The DAO (maltenes) is also shown in the Kern River profile set. The prominent maximum seen in the feed profile (peak 3) is also seen here. This is also the maximum for smaller-sized sulfur-containing compounds and accounts for the majority of the sulfur-containing molecules.

The SDA separation process separates the very large sulfur-containing components from the smaller sulfur-containing compounds, similar to the effect on the metal-containing compounds. But unlike the metal compounds, the majority of the sulfur is found in the DAO fraction. This is not necessarily a disadvantage because these molecules are very amenable to catalytic removal. Desulfurization is one the easiest aspects of refining. It should be noted, however, the distribution of compounds and heteroatoms in this type of processing can be greatly feed dependent,[8] as well as separation solvent dependent.[56] To provide the process with flexibility, several commercial and proposed processes use two-stage or multistage asphaltene removal,[48] with multiple alkane solvents of different solubility parameters. The end result is various grades of DAO

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that will be treated in different parts of the refinery depending upon the quality of the product.

Conclusions

SEC–ICP has opened up several new areas of petroleum process analysis, showing the size behavior of nickel, vanadium, and sulfur in heavy crude oils and during thermal, catalytic, and SDA processing. It has offered insight into new and innovative ways of processing heavy crude oils and residua derived from them as well as helped explain the success of existing processing methods. This has only come about because of a combined, interdisciplinary effort from several fields of science—analytical, inorganic, and organic chemistry, along with chemical and petroleum engineering.

How Bromate Oscillators Are Controlled

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An Introduction to Chemical Oscillators

A solution containing potassium bromate, malonic acid, and a small amount of cerium sulfate in dilute sulfuric acid is a reaction system that probably exhibits the richest and most complex phenomenology of any known nonliving collection of chemicals![1] One of the remarkable observations is that in stirred homogeneous systems the $[Ce^{4+}]/[Ce^{3+}]$ ratio, which can be easily followed by a platinum electrode, shows practically undamped oscillations over a considerable period of

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time, even in closed systems. This reaction is only one example of a class of processes, generally described as *chemical oscillators*, in which some composition variable exhibits regular periodic variations in time or space.[2] A whole family of chemical oscillators with bromate ion as an essential component is now known, and members of this family are often referred to as *bromate-driven oscillators*. More exotic behaviors of bromate-driven oscillators are "trigger waves" in unstirred systems,[3] "facilitation-like behavior",[4] "bistability",[5] or "excitability",[6] which show analogies to propagation of nerve impulses or to dynamic behaviors observed in synapses.[7,8]

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In contrast to the history of biological oscillators, which started with DeMairan's discovery of autonomous circadian rhythms in plants in the early 18th century,[9] chemical oscillating reactions have, with the exception of a few early discoveries in the 19th[10,11] and the early 20th[12] century, only recently received major attention.[13] The majority of chemists before the 1960s simply believed that oscillatory chemical processes were thermodynamically impossible! However, this view changed rapidly when in 1971 a general thermodynamic theory became widely known showing that both biological and chemical oscillators[14] have to be regarded as systems maintained far from equilibrium and governed by nonlinear dynamic laws.[15] One year later, Field, Körös, and Noyes (FKN)[16] described for the first time a detailed mechanism of a chemical oscillator.

Since that time much effort has been concentrated on explaining chemical oscillations in terms of component processes and elementary reactions[17-19] and also in designing systematically new chemical oscillators.[20]

Of the known chemical oscillators most experimental results and theoretical interpretations are available on bromate-driven oscillators. However, in recent years there have been some confusion and misconceptions about the mechanism in these systems. We think that it is now appropriate for a critical assessment of this subject. The main purpose of this paper is to present a review that shows how bromate-driven oscillators are controlled.

The FKN Mechanism and the Oregonator Model

The underlying chemistry of bromate oscillators is the bromination and oxidation of an organic compound by acidic bromate; a catalyst may or may not be present. The catalyst is in general a one-electron redox system with a redox potential between 1.0 and 1.5 V and of the type $M^{(n+1)+}/M^{n+}$ or $M \cdot L_m^{(n+1)+}/M \cdot L_m^{(n)+}$, where M is a transition metal and L is a bidentate ligand. When a catalyst is present, the reacting system is usually referred to as a Belousov–Zhabotinsky (BZ) reaction, because Belousov discovered the first metal-ion-catalyzed, bromate-driven oscillatory system,[21,22] and Zhabotinsky[23,24] performed the first detailed studies with different organic substrates and catalysts. The bromate–malonic acid–sulfuric acid–cerium ion reacting
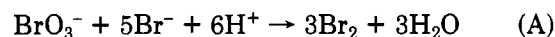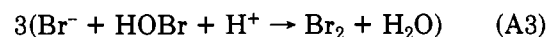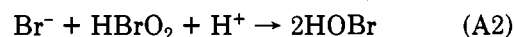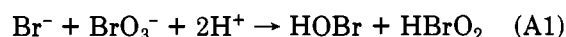
system has been investigated most thoroughly, and the detailed mechanism of the BZ reaction proposed by FKN[16] applies to this system. According to a classification by Noyes,[25] bromate oscillators where a metal-ion or a metal-complex catalyst is present are referred to as "classical" systems.

In the mid-1970s it was found that even in the absence of a catalyst the reaction between acidic bromate and some organic substrates (mostly phenol and aniline derivatives) may exhibit oscillatory behavior.[26] These systems—termed uncatalyzed bromate oscillators—have been characterized by Orbán and Körös[27] and explained[28] by Orbán, Körös, and Noyes (OKN) in terms of a modified FKN[16] mechanism. Model calculations[29] show satisfactory agreement between the OKN mechanism and experimental observations.
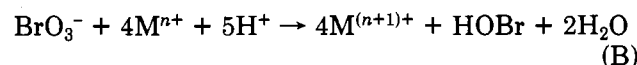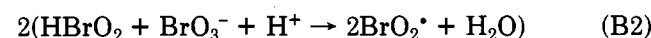
An important characteristic of the mechanism of both catalyzed and uncatalyzed systems is that a key role is attributed to bromide ion, an intermediate of the reaction. Bromide ion has a control function; i.e., the kinetic state of the system depends crucially on its concentration. When the bromide ion concentration is higher than a critical value[30-33]

$$[Br^-] > [Br^-]_{crit} = 5 \times 10^{-6}[BrO_3^-]$$

the reaction between Br^- and BrO_3^- is the dominant process. It has become common to denote the reaction, in this *reduced* state, as "process A". Other important intermediates are hypobromous acid (HOBr) and bromous acid ($HBrO_2$):

$$Br^- + BrO_3^- + 2H^+ \rightarrow HOBr + HBrO_2 \quad (A1)$$

$$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr \quad (A2)$$

$$3(Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O) \quad (A3)$$

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \quad (A)$$

During process A the bromide ion concentration is reduced, and when it falls below the critical value, autocatalytic production of bromous acid begins.[16] The system changes to an *oxidized* state, where process B is dominant.

$$2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+ \quad (B1)$$

$$2(HBrO_2 + BrO_3^- + H^+ \rightarrow 2BrO_2^\bullet + H_2O) \quad (B2)$$

$$4(BrO_2^\bullet + M^{n+} + H^+ \rightarrow M^{(n+1)+} + HBrO_2) \quad (B3)$$

$$BrO_3^- + 4M^{n+} + 5H^+ \rightarrow 4M^{(n+1)+} + HOBr + 2H_2O \quad (B)$$

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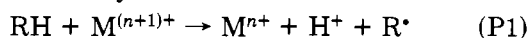(32) Gyenge, R.; Toth, K.; Pungor, E.; Körös, E. *Anal. Chim. Acta* **1977**, *94*, 111.

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In the presence of an easily brominated organic substrate, both Br_2 and HOBr produced by processes A and B, respectively, are expected to brominate the organic compound. Bromination by HOBr is catalyzed by Br^-,[34] producing first Br_2 (reaction A3), which then attacks the organic substrate.

The oscillations observed in bromate-driven oscillators are understood in terms of a switching between process A and process B. Process A consumes bromide ions until $[Br^-]_{crit}$ is reached. Then process B sets in and eventually produces bromide ion indirectly until process A regains dominance. In the FKN mechanism it was at first assumed that bromide ion regeneration is due to a redox reaction occurring between the oxidized form of the metal-ion catalyst and bromo-organics (process C):

$$M^{(n+1)+} + R-H + R-Br \rightarrow$$
$$Br^- + M^{n+} + \text{other products} \quad (C)$$
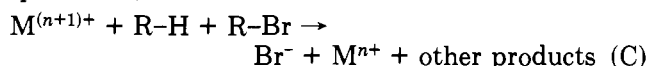
Process C involves radical[35] reactions. Experimental evidence[36] suggests that additional bromide ion may come from intermediate bromo-oxygen species without also passing through bromo-organic species. Of particular interest may be the reactions with HOBr:[37]
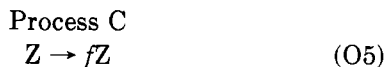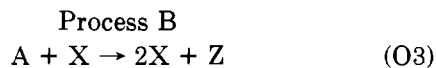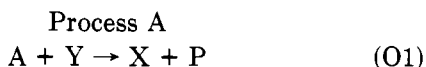
$$RH + M^{(n+1)+} \rightarrow M^{n+} + H^+ + R^\bullet \quad (P1)$$

$$HOBr + R^\bullet \rightarrow ROH + Br^\bullet \quad (P2)$$

$$RH + Br^\bullet \rightarrow Br^- + H^+ + R^\bullet \quad (P3)$$

When bromination of the organic substrate is slow or not possible at all, elementary bromine builds up. Field has shown[38,39] that in this case the control of oscillations still is due to bromide ion, which is provided by the hydrolysis reaction R1:

$$Br_2 + H_2O \rightleftharpoons HOBr + Br^- + H^+ \quad (R1)$$
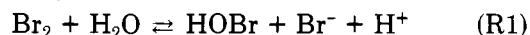
This situation is referred to as bromine-hydrolysis-controlled oscillations.[38,39] Bromine hydrolysis control can occur both in catalyzed and in uncatalyzed systems. The control is ultimately due to Br^- whether or not significant amounts of hydrolyzable Br_2 are also present.

The important role of bromide ion in the catalyzed Belousov–Zhabotinsky reaction is emphasized by the Oregonator model,[40] which is a simplified version of the FKN mechanism. The Oregonator consists of five irreversible pseudoelementary reactions (O1–O5) that simulate the most important component processes of the FKN scheme:

<div align="center">

Process A

$$A + Y \rightarrow X + P \quad (O1)$$

$$X + Y \rightarrow 2P \quad (O2)$$

Process B

$$A + X \rightarrow 2X + Z \quad (O3)$$

$$2X \rightarrow A + P \quad (O4)$$

Process C

$$Z \rightarrow fZ \quad (O5)$$

</div>

where $X \equiv HBrO_2$, $Y \equiv Br^-$, $Z \equiv 2M^{(n+1)+}$, $A \equiv BrO_3^-$, and $P \equiv HOBr$.

The concentration of A is often artificially held constant, leaving X, Y, and Z as the only kinetically active species. Equations O1–O5 are treated as pseudoelementary processes; they result in three coupled, first-order differential equations that may be solved by appropriate numerical methods.[40,41] Several expansions and revisions of the Oregonator exist, but in all Oregonator models the control mechanism relies on bromide ion.[36,37,42-45]

The Source of Bromide Ion

Although the basic form of the FKN mechanism is widely accepted, there has been considerable debate about which chemical reactions actually produce the bromide ion. The original[16] assumption was that during the oscillations bromide was regenerated by reactions between a bromo-organic compound and the oxidized form of the catalyst (process C). This multistep reaction appears in a concise form as reaction O5 in the Oregonator model. This assumption was supported by the observation that in malonic acid containing BZ systems oscillations start only after the concentration of bromomalonic acid (BrMA) has reached a critical value.[46] On the other hand, a number of experimental observations could not be reconciled with the above supposition. In many BZ systems bromide ion cannot be produced by reaction C, because process C is either too slow or does not proceed at all, while in other BZ systems with a high $[MA]/[BrO_3^-]$ ratio (>30) oscillations start immediately after mixing of initial reagents, even when BrMA is absent.[47]

This behavior can now be rationalized by noting that bromide ion can be formed directly from HOBr without passing through BrMA as an intermediate (P1–P3):

<div align="center">

path I

BrMA

$$\nearrow \qquad \searrow$$

$$BrO_3^- \longrightarrow HOBr \longrightarrow Br^- \qquad (R2)$$

path II

</div>

In fact, ^{82}Br-tracer experiments[36] indicate that the path through BrMA is a minor part of the total transition from BrO_3^- to Br^-. A BZ system composed of ^{82}Br-labeled BrMA in concentration above its critical[46] value, an equal concentration of silver nitrate, and the other BZ components (BrO_3^-, MA, Ce^{4+}, and H_2SO_4) was allowed to react until all silver ion was converted to AgBr. The activity of both the isolated AgBr and the filtrate was then measured, and it was found that only 6–8% of the total ^{82}Br activity appeared in the AgBr, while the rest remained in solution.[36]

These results show that in BZ systems most bromide ion originates from bromate, via reduction through oxybromine intermediates to HOBr and then further

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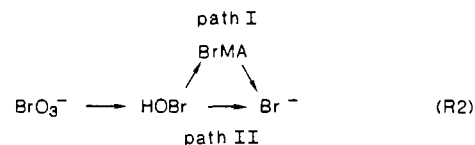(40) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877.

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reduction to bromide, while very little comes from the oxidative cleavage of the C–Br bond.

In the light of the radiotracer experiments, the chemical mechanism was slightly modified by allowing bromide ion to be regenerated from bromate (R2).[36] The limiting stoichiometry (R3) obtained[36,48]

$$2Ce^{4+} + BrO_3^- + \text{organic substrate} \rightarrow$$
$$2Ce^{3+} + Br^- + \text{products (R3)}$$
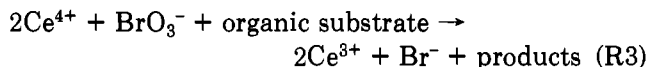
agrees with the condition ($f = 1$)[40] for oscillations in the Oregonator model. Since in the proposed mechanistic model the C–Br bond rupture is omitted, the modified[36] mechanism is applicable to BZ systems containing organic compounds other than malonic acid as well as to uncatalyzed bromate oscillators. This mechanism has been thoroughly analyzed in order to clarify the importance of individual reactions and to reveal the most essential interrelations.[49,50]

Analogous to reactions P1–P3 and R2 (path II) of the extended model,[36] in an amplified Oregonator[37] proposed recently, the regeneration of bromide ion is due to the reaction between radicals (formed by the reaction between the oxidized form of the catalyst and the organic substrate) and HOBr. Although the amplified Oregonator will not describe systems in which Br_2 accumulates or in which high-frequency small-amplitude oscillations around an oxidized steady state are observed, the model is able to simulate excitabilities of reduced and oxidized steady states and temporary bistability in a closed system.[37]

Effects of Added Silver Ion

Silver Ion Perturbed Systems and Excitability. Zhabotinsky noted in his early work the important role of bromide ion as a control intermediate.[51] Vavilin et al.[52] were the first to perturb the bromide ion level of a bromate oscillator by adding small amounts of Ag^+ to the system. They observed a phase shift, but the results were not interpreted in terms of a specific mechanism.

Shortly after Field and Noyes presented the Oregonator model,[40] they found by simulation calculations that bromide-removing reagents may generate an "all-or-none" behavior, now generally referred to as excitability.[53,54] They showed that when a perturbation removes bromide ion such that the resulting concentration falls below the critical value, [Br^-]$_{crit}$, then a single spike of the oxidized form of the metal-ion catalyst is induced. When, on the other hand, the resulting bromide ion concentration after the perturbation is still higher than the critical bromide concentration, then only a slight overshooting occurs, and no spike is observed. Figure 1A shows the theoretical behavior predicted by Field and Noyes, while Figure 1B shows an experimental situation observed later in a closed BZ
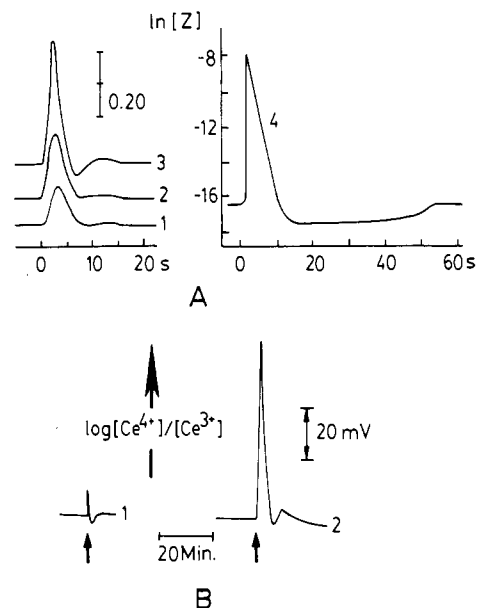
(48) Körös, E.; Varga, M.; Györgyi, L. *J. Phys. Chem.* **1984**, *88*, 4116.
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(54) A discussion of this "all-or-none" behavior can also be found in: Nicolis, G.; Prigogine, I. *Self-Organization in Nonequilibrium Systems*; Wiley: New York, 1977; p 351.

Figure 1. (A) Excitability of the Oregonator model. Perturbant (Ag^+) is added at $t = 0$. Numbering of curves corresponds to initial concentrations of Ag^+ as follows: (1) 1.0×10^{-7} M, (2) 1.5×10^{-7} M, (3) 2.0×10^{-7} M, (4) 2.5×10^{-7} M. The excitation threshold is $(2.05 \pm 0.02) \times 10^{-7}$ M Ag^+. Note that the maximum in [Z] of the supercritical perturbation (4) is about 3000 times larger than the [Z] maxima of the subcritical perturbations (1)–(3). (B) Excitability in a cerium-catalyzed BZ oscillator. Arrows indicate addition of $AgNO_3$. (1) 2.5×10^{-5} M, (2) 3.3×10^{-5} M $AgNO_3$. (From ref 65.)
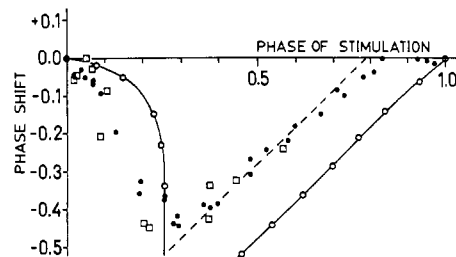

Figure 2. Experimental phase response curves (solid circles and open squares) of BZ reaction and theoretically predicted (open circles) by Oregonator model. Solid circles show experiments performed under a nitrogen atmosphere, while open squares show experiments performed when the reaction medium was in contact with air. (From ref 56.)

system.[55] These calculations and experiments refer to a nonoscillating BZ system with a high bromide ion steady state. However, silver ion induced excitability also can be observed in an oscillating system: whenever the bromide ion concentration is perturbed below its critical concentration, then a new spike of the oxidized form of the catalyst occurs. The situation is concisely described in the form of phase response curves, where the phase shift of the oscillations observed after the perturbation is plotted against the "phase of stimulation", i.e., the point in the cycle (oscillation) where perturbation occurs. Figure 2 shows calculated phase response curves using the original[40] Oregonator and corresponding experiments.[56]

Bromate Oscillators Treated with Excess Silver Ion. When silver ion forces the bromide ion concentration below its critical value, then a single spike is

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(56) Ruoff, P. *J. Phys. Chem.* **1984**, *88*, 2851.

induced in a system that is in an excitable but nonoscillatory reduced state (Figure 1). If the system is oscillatory with oxidizing spikes, silver ion advances the time of the next spike (Figure 2). On the other hand, when silver ion is used in excess, then several repetitive spikes of the oxidized form of the catalyst are observed. In general, one finds that the oscillations observed at the platinum electrode are remarkably well described by the Z variable of the Oregonator, while in contrast to this, the potential changes of a silver wire or a bromide ion selective electrode are not well described by the Y variable. Remarkable in this respect are the observations of Noszticzius[57] and later of Ganapathi-subramanian and Noyes,[58] who under applied excess of silver ion (compared to the bromide ion concentration available in the system) found large-amplitude oscillations at a platinum electrode while the bromide ion selective electrode potential was almost invariant. Because the observed monotonic response of the bromide ion selective electrode was associated with a monotonic bromide ion concentration, the whole situation was mistakenly termed as "non-bromide-controlled oscillations".[57] This class[59] of bromate oscillators appeared for many years to be the perhaps most difficult bromate-driven oscillators to be rationalized within the FKN framework.[60,61] Because of the apparent difficulties of the FKN approach in handling silver ion perturbed systems, the concept of "non-bromide-control" was accepted by some workers, and alternative models were designed.[62]

This class of bromate-driven oscillators now can be understood[63-66] within the framework of the FKN[16] theory by considering the following two points. (1) When silver ion is in excess compared to bromide ion, the bromide ion selective electrode, which consists of a matrix containing both silver ion and bromide ion, exhibits a Nernstian response only to silver ion.[67] (2) The decrease of the effective bromide ion concentration in the presence of silver ion is due to a relatively slow incorporation of bromide ion (present as small oligomers of AgBr) into the silver bromide crystal lattice during precipitation of AgBr. When the silver bromide reaction is coupled to the BZ oscillator, theoretical estimates[63] and model calculations[65] predict that the effective rate constant of bromide ion removal from the solution by process O6 should be on the order of 10^4 M^{-1} s^{-1}.

$$Ag^+(aq) + Br^-(aq) \rightleftharpoons AgBr(s) \qquad (O6)$$
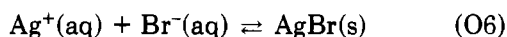
In these studies, process O6 has been approximated by a second-order reaction, which leads to a rate

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(58) Ganapathisubramanian, N.; Noyes, R. M. *J. Phys. Chem.* **1982**, *86*, 5155.
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(60) Field, R. J. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley: New York, 1985; Chapter 2.6.2.
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(65) Ruoff, P.; Schwitters, B. *J. Phys. Chem.* **1984**, *88*, 6424.
(66) Schwitters, B.; Ruoff, P. *J. Phys. Chem.* **1986**, *90*, 2497.
(67) Ganapathisubramanian, N.; Noyes, R. M. *J. Phys. Chem.* **1982**, *86*, 3217 and references therein.
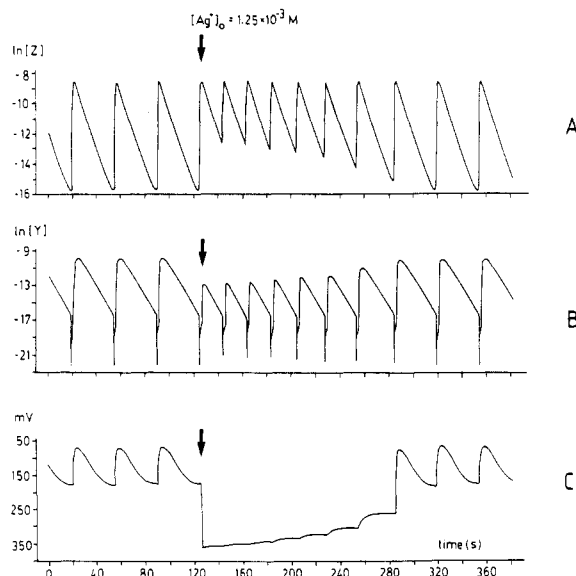

Figure 3. Calculated effect of perturbing an oscillatory Oregonator by 1.25×10^{-3} M Ag^+. The monotonic response of the potential difference between a bromide ion selective electrode and a standard calomel reference electrode is shown in C. (From ref 66.)

equation analogous to the Noyes–Nernst expression of the rate of growth of nuclei to larger crystals:

$$v = k_{O6}(Q - S) = (D/L)A(Q - S)$$

where A is the surface area of the crystals, D is the diffusion coefficient of the crystallizing compound, L is the length of the diffusion path, Q is the total concentration of AgBr in solution, and S is the solubility of coarse crystals of AgBr.[68]

Figure 3 shows the result of a model calculation in which an oscillatory Oregonator has been perturbed by 1.25×10^{-3} M silver ion, and where conditions 1 and 2 from above have been incorporated into the model. Condition 1 is well-known from the use of bromide ion selective electrodes.[67] Commercially available bromide ion selective electrodes consist generally of a matrix of silver bromide and silver sulfide and exhibit Nernstian responses to silver ion or bromide ion, whichever of these ions is in excess.[67] Schwitters and Ruoff[66] deduced a mathematical expression of the bromide ion selective electrode's potential under nonequilibrium conditions when both silver ion and bromide ion are simultaneously present and reacting according to process O6. However, more theoretical work is required for a better understanding of (nonequilibrium) potentials arising from different contributing species.

Several independent experiments have confirmed condition 2. Varga and Körös[69] added an excess of silver ion to a BZ reaction and followed, by titration with bromide ion, the change of excess silver ion during the precipitation process. They found that when process O6 is treated as a second-order reaction, the rate constant value of process O6 is on the order of 10^4 M^{-1} s^{-1}, precisely as predicted earlier by calculations.[63,65]

Kshirsagar et al.[70] have performed a spectrophotometric investigation of process O6. From their exper-

(68) Kolthoff, I. M.; Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*; Macmillian: New York, 1947; p 100.
(69) Varga, M.; Körös, E. *J. Phys. Chem.* **1986**, *90*, 4373.
(70) Kshirsagar, G.; Field, R. J.; Györgyi, L. *J. Phys. Chem.*, in press.

iments they conclude that first a soluble AgBr ion pair is rapidly formed, probably by a diffusion-controlled process. This ion pair and small oligomers of it, most probably $(AgBr)_4$ molecules, react with $HBrO_2$ and BrO_3^-, in the same way as $Br^-(aq)$ does (see reactions A1–A3).[70] The decrease of bromide ion in solution (available to the BZ reaction) can be formally described by process R4. Kshirsagar et al.[70] found that polym-

$$\{AgBr\}(aq) \rightarrow \{AgBr\}(s) \qquad (R4)$$

erization of $(AgBr)_4$ to larger particles where Br^- is no longer available to $HBrO_2$ or BrO_3^- is precisely of the same time scale as suggested by the earlier model calculations![63,65]

Another approach to look for the time scale of process O6 is due to Försterling and Schreiber,[71] who studied spectrophotometrically the silver bromide reaction O6 in competition with the bromide–bromous acid reaction R5. They found that process R5 is considerably more

$$3Br^- + HBrO_2 + 3H^+ \rightarrow 2Br_2 + 2H_2O \quad (R5)$$
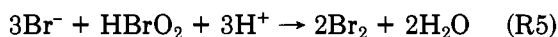
rapid than process O6 and deduced on that basis that a second-order rate constant for effective removal of bromide ion by silver ion must be lower than 3×10^4 M^{-1} s^{-1}.

Noszticzius and McCormick[72] and Vestvik and Ruoff[73] have recently studied the silver bromide reaction by injecting a bromide ion solution into an acidic silver nitrate solution and following the reaction with a silver electrode. While Noszticzius and McCormick[72] found a rapid response of the silver electrode and concluded that a second-order rate constant of process O6 should be at least 2×10^6 M^{-1} s^{-1}, Vestvik and Ruoff[73] found slow or rapid responses, depending on the silver electrode's position in the solution. This casts some doubts about the usefulness of a potentiometric method to study process O6. On the other hand, it is most impressive that three different experimental approaches result in virtually the same silver bromide removal time scale as the theoretically predicted one!

The Control of Oscillations in the Presence of Silver Ion

From above it is apparent that bromate oscillators in the presence of excess silver ion can be understood within the framework of the FKN theory.[16] The experiments[69–71] strongly support the previous[63,65,66] assumption that the control intermediate is bromide ion, which has not yet been bound into the silver bromide crystal lattice. Kshirsagar et al.[70] deduced from their spectrophotometric measurements that in the presence of Ag^+, the Br^- available to reactions A1–A3 is probably present as oligomers of the rapidly formed AgBr(aq), most probably as $(AgBr)_4$ molecules. They further conclude that the control intermediate consists of AgBr(aq) species and term the situation as "AgBr controlled". It is important to realize, however, that it is still the bromide ion that binds to $HBrO_2$, HOBr, and BrO_3^- in reactions A1–A3 that controls the oscillations. Because $Br^-(aq)$ is probably in rapid equilibrium with AgBr(aq), it might be difficult to distinguish experimentally between AgBr or Br^- control.

Table I
Composition of the Reaction Mixture (0.05 M $KBrO_3$, 0.20 M Malonic Acid, 1.0 M H_2SO_4, and 0.002 M Catalyst)

$10^5[Tl^{3+}]$, M	relative time[a]	
	exptl measd[b]	Oregonator model[c]
1.0	1.8	1.1
2.0	2.0	1.6
3.0	2.8	2.8
4.0	3.4	3.6
5.0	4.2	4.6

[a] Relative period time = (time of the second oscillation in the presence of Tl^{3+})/(time of the second oscillation without Tl^{3+}). [b] Cerium-catalyzed system. [c] The period of the Oregonator is 48.75 s.

Perturbations by Bromo-Complex-Forming Metal Ions

In order to clarify the role of bromide ion in bromate oscillators, Körös and co-workers[48,74–77] have used a different approach and studied the effect of Tl^{3+} and Hg^{2+} ions, which form stable water-soluble complexes with bromide ion. Most experiments and simulation calculations have been performed on the Tl^{3+}-perturbed BZ reaction; therefore we discuss this system more extensively than the Hg^{2+}-perturbed one.

BZ Systems with Low Initial Tl(III) Concentration. Körös and Varga[75] found that even at an initial Tl^{3+} concentration of 10^{-5} M, the period length of BZ oscillations is doubled or tripled. At an initial Tl^{3+} concentration of 10^{-4} M the oscillations are quenched. Table I shows the effect of Tl^{3+} on period length in the concentration range $(1.0–5.0) \times 10^{-5}$ M.

BZ Systems with High Initial Tl(III) Concentration. Although oscillations are quenched at an initial Tl^{3+} concentration of about 10^{-4} M, high-frequency oscillations can be observed when the system is treated with an excess of Tl^{3+}, i.e., with initial concentrations higher than 10^{-2} M. As in the case of the silver ion perturbed BZ reaction (Figure 3),[63,78] the system is excited to an oxidized state, and after an induction period small-amplitude, high-frequency oscillations appear.[48,75]

Model Calculations with the Oregonator. Despite the rather diverse effects of Tl^{3+} on BZ systems, the observed phenomena can be explained in a straightforward way within the framework of the FKN[16] theory. Varga et al.[76] extended the original[40] Oregonator model with the following four thallium(III)–bromide equilibria:

$$Tl^{3+} + Br^- \rightleftharpoons TlBr^{2+} \qquad (1)$$

$$TlBr^{2+} + Br^- \rightleftharpoons TlBr_2^+ \qquad (2)$$

$$TlBr_2^+ + Br^- \rightleftharpoons TlBr_3 \qquad (3)$$

$$TlBr_3 + Br^- \rightleftharpoons TlBr_4^- \qquad (4)$$

From a set of estimated[76] rate constants, all phenomena induced by Tl^{3+} of different concentrations could be modeled. With low initial Tl^{3+} concentrations the relative experimental period lengths[48] and those

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(72) Noszticzius, Z.; McCormick, W. D. *J. Phys. Chem.* **1988**, *92*, 374.
(73) Ruoff, P.; Vestvik, J., to be published.

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(77) Györgyi, L.; Varga, M.; Körös, E. *React. Kinet. Catal. Lett.* **1985**, *28*, 275.
(78) Ruoff, P.; Schwitters, B. *Z. Phys. Chem.* (*Wiesbaden*) **1983**, *135*, 171.
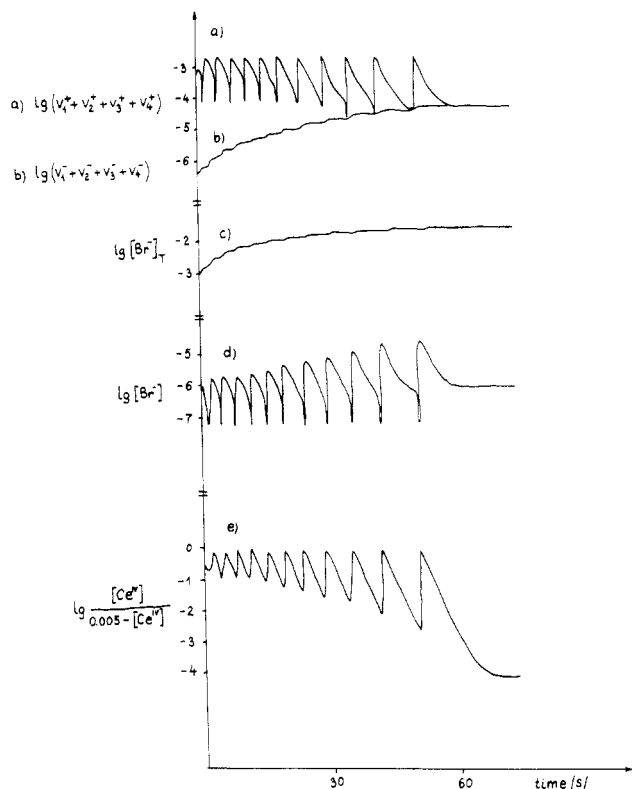
Figure 4. Simulation of the behavior of a Tl^{3+}-perturbed BZ system by the Oregonator model: curve a, logarithm of the sum of the rate of formation; curve b, logarithm of the rate of dissociation; curve c, logarithm of the total bromide ion concentration vs time; curve d, logarithm of uncomplexed bromide ion vs time; curve e, redox potential vs time. Experimental and calculated curves agree rather well. (From ref 76.)

calculated by the Oregonator model, including the bromo-complex-forming reactions 1–4, are given in Table I. They are in excellent agreement with each other.

Also when Tl^{3+} is in excess, experimental and computed dynamics agree rather well. In Figure 4a,b the logarithm of the sum of the rates of formation and dissociation of thallium(III) bromo complexes vs time plots are shown. In Figure 4c,d the total and free bromide ion concentrations are shown. Finally, Figure

4e shows the temporal change of the redox potential calculated from the Tl^{3+}-modified Oregonator model.

Figure 4a shows that the rates of complex formation are periodic. This can be attributed to the fact that they depend on the concentration of the oscillating bromide ion. On the other hand, the rates of complex dissociation show a stepwise change with time.

BZ Systems Perturbed with Mercury(II) Ions. With the mercury(II)-perturbed BZ system an increase in the period time of oscillations is found at low $(10^{-5}$–10^{-4} M) mercury(II) concentrations, and the data show an acceptable agreement between the experimentally measured and calculated values.[77]

Above 10^{-4} M, mercury(II) inhibits the oscillations, which do not reappear at high ($\approx 10^{-2}$ M) mercury(II) concentrations, in contrast to the behavior of the thallium(III)-containing systems.

In this case the results also can be interpreted in terms of the extended Oregonator model in which the rates of formation and dissociation of the mercury(II) bromo complexes (a four-step equilibrium) are included.[77]

Recently we performed calculations using the new (low) set of rate constants,[79] and also with these values good agreement was obtained between experimental and calculated values.

Conclusion

The occurrence of oscillations in the presence of bromide ion removing reagents probably has been the most debated point of bromate oscillators. Even in recent reviews,[60,80] these oscillations have been described to be difficult to explain within the FKN approach. This Account was written to show that a large amount of theoretical and experimental evidence has accumulated that makes it unnecessary to postulate other control intermediates than bromide ion. Although details in many of the component processes in bromate oscillators deserve further investigation, it is evident that bromide ion control is the unifying concept for all bromate oscillators.

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(80) Reference 61, p 16.