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Time Evolution of the Activation Energy in a Batch Chemical Oscillator

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The batch-operated bromate/phosphate/acetone/dual catalyst system was studied at four temperatures between 5 and 35 °C. The dynamics was simultaneously followed by potential measurements with platinum and bromide selective electrodes, and spectroscopically at two different wavelengths. By simultaneously recording these four time series it was possible to characterize the dynamics of the sequential oscillations that evolve in time. The existence of three sequential oscillatory patterns at each temperature allowed estimating the activation energies in each case. Along with the activation energy of the induction period, it was possible to trace the time evolution of the overall activation energy at four different stages as the reaction proceeds. The study was carried out for two different sets of initial concentrations and it was observed that the overall activation energy increases as reactants turn into products. This finding was propounded as a result of the decrease in the driving force, or the system's affinity, of the catalytic oxidative bromination of acetone with acidic bromate, as the closed system evolves toward the thermodynamic equilibrium.

1. Introduction

Multistable, excitable, oscillatory, and even chaotic kinetics are ubiquitous in many reacting chemical systems. Examples of complex dynamics are encountered in heterogeneous solid/gas and solid/liquid interfaces and homogeneous systems.[1−3] In those systems complex behavior emerges when they are refrained from thermodynamic equilibrium and might depend on several constraints connected to the system's dynamics. Temperature is well recognized as one of the main constraints in reacting chemical systems, and a small number of studies concerning its effects on the oscillatory dynamics of some chemical[4−11] and electrochemical[12−15] oscillators have been reported. The effect of temperature in a network of several individual steps, such as in an oscillatory system, might manifest quite divergent results from that seen in an individual reaction once it is a weighted combination of different elementary steps, which commonly are not well-known. The overall activation energy of such a network is the result of a nontrivial combination of several individual steps. Thus, the systematic investigation of properties such as activation energy under different conditions might help uncover different mechanistic aspects of oscillatory reactions. This paper reports the temporal evolution of the overall activation energy in the course of the oscillatory reduction of bromate ions in the $BrO_3^-/H_2PO_2^-$/acetone/Mn(II)-ferroin system,[16−19] in batch.

2. Experimental Section

The experiments were performed in a 90 cm^3 glass reactor covered with a Teflon cap. The reactor was surrounded by a jacket from which water from a thermostated bath was circulated to maintain the set temperature. The reacting mixture occupied 50 cm^3. A magnetic stirrer with a Teflon stirring bar (15 mm long and 5.7 mm in diameter) was used and the rotation speed was fixed at about 1400 rpm. The oscillations were simultaneously accompanied by the potential of a platinum electrode (E_{Pt}) and a bromide selective electrode (E_{Br}), and also spectrometrically at 518 and 356 nm. Both potentials were registered with relation to a standard hydrogen electrode (SHE) prepared with 1.33 mol L^{-1} of aqueous sulfuric acid and connected to the solution mixture through a capillary. An Ocean optics USB 4000 UV−vis spectrometer system equipped with a bifurcated optic fiber and transmission dip probe with an adjustable path (2−10 mm) tip was used. The optical probe was immersed into the reactor vessel via an opening in the lid. Ferroin, $[Fe(phen)_3]^{2+}$, was prepared just before each experiment by mixing 1.10-phenanthroline (phen) with $FeSO_4$ in a stoichiometric ratio. All chemicals were used as received: H_2SO_4 (Mallinckodt 97,5%), $NaH_2PO_2\cdot H_2O$ (Synth), $MnSO_4\cdot H_2O$ (Mallinckodt), $NaBrO_3$ (Vetec), acetone (J.B. Baker 99,7%), $FeSO_4\cdot 7H_2O$ (Merk p.a.), and 1,10-phenanthroline (Riedel-de Haën p.a.). The solutions were prepared with ultrapure water (milli-Q system).

3. Results and Discussion

The bromated/dual substrate/dual catalyst system has been introduced[16] as an interesting system because it presents long-lasting oscillations, gas and precipitate-free evolution, as well as wave formation features. Figure 1 shows the time evolution of the $BrO_3^-/H_2PO_2^-$/acetone/Mn(II)-ferroin system after mixing all the ingredients at 25 °C. Overall, as time evolves four states can be identified: initially the induction period and then the sequential oscillations, named here as types I, II, and III.

Notwithstanding the continuous nature of the transformation from the patterns of type I to III, the specific features such as oscillation amplitude, period, and waveform enabled us to distinguish them at different temperatures. Next, we highlight the key aspects of each pattern. The main feature of the first oscillatory pattern emerging after the induction period, oscillations of type I, is the almost absent oscillation in the absorbance at 356 nm and the rather small oscillations at 518 nm. In addition, such oscillations have a comparatively higher frequency and larger amplitude in the measured potential of both electrodes. Oscillations of type II can be distinguished from the ones of type I mainly on account of the higher oscillation amplitude in the absorbance at 518 nm and also because of the

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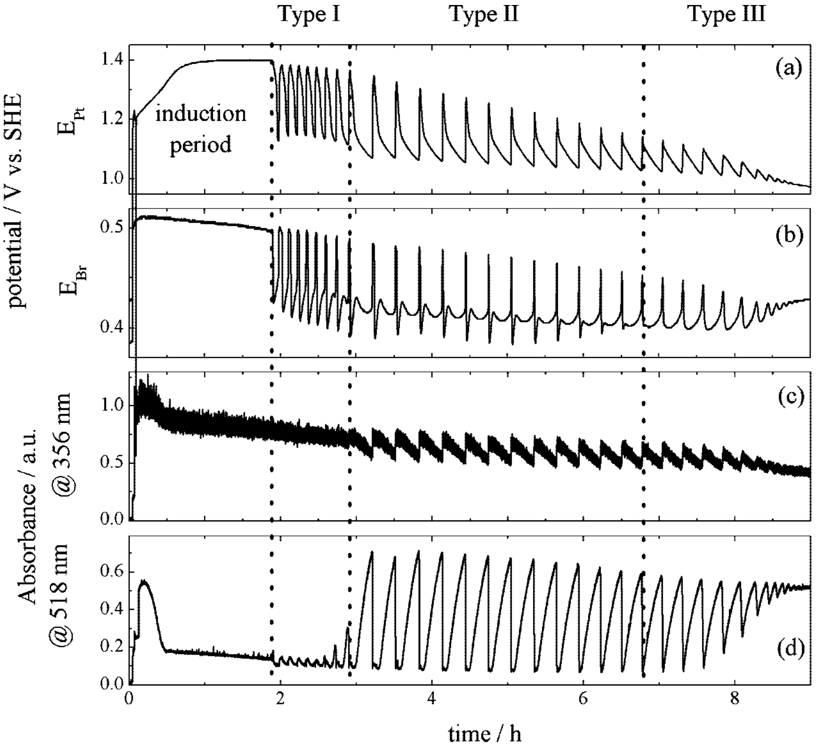

Figure 1. Time evolution of the bromate/dual substrate/dual catalyst at $T = 25$ °C. Initial concentrations: $[BrO_3^-] = 50$ mmol L^{-1}; $[H_2PO_2^-] = 110$ mmol L^{-1}; $[Mn^{2+}] = 3.1$ mmol L^{-1}; $[H_2SO_4] = 1.33$ mol L^{-1}; [acetone] = 320 mmol L^{-1}; [ferroin] = 0.33 mmol L^{-1}.

nonnegligible oscillations at 356 nm. Type II oscillations are also characterized by a lower frequency, a more pronounced relaxation-like feature in the E_{Pt} time trace, and a complex oscillation in the E_{Br} time series, manifested as a small and slow modulation in addition to the main abrupt transition. Finally, oscillations of type III show smaller amplitude in the E_{Pt} time series, and also a simpler behavior in the E_{Br} time series. In addition, a small modulation in the low state absorbance at 518 nm, which is present in the oscillations of types I and II, is absent here.

A noteworthy fact when analyzing the time series given in Figure 1 is the features of sequential oscillations I and II. As is clearly seen, oscillations in the ferroin concentration, as inferred by the absorbance at 518 nm, are very small for type I. Furthermore, oscillations in the ferriin concentration (absorbance at 356 nm) are not seen in this case. On the other hand, oscillations between ferroin/ferriin states are unambiguously detected in oscillations of types II and III. This finding can be interpreted as a direct experimental evidence of the mechanism recently suggested by Kurin-Csorgei et al.[18] for the bromated/dual substrate/dual catalyst batch oscillator. The authors used $[Ru(bpy)_3]^{2+}$ as the second catalyst instead of $[Fe(phen)_3]^{2+}$ as in the present case, and otherwise similar conditions. The dynamic behavior of the bromate/dual substrate/dual catalyst batch oscillator was rationalized in terms of the coupling between two suboscillators: $BrO_3^-/H_3PO_2/Mn(II)$/acetone, and BrO_3^-/BrAc/Ru(II). In this scheme, bromoacetone (BrAc) is initially produced by the first oscillator and then takes part in the second (core) oscillator. Importantly, in the first part of the oscillations the active catalyst is Mn^{2+} whereas the second catalyst, $[Fe(phen)_3]^{2+}$ in the present case, starts playing a role only after some time, or, in other terms, after a critical concentration of BrAc has been reached. Indeed, such a switch between the two main catalysts is clearly shown in the transition between oscillations of types I and II, regarding the absorbance time series depicted in Figure 1c,d.

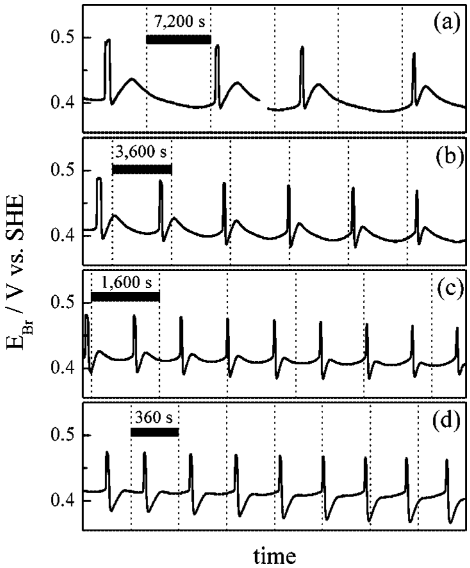

Figure 2. Temperature effect on oscillations of type II: (a) 5 °C, (b) 15 °C, (c) 25 °C, and (d) 35 °C. The remaining conditions are identical to those given in Figure 1.

Oscillations in the $BrO_3^-/H_2PO_2^-$/acetone/Mn(II)-ferroin system were found to be rather resilient and the experiment duration varied typically about 48, 22, 10, and 4 h at 5, 15, 25, and 35 °C, respectively. The effect of temperature on the oscillatory behavior is exemplified in Figure 2 for oscillation of type II. As already pointed out, oscillations retain a similar waveform that allows the classification at different temperatures and the particular features for each pattern presented before are preserved regardless of the temperature.

In the case complex mechanisms such as in the oscillating reactions it is very difficult to assign the, experimentally obtained, apparent activation energy to a single step in the overall process. The concept of activation energy of an

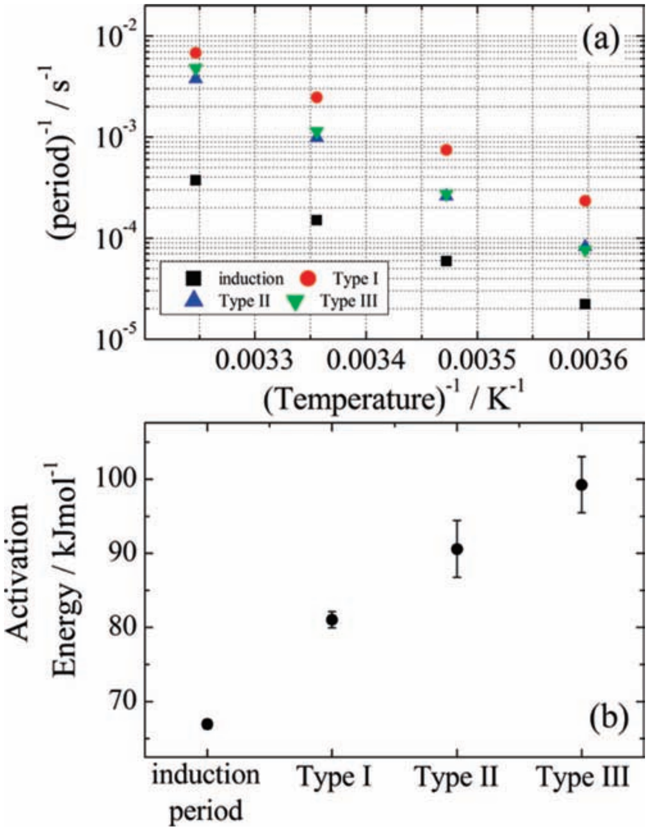

Figure 3. (a) Arrhenius plots using the reciprocal of the induction and of the oscillation period as a function of temperature and (b) temporal evolution of the activation energy estimated for the induction period and oscillations of types I, II, and III.

oscillatory chemical reaction was introduced more than 30 years ago by Körös.[4] The author considers the BZ reaction as "a series of autocatalytic reaction bursts occurring with a certain frequency".[4] Since then, the use of an *overall activation energy* has been employed in several oscillatory systems.[5−9,12−15] A more quantitative treatment introduced by Ruoff and collaborators[20,21] accounts for the temperature dependence of the oscillation period as a function of the reaction rates for each elementary step. The resulting overall activation energy in this description will be the sum of the individual activation energies, weighted by the control coefficients.[20,21]

Between 6 and 12 oscillations were normally used here to estimate the oscillation period, except for some patterns at 5 and 15 °C, where only a few oscillations were observed. Figure 3a shows Arrhenius plots using the reciprocal of the induction period and of the oscillation period, i.e. the oscillation frequency, for the different patterns as a function of 1/temperature. Most of the points are the mean between two different sets of experiments. Figure 3b shows the overall activation energy estimated in each case. Specifically for the induction period and oscillations of type I, the deviations in different experiments were rather small, yet the small scattering in the period and therefore for the activation can be considered small and within an acceptable experimental error.

As given in Figure 3b, the activation energy was found to increase from 67 ± 0.6 kJ mol^{-1} for the induction period to 99 ± 4 kJ mol^{-1} for the type III pattern. Experiments using slightly lower concentrations of bromate (32 mmol L^{-1}), acetone (120 mmol L^{-1}), and ferroin (0.1 mmol L^{-1}) and otherwise identical conditions as those used in Figure 1 were also performed and values between 49 ± 8 and 105 ± 9 kJ mol^{-1} were observed. Such values lie within the range previously observed for the ferroin-catalyzed Belousov−Zhabotinsky (BZ) reaction,[7,14] but are considerably higher than those (ca. 68 kJ mol^{-1}) obtained when Ce^{3+}, Mn^{2+}, or $Ru(dipy)_3^{2+}$ are used as catalysts.[4] The key point to be stressed here is the increase of the activation energy in the course of the batch reaction. This trend also has been observed in previous reports. Burger and Körös[5] found that activation energies estimated for the induction period are usually smaller than those obtained in an oscillatory regime for different BZ mixtures. Strizhak and Didenko[7] have also reported different activation energies for the preoscillatory regime and after oscillations are established for the ferroin-catalyzed BZ reaction. The authors explored the effect of initial ferroin concentration and found that, in any case, the activation energy estimated under the oscillatory regime is higher than that obtained for the induction period.

In all previous reports, the increase of the overall activation energy in time was seen when the system evolves from the induction period to the oscillatory regime. Besides the induction period, the presence of three distinct sequential oscillations in the present case allowed estimating the activation energy at four different states in the course of the reaction. As already stated, the activation energy in oscillatory systems depends on the concentrations of some species involved in the oscillatory cycle. Thus, the different activation energies estimated as the reaction proceeds reflect the different position of the system in the concentration phase space of some essential chemical species. In a batch system, the driving force of the reaction is the high free energy of the reactants, or more precisely the system's affinity.[22] As time evolves the affinity decreases as the systems approach the thermodynamic equilibrium. As in the present case, sometimes a chemical system in the batch evolves toward equilibrium in an oscillatory manner, and oscillations take place around a nonequilibrium point in concentrations phase space. Since the system is closed, the point around which oscillations develop is moving in the phase space as a result of the decrease in its affinity.

The dynamics of the present system is such that it was possible to estimate an apparent activation energy at four different times as the system evolves toward equilibrium. The increase of the activation energy in time, Figure 3b, can be rationalized in terms of the decrease of the driving force as the system approaches the thermodynamic equilibrium. Invoking the concept of "monomolecular kinetics" for an oscillatory system introduced by Körös,[4] the driving force of affinity for this monomolecular reaction is simply the difference between chemical potential times the stoichiometric factor of reactants and products. The decrease of the affinity in time is related to the decrease of the mean energy level of the reactants since they are continuously transformed into products. As a consequence, since the activation energy informs on the difference between the energy of the activated complex and that of the reactants, the increase of the overall activation energy can be taken as proportional to the decrease of the system's affinity. This is true independently on the very position of the activation complex with respect to the reaction coordinate. This interpretation is in line with the seminal work by Evans and Polanyi.[23] Studying a series of reactions of the homologous reactions of the type A + BC = AB + C the authors observed a simple relationship between reactivity and reaction heat. The authors obtained a relationship of the type $\Delta E = -\alpha\Delta H$, where ΔH is the heat realesed during the reaction. The main argument was that the free energy of the reaction varies proportionally to the reaction rate and that changes in the free energy of the transition state are proportional to that in the activation energy.[23] Further experimental data corroborating this scenario can be found for instance in Laidler's classical textbook.[24] As far as the bromated based oscillators are concerned, calorimetric data[25,26] revealed a continuous release of heat as the reaction evolves in time approaching equilibrium. Taking for instance Figure 4 in ref 25 it becomes clear the evolution from the initial (high affinity) state to the final (zero affinity) equilibrium state is via an exothermic oscillatory pathway.

4. Conclusions

We reported in this paper the study of the oscillatory bromate/phosphate/acetone/dual catalyst system operated in batch. The system was investigated at four temperatures between 5 and 35 °C, and its dynamics followed by potential measurements with platinum and bromide selective electrodes, and spectroscopically at two different wavelengths.

The experimental approach introduced here of simultaneously recording four time series allowed the characterization of the dynamics of the sequential oscillations that evolve in time. From the mechanistic point of view, the obtained results corroborate the interpretation provided by Orban and co-workers,[18] in which the dynamic behavior of the bromate/dual substrate/dual catalyst batch oscillator results in the coupling between two suboscillators. Our results indicate that this is indeed the case and that Mn^{2+} acts as the active catalyst in the first part of the oscillations and the second catalyst, $[Fe(phen)_3]^{2+}$, starts playing a role only after some time, presumably after a critical concentration of BrAc has been reached.

The existence of three sequential oscillatory patterns at each temperature studied allowed the estimation of the activation energies at different times. Together with the activation energy of the induction period, it was possible to trace the time evolution of the overall activation energy at four different stages as the reaction proceeds. Despite the two different sets of initial concentrations, the overall activation energy was found to increase in time. This finding was rationalized in terms of the decrease of the system's affinity in the course of the catalytic oxidative bromination of acetone with acidic bromate, as the closed system evolves toward the thermodynamic equilibrium. This result can be considered to be expected to occur whenever a closed system evolves toward the state of thermodynamic equilibrium, provided that a certain step is operative during the whole evolution. Conversely, situations where the overall activation energy decreases as the closed chemical system evolves toward equilibrium might indicate that a change in the leading reaction is occurring in time.

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