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# Uncatalysed Oscillatory Chemical Reactions. Oxidation of 1,4-Cyclohexanedione by Bromate in Perchloric or Orthophosphoric Acid Solution

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## Introduction

In a previous publication [1] we reported that chemical oscillations occur during the oxidation of 1,4-cyclohexanedione (Tetrahydroquinone ≡ THQ) by bromate in acid solution. The system requires no catalyst such as the redox couples $Ce^{4+}/Ce^{3+}$ or $Mn^{3+}/Mn^{2+}$ in the Belousov–Zhabotinskii type reactions. We also showed that this new oscillating reaction takes place not only in the presence of sulfuric acid, as is generally the case, but also in nitric acid solution.

At present we have found that this new uncatalysed oscillating chemical reaction can also occur in a perchloric or orthophosphoric acid solution with characteristics as remarkable (frequency, amplitude and number of oscillations) as those found in the presence of $H_2SO_4$ or $HNO_3$ [1]. It is the only uncatalysed oscillating chemical reaction system known to date which can be observed in four different acid solutions.

## Experimental

Reagents: 1,4-cyclohexanedione (*purum*), $NaBrO_3$ (*puriss.*): Fluka A.G. $HClO_4$ (zur analyse), $H_3PO_4$ (zur analyse): Merck A.G. $NaBrO_3$ was used instead of $KBrO_3$ to avoid the formation of a precipitate of $KClO_4$.

The reaction vessel was a Metrohm EA 880 T-V thermostatted glass reactor. The total volume of solution was always 80 ml. All the experiments were carried out at 35 °C in a $N_2$ atmosphere and the solution was stirred at a constant rate of 1000 r.p.m. [2]. The redox potential was measured by means of a Pt electrode, and the $Br^-$ concentration with a selective electrode (Philips IS 550-Br). The reference electrode was a Hg(II) sulfate electrode.

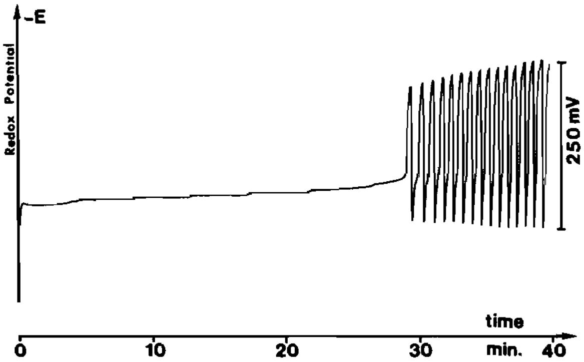

Fig. 1. Redox potentiometric oscillations of the $THQ/BrO_3^-/HClO_4$ system. [THQ] = 0.10 *M*; [$NaBrO_3$] = 0.10 *M*; [$HClO_4$] = 2.0 *M*.

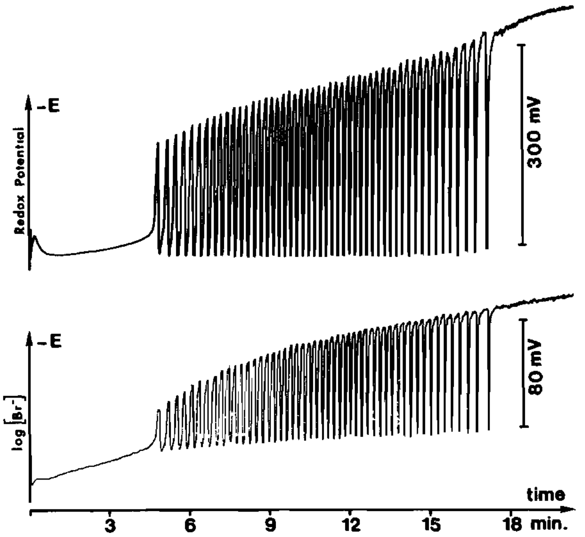

Fig. 2. Simultaneous measurements of the redox potential and the log $Br^-$ concentration of the $THQ/BrO_3^-/H_3PO_4$ system. [THQ] = 0.15 *M*; [$NaBrO_3$] = 0.10 *M*; [$H_3PO_4$] = 5.0 *M*.

## Results and Discussions

The originality of this new oscillating chemical system lies in the fact that the oscillations take place equally well in sulfuric [1], nitric [1], perchloric or orthophosphoric acid solutions. Figure 1 illustrates the redox potentiometric oscillations of the $THQ/BrO_3^-/HClO_4$ system, and Fig. 2 shows the simultaneous measurements of the redox potential and the $Br^-$ ions concentration of the $THQ/BrO_3^-/H_3PO_4$ system. It was not possible to use the bromide-ion selective electrode in the $THQ/BrO_3^-/$

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TABLE I. Influence of the Chemical Composition of the THQ/$BrO_3^-$/$HClO_4$ System on the Oscillatory Phenomenon.

| THQ<br>*M* | $NaBrO_3$<br>*M* | $HClO_4$<br>*M* | $\tau_{ind.}$<br>min | $1/\nu$<br>min | ΔE<br>mV | N |
|---|---|---|---|---|---|---|
| 0.10 | 0.10 | 2.0 | 29.0 | 0.90–0.64–0.90 | 202–323 | 73 |
| 0.10 | 0.10 | 3.0 | 24.8 | 0.36–0.26–0.46 | 105–206 | 162 |
| 0.10 | 0.10 | 4.0 | 21.5 | 0.20–0.16–0.30 | 80–260 | 228 |
| 0.05 | 0.10 | 2.0 | 41.7 | 0.80–0.55–0.90 | 158–277 | 78 |
| 0.15 | 0.10 | 2.0 | 24.7 | 0.81–0.65–1.08 | 212–352 | 52 |
| 0.10 | 0.20 | 2.0 | 48.9 | 0.30–0.22–0.40 | 76–250 | 154 |

TABLE II. Influence of the Chemical Composition of the THQ/$BrO_3^-$/$H_3PO_4$ System on the Oscillatory Phenomenon.

| THQ<br>*M* | $NaBrO_3$<br>*M* | $H_3PO_4$<br>*M* | $\tau_{ind.}$<br>min | $1/\nu$<br>min | ΔE<br>mV | N |
|---|---|---|---|---|---|---|
| 0.10 | 0.10 | 4.0 | 6.0 | 0.75–0.50–0.68 | 182–260 | 21 |
| 0.10 | 0.10 | 5.0 | 5.2 | 0.44–0.22–0.40 | 78–213 | 58 |
| 0.10 | 0.10 | 6.0 | 7.0 | 0.15–0.10–0.25 | 37–232 | 101 |
| 0.05 | 0.10 | 5.0 | 11.4 | 0.24–0.20–0.36 | 65–248 | 62 |
| 0.15 | 0.10 | 5.0 | 4.4 | 0.40–0.20–0.38 | 172–326 | 50 |
| 0.10 | 0.20 | 5.0 | 14.1 | 0.12–0.08–0.15 | 46–190 | 104 |

$HClO_4$ system, as for the $HClO_4$ concentrations used we observed an attack of the electrode membrane which dissolved in the solution thus perturbing the oscillatory phenomenon.

Tables I and II give the variations of the induction period ($\tau_{ind.}$), the period of oscillation ($1/\nu$), the amplitude (ΔE) and the total number of oscillations (N) relative to the chemical composition of the THQ/$BrO_3^-$/$HClO_4$ and THQ/$BrO_3^-$/$H_3PO_4$ systems. Three values were noted for $1/\nu$, corresponding respectively to the beginning, the middle and the end of the oscillations. The two values for ΔE are relative to the first and last oscillations.

We point out that N is very closely related to the acidity of the solution, sharply increasing with the $H^+$ concentration. Thus, for the THQ/$BrO_3^-$/$HClO_4$ sytem in which $HClO_4$ is a strong acid, N = 228 for [$HClO_4$] = 4.0 *M*, while we came up with N = 21 in the system involving $H_3PO_4$ for the same concentration in acid. The behaviour of $\tau_{ind.}$, however, is unexpected: for the same chemical composition, the value of $\tau_{ind.}$ of the THQ/$BrO_3^-$/$HClO_4$ system is more than 3.5 times higher than that of the THQ/$BrO_3^-$/$H_3PO_4$ system.

In all the oscillating chemical systems studied up to now, N increases with the concentration of the organic reductant. The new systems produce the opposite effect: N decreases as THQ increases, which is quite surprising.

## References

1 V. J. Farage and D. Janjic, *Chem. Phys. Letters*, in press.
2 V. J. Farage and D. Janjic, *Chimia*, *35*, 289 (1981).