Hydrothermal Decomposition Rate of Thiodiglycol in Supercritical Water

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Abstract: Supercritical water (SCW) has been used as a reaction medium, primarily for the oxidation of hazardous chemical wastes. It is essential to obtain the hydrothermal reaction kinetics and provide data for the intermediate products if the supercritical water oxidation process is to be developed. In this paper, the hydrothermal decomposition rate of thiodiglycol [(HOC\(_2\)H\(_4\))\(_2\)S, TDG], as the model compound of HD mustard, was investigated in an isothermal continuous tubular reactor under SCW conditions. The reaction temperatures ranged from 386 to 528 °C and the residence times varied from 13 to 87 s at a fixed pressure of 25 MPa. The conversion of TDG was monitored by analyzing the total organic carbon (TOC) content of the liquid effluent samples. By using a first-order global power-law reaction rate expression, the hydrothermal decomposition rate of TDG, based on the TOC disappearance rate, in SCW was regressed from experimental data to a 95% confidence interval. The resulting activation energy was 71.32±5.20 kJ/mol and the pre-exponential factor of the reaction was 5.57(±0.002)×10\(^{-3}\) s\(^{-1}\).

Keywords: hydrothermal decomposition, supercritical water, thiodiglycol, kinetics

Introduction

Thiodiglycol [(HOC\(_2\)H\(_4\))\(_2\)S, TDG] is a refractory and primary hydrolysis product of HD mustard [(CIC\(_2\)H\(_4\))\(_2\)S], which is a chemical warfare agent [1]. TDG is not only a degradation product of HD mustard but also used as a solvent in antifreeze solutions, a dyestuff for printing and in the textile industry, an antioxidant, a vulcanizing agent, an intermediate for other commodities, and a co-stabilizer in the production of polyvinyl chloride [2-5]. Although it has a similar structure and physical properties with respect to those of HD mustard [6], it has relatively nontoxic [4-7]. Thus, it is also used as a model organic sulfur compound and chemical agent simulant. As shown in Table 1, TDG has the same carbon-sulfur (C-S) bond arrangement as does HD mustard and a similar density, but it is more soluble in ambient water than is HD, which greatly facilitates its feed preparation for laboratory studies in supercritical water (SCW).

Given the widespread use of TDG, the finding that it is a common environmental contaminant is not surprising. Thiodiglycol is a refractory chemical compound, meaning that severe conditions are necessary for its remediation because of its high thermal and chemical stability. It is resistant to hydrolysis and photolysis. For example, no photolysis occurred when aqueous solutions were irradiated with sunlight for 14 days; TDG was also resistant to hydrolysis at pH values of 4 ~ 11 over a 96-h period [8].

Further research into the hydrothermal decomposition of TDG in SCW here focuses on measuring its hydrothermal decomposition rate based on the total organic carbon (TOC) disappearance rate. Over the past decade, SCW (T\(_c\) = 374 °C and P\(_c\) = 22.1 MPa) has been growing in importance as a medium for chemical reactions, primarily for the oxidation of hazardous chemical wastes [9-14]. Although SCW has been used successfully as a medium to treat a wide range of hazardous chemical wastes to acceptable destruction efficiency levels, the
reaction kinetics of toxic organic wastes in SCW have not been developed fully. Information regarding the kinetics of the TOC disappearance and the byproducts of the hydrothermal decomposition of TDG is essential for understanding the effects of non-oxidation reactions for the development of future SCW processes.

There have been two experimental studies regarding the hydrothermal decomposition of TDG in SCW [15,16]. However, neither of them developed a kinetic model based on the TOC disappearance kinetics, which is an important method for obtaining reliable kinetic information. Thus, in this study we report experimental results designed to identify the hydrothermal decomposition rate of TDG based on the TOC disappearances rate in SCW. This study contributes to the collective knowledge of reaction kinetics by providing kinetic data for the degradation of TDG and lending insight into the reactive behavior of many hazardous materials in SCW.

### Experimental

#### Apparatus and Procedure

The experiments were conducted in a laboratory-scale, continuous-flow SCW reactor system. A schematic diagram of the experimental apparatus for hydrothermal decomposition in SCW is shown in Figure 1. The system involves two parallel sets of equipment that are almost identical: one for delivering the TDG solution and the other for delivering the distilled and deionized (DDI) water. All of the hot sections of the system were insulated in boxes of ceramic board; the temperature was monitored directly using a thermocouple. The reaction temperature was controlled by using a temperature

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**Table 1.** Physical Properties of TDG and HD Mustard [16]

<table>
<thead>
<tr>
<th>Property</th>
<th>TDG</th>
<th>HD mustard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>HO-C_3H_7-S-C_3H_7-OH</td>
<td>Cl-C_3H_7-S-C_3H_7-Cl</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>122.19</td>
<td>159.07</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>165</td>
<td>217</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>-10</td>
<td>14.5</td>
</tr>
<tr>
<td>Density at 25 °C (g/mL)</td>
<td>1.221</td>
<td>1.2741</td>
</tr>
<tr>
<td>Solubility in distilled water (g/100 g) at 25 °C</td>
<td>completely miscible</td>
<td>0.092</td>
</tr>
</tbody>
</table>

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**Figure 1.** Schematic diagram of the continuous-flow reactor system used for the hydrothermal decomposition of TDG in supercritical water (SCW).
controller (Hanyoung, model DX 7). Prior to each experiment, the TDG solution and the DDI water were degassed with high-purity helium gas to reduce the amount of dissolved oxygen and then they were pumped separately into the reaction system using separate high-pressure pumps (Thermo Separation Product Company). The DDI water was preheated in a 6-m by 1/8-in. (3.175 mm) outer diameter (O.D.) piece of stainless-steel (SS316) tubing. The TDG solution flowed directly into the reactor entrance without being preheated to avoid the degradation of TDG. The solutions were mixed at the reactor entrance in a Hastelloy C-276 cross and then entered the reactor, which had dimensions of a 0.3-m length, 31.7-mm O.D., and 10-mm inside diameter (I.D.), constructed of Hastelloy C-276 tubing with an internal volume of 23.6 cm³. The flow rate ratios of the TDG solution to the preheated DDI water were small, ca. 1:10, to maintain the temperature of the mixed streams as close as possible to that of the reaction temperature. Upon leaving the reactor, the effluent was cooled rapidly in a shell and tube heat exchanger and, afterward, it was filtered, to separate the solid particles, through a 0.5-μm inline metal filter and finally depressurized to ambient conditions by a back-pressure regulator (Tescom Co., model 26-1721-24). After the fluid exited the regulator flashed to atmospheric pressure and was separated into two streams in a gas-liquid separator. The gas flow rate was measured using a soap bubble flow meter, while the liquid flow rate was measured by recording the time required to fill a volumetric flask. The gaseous effluent composition was analyzed using two gas chromatographs, while the liquid effluent samples were collected in glass sample vials, capped with zero headspace, and analyzed using a TOC analyzer and an ion chromatograph (IC).

For each experimental run, the equipment was handled precisely and accurately to minimize errors that are related to control of the experimental conditions. The reactor was stabilized for at least an hour under each set of operating conditions to ensure steady-state operation. Measurements were then taken over the course of another hour, at which point at least four liquid and three gas samples were drawn and at least eight liquid and gas flow rates were recorded. The inlet TOC of the TDG feed concentration was measured from at least four samples—two of each taken at the beginning and at the end of the set of runs—to ensure that the feed concentration remained constant at the temperatures, pressures, and flow rates of the system. Typically, the temperature was held constant (within ± 2 °C) over the length of the reactor, and the pressure was fixed at 25±0.02 MPa as well as over the entire reaction time; the flow rate error ranges of the DDI water and the TDG solution were both maintained to ±2%.

### Materials and Analytical Methods

The TDG feed was prepared from an aqueous solution of TDG (Aldrich, 99+% purity), which was used as received and dissolved in distilled and deionized (DDI) water. The electrical resistance of the DDI water that was used in all of the experimental and analytical processes was ca. 18 MΩ. All of the standard solutions for calibration and identification in the liquid analytical methods were prepared using high-purity chemicals (Aldrich, ACS grade).

Gas samples were analyzed using two Hewlett-Packard model 5890 Series II gas chromatographs equipped with thermal conductivity detectors (TCD); helium was used as the carrier gas. Both gas chromatographs had Rheodyne single-mode injection valves installed to provide on-line sample injection into the gas column. The first gas chromatograph was used to quantify hydrogen sulfide (H₂S) and light hydrocarbons, such as methane (CH₄). This gas chromatograph was equipped with a 9 ft (2.74 m)×1/8 in (3.2 mm) SS Hayesep Q80-100 column. The oven component of the gas chromatograph was operated isothermally at 90 °C with a helium carrier flow rate of 30 mL/min. The second gas chromatograph was used to identify the concentration of light gases, such as oxygen, nitrogen, carbon monoxide (CO), and carbon dioxide (CO₂); it contained a 10 ft (3.05 m)×1/8 in. (3.2 mm) Supelco Carbosieve S-II column. A temperature ramp from 35 to 225 °C (at 32 °C/min) was used.

The TOC concentration of the TDG feed and the liquid phase reactor effluent were analyzed using a TOC analyzer (Shimadzu, model TOC-VCSH), which operated using the combustion catalytic oxidation method, and a highly sensitive nondispersive infrared (NDIR) detector, respectively. Samples were analyzed in triplicate. The relative standard deviation (RSD) for the TOC measurements fell between 0.2 and 2.5%; the results are reported as averages. The TOC conversion used to evaluate the TOC disappearance efficiency in SCW, X, was defined as

\[
X = \left(1 - \frac{[TOC]_f}{[TOC]_i}\right)
\]

(1)

where [TOC]ᵢ and [TOC]ₑ are the concentrations at the reactor inlet and outlet, respectively.

IC (Dionex DX-100) was used to determine the concentration of sulfate of the effluent. The IC system was equipped with an anion column (Star-Ion A300) and an anion self-regenerating suppressor (ASRS-Ultra II). The signal output was recorded using a Hitachi integrator (model D-2500).
Table 2. Hydrothermal Decomposition Experimental Variables and Ranges

<table>
<thead>
<tr>
<th>Experimental Variable</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, $P$</td>
<td>25 MPa</td>
</tr>
<tr>
<td>Temperature, $T$</td>
<td>386 to 528°C</td>
</tr>
<tr>
<td>Residence Time, $t$</td>
<td>13 to 7 s</td>
</tr>
<tr>
<td>Initial TDG Concentration*</td>
<td>0.32 to 10 mmol/L</td>
</tr>
<tr>
<td>Initial TOC Concentration*</td>
<td>1.38 to 99 mmol/L</td>
</tr>
</tbody>
</table>

* TDG and TOC concentrations at the reactor inlet were calculated from the feed stock concentrations and flow rates of the feed streams under the process conditions.

Results and Discussion

Hydrothermal Decomposition

The hydrothermal decomposition experiments were conducted in an isothermal and isobaric flow reactor in the absence of oxygen. The range of conditions explored for these experiments is presented in Table 2. The initial TDG and TOC concentrations were the concentrations at the reactor entrance, as described previously [11]. Because the TOC concentration is used to develop the kinetic rate model, a correlation equation between the TDG concentration ($C_{TDG}$) and the TOC concentration ($C_{TOC}$) was useful when preparing the initial organic feed. The equation is defined as

$$C_{TOC} = 4.443 C_{TDG} + 0.001$$  \hspace{1cm} (2)

Figure 2 shows the correlation between the TDG concentration and the TOC concentration from the data of 58 experiments. The values correlate with a correlation coefficient of $R^2 = 0.9996$. For consistency with all previous experiments conducted at our laboratory, a nominal operating pressure of 25 MPa was selected. This pressure is representative of those used industrially and is far enough above its critical pressure that the physical properties of water (e.g., $\rho$, $\varepsilon$, $K_w$) are not affected by small pressure fluctuations.

The reaction products included gaseous, liquid, and very few solid components. Because the amount of gas produced in the reaction was too low to measure, it was difficult to quantitatively determine the gas fraction. Thus, the carbon balance and sulfur balance could not be determined in these experiments. There was a distinct odor from all of the samples that was due to the presence of $H_2S$, which we determined during the experiments to be one of the reaction products in the gas phase. The other detectable gaseous products were CO, CH₄, CO₂, ethylene (C₂H₄), and ethane (C₂H₆). As for the liquid products, IC analyses indicated the existence of sulfuric acid in small concentrations. The sulfuric acid (H₂SO₄) concentration accounted for less than 1 % of the sulfur fraction in each experiment, indicating that TGD was not transformed into H₂SO₄ as the final product.

Figure 3 presents the resulting conversion of TDG based on the TOC content as a function of the temperature and residence time measured in the hydrothermal decomposition experiments. The hydrothermal decomposition results from 386 to 528°C show an essential increment of the TOC conversion and generally agree with Lachance’s experimental results for TDG hydrolysis in a tubular reactor using SCW [16]. Although hydrothermal decomposition at 528°C resulted in a 92±2 % TOC conversion, there still remained intermediate products that could be harmful to human health (e.g., H₂S). Thus, a further process would be required to degrade these intermediate products.

Rate Expression of Hydrothermal Decomposition of TDG

A the first-order global power-law rate reaction was used to predict the rate of TDG hydrothermal decom-
position in SCW:

\[
\text{rate} = -\frac{d[C_n]}{dt} = k[C_n]
\]  

(3)

where \([C_n]\) is the concentration of the reactant (given in units of mmol/L) and \(k\) is the apparent first-order rate constant (in s\(^{-1}\)). Eq. 3 is easily integrated over the appropriate limits

\[
\int_{t_o}^{t_i} [C_n] \, dt = \int_{t_o}^{t_i} -k \, dt
\]

(4)

Solving Eq. 4 yields:

\[
\ln\left(\frac{[C_n]_{t_i}}{[C_n]_{t_o}}\right) = -k t
\]

(5)

Substituting \(C_n\) with [TOC] and rearranging the equation with respect to the TOC conversion, \(X\), defined by Eq. 1, the following relationship is obtained:

\[
\ln(1-X) = -k t
\]

(6)

Therefore, \(k\) can be determined from the negative slope of the plot of \(\ln(1-X)\) versus the residence time. This calculation was performed for each set of data using the regression tool; the uncertainty in the slope was calculated at 95 % confidence. Figure 4 shows the plot of \(\ln(1-X)\) against the residence time (for each temperature). The negative slope of each linear fit gave the rate constant, \(k\).

The rate constant can be expressed as a function of the temperature in the form of the Arrhenius equation:

\[
ln(k) = \ln(A) - \frac{E_a}{RT}
\]

(7)

or, equivalently:

\[
\ln(k) = \ln(A) - \frac{E_a}{RT}
\]

(8)

where \(A\) is defined as the pre-exponential factor or frequency factor, \(E_a\) is the activation energy, \(R\) is the universal gas constant, and \(T\) is the absolute temperature. From Eq. 8, a plot of \(\ln(k)\) vs. \(1/T\) has a slope of \(-E_a/R\) and an intercept of \(\ln(A)\).

The Arrhenius plot, shown in Figure 5, provides estimates of the global activation energy (71.32±5.20 kJ/mol) and the pre-exponential factor \([5.57(±0.002)\times10^3\, \text{s}^{-1}]\) to a 95 % confidence value. The resulting first-order rate expression for the hydrothermal decomposition of TDG based on TOC is as follows:

\[
-\frac{dt}{d\text{TOC}} = 5.57(±0.002)\times10^3\times10^{(71.32±5.20/RT)} \times \text{TOC}
\]

(9)

Comparison of TOC Conversions Between Hydrothermal and Oxidation Reactions

The rate expression result for the hydrothermal reaction is significantly different than the expression obtained earlier from oxidation experiments [17,18]. The activation energy determined in the hydrothermal reaction is ca. twice that estimated in the oxidation study (71 vs 41 kJ/mol) and the pre-exponential factor is ca. 30 times greater. The cause of this difference is related to the effect of the oxidant. Figure 6 shows a comparison of the TOC conversions obtained from the hydrothermal and oxidation processes at a temperature 475±1 °C, a fixed pressure of 25 MPa, and an initial TOC concentration of 1.64 mmol/L. The oxygen excess used for the oxidation process was 150 %. As is evident in this figure, the hydrothermal process gave a lower TOC conversion when compared with the oxidation process. This finding
indicates that the oxidant enhances the reaction rate of TOC in SCW. The oxidant is also essential for the destruction of the intermediate carbon-based product into CO$_2$ and the oxidation of the sulfur-containing products into H$_2$SO$_4$ [17].

**Conclusions**

The hydrothermal decomposition of thiodiglycol (TDG) was examined in supercritical water (SCW) at residence times of 13 – 7 s and a fixed pressure of 25 MPa. The hydrothermal decomposition results showed an essential increment of the total organic carbon (TOC) conversion in the range 386 – 28 °C. However, the TOC conversion was lower than that of the oxidation process, and intermediate products remained that could be harmful to human health (e.g., hydrogen sulfide), even though the TOC conversion was 92±2% at a temperature of 528 °C. Thus, a further gas treatment process is required to degrade the intermediate products of the hydrothermal reaction. The carbon and sulfur balances could not be calculated because it was difficult to determine their gas fractions quantitatively. The hydrothermal decomposition rate of TDG, based on the TOC disappearance rate, in SCW was predicted by using a first-order global power-law rate equation. The parameters were determined to be 5.57 (±0.002)×10$^3$ s$^{-1}$ for the pre- exponential factor and 71.32(±5.20) kJ/mol for the activation energy.

**Acknowledgment**

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**References**