Kinetics of Oxidation of Benzyl Alcohol with Dilute Nitric Acid

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The oxidation of benzyl alcohol by dilute nitric acid has been selected for the study as a typical method for the manufacture of industrially important intermediate benzaldehyde. All the reactions have been performed in the absence of any solvent. A catalytic amount of sodium nitrite is essential for the generation of active state of nitrogen. Benzyl nitrite is formed in a substantial amount as an intermediate. The effects of various parameters such as the $NaNO_2$ loading, nitric acid concentration, temperature, and molar ratio have been investigated. The stoichiometric requirement of nitric acid for benzyl alcohol conversion has also been determined. The probable mechanism for the oxidation of benzyl alcohol using nitric acid is proposed, showing the reversible formation of benzyl nitrite and its irreversible decomposition to benzaldehyde. The mass-transfer resistance has been eliminated for the investigation of kinetics of all the reactions in the consecutive path. The influence of chloro substitution on the oxidation rates of 2-chlorobenzyl, 4-chlorobenzyl, and 2,4-dichlorobenzyl alcohols has been presented.

1. Introduction

Benzaldehyde (BzH) and substituted benzaldehydes are important perfumery and pharmaceutical intermediates. Benzaldehyde is a starting material for odorants and flavors. Substituted benzaldehydes are used in the manufacture of pharmaceuticals (e.g., 2-chlorobenzaldehyde is used in the manufacture of amlodipin, cloxacillin, and clobenzorex; 4-chlorobenzaldehyde is used in the manufacture of baclofen, chlormezanone, chloropyramine; and 2,4-dichlorobenzaldehyde is used in the manufacture of halofantrine[1]).

The conventional routes for the synthesis of BzH include hydrolysis of the benzal chloride and the vapor/liquid-phase oxidation of toluene. With the former process, it is impractical to obtain the chlorine-free BzH.[2] Furthermore, the chlorination reaction operates at lower conversion levels, requiring a large recycling of recovered toluene. The vapor-phase catalytic oxidation of toluene results in a loss of carbon in the form of carbon oxides, in addition to lower conversion (10%–20%) and poor selectivity (30%–50%). Although the liquid-phase oxidation of toluene prevents the carbon loss, it requires a homogeneous catalyst (such as cobalt, 25–1000 ppm), high pressure (2–70 kg/cm^2), and high temperature (136–160 °C).[2] Also, the BzH that is produced is further oxidized, because it has a lower activation energy than its heat of formation, resulting in poor selectivity.[3] These factors make the process technically and economically unattractive.

Benzyl alcohols are attractive raw materials for the manufacture of BzHs. The oxidation of benzyl and substituted benzyl alcohols to corresponding aldehydes has been investigated over the past forty years, with increased focus during the past twenty years. Several oxidants, such as permanganates,[4,5] dichromates,[6,7] hypohalides,[8,9] peroxides,[10,11] and molecular oxygen[12–14] with or without phase-transfer catalysts (PTCs) and heterogeneous catalysts have been used successfully for the oxidation of benzyl alcohol to BzH. The catalytic

oxidation of benzyl alcohol using molecular oxygen requires a heterogeneous catalyst, high temperature (210 °C), and longer reaction times (>5 h). Although the reported selectivity is quite good (75%–95%), the conversion levels are too low (maximum of 40%).[14]

Practically, in all the previously cited cases, good yields have been obtained, with respect to BzH; however, the conversion levels were lower and/or not been reported in many cases. Furthermore, the inorganic oxidants (along with PTC reagents and their amounts) seem to be cost prohibitive for the large-scale commercial production of aldehydes. In this respect, nitric acid is known to be a favorable oxidizing agent.[15,16] The published literature on the HNO_3-based oxidation of alcohols to aldehydes/ketones has been summarized in Table 1. The oxidation of benzyl alcohols to BzHs by dilute nitric acid (∼10%) in the presence of a catalytic amount of $NaNO_2$, in 40 vol % dioxan as a solvent, was first studied in detail by Ogata et al.[15] They proposed that the reaction proceeded through some intermediate; however, it was not identified. Many other investigators have also studied the oxidation of benzyl alcohol using nitric acid.[17–21] However, the published information suffers from two limitations: (i) oxidation studies have not been performed in the absence of solvent, to make the process commercially more attractive, and (ii) the kinetics of oxidation reaction have not been reported. Due consideration to the formation of benzyl nitrite as an intermediate is needed. The kinetic parameters also must be free from any mass-transfer limitations. These issues have been addressed in the present work.

Thus, benzyl alcohol was reacted with nitric acid in the presence of a catalytic amount of sodium nitrite without any solvent. The oxidation system has been applied for the synthesis of chloro benzaldehydes from corresponding chloro benzyl alcohols as well.

2. Experimental Section

2.1. Method. All the experiments were conducted in a batch manner. A borosilicate glass reactor with an inner diameter (id) of 75 mm and capacity of 400 mL, which was equipped with a pitched-blade downflow

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Table 1. Reported Oxidation of Benzyl Alcohols by Nitric Acid and Nitrous Acid

author	oxidation system	solvent	results
Gray et al.[18]	H_2SO_4 + excess $NaNO_2$	no solvent	(1) formation of BnONO as an intermediate; (2) decomposition of BnONO to BnOH and BzH; and (3) 1st order decomposition with $E = 154.81$ kJ/mol and an F-factor of 10^{13} s^{-1}
Ogata et al.[15]	HNO_3 (20%) + $NaNO_2$	40% dioxan	(1) $NaNO_2$ is needed for the reaction to proceed; (2) minimum acidity of 0.1 M is necessary for the oxidation; (3) first-order dependency on nitric acid and BnOH; (4) $E = 117.28$ kJ/mol; and (5) substitution effect was shown to satisfy Hammett's equation, with a slope of -2.5
Ross et al.[16]	HNO_2 + HNO_3 in H_2SO_4 (50%$-$70%) by $NaNO_2$	no solvent	(1) nitrosonium is an active oxidant; (2) $E = 44.35$ kJ/mol; and (3) substitution effect is shown to follow Hammett's equation, with a slope of -1.4
Gasparrini et al.[20]	20% HNO_3	nitromethane	(1) good yields (95%) of aldehyde; (2) various substitutions with $+\sigma$ and $-\sigma$ have been shown to be oxidized by this system
Nishiguchi and Okamoto[21]	NO_2 in presence of silica gel	no solvent	(1) oxidation of alcohols and ethers to aldehydes and ketones; (2) alky/aryl nitrite used as an intermediate; (3) NO_2 in radical form as an active species; and (4) NO_2 also accelerates the decomposition of the formed nitrite intermediate to aldehyde/ketone
Levina and Trusov[19]	O_2 + HNO_2 in conc. $HClO_4$, H_2SO_4, F_3CCOOH	no solvent	(1) oxidation of BnOH and various other primary and secondary alcohols; and (2) NO^+ used as an active species for the reaction

turbine impeller (25 mm in diameter) and baffle, was used. The reaction temperature was maintained using a constant-temperature bath.

A predetermined quantity of benzyl alcohol was added to the reactor. A measured quantity of sodium nitrite was then added, followed by the addition of aqueous nitric acid that was preheated to the required temperature; the run then was started. Extremely low solubility (4 wt %) of the benzyl alcohol in aqueous nitric acid makes the system have two phases (organic and aqueous). Small quantities of samples of the two-phase mixture were withdrawn at predetermined time intervals. After the sample was withdrawn, it was quickly added to water. As a result, the dissolved nitric acid in the organic phase was extracted back into the aqueous phase and the reaction became quenched. The organic phase (which was separated from the water phase) was used for further analysis. The sample was divided into two parts. The first part was analyzed via gas chromatography (GC), to estimate the amounts of benzyl nitrite, benzaldehyde that had formed, and unconsumed benzyl alcohol. The second part of the sample was analyzed via thin-layer chromatography (TLC), using a Dessagga applicator and scanner to determine the amount of benzoic acid (BzOH) formed.

2.2. Analysis. The various species that participate in the reaction, and their probable paths, can be shown as follows:

$$BnOH \rightarrow BnONO \rightarrow BzH \rightarrow BzOH \qquad (1)$$

BnOH, BnONO, and BzH were analyzed via GC. The GC analysis was performed using a 2-m 10% OV-17 column. Nitrogen was the carrier gas, and the detector was a flame ionization detector. The other parameters were as follows: injection temperature, 350 °C; detector temperature, 350 °C; nitrogen flow rate, 30 mL/min; and temperature programming, 110 °C (isothermal).

For the analysis of BzOH via TLC, precoated silica gel plates (Merck) were used. A portion (0.2 mL) of the sample was diluted to 10 mL with acetone. Known quantities of the diluted sample and the authentic sample of BzOH were applied in the form of 5-mm

bands, using the applicator (Dessagga). The plates were developed in a solvent system that consisted of benzene and methanol (5:1, by volume). A densitometer (Dessagga) was used to analyze the developed plates.

3. Theory of Mass Transfer with Chemical Reaction

In order to estimate the true kinetic parameters, we need to (i) eliminate the mass-transfer resistances, (ii) know the phase in which the reactions occur, and (iii) according to the classification of heterogeneous reactions given by Doraiswamy and Sharma,[22] establish the reaction regime for the present case.

To begin, the following reaction mechanism is proposed; the supporting observations will be explained later.

3.1. Reaction Mechanism.

$$H^+ + NaNO_2 \longrightarrow HNO_2 + Na^+ \qquad \text{Initiation} \qquad (2)$$

$$2R\text{-}CH_2OH + 2HNO_2 \rightleftharpoons 2R\text{-}CH_2ONO + 2H_2O \qquad (3)$$

$$2R\text{-}CH_2ONO \longrightarrow 2R\text{-}CHO + 2HNO \qquad \text{Propagation} \qquad (4)$$

$$HNO + HNO_3 \longrightarrow 2HNO_2 \qquad (5)$$

$$HNO \longrightarrow \tfrac{1}{2} N_2O + \tfrac{1}{2} H_2O \qquad \text{Termination} \qquad (6)$$

The overall reaction is given by

$$2R-CH_2OH + HNO_3 \rightarrow 2R-CHO + \frac{1}{2}N_2O + \frac{5}{2}H_2O \qquad (7)$$
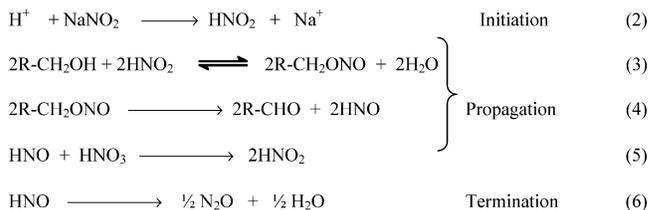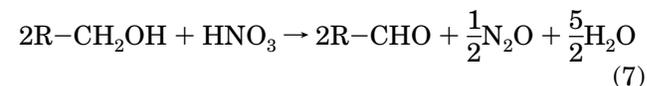
The oxidation reaction of BnOH by dilute nitric acid proceeds via benzyl nitrite (BnONO). HNO_2 is formed by the reaction of $NaNO_2$ and HNO_3. The HNO_2 is the true oxidant and reacts with alcohol to give nitrite ester and, thus, the reaction is initiated. The nitrite ester decomposes in an acidic medium to give aldehyde and HNO or reversibly yielding BnOH back. The excess HNO_3 oxidizes HNO to HNO_2 and the oxidation cycle continues. Thus, as the reaction proceeds, HNO_3 is consumed. HNO finally undergoes self-decomposition to give nitrous oxide and water.

Table 2. Consumption of Nitric Acid for Oxidation of Benzyl Alcohol[a]

BnOH:HNO$_3$ molar ratio	temperature (°C)	batch time (min)	conversion of benzyl alcohol (%)	yield (%)			HNO$_3$ consumed (mol)	ratio of consumed alcohol to HNO$_3$
				BzH	BnOH	BnONO		
1:0.625	70	240	73.18	85.45	1.82	12.73	0.106	2.07
1:0.625	80	240	82.98	94.84	3.5	1.65	0.12	2.07
1:0.625	90	240	86.74	95.11	4.54	0.35	0.148	1.76
1:1.25	70	230	91.90	92.31	2.89	4.80	0.131	2.10

[a] BnOH content = 0.3 mol, HNO$_3$ concentration = 1.59 M, NaNO$_2$ content = 1 g, and speed of stirring = 41.66 rps.

Table 2 shows that the ratio of alcohol consumed to HNO$_3$ at different reaction conditions is ~2.0. This is consistent with the stoichiometric requirement indicated by eq 7. In addition, the gas-phase analysis (Suchak et al., 1989) was performed in an operating plant, using the HNO$_3$ oxidation of benzyl alcohol. It was observed that the gas phase did not contain NO, NO$_2$, N$_2$O$_4$, or N$_2$O$_5$. Thus, it may be concluded that the NO$_x$ that is liberated is in the form of N$_2$O. The liberated N$_2$O in the product gas mixture can be used as a clean and selective oxidant, e.g., for the selective oxidative coupling of methane to ethane (Sugiyama et al.[23]) and for the oxidation of benzene to phenol (Reitzmann et al.[24]).

3.2. Identification of the Phase in Which Reaction Occurs. Benzyl alcohol oxidation by aqueous nitric acid is a typical example of consecutive liquid−liquid heterogeneous reaction. The reactant benzyl alcohol and the reaction products form the organic phase, while the dilute nitric acid forms the aqueous phase. The reaction proceeds through the formation of a benzyl nitrite intermediate, as discussed previously. The formation of benzyl nitrite by the reaction between benzyl alcohol and in-situ-generated nitrous acid may be considered to be similar to the well-known nitration reaction, which occurs in the aqueous phase (see Zaldivar et al.[25] and D'Angelo et al.[26]). Also, in the present case, for a fixed nitric acid concentration, an increase in the volume of the aqueous phase gave a proportionate increase in the rate of reaction (given in kilomoles per second, kmol/s) and the volumetric rate of reaction (given in kilomoles per cubic meter of aqueous phase per second, kmol m^{-3} s^{-1}) remained the same. The relative amount of organic phase did not have any effect on the volumetric rate of reaction. These evidences indicate that the rate-limiting step of the reaction occurs in the aqueous phase.

3.3. Identification of Reaction Regime. Let us write eq 7 in the following form:

$$A + zB \rightarrow \text{products}$$
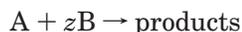
where A and B are the benzyl alcohol and nitric acid, respectively, and z is a stoichiometric coefficient (in the present case, $z = 0.5$). Because the reaction occurs in the liquid phase, the overall oxidation follows these two steps: (i) mass transfer of benzyl alcohol to the aqueous phase and (ii) the reaction between the dissolved benzyl alcohol (A*) and nitric acid (B$_0$). The details that pertain to heterogeneous reactions (consisting of the steps of mass transfer and chemical reaction) have been given by Danckwerts[27] and Doraiswamy and Sharma.[22] They classified these reactions into four regimes, depending on the rates of mass transfer, relative to the rates of chemical reaction in other words, when the rate of chemical reaction is very much slower than the rate of mass transfer, or when the condition given by the following expression is satisfied:

$$k_L a[A^*] \gg \epsilon_L k_{mn}[A^*]^m[B_o]^n \quad (8)$$

where m and n are the orders, with respect to benzyl alcohol and nitric acid, respectively, and ϵ_L is the volumetric fraction of the aqueous phase. Under these conditions, the overall reaction is controlled by the chemical reaction (regime 1) and the volumetric rate of reaction is given by the following equation:

$$R = \epsilon_L k_{mn}[A^*]^m[B_0]^n \quad (9)$$

When the reverse condition given by expression 8 is satisfied, or if the rate of reaction is faster than the rate of mass transfer, the overall rate is controlled by mass transfer (regime 2) and is given by

$$R = k_L[A^*] \quad (10)$$

When the reaction rate increases further, the reaction occurs in a region close to the interface and is completed in the film. The necessary condition for this phenomenon is as follows:

$$\sqrt{M} = \frac{\sqrt{[2/(m+1)]D_A k_{mn}[A^*]^{m-1}[B_0]^n}}{k_L} > 3 \quad (11)$$

For reaction regimes 1 and 2 (determined by eqs 9 and 10), the value of $\sqrt{M}$ (the Hatta number) must be <1, preferentially 0.1.

3.4. Effect of Impeller Speed. Since, in a liquid−liquid system, the values of k_L and a are dependent on the impeller speed, it was believed to be desirable to investigate the effect of impeller speed. For this purpose, 0.3 mol BnOH was reacted with 118 mL of 1.59 M aqueous nitric acid in the presence of 1 g of NaNO$_2$ at 90 °C. The reaction was performed at stirring speeds of 25 and 41.66 rps. Figure 1A shows the conversion of BnOH with time. Variation in the yields of the products—aldehyde, acid, and nitrite—at two speeds is shown in panels B, C, and D, respectively, of Figure 1. The results show that the reaction is not affected by stirring speeds beyond 25 rps, the rate is not dependent on k_L and a, or the reaction is kinetically controlled when the speed exceeds 25 rps. However, as an abundant precaution, all the experiments in the present work have been conducted at an impeller speed of 41.66 rps, to ensure that the reaction proceeds under a kinetically controlled regime and the true kinetic parameter can be evaluated.

For confirmation, it was thought desirable to estimate the values of $\sqrt{M}$ in eq 11. For this purpose, correlations that were proposed by Keey and Glen[28] and Van Heuven and Beek[29] were used for the estimation of the k_L, and the diffusivity was estimated using the procedure that was proposed by Garne and Merchant.[30] Tables 3 and 4 give the values of $\sqrt{M}$ under the range of experimental conditions covered in this work. It can be seen that the values of $\sqrt{M}$ are <0.04. The foregoing evidence clearly indicates that the oxidation reaction
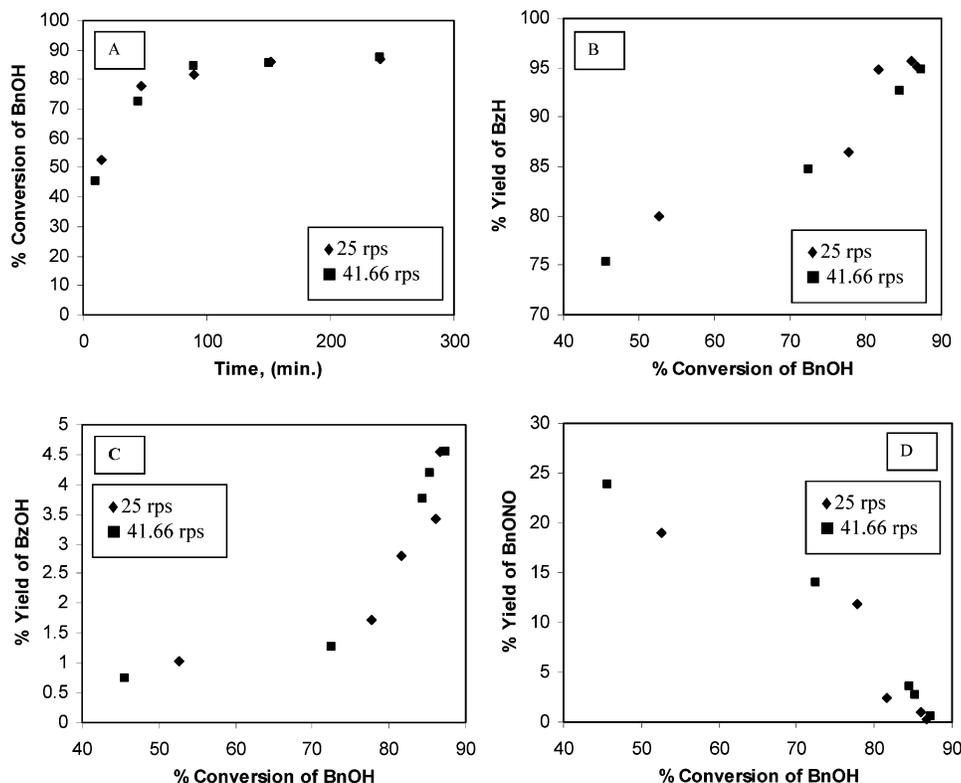
Figure 1. Effect of Impeller speed on the (A) conversion of BnOH (B) Yield of BzH (C) Yield of BzOH (D) Yield of Benzyl nitrite.

Table 3. Mass-Transfer Values at Different Nitric Acid Concentrations

	Value		
parameter	1.59 M	3.18 M	4.77 M
ϵ_L	0.26	0.53	0.80
a ($\times 10^{-2}$ m^2/m^3)	1511	2162	2532
d_D ($\times 10^5$ m)	1.05	1.47	1.89
k_L ($\times 10^5$ m/s)	1.42	0.99	0.85
$\sqrt{M}$ ($\times 10^1$)	0.10	0.20	0.30

Table 4. Mass-Transfer Values at Different Molar Ratios

	Value		
parameter	1:0.625	1:0.94	1:1.25
ϵ_L	0.26	0.18	0.13
a ($\times 10^{-2}$ m^2/m^3)	1511	2162	2532
d_D ($\times 10^5$ m)	1.05	0.91	0.84
k_L ($\times 10^5$ m/s)	1.56	2.73	0.849
$\sqrt{M}$ ($\times 10^1$)	0.10	0.08	0.03

occurs in the bulk of aqueous phase and the overall operation is reaction-controlled.

4. Results and Discussion

The conversion of BnOH (%) and the yield of product (%) were determined using the following formulas:

Conversion of BnOH (%) =

$$\frac{\text{mol of BnOH consumed}}{\text{mol of BnOH charged}} \times 100$$

Yield of product (%) =

$$\frac{\text{mol of product formed}}{\text{mol of BnOH consumed}} \times 100$$

4.1. Effect of Nitric Acid Concentration. To study the effect of concentration of nitric acid, 0.3 mol of BnOH was reacted with different concentrations of HNO$_3$, viz.

1.59, 3.18, and 4.77 M. The amount of HNO$_3$ taken in each experiment was kept constant at 0.1875 mol by appropriately reducing the volume of the aqueous phase to get the desired higher concentration of HNO$_3$. The experiments were performed at 70 °C and 41.66 rps. One gram of NaNO$_2$ was added to the reaction mixture in each case. Figure 2A shows the conversion of BnOH versus time for each case. The rate of reaction increased as the concentration of HNO$_3$ in the aqueous phase increased. Similar results have been reported by Levina et al.[19] Panels B−D in Figure 2 show the variation of yield of BzH, BzOH, and BnONO, with respect to conversion of BnOH. The yield of BzH decreases as the concentration of nitric acid increases, but the decrease in the yield is not pronounced. The yield of benzyl nitrite increases as the concentration of HNO$_3$ decreases.

4.2. Effect of Temperature. The effect of temperature on the yields of various reaction products, with respect to conversion of BnOH, was investigated. BnOH (0.3 mol) was reacted with 118 mL of 1.59 M HNO$_3$ in the presence of 1 g of NaNO$_2$ at 41.66 rps. The results are presented in panels A−D in Figure 3. Figure 3A shows the effect of temperature in the range of 70−90 °C and the corresponding increase the rate of reaction. Panels B and D in Figure 3 show that, when the reaction temperature increases, the yield of BzH increases with simultaneous decreases in the yield of benzyl nitrite. With increasing temperature, the stability of formed benzyl nitrite decreases and it undergoes fast decomposition to BzH. The work of Gray et al.[18] on benzyl nitrites supports the observation. The authors have reported an increased rate of decomposition, with respect to temperature, during the distillation of benzyl nitrite. The variation of BzOH versus the conversion of BnOH for different temperatures is shown in Figure 3C. The effect of temperature can be seen to be insignificant on the yield of BzOH.
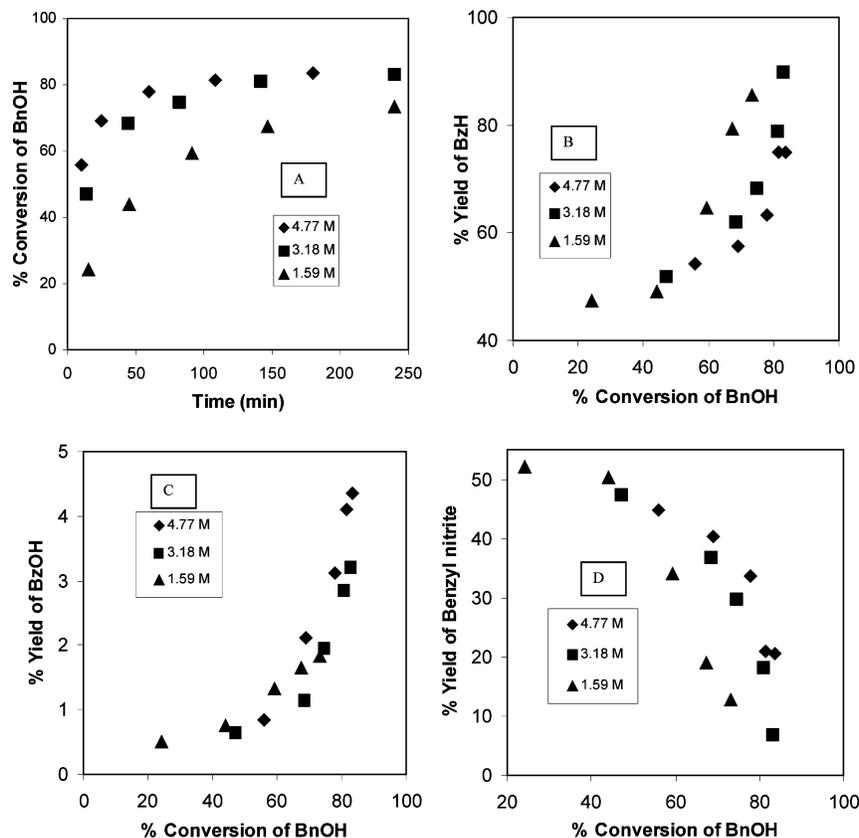
Figure 2. Effect of concentration of nitric acid on the (A) conversion of BnOH (B) Yield of BzH (C) Yield of BzOH (D) Yield of Benzyl nitrite.
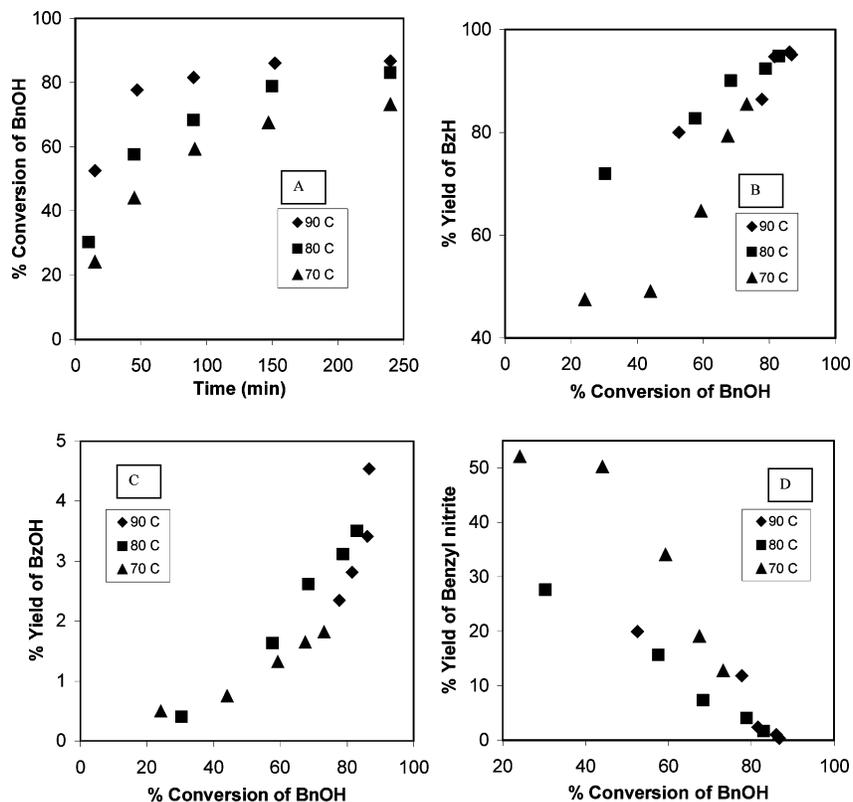
Figure 3. Effect of temperature on the (A) conversion on BnOH (B) Yield of BzH (C) Yield of BzOH (D) Yield of Benzyl nitrite.

4.3. Effect of Sodium Nitrite Loading. In the absence of nitrous acid, the reaction with 0.3 mol of BnOH and 118 mL of 1.59 M HNO₃ (no NaNO₂ added) at 70 °C, the conversion of BnOH was <2%, even after

4 h. It confirms that the nitric acid alone cannot significantly oxidize BnOH. Previous experiments have shown that the addition of a catalytic amount of sodium nitrite initiates the reaction and substantial conversion
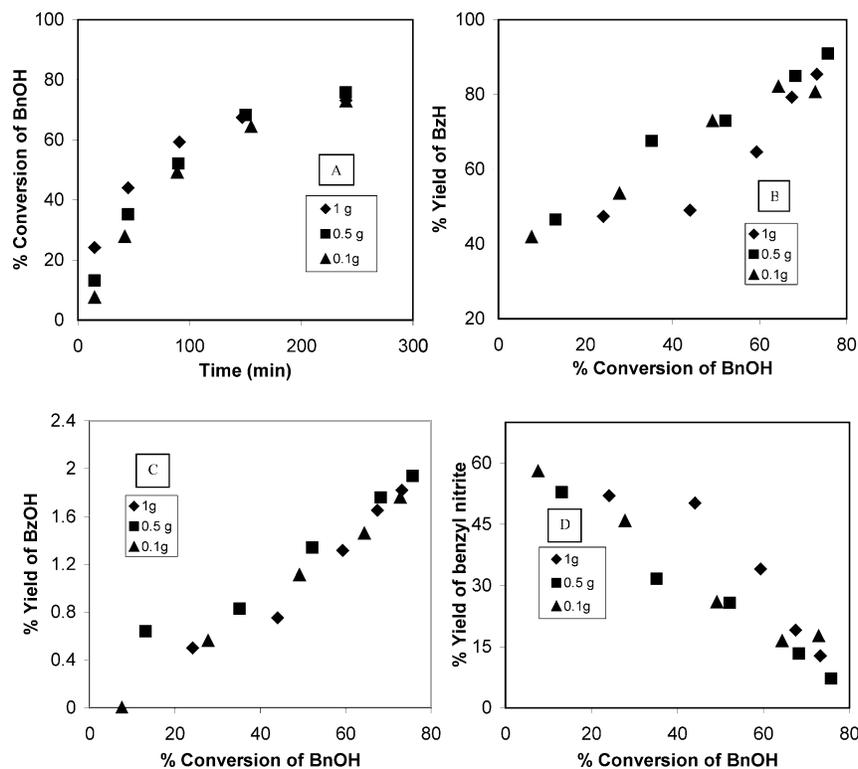
Figure 4. Effect of NaNO₂ loading on the (A) Conversion of BnOH (B) Yield of BzH (C) Yield of BzOH (D) Yield of Benzyl nitrite.

(>80%) of BnOH can be obtained thereafter.[15,16] The oxidation reaction does not proceed when urea is added to the reaction mixture, which is a known scavenger of nitrous acid. Thus, the generation of nitrous acid and its reaction with BnOH can be given as follows:

$$H^+ + NaNO_2 \rightarrow HNO_2 + Na^+ \tag{12}$$

$$HNO_2 + BnOH \rightarrow products \tag{13}$$
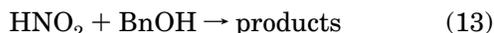
It was decided to investigate the effect of NaNO₂ concentration on the rate of oxidation by varying the loading of NaNO₂ as reported previously. BnOH (0.3 mol) was treated with 118 mL of 1.59 M HNO₃ at 70 °C at a stirring speed of 41.66 rps. Figure 4A shows the conversion of BnOH with time at sodium nitrite loadings of 0.1, 0.5, and 1 g. As stated previously, the reaction occurs to an insignificant extent in the absence of NaNO₂. However, there is a rather sharp increase in the rate of consumption of BnOH after the addition of 0.1 g of NaNO₂. The oxidation rate of BnOH does not increase significantly when NaNO₂ loading is further increased to 1 g. Panels B−D in Figure 4 show the effect of NaNO₂ concentration on the yields of BzH, BzOH, and benzyl nitrite, respectively. As can be seen from Figure 4A, with the increase in NaNO₂ loading, there is a slight increase in the initial conversion rate. This may be due to the high initial concentration of nitrous acid at high NaNO₂ loading. During the reaction, HNO₂ is also generated (eq 5) as a result; the initial NaNO₂ probably does not affect the effective concentration of HNO₂ significantly. Hence, there is no significant difference observed in the progress of the reaction over the range of NaNO₂ used.

4.4. Effect of Different Substrates. Ogata et al.[15] reported the effect of various substituents with a −σ value (electron-releasing groups) and a +σ value (electron-attracting groups) on the oxidation of BnOH. They

have observed that −σ substituents accelerate the reaction, whereas +σ substituents retard the reaction, satisfying Hammett's equation with a ρ-value of −2.25. The formation of BnONO can be considered as an electrophilic substitution reaction involving the benzyl radical. Thus, for such reactions, the electron-donating substituents will increase the electron density on the benzyl ring and will enhance the reaction and vice versa. Ogata et al.[15] estimated the oxidation rates of benzyl alcohol with the various substituents and determined the following order: p-MeO > p-Me > m-Me > H > p-Cl > m-Cl > p-NO₂. The chlorobenzyl alcohols with a +σ value should be more difficult to oxidize, as compared to benzyl alcohol. Therefore, the oxidation system was tested for substituents with +σ values, such as 2-chloro, 4-chloro, and 2,4-dichloro benzyl alcohols, so that it can be further applied to substituents with −σ values.

In the present work, 2-chloro, 4-chloro, and 2,4-dichlorobenzyl alcohols were used. To investigate the progress of reaction for the aforementioned chloro substrates, 0.3 mol of 4-chlorobenzyl alcohol, 2-chlorobenzyl alcohol, and 2,4-dichlorobenzyl alcohol were reacted separately with 236 mL of 4.77 M HNO₃ at 90 °C in the presence of 1 g of NaNO₂ and at a stirring speed of 41.66 rps. Figure 5A shows conversions of different chlorobenzyl alcohols with time. Panels B and C of Figure 5 show the yields of the corresponding aldehydes and acids, respectively. In the case of 4-chlorobenzyl alcohol, almost quantitative conversion of the substrate occurs within 5 min, with the yield of 4-chlorobenzaldehyde being 91%. The rate of consumption of 2,4-dichlorobenzyl alcohol is the slowest, compared to the rate of consumption of 2-chlorobenzyl alcohol and 4-chlorobenzyl alcohol. Nitrite ester was detected in the reaction mixture only in case of oxidation of 2-chlorobenzyl alcohol, showing its initial stability under the studied reaction condition. Figure 5B shows that the yield of 2-chlorobenzaldehyde increases initially and,
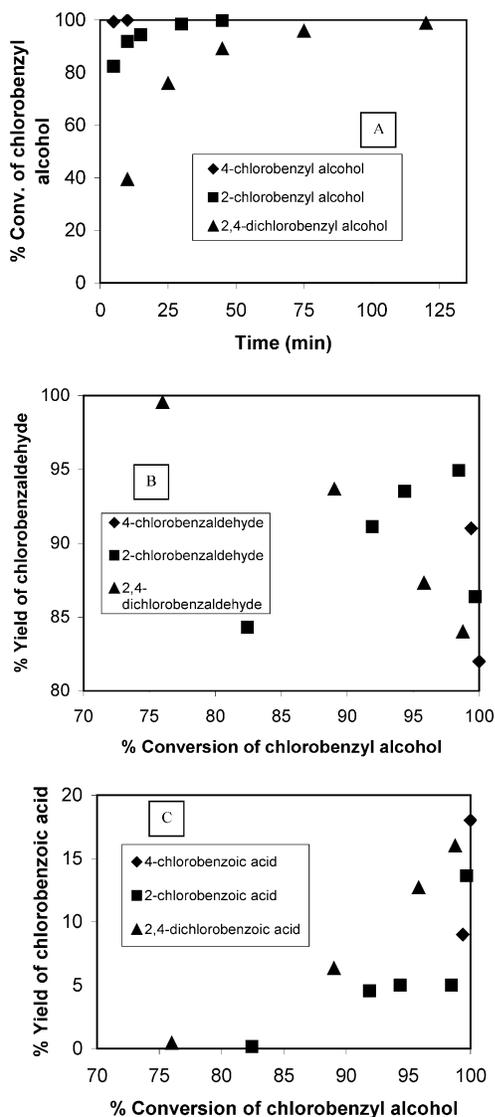
Figure 5. Effect of different substrates on the (A) Conversion of the chlorobenzyl alcohol (B) Yield of chlorobenzaldehdye (C) Yield of chlorobenzoic acid.

because of its further oxidation to 2-chlorobenzoic acid, its yield decreases as the time progress. The initial increase in the yield may be explained by the decomposition of 2-chlorobenzyl nitrite to 2-chlorobenzaldehyde; however, the further decrease in the yields of 2-chlorobenzaldehdye at higher reaction times may be attributed to the overoxidation to its corresponding acid formation. It can be noted that the experimental conditions used for the oxidation of the Cl−BnOH are extreme and thus it resulted to their high conversions. Such extreme conditions were not applied to benzyl alcohol. However, for the similar experimental conditions (T = 90 °C, [HNO$_3$] = 0.7 M, [BnOH] and [4-ClBnOH] = 0.03−0.1, and [NaNO$_2$] = 0.002 M), using dioxan as the solvent, Ogata et al.[15] determined that the reaction rate for BnOH was ∼3 times that of 4-ClBnOH.

4.5. Observations. From the range of parameters covered, the following is a summary of the main observations of the present study, as well as past investigations, which support the proposed mechanism in section 3.1.

(1) NaNO$_2$ acts only as the initiator of the reaction, and its concentration has practically no effect on the progress of the reaction. No reaction occurs in the absence of sodium nitrite.

(2) The estimation of nitrous acid by Ogata et al.[15] shows a continuous increase in its concentration as the conversion of benzyl alcohol increases.

(3) Figures 1−4 show that, in the majority of cases, the extent of benzyl nitrite formation is higher than that of the added NaNO$_2$. This observation further supports that the extent of HNO$_2$ formation is higher than that of the added NaNO$_2$.

(4) Benzyl alcohol does not undergo complete conversion, even at extended time, because of the reversible decomposition of benzyl nitrite to benzyl alcohol.

(5) Gray et al.[18] reported that the decomposition of BnONO results in the formation of benzyl alcohol and benzaldehyde.

(6) The material balance for all the experiments indicated that, for every mole of benzyl alcohol, one-half of a mole of HNO$_3$ is consumed.

4.6. Reaction Kinetics. The oxidation reactions of benzyl alcohol by nitric acid using sodium nitrite as an initiator were monitored by simultaneous measurement of concentration of benzyl alcohol, BzH, benzyl nitrite, and benzoic acid. All the reactions were studied at comparable alcohol amounts and nitric acid concentrations.

Various possible reaction schemes were tested, and the following reaction model is suggested for the benzyl alcohol oxidation to benzyl nitrite and BzH:

$$\text{BnOH (A)} + 0.5\text{HNO}_3 \text{ (B)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{BnONO (C)} \overset{k_2}{\rightarrow} \text{BzH}$$

$$\text{(D)} \xrightarrow[\text{HNO}_3]{k_3} \text{BzOH (E)} \quad (14)$$
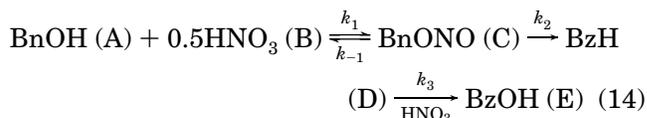
$$\frac{dC_A}{dt} = -\epsilon_L k_1 H_A C_A{}^2 C_B + \epsilon_L k_{-1} H_C C_C \quad (15)$$

$$\frac{dC_C}{dt} = \epsilon_L k_1 H_A C_A{}^2 C_B - \epsilon_L (k_{-1} + k_2) H_C C_C \quad (16)$$

$$\frac{dC_D}{dt} = \epsilon_L k_2 H_C C_C - \epsilon_L k_3 H_D C_D \quad (17)$$

$$\frac{dC_E}{dt} = \epsilon_L k_3 H_D C_D \quad (18)$$

where C_A, C_C, C_D, and C_E are the respective concentrations of alcohol, nitrite, aldehyde, and acid in the organic phase. H_A, H_C, and H_D are the corresponding partition coefficients. Therefore, $H_A C_A$, $H_C C_C$, and $H_D C_D$ are the saturation concentrations of A, B, and C in the aqueous phase. C_B is the concentration of nitric acid in the aqueous phase.

The concentration C_B was obtained in terms of C_A as follows:

$$2(C_{B_0} - C_B) = C_{A_0} - C_A \quad (19)$$

$$C_B = \left[C_{B_0} - \frac{1}{2}(C_{A_0} - C_A)\right] \quad (20)$$

Equations 15−18 were solved simultaneously using the RK4 method, and the values of rate constants were estimated using experimental data with the error minimization technique. A typical plot is shown in Figure 6. The rate constants for all the steps (in eq 14)
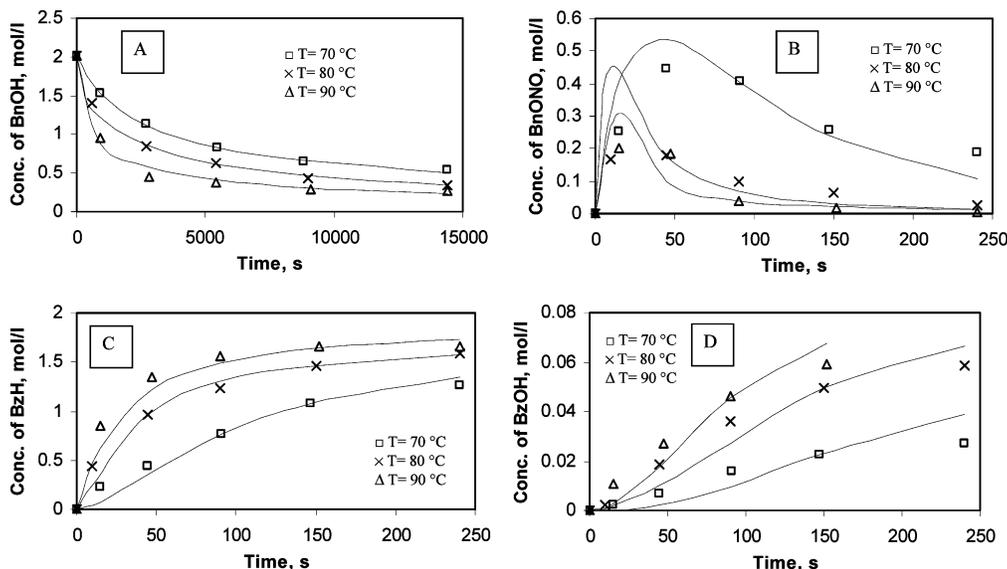
Figure 6. Experimental and fitted data at different temperatures for (A) BnOH (B) BnONO (C) BzH (D) BzOH.

Table 5. Values of Rate Constants at Different Temperatures[a]

	Value		
k-value ($\times 10^2$)	70 °C	80 °C	90 °C
k_1H_A (L mol)$^{-2}$ s^{-1}	1.16	4.14	5.60
$k_{-1}H_C$ (s^{-1})	0.02	6.75	4.50
k_2H_C (s^{-1})	2.39	8.86	14.78
k_3H_D ($\times 10^2$ L mol^{-1} s^{-1})	0.05	0.07	0.08

[a] BnOH content = 0.3 mol, HNO$_3$ concentration = 1.59 M, NaNO$_2$ content = 1 g, and speed of stirring = 41.66 rps.

Table 6. Activation Energy for Different Reactions

	activation energy (kJ/mol)	F-factor
k_1H_A	81.85	3.94×10^{10}
$k_{-1}H_C$	276.42	7.21×10^{38}
k_2H_C	94.62	6.94×10^{12}
k_3H_D	22.05	9.96×10^2

and the corresponding activation energies are given in Tables 5 and 6.

It may be noted that the reaction occurs in the aqueous phase. Because the mass transfer is accompanied by a chemical reaction, the values of the partition coefficients H_A, H_C, and H_D are not known: the values reported in Tables 5 and 6 are those of k_1H_A, $k_{-1}H_C$, k_2H_C, and k_3H_D. Also, to study the effect of nitric acid concentration and mole ratio, the phase ratios were changed. However, (i) because the reaction is kinetically controlled, the interfacial properties (such as effective liquid–liquid interfacial area and the mass-transfer coefficient) are unimportant, in regard to estimation of the kinetic parameters, and (ii) in the entire set of the experiments, the hold-up of the dispersed organic phase did not exceed a volume fraction of 0.45. Also, the impeller speed was kept always higher (41.66 rps), to prevent phase inversion. Thus, according to the regime criteria given by Reeve and Godfrey,[31] the aqueous phase always acted as the continuous phase with the organic phase dispersed in it.

Ogata et al.[15] studied the oxidation of benzyl alcohol in the presence of dioxan as a solvent. They used a mixture of HNO$_3$ and HClO$_4$ as an oxidizing agent. They proposed the formation of either BnONO$_2$ or BnONO as the intermediates. In the present work, an attempt

has been made to identify the probable intermediate. For this purpose, authentic samples of BnONO$_2$ and BnONO were prepared, according to the recommendations of Gray et al.[18] The comparison of the mass spectra of the authentic samples with the actual reaction intermediate confirmed the intermediate to be BnONO and did not have BnONO$_2$. The reaction mechanism and the subsequent rate analysis proposed by Ogata et al.[15] did not consider the formation of this intermediate. Furthermore, they also did not consider the heterogeneous nature of the oxidation reaction.

5. Conclusions

(1) Benzaldehyde (BzH) can be synthesized via the oxidation of benzyl alcohol by dilute nitric acid under milder conditions in the absence of any solvent.

(2) The reaction is a typical example of consecutive slow liquid–liquid reaction.

(3) Beyond 25 rps, the mass-transfer effects were negligible and the overall oxidation was reaction-controlled.

(4) The initial concentration of sodium nitrite does not significantly affect the overall progress of the reaction; however, its presence is necessary for the initiation of the reaction.

(5) During the oxidation of benzyl alcohol, the concentration of nitrous acid increases continuously.

(6) The intermediate formed during the reaction was determined to be benzyl nitrite. It undergoes reversible decomposition toward benzyl alcohol and irreversible decomposition toward BzH. Thus, benzyl alcohol does not undergo complete conversion, even at extended times.

(7) For every mole of benzyl alcohol oxidation, one-half of a mole of HNO$_3$ is consumed.

(8) The reaction kinetics of all the steps (eq 14) has been investigated, and the results have been given in Tables 5 and 6.

(9) The activation energy for benzyl alcohol was determined to be 81.85 kJ/mol. The formation of BzH from benzyl nitrite requires 94.62 kJ/mol of energy.

(10) Chloro-substituted benzyl alcohols can be successfully converted to corresponding aldehydes.

Nomenclature

[A*] = Concentration of A in aqueous phase (mol/L)

a = Interfacial area (m^2/m^3)

BnOH = Benzyl alcohol

BnONO = Benzyl nitrite

BzH = Benzyaldehyde

BzOH = Benzoic acid

C_A = Concentration of benzyl alcohol in the organic phase (mol/L)

C_B = Concentration of nitric acid in the aqueous phase (mol/L)

C_C = Concentration of benzyl nitrite in the organic phase (mol/L)

C_D = Concentration of benzaldehyde in the organic phase (mol/L)

C_E = Concentration of benzoic acid in the organic phase (mol/L)

C_{A0} = Initial concentration of benzyl alcohol in the organic phase (mol/L)

C_{B0} = Initial concentration of nitric acid in the aqueous phase (mol/L)

D_A = Diffusivity of A in the aqueous phase (m^2/s)

d_D = Droplet size (m)

H_A = Partition coefficients of benzyl alcohol

H_C = Partition coefficients of nitrite

H_D = Partition coefficients of aldehyde

k_1 = Rate constant for oxidation of benzyl alcohol ((L/mol)^{2}s^{-1})

k_{-1} = First-order rate constant for decomposition of benzyl nitrite to benzyl alcohol (s^{-1})

k_2 = First-order rate constant for decomposition of benzyl nitrite to benzaldehyde (s^{-1})

k_3 = First-order rate constant for oxidation of benzaldehyde to benzoic acid (s^{-1})

k_{mn} = Rate constant of order $(m + n)$

k_L = True mass transfer coefficient (m/s)

$k_L a$ = Volumetric mass-transfer coefficient (s^{-1})

$\sqrt{M}$ = Ratio of reaction in film to the reaction in the bulk (the Hatta number)

R = Overall rate of reaction (mol L^{-1} s^{-1})

Greek Letters

ϵ_L = Fractional hold-up of the organic phase in the aqueous phase

σ = Sigma values for Hammett's equation

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