Oscillatory Oxidation of Malonic Acid by Bromate

3. CO_2 and BrO_3^--Titration

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The reaction of malonic acid and bromate in the presence of catalytic amounts of cerious ion under oscillating conditions in sulphuric acid was investigated. After two hours reaction time 26 mM bromate were consumed and 42 mM CO_2 produced. No formic acid was detected. Furthermore, ^{14}C-tracer experiments suggest that malonic acid is first brominated and subsequently decarboxylated.

Introduction

In earlier communications we described the results of an investigation of the main products of the oscillating oxidation of malonic acid by bromate[1]. The products were identified as monobromomalonic acid, dibromoacetic acid and CO_2. Also, the relative quantities of the two organic products were determined.

Current hypothesis on the mechanism of the reaction pathway under oscillating conditions stress the importance of the decarboxylation step of the organic acid as well as the oxidation step of bromate ions in the function of the oscillation (see l. c. [2–4]). However, it is not known to what extent these reaction schemes fit the overall pathway. Therefore, we analysed quantitatively the relationship between the amount of bromate used and the amount of CO_2 produced under stationary oscillating conditions, the results of which are reported in this paper.

Material and Methods

1. *Determination of bromate*

Bromate was determined according to the method given in[5] under the following conditions: 2 ml samples of the reaction solution were collected and stored at 0 °C in order to be lateron pipetted into the pre-cooled vessel (0 °C) of a titration apparatus (pH-meter 26 radiometer, Copenhagen) containing 2 ml acidified Na_2SO_3 (purchased from Merck AG, Darmstadt – p.a. grade) solution. The amount of Na_2SO_3 present in the solution was enough to neutralize most of the bromate present. The remaining bromate was titrated under vigorous stirring by a 1.3 M Na_2SO_3 solution using the redox potential recorded by a platinium electrode with a silver chloride electrode as indicator. The bromate content was recalculated under the assumption of a reaction of 3 moles of SO_3^{--} with one mole of bromate.

2. *Determination of CO_2*

A stream of nitrogen gas was bubbled through the reaction solution followed by bottles filled with 0.1 N NaOH (Fixanal obtained from Riedel de Haen AG., Seelze). The amount of CO_2 absorbed was titrated with 1 N H_2SO_4 (Fixanal) at a pH of 7 to 8, using a pH-recorder.

3. *Determination of $^{14}CO_2$*

$^{14}CO_2$ was also trapped with a stream of nitrogen in approximately 5 ml of 0.1 N NaOH. The amount of CO_2 absorbed was titrated as given unter 2. After titration the solution is poured into a scintillation vial filled with 15 ml of Bray-solution[6] and 50 μl of phenylethylamine. The radioactivity was counted in a scintillation counter (Tracerlab-Betamatic model 40).

4. *Isotopics*

^{14}C-labelled malonic acid was obtained from the radio center Amersham with a specific activity to 9.5 μCi/mmole and tested in Bray's solution.

5. *Reaction medium*

The reaction solution was prepared as given previously[1]. The initial concentrations were: $[BrO_3^-] = 0.063$ M; [malonic acid] $= 0.2$ M; $Ce(SO_4)_2 = 10^{-3}$ M in 1 M H_2SO_4 aqueous solution. Total volume 100 ml, room temperature.

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Results

The overall advancement of the oxidation of malonic acid by bromate can be followed by a determination of the amount of bromate consumed and CO_2 produced. Thus, samples were taken at zero time immediately before the addition of cerous ions as well as 10 and 120 min after the initiation of the reaction. The 10-min sample coincides with the initiation of the oscillatory reaction course. At 120 min the oscillation is still proceeding. The results of titrations of bromate by SO_3^{--} are shown in Table I. As expected, the bromate concentration decreases with time and an equivalent amount of CO_2 is produced (see Table I).

Table I. Titration of bromate by SO_3^{--}.

Time of reaction t [min]	$[BrO_3^-]_{(tx)}$ / $[BrO_3^-]_{(t0)}$	Concentration in solution BrO_3^- [M]	Equivalent concentration of CO_2 [M]
0	1.0	0.063	0.0
10	0.86	0.055	—
120	0.57	0.034	0.042

In addition to the determination of the overall production of CO_2, tracer experiments were carried out. In order to find out whether CO_2 is produced from a pooled intermediate or from the primary substrate of the reaction, the amount of radioactivity incorporated into CO_2 from ^{14}C-labelled malonic acid in position 2 was determined after addition of labelled malonic acid at different times to the oscillating system.

In one experiment, labelled malonic acid was added to the solution before the reaction was started by addition of the catalyst. The gas evolved was absorbed between the 15th and 30th min after the initiation of the reaction. In a second experiment, the label was added 20 min after initiation of the reaction and the gas was trapped 5 min later for approximately 20 min.

The amount of tracer found after addition of the label prior to the addition of the catalyst was 4030 dpm per 0.1 mmole of CO_2, whereas later addition yields 1190 dpm for 0.1 mmole of CO_2. The corresponding specific activities are 18.2 and 5.4 μCi/mole respectively. Furthermore, initially, samples of the reacting solution were neutralized by NaOH and assayed for the radioactivity of malonic acid. For 50 μl of the reaction volume a value of 1200 dpm was found corresponding to a specific activity of 60 μCi/mole of malonic acid.

Discussion

On the basis of the chromatographic detection of monobromomalonic acid and dibromoacetic acid as brominated compounds the following overall reaction scheme can be applied:

$$3\,H_2C(COOH)_2 + 2\,BrO_3^- + 2\,H^+ \rightarrow 2\,BrHC(COOH)_2 + H_2O + 3\,CO_2\,, \qquad (A)$$

$$2\,H_2C(COOH)_2 + 2\,BrO_3^- + 2\,H^+ \rightarrow Br_2HC\,COOH + 4\,H_2O + 4\,CO_2\,. \qquad (B)$$

Two hours after initiation of the reaction the ratio of the two brominated compounds with respect to malonic acid are estimated to about 0.14 and 0.023 respectively as shown in[1]. Here, the amount of bromate consumed and CO_2 produced during the two hours of reaction was found to be 0.026 M and 0.042 M respectively. The ratio of CO_2 to BrO_3^- is calculated to 1.6. This ratio should be 1.5 on the basis of reaction (A) and 2.0 on the basis of reaction (B). Since there is about 6.1 times more bromomalonic acid accumulated than dibromoacetic acid (see[1]), the proportion of the extents of reaction (A) and (B) should be 3.05 : 1.

An advancement ζ_A for reaction A of about 0.098 M and ζ_B for reaction B of 0.0032 M can be computed from the amounts of BrO_3^- and CO_2 detected, on the basis of the following equations:

$$\Delta[BrO_3^- = 2\,\zeta_A + 2\,\zeta_B\,,$$
$$[CO_2] = 3\,\zeta_A + 4\,\zeta_B\,.$$

With the computed extents the concentration of the components after 2 hours of reaction are estimated as follows:

$$\begin{aligned}
[H_2C(COOH)_2] &= 0.2 - 3\,\zeta_A - 2\,\zeta_B = 0.164\ \mathrm{M}\,,\\
[BrHC(COOH_2)] &= 2\,\zeta_A = 0.020\ \mathrm{M}\,,\\
[Br_2HC\,COOH] &= \zeta_B = 0.003\ \mathrm{M}\,,\\
[BrO_3^-] &= 0.063 - 2\,\zeta_A - 2\,\zeta_B = 0.037\ \mathrm{M}\,,\\
[CO_2] &= 3\,\zeta_A + 4\,\zeta_B = 0.042\ \mathrm{M}\,,\\
[H^+] &= 2\,\zeta_A - 2\,\zeta_B = 0.026\ \mathrm{M}\,.
\end{aligned}$$

The concentration ratios estimated from the gas chromatographic analysis (see[1]) agree with the values obtained here. Thus, for the set of initial concentrations used, the experimental results are described by the two overall reactions. It should be pointed out, that further reaction leading to oxidation products of malonic acid cannot be excluded on the basis of the present data, however, such reactions should not contribute more than about $10-20\%$ to the overall scheme.

The overall reactions given here do not contain formic acid as final product as suggested elsewhere[4]. Under the conditions used, the chromotropic acid test for formic acid[7] in the reaction mixture as well as in a destilled sample failed to indicate the presence of formic acid. Thus, significant amounts of formic acid are not formed under our conditions used.

The results of the tracer experiments are also in agreement with the reaction scheme. If malonic acid is transformed into brominated acids, it can be assumed that the ^{14}C-label in the two position of malonic acid is fixed. Then, in reaction A the specific activity of CO_2 should be 1/3 of that of malonic acid (C), whereas in reaction B the specific activity of CO_2 should be only 1/4. The expected specific activity of CO_2 generated in both reactions is given by:

$$C^*_{CO_2} = \frac{\zeta_A + \zeta_B}{3\,\zeta_A + 4\,\zeta_B} \cdot C^* \;;$$

a value for the advancements ζ_A and ζ_B obtained after 2 hours of reaction time of 18.5 is computed in agreement with the value measured after addition of the tracer before the reaction is started.

The lower value obtained if the tracer is added lateron to the reaction solution can be explained by the assumption that not malonic acid is decomposed to CO_2 but that malonic acid is first brominated and finally a component of the brominated acid pool is decarboxylated. In order to distinguish between the different possible pathways of the reaction course more tracer experiments are needed. However, one should expect that formic acid contains the tracer, if it could be the essential end-product. Since clearly the tracer is incorporated into CO_2 and the quantitative values obtained for the concentration of the compounds agrees with the one calculated from the reactions A and B, it can be concluded that formic acid is not a major product under the set of initial conditions used in this experiment.

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