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Kinetics of Oxidation of 4-Oxoacids by *N*-Chlorosaccharin in Aqueous Acetic Acid Medium

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Abstract The oxidation kinetics of substituted and unsubstituted 4-oxoacids (**S**) by *N*-chlorosaccharin (NCSA) have been studied in aqueous acetic acid media. The reaction follows first-order kinetics in each of the 4-oxoacids, NCSA and H^+ . The effect of changes in the electronic nature of the substrate reveals that positive charge develops in the transition state. Based on the kinetic results and product analysis, a suitable mechanism has been proposed for the reaction of NCSA with 4-oxoacids.

Keywords Kinetics · Oxidation · 4-Oxoacids · NCSA · Reaction mechanism

1 Introduction

In 4-oxoacids, two carbon atoms separate the carbonyl and carboxyl groups and thus they behave both as oxocompounds and as acids without a direct influence from the other group. Among the various organic compounds employed in these studies, 4-oxoacids are attractive substrates because of their enolization in strong acid media. That enols are reactive species of the substrate has been reported in the literature [1].

N-Chlorosaccharin is a source of a positively charged halogen atom and this reagent has been exploited as an oxidant for a variety of substrates in both acidic and alkaline media [2]. The nature of the active oxidizing species and the mechanism depends on the nature of the halogen atom, the groups attached to the nitrogen and the reaction conditions. The species responsible for this oxidizing character may differ depending on the pH of the medium. The probable reactive species [3] of NCSA in acidic solutions are >NX, HOX, >N⁺HX, or H₂OX⁺, and in alkaline solutions are >NH, HOX, and OX⁻.

In the recent years, studies of the oxidation of various organic compounds by *N*-halo compounds in the presence of perchloric acid have attracted considerable attention [4]. A thorough literature survey revealed that few studies of the oxidation of 4-oxoacids have been

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reported so far [5]. Although the *N*-chlorosaccharin oxidation of a large variety of organic compounds have been studied, there seems to be no reports on a systematic kinetic study of the oxidation of 4-oxoacids by *N*-chlorosaccharin.

We have carried out a systematic study of the reactions of 4-oxoacids (S) by N-chlorosaccharin (NCSA). In this report, we have examined the kinetic and mechanistic aspects of the oxidation of substituted and unsubstituted 4-oxoacids by N-chlorosaccharin in the presence of perchloric acid. The various unsubstituted and substituted 4-oxoacids (S1–S7) employed in the present study are listed below:



S1: Unsubstituted; S2: 4'-Methoxy; S3: 4'-Methyl; S4: 4'-Phenyl; S5: 4'-Chloro; S6: 4'-Bromo; S7: 3'-Nitro.

2 Materials

All of the chemicals used were of p.a. grade. Acetic acid (BDH) was first refluxed over chromic acid for 6 h and then distilled. Solutions of sodium perchlorate, perchloric acid and mercuric acetate were prepared in double-distilled water. Double-distilled water was employed in all kinetic runs.

The parent 4-oxoacid, namely 4-oxo-4-phenylbutanoic acid (S1), and the phenyl substituted 4-oxoacids (S2–S7) were prepared by Friedel-Crafts acylation of the substituted benzene with succinic anhydride. Nitration of the oxoacids was performed under mild conditions to prepare nitro compounds.

3 Experimental section

The reaction was followed potentiometrically by setting up a cell containing the reaction mixture, into which a platinum electrode and a standard calomel electrode were dipped. The Emf of the cell was measured periodically using an Equip-Tronics potentiometer while the reaction mixture was continuously stirred. An electrically operated thermostat was used to maintain the desired temperature with an accuracy of $\pm 0.1^{\circ}$ C. A double-walled 100 mL beaker with inlet-outlet water circulation facility, specially designed for this experiment, was used as the reaction vessel.

The Emf values of the reaction mixtures were determined at definite time intervals. The pseudo-first-order rate constants were computed from plots of $\ln(E_t - E_{\infty})$ versus time. The precision of the values of the rate constant are given in terms of their 95% confidence limits as determined by the student's *t* test [6].

4 Results and discussion

4.1 Order of reaction

The rate of oxidation was found to be first order each in [NCSA] and [S]. Linear plots of $\log_{10}k_1$ versus $\log_{10}[S]$ with unit slope (S1: slope = 1.01 ± 0.03 , r = 0.999; S2: slope = 0.998 ± 0.01 , r = 0.999; S3: slope = 1.02 ± 0.01 , r = 0.989; S4: slope = 1.04 ± 0.03 , r = 0.997; S5: slope = 0.999 ± 0.04 , r = 0.989; S6: slope = 1.03 ± 0.03 , r = 0.999; S7: slope = 1.01 ± 0.02 , r = 0.997) demonstrate the first-order dependence of the rate on [S]. The k_1 values at different [S] are given in Table 1. The k_1 values obtained at different initial concentrations of NCSA reveal that the rates are almost independent of the initial concentration of NCSA (Table 1). This ensures that the order of the reaction with respect to NCSA is one.

The dependence of the reaction rate on the hydrogen ion concentration has been investigated at different initial concentrations of perchloric acid while keeping the concentrations of the other reactants constant. It may be seen that the rate of reaction increases linearly with an increase in the hydrogen ion concentration. This establishes that the reaction rate is first order with respect to the hydrogen ion concentration. A plot of k_1 versus [H⁺] is also linear and passes through the origin (Fig. 1), showing that the reaction proceeds completely through an acid-catalyzed pathway [7].

It was reported earlier in the case of *N*-halo oxidants that, in the absence of mineral acids, HOCl is the reactive oxidant species. Bishnoi *et al.* [7] have observed, for the oxidation of some α -hydroxy acids by NCSA, that the linear increase in the oxidation rate with an increase in [H⁺] indicates that protonation of HOCl occurs to give a cationic chlorine species, see Eq. (1), which is a stronger electrophile and oxidant.

$$HOCl + H_3O^+ \rightleftharpoons H_2O^+Cl + H_2O \tag{1}$$

Thus, the most probable oxidizing species is the hypochlorous acidium ion, (H_2O^+Cl) . The participation of the hypohalous acidium ions in many electrophilic substitution and oxidation reactions is well documented [8].

4.2 Effect of varying the ionic strength

The ionic strength of the reaction medium was changed by the addition of anhydrous sodium perchlorate to study the influence of ionic strength on the reaction rate. It was found that the ionic strength of the reaction medium has no significant effect on the reaction rate.

4.3 Effect of the products

The effect from adding saccharin was studied, which caused a decrease in the oxidation rate. Thus, retardation of the reaction rate upon addition of saccharin suggests that there is a pre-equilibrium step involving a process in which saccharin is a product:

$$NCSA + H_3O^+ \rightleftharpoons H_2O^+Cl + saccharin$$
(2)

If this equilibrium is involved in the oxidation process, then the rate should be an inverse function of the saccharin concentration, which is borne out by the observation that the inverse of the rate constant gives a linear curve (r = 0.999) when plotted against [saccharin]. Similar

prin			$10^4 \times k_1^{a}, s^{-1}$	1					
ge									
$10^2 \times [S]$ mol·dm ⁻³	$10^3 \times [NCSA]$ mol·dm ⁻³	[H ⁺] mol·dm ⁻³	S1	S2	S3	S4	S5	S6	S7
2.0	1.0	0.5	1.72 ± 0.10	5.84 ± 0.60	4.14 ± 0.58	1.84 ± 0.11	1.07 ± 0.17	0.99 ± 0.10	0.26 ± 0.03
4.0	1.0	0.5	3.30 ± 0.17	11.6 ± 0.7	8.27 ± 0.86	3.66 ± 0.13	2.24 ± 0.20	1.96 ± 0.10	0.53 ± 0.06
6.0	1.0	0.5	4.47 ± 0.02	17.0 ± 1.2	12.3 ± 0.9	5.42 ± 0.18	3.15 ± 0.17	2.94 ± 0.12	0.79 ± 0.06
8.0	1.0	0.5	7.33 ± 0.25	22.9 ± 2.2	16.5 ± 0.2	7.42 ± 0.43	4.35 ± 0.22	3.88 ± 0.23	1.06 ± 0.09
2.0	0.8	0.5	1.73 ± 0.05	5.60 ± 0.08	4.18 ± 0.10	1.88 ± 0.05	1.15 ± 0.07	0.92 ± 0.11	0.27 ± 0.02
2.0	0.4	0.5	1.75 ± 0.03	5.66 ± 0.07	4.17 ± 0.11	1.85 ± 0.03	1.11 ± 0.13	0.95 ± 0.10	0.27 ± 0.01
2.0	0.2	0.5	1.74 ± 0.03	5.84 ± 0.18	4.14 ± 0.10	1.84 ± 0.08	1.10 ± 0.04	0.97 ± 0.03	0.27 ± 0.02
2.0	1.0	1.0	3.34 ± 0.14	11.8 ± 0.5	8.24 ± 0.25	3.54 ± 0.26	2.11 ± 0.07	1.98 ± 0.07	0.48 ± 0.04
2.0	1.0	1.2	4.41 ± 0.18	14.2 ± 0.6	9.94 ± 0.26	4.54 ± 0.22	2.51 ± 0.15	2.37 ± 0.11	0.64 ± 0.03
2.0	1.0	1.4	5.46 ± 0.29	16.1 ± 0.1	11.8 ± 0.6	5.35 ± 0.19	2.94 ± 0.17	2.75 ± 0.13	0.81 ± 0.01

Note. The solvent was a 50% acetic acid +50% water (v/v) mixture and the temperature was 303 K. As determined by the potentiometric technique following the disappearance of the oxidant; the error quoted for the k_1 values is the 95% confidence limit of the 'Student t' text [6]. ^{*a*} Estimated from the pseudo-first-order plots over 70% of the reaction.

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Fig. 1 Plots of k_1 versus [H⁺]

for the reaction between S and

NCSA



conclusions were reached in the *N*-chloronicotinamide [9] oxidation of amino acids and in the *N*-bromoacetamide oxidation of some α -hydroxy acids.

4.4 Effect of a free radical inhibitor

The oxidation reactions of S1 with NCSA, catalyzed by perchloric acid, have been investigated at different initial concentrations of acrylonitrile [10]. This reagent neither induces polymerization nor retards the reaction. Under the experimental conditions there is no reaction between NCSA and acrylonitrile. Consequently, it may be inferred that free radicals are not involved in the rate-controlling step of the present reaction.

4.5 Effect of solvent composition

The effect from changing solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 50% to 80%. The pseudo-first-order rate constants were estimated for the oxidation reactions of all of the oxoacids, S1–S7, with NCSA in the presence of perchloric acid at a constant ionic strength. The reaction rate increases markedly with the increase in the proportion of acetic acid in the medium (see Table 2). When the acetic acid content increases in the medium, the acidity of the medium is increased whereas the dielectric constant of the medium is decreased. These two effects cause the rate of the oxidation to increase markedly. The observed effect is similar to those reported for the oxidation of other organic compounds by NCSA [10]. When the acetic acid content of the medium is increased from 50% to 80%, the pH of the medium changes thus leading to an increase in [H⁺] and, hence, catalysis by the acetate ion is untenable.

The enhancement of the reaction rate with an increase in the amount of acetic acid generally may be attributed to two factors, *viz*, (i) the increase in acidity occurring at constant [perchloric acid], and (ii) the decrease in the dielectric constant with an increase in the HOAc content. The plots of $\log_{10}k_1$ against the inverse of the dielectric constant are linear with positive slopes, indicating that an interaction occurs between a positive ion and a dipolar molecule [11]. This supports the postulation of H_2O^+Cl as being the reactive species.

	$10^4 \times k_1$, ^{<i>a</i>} s ⁻¹ (CH ₃ COOH + H ₂ O (v/v), %)					
S	50-50	60–40	70–30	80–20	Slope ^b	r ^b
S1	1.72 ± 0.10	2.54 ± 0.24	3.35 ± 0.14	5.83 ± 0.29	23.8	0.998
S2	5.84 ± 0.60	7.23 ± 0.36	8.31 ± 0.48	9.96 ± 0.60	10.1	0.983
S3	4.14 ± 0.58	5.30 ± 0.25	6.73 ± 0.54	7.94 ± 0.54	12.7	0.985
S4	1.84 ± 0.11	2.36 ± 0.07	3.30 ± 0.14	4.55 ± 0.18	17.6	0.998
S5	1.07 ± 0.17	1.47 ± 0.06	2.20 ± 0.11	3.44 ± 0.01	19.0	0.998
S6	0.99 ± 0.04	1.19 ± 0.05	1.85 ± 0.15	2.87 ± 0.15	14.7	0.994
S7	0.26 ± 0.03	0.52 ± 0.03	0.86 ± 0.07	1.26 ± 0.08	37.9	0.998

Table 2 Effect of the solvent polarity on the rate of reaction where $[S] = 2.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$, $[\text{NCSA}] = 1.0 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, $[\text{H}^+] = 0.5 \text{ mol}\cdot\text{dm}^{-3}$, and the temperature is 303 K

^aEstimated from the pseudo-first-order reaction plots.

^bThese values were calculated from the plots drawn between $\log_{10} k_1$ and 1/D.

4.6 Rate of enolization by the bromination method

It has earlier been reported that oxidation of keto compounds proceeds via enolization of the keto compounds [12]. The rate of enolization of a keto compound is found to be faster than the rate of oxidation. The reactive species of the substrate may be determined by enolization, which is both an acid and base catalyzed reaction that proceeds by a concerted or push-pull mechanism. The rate of enolization was determined by the bromination method for the system under investigation.

4.7 Effect of substituents

The oxidation of 4-oxo-4-phenylbuanoic acid (S1) and substituted 4-oxoacids (S2–S7) was carried out in the temperature range of 303 to 323 K. The observed rate constants increase with temperature for all the studied compounds. The activation parameters for the oxidation of the 4-oxoacid by NCSA have been evaluated from the slopes of the Arrhenius plots.

A close look at the activation parameters presented in Table 3 shows that the activation energies for the oxoacids with electron-releasing substituents are relatively lower than for those with electron-withdrawing substituents. The entropy of activation is negative for all the 4-oxoacids, ranging from -126 to $-232 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The large negative entropy of activation, in conjunction with other experimental data, supports the mechanism outlined in the Scheme 1.

It is interesting to note that the reactivity decreases in the order 4-methoxy > 4-methyl > 4-phenyl > 4-H > 4-Cl > 4-Br > 3-NO₂ for the substituents.

A Hammett's plot for the oxidation of S by NCSA at various temperatures was found to be linear. This Hammett's plot is shown in Fig. 2. The values of the reaction constants (ρ) are reported in Table 4.

The observed ρ values indicate that the reaction is sensitive to the effects of electronic perturbations. It also provides information about the nature of the transition state occurring during the reaction. A reaction involving the development of a positive charge in the transition state is aided by electron-releasing substituents and the resulting ρ values are negative [13–16].

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Table 3	Activation para	umeters and rate co	instants for the oxid	dation of S1-S7 b	y NCSA in aqueou	s acetic acid medium		
	$10^4 \times k_1, s^{-1}$							
S	303 K	308 K	313 K	323 K	E_a kJ·mol ⁻¹	$\Delta H^{\#} \ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$	$\Delta S^{\#} \mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1}$	$\Delta G^{\#} \mathrm{kJ} \cdot \mathrm{mol}^{-1}$
S1	1.72 ± 0.10	2.14 ± 0.17	2.84 ± 0.28	4.00 ± 0.64	34.4 ± 0.55	31.9 ± 0.71	-179.4 ± 0.92	86.2 ± 0.35
S2	5.84 ± 0.60	6.36 ± 0.60	7.84 ± 0.82	8.55 ± 0.58	15.8 ± 0.32	13.3 ± 0.44	-230.8 ± 1.08	83.2 ± 0.16
S3	4.14 ± 0.58	4.72 ± 0.30	5.28 ± 0.40	6.20 ± 0.68	16.3 ± 0.35	13.8 ± 0.07	-231.9 ± 0.96	84.0 ± 0.87
S4	1.84 ± 0.11	2.54 ± 0.10	3.24 ± 0.02	4.58 ± 0.16	35.9 ± 0.22	33.4 ± 0.19	-173.7 ± 1.05	86.0 ± 0.19
S5	1.07 ± 0.17	1.35 ± 0.14	1.66 ± 0.08	2.36 ± 0.26	32.0 ± 0.18	29.5 ± 0.33	-191.5 ± 1.14	87.5 ± 0.58
S6	0.99 ± 0.04	1.12 ± 0.01	1.47 ± 0.01	2.23 ± 0.01	34.2 ± 0.36	31.7 ± 0.66	-184.7 ± 0.68	87.7 ± 0.98
S7	0.26 ± 0.03	0.41 ± 0.01	0.61 ± 0.01	1.04 ± 0.01	55.4 ± 1.02	52.9 ± 0.75	-125.6 ± 0.24	91.0 ± 0.48

 10^{-3} mol·dm⁻³, [H⁺] = 0.5 mol·dm⁻³, and the solvent composition is 50% acetic acid *Note.* [S] = 2.0×10^{-2} mol·dm⁻³, [NCSA] = $1.0 \times +50\%$ water (v/v).





In the present investigation, both the acceleration of the reaction rates from the presence of electron-releasing substituents and the negative value of the reaction constant, ρ , indicate explicitly that the mechanism of oxidation involves the development of positive charge in the transition state.

It is generally recognized that oxidation lead to electron deficient species that are radical cations, radicals or carbocations. These reactions normally have a negative ρ value and the magnitude of the ρ value depends on the extent of electron deficiency. Oxidation reactions involving free radical formation during the rate-controlling step usually have a small negative ρ value and oxidation involving the formation of a carbocation have large a negative ρ value. Based on these arguments we expect to observe a large absolute value for ρ , but the measured values are in the range $\rho = -1.34$ to -0.93. The low ρ value may be attributed to the nature of observed rate constant. The observed rate constant is a composite of several terms as shown in Eq. (12).

The terms shown in Eq. (12) deserve comment. The rate constant k_3 depends on the concentration of the protonated substrate (S⁺). The electron donating substituents tend to delocalize the positive charge on S⁺ and, hence, favor the formation of this positive species. In the rate-limiting step, Eq. (6) of Scheme 1, the formation of the carbocation is facilitated by electron-releasing substituents.

Table 4 Reaction constant values at different temperatures

Temperature K	Reaction constant ^{<i>a</i>} ρ	Correlation coefficient	<i>s</i> *
303	-1.34 ± 0.09	0.998	0.027
308	-1.23 ± 0.17	0.998	0.050
313	-1.11 ± 0.20	0.998	0.057
323	-0.93 ± 0.19	0.998	0.056

Note. The σ values were taken from a reported study [13].

^{*a*}The values were obtained by correlating $\log_{10} (k_2/k_2^{\circ})$ with σ_p for the oxidation reactions of **S1–S7** with NCSA (*s*^{*} is the standard deviation).

Thus, we obtain a slightly lower negative ρ value of (-1.34 at 303 K) because k_{obs} is a composite of the enolization reaction as well as the oxidation of the 4-oxoacids. Hence, in the present investigation the measured ρ value and other findings fit in with the formulation of the mechanism as outlined in Scheme 1.

The dependence of the reaction rate on the structure of the reacting molecule is related to the activation parameters. The decisive term concerning the dependence of the reaction rate on the structure is neither the Gibbs energy nor enthalpy, but the potential energy that is experimentally not accessible. Many authors support the opinion that the activation energy at a certain temperature is a better approximation for the unknown potential energy [17].

The validity of the isokinetic relation can be tested graphically with Exner plots. The isokinetic temperature evaluated from the Exner plots was found to be 378 K. As the experiments have been carried out at temperatures far away from the isokinetic temperature, the application of Hammett's equation to the observed kinetic data is valid. The validity of the isokinetic relationship in the present study implies that all of the 4-oxoacids undergo oxidation by the same mechanism [18].

4.8 Mechanism

A probable mechanism for the oxidation of 4-oxoacids by NCSA has been proposed, based on the experimental results and in analogy with the oxidation mechanisms of oxo compounds with other oxidants.



Scheme 1

5 Derivation of the rate law

Based on kinetic observations and the mechanism proposed, the following rate expressions can be derived by applying the steady-state approximation.

The rate of the reaction is given by

$$\frac{-\mathrm{d}[\mathrm{NCSA}]}{\mathrm{d}t} = k_4 \ [\mathrm{E}][\mathrm{H}_2\mathrm{O}^+\mathrm{Cl}] \tag{8}$$

Applying the steady-state approximation for [E] yields

_

$$\frac{-d[NCSA]}{dt} \frac{k_2 k_3 k_4 [H_3 O^+] [S] [H_2 O^+ Cl]}{k_{-2} k_{-3} [H_3 O^+] + k_4 (k_{-2} + k_3) [H_2 O^+ Cl]}$$
(9)

At high concentration of $[H_3O^+] = 0.5 \text{ mol} \cdot \text{dm}^{-3}$,

$$k_{-2}k_{-3}[\mathrm{H}_{3}\mathrm{O}^{+}] \gg k_{4}(k_{-2}+k_{3})[\mathrm{H}_{2}\mathrm{O}^{+}\mathrm{Cl}]$$

and thus Eq. (9) simplifies to the form:

$$\frac{-d[NCSA]}{dt} = \frac{k_2 k_3 k_4 [H_3 O^+][S][H_2 O^+ CI]}{k_{-2} k_{-3} [H_3 O^+]}$$
$$= \frac{k_2 k_3 k_4 [S][H_2 O^+ CI]}{k_{-2} k_{-3}}$$
(10)

The value of $[H_2O^+Cl]$ can be obtained from Eq. (3) as given in Scheme 1.

$$K_a = \frac{k_{-1}}{k_1} = \frac{[\text{NCSA}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}^+\text{Cl}][\text{saccharin}]}$$

Therefore,

$$[H_2O^+Cl] = \frac{[NCSA][H_3O^+]}{K_a[Saccharin]}$$

Using the value of $[H_2O^+Cl]$ in Eq. (10),

$$\frac{-d[NCSA]}{dt} = \frac{k_2 k_3 k_4 [S][H_3O^+][H_2O^+Cl]}{k_{-2} k_{-3} K_a [saccharin]}$$
(11)

Hence, at higher concentrations of mineral acid, the reaction is first order with respect to the oxoacid (S), [NCSA] and $[H_3O^+]$.

The observed rate constant at high $[H_3O^+]$ is

$$k_{\rm obs} = \frac{k_2 k_3 k_4}{k_{-2} k_{-3} K_a} \tag{12}$$

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5.2 Product analysis and stoichiometry

In a typical experiment, 4-oxoacid $(0.1 \text{ mol}\cdot\text{L}^{-1})$, perchloric acid $(0.5 \text{ mol}\cdot\text{L}^{-1})$ and NCSA $(0.5 \text{ mol}\cdot\text{L}^{-1})$ were mixed in a 50% acetic acid + 50% water (v/v) mixture inside a closed vessel with an outlet, and then allowed to react. The ensuing gas was identified as carbon dioxide. After 24 h the solution was extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the solvent evaporated. The colorless solid obtained was identified as benzoic acid by measuring the mixed melting point and using a chemical method and TLC techniques.

Different sets of reaction mixtures containing different quantities of NCSA and oxoacid, at constant concentrations of perchloric acid and sodium perchlorate, were allowed to react for 24 h at 303 K and then analyzed. The remaining NCSA was assayed iodometrically and the results are in good agreement with 1:1 stoichiometry, and the reaction may thus be represented by:

$$C_{6}H_{5}COCH_{2}CH_{2}COOH + C_{6}H_{4}SO_{2}CONCI + 5H_{2}O \xrightarrow{H^{+}} C_{6}H_{5}COOH + C_{6}H_{4}SO_{2}CONH + 3CO_{2} + 6H_{2} + HCI$$
(13)

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