Bubble-Free Belousov–Zhabotinskii-Type Reactions

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Several single and double substrate bubble-free Belousov–Zhabotinskii-type systems are studied and found to produce CO_2, even though no macroscopic gas formation is observed. The double substrate systems are found to produce the least CO_2 and no precipitate for the concentrations studied. For comparison, the CO_2 production from a malonic acid–bromate–ferroin system is also presented and the result indicates that, besides CO_2, CO plays a major role in the bubble formation in this system.

I. Introduction

Oscillatory chemical systems have been of interest for about two decades.[1] The most extensively studied system is the Belousov–Zhabotinskii (BZ) reaction, which involves the oxidation of an organic acid (usually malonic acid (MA)) by acid bromate in the presence of a metal ion catalyst (usually Ce(III), Mn(II), or ferroin).[2] The reaction is usually studied in a batch (closed) reactor or in a continuous flow (open) stirred tank reactor (CSTR). In a well-stirred reactor (either in batch or CSTR), spatial structures cannot exist, and only temporal structures can be observed. Temporal structures, such as simple and complex oscillations, bistability, and chaos, have been well studied.[3] In unstirred conditions, spatial patterns like target waves[4] and spiral waves[5] can be observed in some BZ systems. This formation of spatial patterns is of great current interest. However, in most variants of the BZ reaction used in these studies, a significant amount of gas evolution occurs, which results in the formation of bubbles. The bubbles can cause problems for delicate experiments in a CSTR involving the study of temporal structures such as chaotic oscillations. The bubbles also interfere with the spatial pattern formation. Hence, it is important to find oscillating chemical systems that are free of bubbles.

Malonic acid is the most common substrate used in studies of the BZ reaction, but unfortunately the gas evolved in this system produces macroscopic bubbles.[6] Recently two BZ-type systems that use acetylacetone (AA)[7] and ethyl acetoacetate (EAA)[8] as organic substrates have been reported as bubble-free. However, these systems produce precipitates for certain reagent concentratons; thus they can only be used in a restricted parameter region for both temporal and spatial studies.

The substrate in the malonic BZ system plays a dual role in the chemical reaction: the reduction of the metal ion catalyst and the removal of bromine. It is of interest to separate these roles by either chemical or physical means. It has been reported that oscillations were observed in some otherwise nonoscillating systems when an inert gas stream, e.g., nitrogen gas, was used to remove the bromine produced during the reaction.[9-11] The reducing substrates used in these reactions were oxalic acid,[9] hypophosphite,[10] and saccharides.[11] The requirement of a gas stream of course defeats the purpose of finding bubble-free systems; however, a chemical removal of Br_2 by acetone is also possible, as demonstrated by Noszticzius[12] in the oxalic acid–acetone system. Rastogi et al.[13] also found numerous new systems by applying acetone as a bromine-removing cosubstrate.

Our method of creating new bubble-free systems was based on the above-mentioned work. We combined the most promising substrates studied by Adamčiková and Ševčik,[10,11] [glucose, arabinose, and hypophosphite ($H_2PO_2^-$)] with acetone as a Br_2

scavenger, and we have compared these systems to the ones with the MA, AA, and EAA substrates. (Although Stroot and Janjic[14] have reported oscillations in an acetone–bromate–manganese system in a highly acidic medium, we could not obtain oscillations for our acid concentrations for the above-mentioned systems when acetone was the only substrate.)

The bubbles evolved in the usual BZ-type reactions, especially the MA substrate BZ system used for spatial pattern studies, contain mainly carbon dioxide.[6] Although no macroscopic gas evolution was observed for our new systems, it is of interest to find out the amount of gas, especially CO_2, produced during the reaction. Thus we measured the CO_2 generated for each of these reactions. Surprisingly, all systems examined produced CO_2, although the amount in some cases was small, not enough to saturate the solution. These results were unexpected for the AA and EAA systems because they have been reported to be free of CO_2.[6] For comparison, we also measured the CO_2 production by a malonic acid BZ system and found that the amount of CO_2 produced was indeed substantially higher than for the bubble-free systems. It was found that the MA–ferroin system, usually used in spatial pattern studies, produced an amount of CO_2 that could only saturate the solution for times much longer than the time of the first appearance of bubbles. This suggests that other gases, most likely carbon monoxide, may play an important role in bubble formation in such BZ systems.

In the next section we will describe the different bubble-free

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TABLE I: Concentrations in M for Oscillations for Bubble-Free BZ Systems

substrates	a	b	NaBrO₃	catalysts	H₂SO₄	k_0, min⁻¹
(a) ethylacetoacetate (EAA)	0.010–0.050		0.030	(ferroin) 0.0002 (Ce(III)) 0.0006	1.0	0.03–0.6
(a) acetylacetone (AA)	0.013–0.018		0.042	(ferroin) 0.0006 (Ce(III)) 0.0003	1.0	0.06–0.2
(a) arabinose–(b) acetone	0.008–0.120	0.008	0.010	(Mn (II)) 0.001	1.0	0.004–0.02
(a) glucose–(b) acetone	0.050	0.008–0.055	0.010	(Mn(II)) 0.001	1.0	a
(a) NaH₂PO₂–(b) acetone	0.015–0.075	0.079	0.010	(Mn(II)) 0.01	2.0	a

*Not applicable.

BZ systems and the detailed measurements of the CO_2 production of these BZ systems. Section III gives the results of CO_2 production for the system studied, and section IV discusses our results.

II. Experimental Section

a. Systems. The experiments were carried out either in batch or in CSTR reactors, and for some cases in both batch and CSTR reactors. The experiments were performed at room temperature (about 25 °C), except for the AA system which was studied in a regulated water bath (29.0 °C). The volume of the reactor for the EAA and for the glucose–acetone systems was 30 mL, while it was 20 mL for the others. Table I shows some typical regions of reagent concentrations for oscillations in a CSTR reactor for the AA, EAA, and arabinose–acetone systems, and in a batch reactor for the glucose–acetone and $H_2PO_2^-$–acetone systems. We will discuss our results based mostly on these concentrations, although we found oscillations for other reagent concentrations. A complete discussion on all concentrations giving oscillations would be beyond the scope of this study.

The EAA system, first reported by Salter and Sheppard,[8a] showed oscillations with either Ce(III) or Mn(II) as catalyst. Here we used double catalyst of Ce(III) and ferroin, the latter for visualization. No oscillation was observed for a sulfuric acid concentration smaller than about 1 M. For acid concentrations of 1–2 M, simple oscillations were observed for normalized flow rate k_0 (total flow rate/volume of reactor) in the range 0.03–0.6 min⁻¹ with concentrations of EAA in the range 0.003–0.05 M and bromate in the range 0.003–0.08 M. Changing the concentrations of Ce(III) or ferroin did not change the oscillations very much. We observed oily drops in the solution at low flow rates, just as was reported by Heilweil et al.,[15] but such oily drops disappeared at high flow rates. The oily drops make the system unsuitable for both temporal studies (at low flow rates) and spatial studies, even though no bubbles were observed at any of the concentrations tested.

The AA system was first studied by Bowers et al.,[7] who observed oscillations using Mn(II) as catalyst. Using a double catalyst of Ce(III) anf ferroin as in the AA system, we observed complex oscillations for AA concentrations smaller than 0.03 M. For AA concentrations greater than 0.03 M, a precipitate was observed, as was reported by Crowley and Field.[16] When Mn(II) was used as the only catalyst a large region of birhythmicity[17] was observed between large-amplitude and small-amplitude oscillations, as shown in Figure 1. In this system precipitate was also observed for concentrations of Mn(II) greater than 0.03 M. Even though no bubbles were observed, the precipitates limit the usefulness of the AA system, like the EAA system.

The arabinose–acetone and glucose–acetone systems are very similar. For the concentration ranges studied, oscillations were observed only when Mn(II) was used as catalyst with acid concentrations greater than 1 M; no oscillations were observed with Ce(III) or ferroin. Adding small amounts of ferroin inhibited the oscillation for the glucose–acetone system in the concentration ranges studied, while oscillations were still observed for the arabinose–acetone systems, but in more restricted ranges. In a batch
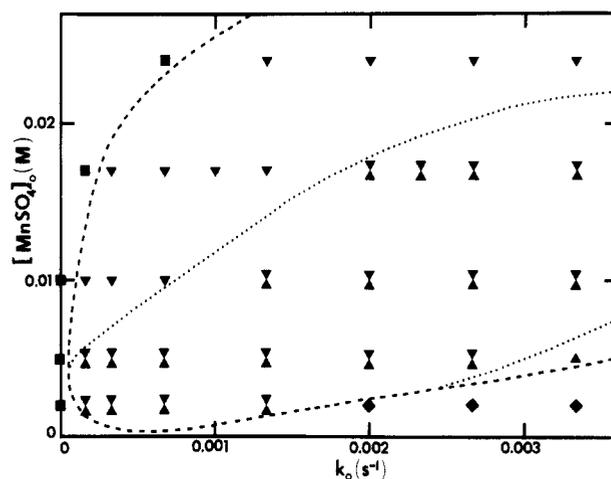

Figure 1. Phase diagram showing regions of oscillations of the BZ system with the substrate AA as a function of the concentration of $MnSO_4$ and normalized flow rate k_0 (total flow rate/reactor volume), for fixed concentrations of $[NaBrO_3]_0$, 0.07 M; $[AA]_0$, 0.02 M; and $[H_2SO_4]_0$, 1.5 M. The symbols are (■) oxidized steady state, (♦) reduced steady state, (▲) small-amplitude oscillatory state, (▼) large-amplitude oscillatory state, and (✗) hysteretic region for states with small- and large-amplitude oscillations. The dotted and dashed lines are guides to the eye for the different regions.
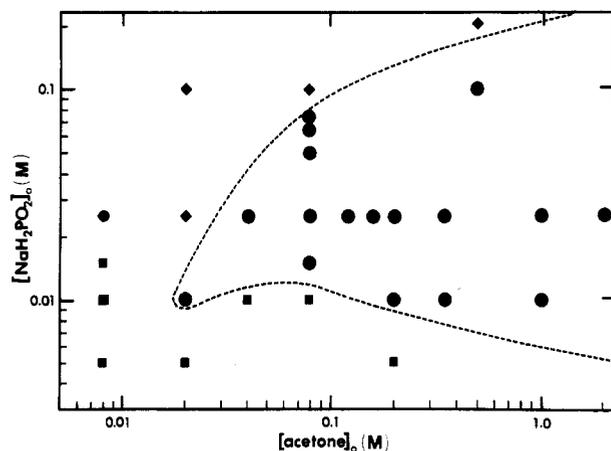

Figure 2. Phase diagram in the $[NaH_2PO_2]_0$–$[acetone]_0$ plane for the $H_2PO_2^-$–acetone system in a batch reactor. Other concentrations are fixed: $[NaBrO_3]_0 = 0.01$ M, $[MnSO_4]_0 = 0.01$ M, and $[H_2SO_4]_0 = 2.0$ M. The symbols indicate the oxidized state (■), the reduced state (♦), and the oscillatory state (●). The dashed line is a guide to the eye to separate oscillatory and steady states.

reactor, 50–100 simple oscillations were observed for these saccharide systems before a steady state was reached. No precipitate or bubbles were observed at any of the reagent concentrations tested. The drawback of these systems is that there is no color change: the reaction is colorless during the oscillations, which limits its usefulness for studies of spatial patterns.

The $H_2PO_2^-$–acetone system, formulated in the same way as the arabinose and glucose systems discussed in the previous section, also oscillated only with Mn(II) as catalyst. Oscillations were also observed with Mn(II) and ferroin as a double catalyst for

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some concentrations far from those shown in Table I. In a batch reactor the concentration of H_2SO_4 had to be greater than 1.5 M in order to get oscillations. The periods of oscillations were usually very long, typically 10 min, as compared to about 1 min for all the other systems we discuss. The color oscillated from colorless to light pink for the system using Mn(II) and from blue to violet for the system using Mn(II)–ferroin. Figure 2 shows a phase diagram of $H_2PO_2^-$ and acetone concentrations for oscillations in a batch reactor when Mn(II) was used as the only catalyst. Spatial patterns were observed in a Petri dish for the double catalyst [Mn(II)–ferroin] system. In a CSTR the period increased from 10 min to the order of hours as the system changed from an oscillatory state to a steady state as the flow rate was varied. Excitability was also observed in the steady state. More detailed studies are underway and will be reported elsewhere. As in the saccharide systems, no precipitates or bubbles were observed at any concentration tested.

b. Carbon Dioxide Measurements. All the reactions discussed in the previous section are bubble-free. The saccharide–acetone and the $H_2PO_2^-$–acetone systems are better candidates for temporal and spatial studies because they are also free of precipitates. Even though there were no bubbles in these reactions, it is of interest to study the amount of gas, particularly CO_2, evolved during the reactions.

We have used a simple method to determine semiquantitatively the amount of CO_2 generated by each reaction in a batch reactor. The apparatus consisted of three test tubes connected in series to form a "closed" system. All reagents of each BZ system, except the catalyst, were introduced into the first test tube. The catalyst for the reaction could be added separately to the solution by a syringe attached at the test tube. A stream of N_2 gas was allowed to bubble through the solution by using a fritted-glass gas dispersion tube to carry away the gases generated in the reaction. The N_2 stream was then directed to the middle test tube which contained a filter paper wetted with high concentrations of MA and H_2SO_4, so that any Br_2 gas carried by the N_2 stream could be removed. The Br_2-free N_2 stream was then directed to the last test tube which contained a titration solution for CO_2. The titration test tube contained 5 drops of 1 mg/mL of phenolphthalein in ethanol added to 6 mL of water. Barium hydroxide stored in a syringe attached to the test tube could be added to the titration solution to produce a pink color. Another gas dispersion tube was used for bubbling the N_2 gas stream through the titration solution. The pink color would gradually fade away as the $Ba(OH)_2$ was consumed by reacting with the CO_2 to form a precipitate. More $Ba(OH)_2$ was added to the titration solution whenever its color changed to that of a reference solution containing the same titration solution to which one drop of 0.05 M $Ba(OH)_2$ was added to give a light pink color.

The experiment was carried out first by introducing the reagents of the BZ system, without the catalyst, into the reacting test tube. Then the whole system was flushed with N_2 gas to remove any residual gases left from preparation. The titration solution was then adjusted to have the same color as that of the reference solution by adding a suitable amount of 0.05 M $Ba(OH)_2$ stored in a syringe attached to the titration test tube. When there was no further change in the color of the titration solution, the catalyst for the BZ reaction was introduced to the reacting solution through another syringe attached to the reacting test tube. At the same time, a known amount of $Ba(OH)_2$ was added to the titration test tube. In doing so, the color of the titration solution changed to bright pink as compared to the light pink color of the reference solution. The time when the catalyst was introduced was noted as the starting time for the reaction. As CO_2 was produced and absorbed by the titration solution, the color of the titration solution started to fade away. The time required for the color to reach that of the reference was recorded and a known amount of $Ba(OH)_2$ was added to recover the bright pink color. This process was continued until enough measurements were taken. As a result, a time series of the total $Ba(OH)_2$ consumed was obtained.

In order to relate the consumption of $Ba(OH)_2$ to the CO_2 production, we calibrated the CO_2 absorption coefficient of the

TABLE II: CO_2 Production of Different BZ Systems[g]

substrates	max CO_2 prodn rate, μmol/(mL min)	total CO_2 prod, μmol/mL	saturn time, h
MA[a]	0.87		0.65
AA[b]	0.11		5.1
EAA[c]	0.094		6.0
glucose–acetone[d]	0.017	4.0	33
arabinose–acetone[e]	0.010	2.45	56
NaH_2PO_2–acetone[f]	0.002	0.25	280

[a] MA = 0.1 M, $NaBrO_3$ = 0.3 M, NaBr = 0.06 M, ferroin = 0.0015 M, H_2SO_4 = 0.3 M. [b] AA = 0.015 M, $NaBrO_3$ = 0.042 M, Ce(III) = 0.00042 M, ferroin = 0.0006 M, H_2SO_4 = 1.0 M. [c] EAA = 0.02 M, $NaBrO_3$ = 0.42 M, Ce(III) = 0.0006 M, ferroin = 0.0002 M, H_2SO_4 = 1.0 M. [d] glucose = 0.05 M, acetone = 0.024 M, $NaBrO_3$ = 0.01 M, Mn(II) = 0.001 M, H_2SO_4 = 1.0 M. [e] arabinose = 0.05 M, acetone = 0.024 M, $NaBrO_3$ = 0.01 M, Mn(II) = 0.001 M, H_2SO_4 = 1.0 M. [f] NaH_2PO_2 = 0.025 M, acetone = 0.35 M, $NaBrO_3$ = 0.01 M, Mn(II) = 0.01 M, H_2SO_4 = 2.0 M. [g] The saturation time was calculated by using the maximum CO_2 production rate.

whole system. The calibration was carried out by replacing the BZ solution with 2 M H_2SO_4 and the catalyst in the syringe by 0.1 M sodium bicarbonate ($NaHCO_3$). By adding a known amount of $NaHCO_3$ into the H_2SO_4 solution, a definite amount of CO_2 was liberated. The same procedure described before was employed to measure the CO_2 generated and from which the total amount of CO_2 absorbed in the titration solution was calculated, thus yielding the absorption coefficient. It was found that the absorption coefficient varied slightly with the N_2 flow rate, increasing from 75% at a N_2 flow rate of 30 mL/min to 90% at a N_2 flow rate of 5 mL/min. There was no significant change in the absorption coefficient measured before and after the measurements of the CO_2 generated by the BZ reactions. An average absorption coefficient value of 0.8 was used for all measurements because the typical N_2 flow rate used in the measurements was 10 to 15 mL/min. The experiment was conducted at room temperature (25 °C) and the N_2 flow rate was controlled manually. The total volume of the BZ solution was typically about 30 mL.

Measurements of CO_2 were performed for the different BZ systems described in the previous section as well as for the MA based BZ system with different catalysts. For the double-substrate systems, the total CO_2 liberated was measured because CO_2 production was small. But for the other systems, the amount of CO_2 generated was beyond the capacity of our apparatus, and hence only the rate of CO_2 production was measured. Furthermore, only the maximum rate was used for comparison. The effect of the N_2 stream on the reaction rate (hence the CO_2 production rate) was found to be small and could be neglected. Thus, the CO_2 production rate measured by using this method could be considered to be that of the reaction without the N_2 stream.

III. Results

Results for the CO_2 production by the double-substrate BZ systems are shown in Figure 3. It is clear that these systems do produce CO_2, although the amount is small. The total amount (obtained by using data taken overnight but not shown in Figure 3) and the maximum rate of CO_2 production are given in Table II for the different reactions. The CO_2 produced in the $H_2PO_2^-$–acetone system came from the oxidation of the acetone, while for the arabinose– and glucose–acetone systems, both arabinose and glucose are primarily responsible for the CO_2 production because of the low acetone concentrations used in these reactions as compared to that used in the $H_2PO_2^-$–acetone system. We estimated the saturation condition from the Bunsen absorption coefficient[18] for CO_2, and for our work we found saturation to occur at a concentration of 0.76 mL of CO_2 at STP in 1 mL of solution. Thus it is clear that the solution will not be saturated. Furthermore, even if the maximum rate of CO_2 production were
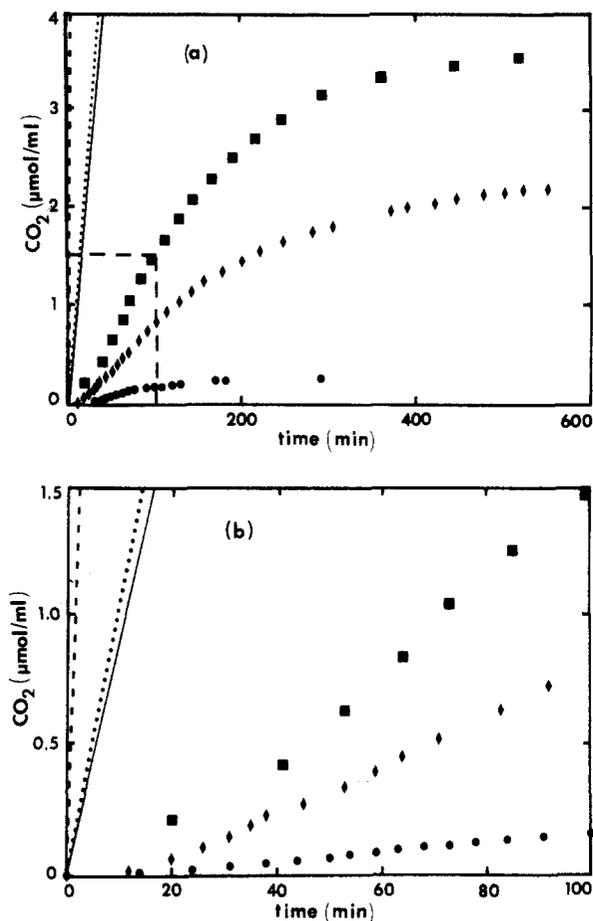
(18) *International Critical Tables*; McGraw-Hill: New York, 1928; Vol III, p 278–279.

Figure 3. The CO_2 generated by different BZ systems in a batch reactor: (●) $H_2PO_2^-$-acetone, (♦) arabinose-acetone, and (■) glucose-acetone. The region near the origin in (a) is shown enlarged in (b). The maximum rates of CO_2 generation for the high CO_2 production BZ systems are given by the dashed line (MA-ferroin), dotted line (AA) and solid line (EAA). The concentrations for each system are given in the footnote of Table II.

used for the entire course of the reaction, the time required to saturate the solution would be days, as given in column 4 of Table II. This confirms that in these systems no bubbles will be formed during the entire course of reaction. For the AA and EAA systems only the maximum rate of CO_2 production was measured, and for both it was about 50 times higher than that of the $H_2PO_2^-$-acetone system. The CO_2 production by the EAA and AA systems was unexpected because they had been reported to be CO_2 free.[6]

For comparison, the CO_2 production by MA-ferroin system with reagent concentrations similar to those used in target pattern studies[19] was also measured. This system is known to produce bubbles, presumably consisting mainly of CO_2. The CO_2 production for the MA-ferroin system was indeed found to be substantially higher than for the other BZ systems we have discussed; it is about 400 times higher than that of the $H_2PO_2^-$-acetone system (see Table II).

The CO_2 production for the MA-Ce(III) system was also measured and found to have a maximum rate of about half of that of the MA-ferroin system. We used the same reagent concentrations as were used by Försterling et al.,[20] who measured the CO_2 production using a flame-ionization method. We found a maximum rate of CO_2 production of 0.3×10^{-6} mol/(mL min), which is consistent with the result 0.16×10^{-6} mol/(ml min) obtained by Försterling et al.[20] This agreement is quite satisfactory considering that the experiments were performed at different

temperatures; here it was 25 °C, while it was 20 °C in ref 20.

We estimated the time required to saturate the solution for these high CO_2 production BZ systems using the maximum rate of CO_2 production, and the results are given in Table II. For the AA and EAA systems, the time is 5 and 6 h, respectively, but for the MA-ferroin system, surprisingly, it is about 40 min! We would like to point out that the saturation time obtained is a lower bound and the actual time will be longer.[21] Thus, one would not expect any bubble formation in the AA or EAA system, which confirms the experimental observations for such systems. As for the MA-ferroin system, bubbles are usually observed within a few minutes or so. This suggests that CO_2 may not be the only source for the formation of bubbles in the MA-ferroin system.

It was shown by Noszticzius[22] and by Bodiss[23] that, in addition to CO_2, there is substantial amount of CO formed in malonic acid BZ systems, especially when ferroin is used as catalyst. After our CO_2 measurements, Olah and Bodiss[24] measured the CO production of the MA-ferroin system using the same concentrations as shown in the footnote of Table II for the MA-ferroin system; surprisingly, they found that 56–59% (by volume) of the total gas produced was CO. Assuming the rate for CO production is comparable to that of CO_2 production, we estimated a maximum CO production rate of 1.3×10^{-6} mol/(mL min) for our MA-ferroin system. Even though this is only slightly greater than the CO_2 production rate, due to the low saturation limit of about 0.023 mL of CO/mL of solution at STP, the saturation time is only about 1 min, which is much faster than that of CO_2 and is consistent with the first appearance of bubbles in such a system. This result suggests that CO is likely to be the main constituent of the bubbles in the early stage of the formation of bubbles.

IV. Discussion

We have studied several bubble-free BZ systems using acetone as a Br_2 scavenger. The substrates used in these systems are acetone with arabinose, glucose, and $H_2PO_2^-$. The arabinose and glucose systems both exhibited simple relaxational oscillations of periods of about 1 min, while the hypophosphite system had substantially longer oscillation periods. Target patterns were observed in the $H_2PO_2^-$-acetone system. No precipitate was observed in these systems, while both the AA and EAA systems had precipitates for certain reagent concentrations. Complex oscillations and birhythmicity was observed in the AA system, while only simple oscillations were observed for the other systems.

Measurements showed that all of the above systems produce CO_2, but the amount of CO_2 liberated is not enough to saturate the solutions and thus does not lead to bubble formation. The $H_2PO_2^-$-acetone system produces the least CO_2, while the EAA and AA systems, surprisingly, produce a substantial amount of CO_2. For comparison, the CO_2 generated from a MA-ferroin system was also measured to be 2–3 orders of magnitude higher than that of the $H_2PO_2^-$-acetone system. The rate of CO_2 production does not depend of course exclusively on the chemical nature of the reagents, but also on the concentrations of the ingredients like bromate and the catalyst, as discussed by Bar-Eli and Haddad.[25]

Despite the amount of CO_2 generated in the MA-ferroin system, it is estimated that it will take a longer time to saturate the solution than the few minutes duration of the observations. However, the saturation time for CO is consistent with the observations. This indicates that CO may play an important role in the formation of bubbles in BZ systems, especially when ferroin is used as catalyst.

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