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Alternative Reaction Channels and Carbene Intermediates in the Ce^{4+}−Malonic Acid and Ce^{4+}−Bromomalonic Acid Reactions. 1. CO_2 Measurements

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The Ce^{4+}−malonic/bromomalonic acid reactions play an important role in the oscillatory Belousov−Zhabotinsky reaction. In this work CO_2 evolution from these reactions was studied with a sensitive and quantitative method, by converting the CO_2 to methane and measuring it with a flame ionization detector. It was found that the stoichiometries depend on the initial conditions in batch experiments or on the mixing rate of reagents in a semibatch reactor. These findings are explained by two main reaction channels: one for recombination and another for decarboxylation. Decarboxylation itself has two separate routes, one is dominant at low while the other at high Ce^{4+} concentrations. In the latter, formation of more than two CO_2 molecules from one malonic/bromomalonic acid molecule was observed. Novel reaction schemes containing carbenes are proposed for these "high Ce^{4+}" decarboxylation channels. To check the new mechanism, HPLC measurements are planned as a continuation of the research.

Introduction

The Belousov−Zhabotinsky reaction—the oxidation of malonic acid by acidic bromate in the presence of Ce^{4+} catalyst and related reactions—is the focus of interest in the past decades because of its interesting dynamics.[1] Currently, its chemical mechanism, the reaction steps, and rate constants are elaborated so that kinetic simulations show a rather good agreement with various types of the observed dynamical phenomena. Though these mechanisms give a detailed description of the inorganic subset including elementary steps, they involve hypothetical composite reactions in the organic subset of the whole BZ reaction. It would be important to understand more details of the latter reactions because these are crucial ones in the negative feedback loop of the autocatalytic process.

The first step in investigating the organic steps of the whole BZ reaction is to examine the reaction of the catalyst, e.g., Ce^{4+} ions, with malonic acid and bromomalonic acid, respectively. Recently a series of papers has identified some primary products of these reactions using the HPLC technique.[2−4] These were 1,1,2,2-ethanetetracarboxylic acid (ETA) and malonyl monomalonate (MAMA) in the Ce^{4+}−malonic acid reaction and bromoethenetricarboxylic acid (BrEETRA) in the Ce^{4+}−bromomalonic acid reaction, products that emerge in the recombination of the primarily formed malonyl or bromomalonyl radicals.

Experimental observations suggest, however, that recombination of the radicals is not the only possibility. For example, it is known that in the Ce^{4+}−malonic acid reaction formic acid can also be an end product. Actually, for a long time it was believed that it is the only one. It is clear that formic acid cannot be a product of a recombination route, as recombination alone can only generate molecules with more than one carbon atom. Formic acid should be formed in a different reaction channel starting also from the malonyl radical but continuing with decarboxylation steps. Such a decarboxylation channel should exist in the Ce^{4+}−bromomalonic acid reaction as well. In that case no formic acid is produced but about 60% of the bromomalonic acid is converted directly into CO_2 when Ce^{4+} is in excess,[4] although BrEETRA does not react further with Ce^{4+}. All these observations suggest that the recombination reaction channel is not unique; it dominates only when the organic radical concentration is relatively high and the Ce^{4+} concentration is relatively low. The other reaction pathway, where the main product is carbon dioxide, involves probably very reactive intermediates that cannot be easily detected. In this study our aim was to get a better insight into these processes by measuring the CO_2 evolved in the reaction of Ce^{4+} and malonic/bromomalonic acid. CO_2 evolution is followed continuously by transferring it into an inert gas stream, converting to methane with H_2, and detecting with a flame ionization detector.[5−7]

Experimental Section

Materials. Malonic acid (Fluka, puriss.), oxalic acid (Reanal, puriss.), $Ce(SO_4)_2$ (Riedel-de-Haen, pro analysi), $(NH_4)_2Ce(NO_3)_6$ (Fluka), and H_2SO_4 (Carlo Erba, RPE) were used as received. Bromomalonic acid was produced following the procedure of Försterling et al.[8]

Reactions. The reaction of malonic acid and bromomalonic acid with Ce^{4+} was examined both in sulfuric acid and in perchloric acid media at room temperature (22 ± 2 °C). Perchloric acid was used because sulfate ions establish a complex with ceric ions so in sulfuric acid medium the oxidation reactions are slower. The acid concentration was 1 M in all

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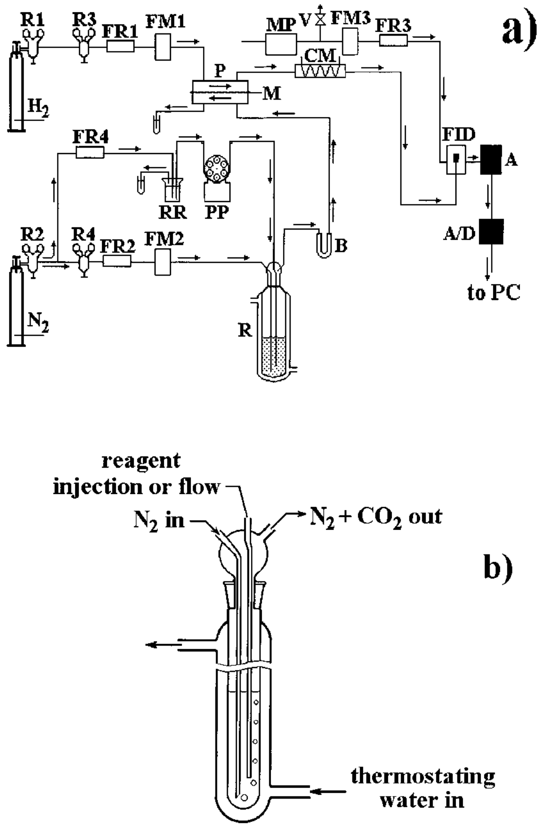


Figure 1. Experimental setup. (a) Various parts and connections of the experimental arrangement: R1−R4, reductors to control H_2 and N_2 gas flows; FR1−FR4 and FM1−FM3, flow resistors and flow meters, respectively; MP, membrane pump for air; V, valve to control the air flow; RR, reagent reservoir; PP, peristaltic pump; R, reactor; B, buffer; P, permeator; M, membrane; CM, catalytic methanizer; FID, flame ionization detector; A, amplifier; A/D, analogue to digital converter; PC, personal computer. (b) The reaction vessel. N_2 was introduced into the bottom of the container with a Teflon tube at a flow rate of 80 ± 2 mL/min. The bubbles were mixing the solution and stripping away the evolved CO_2 on the top. Another tube served for the reagent inlet, either for injection in impulse mode experiments or for continuous flow in semibatch experiments.

cases. In the case of sulfuric acid Ce^{4+} was applied as $Ce(SO_4)_2$, while in case of perchloric acid, Ce^{4+} was as $(NH_4)_2Ce(NO_3)_6$.

Experimental Setup. The experimental setup is shown in Figure 1a. High-purity N_2 (purity: 99.996%) was applied as a carrier gas in the reactor and also for establishing an anaerobic atmosphere in the reagent reservoir. The reaction vessel (Figure 1b) was bubbled with a constant (80 mL/min) N_2 stream to strip the evolved carbon dioxide. In the impulse mode experiments, too high CO_2 peaks could drive the FID signal out of its linear range. To avoid this, a 10 mL buffer volume (B) was applied. A constant fraction of the CO_2 was then transferred to a H_2 stream by selective permeation through a membrane. The permeator was applied to protect the Ni catalyst from larger amounts of oxygen that would otherwise enter into the system at every occasion, opening the reaction vessel. Also, fluctuations in the H_2 gas stream of the flame ionization detector (FID) due to bubbling can be avoided this way. The path of the gas streams in the permeator was a spiral on both sides of the membrane in which the gases were flowing in opposite directions. The spirals were cut into plexiglass disks that hold the silicon rubber membrane mounted between two glass fiber filter papers. The mass transfer was rather effective this way, and the constant fraction of CO_2 permeated from the N_2 side to the H_2 side was close to the theoretical maximum. As permeabilities of permanent gases across silicon rubber are orders of magnitude smaller than that of CO_2, permeation of O_2, N_2 and H_2 did not disturb the measurement. The thin membrane (only a few micrometers thick) was prepared following the method of Marlovits et al.[9] H_2 atmosphere is applied for the catalytic reduction of CO_2 to CH_4 and also necessary for protecting or regenerating the Ni catalyst at its operating temperature (400 °C). The H_2 flow rate was 40 ± 2 mL/min. The flame ionization detector needs some air, too. Its flow rate must be relatively high; otherwise, the FID signal would be sensitive to small fluctuations of the flow rate. Atmospheric air (270 ± 10 mL/min) was pumped to the FID with a membrane pump. (The air was filtered through cotton wool to remove dust particles.) The current of the FID approaches nanoamperes. This current flows through a high (10^9 Ω) resistor. The voltage on the resistor is amplified with a high input impedance amplifier. The amplified signal was measured with an A/D converter connected to a PC. A 12 bit A/D converter (PCL-812PG card of Advantech Co.) was applied, and results were evaluated with the Labtech Notebook 7.1 program.

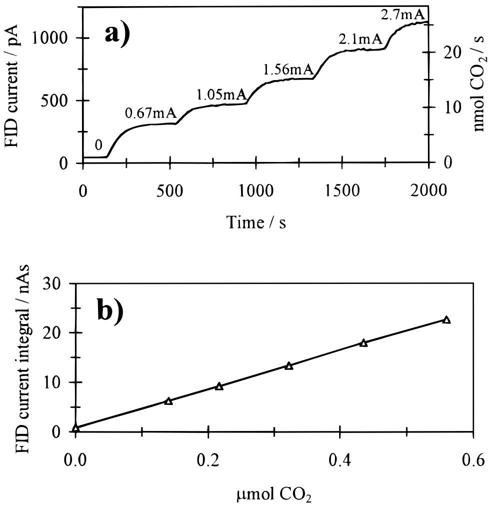


Figure 2. Absolute calibration with CO_2 generated by electrolysis. (a) FID current (pA, left ordinate) and CO_2 current (nmol/s, right ordinate) as a function of time. The electrolyzing currents are given on the plateaus of the curve. A 5 mL aliquot of 0.1 M oxalic acid was electrolyzed in 1 M sulfuric acid medium between Pt electrodes while bubbling with N_2. (b) Calibration curve. The FID current in Figure 2a was integrated when it reached a steady value, and it was given as the function of the amount CO_2 evolved during the time of integration. (The latter one was calculated from the Faraday law, as at the applied current densities oxalic acid gives quantitatively CO_2.)

In the case of semibatch experiments the reagent was pumped with a peristaltic pump (Ismatec Mini-S 840) at a low flow rate, approximately 1−3 μL/s.

Calibration of the Detector. *Absolute Calibration.* CO_2 was generated electrochemically from oxalic acid between Pt electrodes in a sulfuric acid medium. The generator cell was stripped with N_2 similarly to the reactor vessel. After reaching a steady state, the electric signal of the FID was recorded and integrated. In Figure 2 these integrals are depicted as a function of the CO_2 amount generated in the electrochemical cell. The CO_2 evolved was calculated from the Faraday law. As can be seen, the whole measuring system gives a linear response in this range.

Relative Calibration. A relative calibration was made by applying a semibatch reactor with Ce^{4+} inflow into an oxalic acid solution in the reactor. The calibration was repeated every day to check the Ce^{4+} solutions and the stability of the peristaltic

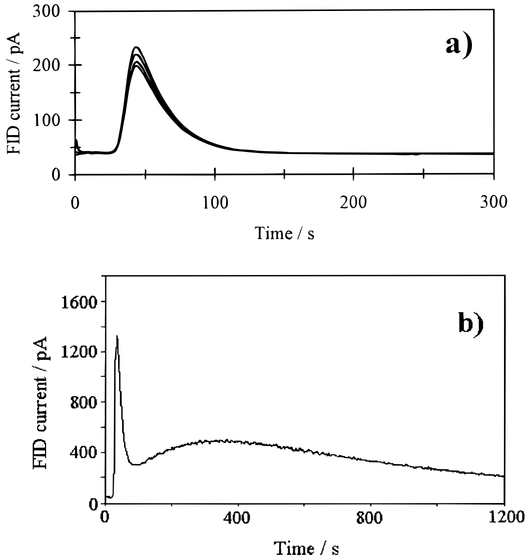


Figure 3. Impulse mode experiments. (a) Injection rate dependent CO_2 amounts in the Ce^{4+}−malonic acid reaction. Four parallel measurements are shown, in each case 1 mL of 5×10^{-3} M $Ce(SO_4)_2$ solution in 1 M H_2SO_4 was present in the reaction vessel and 2 mL of 0.75 M malonic acid in 1 M H_2SO_4 was quickly added. Deviations are caused by the irreproducibility in the rate of the manual injections. (b) A 1.5 mL aliquot of 0.04 M $Ce(SO_4)_2$ solution in 1 M H_2SO_4 was bubbled in the reaction vessel with N_2 for some minutes, and then 1.5 mL 0.02 M malonic acid in 1 M H_2SO_4 was quickly added.

pump. In steady state the CO_2 output in mol/s leaving the reactor with the N_2 carrier gas is equal to the Ce^{4+} input entering the reactor with the reagent flow measured also in mol/s.[10] Thus the stoichiometric coefficient

$$\nu = \frac{n_{CO_2}\,(\text{produced})}{n_{Ce^{4+}}\,(\text{consumed})}$$

for various substrates can be calculated simply as a ratio of the stationary FID currents measured with the substrate and with oxalic acid:

$$\nu = \frac{I_{FID}\,(\text{substrate})}{I_{FID}\,(\text{oxalic acid})}$$

The currents were corrected with the background current of the FID, which was around 40 pA. The main source of the background current was the Ni catalyst emitting some trace contaminants at its operating temperature.

Results

Impulse Mode Measurements. First the Ce^{4+}−malonic acid reaction was investigated. To determine the stoichiometry of the CO_2 evolution, initially a batch reactor was applied. A Ce^{4+} solution was filled into the reactor depicted in Figure 1b. The solution was bubbled with N_2 for few minutes and then a malonic acid solution was quickly injected. Both solutions contained sulfuric acid in a 1 M concentration. The CO_2 generated this way results in one, or sometimes two, peaks in the FID signal (see Figure 3). The peak was integrated and the amount of the CO_2 evolved in the reaction was calculated. The results given by a series of such measurements are displayed in Table 1.

TABLE 1: CO_2 Yield in Impulse Mode Experiments (Number of CO_2 Molecules Produced from One Malonic Acid Molecule (n_{CO_2}/n_{MA}) and by One Ce^{4+} Ion ($n_{CO_2}/n_{Ce^{4+}}$))^a

$n_{MA}/n_{Ce^{4+}}$	$n_{Ce^{4+}}$ (μmol)	n_{MA} (μmol)	n_{CO_2} (μmol)	n_{CO_2}/n_{MA}	$n_{CO_2}/n_{Ce^{4+}}$
1:10	200	20	46.6	2.33	0.233
1:8		25	53.6	2.14	0.268
1:5		40	62.8	1.57	0.314
1:4		50	67.4	1.35	0.337
1:2		100	49.6	4.9×10^{-1}	0.25
1:1		200	36.4	1.8×10^{-1}	0.18
2:1		400	23.5	5.6×10^{-2}	0.12
2.5:1		500	16.1	3.2×10^{-2}	0.081
5:1		1000	9.60	9.6×10^{-3}	0.048
10:1		2000	4.97	2.5×10^{-3}	0.025
20:1		4000	2.55	6.4×10^{-4}	0.013

[a] The Ce^{4+} amount ($n_{Ce^{4+}} = 200$ μmol) was fixed in the experiments. 1 mL MA solution with different concentrations was quickly injected into 2 mL of 0.1 M Ce^{4+} solution in N_2 atmosphere. The amount of the CO_2 evolved was calculated by integrating the FID current peak and comparing the result with that of a calibration experiment applying oxalic acid substrate.

Figure 3 shows two problems of the impulse mode experiments. First, not only the peak height but even the integral might depend on the rate of the injection (see Figure 3a). This was not observed in calibrating experiments with oxalic acid substrate where a stoichiometric ratio of 1 CO_2/1 Ce^{4+} was measured always independently of the injection rate. In the case of malonic acid substrate, however, irreproducible concentration distributions during mixing of the reagents affect the final stoichiometry in some extent. Initial conditions applied in Figure 3a were especially suitable to demonstrate this effect. (Data given in Table 1 were more reproducible.)

A second problem is that in a batch reactor consecutive reactions occur; thus, the main source of the CO_2 evolution can be a different reaction at the beginning and at the end of the experiment. Figure 3b demonstrates this problem clearly. In that experiment the MA:Ce^{4+} ratio was 1:2 but the initial concentrations were 3 times smaller than in Table 1 to show a special feature: a second broad maximum in the rate of the CO_2 evolution. (To see that the second peak is not coming from an unknown contaminant of the malonic acid, malonic acids of different purities and also recrystallized samples were used for this experiment. The result was independent of the purity of the malonic acid.) This unexpected dynamics of the CO_2 evolution is due to the appearance of recombination products ETA and MAMA and their further decarboxylation reactions with Ce^{4+}. At high Ce^{4+} concentrations in an impulse mode experiment the rate of the reaction and consequently the malonyl radical concentration is also high. This favors the recombination reaction because that rate is proportional to the square of the radical concentration. As the concentration of the recombination products is growing and the Ce^{4+} quantity is decreasing, this causes a second maximum in the CO_2 evolution. (Decarboxylation of radicals with four or more carboxylic groups has a much higher probability than that of the malonyl radical.) Our aim is, however, to suppress such processes and study the decarboxylation channel starting from the malonyl radical exclusively. It is obvious that impulse mode experiments cannot meet this condition but only steady-state type CSTR or semibatch experiments where the rate of the reaction can be controlled. Recombination can be suppressed in these reactors by applying low reaction rates.

We decided to apply the semibatch configuration with a continuous inflow of one reagent to the reactor containing a relatively large amount of the other reagent. It is known that in a semibatch reactor in the absence of an outflow no real steady state but only a quasi steady state can be achieved. This was not a serious problem, however, in the majority of our experiments. On the other hand, applying a semibatch reactor we could avoid several technical problems of a CSTR configuration (precise control of several inflows and also of the outflow, CO_2 loss caused by the liquid outflow, etc.).

The results of the impulse mode experiments (Table 1) oriented our semibatch experiments. As can be expected, the number of CO_2 molecules produced from one malonic acid molecule decreases with the increasing malonic acid concentration. It is interesting to observe that this number can be more than 2 at low malonic acid concentrations. The CO_2/Ce^{4+} yield has a maximum also at relatively low malonic acid concentrations. All these suggest that if we want to study the decarboxylation channel of the Ce^{4+}−malonic acid reaction, then a Ce^{4+} excess should be applied. Earlier experiments by Försterling, Pachl, and Schreiber[12] have shown, however, that a relatively high yield of CO_2/Ce^{4+} (close to 0.5) can be achieved when malonic acid is in excess but both Ce^{4+} and malonic acid concentrations and consequently the rate of the reaction is also very low. Thus we can assume that there are two different decarboxylation channels in the reaction. One is active at low while the other is dominant at high Ce^{4+} concentrations. Obviously, we have to apply different parameters in a semibatch experiment if we want to study one or the other channel.

To study the low Ce^{4+} decarboxylation channel, an excess of malonic acid should be placed into the reactor and a slow Ce^{4+} inflow should be applied. As the rate-determining step is the Ce^{4+} inflow to the reactor, the rate of the reaction can be controlled and kept at a low value this way. This is advantageous because at low reaction rates the recombination is slow and malonyl radicals have enough time to decarboxylate.

To study the high Ce^{4+} decarboxylation channel, we have to apply a relatively high concentration of Ce^{4+} in the semibatch reactor and a small inflow of the organic substrate. The low radical concentration associated with the slow rates suppresses the recombination reactions and the high Ce^{4+} concentration accelerates further reactions of the radicals with Ce^{4+}.

Semibatch Experiments with Ce^{4+} Inflow. In the first series of experiments the organic substrates were applied in excess. A 1 mL aliquot of the 0.1 M solution of the organic substrate (malonic, bromomalonic, or oxalic acid) was added into the reactor, and a continuous flow of Ce^{4+} solution was established by a peristaltic pump. The flow rate was low, 1−3 μL/s and it was kept constant for a given series of experiments. (To check this, a relative calibration was made before starting and after finishing a series of experiments. See the Experimental Section.) The rate of the reaction was controlled by the concentration of the Ce^{4+} solution. According to our observations the slow increase in the total volume does not disturb the steady state as the rate of the reaction in a steady state should be equal to the Ce^{4+} input rate. Simultaneous changes in the reagent concentrations are possible, but these should not change the reaction rate itself. For example, toward the end of an experiment the organic substrate concentration could be smaller even by a factor of 2 or 3, but this was counterbalanced by the same increase in the steady-state Ce^{4+} concentration: the CO_2 output rate was constant; see, e.g., Figure 4a,b. Figure 4a shows parallel semibatch experiments with malonic and oxalic acids and Figure 4b shows the same for bromomalonic and oxalic acids. The oxalic acid experiments are shown for comparison only. As can be seen, a steady state is achieved within 100 or 200 s after starting the experiment. (The longer transient in the case of bromomalonic acid suggests that some steps in its decarboxylation channel are slower compared to malonic acid.) Table 2 summarizes the results including experiments with malonic acid both in sulfuric acid and perchloric acid medium and with bromomalonic acid in sulfuric acid medium.

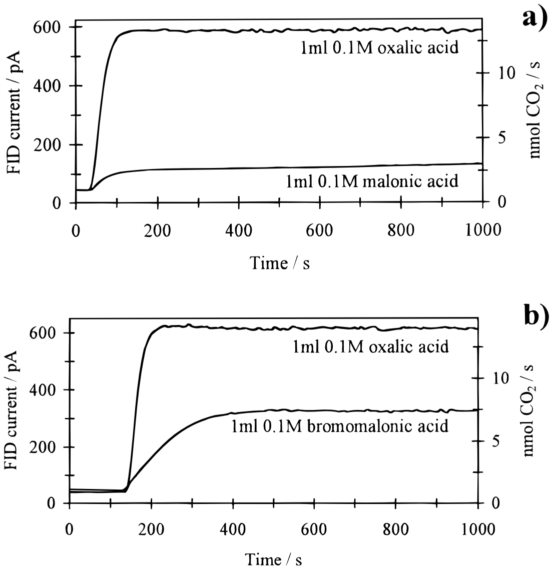


Figure 4. Semibatch experiments. Time evolution of the FID current proportional to the CO_2 evolution rate. The number of CO_2 molecules produced by one Ce^{4+} was calculated from the ratio of the steady-state currents for the given substrate and for oxalic acid. A 5×10^{-3} M Ce^{4+} solution was pumped with a flow rate of 1 μL/s to 1 mL of 0.1 M (a) malonic acid and (b**)** bromomalonic acid (all these solutions were made in 1 M sulfuric acid).

TABLE 2: CO_2 Yield in Semibatch Experiments with Ce^{4+} Inflow (Number of CO_2 Molecules Produced by One Ce^{4+} Ion)[a]

substrate and medium	rate of Ce^{4+} addition (nmol/s)	rate of CO_2 evolution (nmol/s)	$n_{CO_2}/n_{Ce^{4+}}$
MA in H_2SO_4	125.1	2.58	0.02
	12.51	1.70	0.14
	1.25	0.61	0.49
MA in $HClO_4$	136.3	45.8	0.34
	13.63	5.45	0.40
	1.36	0.84	0.62
BrMA in H_2SO_4	131.6	50.7	0.39
	13.16	6.38	0.49
	1.32	1.44	1.09

[a] The reaction vessel contained always 1 mL of 0.1 M solution of the organic substrate in 1 M acid. The Ce^{4+} flow rate was between 1 and 3 μL/S; it was kept constant for a series of experiments. Different Ce^{4+} input rates were established with different Ce^{4+} input concentrations (5×10^{-2} M, 5×10^{-3} M, and 5×10^{-4} M, respectively). The rate of Ce^{4+} addition was calculated from the Ce^{4+} concentration and the applied pumping rate. The ratio $n_{CO_2}/n_{Ce^{4+}}$ was calculated from the ratio of the two steady-state FID signals measured with the substrate and oxalic acid, respectively.

O_2 was excluded from the measurements, but it is known[13] that even tiny amounts can react with organic radicals rapidly. We cannot exclude that especially at the lowest reaction rates trace amounts of oxygen in the N_2 carrier can cause some effect. To check this, a silicon rubber tubing was included into the N_2 flow before the reactor. A low level of oxygen contamination in the N_2 stream was established this way: oxygen from the ambient air could penetrate into the N_2 flow. A soda lime filtering of the air prevented any contamination by CO_2. Results are shown in Table 3. It is clear that oxygen contamination can

TABLE 3: Oxygen Effect in Semibatch Experiments with Ce^{4+} Inflow (Number of CO_2 Molecules Produced by One Ce^{4+} Ion)[a]

substrate and medium	rate of Ce^{4+} addition (nmol/s)	rate CO_2 of evolution (nmol/s)		$n_{CO_2}/n_{Ce^{4+}}$	
		without O_2	with O_2	without O_2	with O_2
MA in H_2SO_4	63.0	2.28	5.13	0.04	0.08
	6.30	1.00	2.28	0.16	0.36
	0.63	0.28	0.28	0.44	0.44
BrMA in H_2SO_4	99.0	44.04	45.76	0.45	0.46
	9.90	4.95	6.51	0.50	0.66
	0.99	0.80	1.85	0.81	1.87
BrMA in $HClO_4$	51.04	25.31	29.07	0.50	0.57
	12.76	7.07	8.81	0.55	0.60
	1.28	1.19	1.72	0.93	1.34

[a] The reaction vessel contained always 1 mL 0.1 M solution of the organic substrate in 1 M acid. Input Ce^{4+} concentrations were 5×10^{-2} M, 5×10^{-3} M, and 5×10^{-4} M in the case of sulfuric acid and 2×10^{-2} M, 2×10^{-3} M, and 2×10^{-4} M in the case of perchloric acid.

TABLE 4: CO_2 Yield in Semibatch Experiments with Organic Substrate Inflow (Number of CO_2 Molecules Produced from One Malonic/Bromomalonic Molecule)[a]

substrate and medium	substrate concn (M)	$n_{CO_2}/n_{\text{substrate}}$
BrMA in H_2SO_4	2×10^{-2}	2.5
BrMA in H_2SO_4	4×10^{-3}	2.6
MA in $HClO_4$	4×10^{-3}	2.6
BrMA in $HClO_4$	4×10^{-3}	2.8

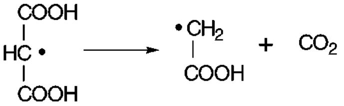
[a] The organic substrates were pumped into the Ce^{4+} solution. The reaction vessel contained initially 2 mL of 0.2 M Ce^{4+} solution in 1 M acid in all experiments. Calibration was made by pumping oxalic acid solutions to the reactor. The concentration of oxalic acid was the same as that of the studied substrate.

increase the CO_2 output considerably from both substrates. It can be seen also that in the case of malonic acid substrate at the lowest reaction rate some natural oxygen contamination[14] was already strong enough to capture all malonyl radicals. Probably, this is why our artificial oxygen source had no additional effect. At higher reaction rates this natural low-level oxygen is consumed in the reaction completely; thus, an additional oxygen source had a strong effect. The experiment with bromomalonic acid substrate was somewhat less sensitive to oxygen at high reaction rates, but the CO_2 output increased dramatically at the lowest rate. All these indicate that the results at the lowest Ce^{4+} input rates are not reliable due to an oxygen effect. Anyway, even if these results with the lowest rates are disregarded, the data in Table 2 clearly demonstrate a rate dependent CO_2 evolution both in the Ce^{4+}−malonic and in the Ce^{4+}−bromomalonic acid reactions. The lower the rate, the higher the CO_2 yield per Ce^{4+} in the low Ce^{4+} decarboxylation channel.

Semibatch Experiments with Malonic/Bromomalonic Acid Inflows. In a second series of experiments to study the high Ce^{4+} decarboxylation channel of the malonic and bromomalonic acids, semibatch experiments were made in a reverse configuration. In these experiments the reactor contained 2 mL of 0.2 M Ce^{4+} solution in 1 M sulfuric or perchloric acid and various solutions of the two substrates dissolved in the same medium were pumped to the reactor slowly (1 μL/s). The results are displayed in Table 4. Malonic acid data in sulfuric acid medium are not shown because we were not able to reach a steady state in this case. This is due to the fact that in sulfuric acid medium the Ce^{4+} is less reactive with the malonyl radical than in perchloric acid; thus, the high Ce^{4+} decarboxylation channel cannot compete effectively with the recombination channel. As a consequence, achieving a steady state is prevented by the accumulation of the recombination products ETA and MAMA, which cause an ever growing CO_2 output in their reaction with Ce^{4+}. A steady state was reached in all other experiments. Table 4 indicates that as an average more than 2.5 carbon atoms, out of the available three per molecule, are oxidized to CO_2 completely.

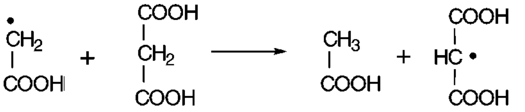
Discussion

Ce^{4+}−Malonic Acid Reaction. *Low Ce^{4+} Decarboxylation Channel.* According to Table 2, the most characteristic result of the semibatch experiments with Ce^{4+} inflow into a reactor containing a high excess of malonic acid is a growing CO_2 output/Ce^{4+} input ratio with a decreasing Ce^{4+} input rate. To explain this result, the following scheme is suggested for the low Ce^{4+} decarboxylation channel. The first step in this channel, after the production of a malonyl radical, is a monomolecular decomposition of this species into an alkyl acetyl radical and a CO_2:



$$\cdot CH(COOH)_2 \longrightarrow \cdot CH_2COOH + CO_2 \qquad (R1)$$

A possible next step could be the recombination of the various radicals. Nevertheless, in a semibatch experiment with low input rate, the radical concentration is relatively low; thus, there is time enough even for a less reactive reaction partner to compete for radicals before they recombine. Especially, the malonic acid molecule can be such a reaction partner because it is in a high excess. Naturally, a reaction between malonic acid and the malonyl radical does not give a net chemical change. On the other hand, a reaction between malonic acid and the acetyl radical gives acetic acid and a new malonyl radical:



$$\cdot CH_2COOH + CH_2(COOH)_2 \longrightarrow CH_3COOH + \cdot CH(COOH)_2 \qquad (R2)$$

This chain reaction could produce several CO_2 molecules per Ce^{4+} depending on the fate of the malonyl radical produced in (R2). Anyway, the chain reaction finally terminates with a recombination even in a semibatch experiment to give mainly ETA and MAMA, but production of some ETRA (ethane tricarboxylic acid) and SA (succinic acid) is also possible. A complete scheme of the low Ce^{4+} decarboxylation channel is given in Figure 5.

Another peculiarity of Table 2 which is worth comment is the effect of the medium. In sulfuric acid the CO_2 output is much lower than in perchloric acid. This difference is especially marked (0.02 vs 0.34) at the highest Ce^{4+} input. This can be explained with the lower reactivity of the Ce^{4+} ions in sulfuric acid medium compared to perchloric acid. (Production of sulfato

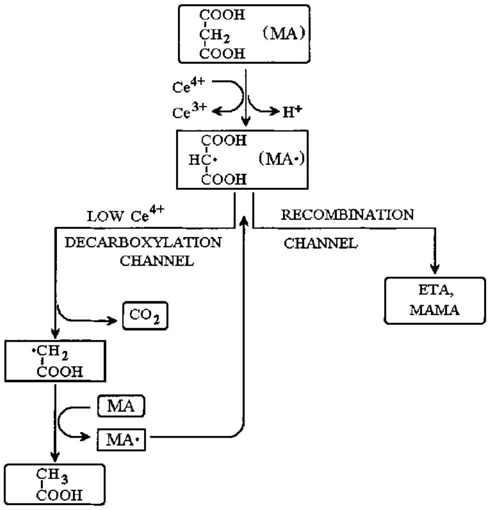
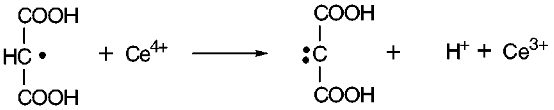


Figure 5. Mechanistic scheme of the low Ce^{4+} decarboxylation channel in the Ce^{4+}−malonic acid reaction.

complexes decreases the redox potential of the Ce^{4+}/Ce^{3+} couple.) Consequently, a second reaction of a malonyl radical with Ce^{4+} has a much higher probability in perchloric acid than in sulfuric acid. We believe that the high CO_2/Ce^{4+} yield in that medium at the highest Ce^{4+} input rate is due to the other, the so-called "high Ce^{4+}" decarboxylation channel, which is active already at lower Ce^{4+} concentrations in perchloric acid than in sulfuric acid medium.

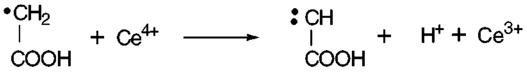
High Ce^{4+} Decarboxylation Channel. According to Table 1 when Ce^{4+} was applied in an 8- or 10-fold excess in the impulse mode experiments, then more than 2 (2.14 and 2.33, respectively) CO_2 molecules were formed from 1 malonic acid molecule in sulfuric acid medium. Semibatch experiments applying perchloric acid medium and a low malonic acid inflow into the reactor where the Ce^{4+} concentration was high (0.2 M) also gave a high CO_2 yield: 2.6 CO_2 (output)/1 malonic acid (input).

The decarboxylation mechanism detailed in Figure 5 cannot explain these results because its end product, acetic acid, still contains two carbon atoms. Even a mechanism with formic acid as an end product could not account for the observed high CO_2 outputs. Consequently, another mechanism is necessary to explain the observations at high Ce^{4+} concentrations. The starting point of this channel is a reaction of the radicals (malonyl or acetyl) with Ce^{4+}:



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{HC}\bullet\\ |\\ \mathrm{COOH}\end{array} + \mathrm{Ce^{4+}} \longrightarrow \begin{array}{c}\mathrm{COOH}\\ |\\ :\mathrm{C}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{H^{+} + Ce^{3+}} \qquad \mathrm{(R3)}$$

or



$$\begin{array}{c}\bullet\mathrm{CH_2}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{Ce^{4+}} \longrightarrow \begin{array}{c}:\mathrm{CH}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{H^{+} + Ce^{3+}} \qquad \mathrm{(R4)}$$

Here, and also in the complete scheme of the high Ce^{4+} decarboxylation channel shown in Figure 6, carbenes[16] as new reactive intermediates are proposed. Why do we assume such "exotic" intermediates? The answer is that other possible and conventionally supposed molecular intermediates in the decarboxylation channel would be too stable against further oxidation by Ce^{4+}. The conventionally supposed intermediates, such as tartronic acid and especially glycolic acid, react with Ce^{4+} rather slowly; therefore, if they would be formed in the reaction, then they could not be flow-through intermediates but they would be end products. For example, glycolic acid could be such a less exotic molecular intermediate which could be formed in (R5):

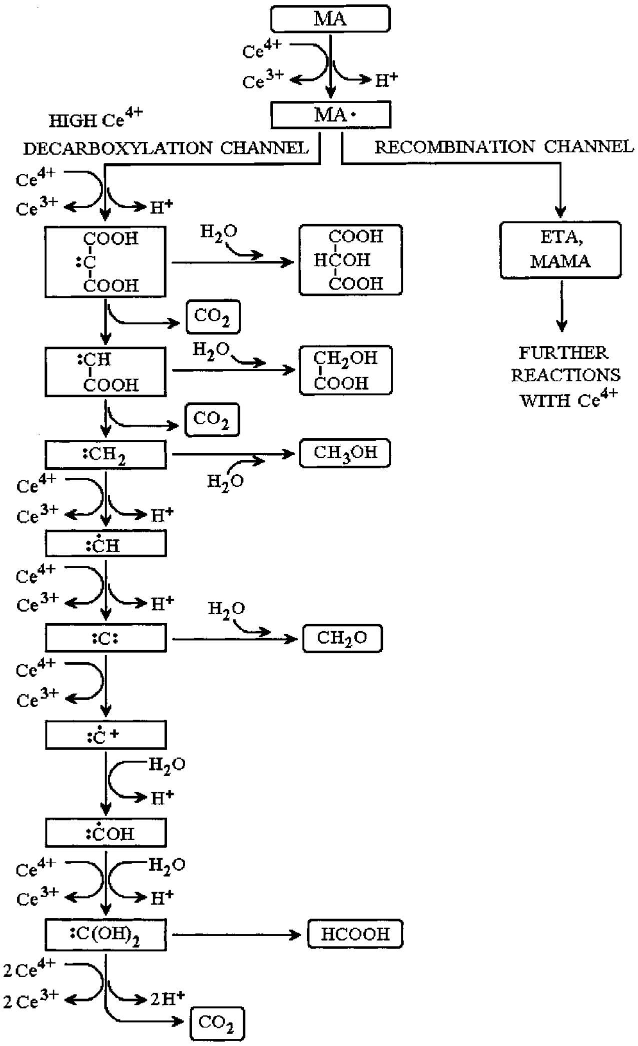


Figure 6. High Ce^{4+} decarboxylation channel of the Ce^{4+}−malonic acid reaction.

$$\begin{array}{c}\bullet\mathrm{CH_2}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{Ce^{4+}} + \mathrm{H_2O} \longrightarrow \begin{array}{c}\mathrm{HOCH_2}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{H^{+} + Ce^{3+}} \qquad \mathrm{(R5)}$$

However, glycolic acid was not detected in the reaction mixture in quantities according to an end product; furthermore, our experiments prove that oxidation proceeds to CO_2 or at least to formic acid on all the three carbon atoms of malonic acid. This excludes the possibility that such molecular intermediates are involved in the oxidation process. Consequently, the decarboxylation reaction has to proceed through more reactive species: ions, radicals, carbenes, and radical-ions (Figures 6 and 7). Carbenes can form transition metal complexes,[17] and this is why we can rationalize the high affinity of Ce^{4+} ions to carbenes and the inhibition of the insertion reactions leading to, e.g., glycolic acid and methanol.

It is interesting to remark that recently Ruoff and co-workers[18] studied the methylmalonic acid−Ce^{4+} reaction by applying high (0.4 M) initial Ce^{4+} concentrations, and they also found a fast reaction channel leading directly to the final product, acetic acid. While they do not assume carbene intermediates, reactions of Ce^{4+} with organic radicals are also suggested in their schemes.

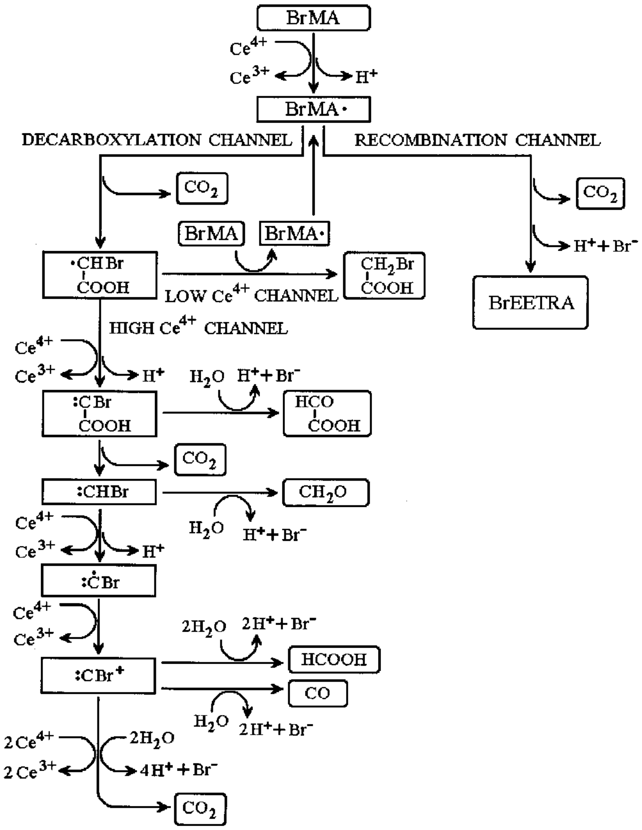


Figure 7. Decarboxylation channels in the Ce^{4+}−bromomalonic acid reaction.

It is clear that the very labile radical and carbene intermediates of the main line cannot be detected by conventional analytical techniques. However, if more stable molecular byproducts appear, these can be detected with sensitive analytical methods. Some possible side reactions producing such byproducts are shown as horizontal lines in Figure 6. As we can see, the possible byproducts of the decarboxylation channel are tartronic acid, glycolic acid, methanol, formaldehyde, and formic acid. It should be stressed again that these compounds are not flow-through intermediates of the suggested reaction scheme but only byproducts "flowing out" from the main line. Nevertheless, it is important to find even trace amounts of them as they give valuable information about the main line of the decarboxylation process. Formic acid is already a well-known product of the reaction, but in our scheme it is not an end product but only one among the possible byproducts. If formic acid were in the main line, then it would be an end product, as it cannot be oxidized further by Ce^{4+}. Nevertheless, our results in Tables 1 and 4 clearly show that by applying an excess of the Ce^{4+} reagent more than two carbon atoms of the malonic acid will be oxidized to CO$_2$. This would not be possible if formic acid were an end product. While our findings support the hypothetical scheme in Figure 6, this does not mean at all that the scheme is now proved convincingly. To study details of the suggested mechanism, HPLC measurements are in progress,[15] focusing on minor byproducts of the Ce^{4+}−malonic acid reaction.

Ce^{4+}−Bromomalonic Acid Reaction. A reaction scheme proposed for this reaction is shown in Figure 7. Reaction steps of the decarboxylation channel are analogous to that of malonic acid (compare with Figures 5 and 6) but the low and high Ce^{4+} decarboxylation channels are integrated into one scheme. This modification is due to the fact that the CO$_2$ evolution is usually 1 order of magnitude higher with the bromomalonic acid substrate compared to malonic acid and considerable CO$_2$ evolution occurs even at high substrate concentrations. Obviously, decarboxylation of bromomalonyl radicals is faster than that of malonyl radicals. A carbene intermediate analogous to the first carbene intermediate of malonic acid cannot be formed in the case of bromomalonic acid. This does not mean, however, that the bromomalonyl radical cannot react with Ce^{4+} but a carbene intermediate can be formed only after loosing a CO$_2$. At low Ce^{4+} concentrations, the decarboxylation of the radical seems to be the dominant reaction. The proposed mechanism is supported by the fact that when Ce^{4+} is in excess, then more than two carbon atoms of the substrate are oxidized to CO$_2$ as an average (see Table 4). To collect some more direct evidence for the scheme, the products of the side reactions will be investigated with HPLC measurements.[15]

Conclusion

Our measurements support that in both the Ce^{4+}−malonic and the Ce^{4+}−bromomalonic acid reactions two different decarboxylation routes exist. Besides the already known low Ce^{4+} decarboxylation channel, the presence of another channel, which is dominant at high Ce^{4+} concentrations, is proved. The details of this new route are presently not known, but it is clear that it should contain intermediates that react with Ce^{4+} quickly. The reaction schemes of the present work propose that these short-lived intermediates are carbenes. To prove these hypothetical schemes, however, further evidence should be collected. These very reactive intermediates might play an important role in the mechanism of the whole BZ reaction because they can be parts of still unknown feedback loops connecting the organic and the inorganic subsets of the oscillating system.

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(19) As one of our referees pointed out, the schemes presented in Figures 5 and 6 support that not all the MA reacts through BrMA in the BZ reaction. Previously it was assumed that (i) the only end product of the Ce^{4+}−MA reaction is formic acid and (ii) the absence of the formic acid as an end product in the total BZ system proves the MA−BrMA pathway. According to the present study, various oxidation channels can appear already in the Ce^{4+}−MA subsystem, which can be active in the complete BZ system as well.

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