

Decomposition kinetics of dimethyl methylphosphate(chemical agent simulant) by supercritical water oxidation

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Abstract: Supercritical water oxidation (SCWO) has been drawing much attention due to effectively destroy a large variety of high-risk wastes resulting from munitions demilitarization and complex industrial chemical. An important design consideration in the development of supercritical water oxidation is the information of decomposition rate. In this paper, the decomposition rate of dimethyl methylphosphonate(DMMP), which is similar to the nerve agent VX and GB(Sarin) in its structure, was investigated under SCWO conditions. The experiments were performed in an isothermal tubular reactor with a H_2O_2 as an oxidant. The reaction temperatures were ranged from 398 to 633 °C at a fixed pressure of 24 MPa. The conversion of DMMP was monitored by analyzing total organic carbon (TOC) on the liquid effluent samples. It is found that the oxidative decomposition of DMMP proceeded rapidly and a high TOC decomposition up to 99.99% was obtained within 11 s at 555 °C. On the basis of data derived from experiments, a global kinetic equation for the decomposition of DMMP was developed. The model predictions agreed well with the experimental data.

Keywords: supercritical water; oxidation kinetics; chemical agent; DMMP

Introduction

Under the provisions of the 1993 International Chemical Weapon Convention, all stockpiled chemical warfare agents (CWAs) are to be irreversibly destroyed. Studies of supercritical water oxidation (SCWO) for treating and destroying CWAs are underway in support of an international program for the destruction of these CWAs stockpiles. SCWO has been known as an efficient and clean technology for the treatment of aqueous organic wastes that derives its effectiveness from the unique solvent properties of water at conditions well above its critical point of 374.3 °C and 22.1 MPa (Fang *et al.*, 2005, 2004, 2000; Veriansyah *et al.*, 2005; Park *et al.*, 2003; Shaw and Dahmen, 2000; Lachance *et al.*, 1999; Rice and Steeper, 1998). When organic compounds and oxygen are brought together in supercritical water (SCW), the oxidation of the organic is rapid and complete to carbon dioxide and water. Heteroatom such as Cl, S, and P are converted to their corresponding mineral acids (HCl , H_2SO_4 , and H_3PO_4), which can be neutralized by using a suitable base to produce salts of relatively low solubility at supercritical conditions. If any organic nitrogen presents the resulting product is primarily molecular N_2 with some N_2O (Killilea, 1992). NO_x gases, typical undesired byproducts of combustion processes, are not formed because the temperature is too low for these oxidation pathways to be favored. Detailed reviews of the technology are available from Brunner (Brunner, 1994; Schmieder

and Abeln, 1999; Gloyna *et al.*, 1994; Savage *et al.*, 1995).

Knowledge of the kinetics of the chemical reactions that occur during SCWO is required to design and analyze SCWO reactors and process (Oh *et al.*, 1996). This realization has motivated numerous previous studies of SCWO kinetics, nearly all of which have concentrated in the kinetics of reactant disappearance. Simply making the reactant disappear, however, by converting into a set of different organic compounds is insufficient for waste treatment by SCWO. Moreover, it is potentially dangerous if the products of incomplete oxidation are more toxic or hazardous than the starting material. It is the oxidation rate of the total organic carbon (TOC) to CO_2 , not the disappearance rate of the initial organic reactant itself, which is of primary applicability to the commercial SCWO process (Frisch and McBrayer, 1996). Indeed, destruction and removal of TOC is the ultimate goal of some SCWO. Thus, the kinetics of TOC disappearance assumes particular significance.

In this paper we describe experiments of dimethyl methylphosphonate(DMMP) which was designed to identify kinetic oxidation rate in supercritical water. DMMP was chosen as a simulant for the nerve agent such as VX and GB since it is structurally similar and has physical properties that are comparable to the actual agent. The chemical structure which can be described DMMP, VX and GB is shown in Fig.1 where R_1 and R_2 are differing functional groups. For DMMP, $R_1 = OCH_3$ and $R_2 = CH_3$; for GB,

$R_1 = F$ and $R_2 = CH(CH_3)_2$; and for VX, $R_1 = SCH_2CH_2N(C_3H_7)_2$, and $R_2 = CH_2CH_3$. Selected physical properties of DMMP and Agent GB are listed in Table I (ANFC, 2002).

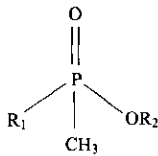


Fig.1 Structure of chemical agent warfare

Table 1 Physical properties of DMMP and GB

Property	DMMP	GB
Molecular weight	124.08	140.1
Boiling point, °C	180	158
Melting point, °C	Pour point : < -50	-56
Density at 25°C, g/ml	1.17	1.09
Solubility in distilled water at 25°C, g/100g	Miscible	Miscible

1 Experimental

1.1 Apparatus and procedure

The experiments were conducted in a laboratory-scale, continuous-flow SCWO reactor system. The experimental set-up is similar to previous published works (Veriansyah *et al.*, 2005). The system involved two parallel sets of equipment that are almost identical, one for delivering the DMMP solution and the other for the oxidant. DMMP and oxidant solution were pumped separately into the system by high pressure pumps (Thermo Separation Product Company). All hot sections of the system were insulated in boxes of ceramic board and the temperature was monitored directly using thermocouple. The temperature of the system was controlled by a temperature controller (Hanyoung DX 7). Oxygen, the oxidant used in these experiments, was prepared by dissolving hydrogen peroxide with deionized water in a feed tank. In order to assure all of H_2O_2 is decomposed to give H_2O and O_2 , the oxidant was pre-heated by flowing through 6 m coiled 1/8-in O.D. SS 316 tubing at 600°C and residence time of more than 14 s. Based on the studies of Phenix *et al.* (2002) and Croiset *et al.* (1997), it has been evidenced that H_2O_2 completely decomposed in the pre-heater even in those experiments carried out at high flow rate and low temperature. DMMP solution was pre-heated by flowing through 0.5 m 1/8-in O.D. SS 316 tubing. The solutions mixed at the reactor entrance in a SS 316 cross and then entered the reactor, which was constructed from a 280 mm length of 18 mm O.D. and 9.5 mm I.D. SS 304 tubing. Upon leaving the reactor, the effluent was cooled rapidly in

a shell and tube heat exchanger and then depressurized to ambient condition by a back-pressure regulator (Tescom Co. 26-1721-24). The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder, and their volumetric flow rates were measured at ambient laboratory conditions.

1.2 Materials and analytical methods

DMMP (Aldrich, 97 wt. %) was the reagent used in the experiments. Hydrogen peroxide (Junsei, 35% w/v aqueous solution) was used as an oxidant. Diluted oxidant solutions were prepared using deionized water.

The concentration of DMMP and liquid-phase reactor effluents were analyzed by TOC Analyzer (Shimadzu TOC-VCPN), which is based on combustion catalytic oxidation method and highly sensitive non-dispersive infrared (NDIR) gas analysis, respectively. Destruction efficiency of TOC, X , defined as follows, was used to evaluate the extent of oxidative decomposition.

$$X = 1 - \frac{[TOC]_f}{[TOC]_i} \quad (1)$$

where $[TOC]_i$ is the initial TOC and $[TOC]_f$ is the residual TOC after reaction.

2 Results and discussion

Forty-one supercritical water oxidation experiments were performed in an isothermal and isobaric tubular reactor. Table 2 provides the experimental ranges and variables. The oxidation reaction in this study can be represented to following stoichiometric Eq. (2).

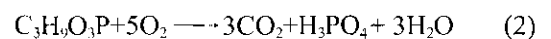


Table 2 Experimental variables and ranges

Experimental variable	Range
Pressure(P), MPa	24
Temperature(T), °C	398–633
Residence time(t), s	4–15
TOC concentration at reactor inlet, mmol/L	2–32
Oxidant concentration at reactor inlet, mmol/L	38–300

In order to develop reliable reaction rate expression, data were taken under various conditions. The global power-law reaction rate can be described as follows:

$$\text{rate} = -\frac{d[C_n]}{dt} = k[C_n]^a [O_2]^b [H_2O]^c \quad (3)$$

where $[C_n]$ is the concentration of reactant (mmol/L); $[O_2]$ is the concentration of oxidant (mmol/L); $[H_2O]$ is the concentration of water; t is the reactor residence time; a , b , and c are the reaction orders of C_n , O_2 , and

H₂O respectively. k is the rate constant, which can be expressed in Arrhenius form in equation as follow:

$$k = A \exp(-E_a/RT) \quad (4)$$

where A and E_a are the pre-exponential factor and activation energy, respectively.

In this study, we assumed the global oxidation of DMMP depends only on the temperature, the reactant concentration, and the oxidant concentration. The water concentration was assumed to have no explicit effect on the reaction rate, as is the case in many reported SCWO kinetic studies, so the global power-law reaction rate can be expressed as:

$$\text{rate} = -\frac{d[C_n]}{dt} = k[C_n]^a [O_2]^b \quad (5)$$

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

$$-\frac{d(1-X)}{dt} = k[TOC]_i^{a-1} (1-X)^a [O_2]^b \quad (6)$$

Since all of experiments were performed at very short contact time, between 4 and 15 s, the method of initial rates can be used to all data(Fogler, 2000; Portela *et al.*, 2001). If the method of initial rate is applied to Eq.(6) with the initial condition $X = 0$ at reaction time $t = 0$, it can be solved analytically to provide Eq. (7) as the relationship between the TOC removal efficiency and the experiment variables.

$$X=1-[1-(1-a)kt[TOC]_i^{a-1} [O_2]_i^{b-1}]^{1/(1-a)} \quad \text{for } a \neq 1 \quad (7)$$

A multi variable non-linear least squares technique was used to estimate the kinetic parameters A , E_a , and the reaction orders. The best-fit values were obtained by minimizing the sum of squares error.

$$s^2 = \sum_i^{N_{\text{exp}}} (X_{\text{exp}} - X_{\text{pred}})^2 \quad (8)$$

where N_{exp} is the number of experiments, X_{exp} is the experimental conversion and X_{pred} is the model predicted DMMP conversion. The quality of data fitting was evaluated by R^2 in ANOVA routine (Johnson and Bhattacharyya, 2001). It has algorithms to estimate 95% confidence interval on each parameter and on the predicted response. Using this procedure and considering all data points, the best-fit global rate expression for TOC of DMMP oxidation in supercritical water was obtained as

$$-\frac{d[TOC]}{dt} = 66.56(\pm 0.48)\exp\left(\frac{-42.00 \pm 0.41}{RT}\right) \cdot [TOC]^{0.96 \pm 0.02} [O_2]^{0.35 \pm 0.04} \quad (9)$$

Fig.2 shows a good comparison between the experimental and prediction TOC decomposition with $R^2=0.986$. The dashed lines, indicating a deviation of $\pm 5\%$ TOC decomposition from the 45 degree line

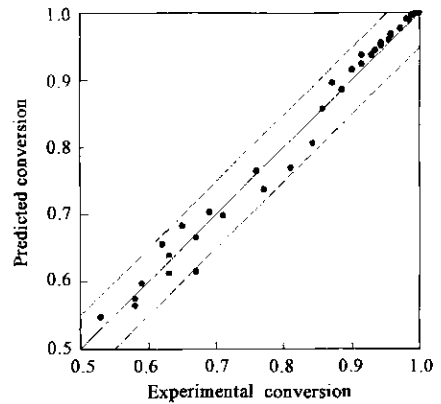


Fig. 2 Parity plot for power-law rate equation for TOC Conversion

(perfect match), contain all data points. This model fits very well with our experimental data.

3 Conclusions

The decomposition kinetics of DMMP was examined from 398 to 633 °C at 24 MPa, residence time of 4–15 s with the initial concentration of DMMP based on TOC was ranged from 2 to 32 mmol/L and the initial oxidant concentration ranged from 38 to 300 mmol/L. Experimental data showed that TOC decomposition greater than 99.99% can be obtained within 11 s at temperature 555 °C.

By taking into account the dependence of reaction rate on oxidant and TOC concentration, all experimental data were used to fit the reaction rate in a non-linear regression analysis, assuming a zero-order dependence on water concentration. Reaction parameter values were determined to be $66.56 \pm 0.48 \text{ L}^{1.31} \text{ mmol}^{-0.31} \text{ s}^{-1}$ for the pre-exponential factor, $42.00 \pm 0.41 \text{ kJ/mol}$ for the activation energy, and for the reaction orders, 0.96 ± 0.02 for DMMP (based on TOC), and 0.35 ± 0.04 for oxidant.

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