J. Phys. Chem. A **1997,** *101,* 1317−1323

Quenching Analysis of the Permanganate−Hydroxylamine Oscillator

Arpád Nagy,* Preben Graae Sørensen, and Finn Hynne

Department of Chemistry and CATS, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Received: August 20, 1996; In Final Form: November 13, 1996⊗

We present the experimental part of a study of the permanganate−hydroxylamine system at a supercritical Hopf bifurcation aiming at deriving a mechanism for the reaction. We report quenching data for the addition of a number of essential species and for substances supposed to remove essential species, as well as for dilution. In particular, we report successful quenchings with colloid manganese dioxide and with Arabic gum, which is supposed to inactivate the surface of the colloid.

1. Introduction

Permanganate ions react in an autocatalytic way with a number of organic and inorganic substrates. A well-known example, often mentioned in textbooks of chemical kinetics as an archetype of autocatalytic redox reactions, is the reduction of permanganate by oxalic acid. The search for nonlinear phenomena in systems containing permanganate ions was initiated by the study of the $KMnO_4-H_2C_2O_4-H_2SO_4$ system in a continuous-flow stirred tank reactor (CSTR), in which kinetic bistability between two steady states was found.[1,2] The first permanganate oscillator,[3] with phosphoric acid as the reaction medium and hydrogen peroxide as the reducing agent, stimulated further investigations of manganese chemistry as a source of new chemical oscillators.

In the last decade, two subgroups of new manganese oscillators were described. The first subgroup consists of permanganate and a reductant,[4−13] and the second one consists of manganese(II) ions and an oxidant.[14−17] A link between these two subgroups is the so-called "minimal permanganate oscillator",[18] based on the Guyard reaction[19] of manganese(II) ions with permanganate. It is interesting that this reaction was described more than 130 years ago and, until now, no realistic model for this reaction has been published. The lack of an adequate model for the Guyard reaction also complicates to a great extent the design of models for other permanganate oscillators.

Most of the permanganate systems[9] oscillate in a reaction medium with a pH value around 3, and only a few of them work at pH around 7. At these values of pH, stable species of manganese are formed in the oxidation states VII, IV, and II. Probably the most important oxidation state for oscillations to occur is the oxidation state IV. The species of manganese in this oxidation state can be present in different forms ranging from soluble species[20] through colloidal particles[21−24] to a precipitate of solid MnO_2. The actual form depends on the concentration of the manganese species, on the concentration and the type of compound stabilizing the colloidal particles in the solution, and on the reactivity of the reducing substrate. Manganese in oxidation states VI and V is stable only in very strong basic solutions,[25,26] and manganese in oxidation state III is stable in a very strong acidic solution.[27,28] At medium pH, the unstable species undergo fast disproportionation processes.

The brief survey of the stability of oxidation states of manganese indicates that a direct kinetic investigation of the elementary steps included in the oscillatory system is practically unrealizable. It is possible to study some of the component processes under conditions which are the same or similar to those of the oscillatory system. This kind of experimental work is helpful for the selection of reactions that should be included in a model and also for the estimation of corresponding rate constants. To get some adequate set of experimental data for the modeling of a permanganate oscillator, stress must be laid upon the methods studying the state of the complete system in a simple oscillatory state. As the method of investigation, we have used the recently developed perturbation method, the quenching method.[29−31]

This method is based on perturbations of an oscillating system close to a supercritical Hopf bifurcation, where a small limit cycle is centered on a saddle focus. This stationary point is unstable in the plane of oscillations and stable in certain other directions that are tangent to the so-called stable manifold. During the oscillations, the point representing the state of the system in concentration space moves around the limit cycle. Quenching is a perturbation that instantaneously shifts the state from a point on a limit cycle to some point on the stable manifold of the saddle focus. On the stable manifold, the system does not oscillate, but it moves back toward the plane, in which the limit cycle is located. At the same time, it may start to spiral out toward the limit cycle. The state of the system in perturbation experiments is monitored by concentration oscillations of some species. A successful quenching is recognized as a temporary stop of oscillations, followed by oscillations of gradually increasing amplitude. The resulting amplitude is increasing until the original limit cycle oscillations are recovered.

If a successful quenching is made by addition of a single species, which is already present in the system, the amount added must be precisely the one required, and the addition must be made in precisely the right phase of an oscillation (to reach the stable manifold). The quenching amount and the quenching phase are a pair of data that can be obtained for each species for which quenching is possible. Another possibility of stopping the oscillations is a quenching by removal of a species. This can be achieved by a shift in concentration space opposite to that of quenching by addition. The quenching in this case is performed by addition of a species which is usually not part of the system and which must react very fast with the species to be removed to form an inactive product. A necessary condition for considering the addition of one species to be equivalent to the removal of another is that addition of the remover can quench the oscillations by precisely the same stoichiometrically

---

* Present address: Department of Physical Chemistry, Comenius University, Mlynská dolina CH-I, SK-842 15 Bratislava, Slovakia.

⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1997.

S1089-5639(96)02559-5 CCC: $14.00

equivalent change of concentration and at precisely the opposite angle (180° shifted) as can the species it is supposed to remove.

The quenching method often can provide a large set of fairly precise data of direct kinetic relevance, which can be used for selection and optimization of models for oscillating reactions, as we have demonstrated previously.[32,33] The possibility of quenching small-amplitude oscillations in a permanganate system was demonstrated in ref 34. The purpose of the present paper is to undertake a detailed experimental study to get the quenching data for the most important manganese species in the oscillatory system.

2. Experimental Section

For the present investigations, we have selected the $KMnO_4-NH_2OH-H_3PO_4$ system, which is the only permanganate oscillator in which small-amplitude oscillations arising from a supercritical Hopf bifurcation have been found so far.

The reaction was run in a CSTR. The reaction cell was made of Plexiglas and was similar to the one described previously.[30] The volume of the cell was 9.2 mL. The reaction mixture was stirred by a propeller with a stirring rate of 700 rpm. The thermostated solutions of $KMnO_4$, NH_2OH, and H_3PO_4 were fed into the reactor through three independent tubes using a peristaltic pump (Ismatec IPN 8). The temperature of the reaction mixture in the cell was kept constant by a two-stage thermostatic control described previously.[30]

The cell was mounted on an optical bench. Polychromatic light from a halogen lamp passed the cell as a parallel beam. The beam was focused on a photodiode, and the desired wavelength of 546 nm was selected with an optical filter placed in front of the diode. The optical path length of the cell was 3 cm. The amplified signal from the diode was applied to a chart recorder and to an A/D converter connected to a PC. Sampling of data was initiated at every 0.4 s, and after five readings, an average value was calculated and stored on the disk. A few measurements were also made with the same cell placed in the sample compartment of a HP 8452A diode array spectrophotometer.

The operating point of the perturbation experiments was chosen on the basis of dynamical phase diagrams of ref 8. The experimental conditions were selected in accordance with the requirement of working close to a supercritical Hopf bifurcation and to have oscillations with a reasonable low period at an acceptable flow rate and without any precipitation of MnO_2 on the walls of the cell. The mixed flow concentrations were $[KMnO_4]_0 = 4.5 \times 10^{-5}$ M, $[NH_2OH]_0 = 4.1 \times 10^{-5}$ M, and $[H_3PO_4]_0 = 2.5 \times 10^{-3}$ M. The temperature was 35.0 ± 0.1 °C. At this temperature, a supercritical Hopf bifurcation was found at a specific flow rate of $j_0 = 4.96 \times 10^{-3}$ s^{-1}. The bifurcation point was determined by linear extrapolation of a plot of the square of the amplitude of the limit cycle oscillations vs the specific flow rate (see Figure 1). By definition, the amplitude is half the peak-to-peak difference for sinusoidal oscillations.

The perturbation experiments were carried out at the specific flow rate $j_0 = (5.3 \pm 0.15) \times 10^{-3}$ s^{-1}. The amplitude of the permanganate oscillations at the operating point was $(5.6 \pm 0.5) \times 10^{-7}$ M, and the frequency of the oscillation was $(9.3 \pm 0.7) \times 10^{-3}$ s^{-1}. The reaction system close to the bifurcation point is very sensitive to small changes of experimental constraints. Therefore, it was most practical to control the amplitude rather than the flow rate. Before each series of perturbations, the flow rate was therefore adjusted so that the amplitude was within the interval specified above.

The additions of species were made manually through a hole in the top of the conical part of the cell by using a pipet with adjustable volume. The concentrations of the solutions used for the perturbations were chosen to correspond to addition of volumes between 5 and 25 μL. The data sampled during a perturbation experiment were stored in the computer, and the recorded datafile was subsequently analyzed by the method described in detail in ref 30. The accuracies of quenching amounts and quenching phases are 10% and 10°, respectively.

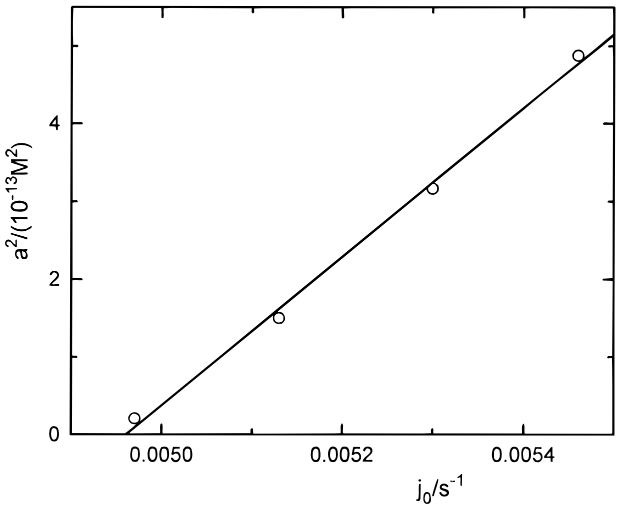

Figure 1. Plot of the square of the amplitude of $[MnO_4^-]$ oscillations as a function of the specific flow rate j_0. The abscissa intercept is the bifurcation flow rate. The linearity of the plot shows the occurrence of a supercritical Hopf bifurcation.

All reagents used for the experiments were of analytical grade and were used without any further purification. The stock solution of $KMnO_4$ was prepared and standardized by the procedure of Kolthoff et al.[35] Hydroxylamine solutions were prepared daily. Four times deionized water, filtered through Super C and Organex-Q cartridges (specific conductivity of less than 0.1 μS/cm), was used as a solvent throughout.

The quenching data for MnO_4^-, Mn^{2+}, NH_2OH, H^+, OH^-, $H_2P_2O_7^{2-}$, F^-, and Arabic gum were obtained by addition of aqueous solutions of $KMnO_4$, $MnSO_4{\cdot}H_2O$, $(NH_3OH)_2SO_4$, $HClO_4$, NaOH, $Na_4P_2O_7{\cdot}10H_2O$, KF, and Arabic gum, respectively. The 0.001 M colloidal solution of MnO_2 in 0.01 M KH_2PO_4 used for perturbations was prepared by the reaction of 4×10^{-4} M $KMnO_4$ with 6×10^{-4} M $MnSO_4$ and is stable for several days. The green 1.65×10^{-5} M solution of MnO_4^{2-} in 0.02 M KOH was prepared by a slightly modified procedure of Sutter et al.[36] A drop (4 μL) of 0.0412 M $KMnO_4$ was mixed with 48 μL of 1 M NaOH. The solution was heated on a hotplate to dryness. The manganate was formed according to the reaction

$$4MnO_4^- + 4OH^- \rightarrow 4MnO_4^{2-} + O_2 + 2H_2O \qquad (1)$$

and was dissolved in 0.02 M KOH. Because the solution of manganate in this medium undergoes slow decomposition, a fresh solution was made immediately before each quenching.

Reagents. $KMnO_4$, $(NH_3OH)_2SO_4$, H_3PO_4, $C_2H_2O_4{\cdot}2H_2O$, H_2SO_4, NaOH, KOH, and $Na_4P_2O_7{\cdot}10H_2O$ were from Merck; $MnSO_4{\cdot}H_2O$ was from Ferak; $HClO_4$ was from Riedel-deHaën; KF was from Fluka; and gum Arabic was from Sigma.

3. Results and Discussion

A. Description of the Oscillatory State. Under the conditions described in the Experimental Section, the system can persist in two stable steady states (SS) and in one oscillatory state. The stable state at relatively high flow rates is the so-called oxidized SS in which manganese is mostly present as

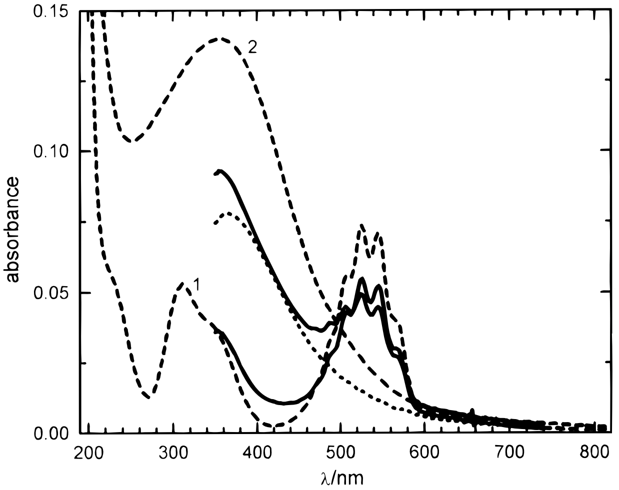

Figure 2. Spectra of the oscillatory reaction mixture in the minimum and maximum of an oscillation at a specific flow rate of $j_0 = 12.76 \times 10^{-3}$ s^{-1} (solid lines), 1×10^{-5} M $KMnO_4$ (dashed line 1), 5×10^{-6} M colloid MnO_2 (dashed line 2), and of an intermediate, probably colloid MnO_2 (dotted line). The optical path length is 3 cm.

permanganate ion. The stable state at relatively low flow rates is the reduced SS in which permanganate ions are mostly reduced to species in oxidation states IV and II. If the system is in the reduced SS and the flow rate is increased stepwise, the SS loses its stability at a specific flow rate of 4.96×10^{-3} s^{-1} at which a transition to an oscillatory state through a Hopf bifurcation occurs. We have studied the transition between the oscillatory state and the reduced steady state carefully without finding any chemical hysteresis. The linear relationship of the square of the amplitude of oscillations on the specific flow rate (Figure 1) and the absence of the hysteresis demonstrate that the Hopf bifurcation is supercritical.

In the initial experiments, the spectra of the oscillating reaction mixture were taken at regular time intervals in the wavelength range from 350 to 740 nm. The spectra at the maximum and at the minimum of an oscillation together with the spectra of permanganate, manganese dioxide, and an intermediate are presented in Figure 2. The qualitative analysis of the spectra indicates that it is possible to monitor spectrophotometrically the oscillations of the two different species. The decrease of the absorbance in the range of 520−580 nm while the absorbance in the range of 350−520 nm is increased and the characteristic structure of the permanganate spectrum show that one of the oscillating species is permanganate. The spectrum of the second species can be obtained by subtracting the spectrum of permanganate, multiplied by a constant, from the spectrum of the reaction mixture. The constant is varied until the characteristic spectral structure of permanganate is not observable in the resulting spectrum after the subtraction. The comparison of the spectra of the intermediate and manganese dioxide supports the assumption that the second oscillating species very probably is a soluble form of manganese dioxide.

If we denote the ratio of molar extinction coefficients of MnO_2 and MnO_4^- ions by r, then r has a maximal value at 420 nm ($r^{420} = 82$) and a minimal value at 546 nm ($r^{546} = 0.55$). These wavelengths were therefore selected for monitoring of the concentration oscillations of MnO_2 and MnO_4^-, respectively. The value of r^{420} is significantly greater then unity, so the recorded absorbance at 420 nm (Figure 3, lower curves) is not affected by oscillations of the MnO_4^- ions. The value of r^{546} is lower but comparable to unity, so the oscillations at 546 nm correspond to the oscillations of the MnO_4^- ions, but they are influenced by the oscillations of MnO_2. This effect is qualitatively observable mainly at higher flow rates, when the average concentration of MnO_2 in the oscillatory system is relatively high and it is decreasing with the decreasing specific flow rate. For the quenching experiments, however, it is important to know the exact value of the amplitude of the permanganate oscillations, because the amount of a species to be added to quench the oscillations is scaled by the amplitude of permanganate oscillations. If we assume that the absorbance of MnO_4^- ions compared to the absorbance of MnO_2 at 420 nm is negligible, then the absorbance of permanganate at 546 nm can be calculated using the formula

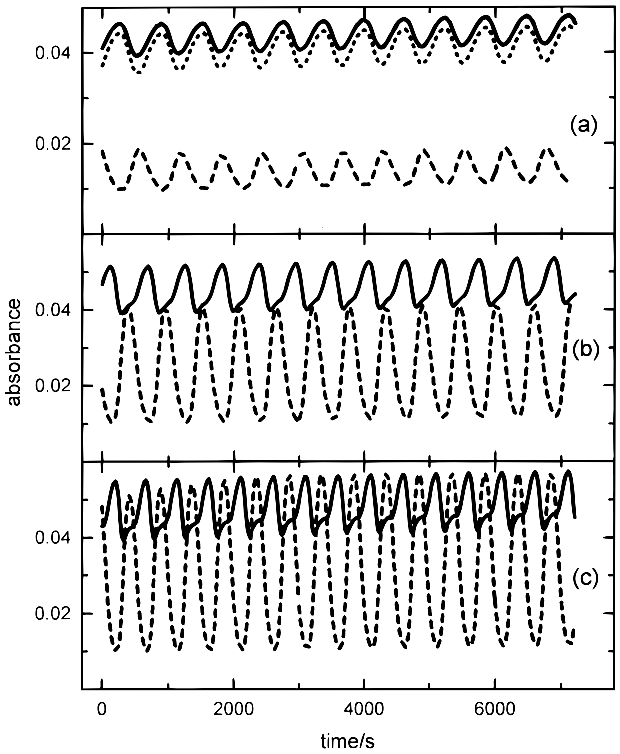

Figure 3. Oscillations of absorbance measured simultaneously at two different wavelengths (420 nm, dashed lines; 546 nm, solid lines) at increasing specific flow rates: (a) $j_0 = 6.13 \times 10^{-3}$ s^{-1}, (b) $j_0 = 9.44 \times 10^{-3}$ s^{-1}, (c) $j_0 = 12.76 \times 10^{-3}$ s^{-1}. The dotted line in a represents the absorbance of MnO_4^- ions calculated according to eq 2. The time traces demonstrate that MnO_4^- ions and MnO_2 oscillate in almost opposite phases. (The difference is −162°.)

$$A^{546}_{MnO_4^-} = A^{546} - \frac{\epsilon^{546}_{MnO_2}}{\epsilon^{420}_{MnO_2}} A^{420} \qquad (2)$$

in which A^{546} and A^{420} are the absorbances of the reaction mixture and $\epsilon^{546}_{MnO_2}$ and $\epsilon^{420}_{MnO_2}$ are the molar extinction coefficients of MnO_2 at 546 and 420 nm, respectively. The time trace at the specific flow rate $j_0 = 6.13 \times 10^{-3}$ s^{-1}, corresponding exclusively to the absorbance of MnO_4^- ions, is shown in Figure 3a together with the uncorrected absorbance at 546 nm. The ratio between the amplitudes determined from the calculated and measured time traces gives the factor by which the measured amplitude has to be multiplied in order to get the correct amplitude of the permanganate oscillations. The correction factor for the specific flow rate at which the perturbation experiments were performed is 1.20.

B. Quenching Results. The oscillations of the permanganate ions in the quenching experiments were measured spectrophotometrically. The experimental setup was arranged in such a way that the voltage of the diode was increasing for increasing concentration of MnO_4^-. The zero phase is defined, by our convention, as the maximum of the first harmonic of the voltage, on the assumption that it corresponds to a maximum

TABLE 1. Basic Quenching Data. Scaled Quenching Amounts ($(q_i/a)^a$) and Phases (ϕ_i) for Addition of Species *i*

species *i*	q_i/a	ϕ_i/deg
NH_2OH	2.4	19
MnO_4^-	3.7	−146
MnO_4^{2-}	0.014	−103
$MnO_{2(col)}$	2.2	−75
Mn^{2+}	35	8
Arabic gum[b]	2.2×10^{-7}	101
$H_2P_2O_7^{2-}$	0.17	−3
F^-	231	21
H^+	1156	77
OH^-	113	−104

[a] The added concentration is scaled by the amplitude **a** of the permanganate oscillations. [b] The absolute quenching concentration is given in units of g/mL.

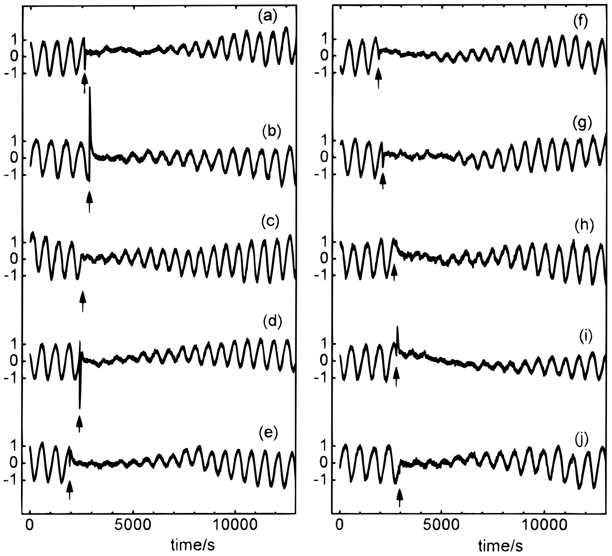

Figure 4. Time series showing successful quenchings by addition of (a) NH_2OH, (b) MnO_4^-, (c) MnO_4^{2-}, (d) MnO_2, (e) Mn^{2+}, (f) Arabic gum, (g) $H_2P_2O_7^{2-}$, (h) F^-, (i) H^+, and (j) OH^-. The instants of the additions are marked by arrows. The scaled quenching concentrations are shown in Table 1, and the phases are shown in Table 1 and in Figure 6.

of the first harmonic of $[MnO_4^-]$. Phases are quoted as principle values in the interval $-180° < \phi \leq 180°$.

If the reaction is run under batch conditions with the same initial concentrations as in the flow experiments, the permanganate is completely reduced to manganous ions. The batch experiment hints that in the oscillatory system, different intermediates of manganese in all oxidation states between VII and II can be present. We tried to make quenchings with manganese species, which we were able to prepare in basic or acidic solutions, in which the concentrations of OH^- or H^+ were so low that their contributions to the quenchings could be ignored. We did not attempt to use Mn(V), which can be prepared only in an extremely basic solution, or Mn(III), which is reasonably stable only in a very acidic medium with an excess of Mn^{2+} ions. The results of the quenching experiments are presented in Table 1 and Figures 4−6. Each of the substances in the table can stop the limit cycle oscillations when the quoted amount is added at the quoted phase.

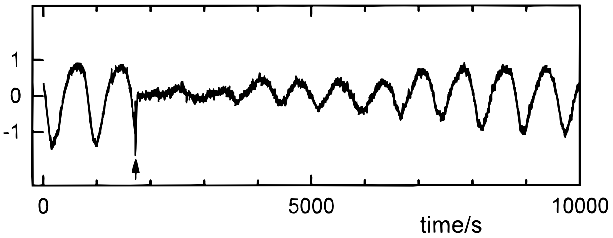

Figure 5. Quenching by dilution with H_3PO_4. The instant of dilution is marked by an arrow. The relative dilution is 0.048, and the phase is 140°.

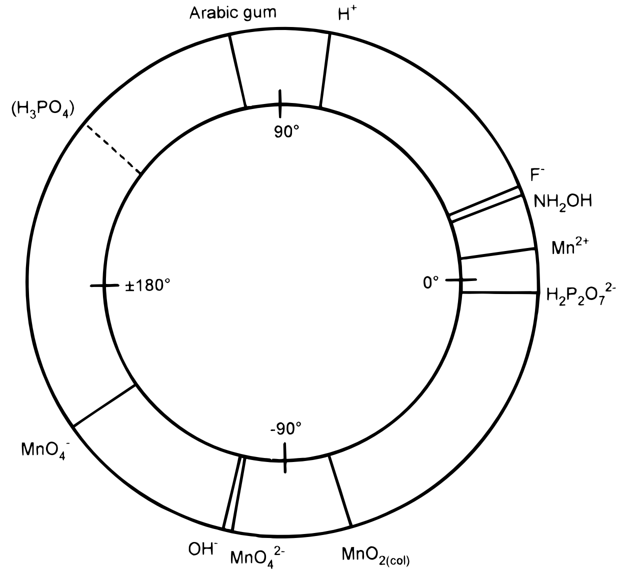

Figure 6. Polar diagram showing the distribution of the quenching phases for quenchings by additions (solid lines) and by dilution (dotted line).

Quenchings with Hydroxylamine and Permanganate. In the permanganate system, the quenchings with NH_2OH and MnO_4^- are possible (Figure 4a,b), unlike the Belousov−Zhabotinsky (BZ) and the Briggs−Rauscher (BR) reactions in which the perturbations with feed species were successful only for Mn^{2+} in BR.[30,37] The oscillations of permanganate in the present system can be easily recorded (Figure 3). In contrast, in the classical oscillatory systems the feed species do not oscillate, or the amplitudes of oscillations are so small that the oscillations are practically not measurable. The average concentration of permanganate in the oscillatory state at the operating point is 10% (± 1%) of the mixed flow concentration and it indicates that the rate of the catalyzed reduction of permanganate by hydroxylamine is relatively high.

Quenching with Manganate. The scaled quenching amount of MnO_4^{2-} in Table 1 shows that manganate is the most efficient quenching species. The quenching phase for MnO_4^{2-} is within the experimental error the same as the one for OH^- ions. The manganate solution was prepared in 0.02 M KOH, and the concentration change of OH^- ions in a successful quenching with manganate is only 19% of the quenching concentration of OH^- ions. To exclude the effect of OH^- ions on the quenching with manganate completely, we made a "blank" perturbation with a solution which was prepared in the same way as the manganate solution but without any manganate. The solution of OH^- ions prepared in this way was then used for the perturbation with the same parameters as in a successful quenching with managanate. The perturbation with this solution did not show any observable effect on the oscillations. In this way, it was possible to prove unambiguously that the quenching with the solution of manganate in 0.02 M KOH can be ascribed essentially to the quenching with manganate (Figure 4c).

Quenching by Addition of Colloid MnO_2, Effect of Colloid Surface. Manganese in oxidation state IV plays a crucial role in all manganese-based oscillators. As can be seen in Figure 2 (dotted line), its prevailing form in the oscillatory system is colloid manganese dioxide. In order to prevent the precipitation of solid MnO_2 in the reaction mixture, the colloidal particles are stabilized by phosphate ions. Under the conditions of the experiments, the reaction has been run continuously for up to 2 weeks without any noticeable precipitation. The quenching with colloidal solution of MnO_2 (Figure 4d) was successful. Presumably the addition of colloidal manganese dioxide increases the area available for the surface reactions in the system. To support the idea that a surface effect is involved, we tried to find a compound that can decrease the surface area in the system. The inhibitory effect of Arabic gum on the autocatalytic oxidation of Mn^{2+} by permanganate was described by Tompkins.[21] Arabic gum is a macromolecular compound, which can cover the surface of colloid particles and decrease their activity. The quenching with Arabic gum was successful (Figure 4f) and the quenching phase for the addition of this compound is opposite to the one for colloid manganese dioxide. The quenching results for MnO_2 and Arabic gum together support our interpretation that the addition of manganese dioxide and Arabic gum, respectively, could be regarded as an increase and a decrease of the surface of colloid MnO_2, which is often assumed to be catalytic.

In the minimal permanganate oscillator,[7] manganese(IV) is supposed to form a supersaturated solution of soluble Mn(IV) which then generates a MnO_2 precipitate autocatalytically as a result of nucleation and surface effects. The autocatalytic species in the Mn(II)−periodate oscillator[14] was identified as soluble $MnO(OH)^+$, and the surface of MnO_2 precipitate acts as an inhibitor, because the autocatalyst is removed from the solution by adsorption on the surface. Another possibility of explaining the effect of the surface was demonstrated in an autocatalytic system of permanganate and methylamine.[40] In this system, the colloid MnO_2 is first formed in a noncatalytic pathway. When the colloid surface is available, the substrate is adsorbed on the colloid and is oxidized by permanganate faster than the substrate in the solution.

The rich variety of possible sources of instability illustrates the complications involved in designing a proper model for the manganese-based oscillators. Unfortunately, the quenching experiments do not allow us to make a direct conclusion about the actual effect of the surface in the permanganate−hydroxylamine system. The quenching results, however, represent a set of reference data for the selection of the most probable mechanism.

Quenching by Decreasing the Concentration of Manganic Ions. Quenching by addition of Mn^{3+} ions could not be carried out, because Mn^{3+} in a solution of appreciable concentration is only stable if the solution contains Mn^{2+} and H^+ in so high concentrations that the effect of their addition completely masks the effect of Mn^{3+}. To get at least some indirect experimental data, we tried to use compounds which can form stable complexes with manganic ions in solution. The concentration of free Mn^{3+} ions in the system can be decreased by addition of these complex-forming agents. Pyrophosphate is particularly effective, and the ion $Mn(H_2P_2O_7)_3^{3-}$ has found use as an oxidant in quantitative inorganic analysis.[35,38] The stabilizing effect of fluoride ions was described by Launer.[39] He believed the fluoride complex to be MnF_4^-. Later studies showed, however, that in solution, different complexes of a general formula MnF_n^{3-n} ($n = 1-6$) can be formed.[41]

Quenching by addition of each compound was successful (Figure 4g,h), but they did not quench the oscillations at exactly the same phase, and the quenching concentrations were significantly different. Under the present conditions, pyrophosphate probably forms a more stable and a less reactive complex because its quenching amount is 1360 times smaller than the one of fluoride ions. Because of the large amount of F^- added in a successful quenching, the effect of it may be due not only to the deactivation of Mn^{3+} ions, but also to other processes such as a change in pH or adsorption on the colloid particles. The quenching with pyrophosphate seems to be more selective, and it allows an estimation of quenching data for the hypothetical addition of Mn^{3+} ions. If we regard the quenching with pyrophosphate as a quenching by removal of manganic ions, then the quenching phase for the addition of Mn^{3+} ions should be 177°. If we assume that the formation of the complex ion $Mn(H_2P_2O_7)_3^{3-}$ is quantitative, then the estimate of the upper limit for the addition of manganic ions is one-third of that of pyrophosphate.

Quenching with Manganous Ions. The manganous ion is the most stable species of manganese, so the quenching could be performed by direct addition of Mn^{2+} ions (Figure 4e). Among all manganese species, Mn^{2+} is the least effective quenching species, because it has the highest quenching concentration (see Table 1).

Quenchings with H^+ and OH^- Ions. Quenching with H^+ was carried out because hydrogen ions are expected to be important to the manganese reactions in acid solution. Quenching with OH^- was made because the chemistry of manganese is strongly dependent on pH and the stability of the various species are very different in acidic and basic media. We find that it is possible to quench the oscillations with H^+ as well as with OH^- and that the quenching phases are opposite (differ by 180°), but the amount required for quenching with H^+ is 10 times that required for OH^-.

The quenching concentrations of H^+ and OH^- are 6.5×10^{-4} M and 7.1×10^{-5} M, respectively, in the experiments. Thus, in a perturbation with H^+, the change of concentration of H^+ (before any reaction has taken place) is smaller than but not small compared to the average value of $[H^+]$ (which is 2.5×10^{-3} M). So the perturbation with H^+ may perhaps be approximately described by linearized theory[31] (which is important to the use of the quenching results for quantitative comparisons with models). But the quenching concentration of OH^- is many orders of magnitude larger than the average value of OH^- (which must be close to its equilibrium value in the phosphoric acid solution, 4×10^{-11} M).

Consequently, perturbation with OH^- certainly cannot be described by linearized theory. But from a chemical point of view, one might account for the addition of OH^- as the removal of the same amount of H^+ provided the recombination reaction

$$H^+ + OH^- \rightarrow H_2O \tag{3}$$

is so fast that other reactions with OH^- can be ignored in response to the perturbation. If this were the case, OH^- should quench with the same amount as H^+ but in opposite phase.

The quenching results for H^+ and OH^- show that although the quenching phases are indeed opposite, the quenching concentrations are different. There are two possible explanations of this fact. Either addition of OH^- does correspond to the removal of H^+ but the stable manifold is curved so different amounts are needed to reach that manifold in the positive and in the negative direction of the $[H^+]$ axis or, alternatively, the system involves fast reactions competing with reaction 3 under the perturbation with OH^-.

The latter alternative is not unlikely. If the added amount of OH^- was uniformly distributed before the reaction, the resulting nonequilibrium concentration of OH^-, 7.1×10^{-5} M, would correspond to the equilibrium concentration of OH^- in a fairly basic solution with pH of about 10. It is obvious that the stirring cannot completely mix the OH^- added in a perturbation before reactions take place. However, this only means that, locally, the nonequilibrium concentration of OH^- could be higher (before reaction with H^+ brings it down). In a nonequilibrium state where $[H^+]$ and $[OH^-]$ are both high, one may have fast manganese reaction with OH^- that are characteristic of basic media but are unimportant in the (acidic) stationary state.

Quenching by Dilution with Phosphoric Acid. Besides quenchings by addition or removal of a single species, it is also possible to quench the oscillations by dilution of the reaction mixture. Quenching by dilution is a special case of removal, when every species present is removed in an amount proportional to the instantaneous concentration of the species. The relations between the quenching data for additions of single species and those for dilution were derived in ref 37. If the reaction mixture is diluted by solution s and the relative dilution and the phase are d_s and ϕ_s, respectively, then the relation takes the form

$$\sum[\exp(-i\phi_j)/q_j](c_j - c_j^{(s)}) = (1 - 1/d_s)\exp(-i\phi_s) \quad (4)$$

where ϕ_j and q_j are the quenching phase and amount for addition of species j and the sum is taken over all species participating in the reaction. If we dilute with a solution containing a species k with concentration $c_k^{(s)}$ equal to its average concentration c_k, the corresponding term $c_k - c_k^{(s)}$ will disappear from the sum on the left-hand side of eq 4.

We have made dilutions with a solution of 2.5×10^{-3} M H_3PO_4, which is the mixed flow concentration of this species. We assume that the average value of $[H^+]$ in the reaction mixture can be approximated by this concentration. The relative dilution for the quenching is 0.048 at the phase of 140°.

The importance of the quenching by dilution can be discussed using eq 4. The equality can be tested if the left-hand side can be calculated. To fulfill this requirement, it is necessary to determine experimentally the quenching data for all species included in the oscillatory system. In practice, it is a very difficult task, because some of the intermediates either are unknown or are so unstable that it is not possible to use them for the perturbations. In contrast, the right-hand side for the dilution has only one term, which is easily accessible. During the perturbation by dilution, the concentrations of all species are decreased and the quenching data for dilution contain the encoded information about the concentration changes of all species of the oscillatory system. Therefore, the quenching by dilution can only be described quantitatively by a model of the oscillatory system in which all significant dynamical species are included. In this sense, the agreement between calculated and experimental quenching data for dilution can serve as a test of the completeness of a model.

4. Conclusion

Studies of permanganate oscillators have been oriented toward the design of new oscillatory systems and to the description of their dynamical behavior. Less attention has been paid to the development of models accounting for the observed phenomena. Undoubtedly, this is due to the fact that the oscillatory permanganate systems are extraordinary complicated. Any oxidation state of manganese between II and VII may be important, and these species may react with each other or with the substrate or derivatives of the substrate in many ways. The presence of colloid Mn(IV) and the possibility of surface catalysis pose additional problems.

A classic approach to establishing a mechanism of a composite reaction is through quantitative kinetic studies of the separate component reactions assumed to be involved. Unfortunately, several of the manganese intermediates are highly unstable under the conditions relevant to the system studied. So although one can get helpful information from the kinetics of some component reactions, kinetically relevant data for the system are scarce.

In general, the results that can be obtained from a study of the complete oscillatory system can only be related to the kinetics of the reactions if a reasonably correct mechanism is known. Our motivation to carry out the present investigation was partly to see how the quenching method works for a system that is completely different from the BZ family of systems and partly, indeed mainly, to provide data for a permanganate oscillator that can help clarify the mechanism of the reaction system.

The results of the quenching experiments are suitable for mechanistic studies for a number of reasons. The results specifically related to each species participating in the reaction can be obtained even if only one species can be monitored experimentally. The only condition is that the species is available for perturbation by addition or a substance can be found that can quickly and selectively remove the species from the reaction mixture.

The quenching results obtained are highly relevant to the kinetics. The quenching concentration and quenching phase for addition of a given species combine to form the corresponding component of a left eigenvector of the Jacobi matrix for the pair of eigenvalues associated with the oscillations. Thus, the components of the eigenvector are experimentally measurable for all species available for perturbation. The experimental quenching results for an oscillatory system can help us in the development of a model for the system. For any suggested model, the quenching data for each species of the model can be calculated easily and compared with the experimental value for that species. Any serious discrepancy is a sign that the model is not correct.

A set of experimental quenching data has the additional advantage that it applies to the system near a Hopf bifurcation. This means it applies to a state that in essence has the simplicity of a stationary state and at the same time can reveal the oscillatory properties of the system. This unique property is extremely important to the use of quenching results for determining a mechanism for an oscillatory reaction. It means that any suggested mechanism can be tested without knowing any rate constants beforehand and without having to integrate the kinetic equations.

The method relies on the representation of stationary reaction velocities in terms of convex parameters and extreme currents, developed by Clarke.[42] This is so because essentially all possible stationary states can be generated directly and the eigenvalues and eigenvectors of the Jacobi matrix calculated. Consequently, all possible Hopf bifurcation points can be obtained with an efficient root-finding algorithm determining the states where the real part of an eigenvalue vanishes. For each supercritical Hopf bifurcation point found this way, the eigenvector can then be compared with the experimental value determined by quenching experiments. If the agreement is satisfactory, one can subsequently calculate the set of rate constants that accounts for the stationary state selected. As a result, one has obtained a model that is likely to be a rather good one.

If one already has a reasonably good mechanism, the comparison with quenching data can determine a set of rate constants that fits the experimental quenching data best. This method we have called "optimization" of models based on a given mechanism.[32,33] Unfortunately, one rarely has a good mechanism without also having a reasonably good set of rate constants, since the mechanism is usually known to be good because it describes the dynamics of the system when associated with the set of rate constants. Optimization in its pure form is therefore most likely to be useful for tuning a set of rate constants to the best possible value. In practice, the most valuable use of quenching data is for choosing between several mechanisms for a reaction at the same time as the best set of rate constants is determined for each mechanism.

Use of the method indicated above for the permanganate oscillator studied in the present paper is a real challenge since so little is known about its mechanism. We have already studied (and discarded) several models based on the species that were found to quench the oscillations and various sets of plausible reactions between these species. Indeed, the conditions of having a supercritical Hopf bifurcation at the experimental flow rate for all inflows and outflows with the correct concentrations (experimentally known or estimated) and with the correct frequency of the emerging oscillations already put very serious constraints on possible models. The additional experimental parameters given in Table 1 provide plenty of additional restrictions to discriminate between mechanisms.

In this connection, we mention that there may be obtained additional relevant quenching data by quenching with nitrogen species other than NH_2OH. However, our experience with models so far has convinced us that we have enough data for our work with models for the moment. Probably the manganese data are most relevant to the manganese part of the mechanism, which is the focus of our interests. For the permanganate−hydroxylamine system, the determination of accurate quenching data for one species usually takes about 2 weeks (when the equipment is running), partly because of the long recovery time for the return from a perturbation.

From the available quenching results, a number of immediate conclusions can be drawn with some confidence. It seems clear that the manganese species that can quench play a role in the mechanism. Thus, permanganate cannot be considered as merely a pool chemical in contradistinction to bromate in the BZ system. The same conclusion applies to hydroxylamine (in contrast with substrates like malonic acid in BZ).

Also, Mn^{2+} cannot be merely a product. It must appear as a reactant in a reaction where at least one other species is produced or consumed. Otherwise, it could not quench the oscillations. (It is not enough that it flows out.) Since Mn^{2+} is not likely to react with any of the nitrogen species formed in the reaction, the Guyard reaction is perhaps responsible for this feature. So this reaction plays a role, and it may or may not be important to the core of the mechanism.

The important role assumed for colloid and/or soluble Mn(IV) is confirmed by the experiments, and the fact that Arabic gum can quench the oscillations suggests that surface reactions are involved.

Manganate is the species (among those tested) that is most efficient for quenching the oscillations, suggesting that reactions involving it are important in the mechanism. Manganate added in a perturbation may partly disproportionate and partly react directly with other species present. The most obvious (stable) products of disproportionation are Mn(IV) and Mn(VII), but it should be noticed that manganate quenches much more efficiently than either MnO_2 or MnO_4^-. So disproportionation is probably not the main reaction of manganate produced in a reaction of the oscillatory system. This fact should be kept in mind when appropriate reactions are selected for a mechanism.

For Mn^{3+}, we have only indirect evidence through the quenching with pyrophosphate. The effect of pyrophosphate can hardly be interpreted in any other way than removal of Mn^{3+}, and its efficiency is remarkable. It corresponds to a relative quenching concentration of only 0.057 for addition of Mn^{3+} if three pyrophosphate ions remove one Mn^{3+}. This suggests that Mn^{3+} is an important participant of the reactions taking place in the oscillatory system. This conclusion agrees with that of ref 14 for the reaction between Mn^{2+} and IO_4^-.

We continue our work on the problem of finding a mechanism of the permanganate−hydroxylamine system by means of the quenching data reported here. We realize that this project is very large and that, quite possibly, we may at best get a model with a number of correct features which naturally should be tested also for its prediction of other dynamical properties including the results of batch experiments of various sorts.

Acknowledgment. We thank Merete Torpe for technical assistance with the experiments. We gratefully acknowledge the financial support from the Center for Chaos and Turbulence Studies. We also express our gratitude to the Danish Natural Science Research Council for a research grant.

References and Notes

(1) Reckley, J. S.; Showalter, K. *J. Am. Chem. Soc.* **1981**, *103*, 7012.
(2) Epstein, I. R.; Dateo, C. E.; De Kepper, P.; Kustin, K.; Orbán, M. *Springer Ser. Synergetics* **1981**, *12*, 188.
(3) Nagy, A.; Treindl, L. *Nature* **1986**, *320*, 344.
(4) Treindl, L.; Nagy, A. *Chem. Phys. Lett.* **1987**, *138*, 327.
(5) Nagy, A.; Treindl, L. *J. Phys. Chem.* **1989**, *93*, 2807.
(6) Fazekas, T.; Mrákavová, M.; Nagy, A.; Olexová, A.; Treindl, L. *React. Kinet. Catal. Lett.* **1990**, *42*, 181.
(7) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 1812.
(8) Nagy, A.; Olexová, A.; Treindl, L. *J. Phys. Chem.* **1991**, *95*, 5809.
(9) Doona, Ch. J.; Kustin, K.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 7484.
(10) Melicherc'k, M.; Mrákavová, M.; Nagy, A.; Olexová, A.; Treindl, L. *J. Phys. Chem.* **1992**, *96*, 8367.
(11) Melicherc'k, M.; Mrákavová, M.; Nagy, A.; Olexová, A.; Sodnomdordz, G.; Treindl, L. *Z. Phys. Chem.* **1992**, *174*, 139.
(12) Melicherc'k, M.; Mrákavová, M.; Nagy, A.; Olexová, A.; Treindl, L. *Collect. Czech. Chem. Commun.* **1995**, *60*, 781.
(13) Melicherc'k, M.; Olexová, A.; Treindl, L. *Collect. Czech. Chem. Commun.* **1996**, *61*, 70.
(14) Orbán, M.; Lengyel, I.; Epstein, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 1978.
(15) Melicherc'k, M.; Sodnomdordz, G.; Treindl, L. *J. Phys. Chem.* **1991**, *95*, 4923.
(16) Melichová, Z.; Olexová, A.; Treindl, L. *Z. Phys. Chem.* **1995**, *189*, 123.
(17) Melichová, Z.; Olexová, A.; Treindl, L. *Z. Phys. Chem.* **1995**, *191*, 259.
(18) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1989**, *111*, 8543.
(19) Guyard, G. *Bull. Soc. Chim. Fr.* **1864**, *1*, 89.
(20) Jáky, M.; Simándi, L. I.; Shafirovich, V. Y. *Inorg. Chim. Acta* **1984**, *90*, L39.
(21) Tompkins, F. C. *Trans. Faraday Soc.* **1942**, *38*, 131.
(22) Doona, Ch. J.; Schneider, F. W. *J. Am. Chem. Soc.* **1993**, *115*, 9683.
(23) Perez-Benito, J. F.; Arias, C. *Int. J. Chem. Kinet.* **1991**, *23*, 717.
(24) Insausti, M. J.; Mata-Perez, F.; Alvarez-Macho, M. P. *Int. J. Chem. Kinet.* **1991**, *23*, 597.
(25) Pode, J. S. F.; Waters, W. *J. Chem. Soc.* **1956**, 717.
(26) Carrington, A.; Symons, M. C. R. *J. Chem. Soc.* **1956**, 3373.
(27) Kalra, H. L.; Ghosh, S. *Z. Phys. Chem. (Leipzig)* **1966**, *231*, 21.
(28) Selim, R. G.; Lingane, J. J. *Anal. Chim. Acta* **1959**, *21*, 536.
(29) Hynne, F.; Sørensen, P. G. *J. Phys. Chem.* **1987**, *91*, 6573.
(30) Sørensen, P. G.; Hynne, F. *J. Phys. Chem.* **1989**, *93*, 5467.
(31) Hynne, F.; Sørensen, P. G.; Nielsen, K. *J. Chem. Phys.* **1990**, *92*, 1747.
(32) Hynne, F.; Sørensen, P. G.; Møller, T. *J. Chem. Phys.* **1993**, *98*, 211.
(33) Hynne, F.; Sørensen, P. G.; Møller, T. *J. Chem. Phys.* **1993**, *98*, 219.
(34) Nagy, A.; Sørensen, P. G.; Hynne, F. *Z. Phys. Chem.* **1995**, *189*, 131.
(35) Kolthoff, I. M.; Belcher, R.; Stenger V. A.; Matsuyama G. *Volumetric Analysis vol. III*; Wiley: New York, 1957; p 73.
(36) Sutter, J. H.; Colquit, K.; Sutter, J. R. *Inorg. Chem.* **1974**, *13*, 1444.
(37) Vukojević, V.; Sørensen, P. G.; Hynne, F. *J. Phys. Chem.* **1993**, *97*, 4091.
(38) Belcher, R.; West, T. S. *Anal. Chim. Acta*, **1952** *6*, 322.
(39) Launer, H. F. *J. Am. Chem. Soc.* **1932**, *54*, 2597.
(40) Mata-Perez, F.; Perez-Benito, J. F. *Can. J. Chem.* **1987**, *65*, 2373.
(41) *Gmelin Handbuch der Anorganischen Chemie. Mangan C4*; Springer-Verlag: Berlin−Heidelberg−New York, 1977; p 88.
(42) Clarke, B. in *Advances in Chemical Physics*; Prigogine, I., Rice, S., Eds.; Wiley: New York, 1980; Vol. 43, p 1.