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Kinetics of Oxidative Decarboxylation of 3,4-Methylenedioxymandelic Acid to Piperonal with Dilute Nitric Acid

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The oxidative decarboxylation of 3,4-methylenedioxymandelic acid (DMA) to piperonal with dilute nitric acid was investigated. This reaction was initiated by $NaNO_2$ and catalyzed by H_2SO_4, but the autocatalytic behavior, which was noted in most nitric acid oxidation reactions, was not observed. Detailed kinetic study showed that the respective reaction orders of $NaNO_2$, H_2SO_4, HNO_3, and DMA were 0.5, 0.5, 1.2, and 1.8, and the activation energy was 59.65 kJ/mol. The gained reaction rate equation provided a good model for the reaction under other temperatures and even the condition of a slightly higher concentration of nitric acid. Additional experimental data suggested that HNO_2 was the reactive species. On the basis of the results, a possible reaction mechanism was proposed.

1. Introduction

The oxidative decarboxylation of mandelic acid derivatives has been successfully used in the synthesis of many aromatic aldehydes, such as piperonal, vanillin, isovanillin, and *p*-hydroxybenzaldehyde. The process can be carried out by oxidation with permanganate in aqueous alkaline medium,[1] quinolinium dichromate,[2] the system of $AgNO_3$ and $Na_2S_2O_8$,[3] molecular oxygen using Cu(II) salt,[3] Bi(0),[4] or cobalt(II) chloride[5] as the catalyst, nitric acid,[6] and so on.

Nitric acid, as an old, low-cost, and effective oxidant, has been widely applied in oxidations of alcohols, ethers, aldehydes, ketones, alkyl halides, organonitrogen compounds, and organosulfur compounds, etc.[7] The nitric acid oxidative decarboxylation of mandelic acid derivatives to corresponding aromatic aldehydes has only been found to be applied in the synthesis of piperonal that was a popular flavor and an important pharmaceuticals intermediate.[8−11] This process was first studied by Cerveny et al.,[6] who found that the product color was brown under a high concentration of nitric acid, while the reaction did not take place at a lower nitric acid concentration. Later, Ube Co. of Japan[12] reported that the reaction selectivity decreased when a high concentration of nitric acid was used, and that high reaction selectivity was obtained by using an organic solvent. Further, the addition of mineral acid such as sulfuric acid was shown to accelerate the reaction. Sidot and Christidis[13] have also found a very small quantity of sodium nitrite could facilitate the start of the reaction, and they performed the reaction by slowly introducing concentrated nitric acid to the reaction mixture.

In this paper, the oxidative decarboxylation of 3,4-methylenedioxymandelic acid (DMA) to piperonal (DMB) with dilute nitric acid was investigated. High reaction selectivity was realized, and pure white product was successfully synthesized in the presence of sodium nitrite and sulfuric acid. Detailed kinetic data were obtained by changing the reaction parameters, and a possible mechanism was proposed.

2. Experimental Section

2.1. Materials. Nitric acid, sodium nitrite, and sulfuric acid were all analytical reagents. DMA was prepared from glyoxylic acid and 1,2-methylenedioxybenzene at 273 K. After recrystallization from water several times, the pure white DMA solid was produced and had a melting point of 430.0−431.0 K.[14]

2.2. Method. All reactions were performed in a stainless steel reaction vessel, as shown in Figure 1. Certain amounts of DMA solid, nitric acid, sulfuric acid, and water were added into the reaction vessel. After purging the vessel with N_2 for 15 min, a small amount of sodium nitrite solution was injected. Then, the reaction vessel was sealed and placed into a circulating water bath where it was held at a constant temperature. After stirring for a certain time, the reaction vessel was moved into a 273.0 K water bath where the reaction mixture was cooled and the reaction subsequently stopped. The outlet valve was then opened to discharge gaseous products, while the residual gaseous products were purged with N_2 for 15 min. The color of gaseous products was viewed though a glass observation pipe. Finally, the reaction mixture was filtrated and analyzed by external standard method of HPLC for the determination of the DMA, DMB, and HNO_3 amounts.

During the reaction process, the reaction system pressure change was recorded. To eliminate the effect of temperature on the system pressure, a blank experiment was carried out. In a nitrogen atmosphere, about 19.0 mL of water was slowly heated from 298.2 to 373.2 K, and the variation of system

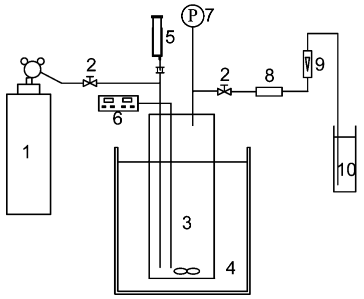

Figure 1. Schematic diagram of experimental equipment: 1, gas cylinder; 2, valve; 3, reaction vessel; 4, water bath; 5, injector; 6, thermometer; 7, pressure gauge; 8, glass observation pipe; 9, flow meter; 10, absorption bottle.

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Table 1. Roles of $NaNO_2$ and H_2SO_4 in Conversion of DMA to DMB with Dilute Nitric Acid[a]

entry	$n(NaNO_2)$ (mmol)	$n(H_2SO_4)$ (mmol)	$n(HNO_3)$ (mmol)	T (K)	DMA conversion (%)
1	0	0	4.5	331.2	1.4
2	0.5	0	4.5	331.2	33.2
3	0	10	0	344.2	1.2
4	0	10	4.5	344.2	2.0
5	0.5	10	4.5	331.2	66.9

[a] Reaction conditions: N_2 atmosphere, $n(\text{DMA}) = 10.0$ mmol, $V_{\text{soln}} =$ 19.0 mL, and reaction time 20 min.

pressure was recorded. The gained variation of system pressure in the blank experiment was then eliminated from the reaction system pressure. Thus, the corrected system pressure was gained and applied in the calculation of DMA and HNO_3 concentrations in the reaction process.

2.3. Kinetic Measurements. The oxidative decarboxylation of DMA ($C_9H_8O_5$) to DMB ($C_8H_6O_3$) by nitric acid could be described by the following equation (detailed information is given in the next section):

$$C_9H_8O_5 + \frac{2}{3}HNO_3 \rightarrow C_8H_6O_3 + CO_2 + \frac{2}{3}NO + \frac{4}{3}H_2O \tag{1}$$

As the reaction proceeded, the system pressure increased. Thus, the corrected system pressure was used to calculate the variations of the concentrations of HNO_3 and DMA during the reaction process (eqs 2−4),

$$n_{\text{gas}} = n_{\text{NO}} + n_{\text{CO}_2} = \frac{5}{2}n_{\text{conv(HNO}_3)} = \frac{5}{3}n_{\text{conv(DMA)}} = \frac{PV_{\text{gas}}}{ZRT} \tag{2}$$

$$C_{\text{HNO}_3} = C^0_{\text{HNO}_3} - \frac{n_{\text{conv(HNO}_3)}}{V_{\text{soln}}} \tag{3}$$

$$C_{\text{DMA}} = C^0_{\text{DMA}} - \frac{n_{\text{conv(DMA)}}}{V_{\text{soln}}} \tag{4}$$

where n_{NO} and n_{CO_2} were the respective molar amounts of the gaseous products NO and CO_2; $n_{\text{conv(HNO}_3)}$ and $n_{\text{conv(DMA)}}$ were the respective molar amounts of conversions of HNO_3 and DMA; $C^0_{\text{HNO}_3}$ and C^0_{DMA} were the respective initial concentrations of HNO_3 and DMA; P was the corrected system pressure; T was the system temperature; V_{soln} was the volume of reaction solution; V_{gas} was the volume of gaseous products, which was equal to the volume of the reaction vessel minus the volume of the reaction solution V_{soln}; and Z was the gas compressibility factor at the end of reaction, which was calculated from eq 2.

3. Results and Discussion

3.1. Preliminary Study. The roles of $NaNO_2$ and H_2SO_4 in conversion of DMA to DMB with dilute nitric acid were studied, and the results are shown in Table 1.

Table 2. Stoichiometry of the Nitric Acid Oxidative Decarboxylation of DMA to DMB[a]

$n(NaNO_2)$: $n(H_2SO_4)$: n(DMA)	HNO_3 conversion (%)	DMA conversion (%)	DMB selectivity (%)	ratio of consumed HNO_3 to DMA
0.01:0.00:1.00	27.0	17.5	95.1	0.694
0.05:0.00:1.00	49.2	33.2	99.1	0.667
0.05:1.00:1.00	98.1	66.9	99.6	0.660

[a] Reaction conditions: N_2 atmosphere; reaction temperature, 331.2 K; $n(\text{DMA}) = 10.0$ mmol; $n(HNO_3) = 4.5$ mmol; $C(HNO_3) = 0.24$ mol/L; and reaction time 20 min.

In the absence of $NaNO_2$, the oxidative decarboxylation of DMA to DMB by dilute nitric acid was difficult (entry 1). However, the conversion of DMA increased from 1.4 to 33.2% by just adding 0.5 mmol of $NaNO_2$ (entry 2). Therefore, a small amount of $NaNO_2$ was found to initiate the reaction.

Sulfuric acid might play two roles in the conversion of DMA to DMB. First, as noted in the textbook,[15] α-hydroxy carboxylic acid decarboxylates to aldehyde just by the action of H_2SO_4. However, the decarboxylation of DMA by 19.0 mL of 0.53 mol/L H_2SO_4 (10.0 mmol) at 344.2 K was very little either without or with HNO_3 (entries 3 and 4). Therefore, H_2SO_4 had little effect on the decarboxylation of DMA to DMB under the above conditions.

Second, H_2SO_4 could catalyze the nitric acid oxidative decarboxylation of DMA to DMB, which is the characteristic of nitric acid oxidation.[7] As shown in Table 1, entries 2 and 5, the conversion of DMA increased from 33.2 to 66.9%, while the DMB selectivity remained above 99% by adding 10.0 mmol of H_2SO_4.

Therefore, $NaNO_2$ was deemed to be the initiator and H_2SO_4 was considered to be the catalyst in the oxidative decarboxylation of DMA to DMB by dilute acid.

3.2. Stoichiometry. As shown in Table 2, the ratio of consumed HNO_3 to DMA was about 2/3, which was the same as that referred to by Sidot and Christidos. In addition, the gaseous products were colorless when the reactions were performed in nitrogen atmosphere, while in an oxygen atmosphere they became a red-brown color typical of NO_2. These phenomena indicated that the reaction produced NO gas, and its reaction equation can be expressed as eq 1.

3.3. Identification of the Phase in Which Reaction Occurs. The oxidative decarboxylation of DMA solid by dilute nitric acid is a heterogeneous solid−liquid reaction. The change of the DMA solid amount had little effect on the reaction rate when the DMA amount far exceeded its solubility, while the reaction was accelerated by increasing the concentration of $NaNO_2$, H_2SO_4, HNO_3, or DMA in reaction solution. Therefore, the reaction rate-limiting step was considered to occur in the liquid phase.

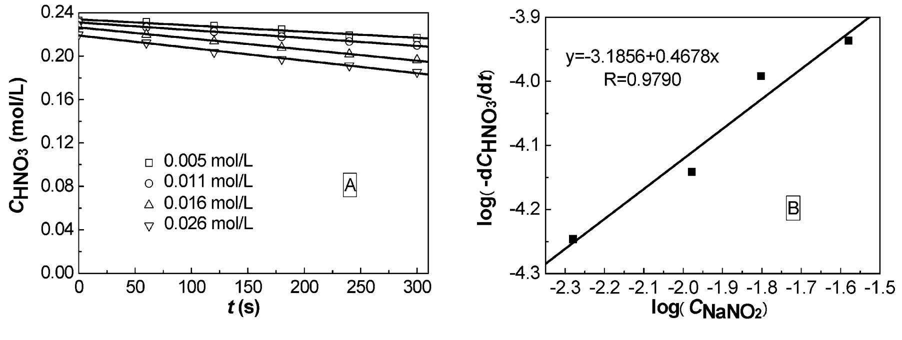


Figure 2. Effect of sodium nitrite concentration on the nitric acid oxidative decarboxylation of DMA, Reaction conditions: N_2 atmosphere; reaction temperature, 331.2 K; $n(\text{DMA}) = 10.0$ mmol; $C(HNO_3) = 0.24$ mol/L.

3.4. Reaction Kinetics. As the oxidative decarboxylation of DMA to DMB with dilute nitric acid was initiated by $NaNO_2$ and catalyzed by H_2SO_4, and its reaction rate-limiting step occurred in the liquid phase, the reaction rate equation can be defined as eq 5,

$$r = -\frac{dC_{HNO_3}}{dt} = kC_{NaNO_2}^{\alpha}C_{H_2SO_4}^{\beta}C_{DMA}^{\delta}C_{HNO_3}^{\gamma} \tag{5}$$

where the respective C_{NaNO_2}, $C_{H_2SO_4}$, C_{DMA}, and C_{HNO_3} were the concentrations of $NaNO_2$, H_2SO_4, DMA, and HNO_3 in liquid phase, and the α, β, δ, and γ were their reaction orders.

3.4.1. Effect of Sodium Nitrite Concentration. To study the effect of sodium nitrite concentration on the reaction rate, some reactions were done with different concentrations of $NaNO_2$, viz., 0.005, 0.011, 0.016, and 0.026 mol/L, as shown in Figure 2. Figure 2A shows that the initial reaction rate can be accelerated by increasing the sodium nitrite concentration. When the sodium nitrite concentration was raised from 0.005 to 0.026 mol/L, the reaction rate r increased from 5.67×10^{-5} to 1.16×10^{-4} mol/(L·s). In addition, taking the logarithm of both sides of eq 5 resulted in eqs 6 and 7 with the negligible change in concentrations of DMA, HNO_3, and H_2SO_4 in the initial reaction period.

$$\log r = \log\left(-\frac{dC_{HNO_3}}{dt}\right) = \log k' + \alpha \log C_{NaNO_2} \tag{6}$$

$$\log k' = \log k + \beta \log C_{H_2SO_4} + \delta \log C_{DMA} + \gamma \log C_{HNO_3} \tag{7}$$

Plotting $\log(-(dC_{HNO_3}/dt))$ vs $\log(C_{NaNO_2})$ yielded a straight line ($R = 0.9790$) with a slope of 0.5, indicating that the $NaNO_2$ order α was about 0.5. The plot with results is shown in Figure 2B. The reaction orders of H_2SO_4, DMA, and HNO_3, viz., β, δ, and γ, were determined using the same method.

3.4.2. Effect of Acidity. The acidity effect on the reaction rate was studied by varying the sulfuric acid amount. As shown in Figure 3A, increasing the acidity of the reaction solution accelerated the reaction rate. Then, plotting $\log(-(dC_{HNO_3}/dt))$ vs $\log(C_{H_2SO_4})$ resulted in a straight line ($R = 0.9938$) with a slope $\beta \approx 0.5$ (see Figure 3B).

3.4.3. Effect of DMA Concentration. To study the effect of the DMA concentration in the aqueous phase on the reaction rate, 2.0 mmol of DMA was reacted with excess HNO_3. The results are given in Figure 4. Figure 4A shows that the DMA concentration in the aqueous phase decreased quickly during the reaction process, which is in accord with eq 8 ($R = 0.9998$).

$$y = 0.05 - 3.54 \times 10^{-4}x + 1.58 \times 10^{-6}x^2 - 3.90 \times 10^{-9}x^3 + 3.90 \times 10^{-12}x^4 \tag{8}$$

From this equation, the reaction rate $-(dC_{DMA}/dt)$ was obtained by a differential method. Plotting $\log(-(dC_{DMA}/dt))$ vs $\log(C_{DMA})$ resulted in the DMA order δ approximately equal to 1.8 (see Figure 4B).

3.4.4. Effect of Nitric Acid Concentration. The effect of nitric acid concentration on the reaction rate was investigated by a differential method also. A small amount of HNO_3 (2.9 mmol) was reacted with 10.0 mmol of DMA. During the reaction process, the nitric acid concentration decreased and fitted eq 9 ($R = 0.9998$).

$$y = 0.12 - 2.37 \times 10^{-4}x + 2.91 \times 10^{-7}x^2 - 2.31 \times 10^{-10}x^3 + 3.23 \times 10^{-26}x^4 \tag{9}$$

A plot of $\log(-(dC_{HNO_3}/dt))$ vs $\log(C_{HNO_3})$ was linear ($R = 0.9981$) with the HNO_3 order $\gamma \approx 1.2$. The results are shown in Figure 5.

3.4.5. Effect of Temperature. Temperature increase had two effects on the reaction rate: it raised both the rate constants k and the DMA concentration in liquid phase when its amount far exceeded its solubility.

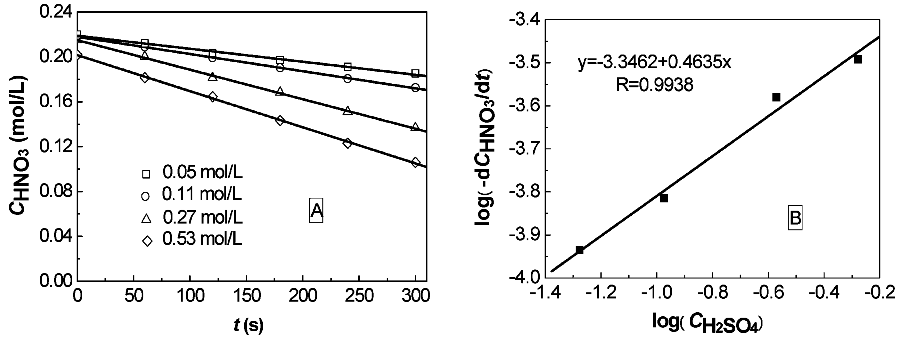


Figure 3. Effect of acidity on nitric acid oxidative decarboxylation of DMA. Reaction conditions: N_2 atmosphere; reaction temperature, 331.2 K; n(DMA) = 10.0 mmol; $C(HNO_3)$ = 0.24 mol/L; and $C(NaNO_2)$ = 0.026 mol/L.

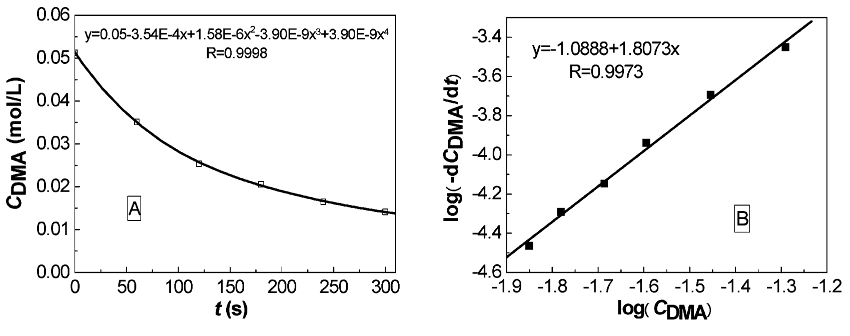


Figure 4. Effect of DMA concentration on the excess nitric acid oxidative decarboxylation of DMA. Reaction conditions: N_2 atmosphere; reaction temperature, 331.2 K; n(DMA):$n(HNO_3)$ = 1.0:2.3; $C(HNO_3)$ = 0.24 mol/L; $C(NaNO_2)$ = 0.026 mol/L; and $C(H_2SO_4)$ = 0.53 mol/L.

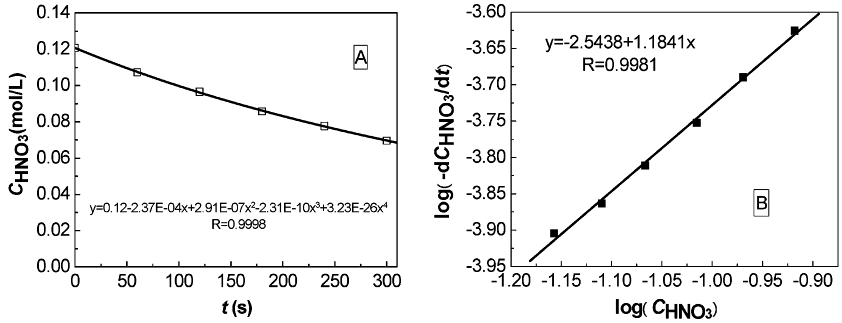


Figure 5. Effect of nitric acid concentration on oxidative decarboxylation of the excess DMA. Reaction conditions: N_2 atmosphere; reaction temperature, 331.2 K; n(DMA):n(HNO_3) = 3.4:1.0; C($NaNO_2$) = 0.026 mol/L; and C(H_2SO_4) = 0.53 mol/L.

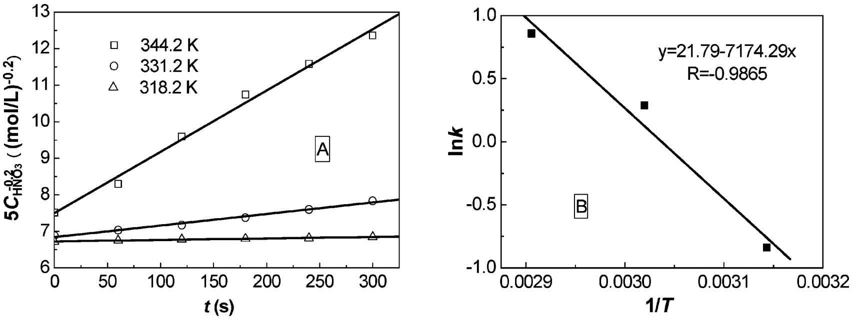


Figure 6. Effect of temperature on the nitric acid oxidative decarboxylation rate constant k. Reaction conditions: N_2 atmosphere; n(DMA) = 10.0 mmol; C(HNO_3) = 0.24 mol/L; C($NaNO_2$) = 0.026 mol/L; and C(H_2SO_4) = 0.53 mol/L.

First, the rate constants k at different temperatures and the activation energy E_a were calculated using eqs 10−12 and 13, respectively.

$$r = -\frac{dC_{HNO_3}}{dt} = kC_{NaNO_2}^{0.5}C_{H_2SO_4}^{0.5}C_{DMA}^{1.8}C_{HNO_3}^{1.2} \tag{10}$$

$$-\int \frac{dC_{HNO_3}}{C_{HNO_3}^{1.2}} = \int kC_{NaNO_2}^{0.5}C_{H_2SO_4}^{0.5}C_{DMA}^{1.8}\,dt \tag{11}$$

$$5C_{HNO_3}^{-0.2} = kC_{NaNO_2}^{0.5}C_{H_2SO_4}^{0.5}C_{DMA}^{1.8}t + c \tag{12}$$

$$k = Ae^{(-E_a/RT)} \tag{13}$$

In eq 12, plotting the $5C_{HNO_3}^{-0.2}$ vs t resulted in a slope of $kC_{NaNO_2}^{0.5}C_{H_2SO_4}^{0.5}C_{DMA}^{1.8}$, *where the concentrations of $NaNO_2$, H_2SO_4, and DMA were constant at the initial reaction period. By this method, the respective rate constants k at 318.2, 331.2, and 344.2 K were calculated about 0.43, 1.33, and 2.36 $(mol/L)^{-3.0}\cdot s^{-1}$ (see Figure 6*A). In addition, the reaction temperature T dependence of the rate constant k was described by Arrhenius eq 13. The natural logarithm from this equation and plotting ln k vs 1/T yielded a straight line with the slope $-E_a/R$ and the intercept of ln A, as shown in Figure 6B. The activation energy E_a and preexponential factor A were 59.65 kJ/mol and 2.90 × $10^9(mol/L)^{-3.0}\cdot s^{-1}$, respectively. Therefore, the reaction rate equation can be defined as

$$r = 2.90 \times 10^9 e^{(-59.65\times10^3/RT)}C_{NaNO_2}^{0.5}C_{H_2SO_4}^{0.5}C_{DMA}^{1.8}C_{HNO_3}^{1.2} \tag{14}$$

Second, the reaction temperature change influenced the DMA solid solubility which was detected by an isothermal method. As shown in Figure 7, when the reaction temperature was raised from 298.2 to 358.2 K, the DMA solubility increased from 0.03 to 0.52 mol/L. The temperature dependence of DMA solubility has been fitted by a fourth-degree polynomial (R^2 = 1.0000). The fitted polynomial is used in eq 14 and yields eq 15 that can be applied in the solid−liquid reaction system. Herein, the reaction temperature has great influence on the reaction rate.

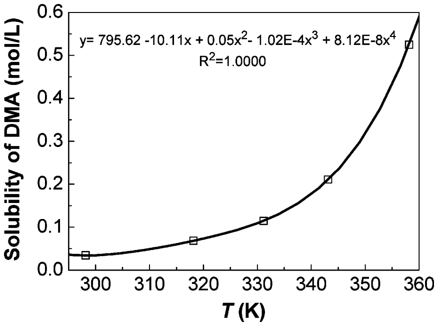


Figure 7. Effect of temperature on the solubility of DMA in water.

$$r = 2.90 \times 10^9 e^{(-59.65\times10^3/RT)}C_{NaNO_2}^{0.5}C_{H_2SO_4}^{0.5}C_{HNO_3}^{1.2}(795.62 - 10.11T + 0.05T^2 - 1.02\times10^{-4}T^3 + 8.12\times10^{-8}T^4)^{1.8} \tag{15}$$

3.4.6. Predictive Capability of the Kinetic Model. To check out the predictive capability of the above reaction rate equation, the initial nitric acid concentrations were modeled and compared with the experimental data. As presented in Figure 8, the experimental and predicted data were in good agreement in the temperature range of 318.2−344.2 K and even slightly higher concentration of nitric acid conditions. The results demonstrated the validity of the proposed kinetic model and its parameters.

3.5. Possible Reaction Mechanism. As summarized by Ogata,[7] nitric acid oxidation has some features such as this reaction being initiated by $NaNO_2$ and catalyzed by sulfuric acid as well as the autocatalytic behavior. The autocatalytic phenomena had been observed in the nitric acid oxidations of formaldehyde,[16] benzyl alcohols,[17] benzyl ethers,[18] benzaldehydes,[19] 2-octanol,[20] and so on.

Horvath et al. studied the autocatalytic oxidation of formaldehyde with nitric acid and proposed the following mechanism:

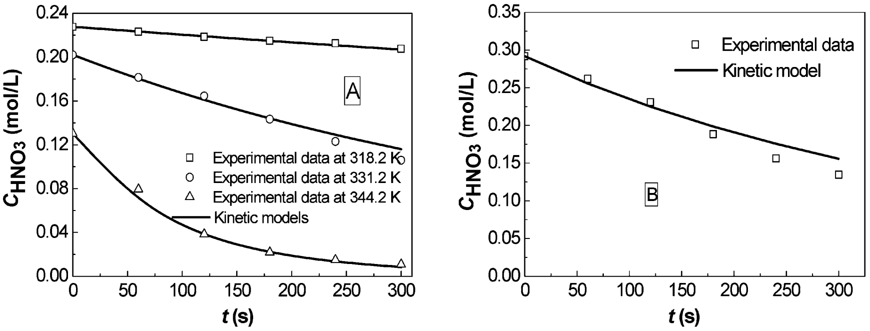


Figure 8. Comparison of reaction kinetics model with experimental data. General reaction conditions: N_2 atmosphere; n(DMA) = 10.0 mmol; $C(NaNO_2)$ = 0.026 mol/L; $C(H_2SO_4)$ = 0.53 mol/L. (A) $C(HNO_3)$ = 0.24 mol/L; reaction temperature, 318.2, 331.2, and 344.2 K. (B) $C(HNO_3)$ = 0.35 mol/L; reaction temperature, 331.2 K.

first, HNO_3 reacted with HNO_2 to give N_2O_4 or two NO_2 molecules, which oxidized formaldehyde to formic acid while producing two HNO_2 molecules. Thus, this proposed mechanism, which started with one HNO_2 and formed two HNO_2 molecules, led to the autocatalytic behavior during the reaction process. This mechanism was similar to that suggested by Ogata et al. in nitric acid oxidations of benzyl alcohol, benzyl ether, and benzaldehyde.

However, a different mechanism of nitric acid oxidation of benzyl alcohol was proposed by Joshi et al.[21] HNO_2, formed by the reaction of $NaNO_2$ and HNO_3, oxidized benzyl alcohol to benzyl nitrite intermediate, which decomposed to benzaldehyde and HNO, and then the latter self-decomposed to produce the gaseous product N_2O or reacted with HNO_3 to give two HNO_2 molecules. Indeed, the authors claimed that the HNO_2 concentration increased continuously during the reaction process, but no autocatalytic behavior was mentioned. In addition, benzyl nitrite as the reaction intermediate was confirmed.

For the nitric acid oxidative decarboxylation of DMA, the autocatalytic reaction character, such as the maximum reaction rate, did not appear in the reaction process. As shown in Figures 2A and 3A, the nitric acid concentration decreased almost linearly even until the nitric acid conversion reached 51.7%.

To determine the reactive species, the following additional experiments using other oxidants (HNO_2 and NO_2) instead of HNO_3 were carried out.

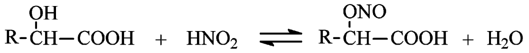
First, HNO_2 ($NaNO_2 + H^+$) was used to oxidize DMA to DMB, and the reaction was performed successfully as reported by the Ube Co.[22] Second, when NO_2 as an oxidant was introduced into the mixture of DMA and H_2O that could react with NO_2 to form HNO_2 and HNO_3,[23] the oxidative decarboxylation proceeded smoothly and gave a DMB yield of 95.0% after 70 min at 331.2 K. However, when adding a certain amount of urea that could rapidly consume HNO_2 to form N_2 and CO_2,[20] the reaction did not take place under the same conditions. Therefore, the reactive species was suggested as HNO_2 rather than NO_2.

The above results enable us to propose a possible mechanism as given in Scheme 1.

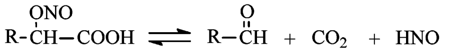
First, $NaNO_2$ reacted with acid and formed HNO_2. Second, the HNO_2 oxidized DMA to a nitrite ester intermediate and initiated the reaction after which the nitrite ester decomposed to DMB, CO_2, and HNO. Finally, the reaction of HNO and HNO_3 produced one HNO_2 molecule again, which promoted the reaction to continue. As the proposed mechanism indicates, the nitrous acid concentration should be constant during the reaction process, which agrees with the absence of autocatalytic behavior.

Scheme 1. Possible Mechanism for the Nitric Acid Oxidative Decarboxylation of DMA

$$NO_2^- + H^+ \rightleftharpoons HNO_2 \qquad (1)$$



$$R\text{-}\overset{\text{OH}}{\text{CH}}-COOH + HNO_2 \rightleftharpoons R\text{-}\overset{\text{ONO}}{\text{CH}}-COOH + H_2O \qquad (2)$$



$$R\text{-}\overset{\text{ONO}}{\text{CH}}-COOH \rightleftharpoons R-\overset{\text{O}}{\overset{\|}{\text{C}}}\text{H} + CO_2 + HNO \qquad (3)$$

$$HNO + 2/3\,HNO_3 \rightleftharpoons HNO_2 + 2/3\,NO + 1/3\,H_2O \qquad (4)$$

The overall reaction was

$$C_9H_8O_5 + 2/3\,HNO_3 \longrightarrow C_8H_6O_3 + CO_2 + 2/3\,NO + 4/3\,H_2O$$

4. Conclusions

The kinetics of oxidative decarboxylation of DMA to DMB by dilute nitric acid was studied. This reaction can be initiated by $NaNO_2$, catalyzed by H_2SO_4, and greatly accelerated by increasing the HNO_3 and DMA concentrations and the reaction temperature. Within a long reaction period, the nitric acid concentration decreased almost linearly, indicating the absence of autocatalytic behavior. The gained reaction rate equation provided a good model for the reaction under different temperatures and even a slightly higher concentration of nitric acid conditions. In addition, a possible reaction mechanism involving HNO_2 as the reactive species was proposed.

Literature Cited

(1) Panari, R. G.; Chougale, R. B.; Nandibewoor, S. T. Oxidation of mandelic acid by alkaline potassium permanganate. A kinetic study. *J. Phys. Org. Chem.* **1998**, *11*, 448.

(2) Nalwaya, N.; Jain, R.; Hiran, B. L. Kinetics and mechanism of oxidation of alpha-hydroxy acids by quinolinium dichromate. *Oxid. Commun.* **2003**, *26* (4), 561.

(3) Bjorsvik, H. R.; Liguori, L.; Minisci, F. High selectivity in the oxidation of mandelic acid derivatives and in O-methylation of protocatechualdehyde: New processes for synthesis of vanillin, iso-vanillin, and heliotropin. *Org. Process Res. Dev.* **2000**, *4* (6), 534.

(4) Favier, I.; Giulieri, F.; Dunach, E.; Hebrault, D.; Desmurs, J. R. Bi^0-catalyzed oxidation of mandelic acid derivatives: Substrate selectivity. *Eur. J. Org. Chem.* **2002**, (12), 1984.

(5) Favier, I.; Dunach, E.; Hebrault, D.; Desmurs, J. R. $CoCl_2$ catalysed decarboxylation-oxidation of mandelic acids by molecular oxygen. *New J. Chem.* **2004**, *28* (1), 62.

(6) Cerveny, L.; Kozel, J.; Marhoul, A. Synthesis of heliotropin. *Perfum. Flavor.* **1989**, *14* (2), 13.

(7) Ogata, Y. Oxidations with nitric acid or nitrogen oxides; In *Oxidation in Organic Chemistry*, Part C; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; p 295.

(8) Braun, U.; Shulgin, A. T.; Braun, G. Centrally active N-substituted analogs of 3,4-methylenedioxyphenylisopr-opylamine (3,4-methylenedioxyamphetamine). *J. Pharm. Sci.* **1980**, *69* (2), 192.

(9) Devakuar, C. Synthesis of sesamol by piperonal. *Agric. Biol. Chem.* **1985**, *49* (3), 725.

(10) Adam, W.; Sahamoller, C. R.; Veit, M.; Welke, B. A convenient synthesis of hispidin from piperonal. *Synth.-Stuttgart* **1994**, (11), 1133.

(11) Shi, X. X.; Liu, S. L.; Xu, W.; Xu, Y. L. Highly stereoselective Pictet-Spengler reaction of D-tryptophan methyl ester with piperonal: convenient syntheses of Cialis (Tadalafil), 12a-epi-Cialis, and their deuterated analogues. *Tetrahedron: Asymmetry* **2008**, *19* (4), 435.

(12) Harada, K.; Aoi, M.; Shirai, M. *Method for producing piperonal*. JP Patent 7258246, 1995.

(13) Sidot, C., Christidis, Y., *Preparation process for piperonal*. U.S. Patent 5095128, 1992.

(14) Xi, H. J.; Gao, Z. X.; Wang, J. G. Synthesis and characterization of the intermediate of piperonal: 3,4-Methylenedioxymandelic acid. *Chem. Res. Appl. (China)* **2009**, *21* (3), 396.

(15) Xu, Sh. Ch. *Organic Chemitry*, 2nd ed.; Higher Education Press: Beijing, China, 1993; p 324.

(16) Horvath, M.; Lengyel, I.; Bazsa, G. Kinetics and mechanism of autocatalytic oxidation of formaldehyde by nitric acid. *Int. J. Chem. Kinet.* **1988**, *20* (9), 687.

(17) Ogata, Y.; Sawaki, Y.; Matsunaga, F.; Tezuka, H. Kinetics of the nitric acid oxidation of benzyl alcohols to benzaldehydes. *Tetrahedron* **1966**, *22*, 2655.

(18) Ogata, Y.; Sawaki, Y. Kinetics of the nitric acid oxidation of benzyl ethers to benzaldehydes. *J. Am. Chem. Soc.* **1966**, *88*, 5832.

(19) Ogata, Y.; Tezuka, H.; Sawaki, Y. Kinetics of the nitric acid oxidation of benzaldehydes to benzoic acid. *Tetrahedron* **1967**, *23*, 1007.

(20) Van Woezik, B. A. A.; Westerterp, K. R. The nitric acid oxidation of 2-octanol. A model reaction for multiple heterogeneous liquid-liquid reactions. *Chem. Eng. Process.* **2000**, *39* (6), 521.

(21) Joshi, S. R.; Kataria, K. L.; Sawant, S. B.; Joshi, J. B. Kinetics of oxidation of benzyl alcohol with dilute nitric acid. *Ind. Eng. Chem. Res.* **2005**, *44*, 325.

(22) Harada, K.; Aoi M.; Shirai M.; Furuya T. *Production of piperonal*. JP Patent 8027144, 1996.

(23) Chacuk, A.; Miller, J. S.; Wilk, M.; Ledakowicz, S. Intensification of nitrous acid oxidation. *Chem. Eng. Sci.* **2007**, *62* (24), 7446.

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