black) regions there is an infinite number of periodic states that have large numbers of oscillations per period. The range in t , over which these states are stable decreases exponentially fast with increasing period; therefore, only those states with a fairly small number of oscillations per period are observable.^{14,28}

Iron and paraformaldehyde are particularly effective in changing the bifurcation structure at low concentrations. On the other hand, most impurities (e.g., calcium, monoesters, acetone, chloroform) on the ppm level have no measurable effect on the dynamics.

We conclude that commercial malonic acid samples should be purified prior to studies of instabilities and complex dynamics. A straightforward three-step purification process was described in section IIIB.

The high sensitivity of the dynamics of the BZ reaction to certain reagents suggests that the bifurcation structure itself could provide a useful test of proposed mechanisms of the reaction. Such experiments are in progress in our laboratory.

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Registry No. BrO_3^- , 15541-45-4; Ce, 7440-45-1; Fe, 7439-89-6; CH_2O , 50-00-0; CH_3OH , 67-56-1; $\text{C}_2\text{H}_5\text{OH}$, 64-17-5; malonic acid, 141-82-2.

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