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Use of methanol and oxygen in promoting the destruction of deca-chlorobiphenyl in supercritical water

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Abstract

The destruction of the well-known PCB, deca-chlorobiphenyl (10-CB), by oxidation and methanolysis in supercritical water (SCW), has been studied in a micro-reactor hydrothermal diamond-anvil cell (DAC, 50 nL) and in larger batch reactors (6 mL). The DAC was coupled to optical and infrared microscopes. In the DAC experiments, 10-CB proved to be stable under pyrolytic conditions, whereas in water, it was hydrolyzed and actually dissolved at temperatures above 475 °C. When partial oxygen was added to the 10-CB/water system, the solubility of 10-CB increased slightly as compared to the pure water experiments, and 10-CB was further decomposed by oxidation. The addition of methanol resulted in further decomposition by methanolysis, as confirmed by FT–IR spectroscopy, and lowered the dissolution temperature to 419 °C. Both oxygen and methanol (25 vol.%) were then used to destroy 10-CB in batch reactors, in which the supercritical water experiments permitted a detailed study of the reaction products of the 10-CB destruction. In the absence of methanol, more than 12 intermediate products were detected by GC–MS, and 99.2% of the 10-CB was destroyed in the presence of 225% excess oxygen at 450 °C within 20 min. When methanol was used in the absence of any excess oxygen, a destruction rate of 100% was achieved at 450 °C within 10 min and only three intermediate products were detected. The enhanced destruction of 10-CB in the presence of methanol is attributed to the homogenous reaction conditions employed and the generation of free radicals.
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1. Introduction

Polychlorinated biphenyls (PCBs; $C_{12}H_{10-m}Cl_m$) are mixtures of synthetic chlorinated aromatic hydrocarbons with the same basic chemical structure and similar physical properties ranging from oily liquids ($m = 1$–4, light, oily fluids; $m = 5$, heavy, honey-like oils) to waxy solids ($m > 5$, greases and waxy substances; $m = 10$, solid) [1,2]. Because of their non-flammability, chemical and thermal stability, high boiling points and low electrical conductivities, PCBs have been used in hundreds of industrial and commercial applications, including electrical equipment (e.g., transformers and capacitors), plasticizers, hydraulics and lubricants, and carbonless copy paper. PCBs are considered to be probable human carcinogens [1–3] and, consequently, their destruction is crucial owing to the potential health risks involved. Technologies to destroy PCB wastes include chemical and biological treatment,

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incineration [4], and supercritical water oxidation. Chemical processes are proven technologies, but are used to destroy lower concentrations of PCBs in contaminated oils. Biological treatment is still at an early stage of development and is not commercially available. Conventional flame-based incineration, however, seems to be ineffective due to the inflammability and chemical stability of PCBs [1]. We propose here a new process involving the oxidation and methanolysis of PCBs in supercritical water (SCW; >374 °C and 22.1 MPa) which should result in the *complete* destruction of PCBs. In the supercritical water oxidation (SCWO) process employed (450–600 °C; 27 MPa [5–7]), PCBs, water, methanol and oxygen form a single phase in which the PCBs are homogeneously and completely destroyed without generating pollutants (e.g., NO_x, PAHs). In particular, we now report the results of an investigation of the oxidation and methanolysis in supercritical water for the most stable PCB, deca-chlorobiphenyl (10-CB; $C_{12}Cl_{10}$, $m = 10$), in a hydrothermal diamond-anvil cell micro-reactor and in batch reactors.

2. Experimental

Solid deca-chlorobiphenyl powder (10-CB; 100–500 μm, 99.0% purity) was used as received from Supelco-Aldrich, Bellefonte, PA. It had a melting point $T_m = 302.5$ °C and a density of 1200 kg/m³. Methanol (99.9% purity) was obtained from Sigma–Aldrich (St. Louis). Hydrogen peroxide 50 wt.% (Fisher ACS certified) was used as an oxygen supplier. Two types of reactors were used in the experiments: (i) a micro-reactor (50 nL), hydrothermal diamond anvil cell (DAC) for visual observation of the phase changes; (ii) larger batch reactors (6 mL) to determine the products of decomposition and the destruction rates of 10-CB.

2.1. Micro-reactor, hydrothermal diamond anvil cell

The phase behavior of 10-CB in supercritical water was investigated using a hydrothermal DAC micro-reactor that has been described earlier [8]. The reaction chamber (50 nL; 500 μm i.d., 250 μm thickness) was sealed by the compression of two opposing diamond anvils and was heated by two electric micro-heaters. The initial density of water (or pressure) was adjusted by changing the applied force to the diamond anvils. Little change was observed in the chamber volume during the reaction process [8]. The temperature of the two diamond anvils was measured with the aid of a data acquisition unit (Strawberry Tree, Model DS-12-8-TC, Sunnyvale, CA). After loading the sample (10-CB + H_2O + methanol/H_2O_2), the mixture was heated and the progress of the reaction was monitored using a stereo-microscope (Olympus SZ11). The images (110X magnification) were recorded on a Panasonic 3 CCD camera (AW-E300) and a VHS recorder (Panasonic AG-5720). Digital imaging analysis of the sample area was achieved using a commercial soft-

ware package (Scion Image, Frederick, MD). After the reaction was complete, the solid residues that had been deposited on the diamond faces were analyzed by FT–IR microscopy (UMA 500, Bio-Rad, Cambridge, MA). Fuller details of the experimental set-up and procedures for these measurements are given in previously published work [9–11].

2.2. Batch reactors

Tubular stainless-steel (316-SS) batch reactors (6 mL; length = 105 mm, o.d. = 12.7 mm) were used to study the oxidation of 10-CB in SCW. Both temperature and pressure were measured with a pressure transducer fitted with a J-type thermocouple (Dynisco E242). In the experiments, approximately 1 and 10 mg of 10-CB, and a 1-mL mixture of {H_2O + methanol + H_2O_2} were loaded into the reactor. After sealing and connecting to the data acquisition system, the reactor was submerged in a fluidized sand bath (Omega FSB-3) and was heated at a rate of 3.5 °C/s up to 450 °C. After a pre-determined period (10–20 min), the reactor was quenched in cold water and the reaction mixture was emptied into a flask. The reactor was washed with water (9 mL) and benzene (10 mL), and the washings were transferred into the same flask. The resulting solution was filtered through a membrane filter. The benzene phase was decanted off from the aqueous phase. The aqueous phase was then analyzed using ion chromatography (Dionex DX-100) to determine the $HCOO^-$, CH_3COO^- and Cl^- anion concentrations. For each ion, three concentrations, blank, 20 ppm and 50 ppm, prepared from standards were used for calibration. The benzene phase was analyzed by gas chromatography-mass spectrometry (GC–MS; GCQ Packages: Polaris MS, Trace 2000 GC, ThermoQuest, Austin, TX). A calibration coefficient for the 10-CB analyses was obtained using blank, 1, 10 and 50 ppm (or 500 ppm for experiments with 10 mg 10-CB) 10-CB standards, and tetradecane was used as an internal standard. Other products were identified using library data without any standard material calibrations.

3. Results and discussion

Experiments concerning the phase behavior of 10-CB in the DAC were conducted under conditions of pure water, {25% vol. methanol + water} solution, at partial (insufficient) oxygen and excess oxygen concentrations. Fig. 1 shows IR spectra of the solid residues obtained from 10-CB decomposition in SCW using pure water, partial oxygen and methanol. Fig. 2 shows visual observation of 10-CB phase transition in SCW when methanol was used.

In the batch experiments, oxidation of 10-CB in SCW was performed at 450 °C, 30 MPa, and 10 or 20 min reaction times, using −36.0, 93.1, 159.5 and 225% excess oxygen concentrations (with 1 mL solution of 0.8–4.2 wt.%
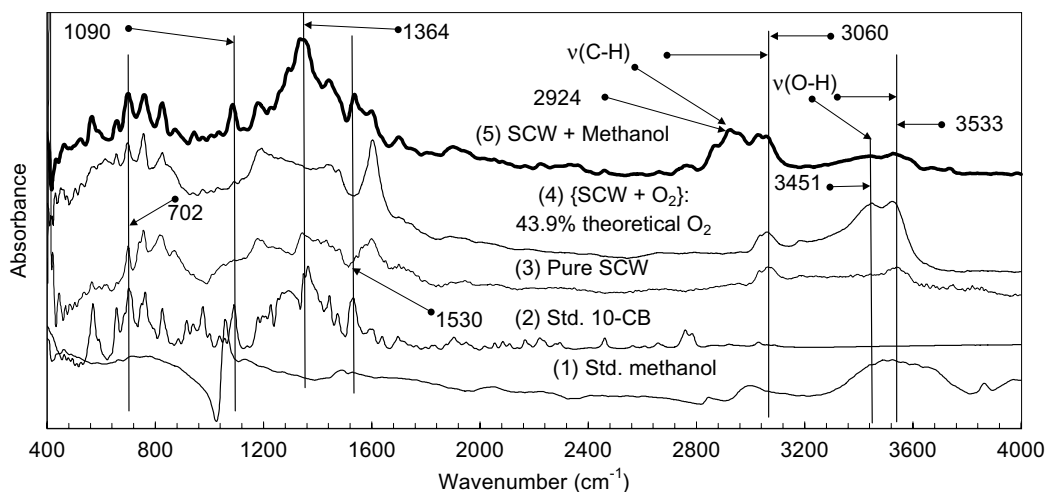
Fig. 1. FT–IR spectra for the standard methanol (#1) and 10-CB (#2), and solid residues produced from pure water (#3), partial oxidation (#4) and methanolysis (#5) in the DAC.
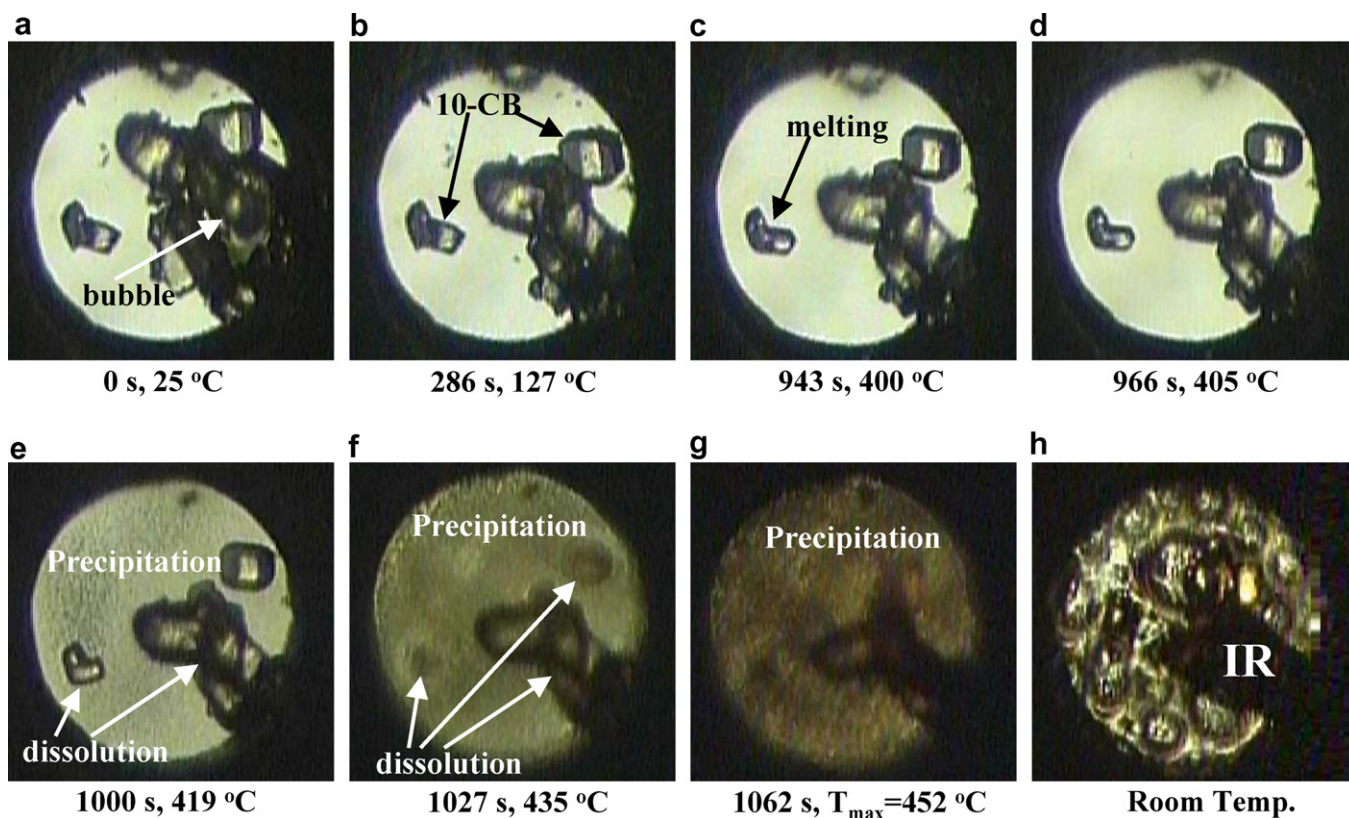

Fig. 2. Visual observation of the 10-CB + water + 25 vol.% methanol mixture when heated to 452 °C at a heating rate of 0.4 °C/s (solution density = 758 kg/m^3) in the DAC.

H_2O_2). Excess oxygen (mol%) was determined as the amount of oxygen above the theoretical requirement for the reaction: $C_{12}Cl_{10} + 5 H_2O + 19/2\ O_2 \rightarrow 12CO_2 + 10HCl$. The destruction of 10-CB in water with methanol was conducted at 200–450 °C for a 10 min reaction time. Fig. 3 illustrates the rate of destruction of 10-CB, with and without, methanol. Fig. 4 shows the GC–MS graphs for the intermediate products from the tests with methanol.

3.1. DAC experiments

The pyrolysis of 10-CB in the DAC was conducted at 450 °C for 20 min. It showed that little chemical reaction occurred, as confirmed by FT–IR spectroscopy [5]. When a mixture of 48 wt.% 10-CB and pure water was heated rapidly in the DAC to a maximum temperature of 599 °C, the air bubble disappeared at 198 °C, at which
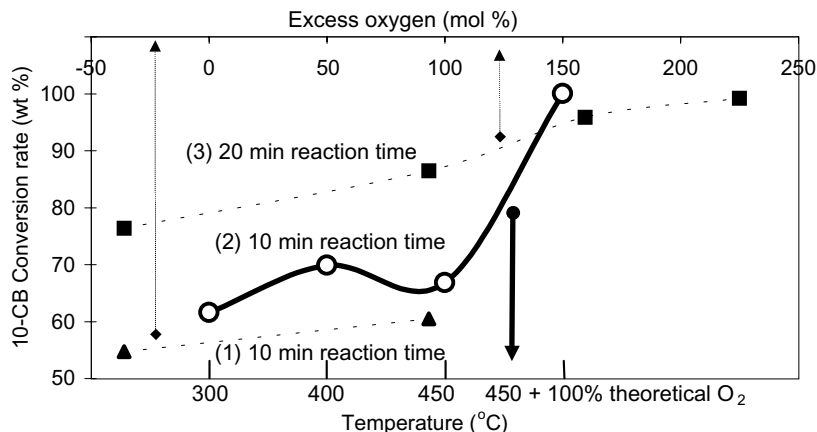
Fig. 3. Destruction rate of 10-CB in water in batch reactors, (1) without methanol at 450 °C and 30 MPa for 10 min reaction time, (2) with methanol at 300–450 °C for 10 min reaction time and (3) without methanol at 450 °C and 30 MPa for 20 min reaction time.

temperature the saturated water density was calculated to be 867 kg/m^3. The DAC experiments follow an isochoric heating path and so the temperature at which the gas bubbles disappear gives a close approximation to the true loaded water density. The 10-CB particles started dissolving at 475 °C. However, the solubility was quite low at the maximum temperature of 599 °C, and so the majority of particles still remained undissolved under these conditions. The undissolved residues remaining on the diamond anvils after the reaction, were analyzed by FT–IR spectroscopy. Fig. 1 (curve 3 vs. 2) shows that the 10-CB has been hydrolyzed on the basis of the C–H and O–H stretching modes at 3060 and 3533 cm^{-1}, respectively. Therefore, 10-CB can be decomposed by hydrolysis.

In the partial oxidation experiments, 44% of the theoretical oxygen (25 wt.% H_2O_2, water density = 917 kg/m^3) was used to oxidize a 34 wt.% 10-CB mixture by heating to 616 °C. The visual observations were similar to those in pure supercritical water but yielded a higher solubility and yellow colored solution. A majority of the 10-CB sample remained heterogeneous and did not dissolve. The IR spectrum (Fig. 1; curve 4 vs. 3) shows that the undissolved residue had an additional O–H band at 3451 cm^{-1} as compared with the spectrum obtained for the above experiment in pure SCW. Apparently, the additional band derives from oxidation. Therefore, adding oxygen can promote both the solubility and the rate of destruction of 10-CB.

Fig. 2 illustrates heating of {10-CB + water + 25 vol.% methanol} system to 452 °C at a heating rate of 0.4 °C/s (solution density = 758 kg/m^3). The dissolution temperature shifted to a much lower temperature of 419 °C (Fig. 2e), as compared to 475 °C for the pure water experiment. A greater solubility of 10-CB and more precipitates were observed, even when a lower reaction temperature was used (max 452 vs. 599 °C). The undissolved residue (Fig. 2h) was analyzed by FT–IR spectroscopy after the DAC was opened. The IR spectrum (Fig. 1; curve 5) indicates that the undissolved residue has an additional C–H band at 2924 cm^{-1}. Apparently, the additional band results

from methanolysis. We cannot obtain IR spectra for the gas inside the DAC (Fig. 2h) because of the strong IR absorption by water and diamond. However, most of gas indicated in Fig. 2h is air (or nitrogen) from the original air bubble (Fig. 2a) after it had dissolved in the mixture of {water + methanol} (Fig. 2b) and re-appeared upon cooling. A small amount of gas such as, CO, CO_2, H_2, CH_4, and C_2H_4 was likely produced from methanol decomposition [12] but the gas is unlikely to be from the reactions of 10-CB with water and methanol [13].

3.2. Oxidation of 10-CB without methanol in batch reactors

3.2.1. Oxidation at less than the theoretically required O_2 concentration

10-CB (10 mg) was oxidized in batch reactors and its destruction rate is depicted in Fig. 3 (curves 1 and 3). Experiments were performed at 64% of the theoretical O_2 required (or −36% excess O_2). When the reaction time was increased from 10 to 20 min, the 10-CB conversion rate rose from 54.7 to 76.4%. GC–MS analysis of the reaction products in the benzene extract phase showed that there were twelve other products consisting mainly of PCBs with low numbers of chlorine atoms, chlorobenzenes and chlorodibenzofurans. Analysis of the anions in the aqueous extract phase gave 9.8 and 7.2 ppm for HCOO$^-$, 0.3 and 0.9 ppm for CH_3COO^-, and 187.3 and 168.2 ppm for Cl$^-$ for the reaction times of 10 and 20 min, respectively.

3.2.2. Oxidation at excess O_2 concentrations

At 93% excess O_2, the 10-CB conversion rate increased from 54.7% to 60.5%, and from 76.4% to 86.6% for reaction times of 10 and 20 min, respectively. The Cl conversion rate, defined as the Cl in 10-CB that is converted to water soluble Cl$^-$, increased from 29% to 50% for 10 min, and from 26% to 66% for 20 min reaction times.

A 160% excess O_2 and 20 min reaction time led to a 95.9% destruction rate of 10-CB. The Cl conversion rate
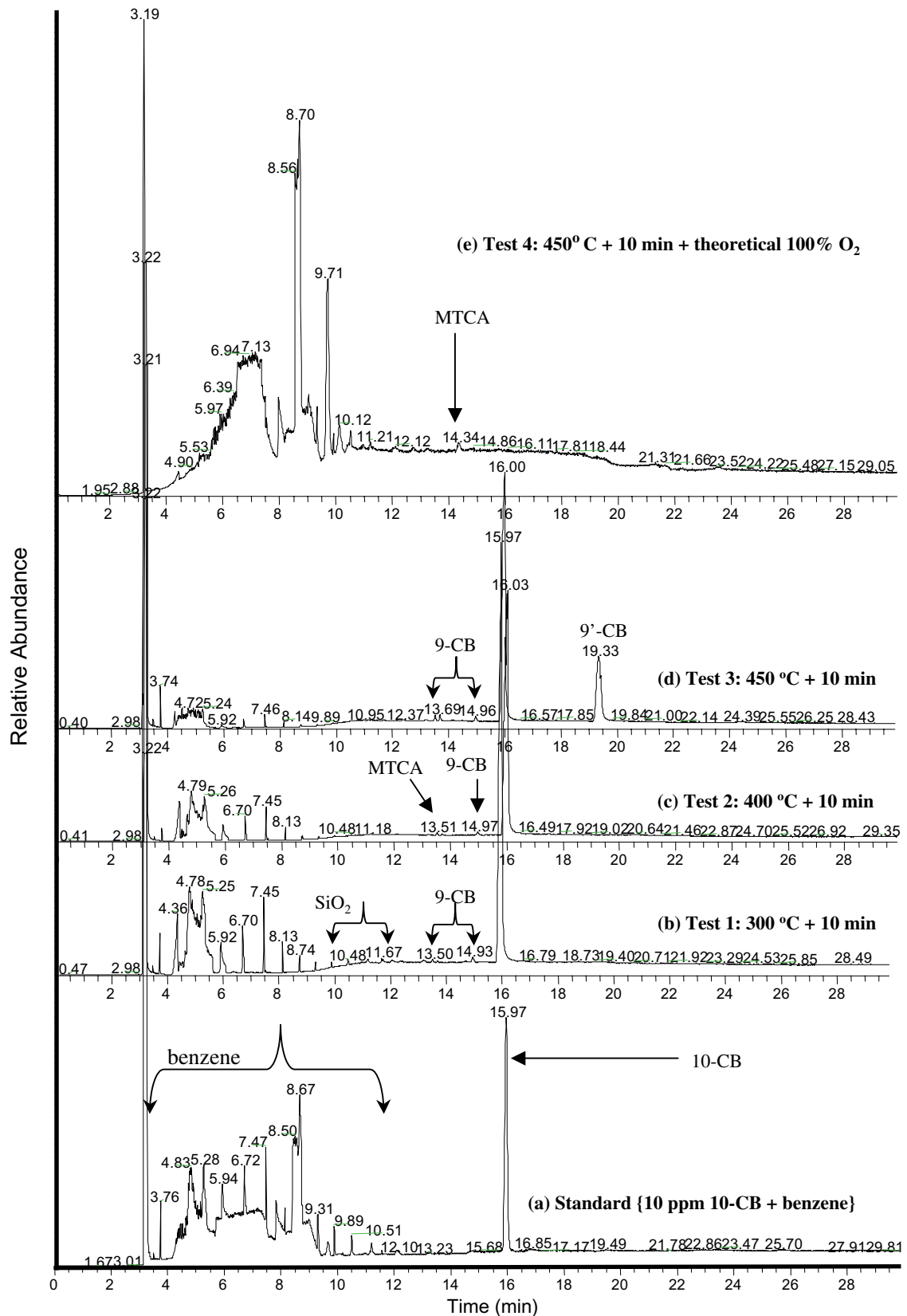
Fig. 4. GC–MS graphs for intermediate products from the tests with 25 vol.% methanol in batch reactors. MTCA: 2,2′-methylenebis[3,4,6-trichloroanisole]; 9-CB: 2,2′,3,3′,4,5,5′,6,6′-nonachloro-1,1′-biphenyl; 9′-CB: 2,2′,3,3′,4,4′,5,5′,6-nonachloro-1,1′-biphenyl.

increased from 66% to 88.1%. A GC–MS spectrum of the benzene extract phase showed that the dinaphthofurans, octa- and nonachlorobiphenyls (8-, 9-CB), pentachlorobenzene and hexachlorodibenzofurans were still present.

When the excess O_2 was increased to 225%, 99.2% of 10-CB was destroyed for a 20 min reaction time. The Cl conversion rate reached its highest value for all the experiments undertaken and was 95.9%.

3.3. Destruction of 10-CB with methanol in batch reactors

Eight experiments (10-CB, 1 mg) were conducted with a 25 vol.% methanol and water mixture at 200–450 °C for 10 min reaction times. Only four of these tests will be discussed here: test 1 at 300 °C; test 2 at 400 °C; test 3 at 450 °C and test 4 at 450 °C with 100% theoretical oxygen (stoichiometric oxygen for complete oxidation methanol, 50% H_2O_2 was used). When methanol was added, even without adding any oxygen and using lower temperatures, the destruction rate (tests 1–3) increased dramatically (Fig. 3; curve 2 vs. 1). The destruction rate at 300 °C is higher than that when oxidized with 100% excess oxygen at 450 °C (61.6% vs. 60.5%). However, the destruction rate is insensitive to temperature in the 300–450 °C range. When 100% theoretical oxygen was used, all the 10-CB was destroyed (Fig. 4e; test 4).

For the GC–MS analysis of the benzene phase for test 1 reacted at 300 °C (Fig. 4b), besides 10-CB, only one intermediate hydrolyzed product (9-CB) with low intensity was detected at 13.5 and 14.9 min. Other weak peaks at 10–12 min were identified as SiO_2, which were probably from sample glass vials or GC column. In this test, a 61.6% destruction rate was achieved, and most of the 10-CB was decomposed to water-soluble products (e.g., HCl, acetic acid). A higher temperature of 400 °C was used in test 2 and an additional weak peak for 2,2′-methylenebis[3,4,6-trichloroanisole] (MTCA) was detected (Fig. 4c). This MTCA most probably results from the methanolysis. At the highest temperature of 450 °C (test 3), a strong peak was detected and identified as an isomer of 9-CB (Fig. 4d), formed by hydrolysis. When 100% theoretical oxygen was added (test 4), no 10-CB peak was detected and only trace amounts of MTCA were found. We did not measure the gas composition in the batch tests, but its composition is similar to that obtained from methanol oxidation under SCW conditions and the gas is most likely composed of CO_2, CO, O_2, H_2, CH_4, and C_2H_4 [12–16].

Croiset and Rice et al. [14–16] have studied H_2O_2 decomposition and alcohol oxidation with H_2O_2 under SCW conditions. It was found that many radicals (e.g., OH, HO_2, H) were produced from the reactions with H_2O_2, which led to an accelerated decay of methanol [12] as compared to adding oxygen gas directly. These radicals also accelerated the destruction of 10-CB in our experiments. Methanol significantly enhances the reaction rates of PCBs in SCW through a free-radical dechlorination step to biphenyl, and then on to methanol- and methoxy-biphenyl [17,18]. In our work, 10-CB was dechlorinated by hydrolysis and methanolysis to lighter PCBs and MTCA,

and subsequently decomposed to water-soluble products via methanolysis, which were further oxidized homogeneously to HCl and CO_2 when O_2 was present.

4. Conclusions

Deca-chlorobiphenyl was completely destroyed in supercritical water with the addition of oxygen and methanol via sequential hydrolysis, oxidation and methanolysis reactions. Oxygen and methanol can promote the dissolution of 10-CB to provide homogeneous reaction conditions for the reactions. Adding methanol is more effective for the destruction of 10-CB to water-soluble products and affords fewer intermediates than does oxidation with excess oxygen. It is suspected that methanol is a major source of highly reactive free radicals involved in promoting the decomposition of PCBs.

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