

DECHLORINATION OF 1-CHLOROOCETADECANE, 9,10-
DICHLOROSTEARIC ACID AND 12,14-DICHLORODEHYDROABIETIC
ACID IN SUPERCRITICAL CARBON DIOXIDE

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Introduction

Pitch deposits are an ongoing problem in the pulp and paper industry. Their main components include fatty and resin acids, which often are chlorinated due to the bleaching process.¹ The complex nature of pitch prevents a direct analysis of its extractives by resulting in a large number of unresolved peaks on a chromatogram during GC analysis; consequently identification of each peak becomes very difficult. Much research has been done on pitch analysis in order to identify its exact chemistry.^{2,3} The origin of the present work is the idea that characterization of pitch deposits and ultimately their elimination may be simplified by reducing the number of chlorinated isomers by applying dechlorination while extraction is performed. The compounds selected for this study, 9,10-dichlorostearic acid (stearic-Cl₂) and 12,14-dichlorodehydroabietic acid (DHA-Cl₂), are the representatives of two major classes of extractives often found in chlorinated pitch deposits. 1-Chlorooctadecane (C₁₈-Cl) is also used as a simplified model of Stearic-Cl₂.

Supercritical fluids have been widely used not only as an extraction fluid but also as reaction media.⁴⁻⁷ Their use in either case has many advantages including reduction of organic solvent usage and faster processes. Palladium catalyzed hydrodehalogenation was carried out in supercritical carbon dioxide (SC-CO₂) for the selected compounds. This reaction was based on previously reported work on PCBs.⁸ The reaction scheme for dechlorination of C₁₈-Cl is as follows.



Optimization of experimental parameters such as pressure, temperature, and the concentrations of reagents (isopropanol and palladium) for dechlorination of C₁₈-Cl, Stearic-Cl₂, and DHA-Cl₂ in SC-CO₂ is reported as well as partial elucidation of the reaction mechanism in SC-CO₂ from the apparent activation energy and the thermodynamic values for desorption of dechlorinated compounds.

Methods and Materials

C₁₈-Cl (96%) was obtained from Aldrich Chemical Co., Stearic-Cl₂ (95 – 99 %) and DHA-Cl₂ (95 – 99 %) were obtained from Helix Biotech, and 5% Pd/γ-Al₂O₃ (reduced) was obtained from Alfa Aesar. Dehydroabietic acid was synthesized from DHA-Cl₂. Stearic acid and optima grade isopropanol was purchased from Fisher Scientific. A stainless steel reaction cell with an internal volume of 2.0 mL was constructed at the Science Technology Centre at Carleton University. Dechlorination in SC-CO₂ was performed in the reaction cell placed in the oven of a

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Suprex MPS/225 supercritical system and mounted atop a magnetic stirrer. The system diagram is shown in Figure 1.

Dechlorination in SC-CO₂ was carried out with 0.0371 g of 5% Pd/ γ -Al₂O₃. The reaction cell containing catalyst was heated for 5 min to the desired temperature, and the mixture was stirred for 5 min, followed by the introduction of 50 μ L of 1000 ppm of chlorinated compound in isopropanol into the cell. The cell was then charged with CO₂ to the desired pressure and the reaction mixture was stirred for 5 min. The outlet and inlet of the reaction cell were opened for 5 min to purge the cell contents into 3 mL of isopropanol in a 5 mL glass vial, concentrated under a stream of N₂ to 0.5 mL, and analyzed by GC/FID. The GC column was a 30 m Megabore DB-5 (0.5 mm id). The GC temperature program used for the analysis of C₁₈-Cl was 160°C for 3 min, followed by a ramp at 12°C/min to 300°C, held for 1 min. Total analysis time was 15.66 min. C₁₈-Cl and octadecane eluted at the 7.8 min and 10.2 min, respectively. For Stearic-Cl₂ and DHA-Cl₂,

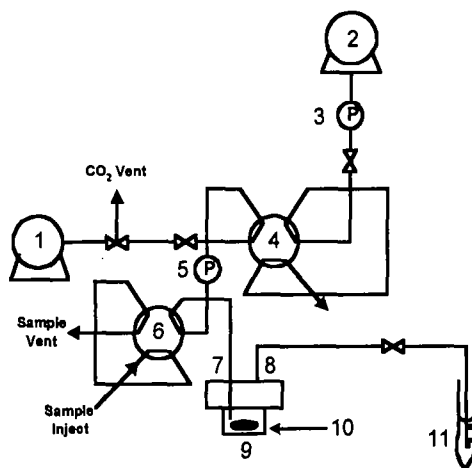


Figure 1: System diagram for dechlorination and extraction in SC-CO₂ (1: CO₂ pump, 2: isopropanol pump, 3: pressure gauge for isopropanol, 4: 6-port valve for isopropanol loop, 5: pressure gauge for the system, 6: 6-port valve for standard injection, 7 and 8: inlet and outlet of the reaction cell, respectively, 9: reaction cell, 10: magnetic stir bar, 11: Reactivial with isopropanol)

the extract was dried under a stream of N₂, methylated using diazomethane, then dissolved in 0.5 mL of isopropanol before the analysis by GC/FID. The GC temperature program used for Stearic-Cl₂ and DHA-Cl₂ was 190°C for 3 min followed by a ramp at 12°C/min to 300°C held for 1 min. Total analysis time was 13.68 min, and methyl esters of stearic acid, Stearic-Cl₂, dehydroabietic acid, DHA-Cl₂ eluted at 4.2 min, 7.1 min, 5.9 min, and 8.5 min respectively.

The dechlorination at 1 atm was performed in a 2 mL autosampler glass vial with exactly half the above amounts of each reaction reagent. The vial was heated to the desired temperature with stirring for 15 min in an oven. After the temperature equilibration, the standard solution was added to the vial and the mixture was stirred for 15 min. The vial was then removed from the oven, centrifuged for 2 min and the suspension was analyzed by GC/FID as above.

The enthalpy and entropy of desorption of stearic acid and dehydroabietic acid were determined by equilibrating 5.0 mL of 50 ppm standard solutions with 0.0050 g of 5% Pd/ γ -Al₂O₃ (0.002 mmol Pd) in a 7 mL glass vial for at least 4 hours at temperatures between room temperature and 80°C. After the equilibration was complete, the suspension was separated from the catalyst by using a syringe filter (0.45 μ m pore) and analyzed by GC/FID as above.

Results and Discussion

Effect of isopropanol concentration

Isopropanol acts both as a hydrogen donor and a solvent at atmospheric pressure, while it only acts as a hydrogen donor in supercritical CO₂. The bulk of the solvent (the CO₂) serves to

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increase the mass transfer of reagents, potentially increasing the overall rate of the reaction. The maximum dechlorination yield was obtained at an isopropanol concentration of 2.5 % (v/v) as indicated in Figure 2. Dechlorination did not proceed in absence of isopropanol, which confirmed its role as a hydrogen donor in the reaction mechanism. The dechlorination yield decreased as the isopropanol concentration increased above 2.5 %, possibly due to adsorption of isopropanol on the polar surface of the catalyst preventing the adsorption of the reactant.

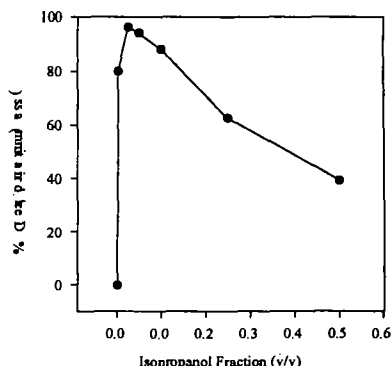


Figure 2: Effect of isopropanol concentration on dechlorination yield of $C_{18}\text{-Cl}$ in supercritical CO_2 ($\text{Pd/Cl} = 100$, $T = 80^\circ\text{C}$, $P = 100$ atm)

Effect of pressure

An increase in pressure decreased the dechlorination yield of $C_{18}\text{-Cl}$, especially at higher temperatures. The pressure needed to be 100 atm or lower in order to achieve a complete dechlorination as indicated in Figure 3. On the contrary, the dechlorination yield of either Stearic- Cl_2 or DHA- Cl_2 was not affected by pressure variation at all. The different behaviors of $C_{18}\text{-Cl}$ and the two acids may possibly be due to the polarity of molecules. While $C_{18}\text{-Cl}$ is a non-polar compound, both Stearic- Cl_2 and DHA- Cl_2 are quite polar. The non-polar CO_2 may compete effectively with $C_{18}\text{-Cl}$ for sites on the surface of the catalyst, and may therefore preferentially occupy more of the surface at high pressure, diminishing the adsorption of the $C_{18}\text{-Cl}$ and slowing its dechlorination. On the other hand, Stearic- Cl_2 and DHA- Cl_2 are much more polar than carbon dioxide, and so would adsorb more strongly than CO_2 and their rates of dechlorination would be less affected by the pressure.

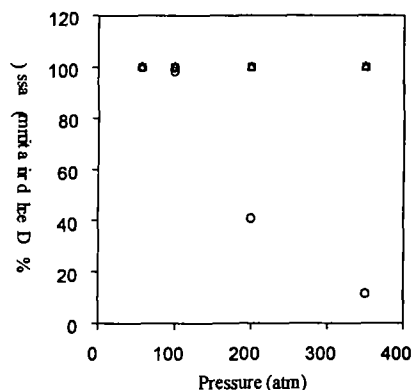


Figure 3: Pressure effect on dechlorination yield of $C_{18}\text{-Cl}$ (O), Stearic- Cl_2 (\square), and DHA- Cl_2 (\triangle) in supercritical CO_2 at 80°C

Effect of Pd/Cl ratio

Dechlorination yield increased as the Pd/Cl ratio was increased, then started to level off at Pd/Cl = 50 for $C_{18}\text{-Cl}$ and 25 for Stearic- Cl_2 and DHA- Cl_2 . Above these values, the yield became independent of the Pd/Cl ratio likely because the reactions became diffusion limited.

Effect of Temperature and Reaction Activation Energy

Increasing the temperature increased the dechlorination yield for all three compounds. The apparent activation energy (E_a) was determined for each compound in SC-CO₂ and for C₁₈-Cl in isopropanol at 1atm (Table 3) by an Arrhenius plot. The reaction rate constants were calculated using the method of initial slopes. The similar results obtained for C₁₈-Cl under different environment suggests that the rate limiting step is same in both cases. In SC-CO₂, C₁₈-Cl and Stearic-Cl₂ also had close E_a values, while that of DHA-Cl₂ was much greater. This difference was considered due to their structural differences. Both C₁₈-Cl and Stearic-Cl₂ are long chain aliphatic molecules while DHA-Cl₂ is aromatic. In the latter, having both chlorines on an aromatic ring would make it more difficult to remove electrons from the C-Cl bond due to its π conjugation system which would interact favorably with the palladium orbitals. This leads to higher electron density in the C-Cl bond through the LUMO, hence the stronger C-Cl bond, leading to a higher value of E_a for the dechlorination reaction, if the rate limiting step is the cleavage of this bond.

Enthalpy of Desorption and Elucidation of Dechlorination Mechanism

The rate limiting step in the heterogeneously catalyzed reactions could be adsorption of the reactants, the surface reaction, or desorption of the products. In the present study, the last possibility was eliminated for Stearic-Cl₂ and DHA-Cl₂ by determining the desorption enthalpy of stearic acid and dehydroabiatic acid (DHA), which were less than half of E_a . Adsorption of octadecane on the catalyst surface was not significant enough to obtain a quantitative data, indicating that adsorption could be the rate limiting step for C₁₈-Cl. For the other two compounds, the rate limiting step is more likely be the surface reaction. There are still some experimental difficulties to overcome in order to fully understand the mechanism of the reaction..

Table 1: Thermodynamic and kinetic parameters for dechlorination of C₁₈-Cl, Stearic-Cl₂ and DHA-Cl₂

	Ea (kJ/mol)		Desorption in isopropanol, 1atm	
	SC-CO ₂	1atm, isopropanol	ΔH (kJ/mol)	ΔS (J/mol·K)
C ₁₈ -Cl	42.6 ± 12.7 %	35.2 ± 9.8 %	Not determined	N.D.
Stearic-Cl ₂	40.1 ± 18.5 %	N.D.	N.D.	N.D.
DHA-Cl ₂	134.9 ± 5.3 %	N.D.	N.D.	N.D.
Stearic acid	N/A	N/A	18.1 ± 11.7 %	38.1 ± 3.4 %
DHA	N/A	N/A	12.1 ± 13.9 %	40.2 ± 2.5 %

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