satisfactorily accounts for the role of the metal concentration in catalyst-inhibitor conversion,<sup>1-6</sup> the abrupt and precipitous drop in the rate of an initiated reaction just above the "critical" metal concentration,<sup>4,5</sup> the preponderance of the cases of the critical phenomenon in low-polarity media,<sup>1-6</sup> the inhibiting effect of transition metals in some autoxidation reactions,<sup>2,26</sup> and the seemingly conflicting solvent effects observed in some autoxidation systems.<sup>4,26-28</sup> In addition to explaining the various experimental findings, the theory provides a rational basis for identifying factors (mentioned above) which are likely to affect the critical phenomenon. The theory and its implications will soon be presented in a later paper.<sup>29</sup>

The inhibiting effect of manganese on the high-pH sulfite autoxidation reaction suggests the use of manganese as an antioxidant in alkali-based SO<sub>2</sub> scrubbing processes, such as the Wellman–Lord and the double-alkali scrubbing processes.<sup>29</sup> As an antioxidant for the undesirable sulfite autoxidation reaction (which would lower the pH and, therefore, the SO<sub>2</sub>-absorbing

(27) N. Uri, Nature (London), 177, 1177-8 (1956).

(28) C. Copping and N. Uri, Discuss. Faraday Soc., No. 46, 202-12 (1968).

(29) Phooi K. Lin, submitted to J. Am. Chem. Soc.

(30) A. V. Slack and G. A. Hollinden, "Sulfur Dioxide Removal from Waste Gases", 2nd ed., Noyes Data Corp., Park Ridge, NJ, 1975, pp 149-248.

capacity of the scrubbing medium), manganese offers significant advantages over the conventional free-radical antioxidants processes.<sup>30</sup> heavy metal sequestrants. Unlike the nonregenerable antioxidants, the inhibiting effect of manganese is long-lasting because manganese stays continuously in a redox cycle which acts as an infinite sink for the sulfite free radicals. Unlike chelating agents which can suppress only the metal-catalyzed reaction, manganese can also inhibit the photocatalyzed and thermal reactions.

## Conclusion

The results of our study establish that (1) alkaline manganese undergoes a pH-dependent catalyst-inhibitor conversion in the autoxidation of sulfite; (2) the phenomenon of catalyst-inhibitor conversion in liquid-phase autoxidation reactions can occur in polar as well as nonpolar media, and it can be induced by factors other than a variation in the metal concentration; (3) the underlying cause of catalyst-inhibitor conversion in liquid-phase autoxidation reactions is the ability of metal ions to tie up and deactivate free radicals through the formation of metal-radical complexes which are unreactive in the propagation chains but active in the termination of the radical chain carriers.

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# Manganese-Catalyzed Autoxidation of Aqueous Hydrazine: Kinetics, Mechanism, and Catalyst–Inhibitor Conversion

## Phooi K. Lim\* and Barry S. Fagg

Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905 (Received: March 3, 1983)

Spectrophotometric evidence and kinetic data suggest that the autoxidation of aqueous hydrazine is a chain reaction propagated by hydrogen peroxide, diimine  $(N_2H_2)$ , and hydrazyl  $(N_2H_3)$ , perhydroxy  $(O_2)$ , and hydroxy (OH) radicals. At 25 °C, the rate constants for the reactions between hydrazyl radical and oxygen and between hydrazyl radical and hydrogen peroxide have been estimated to be 13 and 95  $M^{-1}$  s<sup>-1</sup>, respectively. The manganese-catalyzed reaction shows variable reaction orders over a narrow catalyst concentration range. Below  $5.0 \times 10^{-5}$  M catalyst concentration, the reaction is first order with respect to manganese, oxygen, and hydrazine, respectively, and second order with respect to basicity. Above  $2.0 \times 10^{-4}$  M catalyst concentration, the reaction orders switch to zeroth order for manganese and second order for oxygen. The switch in the reaction orders is caused by a change in the relative contributions of two competing termination reactions in different manganese(II) concentration ranges. The dominant termination reaction switches from the unimolecular adsorption of the perhydroxy radical at a low manganese concentration to the unimolecular adsorption of a manganese-hydrazyl radical complex at a high manganese concentration. The ability of manganese(II) to tie up hydrazyl radical causes manganese to undergo a catalyst-inhibitor conversion at a high metal concentration. A simple and self-consistent reaction mechanism has been developed which correctly predicts the switch in the oxygen order and satisfactorily accounts for all experimental findings. The results of this study support the postulate that the underlying cause of catalyst-inhibitor conversion in any liquid-phase autoxidation reaction is the ability of the metal ion to tie up and deactivate a radical chain carrier through the reversible formation of a metal-radical complex which is unreactive in the propagation chain but active in the termination reaction sequence.

## Introduction

Alkaline manganese(II)-polyol complexes undergo facile autoxidation reaction to form concomitantly manganese(III) complexes and hydrogen peroxide.<sup>1</sup> The observation suggests the use of the manganese-polyol complexes as redox catalysts to promote high-pH autoxidation reactions. The anticipated catalytic properties of the manganese-polyol complexes have been confirmed in several reaction systems,<sup>2</sup> but in the high-pH autoxidation of sulfite, alkaline manganese provides the first known example of a pH-dependent catalyst-inhibitor conversion.<sup>3</sup> Below pH 10.1, manganese functions as a catalyst in the sulfite autoxidation reaction; but above the pH value, manganese reverses its role and becomes a potent inhibitor.

<sup>(26)</sup> K. Okuma, E. Niki, and Y. Kamiya, J. Chem. Soc., Perkin Trans. 2, 59-64 (1977).

<sup>(1)</sup> D. T. Richens, C. G. Smith, and D. T. Sawyer, Inorg. Chem., 18, 706-12 (1979).

<sup>(2)</sup> Phooi K. Lim, John A. Cha, and Barry S. Fagg, Ind. Eng. Chem. Fundam., 23, 29-33 (1984).

<sup>(3)</sup> Phooi K. Lim and G. Terry Hamrick, J. Phys. Chem., preceding paper in this issue.



Figure 1. The high-pH autoxidation of aqueous hydrazine catalyzed by manganese(II)-sorbitol complex.

In a continuing attempt to study the role of manganese in high-pH autoxidation reactions, we have performed a detailed kinetic study of the effect of manganese-sorbitol complex on the high-pH autoxidation of aqueous hydrazine. In this paper, we present the kinetic results and provide a simple and self-consistent rection mechanism which satisfactorily accounts for all the kinetic findings, including the catalyst-inhibitor conversion of manganese.

#### **Experimental Section**

The reaction was studied in 1-L Morton flask reactors made of glass and Teflon. Reagent-grade hydrazine hydrate (Alfa Products, Danvers, MA) was used as received. Deionized and distilled water was used in the preparation of all solutions. Solution pH was controlled with a standard sodium hydroxide or hydrochloride acid solution. The desired reaction temperature was maintained in a water or ice bath, and a constant oxygen pressure was set by an oxygen regulator furnished by Air Products and Chemicals. A vigorous mixing of the reactor solution was achieved magnetically. To avoid oxygen mass transfer limitation, we kept the initial volume of the reactor solution at 200 mL.

The reaction was initiated by draining into the preequilibrated, preoxygenated solution the desired amount of hydrazine monohydrate followed by the manganese-sorbitol complex, the latter was prepared just before use by mixing manganese(II) and sorbitol solutions in a 1:2 stoichiometric ratio. The reactor was purged periodically to remove the nitrogen formed in the reaction.

The reaction was followed by monitoring the hydrazine concentration of the reaction solution as a function of time. At timed intervals, solution samples were withdrawn from the reactor, quenched in measured amounts of excess hydrochloric acid solutions, weighed, and then analyzed for hydrazine by backtitrating the excess acid with a standard sodium hydroxide solution. The endpoint was determined potentiometrically with a Fisher Accumet 750 pH meter. The acid-base titration method gave results closely in agreement with the acidimetric method based on potassium iodate,<sup>4</sup> but being faster and less error-prone, it was adopted in favor over the latter method.

Spectroscopic evidence of reaction intermediates was sought by monitoring the UV absorbance of the reaction solution on a Beckman spectrophotometer.

### **Observation, Results, and Discussion**

Reaction Characteristics and Intermediates. Figure 1 shows the hydrazine concentration-reaction time profile of a representative run for the manganese-catalyzed reaction. Also shown in the figure is the corresponding UV absorbance profile at 230 nm. The reaction is characterized by the presence of an induction period and the release of nitrogen gas bubbles. In all runs, the maximum in the UV absorbance profile coincides with the end of the induction period and the attainment of the maximum oxidation rate (which is used to correlate against kinetic param-



Figure 2. The variation of the hydrazine autoxidation rate with the UV absorbance at different hydrazine concentrations: Evidence suggesting the presence of peroxide and hydrazyl radical.

eters). It is evident from Figure 2 that a direct correlation exists between the oxidation rate and the maximum UV absorbance. We have also observed a similar rate-UV absorbance correlation in the reaction catalyzed by copper.

The data in Figure 2 were obtained with difference initial hydrazine concentrations under otherwise identical reaction conditions. Both the rate and the maximum UV absorbance increase linearly with the hydrazine concentration, but note that the UV absorbance is displaced from the origin by a constant amount. The data are indicative of the presence of two UV-absorbing intermediates in the reaction solution. Evidently, the concentration of one of the intermediates increases linearly with the hydrazine concentration of the other intermediate remains relatively constant.

The identity of one of the intermediates may be shown to be hydrogen peroxide, which is marked by its characteristic broad UV absorbance in the 200-250-nm range. The molar extinction coefficient of hydrogen peroxide at 230 nm is 5030 M<sup>-1</sup> cm<sup>-1</sup> at pH 13 and ca.  $3170 \text{ M}^{-1} \text{ cm}^{-1}$  at pH 12. The identity of the other intermediate may be established from the pulse radiolysis study performed by Hayon and Simic on aqueous hydrazine.<sup>5</sup> Hayon and Simic have presented spectroscopic evidence for the existence of the hydrazyl free radical  $(N_2H_3\cdot)$ , and over the pH range of 9.2-13.4, they have reported that the molar extinction coefficient of the free radical is independent of pH and has a value of 3.5  $\times$  10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup> at its  $\lambda_{max},$  which is 230 nm. It will be shown later that an experimentally consistent reaction mechanism will emerge if the intermediate responsible for the increases in the UV absorbance with increasing hydrazine concentration is identified as the hydrazyl radical and the x intercept in Figure 2 is associated with hydrogen peroxide. According to the proposed mechanism, the steady-state concentration of the hydrazyl radical is directly proportional to the hydrazine concentration whereas the peroxide concentration is independent of the hydrazine concentration but directly dependent on the oxygen pressure.

Visual Observation. At pH 9, the reactor solution is colorless and the reaction is very slow. Above pH 10, the reactor solution has a light yellow color at a low manganese concentration (< 1.0  $\times$  10<sup>-4</sup> M) and a light brown color at a high manganese concentration (> 2.0  $\times$  10<sup>-4</sup> M). The brown color is indicative of the presence of a manganese(III) complex.<sup>1</sup> The solution remains clear for 2–4 days; it then turns dark as the last trace of hydrazine is consumed. A brown precipitate, believed to be a hydrated form

 TABLE I: Effect of Antioxidants on the High-pH

 Manganese-Catalyzed Autoxidation of Aqueous Hydrazine<sup>a</sup>

antioxidant	oxidation rate, M/h
 none	0.177
hydroquinone.	0.189
ascorbic acid	0.206
sodium sulfite	0.210
o-phenylenediamine	0.215

<sup>a</sup> T = 25.0 °C; pH 12.1;  $P_{O_2} = 38$  in. Hg;  $[N_2H_4]_0 = 0.050$  M; [manganese(II)-sorbitol] =  $1.20 \times 10^{-4}$  M; [antioxidant] =  $1.00 \times 10^{-6}$  M (except for the control run).



Figure 3. A first-order rate dependence on the hydrazine concentration.

of manganese dioxide, may sometimes be observed at high manganese concentrations. The observation suggests that the formation of manganese(III) is a necessary step in the manganese catalysis.

Effect of Free-Radical Antioxidants. Free-radical antioxidants at a concentration as low as  $10^{-6}$  M were found to affect the manganese-catalyzed reaction. However, instead of a reaction inhibition as may be expected, the antioxidants actually promoted the reaction. The results in Table I suggests a chain-transfer reaction between the antioxidant free radicals and the hydrazine substrate. Evidently, as a result of the chain-transfer reaction, more hydrazyl radicals are generated to propagate the hydrazine autoxidation reaction.

The Wall Effect. The reaction is sensitive to the nature of the reactor wall. Kinetic data obtained in glass and Teflon reactors are each highly reproducible in the same types of reactors ( $\pm 5\%$  reproducibility in the rate in each case), but the two sets of data differ significantly from each other for the same reaction conditions. For the reaction conditions specified for the control run given in Table I, the oxidation rate in a Teflon reactor is 40% less than that in a glass reactor with the same surface-to-volume ratio. The observation suggests surface participation in the reaction. It will be shown later that the kinetic results are consistent with a unimolecular adsorption of free radicals onto the reactor wall followed by a bimolecular combination of the adsorbed species. The results reported in this paper were all obtained in glass reactors.

Reaction Orders. The results shown in Figures 3-5 indicate that at a low catalyst concentration the manganese-catalyzed reaction is first order with respect to hydrazine, oxygen, and manganese, respectively. However, Figure 5 indicates that the manganese order switches from the first to zeroth order over a narrow catalyst concentration range. The leveling and the subsequent drop in the oxidation rate beyond the  $5 \times 10^{-5}$  M catalyst concentration are surprising, but the results have been confirmed



Figure 4. A first-order rate dependence on the oxygen pressure at a low catalyst concentration.



Figure 5. The rate dependence on the manganese(II) concentration.

repeatedly. Corresponding to the drop in the oxidation rate, there is a lengthening in the induction period accompanied by a drop in the maximum UV absorbance of the reaction solution. The anomalous manganese concentration effect, which is similar to the catalyst-inhibitor conversion of manganese in the autoxidation of tetralin,<sup>6</sup> is, in this case, related specifically to the high pH of the reaction medium since previous studies of the manganesecatalyzed reaction at lower pH values<sup>7,8</sup> have failed to uncover a similar anomaly. The apparent anomaly may be rationalized in exactly the same way the pH-independent catalyst-inhibitor conversion of manganese is accounted for in the sulfite autoxidation reaction,<sup>3</sup> namely, alkaline manganese has the ability to tie up and deactivate free-radical chain carriers in liquid-phase autoxidation reactions. It will be shown later that the switch in the manganese order may be attributed specifically to the reversible formation of a manganese-radical complex between alkaline manganese(II) and the hydrazyl radical.

The results in Figure 6 provide a confirmation of the reaction mechanism which we propose in the section after next to account for the above experimental findings. As predicted by the proposed mechanism, the oxygen order switches from first order at a low

<sup>(6)</sup> Y. Kamiya and K. U. Ingold, Can. J. Chem., 42, 1027-43, 2424-33 (1964).

<sup>(7)</sup> I. Okura, N. K. Thuan, and T. Keii, J. Mol. Catal., 5, 125-30 (1979).
(8) D. M. Wagnerova, E. Schwertnerova, and J. Veprek-Siska, Collect. Czech. Chem. Commun., 38, 756-64 (1973).







Figure 7. The rate dependence on the solution pH.

catalyst concentration to second order at a high catalyst concentration.

pH and Temperature Effects. The pH effect, shown in Figure 7, indicate that the manganese-catalyzed reaction has a pronounced second-order rate dependence on the solution basicity at pH below 12. Above pH 12, the rate increases only modestly with the solution basicity. The strong pH dependence and the distinctive color development of the reaction solution under different pH conditions point to the formation of manganese(III) as the rate-limiting step in the reaction.

The temperature effect is shown in Figure 8. The apparent activation energy, which has been corrected for the variation in the temperature-dependent oxygen solubility, is 16.3 kcal/g mol.

A Proposed Reaction Mechanism and the Confirmation of the Model's Prediction. The reaction mechanism which we propose to account for our experimental findings is shown in Table II. We believe the hydrazine autoxidation reaction is a chain reaction propagated by two reaction chains, namely, reactions 5-7 and 8-10. The reaction species which we propose for the two propagation chains—peroxide, diimine  $(N_2H_2)$ , and hydrazyl  $(N_2H_3)$ , perhydroxy  $(O_2^{-})$ , and hydroxy (OH) radicals—have all been implicated in the aerobic and anaerobic oxidation of hydrazine.5,9-11

(9) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine", Wiley, New York, 1951, p 128.



Figure 8. The rate dependence on the reaction temperature.

TABLE II: Proposed Reaction Mechanism for the High-pH Manganese-Catalyzed Autoxidation of Aqueous Hydrazine

Initiation  

$$Mn^{II}(OH^{-})_{2} + O_{2} \xrightarrow{k_{1}} Mn^{III}(OH^{-})^{2+} + OH + O_{2}^{2-} \text{ slow (1)}$$

$$OH \cdot + N_2 H_4 \xrightarrow{k_2} H_2 O + N_2 H_3 \cdot$$
(2)

$$Mn^{III} + N_2 H_4 \xrightarrow[k_{3r}]{\kappa_3} Mn^{II} N_2 H_3^{2+} + H^+$$
(3)

$$n^{II}N_{2}H_{3}^{2+} \leftrightarrow Mn^{II} + N_{2}H_{3} \cdot$$
(4)
  
Propagation

$$N_2H_3 + O_2 \xrightarrow{R_5} N_2H_2 + HO_2 \cdot (HO_2 \rightarrow H^+ + O_2^-)$$
(5)

$$D_2^- + N_2H_4 \xrightarrow{-2} HO_2^- + N_2H_3^-$$
 (6)

$$N_2H_2 + HO_2^- \longrightarrow N_2 + H_2O + OH^-$$
(7)
$$N_2H_2 + HO_2^- \frac{k_8}{k_1} N_2 + OH^- + OH^-$$
(7)

$$OH + N_3H_4 \xrightarrow{k_9} H_2O + N_2H_4.$$

$$(6)$$

$$N_2H_2 + O_2 \xrightarrow{k_{10}} N_2 + H_2O_2$$
 (10)  
Termination

k.

at low  $[Mn]_T$ 

0,-

Μ

C

+ wall 
$$\xrightarrow{11} 1/_2O_2^{2-} + 1/_2O_2$$
 (11)

at high [Mn] T

$$Mn^{II}N_{2}H_{3}^{2+} + wall \xrightarrow{\kappa_{12}} Mn^{II} + \frac{1}{2}N_{2} + NH_{3}$$
 (12)

The existence and the properties of diimine and the free-radical species are well-known.<sup>11-13</sup> Note that the proposed participation of peroxide and hydrazyl radical in the propagation reactions is also in accord with the evidence presented in connection with Figure 2.

The wall effect implies that the dominant termination reactions are unimolecular in nature. The observation in turn suggests a unimolecular participation of manganese in the initiation reaction sequence. The pronounced pH effect and the visual observation of the reaction solution have led us to propose reaction 1, which forms manganese(III), as a strongly pH-dependent, rate-limting step. To account for the ability of alkaline manganese to tie up free radicals,<sup>3,14</sup> we postulate an equilibrium reaction, namely

<sup>(10)</sup> W. C. E. Higginson and P. Wright, J. Chem. Soc. London, 1551-6 (1955)

<sup>(11)</sup> S. Hunig, H. R. Muller, and W. Thier, Angew. Chem., Int. Ed. Engl., 271-80 (1965). 4.

 <sup>(12)</sup> D. Behar, G. Czapski, J. Rabini, L. M. Dorfman, and H. A. Schwarz,
 J. Phys. Chem., 74, 3209-13 (1970).
 (13) N. Uri, Adv. Chem. Ser., No. 36, 102-12 (1962).

reaction 4, between manganese(II) and the hydrazyl radical. In the proposed manganese-hydrazyl radical complex, manganese can "resonate" between the 2+ and 3+ valence states, and this presumably confers stability to the complex and makes it relatively inert to oxygen attack. At a low manganese concentration, the equilibrium position of reaction 4 is to the right, and, correspondingly, reaction 3 is essentially irreversible. However, at a sufficiently high manganese concentration, reaction 3 becomes reversible and this may account for the brown color of the reactor solution which is indicative of the presence of manganese(III). [Alkaline manganese(II) is colorless in the absence of oxygen.]

Reactions 11 and 12 are believed to be the dominant termination reactions over different catalyst concentration ranges. They each give rise to a first-order termination of a chain barrier and they account for the wall effect.

Applying the usual steady-state assumption, which is justified by the simultaneous attainment of the maximum oxidation rate and the maximum radical concentration, the proposed mechanism leads to the following rate expressions over different catalyst concentration ranges: at low manganese catalyst concentrations:

$$-\frac{d[N_2H_4]}{dt} = \frac{2k_1k_6}{k_{11}} \left[ 1 + \left(\frac{k_8k_{10}}{k_5k_7}\right)^{1/2} \right] [Mn^{II}(OH^-)_2][N_2H_4][O_2]$$
(A)

at high manganese catalyst concentrations:

.......

$$-\frac{d[N_2H_4]}{dt} = \frac{2k_1k_5K_4}{k_{12}} \left[ 1 + \left(\frac{k_8k_{10}}{k_5k_7}\right)^{1/2} \right] \frac{[Mn^{II}(OH^-)_2][O_2]^2}{[Mn^{II}]}$$
(B)

Rate expression A is evidently in agreement with the following experimental findings at a low catalyst concentration: a second-order dependence on the solution basicity and a first-order dependence on the hydrazine concentration, manganese(II) concentration, and oxygen pressure, respectively.

Consistent with the observed shift in the manganese order at high catalyst concentrations, rate expression B shows a zerothorder dependence on the manganese concentration. The rate expression also predicts a second-order dependence on the oxygen pressure, which is a shift from the first-order dependence at a low catalyst concentration. The results shown in Figure 6 confirm the prediction of the model exactly. The successful confirmation of the model's prediction adds to the plausibility of the proposed reaction mechanism.

The data in Figure 2 also permit us to estimate the magnitudes of the rate constants of reactions 5 and 8. If we assume the two reactions make comparable contributions to the overall autoxidation rate,  $k_5$  and  $k_8$  are estimated to be 13 and 95 M<sup>-1</sup> s<sup>-1</sup>, respectively. The above results are based on a molar extinction

(14) M. Pick-Kaplan and J. Rabani J. Phys. Chem., 80, 1840-3 (1976).

The evidence which has been presented in this paper strongly suggests the reversible formation of a metal-free radical complex as the underlying cause of catalyst-inhibitor conversion in liquid-phase autoxidation reactions.<sup>6,15-17</sup> The formation of a metal-radical complex which is unreactive in the propagation chain but active in the termination of a radical chain carrier will bring about a reaction inhibition. For an initiation reaction sequence which is first order with respect to the metal catalyst, a first-order termination of the radical through a dominant unimolecular adsorption of the metal-radical complex will give rise to a zerothorder rate dependence on the catalyst concentration (as is the case with the hydrazine autoxidation reaction). On the other hand, a second-order termination of the radical through a dominant bimolecular self-termination of the metal-radical complex will give rise to reaction inhibition. The relative contributions of the unimolecular and bimolecular terminations of the metal-radical complex may therefore account for the characteristic features of the rate vs. metal concentration plot which shows catalyst-inhibitor conversion: a long plateau region in the intermediate metal concentration range followed by a sharp decline in the high metal concentration range.6,15-17

constant of  $1.3 \times 10^{-3}$  M atm<sup>-1</sup> for oxygen.

### Conclusion

A detailed kinetic study of the manganese-catalyzed autoxidation of aqueous hydrazine indicates that (1) the reaction is propagated by two reaction chains involving hydrogen peroxide, diimine  $(N_2H_2)$ , hydrazyl  $(N_2H_3)$ , perhydroxy  $(O_2^{-1})$ , and hydroxy (OH-) radicals; the rate constants for the reactions at 25 °C between hydrazyl radical and oxygen and between hydrazyl radical and peroxide have been estimated to be 13 and 95 M<sup>-1</sup> s<sup>-1</sup>, respectively; (2) the reaction at a low catalyst concentration is first order with respect to manganese, hydrazine, and oxygen, respectively, and second order with respect to basicity (below pH 12); but at a high metal concentration, the reaction orders switch to zeroth order for manganese and second order for oxygen; (3) the switch in the reaction orders is caused by a change in the dominant termination reaction which is in turn caused by the ability of manganese(II) to tie up the hydrazyl radical; and (4) the experimental findings may be satisfactorily explained in terms of a simple and self-consistent reaction mechanism.

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**Registry No.** Manganese, 7439-96-5; diimine, 302-01-2; hydrazyl, 13598-46-4; hydrogen peroxide, 7722-84-1; hydroquinone, 123-31-9; ascorbic acid, 50-81-7; disodium sulfite, 7757-83-7; o-phenylenediamine, 95-54-5.

<sup>(15)</sup> A. T. Betts and N. Uri, Adv. Chem. Ser., No. 76, 161-81 (1968).
(16) R. A. Sheldon and J. K. Kochi, Oxid. Combust. Rev., 5, 135-242 (1973).

<sup>(17)</sup> J. F. Black, J. Am. Chem. Soc., 100, 527-35 (1978).