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REDOX INTERACTION OF CERIUM(III) AND CERIUM (IV), OR MANGANESE(II) AND MANGANESE(III) IONS WITH BROMATE AND MALONIC AND BROMOMALONIC ACIDS

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Reactions of oxidation of malonic acid by the bromate ion, catalyzed by cerium or manganese ions, in sulfuric acid solutions are accompanied by concentration oscillations of the redox forms of the ions of the catalysts and certain intermediates (oscillating chemical reactions (ocr) of Belousov and Zhabotinykii [1]). It is believed that the mechanism of the action of these catalysts in an oscillating reaction is the same or close, on the basis of the fact that the reactions of oxidation of cerium(III) and manganese(II) ions by the bromate ion have close kinetic parameters [2]. However, the differences between the concentration dependences of the parameters of the oscillations, as well as between the regions of existence of concentration oscillations for reactions with each of these catalysts, are evidence that during an oscillating reaction they act differently [3]. The causes of these differences may be different states of the ions of the catalysts in sulfuric acid solution and a difference in the mechanism and rate of the oxidation of reduced forms of the catalyst by bromate ions and the reduction of their oxidized forms by malonic acid.

It is difficult to use the information available in the literature on the mechanism and rate of these reactions to calculate the rate of interaction of ions of the catalyst with the bromate ion and malonic acid, since in an oscillating reaction the concentrations of the catalyst are significantly (2-5 orders of magnitude) lower than the concentrations of the main components — bromate ions and malonic acid. The present work is devoted to a comparative investigation of the rate of interaction of cerium (III) and cerium(IV) or manganese(II) and manganese(III) ions with an excess of bromate ions, malonic and bromomalonic acids, and the mutual influence of these compounds on the reaction rate.

Measurements of the rates were performed by a spectrophotometric method in solutions of sulfuric acid with a concentration of 1.5 M. The rates of reactions with the participation of manganese ions were measured according to the change in the manganese(III) concentration on a Specol spectrometer at the maximum of the absorption band of manganese(III) ions (480 nm). The rates of reactions in which cerium ions participated were measured according to the change in the cerium(IV) concentration on a Specord UV Vis spectrophotometer in the region of the absorption band of cerium(IV) ions, 320 nm. Measurements of the rates were performed by intensive mixing of the reaction mixture and thermostatic control (298 \pm 0.1 K).

The solutions of the reagents, with the exception of the solution of manganese(III), were prepared according to exact weighed samples of cp grade or analytical grade reagents, followed by dilution with a 1.5 M sulfuric acid solution in distilled water. The concentration of the initial solutions of manganese(III) and cerium(IV) were additionally determined by titration with an iron(II) salt [4]. A solution of manganese(III) was prepared in 5 M sulfuric acid in the presence of manganese(II) (in a 1:4 ratio) according to the well-known procedure [5]. The maximum of the absorption band and the molar extinction coefficient of manganese(III) ions are: in 5 M sulfuric acid $\lambda_{\rm max} = 505$ nm, $\varepsilon = 110$; in 1.5 M sulfuric acid $\lambda_{\rm max} = 480$ nm, $\varepsilon = 79$ (293 K), which is close to the values cited in [6]. A solution of manganese(III) in 1.5 M sulfuric acid was obtained from the initial solution in 5 M sulfuric acid by diluting it with the required amount of ice, cooling the reaction mixture to

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Fig. 1. Kinetic curves of the consumption of manganese(III) ions in solutions: 1) Mn(III) - 0.00024, $CH_2(COOH)_2 - 0.15$ M; 2) in the same solution in the presence of 0.0025 M manganese(II) ions; 3) in solution 2 at the temperature 284 K. The arrows denote moments of addition of a solution of $CH_2(COOH)_2$.

Fig. 2. Kinetic curves of the accumulation of cerium(IV) ions: 1) in a solution of Ce(III) -0.00053, BrO₃⁻ -0.05 M; 2) in a solution of Ce(III) -0.00053, BrO₃⁻ -0.05, CH₂(COOH)₂ -0.15 M; 3) in solution 2 40 min after mixing of the reagents. The arrows denote the moments of addition of the sodium bromate solution.

TABLE 1. Rates of Reduction of Cerium(IV) and Manganese(II) Ions by Bromate Acid $([CH_2(COOH)_2] = 0.15 M)$

C _{Ce(IV)} or C _{Mn(III)}	Reduction o	of Ce(IV) ions	Reduction of Mn(III) ions			
	C _{Ce(III)} , M*	V, moles/liter.	<i>с_{Мп(II)},</i> М*	V, moles/liter· sec		
$1,2 \cdot 10^{-4} \\ 1,6 \cdot 10^{-4} \\ 2,4 \cdot 10^{-4} \\ 3,2 \cdot 10^{-4} \\ 3,6 \cdot 10^{-4} $		$3,6\cdot10^{-6}6,1\cdot10^{-6}1,0\cdot10^{-5}1,4\cdot10^{-5}1,7\cdot10^{-5}$		$8,0\cdot10^{-6}1,2\cdot10^{-5}2,0\cdot10^{-5}3,1\cdot10^{-5}3,3\cdot10^{-5}$		
$4,8\cdot10^{-4}$ 3,2·10 ⁻⁴	$3, 1 \cdot 10^{-3}$	$2, 4 \cdot 10^{-5}$ 1, 1 \cdot 10^{-5}	2,5·10 ⁻³	$4,6\cdot10^{-5}$ $4,5\cdot10^{-5}$		

*The addition was performed before the beginning of the reaction.

270 K. It should be noted that during subsequent heating of the solution of manganese(III) in 1.5 M sulfuric acid obtained from 270 to 293 K, its molar extinction coefficient changed abruptly from 76 to 79, when the temperature 292 K was reached. At the temperature 298 K the solution of manganese(III) in 1.5 M of sulfuric acid obtained was preserved without appreciable decomposition for 10-15 min.

A solution of bromomalonic acid was produced by bromination of malonic acid in solution in the presence of sodium bromide, to which the calculated amount of sodium bromate solution was slowly added with cooling. To obtain 1 M bromomalonic acid, we took solutions of 1.0 M malonic acid, 2.3 M sodium bromide, and added a solution of 1.3 M sodium bromate. The solution of bromomalonic acid obtained (0.95 M) was used in several experiments after preparation. The rate of reduction of cerium(IV) by bromomalonic acid, produced by this method, was the same as in the case of bromomalonic acid produced by bromination of an ether solution of malonic acid with free bromine [7].

The values of the rate of reduction of cerium(IV) and manganese(III) ions by malonic acid, as well as the values of the rates of these reactions in the presence of reduced forms of oxidizing agents, are cited in Table 1. The rate of reduction was determined according to the slope of the original linear portion of the kinetic curve, in the process of which approximately 20-30% of the colored compound - cerium(IV) or manganese(III) Ions by was consumed. As can be seen from Table 1, the reduction of cerium(IV) ions proceeds half as rapidly as

[Ce ^{4+]·104} or [Mn ³⁺]·104, M	Reactions with of cerium (IV)	participation ions	Reactions with participation of manganese (III) ions			
	Supplementary reagents, M	$(\Delta [Ce^{4+}]/\Delta t) \cdot 10^{\circ},$ moles /liter · sec	Supplementary reagents, M	$(\Delta[Mn^{3+}]/\Delta t) \cdot 10^{5},$ moles/liter · sec		
1,6 3,2 4,8 6,4 3,2 3,2 3,2 3,2 3,2 3,2 3,2 3,2		1,7 3,4 5,2 6,4 4,8 8,9 19,7 3,2 3,1	$\begin{bmatrix} \\ \\ \\ \\ \\ \\ \\$	1,0 2,0 3,0 4,6 2,2 3,4 4,0 1,3 1,4		

TABLE 2. Rates of the Reduction of Cerium(IV) and Manganese-(III) Ions by Bromomalonic Acid ([BMA] = 0.05 M)*

*BMA) $CHBr(COOH)_2$, MA) $CH_2(COOH)_2$.

TABLE 3. Parameters of the Oxidation of Cerium(III) and Manganese(II) Ions by Bromate

Initial concentrations of reagents, M		t _{ind} , sec		V _{max} , 10 ⁵ , moles/liter.sec		V _{ocr} ·10 ⁵ , moles/liter·sec		10 ⁴ ,	10 ⁴ ,	
ce ³⁺ or Mn ²⁺	BrO3	CH2(COOH)2	Ce ³⁺	$Mn^{2}+$	Δ[Ce ⁴ +] /Δ <i>t</i>	Δ[M ⁿ³⁺]/Δ <i>t</i>	Δ[Ce ⁴⁺]/Δ <i>t</i>	∆[Mn ³⁺]/∆t	[Ce ⁴⁺] _{max} .	[Min ³⁺]max・ M
0,0011 0,00026 0,00026 0,00053 0,00053 0,00053 0,00053 0,00053 0,001 0,001	0,005 0,01 0,01 0,01 0,05 0,05 0,05 0,05	0,15 0,15 0,15 0,15 0,15	32,0 9,0 45,0 6,0 35,0 2,6 11,0 2,2 9,6	7,5 5,5 16,0 4,0 12,0 2,5 2,5 2,0 2,0	0,030 0,23 0,038 0,54 0,15 1,9 1,3 3,6 3,4	0,11 0,56 0,36 0,97 0,84 6,6 7,3 8,6 12,0		 0,80 7,5 20,0	0,14 0,58 0,13 1,20 0,42 1,40 1,10	0,11 0,30 0,38 0,69 0,72 1,49 1,98 2,8 3,6

that of manganese(III) ions. As is well known [8], cerium(IV) oxidizes malonic acid to formic acid by one-electron steps, with successive formation of tartaric and glyoxylic acids and short-lived radicals. At the rate-determining step, the intermediate complex of cerium-(IV) with malonic acid breaks down, forming solutions of malonic acid:

$$[Ce(IV)...CH_2(COOH)_2] \rightleftharpoons Ce(III) + CH(COOH)_2 + H^+,$$
(1)

$$Ce(IV) + CH(COOH)_{a} + H_{a}O \rightarrow Ce(III) + HCOH(COOH)_{a}.$$
(2)

According to the data of [9], cerium(III) ions do not affect the reaction rate, but according to the data of [10], they slow down the reaction, which we also observed (see Table 1). In the presence of excess malonic acid the reaction rate is proportional to the first power of the concentration of each of the components; the values of the rate constant cited in [8-10] are in the range of 0.5-1.0. The order of the reaction with respect to the cerium(IV) concentration that we found from the data cited in Table 1 is equal to 1.23, which can be explained by an appreciable contribution of reactions of reduction of cerium(IV) by oxidation products of malonic acid. The order of the reaction of oxidation of malonic acid by manganese(III) with respect to the manganese(III) concentration, found analogously, is 1.24.

The reduction of manganese(III) ions by malonic acid, according to the available literature data [11], proceeds by means of rapid formation of a complex

$$Mn^{3+} + CH_2(COOH)_2 \gtrsim [MnCH_2(COO)_2]^+ + 2H^+,$$
(3)

which reduces the next manganese(III) ion and is converted to an active complex of tetravalent manganese $[MnCH_2(COO)_2]^{2+}$:

$$[MnCH_{2}(COO)_{2}]^{+} + Mn^{3+} \neq [MnCH_{2}(COO)_{2}]^{2+} + Mn^{2+}.$$
(4)

The possibility of the formation of an intermediate complex of manganese(IV) permits a twoelectron oxidation of malonic acid without the formation of a radical at the step limiting the rate of the process,

$$[MnCH2 (COO)2]2+ + H2O \rightarrow Mn2+ + CHOH (COOH)2.$$
 (5)

We established that when a solution of malonic acid is added to a solution of manganese-(III) with mixing, a decrease in the optical density, corresponding to the decrease in the concentration of manganese(III), is observed after a short (2-3 sec) induction period. In the presence of manganese(II) ions the duration of the induction period increases, and throughout this time there is an increase in the optical density of the solution (Fig. 1), followed by a decrease in it at a higher rate than in the absence of additions of manganese(II) ions. The increase in the induction period may be a consequence of a slowing of reaction (4) by manganese(II) ions. On the other hand, an increase in the concentration of manganese(II) shifts the following equilibrium to the left:

$$2Mn(III) \not\supseteq Mn(II) + Mn(IV). \tag{6}$$

This should lead to an increase in the rate of reaction (3) and subsequent fast steps of oxidation of tartaric acid to formic acid, which is also manifested in the observed increase in the rate of reduction of manganese(III). When the temperature of the reaction mixture is lowered from 293 to 284 K (Fig. 1), the duration of the induction period is substantially increased, and the value of the optical density remains constant for some time (4-5 sec), 21% higher than the value of the optical density of the initial solution. The increase in the optical density observed in the first moment after mixing of the reagents may be the result of the formation of colored complexes, possessing a larger molar extinction coefficient than manganese(III) ions, in particular, $[MnCH_2(COO)_2]^+$. The complex $[MnCH_2(COO)_2]^{2+}$ is rapidly consumed as a result of the complementary reaction (5) and can scarcely be accumulated in appreciable amounts [11].

The rates of the reduction of cerium(IV) and manganese(III) ions by bromomalonic acid were determined just as in the case of oxidation of malonic acid. From Table 2, which presents the results obtained, it is evident that the reduction of manganese(III) ions proceeds 6-7 times as rapidly as that of cerium(IV) ions and slows down somewhat in the presence of manganese(II) ions. The rate of reduction of cerium(IV) ions is virtually unchanged when cerium(III) ions are added. No synergism of the action of malonic and bromomalonic acids is observed: The resultant rate of reduction both of cerium(IV) ions and of manganese(III) ions by a mixture of malonic and bromomalonic acids is approximately equal to the sum of the rates of the reactions with each of these reducing agents individually. The values of the rate of reduction of manganese(III) ions by bromomalonic acids are approximately the same. The reduction of cerium(IV) ions by bromomalonic acid proceeds 1.5 times as slowly as that by malonic acid.

It is believed that the mechanism of the reduction of cerium(IV) ions by malonic and bromomalonic acids is close. The mechanism of the reduction of manganese(III) ions by bromomalonic acid probably differs from the mechanism of the reduction of manganese(III) ions by malonic acid, as is evidenced by the absence of any increase in the optical density of the solutions in the first moment, when the reagents are mixed in the reaction of bromomalonic acid with manganese(III). Evidently in this reaction a two-electron oxidation of bromomalonic acid is possible, without the formation of an intermediate complex of the manganese(IV) compound:

$$MnCHBr (COO)_{2} \xrightarrow{H_{0}O^{+}} > Mn^{2+} + Br^{-} + HCOH (COOH)_{2}.$$
(7)

The absence of a slow step of oxidation of a complex of manganese(III) with bromomalonic acid, analogous to reaction (4), makes the spectrophotometric recording of the complex $[MnCHBr(COO)_2]^+$ impossible.

The oxidation of cerium(III) and manganese(II) ions by an excess of bromate ions, after an induction period, proceeds with acceleration; then it slows down and equilibrium is established between the reduction products of bromate and the metal ions (Fig. 2). The oxidation of cerium(III) and manganese(II) ions does not go to completion; the maximum concentration of the oxidized form of the reducing agent is substantially below its initial concentration. In the presence of malonic acid, some time after the oxidation of the catalyst (the induction period of the oscillating reaction), periodic concentration oscillations begin.

In an investigation of the oxidation of cerium(III) and manganese(II) ions by bromate, the following parameters were determined according to the slope of the linear portion of the kinetic curve (Fig. 2): the duration of the induction period (tind), the maximum (equilibrium) concentrations of oxidized forms of the metal ions ($[Ce^{4+}]_{max}$ and $[Mn^{3+}]_{max}$), as well as the maximum rate of their oxidation (V_{max}). The rate of oxidation of metal ions by bromate during an oscillating reaction in the presence of malonic acid (V_{ocr}) was found analogously. The values found for the enumerated parameters are cited in Table 3. The influence of malonic acid on the recordable parameters depends on the value of the initial cerium(III) or magnesium(II) and bromate ion concentrations. For the oxidation of cerium(III) by bromate, the duration t_{ind} is increased by a factor of 4-6 under the influence of malonic acid (0.15 M), while V_{max} decreases. For the reaction of manganese(II) with bromate at large concentrations of manganese(II) and bromate ions, the time t_{ind} is unchanged, but V_{max} is increased. The equilibrium concentrations of cerium(IV) ions in the presence of malonic acid are decreased by a factor of 1.5-4.5, while those of manganese(III) ions are increased. The values of V_{ocr} for each of the catalysts are approximately the same as V_{max} in the presence of malonic acid. A comparison of the parameters of the reactions in which these reducing agents participate shows that in the presence of malonic acid V_{max} of the cerium(III)-bromate reaction is 3-6 times lower, while the t_{ind} is 3-5 times greater than in the manganese(II)-bromate reaction.

The values that we found for t_{ind} and V_{max} are in good agreement with those cited in [12] for the oxidation of cerium(III) ions by excess bromate and differ from the results obtained in the presence of an excess of the reducing agent [2]. According to the available literature data, the shape of the kinetic curves of the accumulation of cerium(IV) or manganese(III) ions (Fig. 2) reflects the autocatalytic accumulation of bromous acid and active particles that directly oxidize cerium(III) ions, for example, BrO_2 radicals [13], according to the equation

$$BrO_3^- + Br^- + 2H^+ \not\simeq HBrO + HBrO_2, \tag{8}$$

$$HBrO_{2} + BrO_{3}^{-} + H^{+} \neq 2BrO_{2}^{-} + H_{2}O, \qquad (9)$$

$$BrO_2 + Ce^{3+} + H^+ \gtrsim Ce^{4+} + HBrO_2.$$
 (10)

The induction period of the reaction is believed to be associated with the consumption of bromide ions up to a critical value permitting step (9) to compete with step (8); increasing the bromide ion concentration above $5 \cdot 10^{-6}$ M leads to an inhibition of reaction (9) [13]. In such a case the increase in the induction period of the reaction of cerium(III) with bromate under the influence of malonic acid may be a consequence of a direct (noncatalytic) reduction of bromate by malonic acid, leading to the appearance of a perceptible $(6 \cdot 10^{-6} \text{ M}$ [14]) steady-state concentration of bromide in solution. The value of V_{max} of the cerium-(III)-bromate reaction in the presence of malonic acid may also be increased as a result of an increase in the bromide concentration due to the oxidation of malonic acid by bromate, followed by a competing reaction of reduction of cerium(IV) by malonic acid. Actually, the value of the rate of the reaction of cerium(III) with bromate in the presence of malonic acid is always lower than in its absence (Table 3). However, a comparison of the values of the rate of the cerium(III)-bromate reaction with the values of the rate of this reaction in the presence of malonic acid shows that the slowing of the reaction in the presence of malonic acid (systems 5, 6 and 4, 7, Table 3) is almost entirely (80-90%) the result of the occurrence of a competing reaction of reduction of cerium(IV) by malonic acid. Consequently, the bromide ions liberated as a result of the reaction between bromate and malonic acid affect virtually only the duration of the induction period of the oxidation of cerium(III) by bromate. There is some probability that the decrease in the equilibrium concentration of [Ce⁴⁺]_{max} in the presence of malonic acid is associated with the possibility of rapid consumption of cerium(IV) as a result of its reduction by malonic acid radicals formed in the oxidation of malonic acid by active bromyl radicals 'BrO2.

From the data obtained it also follows that in the absence of malonic acid the cerium-(III)-bromate reaction is characterized by a somewhat longer induction period and proceeds 1.5-4 times more slowly than the manganese(II)-bromate reaction. In the oxidation of manganese(II) by excess bromate (Table 3), the maximum rates of this reaction are 2-3 times as high as in the case of cerium(III). The maximum equilibrium concentrations of manganese(III) ions at bromate concentrations 0.005-0.05 M are half as great as $[Ce^{4+}]_{max}$, which can be explained by the somewhat higher redox potential of the couple Mn^{3+}/Mn^{2+} than of the couple Ce⁴⁺/Ce³⁺, as well as the possibility of consumption of manganese(III) for the reduction of bromide ions.

In contrast to the oxidation of cerium(III) by bromate, the presence of malonic acid in the manganese(II)-bromate reaction leads to an increase in tind only at low (0.005-0.01 M) bromate concentrations; V_{max} of this reaction is decreased under the influence of malonic acid at low bromate concentrations; at high concentrations it is increased; [Mn³⁺]max is increased in the presence of malonic acid (Table 3). The influence of malonic acid, leading to an increase in the values of [Mn³⁺]max and Vmax in the manganese(II)-bromate reaction, is far greater than the apparent increase in these values could be as a result of the increase in the molar extinction coefficient of manganese(III) ions in the presence of malonic acid (a factor of 1.21). The observed increase in $[Mn^{3+}]_{max}$ and V_{max} can evidently be explained by a decrease in the redox potential of the couple Mn^{3+}/Mn^{2+} as a result of complex formation with malonic acid.

Thus, the results of our investigations showed that the rate of interaction of manganese-(II, III) ions with bromate, malonic, and bromomalonic acids is 2-3 times as high as the rate of the analogous reactions with the participation of cerium(III, IV) ions. Therefore the Last induction period in oscillating chemical reactions with the participation of manganese(II, III) ions is shorter than in systems with cerium ions, while in the joint presence of these two catalysts in an oscillating reaction, the dominant influence on the value of the induction period is exerted by manganese(II, III) ions [15]. The differences in the catalytic action of manganese and cerium ions in bromate-malonic acid systems in sulfuric acid solutions are associated with the possibility of formation of relatively stable complex compounds of manganese(III) with malonic acid, which leads to an increase in the reaction rate at individual stages of the oscillating process. This may also be a cause of the increase in the oscillation amplitude of the manganese(III) ions observed under definite concentration conditions when the initial malonic acid concentration is increased [3].

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NATURE OF REACTIVE EXCITED STATE OF PHENAZINE IN '

ITS PHOTOREDUCTION WITH TETRAHYDROFURAN

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The nature of the excited state occurring in the photoreduction of azines (acridine and phenazine) is being thoroughly investigated [1-4]. Most of these articles point out the effect of the nature of the solvent on the electron configuration and the multiplet character of the excited state in which acridine takes part in the photoreduction [5, 6]. However, the causes of this effect remain unexplained. This problem has been studied much less for phenazine.

The present study has been undertaken with the objective to explain the nature of the excited state of phenazine which is responsible for its photoreduction by tetrahydrofuran (THF). It is known that in this solvent the reduction of azines proceeds most efficiently [1, 6]. We have therefore investigated the quantum yield of the overall process of photoreduction and of the elementary processes of luminescence quenching and deactivation of the T state of phenazine as function of the concentration of the reducing agent (in this case THF); the effect of quenching agents of the triplet state (eosin, anthracene) and of a sensitizer (diacetyl) was also investigated. The possibility of sensitizing the photoreduction of phenazine to visible light with diacetyl was also studied.

EXPERIMENTAL PROCEDURE

Absorption spectra were taken on a Specord UV Vis spectrophotometer. The fluorescence and phosphorescence of phenazine were studied by means of an instrument described in [7]. The kinetics of quenching of the T-T absorption of phenazine were recorded with a pulse device [8]. The quantum yields of the photoreduction were determined by means of a ferrioxalate actinometer. The internal filter effect was taken into account as described in [1]. The reference for the assessment of the quantum yields of fluorescence was a deaerated solution of anthracene in toluene (the quantum yield of its fluorescence is equal to 0.28). Phenazine and anthracene were purified by zone melting; the solvents used were toluene and THF, purified as described in [9] and distilled immediately before use. Diacetyl supplied by Kahlbaum was kept in sealed ampuls which were opened immediately before use. All experiments with respect to photoreduction and deactivation of the T states of phenazine were carried out at a residual pressure of $1.3 \cdot 10^{-3}$ Pa. The samples were irradiated with light from a DRSh-1000 mercury lamp (lines 366 and 436 nm, isolated with the corresponding light filters).

RESULTS AND DISCUSSION

In the irradiation with light with $\lambda = 366$ nm in the absence of air oxygen, the photoreduction of phenazine in toluene proceeds extremely slowly. The quantum yield of the reaction in toluene is equal to $\sim 10^{-3}$, a value which is in agreement with the results obtained in [2]. In THF the reaction proceeds to completion within 10-12 min of irradiation, with the formation of dihydrophenazine as the end product which is characterized by an absorption band with $\lambda_{max} = 320$ nm [1, 10]. Admission of oxygen to the reaction space causes complete regeneration of the initial phenazine. It must be pointed out that in the presence of air

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