Degradation of Lactic Acid and Pyruvic Acid in Belousov-Zhabotinskii Reactions

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Dedicated to Friedhelm Schneider on the occasion of his 60th birthday

The temporal degradation of the Belousov-Zhabotinskii substrates lactic acid, pyruvic acid, bromo- and dibromo pyruvic acid is investigated. The only final product of non-brominated substrates is acetic acid. From brominated educts only brominated acetic acids result. The concentrations of the stable products are determined as a function of time. The gross reactions are mainly based on simple consecutive first order reactions. For the pyruvic acid rate constants are determined.

1. Introduction

The investigation of oscillating reactions of the Belousov-Zhabotinskii-type (BZR) seems to have been completed as a result of the precise analysis of the actually oscillating partial systems, the inorganic bromine compounds.

In the beginning this research led Field, Körös and Noyes to the FKN-mechanism [1] which enabled them to interpret the malonic acid/KBrO₃/Ce(H₂SO₄) system. This was followed in 1974 by a more general model of the reaction – the Oregonator model [2], which was modified by Noszticzius and Farkas in 1984 (Explodator model [3]). It is significant that in general only the temporal composition and reaction mechanism of the inorganic bromine species have been described. This is also valid for the reaction kinetic approaches [4]. In the case of other compounds more precise research exists only for the (also oscillating) release of carbon dioxide in the BZR with oxalic acid [5].

Little attention has been paid to the detailed description of the behaviour of organic substrates other than malonic acid [6], although the break-down of these species provides the energy for the oscillating alterations of the concentrations of the inorganic bromine compounds. This is particularly true for biochemical systems with periodical behavior, too [7]. It can furthermore be expected that the degradation of certain substances and their momentary con-

centration level contribute at least to the initiation of the oscillation and its duration.

In the meantime quite a number of different organic substances have been discovered to be suitable for the BZR. Apart from the classical BZR substrates citric acid and malonic acid there are dibromomalonic acid [7] and other derivatives of malonic acid [8], catechol [9], cyclic and aliphatic ketones [10, 11, 12], mandelic acid [13], tartronic and tartaric acid [14], oxalic acid [4, 5], glycolic acid [15], lactic acid [16] and ascorbic acid with its possible degradation products as erythronic acid, glyceric acid and pyruvic acid [17]. Mixtures of biochemically relevant substances like ascorbic acid or NADH with acetone have furthermore been investigated [18].

It should be asked whether – analogeous to the inorganic part of the BZR – generalizations can be made for the organic part of the BZR. Its aim would be to find out the conditions in which, independent of the type of substance, oscillating reactions are possible.

This paper presents a more detailed description of the break-down of substrate molecules during the oscillations. It aims at the identification of stable intermediates and final products as well as at the investigation of temporal changes of concentrations in comparison with the development of the oscillation.

As BZR substrates lactic acid and pyruvic acid were chosen because they play a common role as redox pair (at least in the BZR with lactic acid). This also applies for the glycolysis, which also shows an oscillatory behaviour [19].

In order to verify the possible effect of bromination of substrates on the BZR, the behaviour of

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liable intermediates like monobromo- and di-bromopyruvic acid was also investigated.

2. Methods

2.1 Sampling for kinetic analysis

For the determination of the temporal change of the composition the reaction has to be interrupted at a given time. This is done by adding sodium disulphite, which drastically lowers the redox potential of the solution. Consecutive products are only inert bromide and sulphate ions.

Although this procedure constantly requires new approaches, the yielded c/t-curves can be evaluated like a continuously recorded kinetic measurement. This is due to the excellent reproducibility of the BZR, which is so far-reaching that even the number and the form of the oscillation bands and the duration of periodical behaviour coincide in newly mixed, identical compositions. This can be achieved by following the reaction conditions exactly. In this respect mixturing and constancy of temperature are particulary important. Furthermore an undisturbed gaseous phase is essential as it contains a lot of bromine and volatile organic compounds such as aldehydes or ketones. These substances obviously take part in the BZR as the blow-off with nitrogen immediately leads to perturbations or can even bring the oscillations to an end [17].

2.2 Separation of the organic compounds

During break-down a number of chemically quite silimar and moreover water-soluble substances as carboxylic acids and carbonyl compounds occurs.

The analysis of the organic part of the BZR compositions which aims at the identification and quantitative isolation of the involved substances is not directly possible. This results not only from high concentrations of bromate, elementary bromine, bromoxo compounds, sulphuric acid and high ionic strength, but also from the low concentrations of substrate, intermediates and final products. (It should be noted that the BZR system contains only 4.8 mmol substrate.)

Thus the use of ion exchangers or other chromatographic methods is impossible. Nor will the attempt be successful to separate carbonyl compounds *e.g.* by precipitation as 2,4-dinitrophenylhydrazones. The detectability of the traces of carbonyl compounds is moreover lowered by the presence of hydrogensulphite, which is needed to stop the oscillations.

Of all the methods for the separation of acids and carbonyl compounds from the reaction mixture the extraction with diethyl ether proved to be most effective. That particular method described in [19] in which the BZR compositions are extracted once with the same volume of ether allows only the identification of the compounds, but not their quantitative determination. For that reason the method had to be modified and standardized. It was calibrated for each of the single carboxylic acids as possible compounds of the reaction system. The acids in question were added to sulphuric acid in several different concentrations in a scale according to the BZR compositions and then extracted. The concentrations of the acids in extract were then determined by gaschromatography.

In order to be able to transfer the results of the calibration to the investigation of the BZR systems it was necessary to ensure similar conditions as *e.g.* the concentration of the sulphuric acid and ionic strength. Cerium salt was not added in order to avoid break-down reactions.

2.3 Identification of involved substances and determination of concentrations

The possible intermediates and final products are lactides and lactones, esters of inorganic acids, carboxylic acids, ketones, aldehydes and bromination products.

The acids were identified and their concentration was determined by gaschromatography. Acetic acid could be measured directly. In the case of lactic acid, pyruvic acid and possible brominated acids it was necessary to esterfy them before with diazomethane. For comparision the lactic acid lactide was synthesized. The same was done with possible bromination products.

The identification of carbonyl compounds in question like acetaldehyde, acetoin and diacetyl, which are expected as intermediates, proved to be difficult as sulphite ions and remainders of bromoxo-compounds disturb the usual detection reactions. On the other hand, the intermediates exist only in such low concentrations that the determination by formation of oximes, hydrazones *etc.* is not precise enough. Due to the chemical composition of the reaction solution the enzymatic determination of the aldehyde proved to be impossible. *E.g.* aldehyddehydrogenase/

NAD^+ shows positive effects without substrates, too. Furthermoore, the identification of the carbonyl compounds by GC-MS-system also causes difficulties as the fragments of the molecules are rather similar.

For that reason the concentration of the intermediates was calculated as the sum of the relative concentrations of all reaction partners must add up to 100%.

2.4 Volume determination of carbon dioxide

In the BZR in question carbon dioxide is released. The quantity of the gas gives information about the degradation of the reductant because it is possible to deduce from the number of moles of collected gas the number of remaining C-atoms in the final product. A general problem is the kinetic interpretation of the volume/time curves. When the gas is continuously collected, the reaction is retarded as the oscillation has been disturbed. Besides that, the self-adsorption of the reaction system must be taken into account as this in general results in a small delay of the release of CO_2. For that reason an evaluation of the volume/time curves is only possible within limits.

The bromine vapour, which disturbs the gas measurement, is removed by conducting the gases through a soft PVC hose, which binds bromine. In the gaseous phase there are also small amounts of carbonyls.

3. Experimental Part

3.1 Composition of the BZR solutions

In all cases sulphuric acid ($c = 1.5$ mol l^{-1}) is solvent. The absolute absence of chloride ions is indispensable. For that reason it is necessary to use only water distilled in a quartz apparatus.

The reaction is carried out under constant stirring in a closed thermostatable reaction vessel (*e.g.* Metrohm EA-880-T-20). If not stated otherwise the reaction temperature was 20 °C.

The optimum molar composition of the reaction mixture in all investigated systems is: [substrate] = 0.127 mol l^{-1}, [$KBrO_3$] = 0.198 mol l^{-1}, [$Ce(SO_4)_2$] = 0.0047 mol l^{-1}.

12 ml substrate solution ($c = 0.4$ mol l^{-1}) is added to 25 ml $KBrO_3$ solution ($c = 0.3$ mol l^{-1}). The oscillation is started by adding 0.9 ml Ce(IV)-solution ($c = 0.2$ mol l^{-1}).

In the cases of lactic acid and pyruvic acid sodium salts were used. The dibromopyruvic acid was synthesized according to [20].

3.2 Measurement of the redox potential and the bromide ion activity

Redox electrode: platinum plate (Metrohm EA 211); bromide ion sensitive electrode: Metrohm E 306-Br; reference electrode: mercurous sulphate (Hg/HgSO₄; sat. K_2SO_4, Metrohm EA 406).

3.3 Interruption of the BZR

The reaction is interrupted at the given time by adding 3 g of solid sodium disulphite. The solution heats up in the process. The vessel must be closed quickly after the addition in order to prevent the vaporization of volatile compounds.

3.4 Extraction of the BZR approaches

The solution is extracted five times with 70 ml diethyl ether (free from acetaldehyde) by shaking for two minutes. The united ether phases are dried with 20 g sodium sulphate and then filtered. The residue is washed three times with $10-20$ ml ether each. Afterwards the filtrate is concentrated at 45 °C in the rotation evaporator to a rest volume of $5-10$ ml.

The extraction method is calibrated for each substances in five initial concentrations of simulated set-ups between 0.48 and 4.8 mmol (without addition of cerium salt).

3.5 Preparation of the carboxylic acid ester

Etheric diazomethane solution is added dropwise to the extracts until a weak yellow colouring remains. Then the solution is filled up with diethyl ether to 50 ml. In the case of pyruvic acid it is important to note that its methylester reacts in a slow consecutive reaction, which proved to be of first order, with the excessive diazomethane to 2-methyl-oxirane carboxylic acid methylester [21]. Therefore the GC-analysis should be carried out immediately after the esterification. Otherwise the peak of the oxirane has to be taken into account in the concentration determination of the pyruvic acid. For comparison the oxirane carboxylic acid methylester was synthesized according to [22].

To a small extent a dimerization product of lactic acid is formed, which, however, was not identified further. Its peak was also considered in the concentration determination of the lactic acid.

3.6 GC-Analysis of the acids and esters

For the determination of acetic acid and the methyl esters of lactic acid, pyruvic acid and 2-methyl-oxirane carboxylic acid 5% FFAP on Chromosorb W-HP ($80-100$ mesh; Macherey-Nagel) was used as adsorbent. In order to get the factual momentary

concentrations in the reaction composition, the values determined by GC have to be multiplied with the correction factors which have been obtained in the reference calibration of the extraction method.

3.7 Concentration determination of the intermediates

Under the presumption that there exists mainly a consecutive reaction sequency, the value can easily be calculated as a function of time as for each given moment the sums

[lactic acid] + [pyruvic acid] + [intermediates] + [acetic acid] have resp. [pyruvic acid] + [intermediates] + [acetic acid]
to add up to 4.8 mmol.

3.8 Measurement of the gas volume

For the adsorption of bromine the gas which was released during the BZR is conducted through an approximately 15 cm soft PVC hose into gas syringes. It is collected for a period of three of four hours. The equivalent of 4.8 mmol under the conditions of this investigation is 116 ml carbon dioxide.

The gaseous phase should also be examined with regard to its contents of carbonyls. It must be considered in this respect that bromine and bromoxo-compounds also react with most aldehyde reagents like chromotropic acid, 2,4-dinitrophenylhydrazine or NAD^+/AldDH.

4. Results

The following stable main compounds were identified in the lactic acid-BZR system: lactic acid as educt, pyruvic acid and acetaldehyde as intermediates and acetic acid and carbon dioxide as final products. There are hints for the presence of diacetyl and acetoin. Lactid, lactones and stable brominated compounds could not be detected.

As the pyruvic acid-BZR system proved to be to a large extent a subsystem of lactic acid the results of the degradation of pyruvic acid will be discussed first.

4.1 The pyruvic acid-BZR system

After adding of cerium(IV)-solution to the BZR mixture a great amount of elementary bromine is abruptly released (Landolt effect). The diagram of the potential/time (u/t)-curve (Fig. 1 a) shows that after an initial phase of 1.5 min the oscillation starts. Simultaneously the release of carbon dioxide begins.

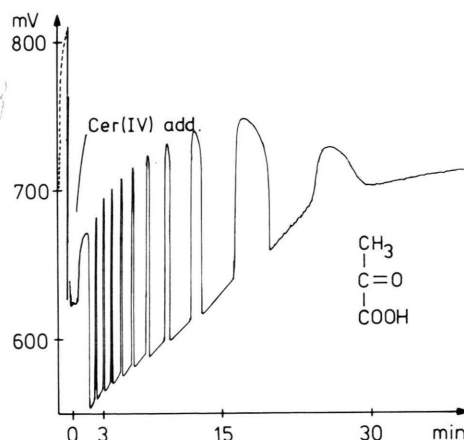The oscillation has a duration of 32 minutes and produces 10 peaks. Their shape remains relatively

Fig. 1a. Redox measurement of pyruvic acid-BZR system at 20 °C (Potentials referring to $Hg/HgSO_4$ (sat. K_2SO_4)).

constant up to an oscillation duration of 5 minutes. Then the frequency decreases.

Fig. 1b shows the temporal alteration of the bromide ions activity. The comparison with Fig. 1a supports the well-known fact that only bromine species contribute to the oscillation phenomenon.

The c/t-curves of substrate and products (Fig. 1c) present a completely different picture. The degradation of the pyruvic acid begins immediately after the adding of cerium(IV)-solution. 45% of it are already transformed after the initial phase of 1.5 minutes. After 5 minutes, when the oscillation frequency decreases significantly, the rest concentration is only about 10%. Later, after an oscillation duration of 17
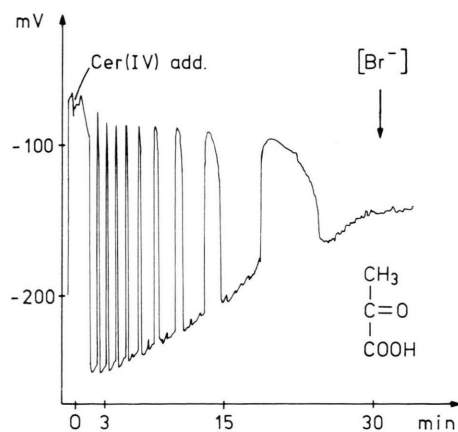

Fig. 1b. Measurement of the bromid ion activity in the pyruvic acid-BZR system.
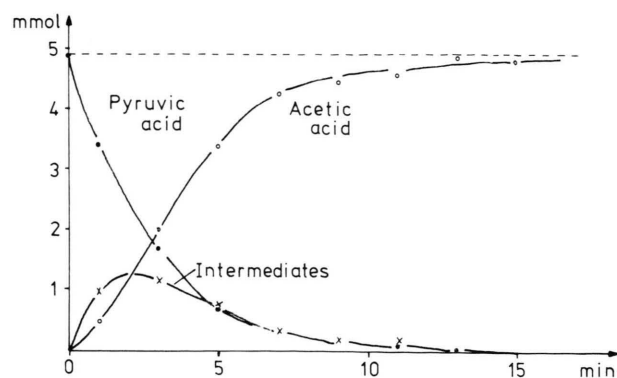
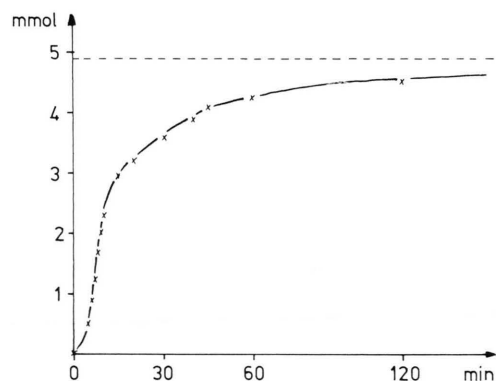Fig. 1c. C/t-curves of the pryruvic acid-BZR system.

Fig. 1d. Release of carbon dioxide in the pyruvic acid-BZR system.

minutes, the acid is gaschromatographically no longer detectable and, thus, the oscillation ends.

The volume/time-curve of CO_2 release (Fig. 1d) shows that the total gas volume is equivalent to the cut-off of one C-atom. This value is attained a while after the fading of the oscillations.

The final product of the break-down of pyruvic acid is acetic acid. The turning point of the c/t-curves of acetic acid hints at the existence of an intermediate product which is in literature generally described as acetaldehyde [16, 23]. There is, however, strong evidence of the presence of acetoin and diacetyl although these could not be identified with certainty. Under the conditions of the BZR they can be formed from acetyl radicals [24]:
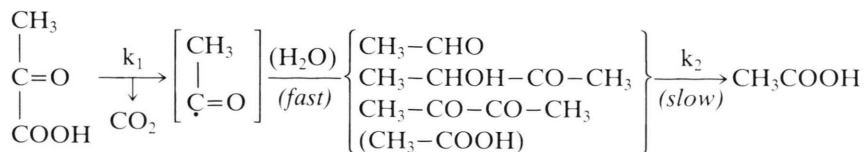
The formed intermediates are decomposed as well, thus, the c/t-curve of them, which has been obtained by difference calculation, shows a maximum.

Acetaldehyde is oxidized by bromate to acetic acid [25]. But under the given experimental conditions acetaldehyde is not a substrate of BZR and does not support the oscillations. It can be shown that this compound even suppresses the oscillations in the given concentrations. On the other hand, diacetyl and acetoin are substrates for BZR. Final product of the break-down is again only acetic acid. The oscillations, however, are not particulary significant (Fig. 2a, b). In the case of acetoin *e. g.* there appears after a long initial phase always only one peak. This proves that the oscillations of the pyruvic acid-BZR system decrease after the degradation of the pyruvic acid in spite of the high reducing capacity of the intermediate products.

The overall consecutive reaction can be formulated as follows:

$$\text{pyruvic acid} \xrightarrow[CO_2]{k_1} \text{intermediates} \xrightarrow{k_2} \text{acetic acid}$$
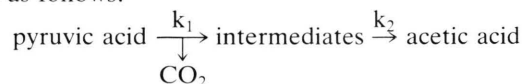
In spite of that the reaction depends furthermore on $[H^+]$ and $[BrO_3^-]$, both partial reactions are with regard to pyruvic acid and the intermediates of first order. This is due to the high concentration of sulphuric acid and the equivalent excess of bromate. The relation of [red]/[ox] is 1:4.7. Thus, k_1 and k_2 are constants of pseudo-first order [14, 16].
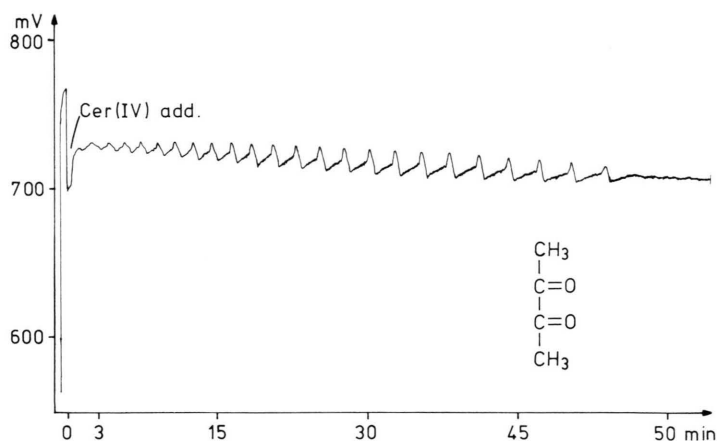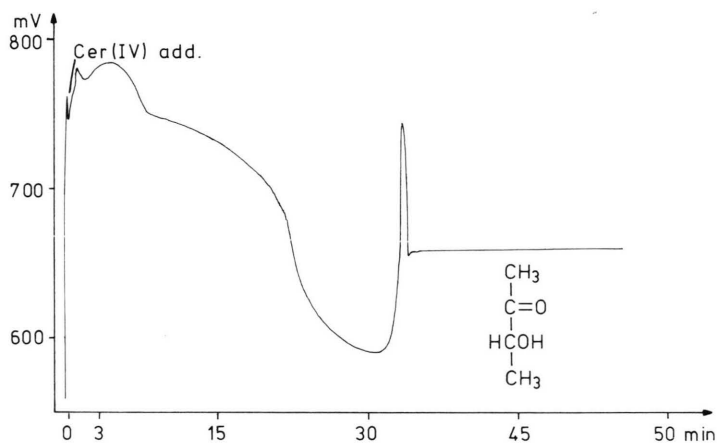
Fig. 2a. Redox measurement of the diacetyl-BZR system.

Fig. 2b. Redox measurement of the acetoin-BZR system.

The rate constant of the decarboxylation of pyruvic acid is $k_1 = 0.372$ min^{-1}. The transfer into the intermediate products proceeds so fast that it does not determine the rate of the total reaction. The value of k_2 cannot be determined precisely enough by numerical evaluation of the c/t-curves. This results from the errors in the concentration measurements. Scale and value of k_2 can, nevertheless, be estimated from the coordinates of the curve maximum point:

$$t_{max} = \frac{\ln(k_1/k_2)}{(k_1-k_2)}$$

The calculated value is $k_2 = 0.70$ min^{-1}. It is confirmed by curve-fitting on the basis of the well-known c/t-functions for consecutive reactions of the type $A \rightarrow B \rightarrow C$.

4.2 The lactic acid-BZR system

After adding cerium(IV) the reaction starts slowly. Only an extraordinarily slow release of bromine occurs. The release of CO_2, however, starts within a few minutes.

Fig. 3a presents the u/t-curve of the reaction. In contrast to pyruvic acid the long initial period is significant, as it correlates with the visible course of the reaction. After 17 minutes the initial phase is over. With the beginning of the oscillations the release of bromine starts, that of CO_2 increases significantly (Fig. 3d).

The course of the u/t-curve (Fig. 3b), recorded by use of a bromide ion sensitive electrode, is similar to the u/t-curve, recorded by use of a platinum elec-
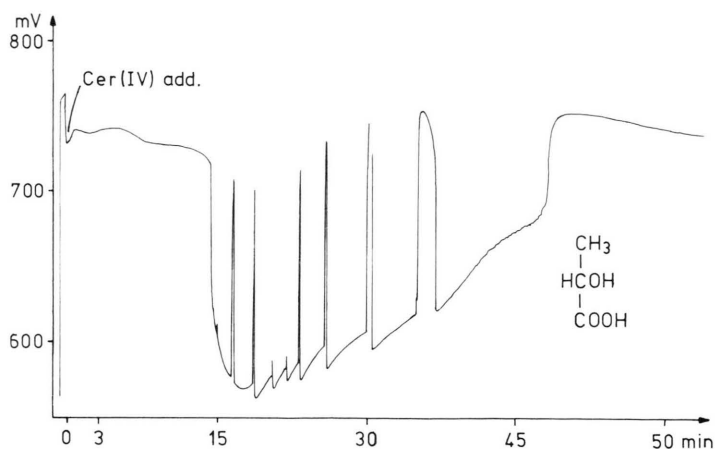
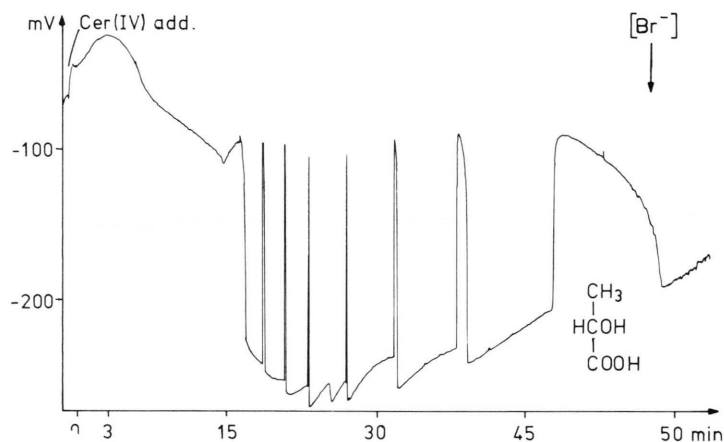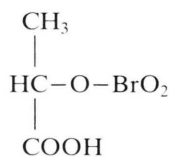Fig. 3a. Redox measurement of the lactic acid-BZR system at 20 °C.

Fig. 3b. Measurement of the bromid ion activity in the lactic acid-BZR system.

trode (Fig. 3a). The bromide ion activity remains very low during this phase, perhaps because other compounds like the bromic acid ester of lactic acid are formed [22]:

$$CH_3 - \overset{|}{HC} - O - BrO_2 - \overset{|}{COOH}$$

At the end of the initial phase the concentration of bromide increases slowly, accompanied by a simultaneously increasing release of bromine. After a certain level a strong release of bromine starts avalanche-like and at the same moment the oscillation begins, too.

From the c/t-curves of the organic compounds (Fig. 3c) it is obvious that the long initial phase correlates with a slow oxidation of the lactic acid to pyruvic acid. The curve reminds of autocatalytic processes or when inhibitions have to overcome.

The long initial phase is apparently necessary for the self-organization of the BZR system with pyruvic acid as substrate. After the masking respectively oxidation of the interfering hydroxyl group of the lactic acid and after reaching a certain level of pyruvic acid (c = 0.7 mmol) it starts to oscillate. In that particular moment the pyruvic acid curve reaches a maximum which signalizes that the oscillation takes place at the expense of this substance. In this respect the lactic acid-BZR is to a large extent a pyruvic acid-BZR with prior substrate formation.
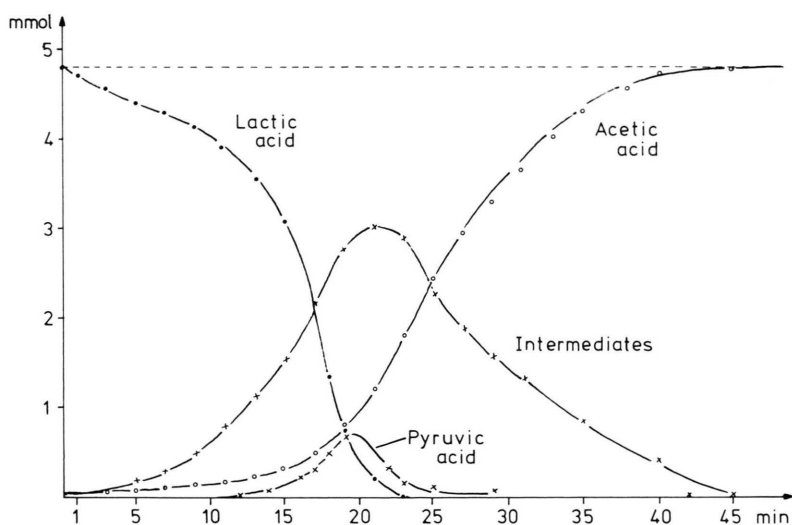
Fig. 3c. C/t-curves of the lactic acid-BZR system.

The c/t-curves of the other intermediates and products lead to the same conclusion. It has to be noted that already during the initial phase carbonylic intermediates (like acetaldehyde, acetoin and diacetyl) and thus also acetic acid have been formed. Pyruvic acid first is found when lactic acid has disappeared to a large degree. The bromic acid ester of the lactic acid which had already been mentioned and is probably primarily formed, could not be detected by GC. This ester decarboxylizes according to [23] under direct formation of acetaldehyde. For that reason CO_2 is already formed a long time before the beginning of the oscillation (Fig. 3d). The release of the total gas quantity is again equivalent to the separation of one C-atom. It is possible that in this reaction at first pyruvic acid is formed very slowly and then is fastly transferred to carbonyl intermediates. This leads to the permanently low concentration of pyruvic acid.

With the disappearance of lactic acid the level of intermediates builds up more strongly. Its maximum appears shortly after the one of pyruvic acid which is typical for consecutive reactions of the type $A \rightarrow B \rightarrow C \rightarrow D$.

The concentration of the intermediates is significantly higher than in the BZR with pyruvic acid as substrate. This is due to the fact that bromate, which
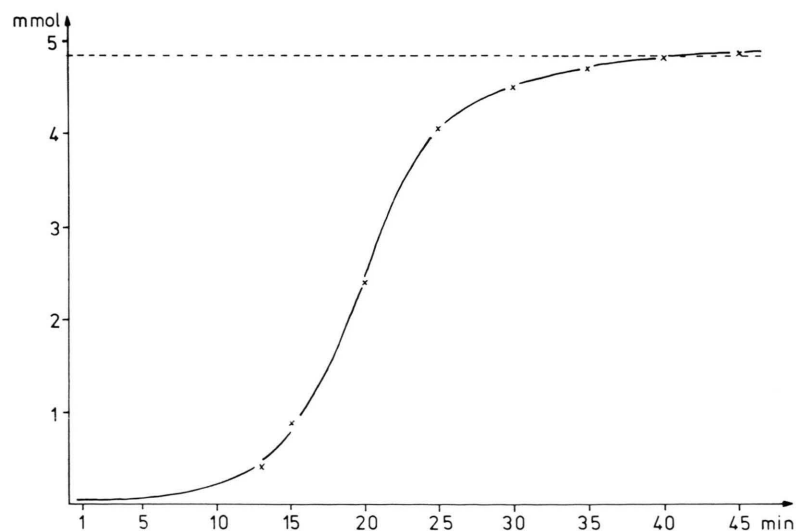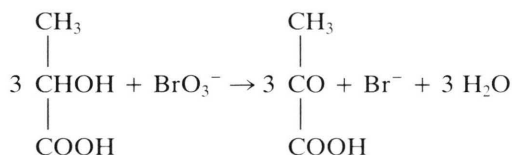

Fig. 3d. Release of carbon dioxide in the lactic acid-BZR system.

is necessary for the oxidation of the carbonyls, has too small a concentration as it is consumed to a great part in the lactic acid oxidation. This can be shown by comparision of the redox equivalents. For a rough calculation of the consumption of bromate by organic reducing substrates can be formulated as follows:

$$3 \; \underset{\overset{|}{COOH}}{\overset{\overset{CH_3}{|}}{CHOH}} + BrO_3^- \rightarrow 3 \; \underset{\overset{|}{COOH}}{\overset{\overset{CH_3}{|}}{CO}} + Br^- + 3 \; H_2O$$

Pyruvic acid is quickly decarboxylized and oxidized as a result of the high bromate concentration and is converted to acetic acid:

$$3 \; CH_3-CO-COOH + BrO_3^- \rightarrow$$
$$3 \; CH_3-COOH + 3 \; CO_2 + Br^-$$

Thus, the result of the gross degradation reaction of lactic acid is:

$$3 \; CH_3-CHOH-COOH + 2 \; BrO_3^- \rightarrow$$
$$3 \; CH_3-COOH + 3 \; CO_2 + 2 \; Br^-$$
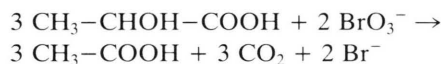
(Bromide ions react with further bromate to bromine.)

The primary oxidation of lactic acid takes up as much bromate as the subsequent oxidative degradation of pyruvic acid, which serves as the "engine" of the oscillation behaviour. Therefore the ratio of the redox equivalents is significantly lower in the beginning of the oscillation than in the case of pyruvic acid as BZR substrate. Redox ratios under 1:2.35 can be found here.

Moreover, hydroxyl compounds are very effective radical scavengers. Consequently they also disturb the build-up of the oscillating bromine system de-pending on radicals. Only when the concentration of hydroxyl groups has passed a certain very low level the oscillation starts. In this context the BZR system with glyceric acid as substrate [17] should be mentioned, which shows a considerably longer initial phase than lactic acid (31 minutes instead of 17 minutes). The same is also valid for acetoin in comparison with diacetyl (Fig. 2a, b).

The duration of the factual oscillation of both BZR systems with lactic acid and pyruvic acid as substrates is surprisingly similar despite the disturbances and concentration differences of bromate. This counts for form and number of the peaks. The pyruvic-BZR system appears relatively stable against disturbances. In the case of lactic acid the peaks are not particularly significant.

Besides the primary consumption of bromate, a further reason for the different behaviour of both systems can be seen in the different concentration levels of the intermediates (Fig. 1c, 3c). As the acetaldehyde disturbs the oscillations they become more irregular as its concentration increases. Acetoin and diacetyl oscillate too slowly and too insignifantly to contribute particularly to the BRZ as long as the bromate level is high enough.

The importance of the gaseous phase for the initial phase becomes clear when one examines the c/t-curve's dependence on pressure for lactic acid (Fig. 3e). For its measurement the differences in the atmospheric pressure were used. The concentration of lactic acid at first decreases, then remains constant on one level before turning into a pressure independent curve. It is remarkable that form and position of the oscillating potential curve prove to be independent from pressure during the initial phase. This is true for the duration, too.
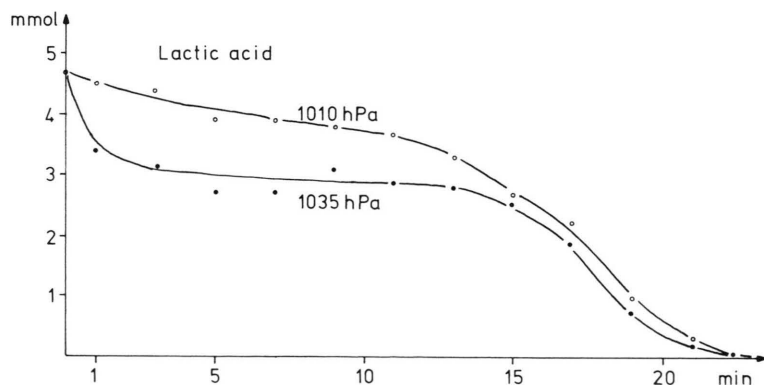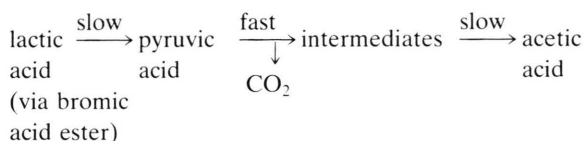

Fig. 3e. Decrease of the lactic acid concentration in dependence of pressure (20 °C).

The gross reaction of the break-down of lactic acid can be described as follows:

lactic acid $\xrightarrow{\text{slow}}$ pyruvic acid $\xrightarrow[\text{CO}_2]{\text{fast}}$ intermediates $\xrightarrow{\text{slow}}$ acetic acid
(via bromic acid ester)

The rate constants could yet not be evaluated due to errors in the concentration determination.

4.3 Dependence on temperature

As during the reaction the temperature increases from 20 to 23 °C the solutions were thermostatized not only before mixing, but also during the entire reaction. The investigation of the course at different temperatures provided the values which are listed in Table I. It can be seen that the half-life period of pyruvic acid resp. lactic acid decreases to a third. This coincides with a significant shortening of the initial phase and an alteration of the oscillatory behaviour (Fig. 4a, b).

Table I. Dependence on temperature.

	20 °C	30 °C
Pyruvic acid:		
$t_{1/2}$	1.87 min	1.0 min
initial phase	1.8 min	0.6 min
oscillation	30 min	10 min
Lactic acid:		
$t_{1/2}$	16.3 min	5.0 min
initial phase	20 min	5.4 min
oscillation	$\approx$50 min	$\approx$18 min

4.4 BZR-Systems with brominated pyruvic acid

Although stable brominated compounds as intermediates or final products have not been found it is of interest to know the effect of the bromination of substrate molecules on the course of the BZR in comparison to non-brominated species. Bromo- and dibromo-pyruvic acid were investigated. (The tribromo-compound proved to be nearly insoluble.)

The results support the observation which was already expressed before that substrate bromination promotes the actual BZR [6]. Thus, the substrate does not influence the potential level of the oscillation band, but influences its appearance. The pyruvic acid oscillation shows only 10 peaks with longer dis-
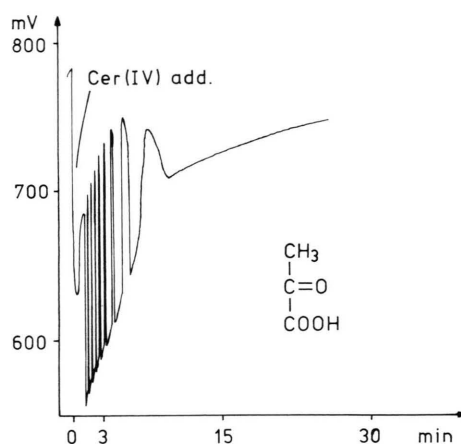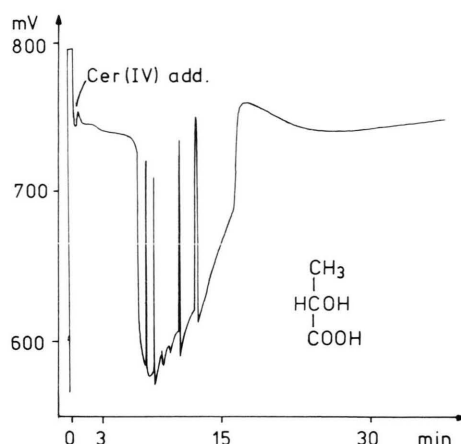

Fig. 4a. Pyruvic acid-BZR at 30 °C.
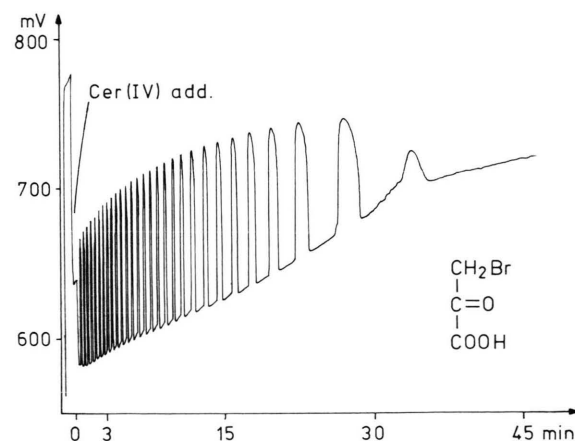

Fig. 4b. Lactic acid-BZR at 30 °C.

Fig. 5a. Redox measurement of the bromo-pyruvic acid-BZR system (20 °C).
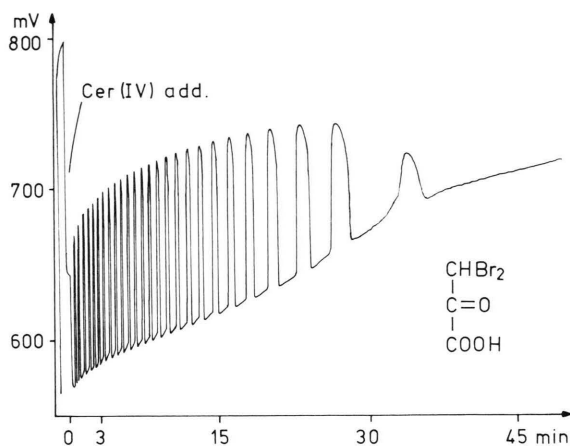
Fig. 5b. Redox measurement of the dibromo-pyruvic acid-BZR system (20 °C).

Table II. Comparison of the BZR with pyruvic acid derivates.

I. Degradation of substrates:

	PA	Br–PA	Br_2–PA
k_1 (min^{-1})	0.37	0.40	0.25
$t_{1/2}$ (min)	1.87	1.73	2.77

II. Formation of final products:

	CH_3–COOH	CH_2Br–COOH	$CHBr_2$–COOH
k_2 (min^{-1})	0.7	0.38	0.3
$t_{1/2}$ (min)	3.4	4.5	6.0

tances between them (Fig. 1a) whereas the brominated substrates show 29 resp. 26 peaks with higher frequencies (Fig. 5a, b).

The c/t-curves point out that accordingly the degradation proceeds differently. Bromo-pyruvic acid is the fastest to be degradated, dibromo-pyruvic acid, however, the slowest. In the latter case this is apparently due to steric reasons. Table II sums up the kinetic parameters and the final products.

[1] R. J. Field, E. Körös, and R. M. Noyes, J. Am. Chem. Soc. **94**, 8649 (1972).
[2] R. J. Field and R. M. Noyes, J. Chem. Phys. **60**, 1877 (1974).
[3] Z. Noszticzius, H. Farkas, and Z. A. Schelle, J. Chem. Phys. **80**, 6062 (1984).
[4] P. Sevcik and J. Dubovska, Coll. Czech. Chem. Commun. **50**, 1450 (1985).
[5] Z. Noszticzius and J. Bódiss, J. Am. Chem. Soc. **101**, 3177 (1979).
[6] G. J. Kasparaek and T. C. Bruice, Inorg. Chem. **10**, 382 (1971).
[7] B. Chance, E. K. Pye, A. K. Gosh, and B. Hess (eds): Biological and Biochemical Oscillators, Academic Press, New York and London (1973).
[8] J. J. Jwo and R. M. Noyes, J. Am. Chem. Soc. **97**, 5422 (1975).
[9] K. D. S. Yadava, Indian J. Chem., Sect. A **16A**, 347 (1978).
[10] P. Stroot and D. Janjic, Helv. Chim. Acta **58**, 116 (1975).
[11] V. J. Varage and D. Janjic, Helv. Chim. Acta **61**, 1539 (1978).
[12] V. J. Farage, P. Stroot, and D. Janjic, Helv. Chim. Acta **60**, 231 (1977).
[13] L. Adamciková and P. Sevcik, Z. Phys. Chem. Neue Folge **132**, 251 (1982).
[14] L. Adamciková and O. Knappová, Coll. Czech. Chem. Commun. **48**, 2335 (1983).
[15] Z. Noszticzius and J. Bódiss, Ber. Bunsenges. Phys. Chem. **84**, 366 (1980).
[16] L. Adamciková and I. Halinárová, Coll. Czech. Chem. Commun. **50**, 1588 (1985).
[17] R. Blume and H. J. Bader, Z. Naturforsch. **39b**, 1795 (1984).
[18] R. P. Rastogi, R. D. Yadava, S. Singh, and A. Sharma, Indian J. Chem. **24A**, 43 (1985).
[19] K. Pye and B. Chance, Proc. Nat. Acad. Sci. **55**, 888 (1966).
[20] L. Bornmann, H. Busse, B. Hess, R. Riepe, and C. Hesse, Z. Naturforsch. **28b**, 824 (1973).
[21] Beilstein E II 3, 624.
[22] F. Arndt, M. Ozansoy, and H. Üstünyar, Rev. Fac. Sci. Istanbul **4**, 83 (1939).
[23] W. D. Emmons and A. S. Pagano, J. Am. Chem. Soc. **77**, 89 (1955).
[24] R. Natarajan and N. Venkatasubramanian, Int. J. Chem. Kin. **VIII**, 205 (1976).
[25] R. P. Rastogi and Ishwar Das, Ind. J. Chem. **23A**, 363 (1984).
[26] V. Avasthi and A. C. Chatterji, Z. Phys. Chem. Leipzig **249**, 17 (1972).
[27] A. T. Winfree, Science **175**, 634 (1972).