

STUDY OF THE MECHANISM OF THE OSCILLATING REACTION BETWEEN BROMATE AND PHENOL

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Dedicated to Professor Dr J. Klikorka on the occasion of his 60th birthday.

In the oscillating reaction of bromate with phenol in the medium of 0.4M-H₂SO₄, the length of the induction period is governed by a kinetic equation for a second-order reaction with a stoichiometry 1 : 1. The concentration of quinones in the reaction mixture increases also according to a kinetic equation for a second-order reaction. The influence of various compounds is discussed, whose additions shorten or prolong the induction period, bring about oscillations in a nonoscillating reaction mixture, or change the frequency of these oscillations. From the comparison of the time dependences of the potential of a platinum and an ion-selective electrodes and of the limiting current of the quinones, a reaction mechanism was proposed.

The mechanism of the recently discovered¹ noncatalysed oscillating reaction between bromate ions and various organic compounds is not known as yet. An interpretation was attempted in the case of a reaction with polyphenols², based on a variant of the Field-Körös-Noyes mechanism³, whose generalization to phenol or other compounds is subject to certain inadequacies (no oscillations of Br⁻ ions are observed during the reaction with phenol⁴, dihydroxyarenes do not show an oscillation behaviour⁹, etc.). Certain characteristic features of the reaction of bromate ions with phenol were already described by us⁴; a detailed study of the reaction mechanism forms the subject of the present work.

In studying the oscillation reaction between bromate ions and phenol, a region was found⁴ in which the composition of the reaction mixture leads to oscillations, whereas outside this region the reaction is characterized by an induction period followed by a sharply distinguished nonoscillating stage. Both stages are clearly visible on the dependence of the potential of a platinum electrode on time (Fig. 1). The oscillations on curve 1 can be interpreted as rising pulses on curve 2 due to interrupting the nonoscillating reaction course. Hence, the study of the behaviour of reaction mixtures giving curves of the type 2 appears of primary importance for the determination of the reaction mechanism, especially if we keep in mind that a nonoscillating curve can be changed to an oscillating one by adding a suitable compound⁴.

EXPERIMENTAL

Chemicals: Sulphuric acid of reagent grade (Lachema, Brno) was used as 0.4M aqueous solution, phenol (Loba Chemie, Wien-Fischamend) as 0.1M solution in 0.4M-H₂SO₄, potassium bromate (Lachema, Brno) as 0.4M solution in 0.4M-H₂SO₄. Other chemicals (Table III) were of highest purity grade. Metal ions were added in the form of sulphates, anions as sodium or potassium salts (0.1M solutions in 0.4M-H₂SO₄). Thiosulphate, sulphide, and sulphite were used as 0.1 aqueous solutions.

Electrodes: Bromide ion-selective electrode (IS) Crytur, platinum foil electrode (Pt), rotating ground gold electrode (Research Institute of Organic Syntheses, Rybitví), and mercurous sulphate electrode (M.S.E.) as reference were used in the measurements.

Apparatus: Six-channel recorder (Rikadenki Kogyo Co., Ltd., Japan) was used to record simultaneously the potential-time curves with the Pt and IS electrodes and the limiting current with the Au electrode. The electromotive force of the cells Pt-M.S.E. and IS-M.S.E. was measured with an emitter follower of own construction for each channel. The limiting current was detected with the emitter follower on another channel as the potential drop on a 1 kΩ resistance in series

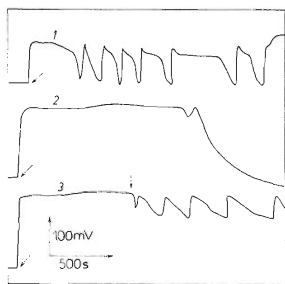


FIG. 1

Oscillating and nonoscillating reaction course. Starting composition of the mixture: 1 0.4M-H₂SO₄ + 7.4 · 10⁻³M-C₆H₅OH + 88.9 · 10⁻³M-KBrO₃; 2 0.4M-H₂SO₄ + 1.85 · 10⁻³M-C₆H₅OH + 22.22 · 10⁻³M-KBrO₃; 3 as 2 but 0.5 cm³ of 0.1M-FeSO₄ added in the instant denoted by a vertical arrow. Solution volume 54 cm³, Pt electrode, 298 K. Inclined arrow denotes addition of the bromate solution

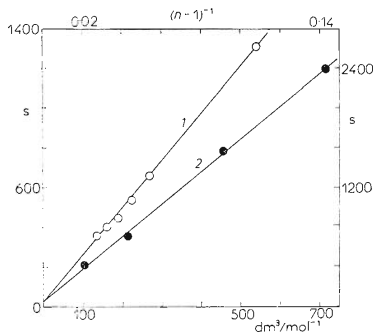


FIG. 2

Dependence of induction period on dilution and starting molar ratio. 1 Dependence of t^* on $[\text{Ph}]_0^{-1}$, left and bottom scale; 2 dependence of t^* on $(n-1)^{-1}$, right and top scale

with the Au electrode polarized at -0.26 V (M.S.E.). This corresponds to the limiting current of quinones, which was well distinguished from the current corresponding to BrO_3^- and H^+ ions. Both the polarisation curve and the dependence of the limiting current on the time, obtained with the Au electrode, were recorded on a Radelkis type polarograph (Budapest).

When only the potential-time curves were needed, they were recorded with a K 200 recorder (Carl Zeiss, Jena), whose high-impedance input ($10^{10} \Omega$) was fed directly with the e.m.f. of the measured cell (Pt-M.S.E. or IS-M.S.E.).

For enthalpiometric measurement of the time dependence of the temperature during the reaction, an isoperibolic calorimeter (*i.e.*, operating at constant temperature of the surrounding medium) (Technical University, Brno) was used in a differential mode: the temperature of the reaction mixture under study and of a reference mixture (without BrO_3^-) was measured with two thermistors 13 NB 09 (Research Institute for Powder Metallurgy, Šumperk) in a bridge circuit with a sensitivity of $2 \mu\text{A}/10^{-3} \text{ K}$. The output of the difference bridge was fed to an EZ 2 recorder (Laboratorní Přístroje, Prague).

All measurements were carried out in a cell with a thermostated mantle piece connected with a U1 thermostat (Prüfgerätewerk Medingen, GFR). The solution was stirred with a magnetic stirrer. The cell holding capacity was 100 cm^3 .

To determine the concentration of BrO_3^- ions, $1-3 \text{ cm}^3$ samples were taken at intervals during the induction period, the reaction was stopped by cooling the sample with solid carbon dioxide and the reaction mixture was extracted three times by ethyl acetate. Bromate in the remaining aqueous phase was determined iodometrically with thiosulphate.

In studying the influence of various substances on the course of $E-t$ curves, both oscillating ($0.4\text{M-H}_2\text{SO}_4 + 7.4 \cdot 10^{-3}\text{M phenol} + 8.89 \cdot 10^{-2}\text{M-KBrO}_3$) and nonoscillating ($0.4\text{M-H}_2\text{SO}_4 + 1.85 \cdot 10^{-3}\text{M phenol} + 2.22 \cdot 10^{-2}\text{M-KBrO}_3$) reaction mixtures were used. The induction period was divided into five approximately equal steps and in each of them, usually 0.5 cm^3 of a 0.1M solution of the chosen substance was added to 54 cm^3 of the reaction mixture.

RESULTS

Induction Period

Curves of the nonoscillating type (Fig. 1, curve 2) were obtained at various dilutions and various initial molar ratios of bromate to phenol, n (Table I). These were used to evaluate the dependence of the induction period on the initial concentration of phenol at constant n , and on the value of n at constant initial phenol concentration. The results can be correlated with the following kinetic equation for a second-order reaction, $\nu_{\text{P}}\text{Ph} + \nu_{\text{B}}\text{BrO}_3^- \rightarrow \dots$,

$$kt\nu_{\text{B}}[\text{Ph}]_0 \left[\frac{(\nu_{\text{P}}[\text{BrO}_3^-]_0)/(\nu_{\text{B}}[\text{Ph}]_0) - 1}{([\text{Ph}]_0/[\text{Ph}])} \right] = \ln \left[\frac{([\text{BrO}_3^-]_0)/([\text{BrO}_3^-]_0)}{([\text{Ph}]_0/[\text{Ph}])} \right], \quad (1)$$

if a certain constant value of the concentration ratio $([\text{BrO}_3^-]_0)/([\text{Ph}]_0)$ is assigned to the end of the induction period t^* . The dependence of t^* on the reci-

procal initial concentration of phenol is linear (Fig. 2, curve 1); the dependence of t^* on $(n - 1)^{-1}$ is also linear (Fig. 2, curve 2) at a stoichiometry $v_P : v_B = 1 : 1^*$.

The stoichiometry of the reaction during the induction period was determined also from the amount of bromate consumed in the reaction with respect to the starting amount of phenol, which is no more present at the end of the induction period in the reaction mixture⁵. The results are given in Table II.

The reaction kinetics during the induction period was followed by measuring the limiting current due to the quinones formed in the reaction mixture in the course of the time.

With a stoichiometry 1 : 1, the increment of the concentration of the products (quinones), x , is proportional to the limiting current I_d , $\lambda x = I_d$, so that $\lambda[\text{Ph}] = \lambda[\text{Ph}]_0 - \lambda x = \lambda[\text{Ph}]_0 - I_d$ and also $\lambda[\text{BrO}_3^-] = \lambda([\text{BrO}_3^-]_0 - x) = \lambda[\text{BrO}_3^-]_0 - I_d$, whereby Eq. (1) takes the form

$$kt[\text{Ph}]_0(n - 1) = -\ln n + \ln [(nI_{d\infty} - I_d)/(I_{d\infty} - I_d)]. \quad (2)$$

The dependence of the last term on the time for various values of n is shown in Fig. 4. Its linearity suggests formally that the reaction is of the second order during the

TABLE I

Length of induction period at various compositions of the starting reaction mixture. (0.4M-H₂SO₄, 298 K)

Initial composition, mol/dm ³		n	Ind. period s	$[\text{Ph}]_0^{-1}$ dm ³ mol ⁻¹
$[\text{Ph}] \cdot 10^3$	$[\text{KBrO}_3] \cdot 10^3$			
9.3	111.6	12	360	135
6.1	72.6	11.9	408	163.6
5.18	61.5	11.86	444	192.8
4.44	53.33	12	540	225
3.7	44.44	12	660	270
1.85	22.22	12	1 320	540
1.58	76.2	48	420	630
1.58	38.1	24	708	630
1.58	19.05	12	1 572	630
1.58	12.7	8	2 400	630

* Values of v_P/v_B close to one (e.g., 0.8 or 1.25) lead also to a practically linear dependence of t^* on $(nv_P/v_B - 1)^{-1}$.

TABLE II
Reaction stoichiometry at the end of induction period at 298 K

n	Medium						
	0.4M-H ₂ SO ₄			0.2M-H ₂ SO ₄			
	[Ph] ₀ · 10 ³ mol dm ⁻³	[BrO ₃ ⁻], mol dm ⁻³	t = t*	[BrO ₃ ⁻] - [BrO ₃ ⁻] [Ph] ₀	[BrO ₃ ⁻], mol dm ⁻³	t = t*	[BrO ₃ ⁻] - [BrO ₃ ⁻] [Ph] ₀
12	7.4	0.0889	0.0807	1.1	0.089	0.080	1.21
	6.11	0.0741	0.0691	0.82	0.0725	0.0654	1.16
	3.7	0.0444	0.0404	1.08	0.0445	0.0400	1.21
	1.85	0.0222	0.0202	1.08	0.02217	0.0198	1.28
8	14.8	0.1190	0.1040	1.01	0.11833	0.1016	1.13
	7.4	0.0592	0.0517	1.01	0.05916	0.0525	0.9
	3.7	0.0291	0.0255	0.97	0.0291	0.0254	0.999
6	14.8	0.0891	0.0724	1.13	0.08917	0.07417	1.01
	11.1	0.0674	0.0583	0.82	0.0666	0.0566	0.9
	7.4	0.0466	0.0384	1.11	0.0466	0.0383	1.12

induction period. The limiting current-time curves (Fig. 3) are remarkable by a pre-induction period (region *a*), which is practically undistinguishable on the potential-time curves.

Fig. 5 shows a simultaneous record of the potential of the Pt and IS electrodes and of the limiting current of quinones. After the induction period is over, the increase of the quinone concentration coincides with the increase of the potential of the Pt and IS electrodes; the drop of the Pt electrode potential has no corresponding counterpart on the other two curves. The total increase of the quinone concentration in the oscillating stage is equal only to 14% of the increase during the induction period. This is in accord with the time dependence of the temperature in the enthalpiometric study of the reaction.

Influence of Various Compounds on the Curves of Both Oscillating and Nonoscillating Types

Since it was shown previously⁴ that a nonoscillating reaction mixture can be caused to oscillate by adding various primary or secondary aliphatic alcohols, we continued

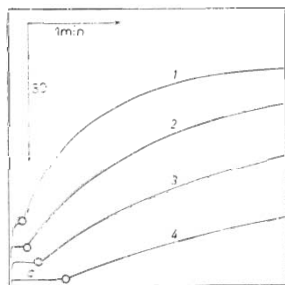


FIG. 3

Dependence of limiting current of quinones on time. Molar ratio of the starting components: 1 48; 2 24; 3 12; 4 6. See Table I for the composition of the reaction mixtures. Ordinate: number of scale divisions; $I_d(t \rightarrow \infty) \approx 39$ divisions for all curves. The curves are shown in their linearized form in Fig. 4 beginning with the point denoted by an open circle

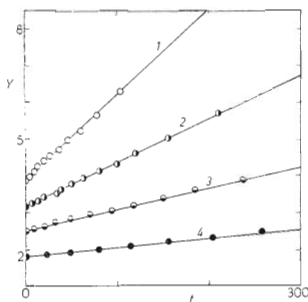


FIG. 4

Linearized dependence of limiting current on time. $Y = \ln [(nI_{d\infty} - I_d)/(I_{d\infty} - I_d)]$. Curve numbers correspond to Fig. 3. Time in seconds

these studies concerning the effect on the nonoscillating (type 2) curves as well as on the oscillating (type 1) curves (length of the induction period, ability to cause oscillations and to stop them, number and frequency of oscillation). The substances were added at different instants during the induction period; they can be divided according to their effect into several groups (Table III). Members of group Ia have a property in common: they catalyse the oxidation of hydroquinone with BrO_3^- ions.

DISCUSSION

Oscillating Stage of the Reaction

The simultaneous records of the potentials of the Pt and IS electrodes and of the limiting current I_d show that the increase of the Pt electrode potential is synchronous with the increase of the quinone concentration and of the IS electrode potential, whose response is not related to Br^- ions but rather to ions with a minimum valency +1, as shown previously⁴. A response of the IS electrode to Br^+ ions in an opposite sense compared to Br^- ions was substantiated experimentally by Noszticzius⁶.

Since stirring of the reaction mixture by bubbling argon does not cause a change in the $E-t$, curves whereas addition of bromine does so to a large extent, we assume that bromine molecules do not constitute a part of the reaction system, hence Br^+

TABLE III

Influence of various additions

Ia	Fe^{2+} , Au^{3+} , VO^{2+}
I	Fe^{2+} , Fe^{3+} , $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$, Au^{3+} , Cr^{3+} , VO^{2+} , $(\text{VO}_3)^-$, I^- , (Br^-) , primary and secondary alcohols
II	Au^{3+} , VO^{2+} , VO_3^- , UO_2 , Mn^{2+} ^a , primary and secondary alcohols
III	CSN^- , $\text{S}_2\text{O}_3^{2-}$ ^c , Br_2 ^b , H_2O_2
IV	Br^- ^c , S^{2-} ^c
V	I^- ^c , Cl^-
VI	$\text{C}_6\text{H}_5\text{OH}$, hydroquinone, H_2O_2 ^b , As^{3+} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, Sn^{2+}
VII	Sb^{3+} , Cu^{2+} , Co^{2+} , NO_2^- , Ce^{3+} , Ce^{4+} , Al^{3+} , Nd^{3+} , MnO_4^- , bubbling with Ar. ClO_3^- , $\text{S}_2\text{O}_8^{2-}$

Notes: Ia shorten the induction period; I bring about oscillations; II suppress oscillations in a later stage, ^a in any stage; III increase the number of oscillations and do not change the frequency or decrease it; IV decrease the frequency; V increase the frequency and number of oscillations; VI prolong the induction period; VII do not influence the curves of either type; ^b effective during the first half of the induction period; ^c effective during the second half of the induction period; () weak effect.

The couple of two consecutive, competitive reactions with a paralelel synthesis of intermediate products (thick lines denote very rapid steps), $M \rightarrow Y \rightarrow N$, is responsible



for the "autocatalytic" character as found earlier¹¹. With this scheme, it was proved by a theoretical analysis and an analogue calculation⁸ that the concentrations of Br(I) and Br(III) oscillate.

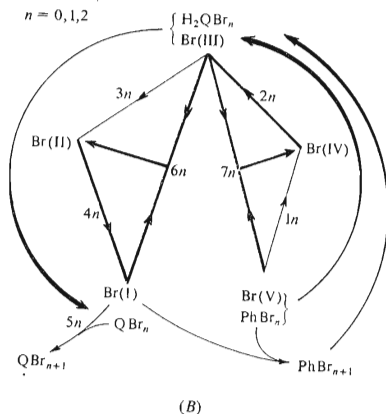
On the basis of the above scheme, certain steps can be assigned to the $E-t$ curves of the Pt and IS electrodes during the oscillation stage (Fig. 6). This is founded by the following considerations: The reaction scheme (A) shows that the autocatalytic decrease of Br(III) coincides with the increase of Br(I), and the autocatalytic increase of H₂Q coincides with that of some form of bromine; the latter cannot be Br(I) since this would imply a time coincidence of the peak of the IS electrode with the abrupt decrease of the Pt electrode potential in contrast to the experimental findings. Hence, the only additional oscillating bromine species is, according to the mentioned kinetic scheme, Br(III). This conclusion is supported by the fact that the reaction between hydroquinone and bromate is very slow, so that H₂Q is in the relatively much more rapid oscillation reaction oxidised with bromine in another oxidation state than +5. This cannot be Br(I), since neither the concentration of Br⁻ ions in the solution nor that of Br₂ changes⁴.

The kinetic scheme (A) elucidates also the fact that the reaction of bromate with dihydroxybenzenes does not oscillate: a reaction in which dihydroxybenzene would be generated is missing.

A theoretical study⁸ of the scheme (A) implies that the oscillation frequency increases with the values of k_5 and k_7 , and that the amplitude of the oscillations increases markedly with decreasing k_6 and less markedly with increasing k_7 or k_5 . From this point of view, the influence of adding compounds of group V can be seen in accelerating the step 5, and the decrease of the frequency by slowing down the step 7 can be attributed to the decrease of active species Br(III) and Br(IV) caused by compounds of group IV. Therefore, the additions are effective only in the second half of the induction period, when a sufficient quantity of Br(III) or Br(IV) can be assumed to be present. Increasing the number of oscillations at constant frequency but with a lower amplitude by compounds of group III can be explained by accelerating the step 6 and by a lower consumption of the "organic fuel" in the course of every oscillation, so that the oscillating stage of the reaction lasts longer.

Since bromo derivatives are formed in step 5 (mono and dibromophenols⁵, bromodihydrobenzenes⁵, bromoquinones⁴, and dibromoquinones⁴ were found in the reaction mixture), some of which can play the role of reducing agents Q_i in steps 1-4, changes of the reducing agent Q_i take place in the course of the oscillations; this is manifested also by a different character of the oscillations on their medium and final stages. This conclusion is supported also by the fact that the oscillations can be eliminated in their medium and final stages by adding compounds of group II.

If we include the bromated intermediate products into the reaction cycle and observe the coincidence of the individual steps in Fig. 6, we obtain the following scheme:



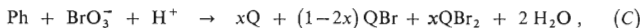
Induction Period

A kinetic analysis of the induction period shows that the reaction proceeds at this stage as one of the second order with a stoichiometry approximately 1 : 1. The kinetic scheme (A) or scheme (B) is reduced to a simple reaction of the second order if the slowest (rate-determining) step is the first one and the intermediate products are present in low stationary concentrations, mainly Br(III) and Br(I). To change this situation, the concentration of Br(III) must increase (an increase of Br(I) would cause a still higher exhaustion of Br(III) by the rapid steps 4 and 6), and this mainly (without external influence) by slowing down step 3n, e.g., owing to the fact that more bromated phenol is a less powerful reducing agent. The transition from the nonoscillating to the oscillating reaction type by lowering the rate constant k_3 was for scheme (A) proved by modelling the process on an analogue computer.

This primary increase of the concentration of Br(III) continues then autocatalytically through steps 2n and 7n with a simultaneous increase of the concentration of the reduced form H_2QBr_n leading to a drop in the Pt electrode potential and an end of the induction period. The latter can be thus considered as the time necessary for the formation of the compound $PhBr_n$ representing the proper reaction component able to react with bromate in an oscillating way. Accordingly, the induction period becomes shorter by up to 80% when the reaction with bromate starts with dibromo-

phenol⁵. The induction period is prolonged by the addition of phenol, hydroquinone, or hydrogen peroxide (added during the first half of the induction period), which can be attributed to increasing the rate of step 3 and thus preventing the oscillations.

It can be inferred from the reaction stoichiometry during the induction period, $\text{BrO}_3^- : \text{Ph} : 1 : 1$, that phenol is converted prevalingly by a four-electron oxidation to quinones according to



where $0 < x < 0.5$. The transitorily formed Br(I) species is consumed to a small extent in a parasitic bromation of phenol to dibromophenol, which acts as a promoter of the oscillations. Accordingly, when studying the dependence of the limiting current or temperature on the time, we found that 86% of the formed products correspond to the nonoscillating stage during the induction period. The latter can be shortened not only by substituting mono- or dibromophenol for phenol⁵ as mentioned above, but also by adding ions of group Ia, whose effect is probably due to redox catalysis. Their accelerating influence on the rate of oxidation of hydroquinone with bromate was proved experimentally in our work.

The appearance or absence of oscillations after the induction period can be discussed as follows. Since not only the rate but also the character of the reaction changes with increasing dilution (the oscillations disappear), the molar ratio of the starting components remaining the same, some reaction steps must be of unequal order. Otherwise, the kinetic equations could be transformed by introducing dimensionless concentrations and time to obtain an invariant solution. The reaction scheme (A) or scheme (B) can be supplemented by first-order reaction steps by assuming that the unstable ion radicals Br(IV) and Br(II) exist as dimers which disintegrate by a first-order reaction. In this connection, it should be noted that a formally similar scheme has been proposed by the critics⁹⁻¹² of the Field-Körös-Noyes mechanism of the Belousov reaction.

The fact that the nonoscillating diluted reaction mixture can be caused to oscillate by adding compounds of group I can be attributed to an acceleration of the bimolecular reaction step with respect to the monomolecular ones to an extent corresponding to more concentrated reaction mixtures, in which oscillations take place.

Preinduction Period

The time dependence of the limiting current shows at the beginning of the reaction a region where the formation of quinones is much slower than in a later stage. This corresponds to the reaction rate in step 1, given by the product of $k_1[\text{BrO}_3^-][\text{Ph}]$, whereas after the formation of the Br(III) species a rapid sequence of steps 2, 7, and others comes into play and the rate is then given as $k_1[\text{BrO}_3^-][\text{P}] + k_7[\text{Ph}]$.

. $[\text{Br(III)}]$. If the concentration of Br(III) is set equal to its stationary value⁸ of $(k_5/k_6) [\text{BrO}_3^-]$, the reaction rate is given as $[\text{Ph}][\text{BrO}_3^-] (k_1 + k_5 k_7/k_6)$ and is much higher than in the preinduction period.

It can be concluded that our experimental findings are in accord with the theoretical behaviour of the reaction scheme (A) or scheme (B), which can be regarded in principle as substantiated, although some details (e.g., dimers of ion radicals) remain open for discussion.

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