Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 5. des Monats bei der Redaktion eingehende Manuskripte können günstigenfalls am 15. des folgenden Monats veröffentlicht werden.

Uncatalyzed and Catalyzed Oscillatory Reactions in the System: 1,2-Dihydroxy-3,5-Benzenedisulfonic Acid Disodium Salt (Tiron) / BrO_3^-/H_2SO_4. Kinetic Study of the Decrease in Tiron Concentration by HPLC.*

Dominique Habashi-Krayenbuhl, Sélim Dogan** and Désimir Janjic***
University of Geneva, Department of Physical Chemistry
30, quai Ernest-Ansermet, CH-1211 Geneva 4 (Switzerland)

Abstract
Oscillatory behaviour in the redox potential of the tiron/BrO_3^-/H_2SO_4 system is reported for the uncatalyzed, the cerium (IV) as well as the ferroin catalyzed systems. The effect of temperature, the rate of decrease in [tiron] were investigated for the catalyzed and uncatalyzed systems. Pentabromoacetone, a reaction product, was isolated from the reaction medium.

Introduction

The most commonly known oscillatory reaction, the Belousov-Zhabotinskii reaction, occurs when malonic acid is added to an aqueous bromate acid solution containing a cerium salt as catalyst [1]. The colour of the mixture changes periodically from yellow to colourless. Measurements of the electrical potential of the working solution show oscillations, reflecting oscillation in intermediate product concentrations. Chemical oscillations have equally been produced with organic substrates other than malonic acid [2]. More recently, it has been found that many aromatic compounds could produce oscillations even without a catalyst [3].
A detailed mechanism was first proposed by *Field* et al. [1] which was modified later to adapt it to new systems [4]. The thermodynamical aspects of these reactions have been reviewed [5].

* Received November 17, 1983
** Present address: Laboratoire Cantonal de Chimie, Case postale 109, 1211 Genève 4 (Suisse)
*** Author to whom correspondence may be addressed

Our choice of tiron as organic substrate was prompted by our interest in the effect on the oscillatory phenomenon of benzene ring substituents other than those previously reported [3]. We found that it could produce oscillations in a BrO_3^-/aqueous sulfuric acid solution. The purpose of our study was to investigate differences between the uncatalyzed system, systems catalyzed by either cerium (IV) or ferroin by means of potentiometric measurements and to compare the effects of temperature on these systems.

A reaction product, pentabromoacetone, was isolated and identified. We then investigated the fate of the organic product: the consumption rate of tiron was measured by HPLC (high-performance liquid chromatography) using an electrochemical detector. The kinetic rate constant for the reaction was calculated for the three afore-mentioned systems at different temperatures and the corresponding activation energies were determined.

Experimental

The redox potentiometric measurements were obtained by means of a platinum electrode and a mercury (II) sulfate reference electrode. A thermostatted and magnetically stirred glass reactor was used, the total volume of solution was always 50 ml.

Liquid chromatography: A Beckman 112 single-piston pump equipped with an Altex 210 injection valve, an Altex Ultrasphere-ODS 5 μm (250 × 4.6 mm) reversed-phase column was used; the flow rate of the eluent was 0.8 ml/min. The detection system consists of a Metrohm 656 electrochemical detector with detecting cell and electrode and a Metrohm 641-VA detector for adjustment of the polarisation potential and for measurement of the current. In our experiments, a polarisation potential of + 800 mV was applied.

Reagents: Tiron, $KBrO_3$ (p.a. Fluka), $Ce(SO_4) \cdot 4\,H_2O$, H_2SO_4 (p.a. Merk), ferroin solution was prepared by the action of $FeSO_4$ on orthophenanthroline.

The elution solvent for HPLC was prepared by dissolving 5g of $(NH_4)_2SO_4$ (p.a. Merck) in 1 l. of aqueous CH_3COOH 5×10^{-2} M and then degassed using ultrasound.

Results

For the uncatalyzed system A, for the cerium (IV) catalyzed system B and for the ferroin catalyzed system C, [tiron] = 2.22×10^{-2} M, [BrO_3^-] = 7×10^{-2} M and [H_2SO_4] = 1.5 M. For systems B and C, [catalyst] = 5×10^{-4} M.

In all experiments, tiron was added to the acidic bromate solution. The solution immediately turns to a dark red colour which slowly dissappears. A white precipitate is slowly formed, the chemical composition of which was found to be pentabromoacetone.

Redox potentiometric measurements. Effect of temperature

Fig. 1(a), 1(b) and 1(c) exemplify the temporal oscillations of the redox potential for systems A, B and C; typical values are given in table 1. In all three systems, one notices a short induction period followed by a jump in potential of about 170 mV. This is followed by a second longer induction period, the duration of which varies from 11 minutes for B to 30 minutes for C at 35.5 °C. The number of oscillations and their frequency increase in the cerium (IV) and ferroin catalyzed systems. As for other chemical oscillators, the induction period decreases

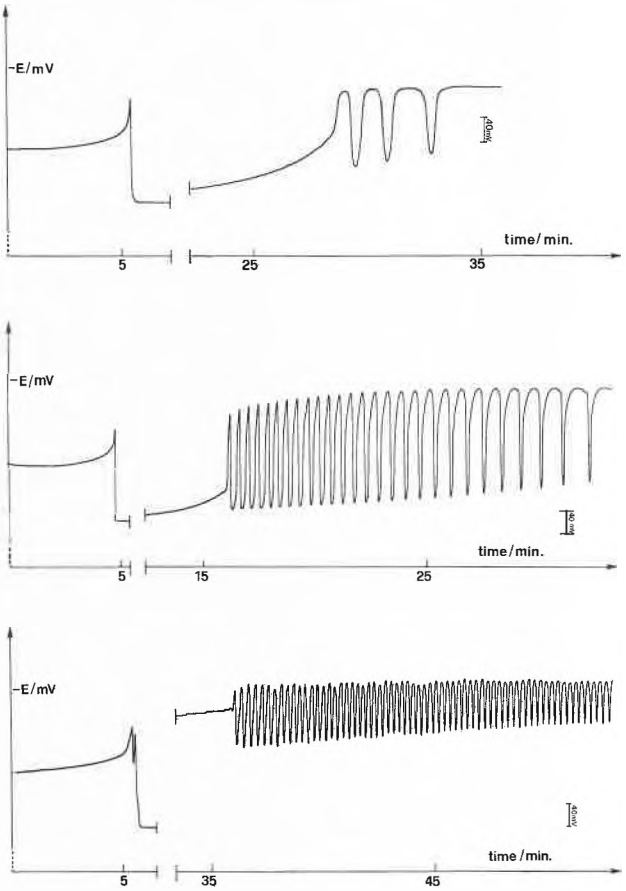

Fig. 1 (a–c): For uncatalyzed system A (1 a), for Ce (IV) catalyzed system B (1 b) and for ferroin catalyzed system C (1 c), [tiron] = 2.2×10^{-2} M, [BrO_3^-] = 7×10^{-2} M, [H_2SO_4] = 1.5 M; for B and C, [catalyst] = 5×10^{-4} M. T = 35.5 °C.

Table 1: Tiron/BrO_3^-/H_2SO_4 system. Influence of the catalysts on the oscillatory phenomenon for T = 35.5 °C. Concentrations A, B, C as for fig. 1.

System	1st $t_{ind.}$ |min|	2nd $t_{ind.}$ |min|	Number of oscillations	Period of 2nd oscillation |min|	Amplitude of 2nd oscillation |mV|
A	5,4	23,2	3	1,4	130
B	4,7	11,3	23	0,45	180
C	5,4	30,5	164	0,3	108

with increasing temperature and ln $1/t_{ind.}$ is a linear function of $1/T$ [6] where $t_{ind.}$ is the total induction period and 25 °C $\leqslant T \leqslant$ 45 °C. The Arrhenius equation is used to calculate the corresponding activation energies. These values are listed in table 2 and are of the same of order of magnitude as those usually found for chemical oscillators [6]. Both without catalyst (A), and with cerium (IV) (B), similar activation energies are observed although the induction period for A is twice that of B. Activation energy is highest for the ferroin catalyzed system for which the induction period is also the longest.

Table 2: Temperature dependence of the induction period. Activation energies for systems A, B, C, concentrations as for fig. 1.

System	E_a $\lvert kJ \cdot mol^{-1} \rvert$
A	73
B	75
C	84

Formation of pentabromoacetone (PBrA)

The reaction medium tiron/BrO_3^-/dilute sulfuric acid brings about the formation of PBrA with or without a catalyst and also for reagent concentrations out of the range of the oscillatory conditions. PBrA occurs in the crystalline form in the reaction vessel. Different methods were used to determine the structure of the white precipitate. Melting point: 78 °C (litt.: 73.2 °C [7]).
UV: Λmax: 261 nm (in CCl_4)
NMR: δ = 6.8 ppm
IR: 1760 cm^{-1} (C=O vibration with halide substituents)
Mass spectrometry: 452 ($HBr_2CCOCBr_3$); 279 ($-COCBr_3$); 251 ($-CBr_3$) 201 ($-COCBr_2H$; 173 ($-CBr_2H$)
Elementary analysis: C_3HBr_5O (452.6)
Calc. C 7.96 H 0.22 Br 88.28%
Found C 8.05 H 0.4 Br 88.18%
The yield of PBrA cannot be measured accurately since the product crystallizes over a period of days in the reaction medium and the quantities of PBrA have small absolute values.

Study of the decrease in tiron by HPLC

Preliminary tests to detect tiron by UV spectroscopy proved it was practically impossible to use this method for quantitative analysis because so many different chemical species in the reaction medium absorb at the absorption wave-length of tiron. We therefore chose the HPLC method coupled to an electrochemical detector. A linear relationship was found between the peak heights and [tiron]. The following method was used to analyse [tiron]: samples of 50 to 100 μl were withdrawn from the beginning of the reaction until the nearly total disappearance of tiron. Time intervals for sampling were chosen so as to have about ten samples per experiment and varied from 1 to 5 minutes depending on reaction temperature. The samples were immediately diluted 100 to 200 times with the elution solvent to stop the reaction and a volume of 20 μl was injected into the column. The same operation was repeated under conditions A, B and C for 21 °C $\leqslant T \leqslant$ 42 °C. In the catalyzed and uncatalyzed systems, [tiron] reaches the limit of detection (about 10% of initial concentration) during the induction period for C, near the beginning of the oscillatory phenomenon for A and during the oscillations for B. The apparent rate constants k_1 for the decrease in [tiron] where k_1 is the slope of the straight line ln [tiron] = f(t) have been calculated, the reaction therefore obeys a first-order rate law. From these rate constants k_1 and using the Arrhenius equation, we calculated activation energies of 70 kJ mol^{-1} for systems A, B and C respectively. We then collected all the values ln k_1 = f(1/T) for A, B and C into a single plot (fig. 2) from which an activation energy of 70 kJ mol^{-1} was found as above. It therefore seems unlikely that the "catalysts" act as such for the consumption of tiron.

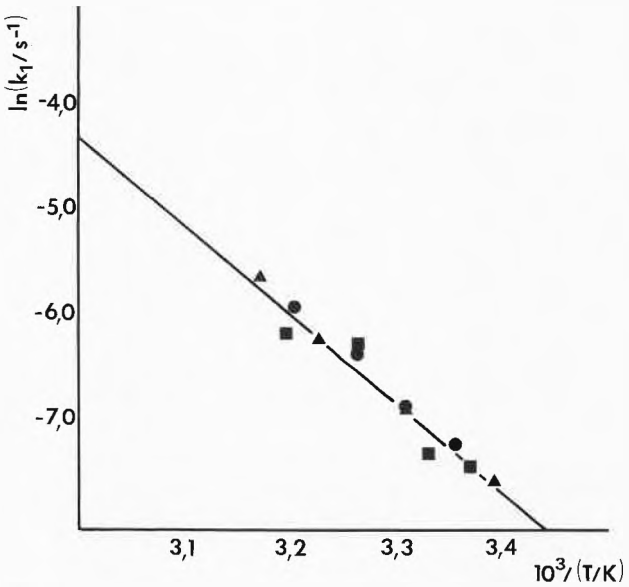

Fig. 2: Arrhenius plot for tiron consumption (systems A (▲), B (●), C (■), concentrations as for fig. (1).

Because of the many reactions involved in the oscillatory phenomenon, we cannot as yet give a satisfactory interpretation of the above results. Our aim is therefore to further investigate the fate of the organic reagent both by analytical and by physicochemical techniqes.

Acknowledgement

The authors wish to thank Mr. *H. Diamantides* for valuable discussions during the course of this work. We are also thankful to Prof. *A. Buchs* for the mass spectrum and Dr. *H. Eder* for the elementary analysis.

References

1 *R. J. Field, E. Körös* and *R. M. Noyes:* J. Am. Chem. Soc. *94*, 8649 (1972).
2 *U. F. Franck:* Angew. Chem. Int. Ed. Engl. *17*, 1 (1978).
3 *M. Orban* and *E. Körös:* J. Phys. Chem. *82*, 1672 (1978).
4 *R. M. Noyes:* J. Am. Chem. Soc. *102*, 4644 (1980).
5 *D. Huber:* Chimia *37* (1983) 292; *R. P. Rastogi* and *R. Shabd:* J. Chem. Ed. *60*, 540 (1983).
6 *V. J. Farage, P. Stroot* and *D. Janjic:* Helv. *60*, 231 (1977); *M. J. Blandamer* and *S. H. Morris:* J. Chem. Soc. Faraday I, *71*, 2319 (1975).
7 *O. Reichard:* Dtsch. Lebensm. Rundsch. *9*, 218 (1966).