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Product distribution and reaction pathways for methylene chloride hydrolysis and oxidation under hydrothermal conditions

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Abstract

The product spectrum, yields, and distribution resulting from hydrolysis of methylene chloride in sub- and supercritical water and post-hydrolysis oxidation in supercritical water have been measured and analyzed to identify and prioritize likely reaction pathways of formation and destruction and their relative importance for all species observed. Reactions with dilute feeds were carried out at 246 bar in a tubular reactor system over temperatures ranging from 25 to 600°C and total residence times of 7 to 23 s. The products detected were formaldehyde, hydrochloric acid, carbon monoxide, hydrogen, methanol, and carbon dioxide, with trace amounts of methane, chloromethane, and other one- and two-carbon chlorinated hydrocarbons in the vapor phase. A complete reaction network for CH_2Cl_2 and its products under hydrolysis conditions was developed. The main route for CH_2Cl_2 breakdown was via subcritical hydrolysis to formaldehyde and HCl, followed by decomposition of formaldehyde to CO and H_2, and subsequent CO conversion to CO_2 and H_2 by the water gas shift reaction. In the presence of O_2, oxidation of HCHO, CO, H_2, and CH_3OH was significant, while CH_2Cl_2 and the chlorinated hydrocarbons exhibited no oxidation conversion below 550°C. By 600°C and a 6 s residence time under oxidation conditions, however, CO_2 and HCl were the only products observed, signifying complete destruction of all compounds (>99.99% of total carbon) under these conditions.

Keywords: Methylene chloride; Hydrolysis; Oxidation; Supercritical water; Reaction pathways

1. Introduction

Oxidation in supercritical water (SCWO) shows strong promise as an innovative and effective means of destroying hazardous organic compounds [1,2]. Owing to the significant drop in the density, dielectric constant, and ability to hydrogen bond that occurs as water is heated above its critical point (374°C, 221 bar), supercritical water is an excellent solvent for non-polar organic compounds and oxygen. With reasonable temperatures, pressures, and residence times (generally 550–650°C, 250 bar, and ≤60 s), organic destruc-

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tion efficiencies $>99.99\%$ can be achieved, with CO_2, H_2O, N_2 (for nitrogen-containing organic species), and mineral acids (for organic species containing halogen atoms, sulfur, and/or phosphorus) as the only products. Some organic compounds are sufficiently reactive to undergo substantial conversion under hydrolysis (oxygen-free) conditions at subcritical temperatures. These less severe operating conditions have attracted interest because they may result in simpler, less expensive equipment. However, a major concern is that some intermediate or end products may be more toxic than the starting material and require further processing. Thus it is important to characterize the complete product spectrum and distribution in order to understand what products form under different operating conditions and to provide information for optimizing system performance for specific applications. In addition, this information is useful in deducing the reaction mechanism(s).

We have studied the hydrolysis and oxidation kinetics of methylene chloride (CH_2Cl_2) in sub- and supercritical water, and the resulting product yields and identities. In an earlier paper [3], we reported on the data, experimental techniques, and preliminary analysis of the experimental results. The experimental data indicate that substantial CH_2Cl_2 hydrolysis occurred under subcritical, non-oxidative conditions, while much more limited or slower reactions occurred under supercritical conditions. To explain this observation, a more recent paper [4] examines the significant effects associated with changes in the solvation characteristics of water from sub- to supercritical temperatures on the CH_2Cl_2 hydrolysis reaction rate. These solvation effects are quantified through the development of a correction factor to the standard Arrhenius form for the rate constant, and incorporated into a global rate expression for CH_2Cl_2 hydrolysis. The present paper focuses on the products identified from the hydrolysis and oxidation of CH_2Cl_2 and their subsequent reactions. The objective is to deduce a reaction network for CH_2Cl_2 destruction that includes the most likely pathways of formation and further breakdown of these products using a combination of evidence from the current experimental data and from the literature.

2. Summary of experimental product data and observations

A tubular flow reactor system was used for the experiments. Aqueous feed solutions of CH_2Cl_2 and of O_2 (or pure water instead of O_2 for hydrolysis runs) were pressurized and heated in separate tubing via a fluidized sandbath up to a temperature between 450°C and 600°C. Both preheater tubes were of Hastelloy C-276, 0.108 cm ID, 0.159 cm OD, and about 2.75 m in total heated length. The two preheater tubes were joined at their ends to a mixing tee connected to 4.7 m of Inconel 625 tubing (0.171 cm ID, 0.635 cm OD) that served as the isothermal main reactor. Hydrolysis conditions always prevailed in the organic feed preheater tubing (even for oxidation runs), while oxidation conditions only existed in the main reactor (during oxidation runs). CH_2Cl_2 and O_2 concentrations ranged from 6 to 38 mmol/l and 14 to 52 mmol/l, respectively at ambient temperature, and from 0.2 to 0.6 mmol/l and 0.56 to 2.08 mmol/l, respectively at the entrance to the main reactor under supercritical conditions. All experiments were isobaric at 246 bar. A more complete description of the experimental system and operating conditions is given by Marrone [5] and Marrone et al. [3].

Liquid and vapor effluent samples were taken after cooling and decompression back to ambient conditions. Products were identified and quantified by a variety of analytical methods including gas chromatography, UV–vis spectroscopy, and ion specific electrode, as detailed in Marrone et al. [3]. The mean carbon mass balance over all runs was 99.9%, with a standard deviation of 6.6%. The mean chlorine mass balance over all runs was 100.0%, with a standard deviation of 5.7%. The major products identified were formaldehyde (HCHO), hydrochloric acid (HCl), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), and methanol (CH_3OH). Small amounts of methane (CH_4) ($\leq 1.4\%$ of the carbon mass balance) were detected during runs at higher sandbath temperatures (≥ 562°C) and residence times. In addition, trace amounts of the following chlorinated hydrocarbons were detected in the vapor phase: chloromethane (CH_3Cl), chloroform ($CHCl_3$), trichloroethylene (C_2HCl_3), and isomers of dichloroethylene (1,1-$C_2H_2Cl_2$, *cis*-1,2-$C_2H_2Cl_2$, and *trans*-1,2-$C_2H_2Cl_2$). Of these, only CH_3Cl was present in quantities large enough to have a statistically significant effect on the carbon and chlorine mass balances. CH_3Cl accounted for <3% of the carbon mass balance, and the next most abundant chlorocarbon, C_2HCl_3, accounted for <0.7%. The other chlorinated hydrocarbons, combined, accounted for <0.1% of the carbon balance. Their presence is noted, however, because of their importance in identifying all possible reaction pathways and because they may be toxic trace products of interest.

Other important observations related to products formed were as follows.

- Although the presence of O_2 did not have a major effect on CH_2Cl_2 breakdown, it did have a significant impact on the number of product species observed and their concentrations compared to those seen under hydrolysis conditions.
- The concentration of HCHO always decreased with increasing sandbath temperature and residence time.
- The number of products identified increased with increasing sandbath temperature up to 550°C.
- Despite the number of different products identified at milder conditions, CO_2 and HCl were the only products detected in oxidation experiments at sandbath temperatures of 600°C and total residence times of 23 s (6 s in the presence of O_2), consistent with what one would expect under SCWO conditions as reported in earlier destruction efficiency studies [2,6].

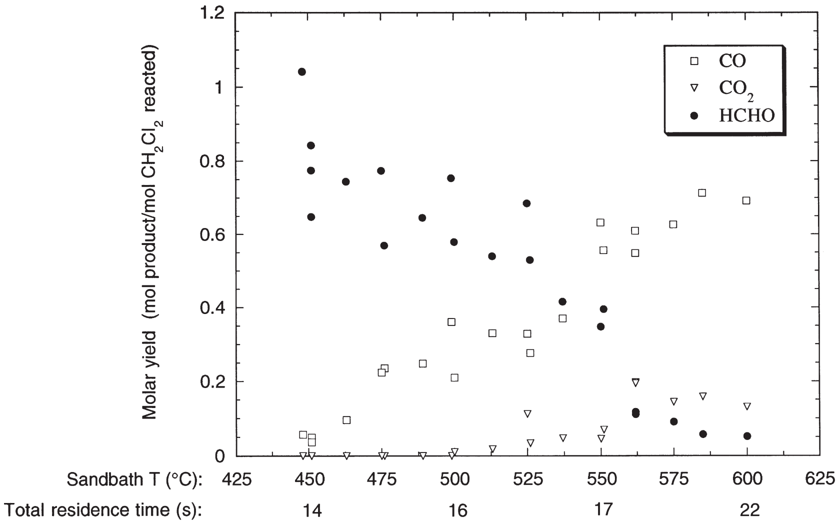
All of these trends, and the relative magnitudes of each product under different operating conditions, can best be observed in the graphs of molar yield versus both sandbath temperature and total residence time contained in Figs. 1 and 2. Here molar yield is defined as moles of product formed per moles of CH_2Cl_2 reacted, and total residence time is the sum of the preheater and main reactor residence times. Each point plotted is for a 6 s residence time in the main reactor at a constant supercritical temperature equal to that of the sandbath (±2–3°C). In order to maintain the same constant residence time in the main reactor over call temperatures studied, the experimental mass flow rate of feed was decreased as the sandbath temperature was increased. The consequence of this procedure was that the CH_2Cl_2 feed experienced different residence times in the preheater tubing, ranging from 7 to 17 s, for different sandbath operating temperatures. All residence times (preheater or main reactor) were calculated from the tube volume, mass flow rate, and temperature dependent density. The decrease in density with increasing temperature which normally results in faster volumetric flow rates was not enough to compensate for the lowered mass flow rates in these experiments, resulting in a net increase in preheater residence time with increasing sandbath temperature, as indicated in Figs. 1 and 2. The residence time is included along with sandbath temperature in these figures because it is known that reaction of CH_2Cl_2, and possibly of some of the products, occurred in the subcritical region of the non-isothermal preheater tubing [4,5].

A significant amount of the residence time of the fluid in the preheater tubing (about 70–80%) was spent at temperatures <390°C. Thus, in principle, the subcritical residence time and preheater temperature profile, as well as supercritical residence time and final fluid (or sandbath) temperature, could all influence the net concentration and distribution of products by affecting the rates of all subcritical (e.g. polar) and supercritical (e.g. free radical) reactions governing product formation and disappearance.

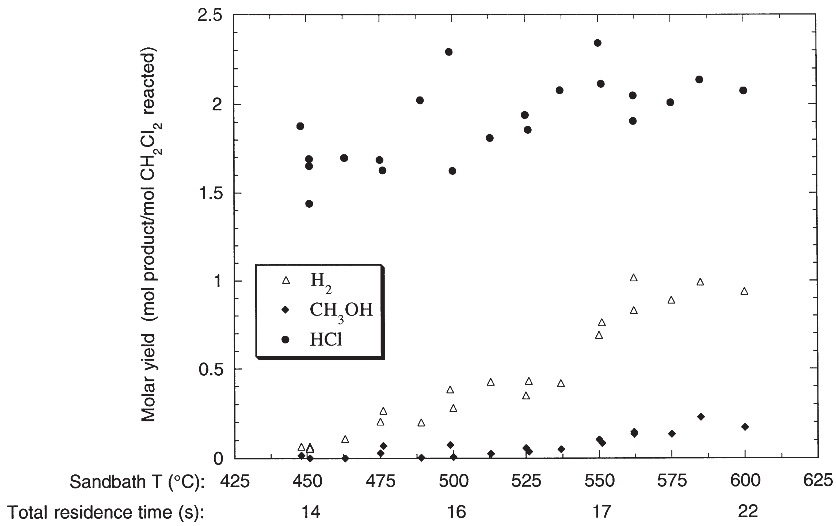
3. Reaction pathways for product formation and destruction

3.1. Formaldehyde

Figs. 1 and 2 show that HCHO is the only product species whose yield decreases continuously with increasing temperature and residence time. At a sandbath temperature of 450°C and total residence time of 14 s under hydrolysis conditions, HCHO accounted for most of the carbon (~94%) in the products. For sandbath temperatures ≥562°C and total residence times ≥18 s, very



(a)



(b)

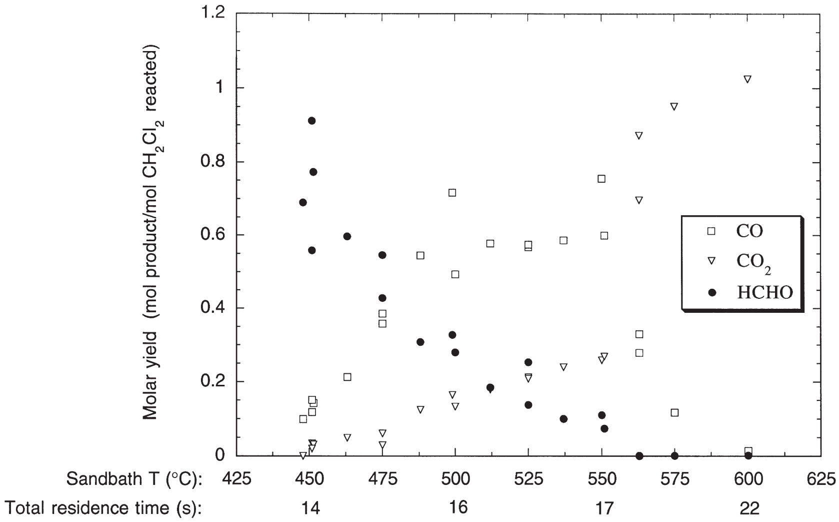
Fig. 1. Molar yield of major products from hydrolysis (oxygen-free) runs as a function of sandbath temperature and total residence time: (a) CO, CO_2, and HCHO; (b) H_2, CH_3OH, and HCl. All data are at 246 bar. Total residence time includes the preheater residence time and the isothermal main reactor residence time of 6 s for all runs.

little HCHO was detected for hydrolysis runs (<10%), and none was found for oxidation runs. These facts suggest that HCHO was a primary intermediate formed from CH_2Cl_2 breakdown. This hypothesis is consistent with the two-step, polar mechanism for subcritical, neutral hydrolysis of CH_2Cl_2 proposed by Fells and Moelwyn-Hughes [7]:

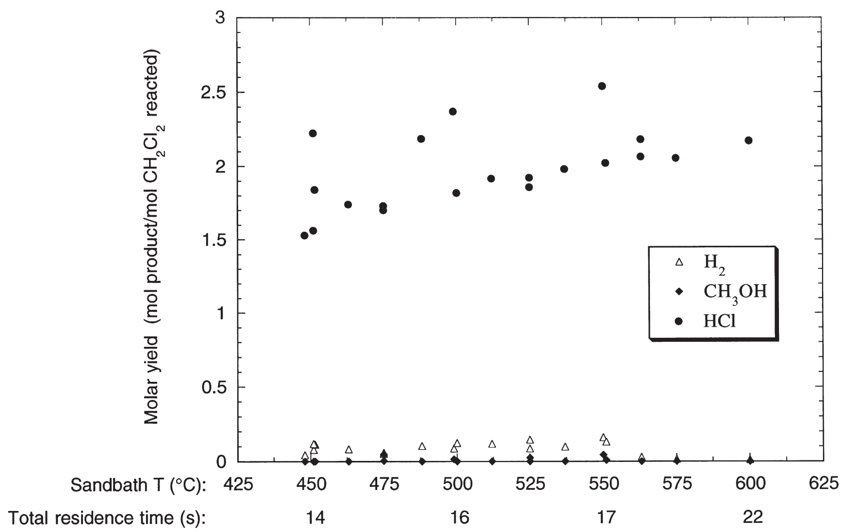
$$CH_2Cl_2 + H_2O \rightarrow CH_2ClOH + HCl \quad (1)$$

$$CH_2ClOH \rightarrow HCHO + HCl \quad (2)$$

Reaction (1) is likely an S_N2 (bimolecular nucleophilic substitution) reaction. The resulting unsta-



(a)



(b)

Fig. 2. Molar yield of major products from oxidation runs as a function of sandbath temperature and total residence time: (a) CO, CO_2, and HCHO; (b) H_2, CH_3OH, and HCl. All data are at 246 bar. Total residence time consists of the preheater residence time and the isothermal main reactor residence time of 6 s for all runs.

ble CH_2ClOH intermediate then undergoes a much faster internal rearrangement in reaction (2) to generate the products. The net reaction stoichiometry is obtained by combining the two reactions:

$$CH_2Cl_2 + H_2O \rightarrow HCHO + 2HCl \quad (3)$$

Significant subcritical hydrolysis of CH_2Cl_2 was made evident in our experiments from the substantial HCl-induced corrosion observed in upstream sections of the preheater tubing [3–5]. Thus, according to reaction (3), HCHO probably also formed early on in the preheater tubing. This would allow ample time for the HCHO to react further to form other products, conceivably by both polar mechanisms under subcritical conditions in the preheater and free radical mechanisms under supercritical conditions. Because relatively few other products were observed in the effluent, the number of possible HCHO reactions is relatively small. Several are known to occur under conditions reasonably similar to those in our experiments.

In the gas phase, HCHO thermally decomposes to CO and H_2 at high temperatures:

$$HCHO \rightarrow CO + H_2 \quad (4)$$

Although the kinetics are extremely slow below 300°C, several investigators cite reaction (4) as the dominant reaction for HCHO above 300°C [8–10]. Klein et al. [11] determined that reaction (4) occurs by a free radical chain mechanism with second-order kinetics in HCHO.

By observing rising CO/H_2 ratios as temperature decreased below 300°C, Fletcher [9] suggested the occurrence of a second surface catalyzed HCHO decomposition reaction:

$$2HCHO \rightarrow CH_3OH + CO \quad (5)$$

Calvert and Steacie [12] confirmed this reaction by detecting both CH_3OH and CO as the major products of a slow, heterogeneous, non-photolytic HCHO decomposition over the temperature range 150–350°C. Longfield and Walters [13] observed the same reaction for temperatures up to 415°C in Pyrex reactors, but saw no significant surface effects on the reaction rate. They also developed an Arrhenius expression for the second-order, gas phase rate constant for reaction (5). It predicts a reaction time on the order of seconds to generate a concentration of CH_3OH similar to that seen in our experiments, although only at the highest operating temperatures (i.e. near 600°C).

In aqueous solution, the above HCHO decomposition reactions do not occur, as evidenced by the lack of formation of any CO or H_2 [10]. Instead, HCHO under these conditions reacts primarily by means of a Cannizzaro reaction, where one molecule of HCHO is oxidized to formic acid and another is reduced to methanol by means of a hydride transfer [14]. This highly polar mechanism has been verified by Fry et al. [15] under basic conditions. The Cannizzaro reaction is unusual not only in mechanism but also in that more than one study claims it to be either a third or fourth order reaction or the sum of a third and fourth order reaction, according to Martin [16]. Although the reaction is normally initiated by nucleophilic addition of OH^-, several researchers have cited that the reaction can also occur when HCHO is heated in the presence of acids [10,17,18]. Under acidic conditions, the nucleophile would likely be H_2O, resulting in the following net reaction:

$$2HCHO + H_2O \rightarrow HCOOH + CH_3OH \quad (6)$$

In the absence of O_2, particularly if H_2 has been formed via reaction (4), HCHO can be directly reduced to methanol [10]:

$$HCHO + H_2 \rightarrow CH_3OH \quad (7)$$

With O_2 present, the primary reaction of HCHO is direct oxidation to either CO or CO_2:

$$HCHO + \tfrac{1}{2}O_2 \rightarrow CO + H_2O \quad (8)$$

$$HCHO + O_2 \rightarrow CO_2 + H_2O \quad (9)$$

In HCHO oxidation studies conducted between 287 and 337°C, Fort and Hinshelwood [19] found evidence that these reactions occurred through a free radical chain mechanism; namely, the existence of induction times, a strong dependence of the reaction rate on HCHO concentration, and a relatively small influence of O_2 on the reaction rate. The studies of Axford and Norrish [20] at 337°C further showed that although both reactions (8) and (9) occur together, reaction (8) predominates. They also showed that as the O_2 concentration decreases, the normally suppressed pyrolytic reaction (4) becomes more prominent. Their proposed mechanism is similar to those postulated for gaseous oxidation of H_2 and CO and that employed by Holgate and Tester [21] in modeling H_2 oxidation in supercritical water, where the OH and HO_2 radicals play a crucial role.

In the present experiments, CH_2Cl_2/water feed solutions were heated from liquid water conditions at the beginning of the preheater tubing (25°C) to more gas-like supercritical conditions in the main reactor (up to 600°C). Thus our reaction conditions overlap all of those encountered in the experiments in the literature cited above. Consequently, all of reactions (4) through (9) may have contributed at some point and to some extent to the observed product spectra over the course of the changing reaction environment. The data in Figs. 1 and 2 allow the importance of each reaction to be assessed. Under hydrolysis conditions, the data clearly show that considerable amounts of CO and H_2 were produced, while much less CH_3OH and no HCOOH were detected. In fact, CO and H_2 were the most abundant products after HCl and HCHO on a molar basis. The increasing CO and H_2 yields with increasing temperature and residence time correlated well with the corresponding decrease in HCHO. For all hydrolysis runs, the combined amount of HCHO, HCl, CO, and H_2 accounted for 90–99.9% of the total mass of products. In addition, after correcting for further CO loss and H_2 production by the water gas shift reaction (see section on CO reactions), the CO to H_2 ratio was always close to one (Table 1). These observations clearly indicate that reaction (4) was the dominant HCHO decomposition reaction in the hydrolysis runs.

In contrast, none of the experimental evidence suggests that any of reactions (5), (6), or (7) alone were dominant. The small measured concentrations of CH_3OH compared to CO indicate that reaction (5) had to be much slower than reaction (4). The low CH_3OH concentrations combined with CO/H_2 ratios near unity indicate that H_2-mediated reduction of HCHO [reaction (7)] could not have been a major reaction. Formic acid was not detected in the present experiments by HPLC with a UV detector. Although this would appear to rule out the Cannizzaro reaction [reaction (6)], it is also possible that some of the HCOOH formed could have reacted further to either CO_2 and H_2, or CO and H_2O, particularly under the highly acidic conditions that existed at subcritical temperatures [22–24]. Extrapolation of data by Van Buren et al. [25] assuming a first order decomposition to CO_2 and H_2 suggests that significant reaction of HCOOH could occur between 450 and 600°C for residence times on the order of seconds, but that complete conversion of HCOOH would only be expected near 600°C. Even without further reaction, any HCOOH formed from reaction (6) may still have gone unnoticed because of a relatively high detection limit for HCOOH (probably near 0.001 M) by the UV detector used. If HCOOH were there at all, however, its concentration [and therefore the importance of reaction (6) for HCHO decomposition] would have been very small, since it could not be greater than the already small concentrations of CH_3OH observed (according to the reaction stoichiometry). The good closure on the carbon balances further implies that there were no missing major products.

Although not individually dominant, reactions

Table 1
Ratio of CO to H_2 before the water gas shift reaction [reaction (11)] and CO conversions assuming the water gas shift reaction was the only CO depletion reaction. All data are from hydrolysis (oxygen-free) runs only. Pre-water gas shift concentrations of CO and H_2 are calculated from the measured values according to the stoichiometry of reaction (11)

Sandbath temperature (°C)	Total residence time (s)[a]	$[CO]_{wgs}/[H_2]_{wgs}$ [b]	Water gas shift conversion (%)[c]
448	14.6	0.87	0
451	14.2	0.73	0
451	14.0	0.74	0
451	14.0	0.66	0
463	14.7	0.89	0
476	15.3	0.89	0
475	15.8	1.09	0
489	15.5	1.24	0
500	17.1	0.94	0
500	15.6	0.81	4
513	16.0	0.85	5
525	16.6	1.84	25
526	17.0	0.77	11
537	17.4	1.12	11
550	19.0	1.05	7
550	16.8	0.90	11
562	18.6	0.98	24
562	18.3	1.17	26
575	19.8	1.03	19
585	22.9	1.04	18
600	21.9	1.02	16

[a] Total residence time shown includes time in preheater tubing plus 6 s in isothermal main reactor.
[b] $[CO]_{wgs}=[CO]+[CO_2]$ = concentration of CO prior to water gas shift reaction assuming no other reactions involving CO. $[H_2]_{wgs}=[H_2]-[CO_2]$ = concentration of H_2 prior to water gas shift reaction assuming no other reactions involving H_2.
[c] Water gas shift conversion $=\dfrac{[CO_2]}{[CO]+[CO_2]}\times 100$.

(5), (6), and (7) are not necessarily insignificant. Exactly how important each of these reactions is, however, is still somewhat difficult to determine conclusively. In general, the fact that the CO/H_2 ratio is always close to one suggests that there should be no further significant sources or sinks for these products under hydrolysis conditions. At the same time, the amount of CH_3OH produced, though small ($<10\%$), was not negligible, particularly at higher temperatures and longer residence times. Although one of these reactions may have been the sole source of the CH_3OH formed, it is also possible that all three of these reactions for CH_3OH production (along with CH_3Cl hydrolysis) could have proceeded separately to some small extent — enough to collectively account for the total amount of CH_3OH observed, while at the same time not resulting in a significant or detectable change in other products used up or generated (i.e. CO, H_2, and HCOOH). Such a scheme would not be inconsistent with both the data and studies in the literature.

The noticeably decreased yields of HCHO at all temperatures and residence times in the oxidation runs compared to the hydrolysis runs [Figs. 1(a) and 2(a)] show that, unlike with CH_2Cl_2 breakdown, O_2 has a significant effect on HCHO breakdown. Aside from the HCHO itself, CO and CO_2 dominate the reaction products, suggesting that reactions (8) and (9) govern HCHO destruction under oxidizing conditions. By 560°C, the HCHO is almost completely reacted, and with further temperature increases, CO and CO_2 yields strongly decline and increase, respectively. These three observations imply that direct oxidation of CO to CO_2 is an important reaction above 560°C.

3.2. Methanol

Most of the possible formation reactions for CH_3OH under the given experimental conditions have already been discussed. One additional pathway of formation is by hydrolysis of CH_3Cl, which is discussed below. Earlier work on CH_3OH hydrolysis and oxidation in supercritical water elucidates the potential for CH_3OH decomposition reactions here. In principle [9], CH_3OH could undergo thermal decomposition in the absence of O_2 to form CO and H_2:

$$CH_3OH \rightarrow CO + 2H_2 \tag{10}$$

However, in experiments using virtually the same apparatus as that of the present study, Webley et al. [26] observed a methanol conversion without O_2 of only 2.1% at a sandbath temperature of 544°C and a main reactor residence time of 6.6 s (a likely total residence time of about 18 s) at 246 bar. This result implies that reaction (10) was probably negligible in the present study and that any CH_3OH measured in the effluent of hydrolysis runs was a true indicator of all that was formed in the course of reaction. This provides further evidence that reactions (5), (6), and (7) were probably of minor importance compared to reaction (4) for HCHO decomposition.

In contrast, methanol is highly susceptible to oxidation in supercritical water. Using the same apparatus, Tester et al. [27] reported a 96% methanol conversion under oxidizing conditions at a sandbath temperature of 530°C, a main reactor residence time of 9.6 s, and 246 bar. Note that in the absence of O_2 in the present work, CH_3OH was conclusively detected only at or above this temperature [Fig. 1(b)]. Thus it is not surprising that CH_3OH was not observed in any of the present oxidation runs [Fig. 2(b)], since complete conversion would be expected just at the point where it would start to form.

3.3. Carbon monoxide

As already discussed, the major CO formation pathway was by homogeneous thermal decomposition of HCHO [reaction (4)], with possibly a small contribution from the heterogeneous reaction that also produces CH_3OH [reaction (5)] and from any HCOOH decomposition. Under hydrolysis conditions, the water gas shift reaction is an important CO sink [28]:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{11}$$

Working on the same experimental apparatus and at similar temperatures as used in the present study, Holgate et al. [29] found that breakdown of CO in the absence of O_2 via the water gas shift reaction [reaction (11)] never resulted in more than a few per cent conversion of CO in the preheater tubing. In the main reactor under isothermal, supercritical conditions without O_2, they reported CO conversions ranging from 1 to 16% at temperatures of 446 to 593°C, respectively, 246 bar, and 7.5 s reactor residence time. If one assumes that reaction (11) was the only CO sink and only CO_2 source, then by stoichiometry the measured concentration of CO_2 divided by the sum of the measured CO and CO_2 concentrations should yield the CO conversion from the water gas shift reaction in the hydrolysis runs of the present set of CH_2Cl_2 experiments. Values of CO conversion estimated in this way (Table 1) vary from 0% up to 26% over the main reactor temperature range of 450–600°C and constant 6 s residence time. These values are in excellent agreement with those of Holgate et al. [29], suggesting that the water gas shift reaction was the most likely pathway for CO loss and CO_2 production in the absence of O_2.

Holgate et al. [29] showed that direct oxidation of CO:

$$CO+\tfrac{1}{2}O_2\rightarrow CO_2 \tag{12}$$

is faster than the water gas shift reaction in the presence of O_2. This fact, coupled with its lack of occurrence in the preheater tubing, indicates that the water gas shift reaction was negligible in the oxidation runs. Over the range of oxidation runs carried out, the CO concentration exhibited a maximum at a temperature of 562°C and 12 s total residence time [Fig. 2(a)]. This behavior implies competing production and destruction reactions for CO. Since thermal decomposition of HCHO can in principle begin in the preheater tubing, it is likely that CO was present when the flow first encountered O_2 at the beginning of the main reactor. Data from Holgate et al. [29] for CO oxidation in supercritical water show a low conversion of 5% at 445°C, 246 bar, and 7.5 s main reactor residence time. The direct oxidation reaction proceeds much faster at higher temperatures, with 60% conversion at 560°C and 93% conversion at 571°C, both for a main reactor residence time of 5 s. Holgate et al. [29] observed this large increase in CO conversion at the same temperature range where the present oxidation experiments found CO yields to maximize and then drop appreciably. Thus the observed behavior of increasing CO yields at lower temperatures and residence times, followed by decreasing CO yields at higher temperatures and residence times, is consistent with the known kinetics of CO oxidation in supercritical water. As expected, at high temperatures and long enough residence times, direct oxidation of CO to CO_2 predominates.

3.4. Hydrogen

H_2 formation occurred by two major pathways under hydrolysis conditions: thermal decomposition of HCHO [reaction (4)] being the primary pathway, followed by the water gas shift reaction [reaction (11)] at supercritical temperatures. The importance of both these reactions is supported by the experimental data and studies in the literature, as pointed out above. In terms of further reactions of H_2, Holgate and Tester [30] concluded that there was no significant net reaction (either pyrolytic or hydrolytic) between H_2 and water in the absence of O_2 under conditions similar to those of the present study. The absence of O_2 together with the relatively high concentrations of H_2 measured, especially at higher temperatures and longer residence times, imply that reducing conditions existed throughout the preheater tubing and also in the main reactor during hydrolysis runs [see Fig. 1(b)]. Note that the maximum molar yield of H_2 based on the stoichiometry of reactions (3) and (4) is 1. Thus it is conceivable that several reduction reactions may have occurred in these regions, explaining the presence of other observed products (e.g. reduction of HCHO to CH_3OH, of CH_2Cl_2 to CH_3Cl, and of CH_3Cl to CH_4). The experimental data, however, suggest that none of these reactions should be major sinks for H_2 because: (1) reduction of HCHO is only one of four possible reactions that collectively produced a relatively small amount of CH_3OH (see above); (2) concentrations of CH_3Cl never exceeded 3% of the total carbon balance; and (3) only trace amounts of CH_4 were detected. The closeness of CO/H_2 ratios to unity in the hydrolysis runs further suggests that, in general, only minimal consumption of H_2 by other reactions could have occurred.

The H_2 yields in the oxidation runs were much lower than those from the hydrolysis runs, with no H_2 detected above 562°C and 6 s exposure to O_2 (main reactor residence time) [Figs. 1(b) and 2(b)]. Comparison of the H_2 and CO yield data in Figs. 1 and 2 implies that direct H_2 oxidation, i.e.

$$H_2+\tfrac{1}{2}O_2\rightarrow H_2O \tag{13}$$

is much faster than CO oxidation, at least up to temperatures of 562°C where CO concentrations start to drop substantially with increasing temperature. Holgate and Tester [30] found 98% conversion of H_2 by oxidation in supercritical water at a temperature of 571°C, main reactor residence time of 5 s, and pressure of 246 bar using double the stoichiometric amount of O_2 at the main reactor inlet. Almost all of the present experiments were fuel-lean relative to H_2. Under such conditions at 560°C and 246 bar, Holgate and Tester [31] showed that H_2 oxidation was faster than H_2 production via the water gas shift reaction over a main reactor residence time range of 3–8 s. They also determined that H_2 oxidation proceeds more rapidly than CO oxidation at 550°C, but that the rates become comparable at 560°C. Thus, H_2 concentrations measured in the present study are consistent with earlier data and conclusions.

3.5. Hydrochloric acid and carbon dioxide

HCl and CO_2 are the final products of CH_2Cl_2 destruction under oxidation conditions at high enough temperatures and long enough residence times (600°C and 23 s in the present experiments). HCl was always the dominant chlorinated product in both hydrolysis and oxidation experiments, accounting for >97% of the chlorine from CH_2Cl_2 conversion. HCl molar yields were also roughly constant at 2 for both hydrolysis and oxidation experiments [Figs. 1(b) and 2(b)]. CO_2 concentrations were much less in hydrolysis runs compared to oxidation runs, because CO_2 could only be formed from the water gas shift reaction under hydrolysis conditions, whereas oxidation of all carbon-containing species could produce CO_2 under oxidation conditions.

3.6. Other reactions of CH_2Cl_2

Although subcritical hydrolysis [reaction (3)] accounted for most of the breakdown of CH_2Cl_2 observed in the present experiments, there was evidence suggesting the occurrence of additional side reactions of CH_2Cl_2. Various chlorinated hydrocarbon compounds (e.g. $CHCl_3$, C_2HCl_3, $C_2H_2Cl_2$) were detected in small, but temperature-dependent quantities in the vapor effluent from both hydrolysis and oxidation runs. The maximum concentrations of these products (inferred from peak sizes and areas resulting from gas chromatography with an electron capture detector) occurred in hydrolysis runs at the highest sandbath temperatures and residence times (600°C, 23 s). For oxidation runs, slightly larger peaks were observed compared to hydrolysis runs up to a maximum at 550°C and 17 s. Above these conditions, all peak sizes rapidly decreased towards zero with increasing sandbath temperatures and residence times.

The presence of most of these compounds, including $CHCl_3$, C_2HCl_3, and all three isomers of $C_2H_2Cl_2$, cannot easily be explained by any polar mechanism. Thus they were likely formed via free radical mechanisms under supercritical conditions, possibly as recombinations of radical fragments from CH_2Cl_2 pyrolysis or oxidation. Taylor et al. [32] observed exactly the same products (along with HCl) in the same order of abundance from the oxidative pyrolysis of CH_2Cl_2, which they accounted for by a free radical, 28-reaction network. In the present experiments, the extremely low concentrations of these compounds are consistent with the relatively low CH_2Cl_2 conversions observed in the supercritical main reactor.

Of all the chlorinated hydrocarbons detected, CH_3Cl is unique in that it was present in the greatest amount (up to 2.9% of the total carbon balance), and could participate in non-free radical reactions. The most likely source of its formation was via reduction of CH_2Cl_2. With appreciable amounts of H_2 present in hydrolysis runs from HCHO thermal decomposition (as mentioned earlier), H_2 could clearly have been the reducing agent:

$$CH_2Cl_2+H_2 \rightarrow CH_3Cl+HCl \quad (14)$$

Other possibilities for the reducing agent include either iron or nickel in the tube wall functioning through a surface reaction (see below). Once formed, CH_3Cl could either be reduced further to CH_4 or hydrolyzed to CH_3OH and HCl via a polar S_N2 mechanism:

$$CH_3Cl+H_2 \rightarrow CH_4+HCl \quad (15)$$

$$CH_3Cl+H_2O \rightarrow CH_3OH+HCl \quad (16)$$

The fact that: (1) CH_4 was detected only in small quantities and only at higher sandbath temperatures and longer residence times (18 s at 562°C, 19 s at 550°C); (2) CH_3OH concentrations were much greater than those of CH_4; and (3) CH_3Cl hydrolyzes more rapidly than CH_2Cl_2 [33] imply that reaction (16) rather than reaction (15) was likely the more important reaction for CH_3Cl destruction under hydrolysis conditions. Because there are other possible CH_3OH sources [i.e. reactions (5), (6), and (7)], the CH_3OH concentrations cannot be used to determine the total amount of CH_3Cl produced. However, even if one assumes that all the CH_3OH detected formed from reaction (16), the total amount of CH_3OH, residual CH_3Cl, and CH_4 typically accounted for $<12\%$ of the total carbon in the effluent, implying that CH_3Cl formation was not a major sink for CH_2Cl_2. This at best modest role for reactions (14), (15), and (16) may be due to the need for certain reactants to be formed before these reactions could begin. For example, with H_2 as the reducing agent, reaction (14) could not become important until after CH_2Cl_2 hydrolysis and HCHO decomposition had proceeded to build up enough H_2. Thus by the time there was enough H_2, there may have been insufficient time left under polar, subcritical conditions for reaction (16) to proceed to any significant extent. (We are not aware of any evidence for CH_3Cl hydrolysis in a gas-like free radical environment.) Quantitative support for this hypothesis would require further measurements and detailed kinetic modeling computations. However, qualitatively this reasoning is supported by observations of increasing amounts of CH_3Cl, CH_3OH, and CH_4 at higher sandbath temperatures owing to longer residence times in the preheater tubing [4,5].

3.6.1. Direct oxidation

Recall that in our experimental system, the feed exposed to O_2 in the main reactor during oxidation runs was a mixture of unconverted CH_2Cl_2 plus the diverse products from reactions in the preheater under sub- and supercritical temperatures. Typical CH_2Cl_2 concentrations and O_2/CH_2Cl_2 molar ratios at the inlet to the main reactor were $0.2–0.6\times10^{-3}$ mol/l and 1.0–4.0, respectively. Consequently, our CH_2Cl_2 oxidation experiments explore the reactions in supercritical water of very dilute CH_2Cl_2/hydrolysis product mixtures in a stoichiometric excess of O_2. Below 525°C, these experiments resulted in little or no further conversion of CH_2Cl_2 beyond that obtained from otherwise similar hydrolysis runs (i.e. in the absence of O_2). Even above 525°C, oxidation and hydrolysis conversions of CH_2Cl_2 were closer than that observed for many other compounds studied [3], although part of this is due to the significant hydrolysis that CH_2Cl_2 undergoes. Concentrations of CH_3Cl and the other chlorinated hydrocarbons also showed no decrease in oxidation experiments below 550°C.

A slow oxidation reaction of CH_2Cl_2 at lower temperatures would not be that surprising given the fact that chlorinated hydrocarbons are known to be combustion inhibitors [34]. Andelman [35] has also reported that chlorinated compounds had the greatest half lives for reaction with alkoxy radicals compared to several other organic compounds including alkanes, olefins, ethers, and ketones. Despite what was observed below 550°C, however, it must be emphasized that CH_2Cl_2 conversion was 100% (within statistical error) at a temperature of 600°C and residence time of 6 s in the main reactor, and no products other than CO_2 and HCl were detected in the effluent. From a practical perspective, this finding strongly supports the notion that dilute concentrations of CH_2Cl_2 and several other C_1 and C_2 chlorinated hydrocarbons can be efficiently destroyed by oxidation in supercritical water at still reasonable temperatures and residence times (600°C, <10 s).

3.6.2. Surface reactions

There is further evidence, both in our work as well as in the literature, that additional CH_2Cl_2 reactions may have occurred under "hydrolysis" conditions, without further affecting the product spectrum. At all temperatures, experimentally measured values of CH_2Cl_2 hydrolysis conversion were greater than the conversion predicted at the end of the preheater tubing by extrapolating an empirical correlation for the rate constant developed by Fells and Moelwyn-Hughes [7,4,5]. This correlation of Fells and Moelwyn-Hughes was based on data from experiments they carried out from 80 to 150°C in Pyrex ampoules. Discrepancies between calculated and experimental values were larger at sandbath temperatures above 550°C and total residence times longer than 17 s. It is possible that extrapolation of their correlation over the extended temperature range of our experiments is not appropriate, especially given the drastic changes in water properties from ambient to supercritical conditions. However, the fact that higher conversions were observed in the high-nickel alloy tubing of the present experiments, compared to those in the Pyrex reactors of Fells and Moelwyn-Hughes, does hint that some of the discrepancy could be due to an additional metal-catalyzed surface reaction for CH_2Cl_2 breakdown.

Evidence in the literature does support the possibility of a surface reaction taking place. It has been known for some time that chlorinated organic compounds in water can undergo degradation when in the presence of metals [36,37]. The process is believed to be a redox reaction where the chlorinated organic compound is reduced and the metal is oxidized. Gillham and O'Hannesin [37] studied the degradation of 14 chlorinated methanes, ethanes, and ethenes (including CH_2Cl_2) in water by zero-valent iron under ambient conditions. For most compounds, they found that the presence of iron metal increased destruction rates, relative to those for iron-free hydrolysis, by 3 to 13 orders of magnitude. A subsequent similar study by Matheson and Tratnyek [38] specifically focused on the sequential reduction of the chlorinated methanes with iron. The data from both studies support a mechanism that requires direct contact between the organic compound and metal surface. Interestingly, however, CH_2Cl_2 was the only compound in both studies that showed no rate enhancement in the presence of iron, for which no explanation was given. Unlike that observed for the other compounds, Matheson and Tratnyek did not detect any measurable amount of CH_2Cl_2 degradation until after several months. That conversion which was detected was much more likely to have occurred by homogeneous hydrolysis rather than surface reduction based on the magnitude of the observed rate at ambient temperature and the fact that no CH_3Cl or CH_4 was found. Despite this result, they speculate that conditions may exist where CH_2Cl_2 does undergo significant destruction by surface reduction.

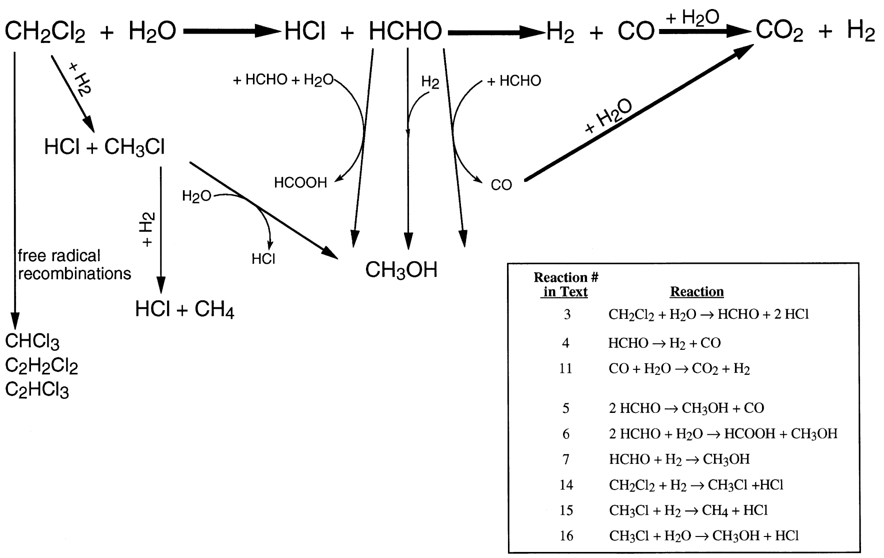
Catalytic reactions also warrant consideration for chlorinated compounds. In supercritical water, Houser and Liu [39] observed a strong catalytic effect of Inconel 600 reactor walls in the decomposition of 1-chloro-3-phenylpropane and 4-chlorophenol, as compared to control experiments in Vycor ampoules. Specifically regarding CH_2Cl_2, Bond and F. Rosa Calzadilla [40] found that CH_2Cl_2 hydrolysis with water vapor can be catalyzed by the acidic oxide catalysts γ-Al_2O_3 and TiO_2, from 259 to 500°C at atmospheric pressure. For either catalyst, the mechanism is hypothesized to involve chemisorption of both the organic compound and water to Lewis acid sites (i.e. Al or Ti), followed by attack of the resulting Cl–metal bonds by the water to form HCl and CO_2 and regenerate the surface. They also noted that HCl was detected long after the chlorinated feed was stopped, a trend also observed in our experiments. The authors did not provide an explanation for this persistence of HCl, but the implication is that it continues to form from reaction of the chlorinated organic compound already sorbed onto the catalyst surface. CH_2Cl_2 oxidation is also subject to catalysis, as was found by Papenmeier and Rossin [41] in experiments conducted with dry and humid air in the presence of a 3% Pt/κ–δ Al_2O_3 catalyst between 300 and 400°C at atmospheric pressure. Their data are consistent with a reaction mechanism involving adsorption and reaction of CH_2Cl_2 with oxygen sorbed on the Pt.

The literature on surface reactions of CH_2Cl_2 and other chlorinated compounds is intriguing in the present context. On the one hand, earlier studies confirm the possibility that the chlorinated methanes can undergo surface reactions (both reduction and oxidation). On the other hand, not all of the experimental conditions (temperatures, pressures/densities, and the metal/catalyst surfaces used) overlap those of our experiments. It is therefore difficult to unequivocally determine the importance of surface reactions in our system. The high-nickel alloy tubing used in our experiments (Hastelloy C-276 and Inconel 625) contains only 5 wt% of iron. Because the activity of nickel as a catalyst is greater than that of iron for reduction reactions such as hydrogenation [42], and because of the common use of nickel as a catalyst for many reactions in organic chemistry, it is tempting to propose that the walls of the Hastelloy C-276 and/or Inconel 625 tubing provided an equally active or even more active catalyst surface. The higher temperatures in our experiments would also likely promote faster reaction rates compared to that at ambient temperature. However, there are also equally compelling reasons to believe that surface reactions may not have occurred to any significant extent, if at all, relative to the known homogeneous reactions discussed above [i.e. reactions (3), (4), and (11)]. The small concentrations of reduced products (CH_3Cl and CH_4), along with the fact that no evidence for a reduction reaction with iron was seen for CH_2Cl_2 by Gillham and O'Hannesin [37] and Matheson and Tratnyek [38], oppose a surface reduction being important. The lack of any appreciable amount of CO_2 formation until higher temperatures and longer residence times does not support the purely catalytic reactions described above, although it is conceivable that partially oxidized products such as HCHO rather than CO_2 could form via catalysis.

Thus the presence and extent of CH_2Cl_2 surface reactions in our experimental system is uncertain. To resolve this issue, we are currently conducting a series of controlled batch experiments to determine if Hastelloy C-276 has an effect on the rate of CH_2Cl_2 hydrolysis and reduction. In these experiments, metal surface area-to-fluid volume ratios will be varied considerably, over the full range of low subcritical to near supercritical temperatures.

4. Proposed reaction network

Based on our experimental data, relevant studies in the literature, and the preceding discussion, we



Reaction # in Text	Reaction
3	$CH_2Cl_2 + H_2O \rightarrow HCHO + 2\,HCl$
4	$HCHO \rightarrow H_2 + CO$
11	$CO + H_2O \rightarrow CO_2 + H_2$
5	$2\,HCHO \rightarrow CH_3OH + CO$
6	$2\,HCHO + H_2O \rightarrow HCOOH + CH_3OH$
7	$HCHO + H_2 \rightarrow CH_3OH$
14	$CH_2Cl_2 + H_2 \rightarrow CH_3Cl + HCl$
15	$CH_3Cl + H_2 \rightarrow CH_4 + HCl$
16	$CH_3Cl + H_2O \rightarrow CH_3OH + HCl$

Fig. 3. The proposed reaction network for CH_2Cl_2 breakdown under hydrolysis conditions in sub- and supercritical water.

have proposed a reaction network for CH_2Cl_2 hydrolysis in sub- and supercritical water (Fig. 3). This scheme accounts for all products detected experimentally by one or more reaction pathways. The most prominent reactions of CH_2Cl_2 hydrolysis, HCHO thermal decomposition, and the water gas shift reaction are shown at the top with larger arrows and font to indicate their importance. An analogous reaction network for post-hydrolysis oxidation of CH_2Cl_2 can be written by adding to Fig. 3 pathways for oxidation to CO and CO_2 and/or H_2O for each species (except HCl). These oxidation pathways should be considered major reactions for all compounds except CH_2Cl_2 and the chlorinated hydrocarbons. Oxidation of these species does not become important until high temperatures and residence times (i.e. $>550°C$, 17 s).

5. Summary and conclusions

A number of conclusions can be drawn from this analysis of the products of CH_2Cl_2 hydrolysis and post-hydrolysis oxidation based on the experimental data and results of studies in the literature. The breakdown of CH_2Cl_2 and further reaction of its products can occur via both polar and free radical pathways. Under the experimental conditions explored, the dominant reaction for CH_2Cl_2 was hydrolysis to HCHO and HCl, which begins at subcritical temperatures by a polar substitution mechanism. HCHO may react via more than one pathway, but the data indicate that decomposition to CO and H_2 was the major reaction under oxygen-free conditions, followed by conversion of CO to CO_2 via the water gas shift reaction. CH_3OH, which appeared in smaller quantities and only at higher temperatures and residence times, likely formed via some combination of lesser reactions involving HCHO reduction and/or CH_3Cl hydrolysis. The observed concentrations and behavior of CO, H_2, and CH_3OH were all consistent with those found in earlier studies performed in supercritical water.

Oxidation, which occurred in these experiments only under supercritical conditions and only after reaction occurred in the preheater tubing, resulted in significantly lower concentrations of the nonchlorinated products and H_2 in favor of CO, CO_2, and H_2O, emphasizing the importance of these oxidation reactions. CH_2Cl_2 and the other trace chlorinated hydrocarbons showed some resistance to oxidation below temperatures of 550°C, but their concentration rapidly decreased toward zero above this temperature. Conflicting evidence makes it difficult to determine whether any surface reduction or catalytic reactions of CH_2Cl_2 occurred with the Hastelloy C-276 or Inconel 625 tubing used. If surface reactions of CH_2Cl_2 did occur, however, the current data indicate that they would probably be less important than the homogeneous hydrolysis reaction. Although the data of this study demonstrate the ease with which some hazardous organic compounds such as CH_2Cl_2 may decompose at less extreme conditions, our results also show the importance of having higher (supercritical) temperatures (i.e. above 550°C) and oxidant present to ensure complete destruction of all carbon-containing by-products to CO_2.

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