

Article

Kinetics of Hydroxychlorination of Styrene Using Hydrogen Peroxide and Hydrochloric Acid

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Abstract

Styrene chlorohydrin is an important intermediate used in the manufacturing of high-value specialty chemicals. This paper focuses on understanding the kinetic aspects of styrene chlorohydrin production using hydrogen peroxide and hydrochloric acid. For this two-phase non-catalytic system, lab-scale initial rate experiments are conducted to assess the impact of key design parameters, such as reaction temperature, speed of agitation, and phase volume fraction, on the observed reaction rate. Based on these studies, it has been shown that this reaction takes place in the aqueous phase and the apparent order of reaction with respect to styrene, hydrogen peroxide and hydrochloric acid is approximately one, one and two, respectively. The corresponding Hatta number values are much smaller than one and the enhancement factor is approximately one, confirming that the system operates in regime I. Subsequently, a detailed reaction mechanism is proposed to capture the composition profiles of styrene chlorohydrin as well as the other major side products. The proposed model is then validated against composition trends observed in full-batch experiments. The model captured concentration profiles accurately, yielding sum of squared error (SSE) values around three. This model can be utilized to design and optimize the commercial manufacturing process for styrene chlorohydrin.

Keywords: hydroxychlorination; mass transfer with chemical reaction; heterogeneous liquid-liquid system; regime I

1. Introduction

Styrene chlorohydrin ($C_6H_5-CHOH-CH_2Cl$) is an important intermediate used in specialty chemicals manufacturing. Styrene chlorohydrin and its derivatives are integral to modern industrial and chemical applications, offering flexibility and efficiency when producing high-value compounds. As a member of the chlorohydrin family, it contains one chlorine atom along with an alcoholic hydroxyl group. Due to the presence of the OH and Cl groups, it has significant solvent potential and serves as a versatile raw material for producing glycols, acetates, nitrates, oxides, and other derivatives. Its reactivity makes it suitable for synthesizing oxidized olefin derivatives [1]. It acts as an intermediate in chemical synthesis for key products like phenyl ethyl alcohol (a perfume ingredient), styrene oxide, ω -bromostyrene [2] and pharmaceutical drugs such as synthomycin and levomycetin [3,4]. Furthermore, it can be easily converted into epoxides, amino alcohols, and hydroxy acids. It is also used to formulate plasticizers for lacquers (especially cellulose



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ester lacquers), resins, and plastics and as a solvent in refining oil fractions and in high-boiling solvents for paints, varnishes, and coatings [5].

Different synthesis routes for styrene chlorohydrin, such as hydroxychlorination of styrene [6], ring opening of styrene oxide [7], metal–organic reaction with benzaldehyde [8], 1,2-difunctionalization of styrene [9], oxidative chlorination of styrene [2] as well as biochemical synthesis routes [10], have been proposed in the literature.

Styrene chlorohydrin is primarily synthesized via hydroxychlorination of styrene using hypochlorous acid (HOCl) [11]. However, HOCl's instability above 1–2% concentration limits the overall performance [12]. While in situ HOCl generation from hypochlorites and acids is common, it is still constrained by HOCl instability [13]. Furthermore, direct reaction of styrene with HOCl is also associated with the production of side products like styrene dichloride or benzaldehyde. Another approach for the synthesis of styrene chlorohydrin involves ring opening of styrene oxide with various chlorine sources such as HCl [14], metal chlorides [7] or ionic liquids [15]. However, these methods suffer from limitations such as the need for in situ preparation of reagents, slow reaction kinetics, elevated temperature requirements, low atom efficiency and prior synthesis of styrene oxide. The addition of organometallic reagents to carbonyl groups is a well-established method for forming carbon–carbon bonds. For chlorohydrin synthesis via such additions, carbenoid reagents bearing both metal–carbon and carbon–chlorine bonds can be used. Accordingly, Clososki et al. used benzaldehyde and stabilized $\text{ClCH}_2\text{MgCl} \cdot \text{LiCl}$ to prepare styrene chlorohydrin using a low-temperature process [8]. The high cost and thermal sensitivity of these reagents make them unsuitable for industrial-scale production of styrene chlorohydrin. On the other hand, a few reagent systems have been reported in the literature for direct transformation of carbon–carbon double bonds to the corresponding 1,2-difunctionalized alkane i.e., the chloroalcohol derivative. These reagents include 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) in *N*-tosyl-L-threonine (NTsLT)/*t*-BuOH/water [9] or *N*-chlorosuccinimide (NCS)/thiourea in THF/ H_2O [16]. However, due to high reagent cost and the need to use strong acid as a chlorinating agent, these methods have limited practical importance. Lastly, enantiomerically pure styrene chlorohydrin can be obtained by microbial reduction of α -haloacetophenones [10] or by kinetic resolution using lipases [17]. However, such biochemical reactions are slow, sensitive to operating conditions, and require costly enzymes.

Owing to the limitations of the above-mentioned approaches, there is a need to develop a simple, efficient and sustainable method for the production of styrene chlorohydrin. From a green chemistry point of view, avoiding toxic and/or hazardous reagents and solvents, diminishing the energy consumption, obtaining high atom efficiency and using healthy and safer reaction processes are highly desirable. To this end, oxidative chlorination via in situ generation of the chlorinating agent from the oxidation of chloride ion with a suitable oxidant has emerged as a powerful tool for the production of chlorinated synthons [18]. Accordingly, styrene chlorohydrin can be produced from hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) as a water-soluble oxidant [2].

The process of preparing styrene chlorohydrin from styrene, HCl and H_2O_2 is challenging due to the intricate coupling of reaction kinetics and mass transfer effects. Specifically, in this two-phase system, styrene and its derivatives occupy the organic phase whereas HCl, H_2O_2 and water formed in the reaction occupy the aqueous phase. For optimization and scale up of this system, it is important to identify the regime of this system [19]. Based on the rate-controlling step, the corresponding kinetic mechanism can then be formalized. For example, if the reaction is kinetically controlled then the reaction kinetics would be required for further analysis. On the other hand, if the mass transfer rate governs the overall process, then the estimation and optimization of the corresponding mass transfer

coefficient would be required. While preliminary kinetic studies on hydroxychlorination of styrene were pursued by Novikov et al. [6], the detailed reaction mechanism and the impact of mass transfer have never been formally explored for this system.

Motivated by this, this paper focuses on the mass transfer and kinetic aspects of this styrene/HCl/H₂O₂ system. Specifically, initial rate experiments are conducted to analyze the impact of key operational factors, such as speed of agitation, phase volume fraction, and reaction temperature to identify the controlling regime for this reaction. Subsequently, full-batch experiments are carried out to establish a detailed rate model for this system, which can be used to optimize the process (e.g., maximization of styrene chlorohydrin selectivity).

The rest of the paper is organized as follows. Section 2 details the reactions and mass transfer processes involved in this system, describes the experimental setup and specifies the analysis methods employed in this work. Furthermore, the approach used to identify the rate limiting step and the corresponding mechanism are also presented. Section 3 presents the results obtained from the initial rate as well as the full batch experimental studies. Lastly, Section 4 presents an analysis of these results and draws key conclusions concerning this reaction system.

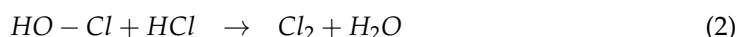
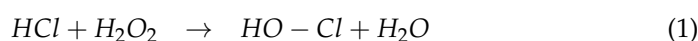
2. Materials and Methods

This section describes the chemistry of the reaction system, the experimental setup and analytical techniques used to estimate compositions, and the methodology followed to identify the key kinetic and mass transfer aspects of this system.

2.1. Reaction and Mass Transfer Aspects

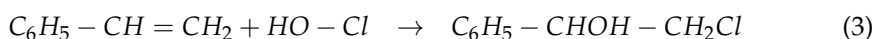
Styrene hydroxychlorination by aqueous hydrogen peroxide and hydrochloric acid is an example of a liquid–liquid heterogeneous reaction system. While styrene forms the organic phase, hydrogen peroxide and hydrochloric acid occupy the aqueous phase. The main reactions taking place in this system are described below.

1. HCl and H₂O₂ react to form hypochlorous acid. Furthermore, HOCl can react with another molecule of HCl to form aqueous chlorine [20].



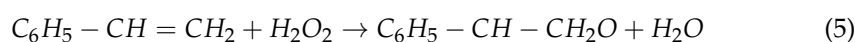
Because both species reside in the aqueous phase, these reactions take place entirely within it.

2. Styrene reacts with HOCl to form styrene chlorohydrin which is the product of interest. In a parallel reaction, styrene can also react with aqueous chlorine to form undesired product styrene dichloride [21].

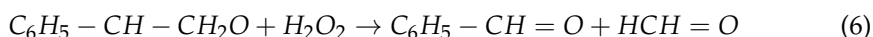


Depending on the reacting phase, either/both of the reactants will move towards the reacting phase for this reaction to take place. For example, if the reaction takes place in the aqueous phase, styrene will diffuse into the aqueous phase.

3. Similarly, styrene can also react directly with H₂O₂ to form styrene oxide, another undesired product [22].



4. Lastly, styrene oxide can be further oxidized to benzaldehyde and formaldehyde [23].



After all the reactions are completed to their respective extents, the unreacted reactants and products migrate to their preferred phases. Specifically, HCl and H₂O₂ return to the aqueous phase, whereas the organic phase consists of unreacted styrene, styrene chlorohydrin, styrene dichloride, styrene oxide, benzaldehyde and formaldehyde.

2.2. Experimental Setup

The experiments described in this paper were conducted in a 250 mL three-neck jacketed glass reactor equipped with a removable baffle and a four-blade turbine agitator as schematically depicted in Figure 1. The reaction setup included a circulating water bath to maintain isothermal conditions. Each experimental run commenced with the preparation of reactant solutions at the desired concentrations using deionized water and n-heptane as diluent for the aqueous and organic phases, respectively.

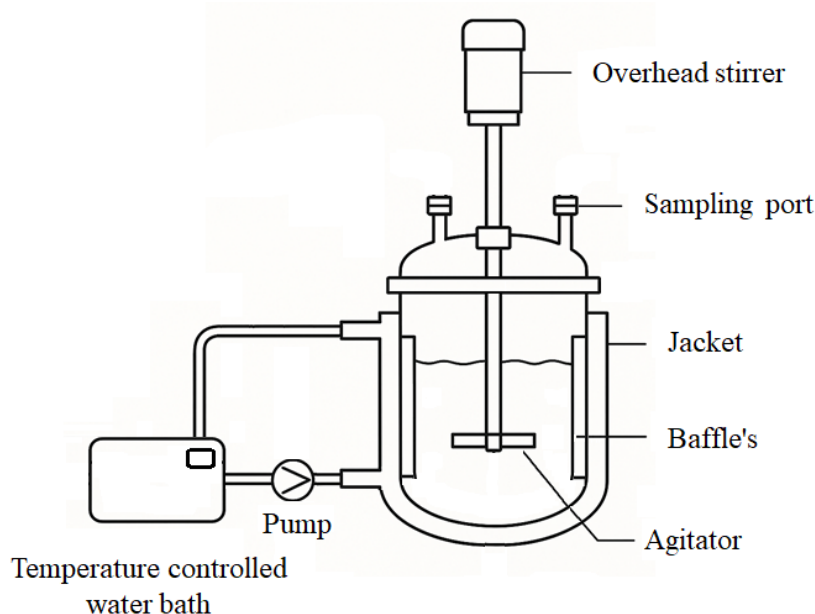


Figure 1. Schematic diagram of the experimental setup.

Each experimental run was started by charging the reactor with reagents at the required preheated temperature and a specified impeller speed. Small quantities of reaction mixture (organic and aqueous) were withdrawn periodically for analysis of composition.

2.3. Analysis Method

Gas chromatography (GC) was employed for the analysis of organic species, while ion chromatography (IC), high-performance liquid chromatography (HPLC) and titration were used for the analysis of aqueous species. The specific details are presented below.

- GC: The GC analysis was carried out with Thermofisher trace 1110 GC coupled with 28 a DB-5 MS capillary column, with nitrogen serving as the carrier gas and a flame 29 ionization detector employed as the detector. The specific parameters included 1 µL of injection volume, whereas injection and detector temperature set to 280 °C, a nitrogen (carrier gas) flow rate of 1 mL/min with a split ratio of 1:80, and temperature programming set as follows: 50 °C with a 2 min hold, a ramp from 50 °C to 135 °C (at a rate of 30 °C/min) with a 5.5 min hold, a ramp from 135 °C to 182 °C (at a rate of

30 °C/min) with a 7 min hold, and a final ramp from 182 °C to 300 °C (at a rate of 30 °C/min) with a 2 min hold. GC samples were prepared using 10 µL from the organic reaction mixture phase diluted with 1000 µL of 1,2 dichloroethane solvent.

- IC: The chloride anions in aqueous media were analyzed with a Thermoscientific Dionex Aquion ion chromatography instrument coupled with an AS-11 Column 4.5 mM sodium carbonate and 0.8 mM sodium bicarbonate mobile phase with 1 mL/min flow.
- Titration: The strength of hydrochloric acid was determined by titration against 0.1 M sodium carbonate (Na_2CO_3). Standardization of Na_2CO_3 was performed using 0.1 M oxalic acid. Phenolphthalein was used as an indicator during standardization and to determine the strength of HCl.
- HPLC: The aqueous styrene concentration was determined using a Scientific Dionex Ultimate 3000 system coupled with a UV detector. An aliquot of 10 µL from the aqueous phase was initially diluted with 1000 µL of acetonitrile, followed by a second dilution of 25 µL of the mixture with 1000 µL of acetonitrile for a 10 µL HPLC injection. The samples were analyzed at an Isocratic (1 mL/min) mobile phase composed of Acetonitrile (75%) and water (25%) for 15 min at 254 nm wavelength using COSMOSIL 5C18-MS-II packed column.

2.4. Approach to Identify Rate Determining Step

As the reaction system involves two phases, reactants have to diffuse to a reaction zone. Depending on the specific conditions, the reaction zone may either lie directly at the interface or extend into one or both the phases near the interface. The location of the reactive region is determined by the balance between reaction velocity and diffusion rates. In the limiting case where the intrinsic reaction rate is much slower than mass transfer, the system is kinetically controlled and the reaction occurs uniformly in one of the phases. In this case, the observed rate of reaction is the same as the intrinsic rate of reaction. Conversely, if the intrinsic reaction rate is much faster than the mass transfer rate, the rate of chemical conversion is controlled by mass transfer. In this case, the observed rate of reaction is the same as the intrinsic mass transfer rate. To this end, it is important to first determine the location of the reaction regime based on the relative rates of reaction and mass transfer.

Let us consider a general heterogeneous reaction $A + zB \rightarrow P$. For the main reaction (3) of our system, if the reaction takes place in the aqueous phase, styrene and hypochlorous acid can be considered as A and B , respectively, and z is 1. This heterogeneous reaction with mass transfer can belong to one of the following four regimes [19].

1. Regime I: This kinetically controlled regime captures the case when the rate of chemical reaction is much slower than the rate of mass transfer. For this case, the observed volumetric rate of reaction (r_{obs}) can be written as

$$r_{obs} = \varepsilon_L k [A^*]^m [B_0]^n \quad (7)$$

where ε_L represents the fractional holdup of the aqueous phase, $[A^*]$ represents the saturation concentration of styrene in the aqueous phase, $[B_0]$ represents the bulk concentration of hypochlorous acid and m and n represent the order of reaction with respect to styrene and hypochlorous acid, respectively. It can be noted that, in this case, the observed rate of reaction is a function of the volume fraction of the reaction phase, the intrinsic rate constant (and thus reaction temperature) and species concentration of both the reacting components.

2. Regime II: This regime represents a slow reaction system. In this case, the rate of reaction is faster than the rate at which A enters the reacting phase. In this regime, the

overall rate is controlled by the rate at which A is transferred to the reacting phase and the observed rate can be given by the following expression.

$$r_{obs} = k_L \underline{a} [A^*] \quad (8)$$

where k_L represents the mass transfer coefficient for styrene and $\underline{a}$ represents the interfacial area. It can be noted that, in this case, the observed rate of reaction is a function of the intrinsic mass transfer coefficient (and thus the speed of agitation), the interfacial area and concentration of only the diffusing species (A).

3. Regime III: This regime represents fast reaction and the reaction takes place inside the film surrounding the interface. For this case, the observed rate of reaction can be given by the following expression.

$$r_{obs} = [A^*] \sqrt{\frac{2}{m+1} D_A k [A^*]^{m-1} [B_0]^n} \quad (9)$$

where D_A is the diffusivity of A. For this regime, the observed rate of reaction is a function of species concentration of both the reacting components, but is independent of the reacting phase volume fraction.

4. Regime IV: This regime represents instantaneous (very fast) reaction. For this regime, the observed rate of reaction can be written as

$$r_{obs} = \frac{k_L [B_0] D_B}{z D_A} \quad (10)$$

where D_B is the diffusivity of B. For this regime, the observed rate of reaction is a function of the intrinsic mass transfer coefficient and bulk phase concentration of B.

Based on Equation (7)–(10), it can be seen that the regime of reaction can be determined by studying the variation in the observed rate of reaction with temperature (intrinsic rate constant), speed of agitation (intrinsic mass transfer coefficient), phase volume fraction and species concentration. To this end, initial rate studies are conducted to determine the reaction phase and the corresponding regime of the system. Specifically, the following experiments are conducted.

1. Variation in phase volume fraction.
2. Variation in speed of agitation.
3. Variation in reaction temperature.
4. Variation in initial concentration.

For each of these experiments, the initial rate of consumption of styrene is computed by the slope of styrene concentration profile at the start of the reaction. Subsequently its correlation with various factors is analyzed to establish regime and reaction phase.

2.5. Approach to Formulate Kinetic Model

In order to formulate a detailed kinetic model of this reaction system, mass balance equations are written for the key reactants and products based on reactions (1)–(6). For a batch system, assuming that the reaction takes place in the aqueous phase following regime I, the dynamic evolution of various species is governed by the following equations.

$$\begin{aligned}
\frac{dC_{HCl}}{dt} &= -k_1 C_{HCl} C_{H_2O_2} - k_2 C_{HOCl} C_{HCl} \\
\frac{dC_{H_2O_2}}{dt} &= -k_1 C_{HCl} C_{H_2O_2} - k_5 C_S C_{H_2O_2} - k_6 C_{SO} C_{H_2O_2} \\
\frac{dC_{HOCl}}{dt} &= k_1 C_{HCl} C_{H_2O_2} - k_2 C_{HOCl} C_{HCl} - k_3 C_S C_{HOCl} \\
\frac{dC_S}{dt} &= -k_3 C_S C_{HOCl} - k_4 C_S C_{Cl_2} - k_5 C_S C_{H_2O_2} \\
\frac{dC_{Cl_2}}{dt} &= k_2 C_{HOCl} C_{HCl} - k_4 C_S C_{Cl_2} \\
\frac{dC_{SCH}}{dt} &= k_3 C_S C_{HOCl} \\
\frac{dC_{SDC}}{dt} &= k_4 C_S C_{Cl_2} \\
\frac{dC_{SO}}{dt} &= k_5 C_S C_{H_2O_2} - k_6 C_{SO} C_{H_2O_2} \\
\frac{dC_{BNZ}}{dt} &= k_6 C_{SO} C_{H_2O_2} \\
\frac{dC_{FM}}{dt} &= k_6 C_{SO} C_{H_2O_2}
\end{aligned} \tag{11}$$

where C_i refers to the concentration of species i in the aqueous phase. Subscripts HCl , H_2O_2 , $HOCl$, S , Cl_2 , SCH , SDC , SO , BNZ and FM refer to hydrochloric acid, hydrogen peroxide, hypochlorous acid, styrene, chlorine, styrene chlorohydrin, styrene dichloride, styrene oxide, benzaldehyde and formaldehyde, respectively. k_1 to k_6 represent kinetic rate constants for reactions (1)–(6), respectively. The above model is simplified by considering quasi-steady state approximation for some of the intermediate species. Furthermore, the aqueous phase concentration of styrene, styrene chlorohydrin, styrene dichloride and benzaldehyde is expressed in terms of their organic phase concentration using the corresponding partition coefficients. Accordingly, the reduced kinetic model is given by Equation (12).

$$\begin{aligned}
\frac{dC_{HCl}}{dt} &= -k_1 C_{HCl} C_{H_2O_2} - k_2 \left(\frac{k_1 C_{HCl} C_{H_2O_2}}{k_2 C_{HCl} + k_3 \left(\frac{C_S^{org}}{P_S} \right)} \right) C_{HCl} \\
\frac{dC_{H_2O_2}}{dt} &= -k_1 C_{HCl} C_{H_2O_2} - 2k_5 \left(\frac{C_S^{org}}{P_S} \right) C_{H_2O_2} \\
\frac{dC_S^{org}}{dt} &= P_S \left[-k_3 \left(\frac{C_S^{org}}{P_S} \right) \left(\frac{k_1 C_{HCl} C_{H_2O_2}}{k_2 C_{HCl} + k_3 \left(\frac{C_S^{org}}{P_S} \right)} \right) - \left(\frac{k_1 k_2 C_{HCl}^2 C_{H_2O_2}}{k_2 C_{HCl} + k_3 \left(\frac{C_S^{org}}{P_S} \right)} \right) \right. \\
&\quad \left. - k_5 \left(\frac{C_S^{org}}{P_S} \right) C_{H_2O_2} \right] \\
\frac{dC_{SCH}^{org}}{dt} &= P_{SCH} k_3 \left(\frac{C_S^{org}}{P_S} \right) \left(\frac{k_1 C_{HCl} C_{H_2O_2}}{k_2 C_{HCl} + k_3 \left(\frac{C_S^{org}}{P_S} \right)} \right) \\
\frac{dC_{SDC}^{org}}{dt} &= P_{SDC} k_2 C_{HCl} \left(\frac{k_1 C_{HCl} C_{H_2O_2}}{k_2 C_{HCl} + k_3 \left(\frac{C_S^{org}}{P_S} \right)} \right) \\
\frac{dC_{BNZ}^{org}}{dt} &= P_{BNZ} k_5 \left(\frac{C_S^{org}}{P_S} \right) C_{H_2O_2}
\end{aligned} \tag{12}$$

where P_i represents the partition coefficient for component i . It can be noted from Equation (12) that there are four unknown kinetic parameters (k_1 , k_2 , k_3 , and k_5) and four partition coefficients (P_S , P_{SCH} , P_{SDC} and P_{BNZ}). To estimate these parameters, full-batch experiments are carried out and the composition of key variables in both the phases (organic and aqueous) is measured/estimated. Specifically, multiple batch runs were conducted for varying ratio of initial amount of the three raw materials (styrene, HCl and H_2O_2). At the end of every hour, aqueous and organic samples were taken out for analysis. The organic phase composition of styrene, styrene chlorohydrin, styrene dichloride and benzaldehyde was estimated using GC. The corresponding details are provided in the supplementary text. The aqueous phase composition of chloride ions was estimated using ion chromatography, as described in Section 2.3. The aqueous phase H_2O_2 concentration can be measured by UV spectroscopy or via the $KMnO_4$ titration method. However, the presence of Cl^- ions in the aqueous phase interferes with both these estimation methods [24]. Therefore, instead of actual measurement, the corresponding aqueous phase concentration of H_2O_2 was estimated by closing the material balance of the system. While this adds some level of uncertainty to the estimated kinetic parameters, we believe that those variations are within the acceptable levels of measurement error. Subsequently, the equation system (12) was numerically integrated using MatLab's ode15s function and the unknown parameters were estimated by minimizing the error between the predicted and actual values of species concentration.

3. Results

3.1. Initial Rate Studies

As mentioned in the previous section, initial rate studies were conducted by varying overall system operating parameters such as phase volume fraction, operating temperature, speed of agitation and the initial concentration of reacting species. The specific details of these studies are given below.

3.1.1. Variation in Phase Volume Fraction

For this set of experiments, pure styrene was taken as the organic phase. This was contacted with aqueous phase containing HCl and H_2O_2 . The corresponding initial concentrations of styrene (organic phase), HCl (aqueous phase) and H_2O_2 (aqueous phase) were 8.61, 3.67 and 4.57 mol/L, respectively. The reaction was carried out at 30 °C and 600 RPM agitation. For a total liquid volume of 60 mL, the aqueous phase volume fraction was varied from 65% to 85%. The corresponding variation in the initial rate of consumption of styrene on molar as well as volumetric basis is given in Table 1.

Table 1. Effect of aqueous phase volume fraction on rate of consumption of styrene.

ε_L	Molar Rate (mol/h $\times 10^3$)	Volumetric Rate—Overall (mol/L·h)	Volumetric Rate—Aqueous (mol/L·h)
0.65	4.3 $\pm$ 0.03	0.071 $\pm$ 0.001	0.109 $\pm$ 0.001
0.75	5.1 $\pm$ 0.09	0.086 $\pm$ 0.002	0.114 $\pm$ 0.002
0.85	6.8 $\pm$ 0.24	0.114 $\pm$ 0.004	0.134 $\pm$ 0.005

3.1.2. Variation in Speed of Agitation

In this set of experiments, for the same initial feed composition and total volume as the previous case, and with an aqueous phase volume fraction of 0.75, the speed of agitation was varied between 200 and 1200 rpm. This variation was studied for two

different reaction temperatures, 30 °C and 45 °C. The corresponding variation in the initial rate of consumption of styrene is given in Table 2.

Table 2. Effect of speed of agitation on the rate of consumption of styrene.

Speed (rpm)	Molar Rate (mol/h $\times 10^3$)	Volumetric Rate—Overall (mol/L·h)	Volumetric Rate—Aqueous (mol/L·h)
Reaction temperature = 30 °C			
200	2.0 $\pm$ 0.10	0.033 $\pm$ 0.002	0.044 $\pm$ 0.002
400	4.9 $\pm$ 0.16	0.082 $\pm$ 0.003	0.109 $\pm$ 0.004
600	5.1 $\pm$ 0.09	0.086 $\pm$ 0.002	0.114 $\pm$ 0.002
800	4.7 $\pm$ 0.06	0.079 $\pm$ 0.001	0.105 $\pm$ 0.001
1000	3.7 $\pm$ 0.04	0.061 $\pm$ 0.001	0.082 $\pm$ 0.001
1200	3.6 $\pm$ 0.23	0.061 $\pm$ 0.004	0.081 $\pm$ 0.005
Reaction temperature = 45 °C			
200	13.1 $\pm$ 3.02	0.219 $\pm$ 0.050	0.292 $\pm$ 0.067
400	25.3 $\pm$ 1.30	0.422 $\pm$ 0.022	0.562 $\pm$ 0.029
600	25.9 $\pm$ 0.21	0.431 $\pm$ 0.003	0.574 $\pm$ 0.005
900	23.4 $\pm$ 0.97	0.390 $\pm$ 0.016	0.519 $\pm$ 0.021
1200	17.9 $\pm$ 0.43	0.299 $\pm$ 0.007	0.398 $\pm$ 0.010

3.1.3. Variation in Reaction Temperature

For this study, the reaction was carried out at four different temperatures using the temperature-controlled water bath. The speed of agitation was kept at 600 rpm and all the other parameters were kept the same as in the previous study. The corresponding results are tabulated in Table 3.

Table 3. Effect of reaction temperature on rate of consumption of styrene.

Temperature (°C)	Volumetric Rate—Overall (mol/L·h)	Volumetric Rate—Aqueous (mol/L·h)	Solubility ¹ (mol/L)
20	0.038 $\pm$ 0.004	0.050 $\pm$ 0.005	0.0032
30	0.086 $\pm$ 0.002	0.114 $\pm$ 0.002	0.0036
40	0.241 $\pm$ 0.013	0.321 $\pm$ 0.018	0.0040
45	0.431 $\pm$ 0.004	0.574 $\pm$ 0.005	0.0042

¹ Styrene solubility in water [25].

3.1.4. Variation in Initial Concentration

For these studies, the concentration of one of the reacting species was varied while the concentration of the other species as well as the other reaction parameters were kept the same as in the previous studies. To study variation with respect to styrene concentration, the concentration of styrene in the organic phase was varied by using n-Heptane as a diluent. The corresponding results are given in Table 4.

3.2. Full-Batch Studies

For these studies, full-batch experiments were conducted using two different initial concentrations. Specifically, for the first run, the molar ratio of styrene to hydrochloric acid and hydrogen peroxide was taken as 1:1.3:1.6. Similarly, for the second run, this ratio was changed to 1:1.3:3.1. For these experiments, the speed of agitation was kept at 600 rpm, the aqueous phase volume fraction was fixed at 0.75 and the reaction temperature was set at 45 °C. For both the cases, the reaction was continued till styrene conversion exceeded 90%. The corresponding concentration-time data is given in Table 5. Here, selectivity towards the desired product, styrene chlorohydrin, is defined as the amount of the desired product

formed as a fraction of the total limiting reagent (styrene) reacted. Similarly, the yield of styrene chlorohydrin is computed as the amount of the desired product formed as a fraction of the total limiting reagent (styrene) in the feed.

Table 4. Effect of reactant's initial concentration on rate of consumption of styrene.

C_S^{org} (mol/L)	C_S (mol/L $\times 10^3$)	C_{HCl} (mol/L)	$C_{H_2O_2}$ (mol/L)	Volumetric Rate—Aqueous (mol/L·h)
4.00	1.34	3.67	4.57	0.092 ± 0.003
5.00	1.56			0.114 ± 0.002
6.00	1.64			0.128 ± 0.024
7.00	1.94			0.134 ± 0.001
8.61	2.36	3.67	1.00	0.026 ± 0.001
			2.00	0.050 ± 0.005
			6.00	0.171 ± 0.004
			8.00	0.274 ± 0.007
8.61	2.36	3.67	1.24	0.011 ± 0.002
			1.89	0.013 ± 0.001
			2.51	0.028 ± 0.004
			3.13	0.059 ± 0.005
			3.67	0.114 ± 0.002

Table 5. Concentration–time data for full-batch experiments.

Time (h)	C_S^{org} (mol/L)	C_{HCl} (mol/L)	$C_{H_2O_2}$ (mol/L)	C_{SCH}^{org} (mol/L)	C_{SDC}^{org} (mol/L)	C_{BNZ}^{org} (mol/L)	Selectivity (%)	Yield (%)
Run I: S:HCl:H ₂ O ₂ = 1:1.3:1.6								
0	8.83	3.67	4.56	0.00	0.00	0.00	-	0.0
1	5.42	1.97	3.31	1.98	1.09	0.34	58.1	22.4
2	3.94	1.61	2.78	3.08	1.34	0.47	63.0	34.9
4	2.82	1.29	2.41	4.05	1.53	0.44	67.4	45.9
6	2.03	1.05	2.17	4.88	1.54	0.39	71.8	55.3
12	1.25	0.79	1.92	5.60	1.63	0.35	73.9	63.4
18	0.82	0.67	1.77	6.00	1.64	0.37	74.9	68.0
Run II: S:HCl:H ₂ O ₂ = 1:1.3:3.1								
0	8.83	3.67	8.99	0.00	0.00	0.00	-	0.0
1	3.10	0.87	6.92	3.48	1.75	0.49	60.7	39.4
2	2.25	0.78	6.65	4.25	1.91	0.42	64.6	48.1
4	1.37	0.52	6.35	5.08	1.93	0.45	68.1	57.5
6	0.96	0.38	6.19	5.32	2.02	0.53	67.6	60.2
12	0.38	0.20	6.06	6.07	2.04	0.34	71.8	68.7

4. Discussion

Let us now analyze the results to establish the key kinetic aspects of this system.

4.1. Rate Controlling Step

Let us first identify the reacting phase. Figure 2 captures the variation in the initial rate of styrene consumption with aqueous phase volume fraction. It can be seen that, for the same initial concentration of the reactants, there is a proportionate rise in the net rate of consumption of styrene (on a molar basis or a total volume basis) with an increment in aqueous phase volume fraction. On the other hand, there is marginal variation in the volumetric rate computed on the basis of aqueous phase volume. Based on this, it can be argued that the reaction is taking place in the aqueous phase, potentially following regime I kinetics (see Equation (7)).

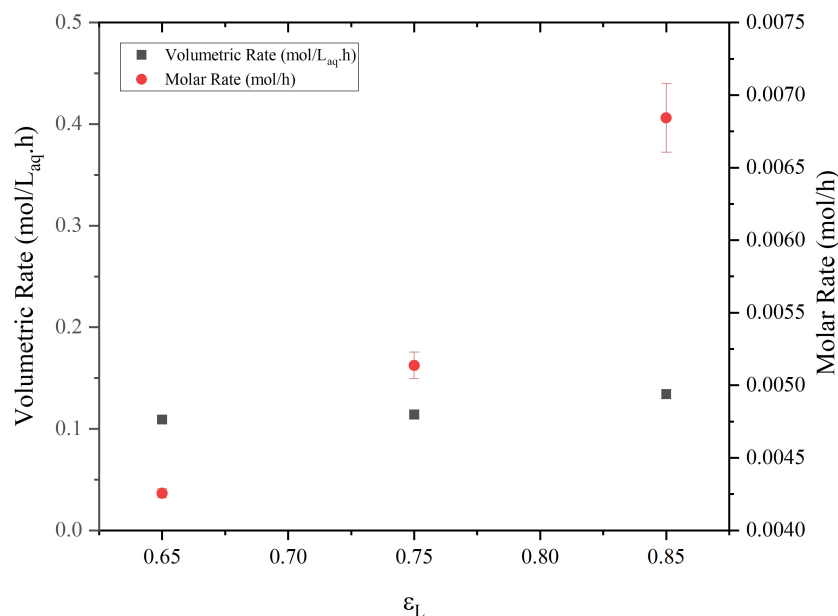


Figure 2. Effect of aqueous phase volume fraction on initial rate of consumption of styrene.

Let us now assess the impact of mass transfer on the overall rate of reaction. As the speed of agitation directly impacts k_L and a , its impact on the observed rate of reaction helps us to assess the relative importance of mass transfer and intrinsic reaction rates. Figure 3 depicts the corresponding variation. It can be observed that there is a significant increase in the overall as well as the volumetric rate of reaction when the speed of agitation is increased from 200 rpm to 400 rpm, indicating the strong impact of mass transfer on reaction. However, when the system is agitated within 400 rpm to 800 rpm, the impact of the mass transfer on the reaction is negligible. When the speed of agitation was increased beyond this, intense turbulence led to reaction material being thrown up to the wall of the reactor, resulting in a reduced reaction rate. It can thus be concluded that the system falls within kinetically controlling regime I for impeller speed in the range of 400 to 800 rpm. Therefore, to evaluate intrinsic kinetic parameters, subsequent experiments were performed at an impeller speed of 600 rpm.

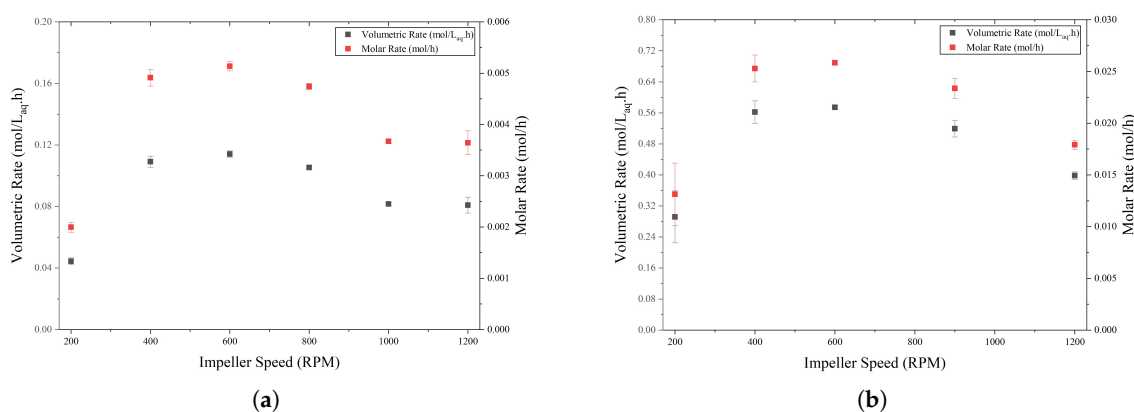


Figure 3. Effect of speed of agitation on initial rate of consumption of styrene. (a): Reaction temperature = 30 °C. (b): Reaction temperature = 45 °C.

To ensure that the system falls under the kinetically controlled regime, it is necessary to establish impact of temperature on the volumetric rate of reaction. From Figure 4a, it can be seen that the volumetric rate of reaction increases with temperature. For a kinetically controlled system, the corresponding rate constant k should obey the Arrhenius equation.

From Figure 4b, it can be seen that the apparent rate variation with temperature follows Arrhenius law with activation energy of 18.08 kcal/mol. If the reaction follows regime I, the corresponding styrene concentration in the aqueous phase will be equal to its solubility $[A^*]$. As styrene solubility is also a function of temperature (as tabulated in Table 3), the corresponding rate is scaled by $[A^*]$ to compute the apparent rate constant. From Figure 4c, it can be noted that the apparent rate constant also obeys Arrhenius law and accordingly, the true activation energy is 16.13 kcal/mol. This further substantiates that the reaction is kinetically controlled and follows regime I.

Let us now assess the impact of the initial concentration of the three reactants on the reaction rate. Figure 5 depicts the corresponding variations. It can be seen that the aqueous phase volumetric rate increases with the increasing initial aqueous phase concentration of styrene. Based on the corresponding log–log plot, it can be noted that the corresponding apparent order of reaction is one. Similarly to styrene, with the increase in concentration of hydrogen peroxide, the initial volumetric rate also increases with an apparent order of one. For the case of HCl, the variation in rate with concentration is much stronger and the corresponding apparent order is 2.1. This higher order with respect to HCl suggests involvement of HCl in multiple rate-controlling steps. As per the kinetic model presented in Equation (12), the dependence of the rate of styrene consumption on Styrene concentration is between 0 and 1, the dependence on H_2O_2 concentration is 1, and the dependence on HCl concentration is between 1 and 2. Thus, the observed apparent order of reaction with respect to each species matches closely with the proposed kinetic model.

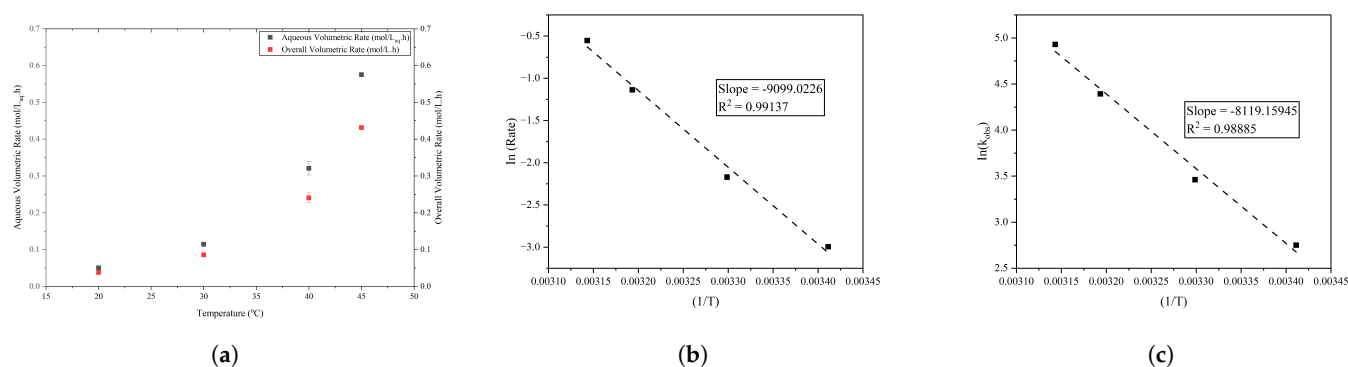


Figure 4. Effect of temperature on the initial rate of consumption of styrene. (a): Variation with temperature. (b): Arrhenius plot for apparent rate. (c): Arrhenius plot for apparent rate constant.

Lastly, for the two full-batch experiments, we computed the Hatta number and (mass transfer) enhancement factors. The corresponding Hatta number values obtained were 6.33×10^{-4} and 2.27×10^{-5} , respectively. Accordingly, the enhancement factors for both the runs were approximately equal to 1. Both these values further substantiate kinetically controlled regime I operation for this system.

Based on these studies, it can be concluded that this heterogeneous system, when agitated between 400–800 rpm, follows kinetically controlled Regime I behavior, with reaction taking place in the aqueous phase. Furthermore, the apparent order with respect to styrene and H_2O_2 is one, whereas for HCl, it is higher than one.

4.2. Reaction Mechanism

Figure 6 depicts the concentration trajectories of key species in the reaction system for full-batch experiments. It can be noted that the higher concentration of H_2O_2 in run II resulted in faster overall reaction. This is consistent with the kinetically controlled reaction and positive order with respect to H_2O_2 . For both the initial concentrations, styrene chlorohydrin is preferred over styrene dichloride and the corresponding selectivity values

are higher than 50%. As the end of the batch, for both the cases, the yield for styrene chlorohydrin is around 68%.

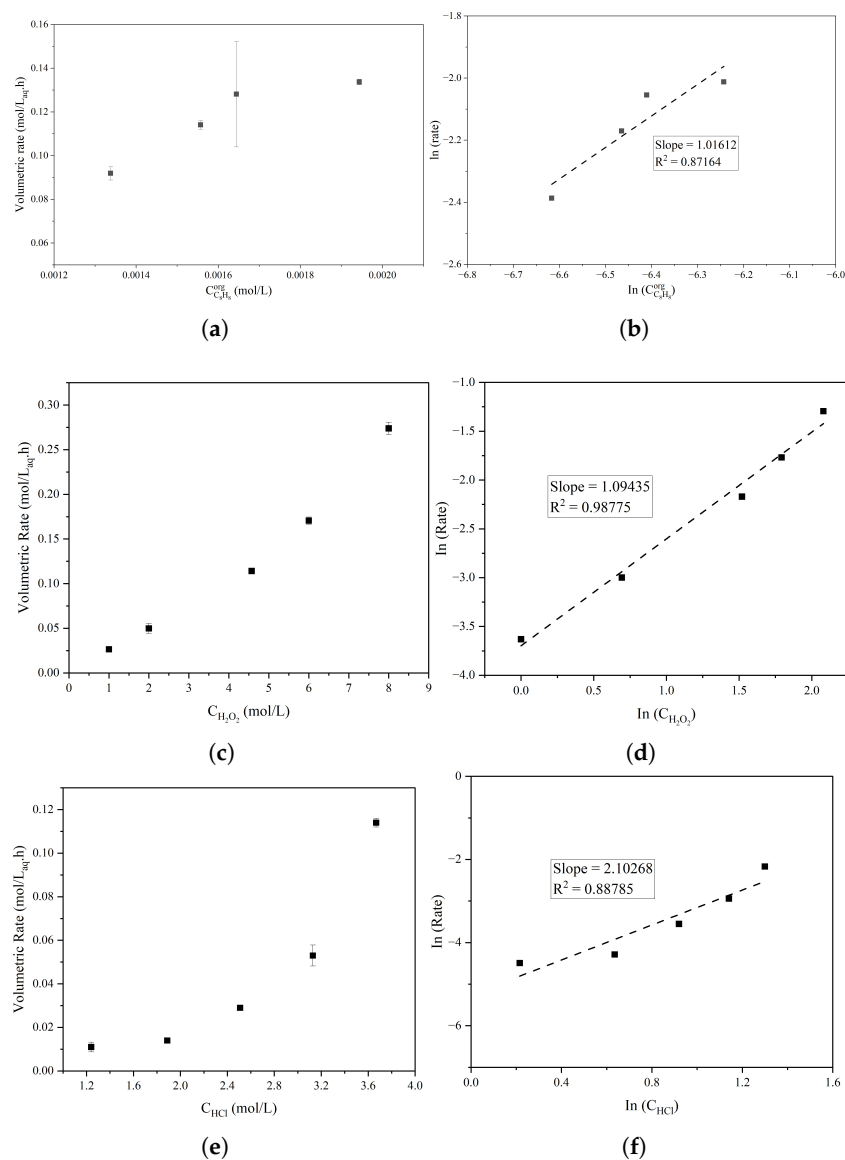


Figure 5. Effect of reactant concentration on initial rate of consumption of styrene. (a,b): Variation with Styrene concentration. (c,d): Variation with H_2O_2 concentration. (e,f): Variation with HCl concentration.

The model parameters obtained by fitting these profiles against Equation (12) are given in Table 6. The corresponding predicted concentration profiles are also included in Figure 6. It can be noted that the kinetic model (12) captures reaction kinetics fairly well for both the experimental runs. Specifically, the SSE (sum of squared error) values for composition prediction over the entire batch for set I and set II are 2.83 and 3.15, respectively. The parity plots for each key concentration are presented in Figure 7. It can be noted that the model is able to predict the concentrations of all the key reactants (styrene, HCl and H_2O_2) as well as the main product (styrene chlorohydrin) and main byproduct (styrene dichloride). However, there is a significant error in predicting the concentration of benzaldehyde. It can be seen from Figure 7f that the model predominantly underpredicts the benzaldehyde concentration. Based on our knowledge, other than the reactions considered in this paper, there is no additional mechanism for benzaldehyde formation in this system. Given that the concentration of benzaldehyde is quite small, there

is a possibility of analytical uncertainty when determining its concentration. Based on this, the discrepancy in benzaldehyde concentration prediction can be attributed to its relatively smaller concentration compared to the other species, leading to a smaller impact on the overall objective function (minimization of squared prediction error).

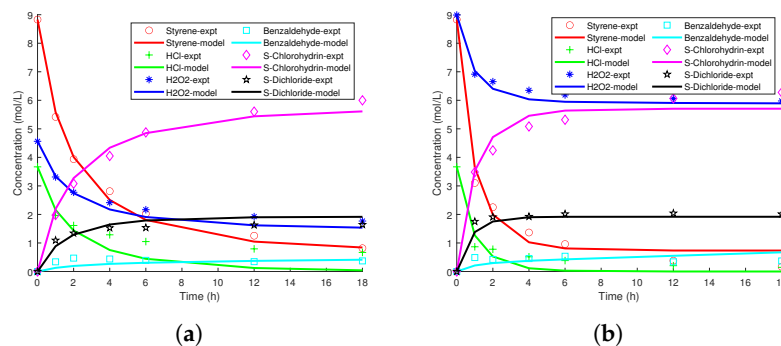


Figure 6. Temporal profiles for key component concentrations. (a): run I. (b): run II.

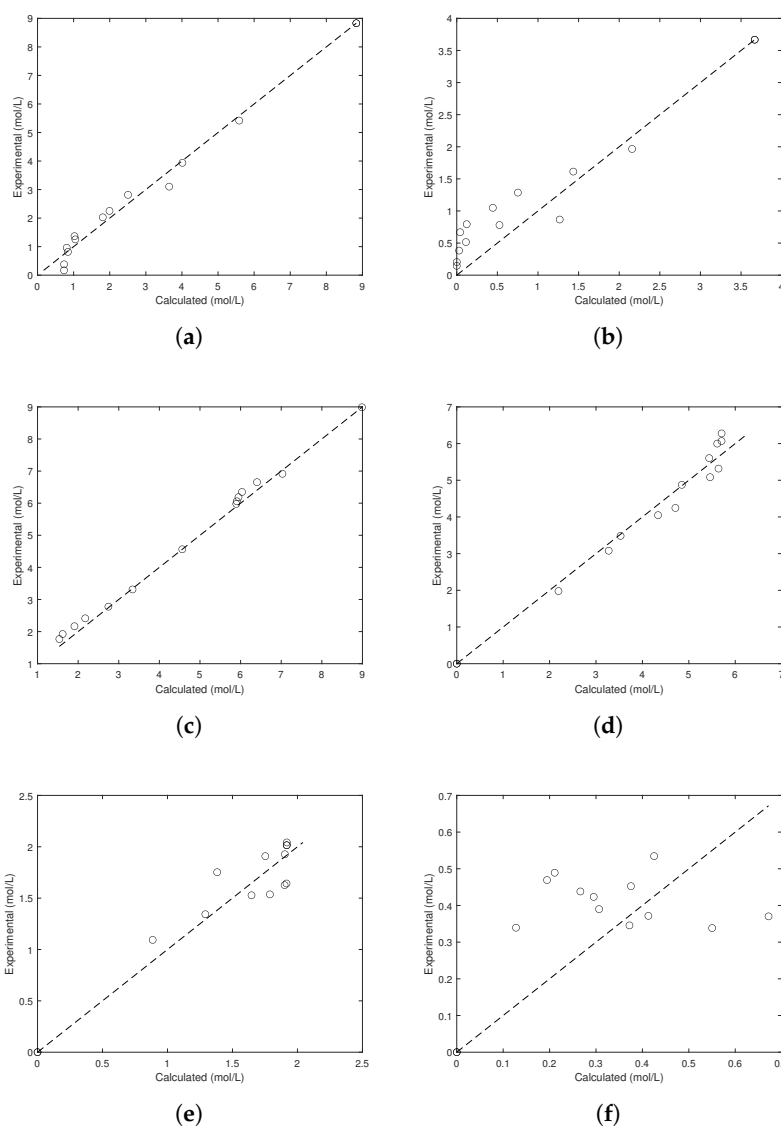


Figure 7. Parity plots for key component concentrations for full-batch experiments. (a): Styrene. (b): HCl. (c): H₂O₂. (d): Styrene chlorohydrin. (e): Styrene dichloride. (f): Benzaldehyde.

Table 6. Estimated kinetic parameters.

Parameter	Value (L/mol·s)	Parameter	Value (—)
k_1	3.00×10^{-5}	P_S	2.68
k_2	5.08×10^{-5}	P_{SCH}	2.40
k_3	7.44×10^{-4}	P_{SDC}	2.97
k_5	2.78×10^{-7}	P_{BNZ}	18.51

5. Conclusions

In this paper, we explored the kinetic aspects of hydroxychlorination of styrene using hydrochloric acid and hydrogen peroxide. For this heterogeneous liquid–liquid system, initial rate as well as full-batch experiments were performed to identify key rate-controlling steps and propose a detailed rate model. Based on the initial rate experiments, it was shown that this reaction takes place inside the aqueous phase. It is kinetically controlled and follows regime I. The apparent order of reaction with respect to styrene, hydrogen peroxide and hydrochloric acid is one, one and two, respectively. Subsequently, a detailed kinetic model was proposed to capture the dynamic evolution of key reaction species and was simplified by adopting quasi-steady-state assumption for some of the intermediate species. The various rate parameters for this model were estimated by conducting full-batch experiments. The proposed model accurately captures the evolution of key raw materials as well as the products. For the considered experiments, the styrene chlorohydrin yield was 68–69% with selectivity of 72–75%. The proposed model can be used to optimize reaction conditions to further improve yield and selectivity.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr14152398/s1>, Product identification and composition estimation.

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Abbreviations

The following abbreviations are used in this manuscript:

a	Interfacial area
$[A^*]$	Saturation concentration of styrene in the aqueous phase
BNZ	Benzaldehyde
C_i	Concentration of species i in aqueous phase
C_i^{org}	Concentration of species i in organic phase
D_i	Diffusivity of component i
ε_L	Fractional holdup of aqueous phase
FM	Formaldehyde
k	Kinetic rate constant

k_L	Mass transfer coefficient
P_i	Partition coefficient for component i
S	Styrene
SCH	Styrene chlorohydrin
SDC	Styrene dichloride
SO	Styrene oxide

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