Kinetics of the reaction of ozone with 2,4,6-trichlorophenol

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Abstract

The kinetics of the aqueous phase reaction between ozone and 2,4,6-trichlorophenol was studied in this work using a wetted-sphere absorber. Ozone absorption rates into an aqueous solution of trichlorophenol were interpreted to give an expression for the second-order kinetic rate constant as $k_2 = 8.19 \times 10^{21} \exp(-11630/T)$ l/g mol s. Stoichiometry experiments showed that one mole of ozone reacts with one mole of 2,4,6-trichlorophenol.

1. Introduction

With the development of large-scale ozone generators along with reduced installation and operating costs, there has been increasing interest in using ozone (O_3) to treat waste-water effluents containing hazardous organic and inorganic compounds which are difficult or expensive to remove by conventional aeration, biodegradation, physical adsorption, etc. [1–6]. Its powerful oxidizing capabilities and the absence of hazardous decomposition products make ozone a potentially useful pretreatment agent for converting refractory compounds into substances which are treatable by one or more of the conventional methods of chemical breakdown. In some cases, ozone treatment alone may be sufficient to meet pollution standards.

Aqueous ozone oxidizes organic micropollutants in several ways including direct reaction, radical-type reactions involving $\cdot OH$ and $HO_2^\cdot$, and ozonolysis. The latter oxidation path involves attachment of ozone at double and triple carbon–carbon bonds to form ozonides which decompose quickly. Thermodynamically, the oxidation potential of ozone in water at a hydrogen-ion activity of unity is -2.07 V compared to chlorine which is -1.36 V [6–8].

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Aqueous ozonation of aromatic compounds appears to involve both ozonolysis and direct attack at individual carbon atoms [1]. Phenols are more reactive toward ozone than are most aromatics, and phenol itself is oxidized to carbon dioxide, formic acid, glyoxal and oxalic acid [1, 9].

The overall kinetics of nearly all reactions between organic compounds and ozone reported in the literature are first order with respect to both ozone and organic concentrations or second-order overall [10–12] . Comparisons of rate constants with chemical structures of the reacting groups show that nearly all reactions of ozone are highly selective and electrophilic from a kinetics point of view. With only a few exceptions, most of the kinetic measurements of ozone oxidation have been made at only one temperature so that activation energies are generally not available.

Studies have shown that the solubility of ozone in water obeys Henry's law [12, 13] which relates the partial pressure of ozone in the gas phase to its mole fraction in the liquid phase at equilibrium. The dependence of the Henry's law coefficient for the physical solubility on temperature and pH was found to be [14]:

$$H = 3.84 \times 10^7 [OH^-]^{0.035} \exp(-2428/T) \tag{1}$$

where the dimensions of H, $[OH^-]$ and T are atm/mole fraction, g mol/l and °K, respectively.

The objectives of this work were to obtain the stoichiometry and the kinetic rate law for the ozone oxidation in aqueous solution of 2,4,6-trichlorophenol. A wetted-sphere absorber was used to obtain the kinetics data. Trichlorophenol was chosen as representative of the class of chlorinated aromatic compounds known to be refractory to common waste-water treatment processes.

2. Experimental apparatus and procedure

All aqueous solutions used in this work were prepared using deionized water. The ozone–oxygen mixtures were obtained by a Welsbach ozone generator (Model T-408). Aqueous organic solutions were prepared by dissolving a measured amount of the organic compound into a known volume of water.

2.1. Kinetics experiments

A wetted-sphere absorber as shown in Fig. 1 was used to determine the reaction kinetics. The absorption chamber is made of a 31 cm long, 7.6 cm i.d. Pyrex glass cylinder and is enclosed by a constant-temperature jacket constructed from a 31 cm long, 16.5 cm i.d. Pyrex glass cylinder. Both cylinders are sandwiched between two stainless steel flanges and the ends are sealed with Teflon gaskets. Water to the jacket is supplied from and recycled to a constant-temperature circulating bath.

The liquid feed is pumped to a surge tank, then through a rotameter and through a coil in the constant-temperature jacket. It is then fed to a 1 cm i.d. delivery glass tube. The surge tank which is topped by a closed space of nitrogen gas helps in eliminating pump pulses. The delivery glass tube can slide in the vertical direction and

A   From Gas Supply
B   From He Supply
C   To Fume Hood
D   Solution Supply
E   Manometer
F   Liquid Distributor
G   Wetted Sphere
H   Absorption Chamber
I   Water Jacket
J   Receiver Tube
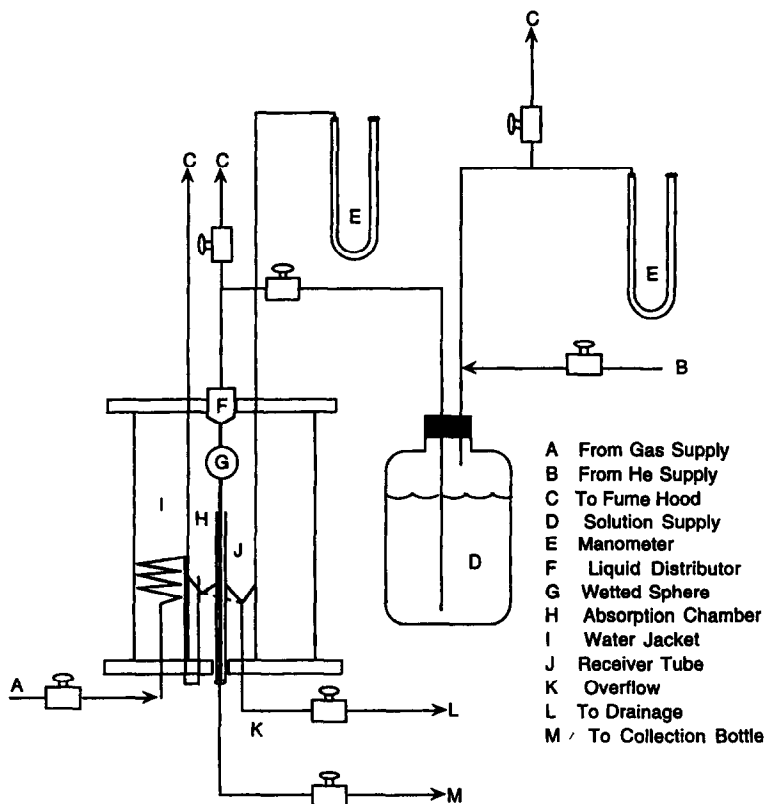K   Overflow
L   To Drainage
M   To Collection Bottle

Fig. 1. Schematic drawing of wetted-sphere apparatus.

can be locked in position by a swage-lock nut with Teflon ferrules. The gas supply is fed to a saturator, then through a coil in the constant-temperature jacket. It is then introduced into the absorption chamber at the base and is exhausted at the top of the chamber.

The sphere, a Hastelloy C ball of 3.76 cm diameter, was mounted on a 0.4 cm diameter Hastelloy rod. The part of the rod above the sphere was accurately centered in the orifice of the liquid feed distributor. This was achieved by axially mounting the rod onto a Teflon alignment block which, in turn, was a concentric tight fit in the liquid feed distributor. The liquid feed enters at the top and passes through the alignment block via eight holes which ensure even flow out of the orifice. After passing over the sphere the liquid runs down a short length of rod into a 0.9 cm i.d. receiving tube. The liquid is maintained at the top of this tube by a constant level device.

The sphere is fixed at 0.3 cm from the liquid feed orifice. This distance was chosen because at longer distances the liquid tended to break away from the rod and produced uneven distribution over the sphere. This condition is undesirable since it would alter the contact time and surface area by unpredictable amounts. At shorter

distances, the liquid tended to spray out over the ball even at moderate flow rates. The length of rod between the sphere and the receiving tube was fixed at 2.0 cm, since it was found experimentally by Davidson and Cullen [15], Goettler [16], Wild and Potter [17], and Tomcej et al. [18] that for distances less than 2.0 cm the rate of absorption drops appreciably owing to a 'stagnant layer' end effect. When the distance was greater than 2.0 cm 'rippling' effects became significant.

Freshly degassed liquid is initially fed to the distributor at high flow rates to ensure complete wetting of the sphere. When the liquid film has stabilized the flow rate is reduced to the desired rate.

The oxygen stream containing about 3 mol% ozone was saturated with water vapor at the temperature of the experiment before entering the absorption chamber. The gas was saturated by sparging through pure water at the temperature of the experiment. The water in the sparge vessel also becomes saturated with the gas. Since the liquid at the gas/liquid interface on the sphere is also saturated with ozone at the partial pressure of ozone in the absorption chamber, this equilibrium concentration was determined experimentally by measuring the ozone concentration for the water in the sparge vessel.

All of the experiments were done under atmospheric pressure. The temperature of the system is monitored by thermometers in the constant-temperature jacket, in the absorption chamber, and in the liquid feed distributor. The temperatures were controlled to within $\pm 0.3\,°C$.

A Model 5400 Perkin-Elmer gas chromatograph was used to analyze quantitatively for the molar concentrations of 2,4,6-trichlorophenol. It was equipped with a flame ionization detector (FID), a pre-column flash vaporizer and flow splitter, and a display console coupled with a menu-driven computerized processor. Chromatographic-grade cylinder helium was used as the carrier gas, and the analyses were performed isothermally. Ultra-pure hydrogen for the FID was generated by an LDC/Milton-Roy Elhygen Mark V electrolytic unit, and purified cylinder air was used for burning the hydrogen in the FID. A 30 m Alltech SE54 capillary column connected to the FID was used with pre-column flow splitting.

GC samples from the reactor feed lines were taken directly with a Hamilton microsyringe through a septum in a T-connector and contained only water and the individual organic compounds. To analyze the product stream leaving the reactor, small aliquots (10–20 cm³) of the product stream were first treated with an indigo dye injection to destroy the residual ozone (if any existed) and thus quench the reaction. These quenched aliquots were then sampled with the Hamilton microsyringe for GC analysis and contained water, unreacted organic (if not all consumed), excess indigo dye, ozone-bleached dye (if excess ozone existed) and products of the ozone-organic reaction. The GC sample sizes varied between 1 and 5 μl and were injected into the GC flash vaporizer with the Hamilton microsyringe. Flash-vaporized samples containing 2,4,6-trichlorophenol were carried through the pre-column splitter prior to entering the capillary column. The concentration of ozone in the aqueous feed and product streams of each reactor was measured using a standard indigo-dye method [15]. This method is very specific for ozone and is based on an instantaneous reaction

between aqueous ozone and aqueous indigo dye, producing a quantitative color change (bleaching action) which is detectable in a visible-range spectrophotometer or colorimeter. Blank samples containing no trichlorophenol were analyzed in the GC and no evidence of any dissolved organics in the deionized water used to make up the solutions was seen.

Two reagents were used in this method. The first was the aqueous dye which was made by diluting 0.6000 ± 0.0001 g of potassium indigo trisulfonate and 2.2924 ± 0.0001 g of 85% H_3PO_4 to one liter with DI water. The second was a buffer which was made by diluting 28 g of $NaH_2PO_4 \cdot H_2O$ and 35 g of 85% H_3PO_4 to one liter with DI water.

In measuring the concentration of aqueous ozone, 1 ml of the indigo dye solution and 10 ml of the buffer solution were first added to a 100 ml volumetric flask. To this mixture, a known volume of aqueous ozone was added from a syringe. If a blue color remained, the volumetric flask was filled with DI water to the mark. Aliquots of this solution were poured into a photometer sample tube which was then inserted into the measuring part of a Bausch and Lomb Spectronic 20 spectrophotometer/colorimeter (Spec 20) with a wavelength setting of 600 nm. The absorbance was recorded.

A blank was prepared in the same manner as stated above without the addition of aqueous ozone. The difference in absorbances between the sample and the blank was used to calculate the concentration of ozone in the sample from an adapted version of Beer's law.

2.2. Stoichiometry experiments

Batch reactor experiments were performed to find the stoichiometric ratio between 2,4,6-trichlorophenol and ozone. A known volume of the aqueous organic with a known concentration was placed in a well-stirred flask. A known volume of a known concentration of aqueous ozone was added to the flask and allowed to react to completion, which always took less than 15 min. The concentration of the unreacted aqueous organic was then measured in the GC, thus permitting calculation of the moles of organic consumed by the known moles of ozone initially added.

3. Results and discussion

The results of the stoichiometry experiments are shown in Table 1. It is seen that the data indicate that one mole of ozone reacts with one mole of 2,4,6-trichlorophenol.

3.1. Kinetics experiments

Gas absorption accompanied by a second-order chemical reaction is not described explicitly by any analytical equation under conditions where the penetration theory applies. However, a good approximation for the enhancement factor due to the

Table 1
Stoichiometry for the reaction between 2,4,6-trichlorophenol and ozone

Wt. of org. solution (g)	Wt. of O_3 solution (g)	Init. conc. of org. (mol/cm^3)	Init. conc. of O_3 (mol/cm^3)	Final conc. of org. (mol/cm^3)	Mole ratio (n org/n O_3)
9.90	19.50	3.80×10^{-7}	6.67×10^{-8}	8.10×10^{-8}	1.06
10.00	20.00	3.80×10^{-7}	6.67×10^{-8}	7.50×10^{-8}	1.16
10.00	19.60	5.90×10^{-7}	1.04×10^{-7}	1.20×10^{-7}	1.15
10.00	20.00	5.90×10^{-7}	1.04×10^{-7}	1.12×10^{-7}	1.22
55.50	30.70	1.63×10^{-6}	1.58×10^{-7}	1.00×10^{-6}	0.86
28.90	26.30	1.63×10^{-6}	1.58×10^{-7}	7.66×10^{-7}	1.15

chemical reaction is given by Brian et al. [19].

$$E = \frac{\left[\left(M\dfrac{E_i - E}{E_i - 1}\right)\right]^{1/2}}{\tanh\left[\left(M\dfrac{E_i - E}{E_i - 1}\right)\right]^{1/2}}, \tag{2}$$

where $M = (\pi/4)k_2 C_0 t$, k_2 is the second-order rate constant (cm^3 g^{-1} mol^{-1}s^{-1}), C_0 is the concentration of the organic compound, t is the gas/liquid contact time for the wetted sphere absorber (s), $E = k_c/k_c^0$, k_c is the mass transfer coefficient for chemical reaction conditions (cm/s), k_c^0 is the mass transfer coefficient under physical absorption conditions (cm/s) and E_i is the enhancement factor under conditions where the reaction may be considered to be instantaneous.

The second-order rate constant was determined from the absorption rate data by solving Eq. (2) iteratively for M. For these calculations E_i was approximated as [20]

$$E_i = 1 + \frac{C_0}{C_A^*}, \tag{3}$$

where C_A^* is the liquid phase concentration of O_3 at the gas/liquid interface, g mol/cm^3. The enhancement factor, E, was determined from the measured rate of O_3 absorption, R_A, and the theoretical solution of Olbrich and Wild [21] for physical absorption with laminar flow over a sphere. The Olbrich and Wild solution is given as

$$R_A^0 = QC_A^*[1 - \beta_i \exp(-\gamma_i \alpha)], \tag{4}$$

where R_A^0 is the rate of physical absorption, (g mol/s), Q is the volumetric flow rate of liquid (cm^3/s), β_i, γ_i are the constants given by Olbrich and Wild, $\alpha = 3.36\pi(2\pi g/3v)^{1/3} r_s^{7/3} Q^{-4/3} D_A$, $g = 981$ cm/s^2, v is the kinematic viscosity (cm^2/s), r_s is the radius of sphere (cm), D_A is the liquid-phase diffusion coefficient of O_3 (cm^2/s).

The experimental absorption rates, R_A, were calculated from the measured liquid flow rate and from the measured depletion of trichlorophenol.
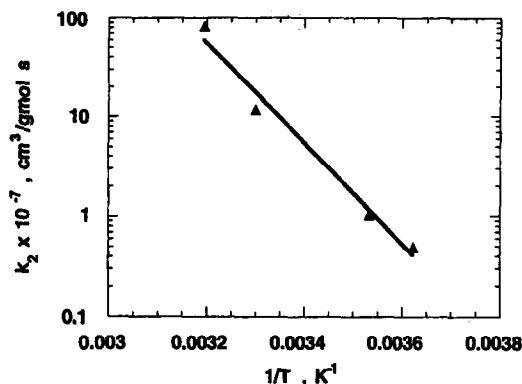
$$R_A = Q(C_1 - C_2), \tag{5}$$

Fig. 2. Second-order rate constant for the reaction between 2,4,6-trichlorophenol and ozone.

where C_1 is the organic concentration in inlet stream (g mol/cm^3), and C_2 is the organic concentration in outlet stream (g mol/cm^3).

The enhancement factor is then calculated from

$$E = R_A / R_A^0 \tag{6}$$

Fig. 2 shows an Arrhenius plot of the second-order rate constant vs. the inverse of the absolute temperature. As indicated in this figure, the data follows the Arrhenius relationship and are well-correlated by

$$k_2 = 8.19 \times 10^{21} \exp\left(\frac{-11\,630}{T}\right) \text{1/g mol s.} \tag{7}$$

The expression for the second-order kinetic rate constant given by Eq. (7) was obtained by a least-squares fit of the data taken over the temperature range 3–40 °C. The activation energy for the reaction between ozone and 2,4,6-trichlorophenol as determined from Eq. (7) is 23 030 cal/g mol.

For these calculations the diffusivity of O_3 in water was calculated using the predictive equation proposed by Akgerman and Gainer [22]. At 25 °C the diffusivity of O_3 in water is calculated as 2.01×10^{-5} cm^2/s.

For the experiments reported here the pH of the solutions used was not controlled and was measured as 4.9 ± 0.1 with the slight variation due to variation in the concentration of trichlorophenol (1.8×10^{-7} to 10.8×10^{-7} g mol/cm^3).

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