ACCOUNTS OF CHEMICAL RESEARCH

VOLUME 10 NUMBER 8 AUGUST, 1977

Mechanisms of Chemical Oscillators: Experimental Examples[1]

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Received February 25, 1977

In a previous Account,[1] we discussed the possibilities for concentration oscillations in closed chemical systems and illustrated the principles by means of the Oregonator[3] model consisting of the following five steps.

$$A + Y \rightarrow X \quad (M1)$$

$$X + Y \rightarrow P \quad (M2)$$

$$B + X \rightarrow 2X + Z \quad (M3)$$

$$X + X \rightarrow Q \quad (M4)$$

$$Z \rightarrow fY \quad (M5)$$

If [X] is always small compared to the other concentrations, the first four steps can be combined in pairs to generate the stoichiometries of processes Mi and Mii.

$$A + 2Y \rightarrow P \quad (Mi)$$

$$2B \rightarrow 2Z + Q \quad (Mii)$$

As we discussed before,[1] certain combinations of values for the rate constants and the stoichiometric factor f permit the concentrations of X, Y, and Z to undergo repetitive oscillations while processes Mi, Mii, and M5 cause A and B to be converted irreversibly to P and Q.

We discuss here a number of chemical systems that exhibit temporal or spatial periodicities. Whenever appropriate, these discussions of mechanism will be numbered to emphasize how the detailed chemistry relates to the Oregonator model.

The Belousov–Zhabotinsky Reaction

An acidic bromate solution can oxidize various organic compounds, and the reaction is catalyzed by species like cerous and manganous ions that can generate 1-equiv oxidants with quite positive reduction potentials. Belousov[4] first observed oscillations in $[Ce^{IV}]/[Ce^{III}]$ in such a system, and Zhabotinsky made extensive studies of both temporal[5] and spatial[6] oscillations. This system is by far the most studied and best understood of any chemical oscillator.

Brief biographical sketches of the authors appear on page 214 of this volume.

Basic Mechanism. The chemical mechanism of the temporal oscillations has been elucidated by Field, Körös, and Noyes.[7] If an acidic solution of potassium bromate contains a comparable amount of malonic acid, a plausible stoichiometry for net chemical change is given by process A_T. That stoichiometry is not affected by a small amount of cerium ion catalyst.

$$2BrO_3^- + 3CH_2(CO_2H)_2 + 2H^+ \rightarrow 2BrCH(CO_2H)_2 + 3CO_2 + 4H_2O \quad (A_T)$$

Although eq A_T represents the change of major reactants whose free-energy difference drives the chemical processes, bromate ion attacks organic substrates only very slowly by direct reaction. However, thermodynamic considerations show that it can also oxidize both bromide ion and cerium(III).

If reduction of bromate is initiated by bromide, the processes of importance are A1, A2, and Ax. If we

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

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

$$HOBr + CH_2(CO_2H)_2 \rightarrow BrCH(CO_2H)_2 + H_2O \quad (Ax)$$

assume that proton transfer equilibria are rapidly established and make the assignment $A = BrO_3^-$, $X = HBrO_2$, and $Y = Br^-$, the analogy to steps M1 and M2 of the Oregonator is obvious. Step Ax has no analogue in the Oregonator and serves merely to consume the product HOBr from the first two steps; the stoichiometry is the same whether Ax takes place directly or through intermediate Br_2 formed from HOBr and Br^-. Then overall reaction Ai is a direct analogue of Mi.

$$BrO_3^- + 2Br^- + 3CH_2(CO_2H)_2 + 3H^+ \rightarrow 3BrCH(CO_2H)_2 + 3H_2O \quad (Ai)$$

(1) Paper No. 19 in the series Oscillations in Chemical Systems. Paper No. 18 is R. J. Field and R. M. Noyes, *Acc. Chem. Res.*, **10**, 214 (1977).
(2) Present address is University of Montana.
(3) R. J. Field and R. M. Noyes, *J. Chem. Phys.*, **60**, 1877 (1974).
(4) B. P. Belousov, *Ref. Radiats. Med.*, **1958**, 145 (1959).
(5) (a) A. M. Zhabotinsky, *Dokl. Akad. Nauk SSSR*, **157**, 392 (1964); (b) *Biofizika*, **9**, 306 (1964).
(6) A. N. Zaikin and A. M. Zhabotinsky, *Nature (London)*, **225**, 535 (1970).
(7) R. J. Field, E. Körös, and R. M. Noyes, *J. Am. Chem. Soc.*, **94**, 8649 (1972).

Although thermodynamic data indicate that cerium(III) can reduce bromate either to HOBr or to Br_2, Ce(III) is a 1-equiv reductant, and bromate is such a weak 1-equiv oxidant it cannot initiate the reaction. However, BrO_2 radicals are strong enough 1-equiv oxidants to attack Ce(III) directly. The mechanism of cerium oxidation is then given by processes A3a, A3b, and A4[8]. If we make the additional assignments B =

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2 + H_2O \quad (A3a)$$

$$BrO_2 + Ce^{3+} + H^+ \rightarrow HBrO_2 + Ce^{4+} \quad (A3b)$$

$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \quad (A4)$$

BrO_3^- and Z = $2Ce^{4+}$, then step M3 of the Oregonator is equivalent to the sequence A3a + 2(A3b), with step A3a rate determining, and step M4 is equivalent to step A4. The stoichiometry of process Aii differs from a

$$BrO_3 + 4Ce^{3+} + 5H^+ \rightarrow HOBr + 4Ce^{4+} + 2H_2O \quad (Aii)$$

simple interpretation of process Mii because half the bromate that reacts by step A3a is regenerated by step A4 while the Oregonator model made no effort to include this kinetically unimportant refinement. Of course step Ax can easily be added to the stoichiometry of process Aii.

Ce(IV) is a strong oxidant that can attack various of the organic species in the system. Studies by Jwo[9] show that the overall chemistry is very complex, but the reactions are kinetically first order in Ce(IV). If malonic acid is present in large excess over other organic species, it reacts preferentially with cerium(IV) to produce malonyl radicals which abstract hydrogen from bromomalonic acid to initiate a complicated sequence whose overall stoichiometry is approximated by process A5a.

$$BrCH(CO_2H)_2 + 2Ce^{4+} + {}^3/_2H_2O \rightarrow Br^- + {}^1/_2HOCH(CO_2H)_2 + CO_2 + {}^1/_2HCO_2H + 2Ce^{3+} + 3H^+ \quad (A5a)$$

If malonic acid is present in stoichiometric deficiency with respect to bromate, the brominated form becomes the chief organic species. More elementary bromine then builds up during the time when cerium(IV) is present, and the overall stoichiometry can be approximated by processes A5b and A5c. Either A5a or

$$BrCH(CO_2H)_2 + 4Ce^{4+} + 2H_2O \rightarrow Br^- + 2CO_2 + HCO_2H + 4Ce^{3+} + 5H^+ \quad (A5b)$$

$$HOBr + HCO_2H \rightarrow Br^- + CO_2 + H^+ + H_2O \quad (A5c)$$

A5b + A5c produces one bromide ion for each two Ce(IV) consumed and generates the stoichiometry of step M5 of the Oregonator with $f = 1$; this is precisely the stoichiometry of maximum susceptibility to oscillation. Of course only the sequence A5b + A5c generates the stoichiometry of process A_T. Figure 1 may help the reader to grasp the stoichiometric relationships for this particular overall result.

The above discussion shows that the Oregonator does indeed model the essential features of the chemical mechanism, although the chemistry presented here is much oversimplified. Edelson[10] has shown that a model

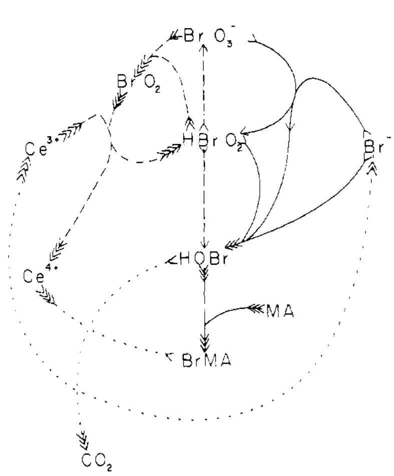

Figure 1. Schematic representation of chemical mechanism of Belousov–Zhabotinsky reaction. Barbs approaching or leaving each species indicate numbers of molecules formed or destroyed to generate process A_T. Solid paths generate stoichiometry of nonradical process Ai; dashed paths generate stoichiometry of partly radical process Aii; dotted paths generate stoichiometry of process A5.

much like this chemistry does reproduce many experimental features. Unfortunately, the model equations presented in that paper are not precisely the same as those for which calculations are shown. We are now attempting to refine the chemical detail further to reproduce the wide range of experimental observations. Although this work is not yet complete, it is clear that the main chemical features of this remarkable system are understood.

Modifications in Closed Systems. Reactions A1, A2, A3a, and A4 are confined specifically to oxybromine chemistry, and it is not surprising bromate appears to be an essential component in any Belousov–Zhabotinsky system. However, all the other components are subject to substitution. The following comments are suggestive, but should not be considered a thorough review.

The cerium(III) catalyst discussed above is a weak 1-equiv reducing agent. Körös et al.[11] have shown that Mn^{2+}, $Fe(phen)_3^{2+}$, and $Ru(bpy)_3^{2+}$ also serve as catalysts. An effective catalyst couple must apparently have a reduction potential roughly between 1.0 and 1.5 Volt/equiv. It is not yet clear to what extent kinetic as well as thermodynamic factors contribute to determining catalyst efficacy.

Kasperek and Bruice[12] list a number of organic acids that did and did not generate oscillations in their hands. Although specific requirements are not entirely clear, a satisfactory organic substrate should be easily brominated, and the resulting bromo compound should react with the oxidized form of the catalyst with liberation of bromide ion. The species that gave oscillations for Kasperek and Bruice[12] are acids that also produce carbon dioxide during oxidation, but Bowers et al.[13] observed oscillations with 2,4-pentanedione ($CH_3COCH_2COCH_3$) which generates no gaseous products during the oscillatory reaction. Stroot and

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(9) (a) J. J. Jwo and R. M. Noyes, *J. Am. Chem. Soc.*, **97**, 5422 (1975); (b) R. M. Noyes and J. J. Jwo, *ibid.*, **97**, 5431 (1975).
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(11) (a) E. Körös, L. Ladányi, V. Friedrich, Zs. Nagy, and Á. Kis, *React. Kinet. Catal. Lett.*, 1, 455 (1974); (b) E. Körös, M. Burger, V. Friedrich, L. Ladányi, Zs. Nagy, and M. Orban, *Faraday Symp. Chem. Soc.*, **9**, 28 (1974).
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Janjic[14] report other ketone substrates that exhibit oscillations.

The Belousov–Zhabotinsky reaction requires a strong acid, and H_2SO_4 has usually been used. At least in our hands, $HClO_4$ is an unsatisfactory acid with cerium catalyst, apparently because Ce^{3+} is too weak a reducing agent in this medium. There is no obvious reason why $HClO_4$ could not be used with some catalyst couples having smaller reduction potentials. Körös[15] reports that nitric acid can be substituted for sulfuric and that the frequency of oscillation is thereby increased; nitrogen oxide radicals may be involved with this enhanced behavior. Even the weaker acid H_3PO_4 can generate oscillations.[16] Of course HCl is also a strong acid, but it is unsatisfactory because chloride ion inhibits the oscillations; Jacobs and Epstein[17] have elucidated the mechanism of that inhibition.

Periods observed for oscillation are usually about a minute to within a factor of ten, but Dayantis and Sturm[18] report some concentrated solutions that oscillate with periods as small as about a tenth of a second.

Spatial Periodicities. Belousov–Zhabotinsky systems certainly provide the best known examples of spatial structures. The phenomenon was first reported by Busse[19] and by Zhabotinsky.[6] Winfree[20] developed a particularly effective set of concentrations for illustrating this behavior. Regions of oxidation where process Aii is dominant move by reaction and diffusion into reducing regions of excess bromide ion where Ai is dominant, and the reactions of A5 in the trailing edge serve to accomplish the transition from oxidized catalyst to excess bromide. The distinctions between phase and trigger waves and the peculiar spiral and scroll phenomena were discussed briefly with references in the previous Account.[1] Recent applications include the observation of Showalter[21] that trigger waves of oxidation can be generated electrolytically at will and a report by Jessen et al.[22] that the manganese pentanedione system can generate trigger waves without the accompanying carbon dioxide evolution that sometimes disturbed Winfree.[20]

Flow Systems. Chemical engineers have long known that reactions which exhibit only stable steady states and monotonic behavior in a stirred batch reactor may exhibit unstable steady states and nonmonotonic behavior in a stirred-flow reactor.[23] Often the necessary feedback arises because the rate of a strongly exothermic reaction increases rapidly with temperature, and linking of this effect with the flow kinetic terms can destabilize the steady state.[24] The Belousov–Zhabotinsky reaction exhibits other more complex features when it is run in a stirred-flow reactor. Papers are appearing frequently, and the following discussion is suggestive rather than complete.

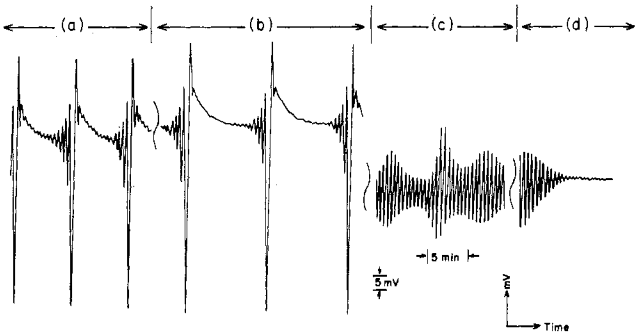

Figure 2. Effect of different sodium bromate feed rates on Belousov–Zhabotinsky oscillations in a stirred-flow reactor. Total flow rate was 4.7 mL min^{-1}. Bromate flow rates during different periods were (a) 1.28 mL min^{-1}, (b) 1.32 mL min^{-1}, (c) 1.33 mL min^{-1}, (d) 1.36 mL min^{-1}. Reproduced with permission from K. R. Graziani, J. L. Hudson and R. A. Schmitz, *Chem. Eng. J.*, **12**, 9 (1976).

If flow rates are adjusted properly, the system may exhibit repetitive pulses of a few oscillations separated by periods of steady reaction. This phenomenon has been observed apparently independently by workers in Russia,[25] Denmark,[26] Germany,[27] Czechoslovakia,[28] France,[29] and U.S.A.[30] Figure 2 illustrates the sharpness with which the effect can be produced by changes in flow rate, and the phenomenon apparently is restricted to a narrow range of conditions between those for limit cycle oscillations and steady reaction. Noyes[31] has rationalized the observations by noting that bromomalonic acid (BrMA) is produced more rapidly during steady reaction in the oxidized condition (process Aii dominant) than the average rate during oscillation. A proper flow rate may remove BrMA more rapidly than it is produced during oscillation but less rapidly than during steady reaction, and the system may alternate between the two conditions.

Graziani et al.[30] point out that the above observations suggest the possibility of hysteresis and of bistability with two different states stable to small perturbations at the same flow rate. They also show that such a conclusion is consistent with the FKN mechanism,[7] but they did not obtain convincing experimental evidence. More conclusive evidence has been reported by de Kepper et al.[29] and by Marek and Svobodová.[28]

The latter authors[28] also report some interesting observations of phase linking by using a short tube to connect two stirred-flow reactors oscillating at the same frequency but in different phase. Both reactors approached a single new frequency one-quarter of the original one. Such behavior is expected from the theory of synchronized oscillators.[32] Marek and Stuciil[33] have carried out a more complete study of the synchroni-

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zation of oscillating Belousov–Zhabontinsky systems.

Other Oscillating Solution Reactions

The Bray–Liebhafsky Reaction. Over 50 years ago, Bray[34] concluded from thermodynamic considerations that the iodate–iodine couple should be almost ideal to catalyze the decomposition of hydrogen peroxide. He found the anticipated catalysis but also discovered it was not always smooth and that bursts in oxygen evolution were sometimes accompanied by alternating destruction and formation of iodine. Spectrophotometric measurements of iodine can be coupled with potentiometric measurements of iodide and of oxygen.[35] The reaction was studied extensively by Liebhafsky[36] at two widely separated periods during his career, and the mechanism has now been elucidated by Sharma and Noyes.[37]

Thermodynamic considerations indicate that reactions Bi and Bii are both almost irreversible.

$$2IO_3^- + 5H_2O_2 + 2H^+ \rightarrow I_2 + 5O_2 + 6H_2O \quad \text{(Bi)}$$

$$I_2 + 5H_2O_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O \quad \text{(Bii)}$$

The steps B1, B2, and Bx exhibit obvious similarities

$$IO_3^- + I^- + 2H^+ \rightarrow HIO_2 + HOI \quad \text{(B1)}$$

$$HIO_2 + I^- + H^+ \rightarrow 2HOI \quad \text{(B2)}$$

$$HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O \quad \text{(Bx)}$$

to the analogously numbered A reactions except that step Bx regenerates the iodide ion consumed in steps B1 and B2. If these steps are combined with the reversible hydrolysis of elementary iodine, the stoichiometry of process Bi can be generated with kinetic behavior resembling steps M1 and M2 of the Oregonator.

Process Bi results from direct 2-equiv oxidation of a hydrogen peroxide molecule. Although iodide ion is also thermodynamically capable of reducing hydrogen peroxide by a 2-equiv process, the reaction is too slow to be significant in this system. On the other hand, thermodynamic considerations indicate that the radicals I and IO_2 are incapable of oxidizing hydrogen peroxide by hydrogen atom abstraction but are capable of reducing it with hydroxyl radical formation. It therefore appears that process Bii is at least partly radical in nature.

The situation is further complicated because HOI will not be oxidized by a direct 1-equiv radical reaction. A mechanism that seems to be consistent with everything that is known about the system and its component parts is given by steps B3a–g and B4. Of course B3a is an

$$IO_3^- + HIO_2 + H^+ \rightarrow 2IO_2 + H_2O \quad \text{(B3a)}$$

$$IO_2 + H_2O_2 \rightarrow IO_3^- + H^+ + OH \quad \text{(B3b)}$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad \text{(B3c)}$$

$$HO_2 + I_2 \rightarrow I^- + I + O_2 + H^+ \quad \text{(B3d)}$$

$$I + O_2 \rightleftarrows IOO \quad \text{(B3e)}$$

$$IOO + I^- + H^+ \rightarrow HOI + IO \quad \text{(B3f)}$$

$$IO + H_2O_2 \rightarrow HIO_2 + OH \quad \text{(B3g)}$$

$$2HIO_2 \rightarrow IO_3^- + HOI + H^+ \quad \text{(B4)}$$

exact analogue of A3a, and the sequence B3a + 2(B3b) consumes one HIO_2 while producing two OH radicals. The sequence B3c to B3g is a hydroxyl radical catalyzed oxidation of iodine. (Of course the IOO peroxy radical is a different species from the IO_2 radical derived from iodic or iodous acid.) Whenever the average chain length exceeds 0.5, occurrence of step B3a initiates autocatalytic generation of HIO_2 in a mechanism very similar to the sequence A3a + A3b in the Belousov reaction or the step M3 in the Oregonator. Autocatalysis does not lead to indefinite buildup of $[HIO_2]$ because of higher order step B4 just like steps A4 and M4 in the other mechanisms.

The radical mechanism developed here does not generate the stoichiometry of process Bii. The HOI produced in steps B3f and B4 will react by Bx. A careful analysis leads to the conclusion that this mechanism generates the approximate stoichiometry of process Bii′ which differs from that of process Bii by

$$I_2 + 11H_2O_2 \rightarrow 2IO_3^- + 3O_2 + 2H^+ + 10H_2O \quad \text{(Bii}'\text{)}$$

the additional catalytic decomposition of six molecules of hydrogen peroxide. If chains are terminated by reactions of the sluggish HO_2 radicals, an apparently accidental combination of circumstances generates the stoichiometry of Bii′ regardless of the length of the radical chains! This revised stoichiometry explains the well-known but previously puzzling fact that the rate of oxygen evolution increases greatly when iodine is being oxidized by iodate even though the stoichiometry of Bii produces no oxygen whatsoever.

The average length of the chain B3c–g is increased by increasing amounts of both I_2 and O_2. At low concentrations of iodine, the chain length will be less than 0.5 and net process Bi will dominate. When enough iodine has been formed, the chain length reaches the critical value, and the system switches to dominance by process Bii′. After this switch, the solution becomes grossly supersaturated with dissolved oxygen, and the chain length increases because of the effect on steps B3e and B3f. Therefore, the concentration of iodine must fall significantly before the system switches back to dominance by process Bi. The relief of supersaturation by dissolved oxygen introduces the slow restoration step analogous to M5 in the Oregonator; the system would otherwise go to a stable steady state.

The simple Oregonator model is not strictly applicable to the Bray reaction, but many features are still valid. Edelson[38] is attempting to model the experimental observations by means of the proposed mechanism.

The Briggs–Rauscher Reaction. Briggs and Rauscher[39] added manganous ion and malonic acid to a Bray system of acidic iodate and hydrogen peroxide. They discovered dramatically enhanced oscillations with a period of only a few seconds. Cooke[40] has begun to obtain the sort of information necessary to elucidate the mechanism, and Pacault et al.[41] have reported

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(41) (a) A. Pacault, P. Hanusse, P. de Kepper, C. Vidal, and J. Boissonade, *Acc. Chem. Res.*, **9**, 438 (1976); (b) A. Pacault, P. de Kepper, P. Hanusse, and A. Rossi, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **281**, 215 (1975); (c) P. de Kepper, A. Pacault, and A. Rossi, *ibid.*, **282**, 199 (1976); (d) P. de Kepper, *ibid.*, **283**, 25 (1976).

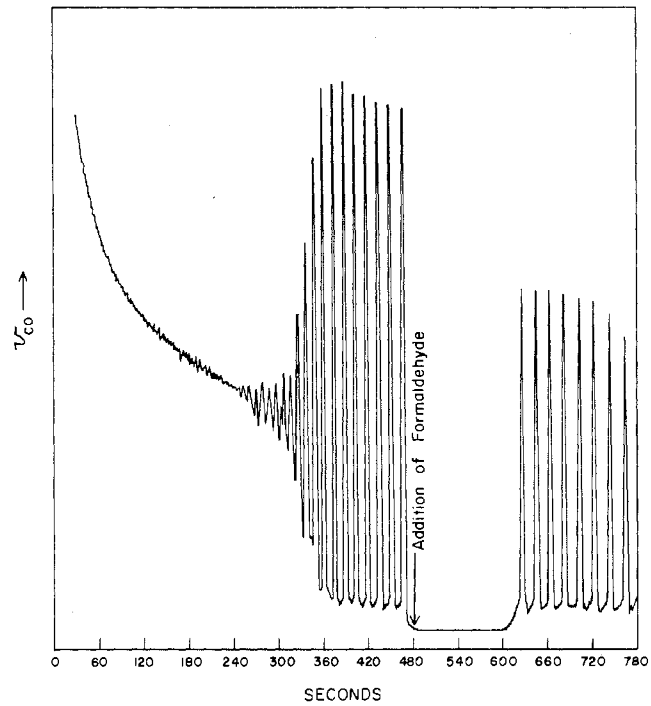

Figure 3. Rate of carbon monoxide production (in arbitrary units) at 55 °C by a stirred solution prepared from 4.0 mL of 88% aqueous formic acid and 10.0 mL of concentrated (ca. 97%) sulfuric acid. An addition of 0.3 mL of 37% formaldehyde solution was made at the time indicated.

interesting observations of multiple stationary states in a stirred-flow reactor. It appears that iodate is reduced and malonic acid is oxidized during the reaction, but it is not even clear whether hydrogen peroxide is a net oxidant or reductant or whether only its catalyzed decomposition contributes free energy as it does in the Bray–Liebhafsky reaction. Much more work will be needed before the mechanism is understood.

The Morgan Reaction. Formic acid could conceivably decompose either by Cα or by Cβ. Standard

$$H(CO)OH \rightarrow CO + H_2O \qquad (C\alpha)$$

$$H(CO)OH \rightarrow CO_2 + H_2 \qquad (C\beta)$$

free-energy changes for both are negative by a few kilocalories/mole, with Cβ slightly favored.

In concentrated sulfuric acid medium, virtually all of the observed products correspond to Cα. Over 60 years ago, Morgan[42] reported an oscillatory evolution of gas. Although these observations precede all other reports of homogeneous condensed-phase oscillators, the system has been generally ignored. Showalter[43] has recently reexamined it and has established that the basis of the oscillations is indeed chemical. The kinetic behavior may be grossly affected by small additions of species like formaldehyde, sodium nitrite, or ferrous sulfate, and the mechanism appears to be free radical rather than the acid catalysis that might have been expected. A typical experiment is shown in Figure 3.

Further mechanistic studies[43] have implicated iron salts and perhaps nitrates, always present at the part per million level in sulfuric acid. Reactions with C prefixes summarize the mechanism presently favored. Those equations do not specifically note rapid protolytic equilibria between species like OH and H_2O^+ or

$$H(CO)OH + H^+ \rightleftarrows CO(solv) + H_2O + H^+ \qquad (Ci)$$

$$Fe^{2+} + nCO(solv) \rightleftarrows Fe(CO)_n{}^{2+} \qquad (C3a)$$

$$Fe(CO)_n{}^{3+} + H_2O \rightleftarrows Fe(CO)_n{}^{2+} + H_2O^+ \qquad (C3b)$$

$$OH + H(CO)OH_2{}^+ \rightarrow H_2O + CO(solv) + H_2O^+ \qquad (C3c)$$

$$2OH \rightarrow H_2O_2 \qquad (C4)$$

$$CO(solv) \rightleftarrows CO(g) \qquad (C5a)$$

$$H_2O_2 + 2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \qquad (C5b)$$

$$H_2O_2 + H(CO)OH \rightarrow 2H_2O + CO_2 \qquad (C5c)$$

$$2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2 \qquad (C5d)$$

H(CO)OH and $H(CO)OH_2{}^+$.

Reaction Ci is a general-acid-catalyzed dehydration that slowly produces CO without any radical component. As iron ions become carbonylated, Fe(III) becomes a stronger oxidizing agent and the equilibrium of C3b becomes more favored—although the equilibrium constant will always be many orders of magnitude less than unity. Of course H_2O^+ is a protonated hydroxyl radical, and the sequence of the C3 steps provides autocatalysis resembling step M3 of the Oregonator.

As radicals are destroyed by second-order step C4 rather than by first-order step –C3b, the concentration of Fe(II) increases until equilibrium C3b becomes so unfavorable that radical-catalyzed reaction C3c is suppressed.

If step C5a is faster than C5b, carbon monoxide is then effectively removed before $[Fe^{III}]/[Fe^{II}]$ becomes large enough for the autocatalytic radical C3 sequence to again become significant.

This mechanism resembles the Oregonator in many ways if the hydroxyl radical is equated with intermediate X while Fe(II) and dissolved carbon monoxide are regarded as phase-determining intermediates. However, this mechanism exhibits an interesting variation from the Oregonator in that the nonradical reaction Ci and steps C3a–C5b (equivalent to process Mii + M5 of the Oregonator) both generate the same stoichiometry expressed by process Cα.

A pathway alternative to step C5b is the combination C5c + C5d which generates the stoichiometry of steps C5b + Cβ. Arguments in favor of this general mechanism for the Morgan reaction are being developed in another manuscript to be submitted soon.

An important potential application of the Morgan reaction arises because at elevated carbon monoxide pressure the system reaches a true equilibrium with a significant concentration of formic acid still present. If the pressure is then lowered, the system can be driven far enough from equilibrium to generate renewed oscillations. It is generally recognized that a system must be sufficiently far removed from equilibrium before oscillations are possible, but nobody has really established how far is sufficient. Preliminary very crude measurements[43] suggest that oscillations will not occur unless the system differs from equilibrium by at least $RT \ln 3$ for the $-\Delta G$ of process Cα.

Ammonium Nitrite Decomposition. It has long been known that aqueous solutions of ammonium nitrite, NH_4NO_2, decompose when heated and produce elementary nitrogen. Degn[44] has reported that the gas

(42) J. S. Morgan, *J. Chem. Soc., Trans.*, **109**, 274 (1916).
(43) K. Showalter and R. M. Noyes, unpublished observations.
(44) H. Degn, informal report at European Molecular Biology Organization Workshop, Dortmund, Oct 4–6, 1976.

may be evolved in oscillatory pulses with a period of tens of seconds. Smith[45] has confirmed this claim and has observed similar behavior from solutions of methylammonium nitrite, $CH_3NH_3NO_2$. It is too early to say much about the probable mechanism, but a radical component is suggested by the visual observation of nitrogen dioxide in the evolved gas. It appears doubtful that nitrogen gas itself is a chemically reactive product the way the evolved gas is in the Bray–Liebhafsky and Morgan reactions.

The Mason Reaction. DePoy and Mason[46] have reported oscillations of up to 15% in the concentration of aqueous dithionite, $S_2O_4^{2-}$, during its autocatalytic disproportionation. The analytical method involved measurements at different times rather than a continuous recording of some property. It may be that massive concentrations of some intermediate build up and then break down with regeneration of some of the original dithionite. It may also be that the analytical method is measuring some intermediate species in addition to dithionite. It seems difficult in any other way to reconcile the observations with the thermodynamic requirement[1] that concentrations of reactant species can not oscillate.

Photochemically Driven Oscillators. In all of the above examples, oscillations are driven by the free-energy change of an irreversible chemical reaction. Nitzan and Ross[47] showed theoretically that continuous illumination of a homogeneous system could initiate oscillations, hysteresis, and similar instabilities. Yamazaki et al.[48] have reported photochemically driven oscillations during irreversible chemical processes arising from ultraviolet irradiation of 1,5-napthyridine. Turro[49] has reported oscillations in the photostationary state sometimes attained when the peroxide of 9,10-diphenylanthracene is simultaneously being formed photochemically and destroyed thermally. Such a phenomenon could be accommodated[50] to an Oregonator type of mechanism involving singlet oxygen as an intermediate. If such a system does undergo no net chemical change while concentrations of species oscillate during continuous radiation, the observation may have practical implications.

Oscillations in Heterogeneous Condensed Systems

Oscillatory Electrode Reactions. It has long been known that electrochemical systems may oscillate as changing electrode surfaces affect conductivity and/or potentiometric behavior[51]. No effort will be made to review the field here.

The "beating mercury heart" phenomenon involves pulsation of a mercury globule near a corroding electrode not necessarily touching the mercury. Surface charge density changes the surface tension of the mercury and hence the shape of the globule; the shape change alters capacity and/or conductivity of the system. Lin, Keizer, et al.[52] have recently explained oscillations driven by the solution of aluminum in aqueous alkali.

Periodic Precipitation Phenomena. If silver nitrate solution is added at one point to a sheet of gel impregnated with potassium chromate, silver chromate precipitates in concentric rings. The phenomenon was discovered by Liesegang[53] and has been observed with several sparingly soluble salts. The subject was reviewed by Stern,[54] and the theory has been extended by Flicker and Ross.[55] When crystallization is initiated in a supersaturated region, ions diffuse from the surroundings to the growing crystals. Silver ions diffusing outward beyond those crystals must traverse a region of depleted chromate before the medium again becomes sufficiently supersaturated for nucleation to occur.

A similar banding with periods up to 2 m has been observed in igneous rocks that formed from large bodies of magma cooling at great depths. Most geologists since Darwin have attempted to invoke gravitational field effects to explain differentiation in such magmas. McBirney and Noyes[56] have shown that the non-Newtonian viscosities of the fluid magmas would not permit gravitational differentiations, and the effect has been explained by a molecular model based on supersaturation and diffusion much as occurs with Liesegang rings.

Oscillations During Gas Reactions

Heat capacities of dilute gases are much less per unit volume than are those of liquids, and temperatures can be greatly altered by sudden changes in reaction rate. Because reaction rates are strongly dependent upon temperature, various reactions can be accelerated or retarded by the thermal consequences of their occurrence, and the possibilities for oscillatory behavior are thereby enhanced.

Explosions due to chain branching autocatalytic oxidations have been known for centuries. Oscillations have also been reported during oxidation and chlorination of some hydrocarbons. Appropriate references are provided by Gray et al.[57] who also report their own observations of propane oxidation. It is not yet clear whether any of these systems generate unstable steady states under truly isothermal conditions.

Dickens et al.[58] report oscillatory flames during the oxidation of "dry" carbon monoxide. The system is very complicated, and about a part per million of water could accelerate the rate by orders of magnitude. Yang[59] has suggested an isothermal model that generates an unstable steady state. However, that model requires an unidentified excited electronic state of carbon dioxide with peculiar kinetic properties. Pilling and Noyes[60] have argued that the Yang model is im-

(45) K. Smith and R. M. Noyes, preliminary observations.
(46) P. E. DePoy and D. M. Mason, *Faraday Symp. Chem. Soc.*, **9**, 47 (1974).
(47) A. Nitzan and J. Ross, *J. Chem. Phys.*, **59**, 241 (1973).
(48) I. Yamazaki, M. Fujita, and H. Baba, *Photochem. Photobiol.*, **23**, 69 (1976).
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(52) S. W. Lin, J. Keizer, P. A. Rock, and H. Stenschke, *Proc. Natl. Acad. Sci. U.S.A.*, 71, 4477 (1974).
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(57) P. Gray, J. F. Griffiths, and R. J. Moule, *Faraday Symp. Chem. Soc.*, **9**, 103 (1974).
(58) P. G. Dickens, J. E. Dove, and J. W. Linnett, *Trans. Faraday Soc.*, **60**, 539 (1964).
(59) (a) C. H. Yang, *Combust. Flame*, **23**, 97 (1974); (b) C. H. Yang and A. L. Berlad, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1661 (1974); (c) C. H. Yang, *Faraday Symp. Chem. Soc.*, **9**, 114 (1974).

plausible and have shown the isothermal steady state must be stable if only known reactions of species in ground electronic states are considered. Explosions can be modeled if thermal gradients due to conduction are added, but turbulence apparently must be invoked also if oscillations are to be explained. A recent paper by McCafrey and Berlad[61] suggests that heterogeneous effects may also be necessary in order to account for oscillations.

Oscillations in Biological Systems

Living organisms are open chemical systems constantly subject to external influences and invariably far from equilibrium! Numerous oscillatory responses have been observed with periods ranging from seconds to at least a year.[62] Some of these responses are undoubtedly initiated by external stimuli, but others like human "jet lag" are in opposition to those stimuli and must originate in the chemistry of the individual concerned.

No effort will be made to review the field. None of the chemical mechanisms has been elucidated in detail, but glycolysis has been studied extensively. Boiteux and Hess[63] have summarized the evidence that the key step contributing to instability involves the conversion of fructose 6-phosphate to fructose 1,6-bisphosphate catalyzed by phosphofructokinase. The activity of this enzyme is strongly influenced by the product of the reaction it catalyzes. A model that leads to an unstable steady state has been proposed by Goldbeter and Lefever.[64] That model involves a process third order in reactive intermediates as invoked for the Brusselator model of Prigogine and Lefever.[65] It is not clear whether or not existing experimental data could also be accommodated to an Oregonator model[3] based on switching between pseudo steady states.

The dynamics of populations of individual species introduce still more complexities, especially when those populations are not uniformly distributed through the space of interest.[66] Although some oscillations in predator–prey populations bear superficial resemblances to the chemical oscillators discussed here, the systems involved are so different that any comparisons should be handled with great caution.

Characteristics of Known Chemical Oscillators

The above discussion illustrates that chemical instabilities may arise for several different reasons. Thus periodic precipitation phenomena involve kinetics of nucleation in supersaturated systems. Electrode reactions and localized trigger wave initiation require a heterogeneity in the system, and phase waves require a gradient in a system that would be oscillatory even if uniform. All presently known gas-phase oscillators seem to require a coupling with the thermal effects associated with very exothermic processes, although there is no reason why isothermal gas oscillators could not occur. Probably enzyme kinetics are not yet well enough established to determine whether biological oscillations involve switching between pseudo steady states (Oregonator) or third order in intermediates (Brusselator) types of mechanisms.

At the present time, the best understood homogeneous oscillators involve ionic reactions in aqueous solution. It is interesting that many of the best established examples include gas evolution as one of the processes. In the Bray–Liebhafsky[37] and Morgan[43] reactions, the evolved gas is chemically reactive and its rate of evolution is critical to the possibility of oscillations. In the Belousov–Zhabotinsky[7] reaction, the evolved gas seems to be inert chemically, and completely gas-free systems can exhibit both temporal[13] and spatial[22] periodicities. It is too early to say whether or not gas evolution is chemically significant for the ammonium nitrite[45] and photochemically driven[49] oscillators.

So few mechanisms are yet understood that it is risky to generalize. However, enough homogeneous solution mechanisms have been elucidated that we can suggest a few features that are probably worth looking for when studying other oscillators:

(a) The major reactants must undergo at least two key processes (like Mi and Mii) that produce or consume phase-determining intermediates. Both key processes must be strongly favored thermodynamically.

(b) The rate of one of the key processes can be switched on or off relative to the other. This switching is a kinetic effect free of thermodynamic constraints. For the systems whose mechanisms are understood, one and only one of the two key processes involves free radicals in its mechanism.

Unless d-orbital shells are only partially filled, most molecules have an even number of electrons. The sum or difference of two even numbers is always even, and the sum or difference of an even and an odd number is always odd. Therefore radical and nonradical processes can take place independently of each other just as seems to be required for processes Mi and Mii.

Most organic free radicals tend to be high-energy species that react rather indiscriminantly and should be avoided in biological processes. This argument suggests that transition elements in the third row of the periodic table may be involved in the 1-equiv oxidations and reductions that are required for one of the processes; such reactions might be coupled to transitions between S–H and S–S bonds in proteins. Many of those transition elements are essential to life but are needed only in trace amounts. It is tempting to suggest they may be incorporated in some of the enzyme systems needed for biological control mechanisms.

(c) The switching between the two key processes involves a stiffly coupled intermediate (X in the Oregonator) that is formed and destroyed by processes the same order in its concentration. Small dominance by either formation or destruction can greatly alter the concentration of that intermediate and switch the system to major dominance by one or the other of the key processes.

(d) A final process must overcome the effects of the two key processes on the concentrations of the PDI. This final process (such as step M5 in the Oregonator) must have a sufficiently small time constant that the system will repeatedly overshoot its mathematical steady state. Whenever the rate constant for this

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(64) A. Goldbeter and R. Lefever, *Biophys. J.*, 12, 1302 (1972).
(65) I. Prigogine and R. Lefever, *J. Chem. Phys.*, 48, 1695 (1968).
(66) R. May, "Stability and Complexity in Model Ecosystems", Princeton University Press, Princeton, N.J., 1973.

restoration process exceeds a certain value, the system will go to that steady state. Such a steady state may be only marginally stable, so that the system can still be excited by a suitable perturbation.

In many of the known solution oscillators, this final process is escape of a gas. Many metabolic processes in living organisms produce carbon dioxide, which then affects cytoplasmic pH. If pH is important to the processes leading to oscillation, diffusive escape of carbon dioxide through cell walls could be the slow process permitting the delayed feedback necessary for oscillation.

We wish to emphasize the biological suggestions we have made above are purely speculative without any experimental justification. However, they arise from direct analogies with now established mechanisms in simpler chemical systems. We make no claim they are valid, but we believe they are provocative. We hope they will suggest further tests by which these crude ideas may be substantiated or rejected.

Notes Added in Proof

Bowers and Rawji[67] have also studied the Morgan reaction[42,43] of formic acid dehydration. They believe the oscillations are caused by physical rather than by chemical effects.

Bose, Ross, and Wrighton[68] have independently observed photochemically induced oscillations in the fluorescence of anthracene and of dimethylanthracene similar to those found by Turro[49] for the diphenyl derivative.

Much of the work described here was supported either by the National Science Foundation or by the Atomic Energy Commission.

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A Transition-State Probe

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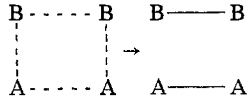
Received February 2, 1977

A central problem in chemistry is that of increasing our knowledge of transition states. The lifetime of the transition state is so short relative to the time scale of the majority of our investigative techniques that direct observations are normally not possible. Thus, in solution chemistry, conclusions regarding transition-state geometry may be inferred from calculation following kinetic studies; the possibility of the *direct* measurement of a transition-state property is lost due to collisions which precede the determination of the experimental parameter (e.g., rate of product formation). Clearly, if we wish to obtain information about transition-state geometry, then it would be extremely useful to know what happens to the electronic energy stored in the stretched bonds of the transition state (e.g., **1**) as it passes to more stable products (e.g., **2**).



1 **2**

Let us consider first a hypothetical and extreme case where the geometry of **1** was such that the A–A and B–B bond lengths were close to their equilibrium values in the products **2**, and the excess electronic energy of **1** over **2** could then be regarded as lying in the form of a potentially repulsive interaction along the two A--B bonds in **1**. Thus, as the transition state was converted to products, a quantity of energy close to the reverse activation energy would appear as kinetic energy (mutual repulsion) of the products. In the reverse process (**2** → **1**), such a model would correspond to an activation energy being supplied by collision of A–A and B–B due to relative translation along the A → B directions, without the requirement of vibrational excitation of A–A and B–B.

As a second and opposite extreme, we might envisage a situation where the A–A and B–B bond lengths in **1** were far from their equilibrium values in the products **2**, such that the excess electronic energy of **1** over **2** would appear as vibrational energy of the products **2**, which would drift apart without mutual repulsion. Here, in the reverse process (**2** → **1**), the activation energy would be supplied almost exclusively as vibrational energy of A–A and B–B, a large relative translational (collisional) energy of the two molecules not being required.

Information on the presence or absence of large mutual repulsions of A–A and B–B as a transition state **1** collapses to products in a period comparable to vibrational frequencies (10^{-13} s) can only be obtained by direct observation of the behavior of isolated **1**, i.e., in the absence of collisions. Such conditions can be found in a molecular beam. The measurement of mutual repulsion of two particles formed by the collapse of a transition state is facilitated if the transition state itself carries a charge and the products correspond to a charged molecule and a neutral molecule. The ionic product can then be passed through a magnetic field

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