The 1,4-Cyclohexanedione−Bromate−Acid Oscillatory System. 3. Detailed Mechanism

István Szalai and Endre Körös*

Department of Inorganic and Analytical Chemistry, L. Eötvös University,
1518 Budapest, P.O. Box 32, Hungary

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1,4-Cyclohexanedione (CHD) in its reaction with acidic bromate undergoes aromatization and one of the main resulting products 1,4-dihydroxybenzene (H_2Q) is further oxidized and brominated to 1,4-benzoquinone and bromoorganics. The kinetics of H_2Q formation, of the reaction of CHD and Br_2, as well as of the reaction between H_2Q and bromate ion, were followed spectrophotometrically. The latter reaction exhibited Landolt (clock)-type dynamics. On the basis of our earlier analytical and present kinetic investigations, a detailed mechanistic model has been suggested that could well simulate the temporal oscillations of the title system. H_2Q plays an essential role in the mechanism and is responsible for the unusual behavior (200−300 oscillations) of this chemical oscillator. We pointed to the relation that may exist between the CHD−bromate−acid system and those reported as oscillatory Landolt-type reactions [e.g., $IO_3^- - SO_3^{2-} - Fe(CN)_6^{4-}$].

Introduction

Uncatalyzed bromate oscillators, UBOs, (i.e., reacting systems that exhibit oscillatory dynamics even in the absence of a metal-ion, metal-complex catalyst) were discovered in 1977−78;[1,2] many systems were characterized[3] and a skeleton mechanism was proposed[4] that has been modified by Herbine and Field.[5] In later years, an extended mechanism[6] was suggested, and also, reduced models were published in the literature.[7]

Generally, UBOs are composed of an aromatic (mostly a phenol or an aniline derivative), bromate ion, and sulfuric acid. The overall reaction is the parallel running oxidation and bromination of the organic substrate that results in a variety of products depending on the chemical composition of the reacting system. Under batch configuration, most UBOs exhibit a few, highly damped temporal redox-potential and bromide-ion-concentration oscillations. So far, only sporadic attempts have been made to unravel which are the intermediates and products of the oscillatory bromate−aromatic reaction. The phenol−bromate reacting system has been investigated in some detail. Thin layer chromatography[8] and HPLC techniques[9] were used to follow the temporal course of the reaction. In the form of oxidation products, 1,2-benzoquinone and 1,2-dihydroxybenzene, as well as bromination products, mono-, di-, and tribromophenols have been identified and their concentrations determined at frequent intervals. On the basis of these qualitative results, Györgyi et al.[6] proposed a more detailed mechanistic model that simulated well the dynamic behavior of some UBOs.

A rather unexpected observation communicated by Farage and Janjic[10]—an alicyclic diketone, the 1,4-cyclohexanedione (CHD), reacted with acidic bromate in an oscillatory manner, and under optimal chemical conditions 200−300 high frequency oscillations were recorded—prompted us to investigate this reacting system more thoroughly. The mentioned authors studied only the effects of temperature, oxygen, catalyst, and stirring on the dynamics of the reaction, and did not consider, however, its chemistry and made no suggestion regarding the mechanism of the reaction.

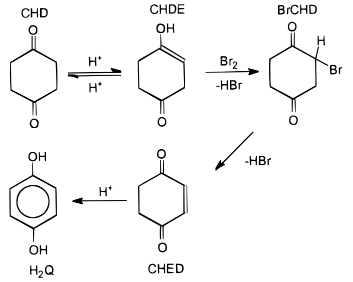

Figure 1. Mechanism of the formation of 1,4-dihydroxybenzene.

To some extent the Farage−Janjic system was unique, because all systems studied previously that contained alicyclic mono- or diketones (e.g., cyclopentanone, cyclohexanone, and 1,3-cyclohexanedione) reacted with bromate ion in an oscillatory manner only in presence of a metal-ion catalyst.

Druliner and Wasserman reported that the oxidation of cyclohexanone with dioxygen catalyzed by the Co(II)−Br^- system resulted in the cleavage of the alicyclic ring and a variety of aliphatic compounds (e.g., adipic, glutaric, succinic, and capronic acids) were the products of the reaction.[11] Oxidation of CHD with various oxidizing agents, on the other hand, does not yield aliphatic products. Manganese(IV) oxide and iron(III) chloride in aqueous sulfuric acid oxidize CHD to 1,4-benzoquinone (Q);[12] bromine in chloroform and selenium(IV) oxide in dioxane convert CHD to 1,4-dihydroxybenzene (H_2Q).[13] Most probably H_2Q is formed via the enolization of 2-cyclohexene-1,4-dione[14] (Figure 1). Also, the oxidation of CHD with phosporous(V) chloride results in an aromatic product, the 1,4-dichlorobenzene.[15]

The reaction between CHD and bromate ion has not been investigated earlier. In order to construct a chemical mechanism, knowledge obtaining the chemistry of the bromate−CHD reaction was of prime importance. In two previous papers we have reported on our investigations along this line.[16,17] We followed the temporal course of the reaction by analyzing samples, withdrawn at regular intervals, using GC/MS tech-

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niques. In the reaction mixture we could identify H_2Q and Q as well as 2-bromo-1,4-cyclohexanedione, 2-bromo-1,4-dihydroxybenzene, and 2-bromo-1,4-benzoquinone. Thus we established that bromate ion in dilute sulfuric acid did not cleave the alicyclic ring but the first step of oxidation was an aromatization process. This fact accounted for the absence of carbon dioxide evolution during the course of the reaction and provided us the possibility to study chemical wave and pattern formations in the CHD−bromate−ferroin−sulfuric acid system under bubble-free conditions.[18,19]

In the present communication we report on the chemical mechanism of the title oscillatory system.

Chemicals and Experimental Methods

H_2SO_4 (Chemolab 96%), 1,4-cyclohexanedione (Aldrich 98%), KBr (Reanal p.a.), 1,4-dihyroxybenzene (Merck 99%), and 1,4-benzoquinone (Merck 98%) were used without further purification. $NaBrO_3$ (Fluka p.a.) was recrystallized twice from water. All solutions were prepared from bidistilled water.

The absorption spectra were taken on a Milton Roy 3000 diode array spectrophotometer in a quartz cell (path length, 1 cm; volume, 3 cm^3). The oscillatory reaction was monitored on a chart recorder (Kipp-Zonen BD-41) by using a smooth Pt electrode (Radelkis) and a $Hg/Hg_2SO_4/K_2SO_4$ reference electrode (Radiometer). The analog signals were digitalized by a 12 bit AD converter (Labtech PCL-711 S) and processed by a PC. The temperature was kept at 20.0(± 0.1) °C, and the solutions in the cell were mixed by a magnetic stirrer.

The parameter estimations were carried out by using program ZITA.[20] The simulations were done with the program LSODE.[21]

Results

Reaction of 1,4-Cyclohexanedione and Bromine in Sulfuric Acid. According to the literature[12,13] and our previous results,[16] the following scheme was suggested for the bromination of CHD in a sulfuric acid solution:

$$\mathrm{CHD} + \mathrm{H}^+ \rightleftharpoons \mathrm{CHDE} + \mathrm{H}^+$$
$$v_{11} = k_{11}[\mathrm{CHD}][\mathrm{H}^+] = k'_{11}[\mathrm{CHD}] \quad v_{-11} = k_{-11}[\mathrm{CHDE}][\mathrm{H}^+] \quad \text{(R11)}$$

$$\mathrm{CHDE} + \mathrm{Br}_2 \rightarrow \mathrm{BrCHD} + \mathrm{H}^+ + \mathrm{Br}^-$$
$$v_{12} = k_{12}[\mathrm{CHDE}][\mathrm{Br}_2] \quad \text{(R12)}$$

$$\mathrm{BrCHD} \rightarrow \mathrm{CHED} + \mathrm{Br}^- + \mathrm{H}^+$$
$$v_{14} = k_{14}[\mathrm{BrCHD}][\mathrm{H}^+] = k'_{14}[\mathrm{BrCHD}] \quad \text{(R14)}$$

$$\mathrm{CHED} + \mathrm{H}^+ \rightarrow \mathrm{H_2Q} + \mathrm{H}^+$$
$$v_{15} = k_{15}[\mathrm{CHED}][\mathrm{H}^+] = k'_{15}[\mathrm{CHED}] \quad \text{(R15)}$$

(CHDE = enol form of CHD; BrCHD =
2-bromo-1,4-cyclohexanedione, CHED =
2-cyclohexene-1,4-dione, H_2Q = 1,4-dihyroxybenzene)

We observed the formation of H_2Q as the end product of the reaction in the spectrum of the reaction mixture (Figure 2).

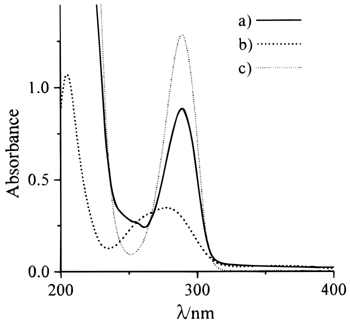

Figure 2. Formation of 1,4-dihydroxybenzene as the end product of bromination. Initial concentrations: $[\mathrm{CHD}]_0 = 10^{-2}$ mol dm^{-3}, $[\mathrm{Br_2}]_0 = 5 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{H_2SO_4}]_0 = 1.0$ mol dm^{-3}. (a) Spectrum of the reaction mixture after 15 h. (b) Spectrum of 9.5×10^{-3} mol dm^{-3} CHD. (c) Spectrum of 5×10^{-4} mol dm^{-3} H_2Q.

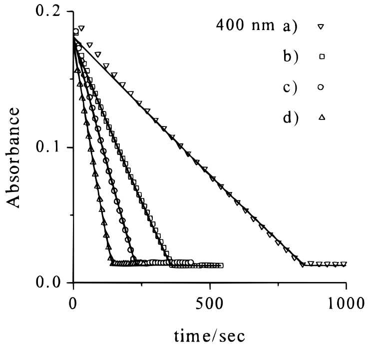

Figure 3. Bromination of CHD. Experimental conditions: $[\mathrm{CHD}]_0 = 10^{-2}$ mol dm^{-3}, $[\mathrm{Br_2}]_0 = 10^{-3}$ mol dm^{-3}, 20 °C. (a) $[\mathrm{H_2SO_4}]_0 = 0.5$ mol dm^{-3}. (b) $[\mathrm{H_2SO_4}]_0 = 1.0$ mol dm^{-3}. (c) $[\mathrm{H_2SO_4}]_0 = 1.5$ mol dm^{-3}. (d) $[\mathrm{H_2SO_4}]_0 = 2.0$ mol dm^{-3}. The solid lines are the fitted curves. Absorption coefficients: $\epsilon^{400}_{\mathrm{Br_2}} = 171$ mol^{-1} dm^3 cm^{-1}, $\epsilon^{400}_{\mathrm{CHD}} = 1.4$ mol^{-1} dm^3 cm^{-1}.

TABLE 1: First Order Rate Constants of the Enolization of CHD[a]

$[\mathrm{H_2SO_4}]$/ mol dm^{-3}	$[\mathrm{H}^+]_T$/ mol dm^{-3}	k'_{11}/s^{-1}	CoD
0.5	0.63	$1.24 \times 10^{-4} (\pm 6.2 \times 10^{-6})$	0.985
1.0	1.29	$2.92 \times 10^{-4} (\pm 5.6 \times 10^{-6})$	0.983
1.5	1.96	$4.60 \times 10^{-4} (\pm 5.4 \times 10^{-6})$	0.997
2.0	2.65	$7.63 \times 10^{-4} (\pm 1.0 \times 10^{-5})$	0.998

[a] CoD $= 1 - [\sum_{i=1}^{n} (y_i - f(x_i))^2]/[\sum_{i=1}^{n} (y_i - \bar{y})^2]$ indicates the goodness of fit. The data are given at 95% significance level. We used H^+ ion concentrations reported by Robertson and Dunford.[31]

The reaction of CHD and Br_2 was monitored at three wavelengths (240, 290, and 400 nm) and the kinetics measured at different initial concentrations of CHD, Br_2, and H_2SO_4, respectively. The bromination of CHD was followed at 400 nm (absorbance maximum of bromine). CHD was always in excess (8−20 times) in these experiments. The obtained curves showed a pseudo zeroth-order kinetics (Figure 3) indicating that the rate-determining step was the enolization of CHD (R11). From these experiments we could estimate only k'_{11}. The total absorbance was calculated from the absorbance of CHD and Br_2. We used $pK_{11} = 6.39$[22] and $k_{12} = 2.8 \times 10^9$ mol^{-1} dm^3 s^{-1}[23] for the parameter estimation (these values have been reported for cyclohexanone). At a given acidity the estimation was made simultaneously on the data measured at different initial concentrations of CHD and bromine. Table 1 shows the results of parameter estimations. From the dependence of k'_{11} on acidity we estimated the second order rate constant, $k_{11} = 2.13 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} ($\pm 3.9 \times 10^{-5}$). Keeffe et al.

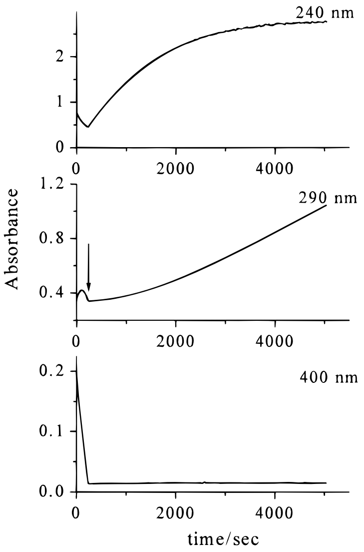

Figure 4. Formation of CHED and H_2Q after the bromination of CHD. Experimental conditions: $[CHD]_0 = 10^{-2}$ mol dm^{-3}, $[Br_2]_0 = 1 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4]_0 = 1.5$ mol dm^{-3} , 20 °C.

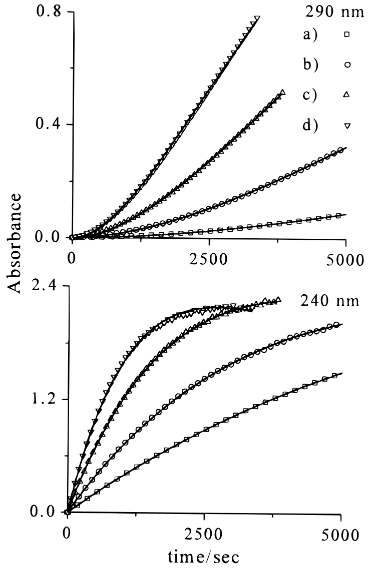

Figure 5. Formation of CHED and H_2Q at different acidities. Experimental conditions: $[CHD]_0 = 10^{-2}$ mol dm^{-3}, $[Br_2]_0 = 10^{-3}$ mol dm^{-3}, 20 °C. (a) $[H_2SO_4]_0 = 2.0$ mol dm^{-3}. (b) $[H_2SO_4]_0 = 1.5$ mol dm^{-3}. (c) $[H_2SO_4]_0 = 1.0$ mol dm^{-3}. (d) $[H_2SO_4]_0 = 0.5$ mol dm^{-3}. The solid lines are the fitted curves.

reported nearly the same value for cyclohexanone (2.36×10^{-4} mol^{-1} dm^3 s^{-1}).[22]

We followed the slow formation of H_2Q (at 290 nm) and CHED (at 240 nm) after the bromination reaction (Figure 4) and from these curves calculated the rate constants for R13 and R14. Parameter estimation started when bromine was consumed (arrow it in Figure 4), and absorbance was set to zero. (Absorbances of CHD and BrCHD were neglected.) The total absorbance was calculated from the absorbance of CHED and H_2Q ($\epsilon^{290}_{H_2Q} = 2560$ mol^{-1} dm^3 cm^{-1}, $\epsilon^{240}_{H_2Q} = 515$ mol^{-1} dm^3 cm^{-1}) only. The initial concentration of BrCHD was set equal to the initial concentration of bromine. After this simplification four parameters remained to be estimated (k'_{14}, k'_{15}, ϵ^{240}_{CHED}, ϵ^{290}_{CHED}). Agreement between fitted curves and experimental data are good (Figure 5). The results of parameter estimation are compiled in Table 2. Our values for k'_{15} and ϵ^{240}_{CHED} agree well with those reported by Garbisch ($k'_1 = 2.2 \times 10^{-4}$ s^{-1} in 0.33 mol dm^{-3} sulfuric acid and $\epsilon^{233}_{CHED} = 1.51 \times 10^4$ mol^{-1} dm^3 cm^{-1} in ethanol)[14] who followed reaction R15 by NMR. We derived the second order rate constants from the acidity dependence and obtained that $k_{14} = 5.0 \times 10^{-5}$ mol^{-1} dm^3 s^{-1} ($\pm$ 9.1×10^{-6}) and $k_{15} = 1.94 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} ($\pm 2.56 \times 10^{-5}$).[24]

Reaction of Bromate and 1,4-Dihydroxybenzene in Sulfuric Acid. One of the most important steps in the mechanism of bromate oscillators is the autocatalytic reaction between bromate ion and bromous acid. This reaction requires a reducing agent that converts $BrO_2^{\bullet}$ to $HBrO_2$:

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2\,BrO_2^{\bullet} + H_2O \qquad (A1)$$

$$BrO_2^{\bullet} + M^{n+} + H^+ \rightarrow HBrO_2 + M^{(n+1)+} \qquad (A2)$$

$$(M^{n+} \text{ is a catalyst, e.g., } Ce^{3+} \text{ or } Mn^{2+})$$

We assumed that in the title oscillatory system H_2Q (and the semiquinone radical) could play this role.

We followed the bromate−H_2Q reaction at 400 nm (main contribution from Q and Br_2), at 240 nm (main contribution from Q) and at 290 nm (main contribution from H_2Q) and observed a typical clock-type reaction (Figure 6). Reactions B1−B3 summarize the common characteristics of the halogen-based clock systems.[25]

$$3H_2R + XO_3{}^- \rightarrow 3R + X^- + 3H_2O \qquad (B1)$$

$$5X^- + XO_3{}^- + 6H^+ \rightarrow 3X_2 + 3H_2O \qquad (B2)$$

$$H_2R + X_2 \rightarrow R + 2X^- + 2H^+ \qquad (B3)$$

$$k_{A1} < k_{A2} \ll k_{A3} \text{ and } [H_2R]_0 < 3[XO^-{}_3]_0$$

$$(X = \text{halogen, } H_2R = \text{reductant})$$

These reactions are the main stoichiometric steps. In our case, when X = Br, the rate determining step of B2 is R3.

$$Br^- + BrO_3{}^- + 2H^+ \rightleftharpoons HOBr + HBrO_2 \qquad (R3)$$

We inserted reactions R17 and R16 as B1 and B3 into our model. (Reaction R17 is the first step of the reduction of bromate by H_2Q.)

$$H_2Q + Br_2 \rightarrow Q + 2Br^- + 2H^+ \qquad (R16)$$

$$H_2Q + BrO_3{}^- + H^+ \rightarrow Q + HBrO_2 + H_2O \qquad (R17)$$

We could not find any kinetic data in the literature on reactions R16 and R17. The reaction between H_2Q and bromine is fast, and by comparing the experimental data and the simulation a value of 3×10^4 mol^{-1} dm^3 s^{-1} was obtained for k_{16}. The order of k_{16} is the same as the order of the rate constant of the reaction between H_2Q and Fe(III), Co(III), Ce(IV), and Mn(III).[26]

We assumed that by removing bromine the kinetics might become autocatalytic and therefore added CHD to the reaction mixture (Figure 7). At low CHD concentrations, the rate of reaction decreased, and at the end, an autocatalytic step appeared (curve b in Figure 7). At high CHD concentrations the reaction became faster and autocatalytic (curve d in Figure 7). The absorbance was calculated from the absorbance of H_2Q, Q, and

TABLE 2: Results of Parameter Estimation for Reactions R14 and R15

$[H_2SO_4]$/ mol dm^{-3}	$[H^+]_T$/ mol dm^{-3}	k'_{14}/s^{-1}	k'_{15}/s^{-1}	ϵ^{240}_{CHED} mol^{-1} dm^3 cm^{-1}	ϵ^{290}_{CHED} mol^{-1} dm^3 cm^{-1}	CoD
0.5	0.63	$2.93 \times 10^{-5} (\pm 6.4 \times 10^{-7})$	$1.11 \times 10^{-4} (\pm 2.910^{-6})$	$1.43 \times 10^4 (\pm 378)$	58.7 (±5.78)	0.9999
1.0	1.29	$6.45 \times 10^{-5} (\pm 8.2 \times 10^{-7})$	$2.52 \times 10^{-4} (\pm 3.7 \times 10^{-6})$	$1.29 \times 10^4 (\pm 214)$	56.8 (±8.76)	0.9999
1.5	1.96	$1.14 \times 10^{-4} (\pm 1.2 \times 10^{-6})$	$4.71 \times 10^{-4} (\pm 5.8 \times 10^{-6})$	$1.40 \times 10^4 (\pm 200)$	31.8 (±12.22)	0.9999
2.0	2.65	$1.74 \times 10^{-4} (\pm 2.1 \times 10^{-6})$	$7.86 \times 10^{-4} (\pm 1.4 \times 10^{-5})$	$1.44 \times 10^4 (\pm 294)$	28.2 (±20.4)	0.9996

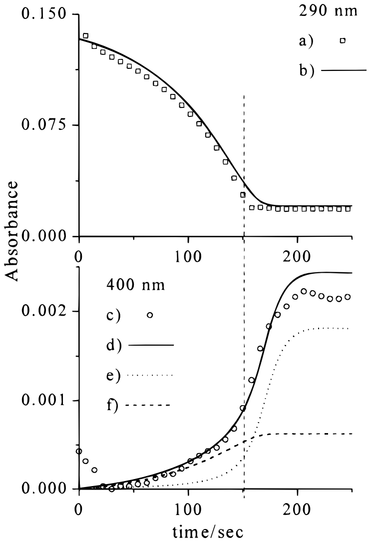

Figure 6. Absorbance changes during the bromate−1,4-dihydroxybenzene reaction. Experimental conditions: $[H_2Q]_0 = 5 \times 10^{-5}$ mol dm^{-3}, $[BrO_3^-]_0 = 8 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4]_0 = 1.0$ mol dm^{-3}, 20 °C. (a,c) Experimental data. (b,d) Simulated absorbances (R1−R18, R20). (e) Simulated absorbance of bromine. (f) Simulated absorbance of 1,4-benzoquinone. Absorption coefficients: $\epsilon^{400}_Q = 15$ mol^{-1} dm^3 cm^{-1}, $\epsilon^{290}_Q = 395$ mol^{-1} dm^3 cm^{-1}.

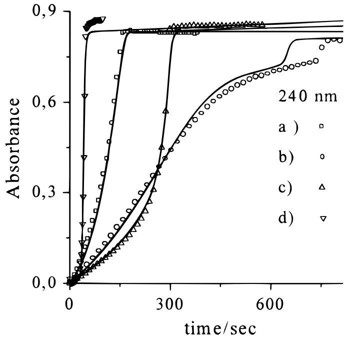

Figure 7. The effect of CHD on the reaction of bromate and H_2Q. Experimental conditions: $[H_2Q]_0 = 5 \times 10^{-5}$ mol dm^{-3},$[BrO_3^-]_0 = 8 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4]_0 = 1,0$ mol dm^{-3}, 20 °C (a) Without CHD. (b) $[CHD]_0 = 5 \times 10^{-4}$ mol dm^{-3}. (c) $[CHD]_0 = 2 \times 10^{-3}$ mol dm^{-3}. (d) $[CHD]_0 = 1 \times 10^{-2}$ mol dm^{-3}. Solid lines are the simulated curves (R1−R18).

CHED ($\epsilon^{240}_Q = 16500$ mol^{-1} dm^3 cm^{-1}, $\epsilon^{240}_Q = 14200$ mol^{-1} dm^3 cm^{-1}). We included three additional reactions into the model for the simulation:

$$H_2Q + BrO_2^{\bullet} \rightarrow HQ^{\bullet} + HBrO_2 \qquad (R8)$$

$$HQ^{\bullet} + BrO_2^{\bullet} \rightarrow Q + HBrO_2 \qquad (R9)$$

$$H_2Q + HOBr \rightarrow Q + Br^- + H^+ + H_2O \qquad (R18)$$

Upon considering the literature,[26] we had taken R9 as a diffusion controlled reaction ($k_9 = 8 \times 10^9$ mol^{-1} dm^3 s^{-1}). Upon the comparison of the experimental data and simulations, the following rate constants were suggested: $k_8 = 8 \times 10^5$ mol^{-1} dm^3 s^{-1}, $k_{17} = 2 \times 10^{-2}$ mol^{-2} dm^6 s^{-1}, and $k_{18} = 6 \times 10^5$ mol^{-1} dm^3 s^{-1}. These values satisfy the expected condition: $k_{17} < k_3 \ll k_{16}$ ($k_3 = 1.2$ mol^{-3} dm^9 s^{-1}). The agreement of the simulated curves with the experimental data is acceptable (Figures 6 and 7).

Oscillatory Behavior. We monitored the temporal change of the redox potential during the reaction of bromate ion and CHD in a sulfuric acid solution and assumed that the potential of Pt electrode mainly depended on the H_2Q/Q redox couple. Our model (Table 3) suitably simulated the oscillatory phase of the reaction; however, the induction period in the simulation was considerably longer than the experimentally measured one. In order to reduce the length of the induction period, we suggested a direct reaction between bromate and CHD (Figure 8).

$$CHD + BrO_3^- + H^+ \rightarrow H_2Q + HBrO_2 + H_2O \qquad (R19)$$

With this modification the induction period in the simulation became somewhat shorter (Figure 9). Unfortunately, we have no direct experimental proof on this reaction. Our aim was to suggest a chemical mechanism that accounted for the oscillatory behavior of the CHD−bromate−acid reacting system and focused on reactions, which are most probably important from this point of view. The shape and frequency of the simulated oscillations are very similar to the curves measured experimentally (Figure 10). We could also simulate qualitatively the potential change after the termination of oscillations. The system for a certain period of time remained in the “reduced” state that indicated the accumulation of H_2Q. After the consumption of H_2Q, a fast bromine production (“clock” behavior) was triggered (Figure 11).

Discussion

Similar to other bromate oscillators, the very special chemistry of bromate ion, that is, depending upon the actual bromide ion concentration, two-electron (oxygen transfer) and one-electron processes occur alternately, makes the CHD−bromate−acid system oscillatory. Its unusual organic chemistry, however, deserves special attention.

At room temperature, CHD reacts with bromate very slowly, and in order to shorten the induction period, runs have been performed at elevated temperatures (above 30 °C). The reason for the slow reaction is that as against the so far applied organics, which are mostly phenol or aniline derivatives, the oxidation of CHD with BrO_2 is not a favored reaction, because CHD is a symmetric and is toward a single hydrogen abstraction reaction ($BrO_2^{\bullet} + RH \rightarrow HBrO_2 + R^{\bullet}$) a rather unreactive molecule. Therefore, it is more likely that bromate ion attacks one of the $-CH_2-CH_2-$ units of CHD, producing a chelate-type activated complex, not uncommon when certain oxyanions (e.g., MnO_4^- or IO_3^-) react with an organic compound, that decomposes according to Figure 8.

The CHD−bromate reaction cannot be followed directly; however, our recent calorimetric studies[27] seems to provide an indirect support for our assumption. In the caloric experiments

TABLE 3: Mechanistic Model of the CHD−Bromate−Acid Oscillatory System

				ref
R1	$Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O$	$k_1 = 8 \times 10^9$ mol^{-2} dm^6 s^{-1}	$k_{-1} = 80$ s^{-1}	32
R2	$Br^- + HBrO_2 + H^+ \rightleftharpoons 2HOBr$	$k_2 = 2.5 \times 10^6$ mol^{-2} dm^6 s^{-1}	$k_{-2} = 2 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}	32
R3	$Br^- + BrO_3^- + 2H^+ \rightleftharpoons HOBr + HBrO_2$	$k_3 = 1.2$ mol^{-3} dm^9 s^{-1}	$k_{-3} = 3.2$ mol^{-2} dm^6 s^{-1}	33
R4	$HBrO_2 + H^+ \rightleftharpoons H_2BrO_2^+$	$k_4 = 2 \times 10^6$ mol^{-1} dm^3 s^{-1}	$k_{-4} = 1 \times 10^8$ s^{-1}	34
R5	$HBrO_2 + H_2BrO_2^+ \rightarrow HOBr + BrO_3^- + 2H^+$	$k_5 = 1{,}7 \times 10^5$ mol^{-1} dm^3 s^{-1}		34
R6	$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons Br_2O_4 + H_2O$	$k_6 = 48$ mol^{-2} dm^6 s^{-1}	$k_{-6} = 3.2 \times 10^3$ s^{-1}	33
R7	$Br_2O_4 \rightleftharpoons 2BrO_2^\bullet$	$k_7 = 7.5 \times 10^4$ s^{-1}	$k_{-7} = 1.4 \times 10^9$ mol^{-1} dm^3 s^{-1}	33
R8	$H_2Q + BrO_2^\bullet \rightarrow HQ^\bullet + HBrO_2$	$k_8 = 8 \times 10^5$ mol^{-1} dm^3 s^{-1}		*a*
R9	$HQ^\bullet + BrO_2^\bullet \rightarrow Q + HBrO_2$	$k_9 = 8 \times 10^9$ mol^{-1} dm^3 s^{-1}		*a*
R10	$2\ HQ^\bullet \rightleftharpoons H_2Q + Q$	$k_{10} = 8.8 \times 10^8$ mol^{-1} dm^3 s^{-1}	$k_{-10} = 7.7 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}	35
R11	$CHD + H^+ \rightleftharpoons CHDE + H^+$	$k_{11} = 2.13 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}	$k_{-11} = 5.2 \times 10^2$ mol^{-1} dm^3 s^{-1}	*a*
R12	$CHDE + Br_2 \rightarrow BrCHD + H^+ + Br^-$	$k_{12} = 2.8 \times 10^9$ mol^{-1} dm^3 s^{-1}		23
R13	$CHDE + HOBr \rightarrow BrCHD + H_2O$	$k_{13} = 2.8 \times 10^9$ mol^{-1} dm^3 s^{-1}		23
R14	$BrCHD \rightarrow CHED + Br^- + H^+$	$k_{14} = 5 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}		*a*
R15	$CHED + H^+ \rightarrow H_2Q + H^+$	$k_{15} = 1.94 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}		*a*
R16	$H_2Q + Br_2 \rightarrow Q + 2Br^- + 2H^+$	$k_{16} = 3 \times 10^4$ mol^{-1} dm^3 s^{-1}		*a*
R17	$H_2Q + + H^+ BrO_3^- \rightarrow Q + HBrO_2 + H_2O$	$k_{17} = 2 \times 10^{-2}$ mol^{-2} dm^6 s^{-1}		*a*
R18	$H_2Q + HOBr \rightarrow Q + Br^- + H^+ + H_2O$	$k_{18} = 6 \times 10^5$ mol^{-1} dm^3 s^{-1}		*a*
R19	$CHD + BrO_3^- + H^+ \rightarrow H_2Q + HBrO_2 + H_2O$	$k_{19} = 1 \times 10^{-5}$ mol^{-2} dm^6 s^{-1}		*a*

[a] The value comes from our parameter estimations or simulations. The values refer to a temperature of 20 °C. $[H_2O] = 55$ mol dm^{-3} is included in the rate constant. CHD = 1,4-cyclohexanedione; CHDE = enol form of CHD; BrCHD = 2-bromo-1,4-cyclohexanedione, CHED = 2-cyclohexene-1,4-dione, H_2Q = 1,4-dihydroxybenzene; Q = 1,4-benzoquinone, $HQ^\bullet$ = semiquinone radical.

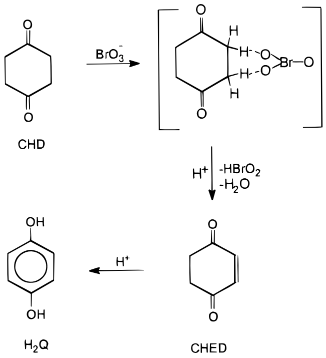

Figure 8. Reaction of CHD and bromate ion.

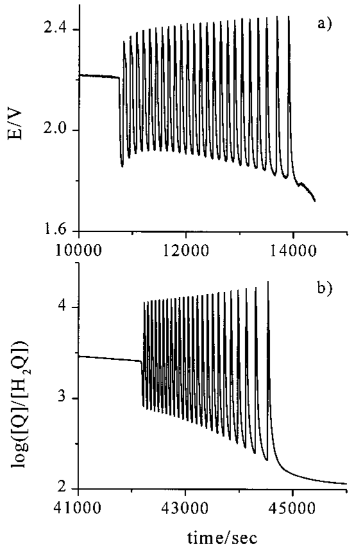

Figure 9. Oscillations during the bromate−CHD reaction. Experimental conditions: $[CHD]_0 = 0.10$ mol dm^{-3}, $[NaBrO_3]_0 = 0.10$ mol dm^{-3}, $[H_2SO_4]_0 = 1.0$ mol dm^{-3}, 20 °C. (a) Measured redox potential. (b) Simulation (R1−R19).

we observed that, during the induction (preoscillatory) period of the CHD−bromate reaction, the rate of heat evolution was a constant, low value, indicating a slow exothermic reaction.

H_2Q plays a central role in the function of the oscillatory system. When during the reaction a considerable amount of H_2Q (10^{-5}−10^{-4} mol dm^{-3}) accumulates, a direct reaction between bromate and H_2Q takes its role. As oxidation product 1,4-benzoquinone is formed, and in a parallel running reaction, bromine, the reduction product of bromate ion, brominates CHD. Via the formation of BrCHD, as an intermediate, CHD is converted to H_2Q by HBr elimination. Bromide ions act as inhibitors when through a series of oxygen transfer reactions

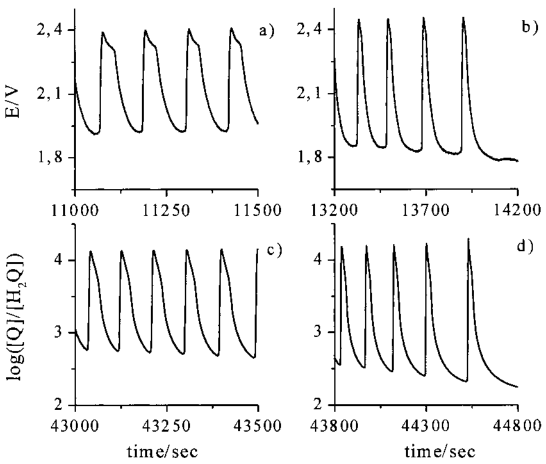

Figure 10. Start and termination of the oscillations. (a,b) Measured redox potential (the conditions are same as in Figure 9). (c,d) Simulated curve.

$$BrO_3^- \xrightarrow{Br^-} HBrO_2 \xrightarrow{Br^-} HOBr \xrightarrow{Br^-} Br_2 \text{ (and/or R−Br)}$$

their concentration drops below a critical value. Because H_2Q is generated slowly, however continuously, even under a batch configuration a high number (200−300) of oscillations can be recorded.

By considering the mechanism of the CHD−bromate−acid oscillator, we are inclined to claim that some kind of analogy exists between this system and the $IO_3^- - SO_3^{2-} - Fe(CN)_6^{4-}$ one, the latter studied thoroughly by Edblom et al.[28] The H_2Q−bromate reaction is of a clock type, same as the $IO_3^- - SO_3^{2-}$ reaction. The latter one can be converted to an oscillatory system by the addition of a second reducing agent. Hexacyanoferrate(II) ion proved to be most suitable reductant for this purpose. A somewhat similar situation seems to exists when

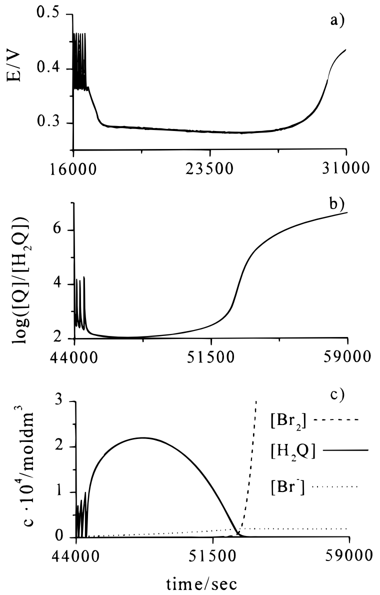

Figure 11. Redox potential change after the oscillation. (a) Measured redox potential (the conditions are same as in Figure 9). (b,c) Simulated curves.

the reaction mixture contains H_2Q, bromate ion, and CHD, where the role of CHD is comparable to that of hexacyanoferrate(II) ion in the Edblom et al. system. Similar systems have been reported also during the late seventies by Rábai et al.[29] They observed the appearance of three extrema in halide ion concentration vs time curves when malonic acid was added to a variety of Landolt-type systems (e.g., $IO_3^- + SO_3^{2-}$, $IO_3^- + AsO_3^{3-}$, $BrO_3^- +$ ascorbic acid). Later Rábai and Beck[30] observed that in the $IO_3^- + S_2O_3^{2-} + HSO_3^-$ reacting system a few, high amplitude, damped oscillatory pH changes occurred even under batch configuration in narrow concentration ranges of the reactants.

A major difference between the previously reported Landolt-type (oligo)oscillators and the CHD−bromate−acid system is that in the latter one of the reducing agents (H_2Q) is *generated* during the reaction; in the former one, however, both reductants should be present at the start of the reaction.

Our observation might open a novel way to search for batch oscillators that exhibit a rather prolonged oscillatory phase due to the small portions of reactants (on the order of 10^{-5} mol dm^{-3}) consumed in a single oscillatory step. Attempts should be made to try to find reactions, which produce such rather stable intermediates, that can convert Landolt-type reactions to oscillatory ones.

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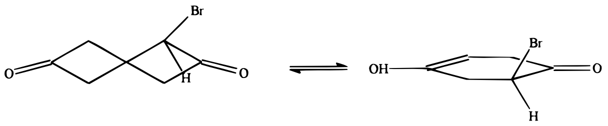
(24) R15 is a HBr elimination from the BrCHD and it is rather unusual that the rate of elimination increases with an increase in acid concentration. This can be explained in terms of an enolization preequilibrium:



The enol form of BrCHD has a planar geometry with three sp^2 carbon atoms that generate a strained state, thus facilitating the splitting off of the HBr unit.
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