Principal Component Analysis for Reducing the Edelson–Field–Noyes Model of the Belousov–Zhabotinsky Reaction

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Principal component analysis is a general method of extracting kinetic information from the array of sensitivity coefficients computed for several species of a reacting system. Eigenvectors corresponding to small eigenvalues indicate unimportant reactions and/or the validity of simplifying kinetic assumptions, thereby enabling one to optimally reduce the mechanism. Application of the method to the Edelson–Field–Noyes mechanism of the Belousov–Zhabotinsky reaction yields Oregonator-type simple models and clearly shows the kinetic approximations required for such reductions. The relative significance of individual reactions in the EFN mechanism is also determined over different subintervals of the period.

Introduction

The Edelson–Field–Noyes (EFN) model[1-4] is an ambitious effort to describe the detailed chemistry of the Belousov–Zhabotinsky reaction by slightly expanding the Field–Körös–Noyes[5] mechanism. The aim of the present paper is reducing the EFN model by the recently published method of principal component analysis.[6] Derivation of greatly simplified models for the BZ reaction is obviously not new. The famous Oregonator of Field and Noyes[7] was obtained on the basis of chemical considerations and application of the classical approximation techniques of chemical kinetics, e.g., the rate-determining-step and quasi-steady-state approximations. The Oregonator has been modified by several authors[8-10] to accommodate better a number of observed phenomena.

The relations between the complete model and a set of simplified ones has also been explained in terms of singular perturbation theory applied to the corresponding differential equations.[11-12] The aim of our analysis is, however, completely different. Instead of explaining what has been previously done, the method of principal components offers a rational basis for deriving the simplest model which is in substantial agreement with the detailed chemistry of the EFN mechanism. First, measuring the relative reaction significance the method offers an objective condition for weeding out the less important steps of the mechanism. Second, revealing dependencies among the parameters the method may suggest simplifying kinetic assumptions.

Though the present paper may be considered as a "test" application of a general method of simplifying kinetic models, the result seems to be interesting in itself. The derived skeleton model consists of eight reactions and preserves the essential oscillatory features of the original EFN model. Selecting $HBrO_2$, Br^-, and Ce^{4+} as concentration variables, we obtain a subset of the reactions that form the modified Oregonator due to Showalter, Noyes, and Bar-Eli,[8] rather than the original Oregonator model. Taking HOBr as an additional concentration variable gives a further reaction recently proposed by Noyes.[10] It should be emphasized

that this tremendous simplification of the EFN model has been attained by weeding out the less important 14 reactions and by applying one rate-determining-step assumption, all suggested by the results of principal component analysis.

Results also give further insight into the EFN mechanism by exhibiting the relative importance of its reactions over different subintervals of the oscillation period.

Principal Component Analysis of Kinetic Models

In sensitivity studies one usually computes the normalized sensitivity coefficients $\partial \ln y_i(t_j,k)/\partial \ln k_l$ for the species concentrations $y_1(t_j,k)$, ..., $y_m(t_j,k)$ at selected time points t_1, t_2, ..., t_q and the nominal values $k^0 = (k_1^0, k_2^0, ..., k_p^0)^T$ of the parameters. The main objective is to determine the relative importance of elementary reactions or certain groups of reactions in the complex mechanism. As shown by Vajda, Valkó, and Turányi,[6] principal component analysis offers an effective means for extracting this useful information from the $mq \times p$ array S of sensitivity coefficients by performing an eigenvalue–eigenvector decomposition of the cross-product matrix S^TS. The basic concept of the method is the response function

$$Q(k) = \sum_{j=1}^{q} \sum_{i=1}^{m} \left[\frac{y_i(t_j,k) - y_i(t_j,k^0)}{y_i(t_j,k^0)} \right]^2 \tag{1}$$

which is a compact way of exhibiting concentration effects brought about by a variation $\Delta k = k - k^0$ in rate coefficients. With the notations

$$\alpha_l = \ln k_l, \quad l = 1, 2, ..., p \tag{2}$$

the classical Gauss approximation[13] yields

$$Q(k) \approx \tilde{Q}(\alpha) = (\Delta \alpha)^T S^T S (\Delta \alpha) \tag{3}$$

where $\alpha_l^0 = \ln k_l^0$ and $\Delta \alpha = \alpha - \alpha^0$. Let U denote the a matrix of normalized eigenvectors u_i of S^TS such that $u_i^T u_i = 1$, $i = 1$, 2, ..., p. Then the new set

$$\Psi = U^T \alpha \tag{4}$$

of parameters called principal components[13] leads to the canonical form

$$\tilde{Q}(\Psi) = \sum_{i=1}^{p} \lambda_i (\Delta \Psi_i)^2 \tag{5}$$

of the response function 3, where $\Delta \Psi = U^T \Delta \alpha$ and $\lambda_1 > \lambda_2 > ... > \lambda_p$ denote the eigenvalues of S^TS at k^0. Expression 5 is very

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(2) Edelson, D.; Noyes, R. M., Field, R. J. *Int. J. Chem. Kinet.* **1979**, *11*, 155–64.
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(9) Bar-Eli, K.; Haddad, S. *J. Phys. Chem.* **1979**, *83*, 2944–52.
(10) Noyes, R. M. *J. Chem. Phys.* **1984**, *80*, 6071–6078.
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(12) Wolfe, R. J. *Arch. Ration. Mech. Anal.* **1978**, *67*, 225–50.

(13) See, e.g., Bard, Y. *Nonlinear Parameter Estimation*; Academic Press: New York, **1974**; p 184.

REACTIONS IN THE MODEL

Model	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	A
A
B
C
D
E
F
G

▨ Reaction present in the model

Figure 1. Summary of the derived models.

informative. In fact, if we move from α^0 along the eigenvector u_i in the space of transformed parameters (2), then $\Delta\Psi_j = 0$ if $i \neq j$. Thus $\bar{Q}(\Psi) = \lambda_i(\Delta\Psi_i)^2$ and hence λ_i measures the significance of reactions which are present with significant (say, >0.2) coefficients in the principal component Ψ_i. Principal components corresponding to the larges eigenvalues then obviously define the "influental" part of the mechanism. Giving mechanistic interpretation to certain forms of eigenvectors, the presence of small eigenvalues (i.e., $\lambda_i \approx 0$) also has kinetic consequences. The simplest case is $\Psi_i \approx \alpha_j$ (i.e., α_j is a dominant term in the principal component Ψ_i), then (5) is not sensitive to the changes in α_j and step j is a candidate for weeding out from the mechanism. The most important feature of our analysis is, however, the uncovering of parameter interactions. To show the simplicity of this result assume that $\lambda_i \approx 0$ and the corresponding normalized eigenvector is

$$u_i = (0.707, 0.707, 0, ..., 0) \tag{6}$$

Then $\bar{Q}(\Psi) \approx 0$ along the line $\Delta\alpha_1 = \Delta\alpha_2$ and according to (2) this line defines the curve $k_1/k_2 = $ constant in the space of original parameters. Thus the response function 1 depends only on the ratio k_1/k_2 and does not depend on k_1 and k_2 separately. Since application of quasi-steady-state or rate-determining-step assumptions frequently leads to such nonlinear parameter combinations appearing in rate equations, the uncovered parameter interactions may suggest applicability of approximations. Similar mechanistic interpretation exists for the case of several interacting parameters,[6] but such an extension is not required in the present paper.

To classify an eigenvalue as "small" or "large" we have only approximate rules. As detailed in our previous paper,[6] approximations involving eigenvalues $\lambda_i < 10^{-4}mq$ usually lead to small ($\leq 1\%$) average changes in concentrations (e.g., the corresponding reactions may be eliminated from the mechanism). On the other hand, the eigenvalues $\lambda_1, \lambda_2, ..., \lambda_s$ may be considered as the "large" ones if $\sum_{i=1}^{s}\lambda_i/\sum_{j=1}^{p}\lambda_j > 0.99$, though this criterion frequently selects only one or two eigenvalues vastly greater than the rest. Between the set of these influental reactions and the set of non-influental ones there exist reactions of transitional importance, whose elimination usually implies significant concentration effects but does not necessarily change the kinetic behavior substantially. Therefore, a really deep simplification of a kinetic model as given in this paper requires a trial-and-error procedure. This does not decrease usefulness of principal components, since by ranking reaction groups the method clearly suggests the candidate reactions for simplifying the model, whereas each simplification step can separately be validated by solving the kinetic equations and checking concentration deviations.

A further degree of freedom in the method is the choice of sample points $t_1, t_2, ..., t_q$ which obviously influence the eigenvalues and eigenvectors (e.g., selecting points within the induction period of a chain reaction one will not find the parameter combinations indicating a quasi-steady-state assumption valid only after the considered time interval). Though analyzing oscillating reactions results are essentially independent of the choice of sample points within the period, a better separation of large and small eigenvalues

can be attained by selecting more points in the neighborhood of some characteristic times with minimum or maximum concentrations for one or several species. On the other hand, as will be discussed also in this paper, reaction significance can be different at different stages of the process and hence to measure the total sensitivity of the system over the entire period some sample points should be placed in each stage.

A specific feature of oscillating systems is the possibility of separating the secular terms[17] in the sensitivity coefficients, thereby increasing the information content of the results. The presence of secular terms, however, only slightly increases the largest eigenvalues in latter periods, whereas the eigenvectors are completely unchanged. Therefore, in this paper we restrict our consideration to simple sensitivity coefficients computed according to the well-known methods of solving the sensitivity equations.

Reducing the EFN Model via Principal Component Analysis

The EFN mechanism consists of 26 reactions among 18 chemical species. Though Table I lists 32 reactions as originally published by Edelson, Noyes,[2] and Field, our analysis involves only the 26 reactions with originally nonzero rate coefficients. To keep similarity with the available sensitivity results we adopt the conditions used by Edelson,[4] thereby restricting considerations to open systems with a number of species maintained at constant concentrations. Initial conditions are also indicated in Table I. We computed normalized sensitivity coefficients at 13 time points, 20.0, 32.0, 32.03, 32.115, 33.45, 40.0, 60.0, 68.0, 68.726, 71.7, 80.0, 100.0 and 120.0 s, within each period with a period time of 114.12 s. Sample points are more densely allocated in the neighborhood of characteristic time points (i.e., 32.115 and 71.7 s, corresponding to minimum and maximum Br^- concentrations, respectively). Solving the sensitivity equations by the recently published decomposed direct method,[14] normalized sensitivities were computed at these time points for several periods. The S^TS matrix was formed separately for each period, taking into account only the corresponding sample points. Table II shows eigenvalues and significant (i.e., ≥ 0.2) entries of eigenvectors of S^TS for period 2. In further periods we obtained similar results, whereas in period 1 the only significant difference was the increased importance of step 1.

According to the discussion in the previous section, the results of Table II give conclusions as follows:

(i) Since $\lambda_i \leq mq \times 10^{-4} = 1.56 \times 10^{-2}$ for $20 \leq i \leq 26$, steps 2, 25, 23, 28, 17, 4, and 20 are unimportant and can be dropped. Table III shows the period time, minimum and maximum concentrations both for the complete mechanism of 26 reactions and for reduced mechanism of 19 reactions (see columns A and B, respectively). We note that Figure 1 offers a summary of the various reduced models involved in this paper. Each letter A–G

(14) Valkó, P., Vajda, S. *Comput. Chem.* **1985**, *8*, 225-72.

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TABLE I: Reactions of the EFN Mechanism and Initial Conditions[a]

no.	reaction	rate constant
1–2	$2H^+ + Br^- + BrO_3^- \rightleftharpoons HOBr + HBrO_2$	$2.10 \ M^{-3} \ s^{-1}$ $1.00 \times 10^4 \ M^{-1} \ s^{-1}$
3–4	$H^+ + HBrO_2 + Br^- \rightleftharpoons 2HOBr$	$2.00 \times 10^9 \ M^{-2} \ s^{-1}$ $5.00 \times 10^{-5} \ M^{-1} \ s^{-1}$
5–6	$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O$	$8.00 \times 10^9 \ M^{-2} \ s^{-1}$ $2.00 \ M^{-1} \ s^{-1}$
7–8	$CH_2(COOH)_2 \rightleftharpoons (OH)_2C{=}CHCOOH$	$3.00 \times 10^{-3} \ s^{-1}$ $2.00 \times 10^2 \ s^{-1}$
9–10	$Br_2 + (OH)_2C{=}CHCOOH \rightleftharpoons H^+ + Br^- + BrCH(COOH)_2$	$6.00 \times 10^4 \ M^{-1} \ s^{-1}$ 0
11–12	$HOBr + (OH)_2C{=}CHCOOH \rightleftharpoons H_2O + BrCH(COOH)_2$	0 0
13–14	$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2BrO_2^{\cdot} + H_2O$	$1.00 \times 10^4 \ M^{-2} \ s^{-1}$ $3.64 \times 10^5 \ M^{-2} \ s^{-1}$
15–16	$BrO_2^{\cdot} + Ce^{3+} + H^+ \rightleftharpoons Ce^{4+} + HBrO_2$	$6.50 \times 10^5 \ M^{-2} \ s^{-1}$ $2.40 \times 10^7 \ M^{-1} \ s^{-1}$
17–18	$Ce^{4+} + BrO_2^{\cdot} + H_2O \rightleftharpoons BrO_3^- + 2H^+ + Ce^{3+}$	$1.70 \times 10^{-1} \ M^{-2} \ s^{-1}$ $1.30 \times 10^{-4} \ M^{-3} \ s^{-1}$
19–20	$2HBrO_2 \rightleftharpoons HOBr + BrO_3^- + H^+$	$4.00 \times 10^7 \ M^{-1} \ s^{-1}$ $2.00 \times 10^{-10} \ M^{-2} \ s^{-1}$
21	$Ce^{4+} + CH_2(COOH)_2 \rightarrow {\cdot}CH(COOH)_2 + Ce^{3+} + H^+$	$1.00 \ M^{-1} \ s^{-1}$
22	${\cdot}CH(COOH)_2 + BrCH(COOH)_2 + H_2O \rightarrow Br^- + CH_2(COOH)_2 + HO\dot{C}(COOH)_2 + H^+$	$1.00 \times 10^4 \ M^{-2} \ s^{-1}$
23	$Ce^{4+} + BrCH(COOH)_2 + H_2O \rightarrow Br^- + HO\dot{C}(COOH)_2 + Ce^{3+} + 2H^+$	$7.30 \times 10^{-3} \ M^{-2} \ s^{-1}$
24	$2HO\dot{C}(COOH)_2 \rightarrow HOCH(COOH)_2 + O{=}CHCOOH + CO_2$	$1.00 \times 10^9 \ M^{-1} \ s^{-1}$
25	$Ce^{4+} + HOCH(COOH)_2 \rightarrow HO\dot{C}(COOH)_2 + Ce^{3+} + H^+$	$2.13 \ M^{-1} \ s^{-1}$
26	$Ce^{4+} + O{=}CHCOOH \rightarrow O{=}\dot{C}COOH + Ce^{3+} + H^+$	$5.00 \times 10^1 \ M^{-1} \ s^{-1}$
27	$2O{=}\dot{C}COOH + H_2O \rightarrow O{=}CHCOOH + HCOOH + CO_2$	$1.80 \times 10^7 \ M^{-2} \ s^{-1}$
28	$Br_2 + HCOOH \rightarrow 2Br^- + CO_2 + 2H^+$	$6.00 \times 10^{-3} \ M^{-1} \ s^{-1}$
29	$HOBr + HCOOH \rightarrow Br^- + H^+ + CO_2 + H_2O$	0
30	$2{\cdot}CH(COOH)_2 + H_2O \rightarrow CH_2(COOH)_2 + HOCH(COOH)_2$	$1.80 \times 10^7 \ M^{-2} \ s^{-1}$
31	$Br_2 + BrCH(COOH)_2 \rightarrow Br_2CHCOOH + Br^- + H^+ + CO_2$	0
32	$HO\dot{C}(COOH)_2 + BrCH(COOH)_2 + H_2O \rightarrow Br^- + HOCH(COOH)_2 + HO\dot{C}(COOH)_2 + H^+$	0

[a] Initial conditions: $[BrO_3^-]^b = 6.3 \times 10^{-2}$, $[Br^-] = 3.0 \times 10^{-5}$, $[Ce^{3+}] = 1.0 \times 10^{-3}$, $[H^+]^b = 1.05$, $[BrCH(COOH)_2]^b = 1.0 \times 10^{-3}$, $[CH_2(COOH)_2]^b = 2.5 \times 10^{-1}$, $[H_2O]^b = 55.0$, $[HCOOH]^b = 5.0 \times 10^{-4}$, $[HOCH(COOH)_2]^b = 4.0 \times 10^{-3}$, $[O{=}CHCOOH]^b = 2.0 \times 10^{-3}$. [b] Maintained at constant concentration.

refers both to a specific model and to the corresponding column in Table III that characterizes oscillations generated by the model in an open system. As seen from Table III, weeding out the seven less important reactions gives negligible deviations. According to the principal components Ψ_{17} and Ψ_{18}, the next reaction of low significance is 18, whose elimination also implies only small deviations in the kinetic behavior (see column C in Table III).

(ii) As shown by Ψ_{19}, the response function depends only on the ratio k_5/k_6, thus steps 5 and 6 should practically be always at equilibrium with the quasiequilibrium concentration

$$[Br_2]_e = \frac{k_5}{k_6} \frac{[HOBr][Br^-][H^+]}{[H_2O]} \quad (7)$$

Similarly, though λ_{18} slightly exceeds the critical value $mq \times 10^{-4} = 1.56 \times 10^{-2}$, Ψ_{18} shows the response mainly depending only on the ratio k_7/k_8, and thus

$$[(OH)_2C{=}CHCOOH]_e = (k_7/k_8)[CH_2(COOH)_2] \quad (8)$$

Dependence of the concentrations on the equilibrium constants k_5/k_6 and k_7/k_8 indicates that the rate-determining step in the reaction sequence 5–6–7–8–9 is the bromination reaction 9. It should be emphasized that in spite of the small eigenvalues stemming from parameter interactions all these steps are quite influental as shown by Ψ_1 and Ψ_5, both corresponding to large eigenvalues. This agrees with the conclusion of Edelson[4] on the rate-controlling role of the enolization and bromination of malonic acid on the period. Using (7) and (8) for step 9 we obtain the rate expression

$$r_9 = k_9 \frac{k_5}{k_6} \frac{k_7}{k_8} \frac{1}{[H_2O]} [H^+][HOBr][Br^-][CH_2(COOH)_2] \quad (9)$$

which formally corresponds to the reaction

$$HOBr + Br^- + CH_2(COOH)_2 + H^+ \rightarrow$$
$$H^+ + Br^- + BrCH(COOH)_2 + H_2O \quad (A)$$
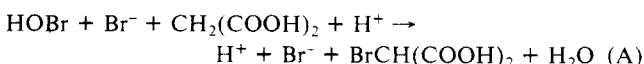
This reaction with the rate coefficient $k_A = 6.545 \times 10^7 \ M^{-3} \ s^{-1}$ will be referred to as reaction A. Replacing steps 5, 6, 7, 8, and 9 of model C by reaction A, the resulting set of 14 reactions gives the period time and concentrations shown in column D of Table III.

(iii) The reduced set retains 13 reactions of the original EFN mechanism. According to their relative importance these reactions can be divided into two further classes. In fact, $\sum_{i=1}^{10}\lambda_i/\sum_{i=1}^{26}\lambda_i = 0.9999$, in $\Psi_1-\Psi_{10}$ the significant parameters are only the rate coefficients of steps 22, 1, 3, 13, 26, 21, 15, and 16, thereby forming the influental part of the mechanism. The second class is formed by steps 24, 27, 19, 14, and 30 in $\Psi_{11}-\Psi_{16}$, corresponding to the eigenvalues $0.15 \leq \lambda_i \leq 3.17$. As shown in column E of Table III, elimination of these reactions of "transitional" importance implies considerable changes in period and concentrations. Essentials of dynamic behavior are, however, preserved and the reduced mechanism of nine reactions exhibits stable limit cycle oscillations.

It is interesting to note that without the rate-determining-step assumption in step (ii), we also obtain oscillations eliminating the unimportant (i) and moderately important (iii) reactions of the EFN mechanism. The resulting set of 13 reactions gives, however, increased period and Br⁻ concentrations as shown in column F of Table III. Thus simplication steps (ii) and (iii) have opposite effects on the period, and the change in the results from introducing the rate-determining step A in (ii) is far more significant than that of eliminating some reactions of transitional importance in (iii).

Simplification steps (i)–(iii) result in the model E of 9 reactions listed in Table IV. Now we relate this mechanism to other simplified models of the BZ reaction. It may be readily verified that our reactions form a subset of the modified Oregonator reported by Showalter, Noyes, and Bar-Eli.[8] Selecting $HBrO_2$, Br⁻, and Ce^{4+} as concentration variables, step A produces no net chemical change and can be dropped. The reaction
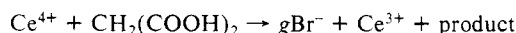
$$Ce^{4+} + CH_2(COOH)_2 \rightarrow gBr^- + Ce^{3+} + product$$

TABLE II: Eigenvalues and Eigenvectors for the EFN Model

no.	λ	dominant elements of the principal component[a]							
		7	9	8	22	1			
1	2.29×10^9	0.53	0.50	-0.50	0.26	0.22			
		22	13	26	21	1	30		
2	4.67×10^6	-0.53	0.40	0.40	-0.37	0.31	0.26		
		1	3	13	22	21	8	7	
3	8.99×10^1	0.52	-0.52	0.38	0.23	0.22	0.21	-0.21	
		15	16	21	13	14	1		
4	5.21×10^1	0.58	-0.46	0.35	0.35	-0.26	0.25		
		21	5	6	26	1	13		
5	3.06×10^1	0.49	-0.42	0.42	0.34	0.31	-0.25		
		21	15	6	5	22	3	26	16
6	2.44×10^1	-0.63	0.31	0.30	-0.30	0.29	0.28	0.24	0.21
		26	22	27					
7	1.19×10^1	0.67	0.63	0.21					
		9	7	8	13	1	15		
8	6.93	0.66	-0.35	0.34	-0.26	0.25	0.25		
		13	9	15	1	3	5	6	
9	6.16	-0.52	-0.44	0.44	0.31	-0.25	0.23	-0.23	
		3	1	5	6	15	9	19	
10	4.43	0.55	0.44	0.32	-0.32	-0.25	-0.20	-0.20	
		24	27	30					
11	3.17	0.85	-0.32	-0.22					
		27	24	30					
12	2.86	0.81	0.44	0.22					
		14	16	13	15	3	19		
13	1.97	0.52	0.51	0.37	0.35	0.30	0.25		
		19	16	14	15				
14	1.18	0.63	-0.56	0.41	0.24				
		19	14	16					
15	6.47×10^{-1}	0.67	-0.62	0.34					
		30	18	26	27				
16	1.50×10^{-1}	0.79	0.45	-0.25	0.22				
		18	20	27					
17	8.41×10^{-2}	0.85	-0.34	0.21					
		8	7	18					
18	3.89×10^{-2}	0.70	0.67	-0.21					
		5	6						
19	2.18×10^{-3}	0.71	0.70						
		2							
20	8.01×10^{-4}	1.00							
		25							
	5.42×10^{-5}	1.00							
		23							
22	3.02×10^{-7}	0.99							
		28							
23	9.62×10^{-9}	0.99							
		17							
24	3.93×10^{-9}	1.00							
		4							
25	1.46×10^{-16}	1.00							
		20							
26	9.10×10^{-20}	1.00							

[a] The top line refers to the rate constant for the reactions listed in Table I. The bottom line lists eigenvector components of magnitude ≥ 0.20.

TABLE III: Period and Concentrations Computed from the Complete and Different Reduced Models

	model						
	A	B	C	D	E	F	G
period, s	114.1	112.3	112.2	29.6	37.8	174.5	43.7
$[Br^-]^a$	1.39×10^{-9}	1.32×10^{-9}	1.32×10^{-9}	5.13×10^{-10}	3.79×10^{-10}	1.73×10^{-9}	3.75×10^{-10}
	1.09×10^{-4}	1.09×10^{-4}	1.09×10^{-4}	5.42×10^{-5}	2.68×10^{-4}	5.98×10^{-4}	2.68×10^{-4}
$[HBrO_2]^a$	6.97×10^{-11}	6.97×10^{-11}	6.97×10^{-11}	7.07×10^{-11}	6.98×10^{-11}	6.95×10^{-11}	6.88×10^{-11}
	3.41×10^{-6}	3.42×10^{-6}	3.42×10^{-6}	3.14×10^{-6}	1.64×10^{-5}	1.62×10^{-5}	1.64×10^{-5}
$[Ce^{4+}]^a$	3.14×10^{-7}	2.72×10^{-7}	2.70×10^{-7}	4.07×10^{-7}	3.98×10^{-7}	2.63×10^{-7}	6.23×10^{-7}
	2.27×10^{-4}	2.29×10^{-4}	2.29×10^{-4}	2.28×10^{-4}	9.93×10^{-4}	9.95×10^{-4}	9.99×10^{-4}
$[BrO_2]^a$	1.51×10^{-10}	1.51×10^{-10}	1.37×10^{-10}	1.46×10^{-10}	1.44×10^{-10}	1.35×10^{-10}	1.53×10^{-10}
	8.10×10^{-6}	8.08×10^{-6}	8.10×10^{-6}	7.57×10^{-6}	9.52×10^{-4}	2.13×10^{-3}	9.36×10^{-4}

[a] Top and bottom lines refer to minimum and maximum concentrations, respectively.

of Oregonator-type models[7-9] can be regarded as a schematic sum of steps 21, 22, and 26 of our reduced mechanism and hence the stoichiometric factor g is $r_{22}/(r_{21} + r_{26})$, where the r's denote reaction rates. Though it is not justified, assume a quasi-steady-state for the malonyl radical. Taking into account that in our computations [O=CHCOOH] is maintained at a constant concentration of 2×10^{-3}, we obtain

$$g = \frac{r_{22}}{r_{21} + r_{26}} = \frac{[CH_2(COOH)_2]}{[CH_2(COOH)_2] + 0.1} \qquad (10)$$

TABLE IV: Reactions of the Reduced EFN Models

no.	no. in the EFN model	reaction	rate coefficient
1	1	$2H^+ + Br^- + BrO_3^- \rightarrow HOBr + HBrO_2$	$2.10\ M^{-3}\ s^{-1}$
2	3	$H^+ + HBrO_2 + Br^- \rightarrow 2HOBr$	$2.00 \times 10^9\ M^{-2}\ s^{-1}$
3	13	$HBrO_2 + BrO_3^- + H^+ \rightarrow 2BrO_2{\cdot} + H_2O$	$1.00 \times 10^4\ M^{-2}\ s^{-1}$
4-5	15-16	$BrO_2{\cdot} + Ce^{3+} + H^+ \rightleftharpoons Ce^{4+} + HBrO_2$	$6.50 \times 10^5\ M^{-2}\ s^{-1}$
			$2.40 \times 10^7\ M^{-1}\ s^{-1}$
6	21	$Ce^{4+} + CH_2(COOH)_2 \rightarrow {\cdot}CH(COOH)_2 + Ce^{3+} + H^+$	$1.00\ M^{-1}\ s^{-1}$
7	22	${\cdot}CH(COOH)_2 + BrCH(COOH)_2 + H_2O \rightarrow Br^- + CH_2(COOH)_2 + HOC{\cdot}(COOH)_2 + H^+$	$1.00 \times 10^4\ M^{-2}\ s^{-1}$
8	A[a]	$HOBr + Br^- + CH_2(COOH)_2 + H^+ \rightarrow H^+ + Br^- + BrCH(COOH)_2 + H_2O$	$6.545 \times 10^7\ M^{-3}\ s^{-1}$
9	26[b]	$Ce^{4+} + O{=}CHCOOH \rightarrow O{=}C{\cdot}COOH + Ce^{3+} + H^+$	$5.00 \times 10^{-1}\ M^{-1}\ s^{-1}$

[a] Obtained from steps 5, 6, 7, 8, and 9 of the EFN model. Taken into account only in closed systems. [b] Not contained in the reduced model G.

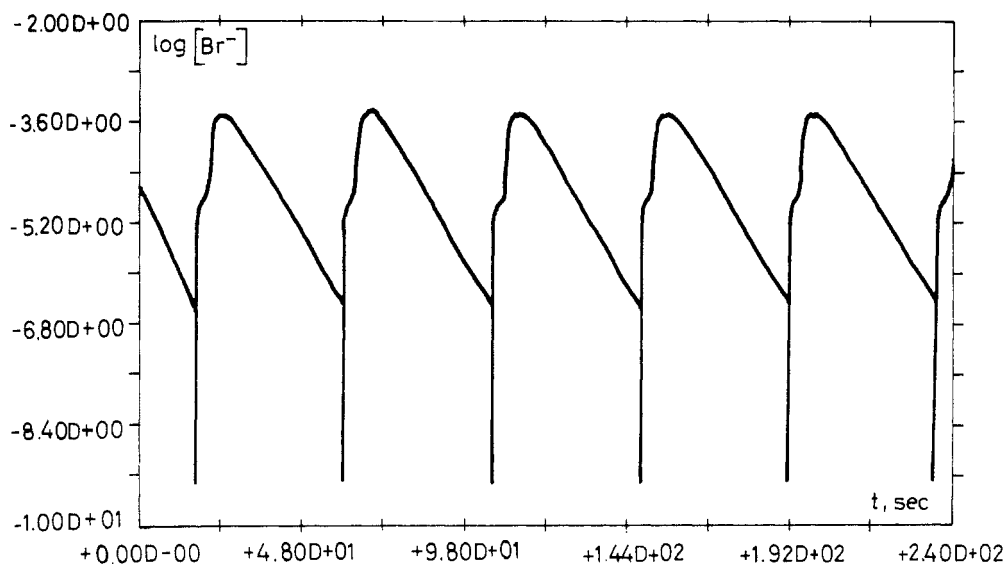**Figure 2.** Bromide oscillations computed from model G in an open system.

and hence $g = 0.71$ under the conditions of this study. Though [O=CHCOOH] is quite close to 2×10^{-3} also in the solution of the complete EFN model, eq 10 is an overestimation of the real stoichiometric factor since its value is significantly decreased by the presence of step 30 in the complete mechanism. In fact, adding step 30 to the 14 reactions of the simplified model F yields nonoscillatory behavior. Though relation 10 is approximate, it explains why the solution of the EFN model does not oscillate at low malonic acid concentrations. With decreasing [CH$_2$(CO-OH)$_2$], g goes below its lower critical value. This is caused by step 26 providing a channel for the reduction of Ce^{4+} without the simultaneous regeneration of bromide. We note that dropping also step 26 gives $g = 1$, independent of the malonic acid concentrations. The period and concentrations are, however, only moderately changed compared to model E as shown in column G of Table III. Since in an open system reaction A does not influence the concentration variables HBrO$_2$, Br$^-$, and Ce^{4+}, this simplest skeleton model consists of reactions 1–7 of Table IV. Figure 2 shows Br$^-$ concentrations generated by this simple mechanism.

Note that eliminating reaction steps also reduces the number of concentration variables. The number of variables is 12 in models A, B, and C, and it is reduced by one in each simplification step as we proceed to further models in Table III. In the simplest model G we have the species Br$^-$, Ce^{3+}, Ce^{4+}, HOBr, HBrO$_2$, BrO$_2$·, and ·CH(COOH)$_2$. Construction of an Oregonator-type model further reduces the number of variables, since introducing the schematic sum of steps 21 and 22 eliminates ·CH(COOH)$_2$. In addition, the original Oregonator eliminates BrO$_2$· by a further quasi-steady-state approximation and disregards as HOBr not influencing the reaction rates.

We emphasize that the results of principal component analysis do not justify the reduction of the EFN mechanism into the original Oregonator by eliminating BrO$_2$·. In fact, the validity of a further quasi-steady-state or rate-determining-step assumption

would have lead to a further small eigenvalue indicating close relations among steps 13, 15, and 16. The response function is, however, independently influenced by these reactions (see step 13 in principal components Ψ_2 and Ψ_3) though k_{15} and k_{16} are somewhat correlated according to Ψ_4 and Ψ_6.

Our results, however, indicate that the modified Oregonator of Showalter, Noyes, and Bar-Eli[8,9] can be further simplified. In fact, steps 2 and 4 of the EFN mechanism are completely noninfluental. Though step 14 is slightly more important, it can also be dropped and hence we agree with Field and Noyes[7] in assuming the first three reactions of Table IV to be irreversible. The only reversible reaction of the skeleton model should be steps 15 and 16 introduced by Showalter, Noyes, and Bar-Eli[8] in order to compute trajectories resembling those observed in flow systems. Furthermore, the disproportionation of HBrO$_2$ (i.e., step 19 in Table I) turns out to be of transitional importance in the EFN mechanism and can be eliminated when forming the simplest skeleton model. Notice that this is possible due to steps 15 and 16 in the reduced model, while in the original Oregonator the disproportionation step is necessary to prevent the rise in [HBrO$_2$].

According to our discussion the skeleton of the EFN model in a closed system is formed by the eight reactions 1, 3, 13, 15, 16, 21, 22, and A listed in Table IV (note that step 26 is dropped). It is important to note that reaction A is just step R6α introduced by Noyes in his recent revision of the Oregonator,[10] thus this step is implicitly contained also in the EFN model. With the derived rate constant k_A our mechanism gives rise to oscillations also in a closed system and these oscillations can be extended to low concentrations of malonic acid because of the constant value of the stoichiometric factor g. Responses computed in closed system for three different initial concentrations of malonic acid are listed in Table V. Initial conditions for BrO$_3^-$, Br$^-$, Ce^{3+}, and H$^+$ are those given in Table I.

Finally, we show a further goal of the present study. As will be discussed in the next section, the steps of the EFN mechanism
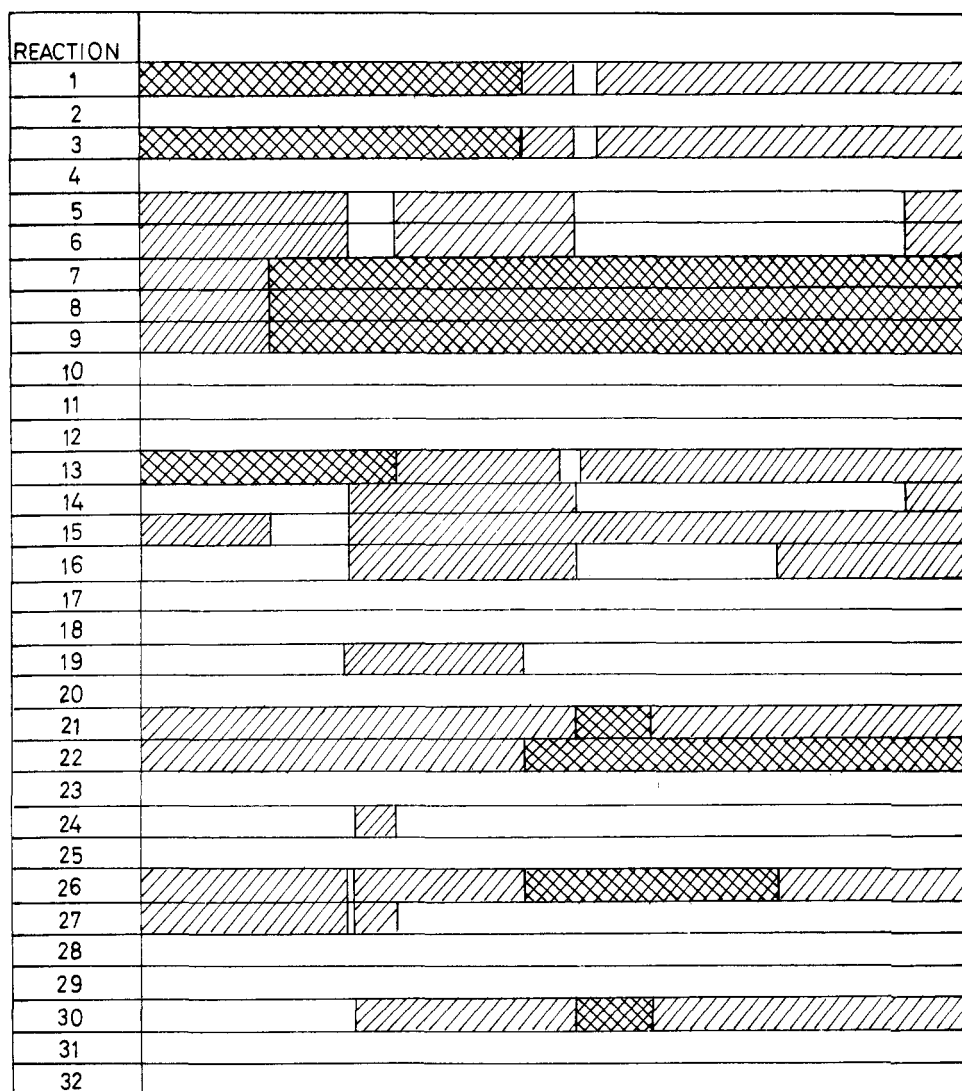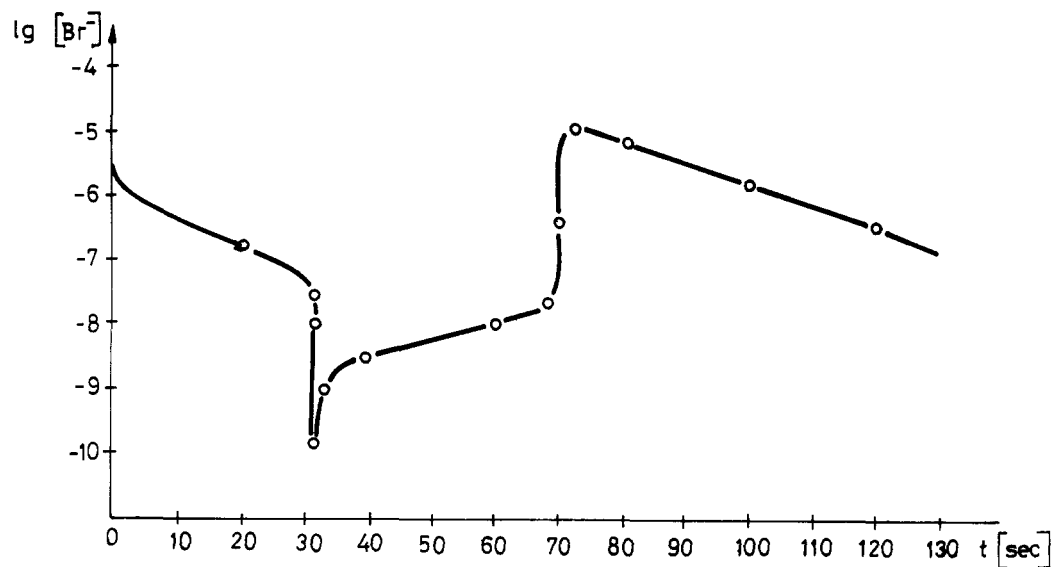
Figure 3. Significance of reactions in the EFN mechanism over subintervals of the period.

are divided into three more-or-less independent groups of reactions labeled A, B, and C.[15] Steps 21–32 of process C regenerate Br⁻ by the oxidation of brominated organic compounds. According to the chemical and experimental evidence recently evaluated by Varga et al.,[16] this part of the EFN mechanism should be substantially altered. Revision of the mechanism is partly model-based; thus the assumed new reactions should be added to carefully checked reactions of the groups A and B. For reducing compu-

TABLE V: Period and Br⁻ Concentrations Computed from Model G in Closed System Considering Period 1

	initial [CH₂(COOH)₂], M		
	0.1	0.25	0.6
period, s	97.2	53.0	43.1
[Br⁻]ᵃ	3.00×10^{-8}	3.08×10^{-8}	3.56×10^{-8}
	2.46×10^{-4}	5.32×10^{-4}	1.02×10^{-3}

ᵃTop and bottom lines refer to minimum and maximum concentrations, respectively.

tational efforts when revising the mechanism, it is advantageous to use a minimum set of reactions. Our model was primarily constructed to meet this requirement. Since it is only a starting point for further investigations, no systematic comparison of calculations with experiments is given here.

Some preliminary results on the behavior of this modified mechanism have already been published.[16]

Dynamics of Reaction Significance

Eigenvalues and eigenvectors offer a compact way of exhibiting the relative importance of reactions in the mechanism. However, the response function 2 measures only the total sensitivity of the system over the selected time points of the period, whereas reaction significance can be different at different stages of the process. For greater insight, principal components were also computed separately at each time point from the corresponding sensitivity coefficients. According to the summary of results shown in Figure 3, elimination of step 30 from the EFN model was not completely justified since this reaction is quite important at some part of the period. Similarly, steps 14 and 19 are moderately important in the low bromide production stage. In fact, according to Figure 2 this part of the period is quite short in the results of model G. Therefore, using the reduced model for revising the EFN mechanism steps 14, 19, and 30 were also retained.[16]

It is interesting to compare Figure 3 with theoretical expectations. Listing only important and moderately important steps, the three groups in the EFN mechanism are A = {1, 3, 5, 6}, B = {13, 14, 15, 16, 19}, and C = {7, 8, 9, 21, 22, 26, 30}. In terms of these groups the FKN mechanism was explained as follows.[15] At high bromide ion concentration process A predominates consuming Br⁻. Then it practically stops and process B begins. This quickly produces Ce⁴⁺, which in turn produces a burst of bromide through process C. A high Br⁻ concentration restarts process A. Figure 3 clearly shows how process A with some delay losses its significance at low bromide concentration. Step 13 of process B is, however, quite important also at this stage of the period which

may be caused by a continuous buildup of BrO₂ concentration. Further reactions of process B really become important only when the minimum bromide ion concentration is reached. Steps 21, 22, 26, and 30 of process C are also clearly separated in time from the other groups. Steps 7, 8, and 9 are, however, significant over a much longer part of the period. This observation agrees with results of the previous section, since steps of process C are assumed to regenerate Br⁻. If the rate-determining-step assumption is applied, however, reactions 5, 6, 7, 8, and 9 may be represented by the single reaction A which obviously does not contribute to this process.

For interpretation of the sensitivity results in determining reaction significance one remark seems to be appropriate. Assume that step i is significant over some part $[t_0, t_1]$ of the period, but on $[t_1, t_2]$ the reaction becomes very slow and practically does not contribute to concentration changes. Even in this case, however, the concentrations may be quite sensitive to Δk_i on $[t_1, t_2]$ because of indirect effects, i.e., concentration changes brought about by Δk_i over $[t_0, t_1]$. Therefore, changes in reaction significance do not strictly follow the changes in reaction rates.

Conclusion

The EFN mechanism of the BZ reaction has been reduced by eliminating its less important steps and applying a rate-determining-step assumption in order to obtain a tractable model for further studies. A generally accepted method of solving such problems is sensitivity analysis, resulting in a mass of numerical information in the form of sensitivity coefficients. As shown in the paper, principal components offer an effective means for extracting useful kinetic information from these derived sensitivity tables. Eigenvectors reveal interacting reaction sequences and the corresponding eigenvalues measure the significance of these separate parts in the mechanism, enabling us to identify the 14 less important reactions. Furthermore, the uncovered dependences among the parameters confirm the validity of a rate-determining-step assumption. It is quite agreeable that our resulting model agrees with previously published skeleton models. In particular, a reversible reaction introduced Showalter, Noyes, and Bar-Eli into the original Oregonator is shown to be important. There appears also a further reaction recently proposed by Noyes revising the Oregonator model. Our simple mechanism exhibits oscillations also in a closed system. The contribution of the paper is, however, in providing a rational basis for each step of the simplification procedure, partly intuitive in previous publications.

Results are checked by studying reaction significance at different time points of the period separately.