3118 *J. Phys. Chem. A* **1998,** *102,* 3118−3120

# HPLC Studies on the Photochemical Formation of Free Radicals from Malonic Acid

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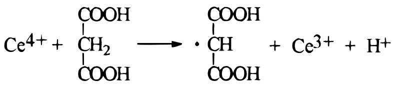
*Received: December 8, 1997; In Final Form: February 20, 1998*

In the Belousov Zhabotinsky reaction, malonyl radicals formed during the oxidation of malonic acid by $\mathrm{Ce^{4+}}$ play an important role in the mechanism of the negative feedback loop. In the past, we have analyzed the end products in the $\mathrm{Ce^{4+}}$−malonic acid reaction applying HPLC technique. For comparison, we generated malonyl radicals by UV irradiation of solutions of malonic acid and we identified the reaction products. Two of these are the same as in the $\mathrm{Ce^{4+}}$−malonic acid reaction, but some additional products are also formed. To explain our experimental results, a new reaction path is proposed where malonyl radicals and hydrogen atoms are the first intermediates in the photochemical decomposition of the malonic acid. Mechanistic differences between this photochemical decomposition and the $\mathrm{Ce^{4+}}$−malonic acid reaction are also discussed.

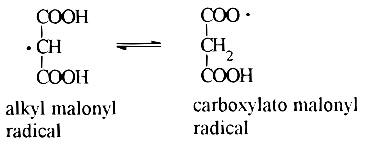
## Introduction

The Belousov−Zhabotinsky reaction is one of the most studied chemical oscillators.[1−3] In its classical form it is the oxidation of malonic acid by acidic bromate catalyzed by the $\mathrm{Ce^{4+}/Ce^{3+}}$ redox couple. The organic radicals play an important role in the mechanism of this reaction. For example, an additional negative feedback loop via organic radicals was discovered.[4,5] Using HPLC and NMR techniques, it was found that the primary products of the $\mathrm{Ce^{4+}}$−malonic acid reaction are 1,1,2,2-ethanetetracarboxylic acid (ETA) and monomalonyl malonate (MAMA).[6,7] These compounds are the recombination products of malonyl radicals (R1−R4).



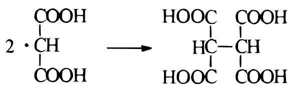
$$\mathrm{Ce^{4+}} + \begin{array}{c}\mathrm{COOH}\\|\\\mathrm{CH_2}\\|\\\mathrm{COOH}\end{array} \longrightarrow \begin{array}{c}\mathrm{COOH}\\|\\\cdot\,\mathrm{CH}\\|\\\mathrm{COOH}\end{array} + \mathrm{Ce^{3+}} + \mathrm{H^+}$$

**(R1)**



$$\begin{array}{c}\mathrm{COOH}\\|\\\cdot\,\mathrm{CH}\\|\\\mathrm{COOH}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{COO}\,\cdot\\|\\\mathrm{CH_2}\\|\\\mathrm{COOH}\end{array}$$

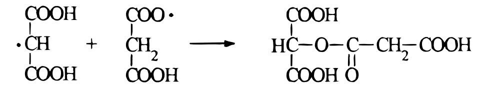
**(R2)**



$$2\;\cdot\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{CH}\\|\\\mathrm{COOH}\end{array} \longrightarrow \begin{array}{cc}\mathrm{HOOC} & \mathrm{COOH}\\| & |\\\mathrm{HC}- & \mathrm{CH}\\| & |\\\mathrm{HOOC} & \mathrm{COOH}\end{array}$$

(ETA)

**(R3)**

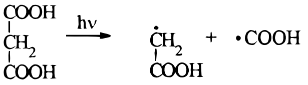


$$\begin{array}{c}\mathrm{COOH}\\|\\\cdot\,\mathrm{CH}\\|\\\mathrm{COOH}\end{array} + \begin{array}{c}\mathrm{COO}\,\cdot\\|\\\mathrm{CH_2}\\|\\\mathrm{COOH}\end{array} \longrightarrow \begin{array}{l}\mathrm{COOH}\\|\\\mathrm{HC{-}O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CH_2{-}COOH}\\|\\\mathrm{COOH}\end{array}$$

(MAMA)

**(R4)**

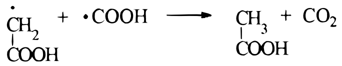
Organic radicals can be also produced by UV irradiation. The photochemistry of malonic acid was studied with various methods (observation of transient spectra, ESR, CIDNP).[8−11] Kaiser et al.[9−11] assumed that in water the primary process during the UV irradiation of organic acids is the α-cleavage reaction (R5). They studied the photochemistry of various organic acids and malonic acid was only one of them. In the malonic acid case, they attributed the ESR signals to $^\bullet\mathrm{CH_2COOH}$ and to $^\bullet\mathrm{COOH}$ radicals.



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{CH_2}\\|\\\mathrm{COOH}\end{array} \xrightarrow{h\nu} \begin{array}{c}\dot{\mathrm{C}}\mathrm{H_2}\\|\\\mathrm{COOH}\end{array} + \cdot\,\mathrm{COOH}$$

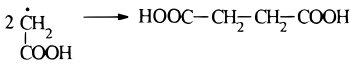
**(R5)**

In the CIDNP studies they found that the products are acetic acid and succinic acid according to reactions R6 and R7:[10] It is important to remark that they did not detect any recombination products of $^\bullet$COOH radicals and the direct identification of carboxyl radicals with the ESR technique is somewhat uncertain.



$$\begin{array}{c}\dot{\mathrm{C}}\mathrm{H_2}\\|\\\mathrm{COOH}\end{array} + \cdot\,\mathrm{COOH} \longrightarrow \begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{COOH}\end{array} + \mathrm{CO_2}$$

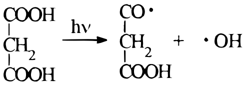
**(R6)**



$$2\,\begin{array}{c}\dot{\mathrm{C}}\mathrm{H_2}\\|\\\mathrm{COOH}\end{array} \longrightarrow \mathrm{HOOC{-}CH_2{-}CH_2{-}COOH}$$

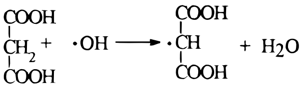
**(R7)**

Kaiser and co-workers[11] also found alkyl malonyl radicals during the UV irradiation of malonic acid. They suggested that there was another primary process, the O,CO bond cleavage (R8). This would lead to hydroxyl and acyl-type radicals. The



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{CH_2}\\|\\\mathrm{COOH}\end{array} \xrightarrow{h\nu} \begin{array}{c}\mathrm{CO}\,\cdot\\|\\\mathrm{CH_2}\\|\\\mathrm{COOH}\end{array} + \cdot\,\mathrm{OH}$$

**(R8)**



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{CH_2}\\|\\\mathrm{COOH}\end{array} + \cdot\,\mathrm{OH} \longrightarrow \cdot\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{CH}\\|\\\mathrm{COOH}\end{array} + \mathrm{H_2O}$$

**(R9)**

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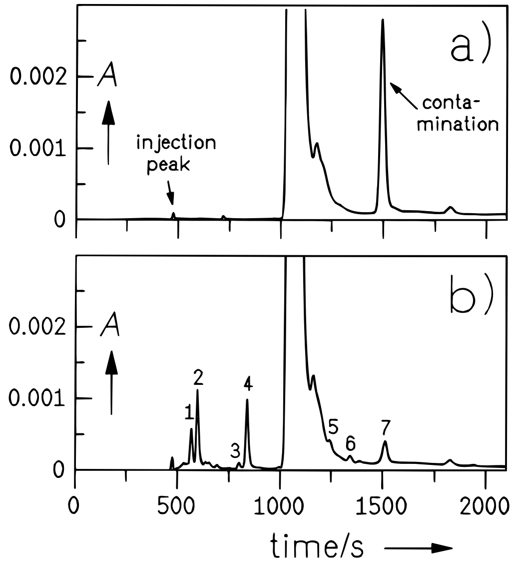


**Figure 1.** HPLC spectra (absorption *A* versus time) of a 2 M malonic acid solution in 1 M sulfuric acid: (a) Before illumination; (b) after 6 h of illumination with UV light. The peak at $t_{ret} = 1495$ s corresponds to a contamination in malonic acid which disappears under UV irradiation within 1 h. Note that the new peak 7 appears at $t_{ret} = 1511$ s.

reactive $^{\bullet}$OH radical would certainly abstract an H-atom from the acid and in this way generate the observed alkyl malonyl radical (R9). Direct evidence for this mechanism was not possible, however, because the assumed acyl-type radical was not detectable in their ESR experiments.

Our aim here is to generate malonyl radicals with UV irradiation and to study in this way their reactions in the absence of $Ce^{4+}$. Naturally the HPLC technique applied here is not able to detect the organic free radicals themselves but only their recombination products. Knowledge of these secondary products, however, can help to identify the primary radicals participating in these reactions.

## Experiments

The HPLC experiments were performed with Shimadzu equipment (LC-10AS pump, CTO-10A column oven, SPD-10A dual-wavelength UV detector working at 220 nm, 8-nm bandwidth, 8-$\mu$L cell volume) using an ion-exchange column (Merck, Polyspher OA KC column with a length of 30 cm and diameter of 9.5 cm). The temperature was controlled at 45 °C with the column oven. The eluent was 0.01 M $H_2SO_4$ (flow rate of 0.40 mL/min.). The sample was injected using a Rheodyne 7010 injector with a 20-$\mu$L sample loop.

The irradiation was performed in a closed quartz cell with an optical path length of 1 cm. The solutions were purged with nitrogen for 30 min before the irradiation. The light source was a 200-W Hg lamp (the light intensity was 640 W/m$^2$). The samples were diluted 100 times with water before the injection into the HPLC instrument.

$H_2SO_4$ (Merck 95%) was used without further purification. Malonic acid (Fluka puriss.) was recrystallized twice from water. All solutions were prepared with doubly distilled water.

## Results

We studied the products of UV irradiation of malonic acid in sulfuric acid (Figure 1) and in water. One problem was a contaminant in the malonic acid resulting in a peak at a retention time of 1495 s. We were not able to identify it. However, this compound disappears completely within 1 h of UV irradiation. The observed HPLC peaks of the irradiation products are summarized in Table 1, and the concentrations of these products were calculated from calibration curves of Sirimungkala.[12]

**TABLE 1: Retention Times $t_{ret}$ and Concentrations *c* of Products in a Solution of 2 M Malonic Acid after 6 h of UV Irradiation**

| | | | $c/10^{-5}$ M | |
|---|---|---|---|---|
| peak | $t_{ret}$/s | compound | in 1 M $H_2SO_4$ | in water |
| 1 | 570 | MAMA | 0.62 | 0.26 |
| 2 | 600 | ETA | 1.9 | 0.8 |
| 3 | 800 | tartonic acid | 0.23 | |
| 4 | 840 | ETRA | 4.7 | 3.4 |
| 5 | 1240 | succinic acid | 2.3 | 1.5 |
| 6 | 1345 | unidentified | | |
| 7 | 1511 | acetic acid | 13 | 17 |

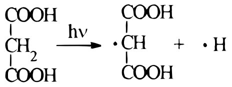
The identified products were monomalonyl malonate, 1,1,2,2-ethanetetracarboxylic acid, tartronic acid, 1,1,2-ethanetricarboxylic acid (ETRA), succinic acid, and acetic acid. The products of photochemical decomposition of malonic acid in water and sulfuric acid are the same, but in water we got less products (except acetic acid) according to smaller quantum yield.[8,13]

## Discussion

Apparently acetic acid is the main reaction product. First we tried to interpret our results accepting the reaction scheme suggested by Kaiser et al.[9−11] According to their theory, acetic acid is formed in R6, a reaction between acetyl and carboxyl radicals. Moreover, it is also assumed that these radicals are formed in a 1:1 stoichiometric ratio from malonic acid in its photochemical decomposition (R5). If their scheme is correct, then recombination products of both radicals should appear. Indeed, succinic acid, a recombination product of acetyl radicals (see R7), was found both in Kaiser's and in our experiments. The other expected recombination product would be oxalic acid (a recombination product of two carboxyl radicals). In contrast, no oxalic acid was found either in our or in Kaiser's experiments. Within Kaiser's scheme, this result can be explained only if we assume that the recombination reaction between carboxyl radicals is much slower than R6 or R7. This is not very probable. Another assumption which is also hard to accept is that $CO_2$ is a product of R6. The main product of a recombination reaction between acetyl and carboxyl radicals should be malonic acid. On the other hand, without R6 we have no explanation within this scheme for the experimentally observed $CO_2$ evolution.[14]

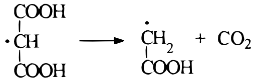
A further problem of the scheme is the generation of malonyl radicals. The appearance of MAMA and ETA among the reaction products (see Table 1) proves that malonyl radicals are important intermediates in the photochemical degradation of malonic acid. In Kaiser's scheme, malonyl radicals emerge in a sequence where the first intermediates are hydroxyl and acyl-type radicals. We did not observe, however, any recombination products of either the hydroxyl or the acyl-type radicals. Consequently, there is no direct (ESR) or indirect (HPLC) evidence that alkyl malonyl radicals are formed according to the sequence R8 and R9.

The above considerations show that, at least in the case of malonic acid, it is rather difficult to explain the experimental findings with the mechanism proposed by Kaiser et al.[9,10] Therefore, we suggest a new reaction path for the formation of alkyl malonyl radicals: This sequence explains the formation



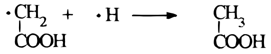
$$HOOC-CH_2-COOH \xrightarrow{h\nu} HOOC-\dot{C}H-COOH + \cdot H$$

**(R10)**



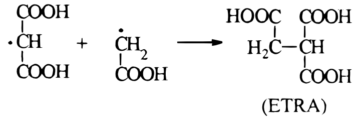
$$HOOC-\dot{C}H-COOH \longrightarrow \dot{C}H_2-COOH + CO_2$$

**(R11)**



$$\cdot CH_2-COOH + \cdot H \longrightarrow CH_3-COOH$$

**(R12)**



$$HOOC-\dot{C}H-COOH + \dot{C}H_2-COOH \longrightarrow \underbrace{HOOC-H_2C-CH(COOH)_2}_{\text{(ETRA)}}$$

**(R13)**

of acetic acid as well as the formation of $CO_2$. We have only three types of radicals with the carboxylato type formed in reaction R2. The recombination of these radicals in reactions R3, R4, R7, and R13 can produce the detected products, ETA, MAMA, ETRA, and succinic acid; tartronic acid appears as a hydrolysis product of MAMA.[7] (The hydrolysis of the ester MAMA is slower in water than in 1 M sulfuric acid medium. This explains why tartronic acid appeared only in experiments performed in 1 M sulfuric acid but not when the medium was pure water.) In this case, we do not need ·COOH and the undetected ·OH and acyl-type radicals to explain the formation of products. Our conclusion is that the primary reaction during the UV irradiation of malonic acid is the reaction R10 instead of R5. Accordingly, we can neglect reactions R6, R8, and R9 too; this means that the decomposition of malonic acid under UV irradiation is different from the decomposition of the other acids studied by Kaiser et al.[9−11]

Our findings can shed some light on the mechanism of the Ce$^{4+}$−malonic acid reaction[6,7] as well. In both cases, the most important reactions are recombinations. During the oxidation of malonic acid by Ce$^{4+}$, the primary reaction products are ETA and MAMA only. In this case, acetic acid, succinic acid, and ETRA are not formed. In other words, recombination products of the acetyl radical are missing. Naturally H-atoms necessary for the acetic acid production are also absent but succinic acid and ETRA should still appear because their formation requires only acetyl radicals. The absence of these products strongly suggests that acetyl radicals, unlike malonyl radicals, can react with Ce$^{4+}$. To reveal the products and the mechanism of this reaction requires further research, however.

**Acknowledgment.** We thank H. Schreiber and J. Oslonovitch for discussions and for their help in the experiments. The authors thank the Deutsche Forschungsgemeinschaft, the Stiftung Volkswagenwerk, and the Fonds der Chemischen Industrie for financial support. Additionally, Z.N. was supported by OTKA (T-017041) and FKFP (0287/1997) grants, and I.S. was supported by OTKA (F 017073) and MHB (44/96/I) grants.

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(12) Sirimungkala, A. Ph.D. dissertation, Philipps-Universität, Marburg/Lahn, Germany, 1996.

(13) As one of our Reviewers pointed out, there is a larger amount of recombination products (like MAMA and ETA) and a smaller amount of the decarboxylation product acetic acid in sulfuric acid medium than in water. The observation suggests that sulfuric acid slows down the decarboxylation of malonyl radicals. This behavior is in contrast with that of malonic acid, where sulfuric acid facilitates decarboxylation of the molecule.

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