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Total Mineralization of Carbon Tetrachloride under Basic Phase Transfer Conditions

Elza Snir and Yoel Sasson*

Casali Institute of Applied Chemistry, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Abstract:

Complete dechlorination of carbon tetrachloride to the mineral level was realized under mild conditions in the presence of a solid caustic base, a quaternary ammonium phase transfer catalyst and a cocatalyst such as an alcohol which functioned also as a solvent. The solvent and the catalyst could be readily recovered and recycled after completion of the process. The reaction is sufficiently fast to avoid neutralization of the formed carbon dioxide, and consequently the overall stoichiometry of the process is: $CCl_4 + 4NaOH \rightarrow 4NaCl + CO_2 + 2H_2O$. The key step in the reaction mechanism is the extraction of alkoxide anion by the phase transfer catalyst followed by consecutive nucleophilic substitution and hydrolysis of the substrate.

Introduction

Carbon tetrachloride (CT) is a perchlorinated biorefractory contaminant that has been used in the past in a wide range of commercial, industrial and military applications. It has been applied as a solvent, heat transfer medium, cleaning solvent, pesticide, refrigerant aerosol propellant, and as an intermediate for the production of chlorofluorocarbons (CFC). Even though CT was banned in 1990 at the London Conference due to its potential impact on the ozone layer depletion, it is still being formed as a byproduct in various chlorination processes. CT is classified as a Group B2 carcinogen and is highly toxic to the liver, lung and kidneys. CT does not degrade naturally (although some anaerobic microorganisms, such as methanogens, are capable of reductive dechlorination[1]) and thus accumulates in the environment, causing heavy damage to the ecosystem. Clean and effective methods for destruction of CT are hence being sought by researchers.

Simple adsorption of CT, such as by activated carbon, is not practical mainly because the regeneration of the saturated actived carbon is not straightforward and subsequent replacement of the adsorbent would be frequently required.[2] Incineration is thus currently the most widely used solution,[3] but the high temperatures required (>1300 °C) result in formation of highly toxic byproducts such as dioxins and furans. Catalytic incineration provides a partial solution to this problem,[4] particularly when performed in the presence of hydrogen donor molecules such as toluene or methane.[5]

Numerous alternatives have been reported for alternative destruction methods of CT and other chlorinated hydrocarbons (CHC). Typical are catalytic oxidative, reductive or hydrolytic degradation and reaction with zero-valent metal such as zero-valent iron (ZVI). Electrochemical[6] and photochemical[7] methods are less common.

Destructive adsorption of CT was realized at 200–300 °C in a gas-phase reaction in the presence of steam and solid alkaline-earth oxides (i.e., SrO, BaO)[8] or lanthanide oxides (i.e., La_2O_3, Pr_2O_3), particularly when supported on alumina.[9] It was shown that the gaseous CT and the solid metal oxide form carbon dioxide and a metal chloride. The latter simultaneously reacts with steam to form HCl and regenerate the metal oxide. The authors claimed an unprecedented destruction rate of 0.289 g of CCl_4 h^{-1} g^{-1} catalyst at 350 °C. This is a simple technology that produces a useful byproduct (HCl), but since the intermediate in the catalytic cycle was phosgene, which in certain instances turned up in the final product mixture, it is highly unlikely to be applied in practice.

Degradation of CT using the modified Fenton reagent[10] was found to be principally suitable for in situ treatment of contaminated soil and groundwater, particularly when dense non-aqueous-phase liquid (DNAPL) was present.[11] Interestingly, it was established that the reactive species in these processes was not the typical hydroxyl radical but rather the less reactive superoxide anion.[12]

Reductive dechlorination by zero-valent metals was advocated as the technology of choice for treatment of CT-contaminated water.[13] Indeed, rapid conversion of highly diluted CT (μM level) could be measured, particularly under anaerobic conditions, but unfortunately the dehalogenation process came

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* Author to whom correspondence may be sent. E-mail: ysasson@huji.ac.il.

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to a standstill at dichloromethane, although some improvement was realized when a Cu/Al bimetallic alloy was applied.[14]

The best technology for detoxification of CT (and other CHCs) in bulk is catalytic hydrogenolysis using hydrogen or hydrogen donors as primary reducing agents. Palladium is the catalyst of choice for both gas- or liquid-phase reactions,[15] but other transition-metal catalysts have been used as well.[16] An identical process has been the foundation of the transformation of CFCs to the more ozone-friendly derivatives HCFCs via catalytic hydrodechlorination.[17] When applied to CT destruction, the main shortcoming of catalytic hydrodehalogenation is its selectivity which, with any metallic catalyst (with very few exceptions[18]), is mainly directed to the formation of chloroform although a small amount of methane is also formed.[19] Chloroform is the only product obtained also when a hydrogen donor such as isopropanol is applied in the presence of a homogeneous Ru(II) catalyst.[20] If total mineralization is required, a successive step is necessary for the decomposition of chloroform, e.g. via basic hydrolysis.

In this study we have developed conditions for the direct aqueous hydrolysis of CT in the presence of sodium hydroxide. The main tool for this unexpected reaction is quaternary ammonium phase transfer catalysis combined with an alcohol cocatalyst. It was previously proven that the direct extraction of hydroxide anion in phase transfer systems is practically unfeasible (eq 1).[21]

$$Q^+X^-_{(org)} + OH^-_{(aq)} \rightleftharpoons Q^+OH^-_{(org)} + X^-_{(org)} \tag{1}$$

However, upon addition of alcohols, basicity could be transferred into the organic phase via the extractable alkoxide anions (eq 2).[22]

$$Q^+X^-_{(org)} + OH^-_{(aq)} + ROH \rightleftharpoons Q^+OR^-_{(org)} + X^-_{(org)} + H_2O \tag{2}$$

This phenomenon has been used in several phase transfer systems.[23] The efficacy of the extraction is determined by the pK_a of the alcohol and the extraction coefficient of the alkoxide anion (see Figure 1). In this study we have explored the cocatalytic effect of alcohols on the phase transfer catalyzed hydrolytic destruction of carbon tetrachloride under mild conditions.

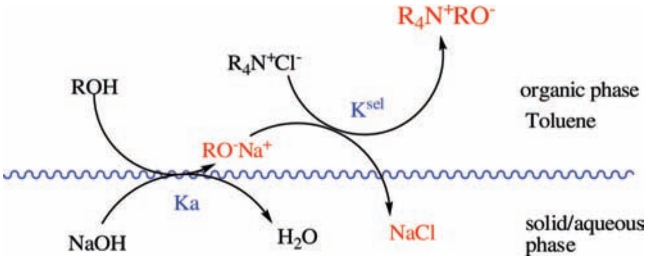

Figure 1. **Extraction of alkoxide anions in the presence of phase transfer catalysts.**

Results and Discussion

When CT (neat or in a solvent such as toluene) was heated to reflux in the presence of 6 equiv of a concentrated aqueous solution of sodium hydroxide, no reaction was observed after several hours. Addition of 5 mol% of a typical phase transfer catalyst such as Aliquat 336[24] or tetra-*n*-butylammonium bromide (TBAB) initiated a very slow hydrolytic reaction. Conversely, upon addition of a small amount of alcohol such as isopropanol or *n*-hexanol to the above mixture, a highly exothermic transformation ($\Delta H = -949$ kJ/mol CT) was realized according to the following stoichiometry: (eq 3)

$$CCl_4 + 6NaOH_{(aq)} \xrightarrow[\text{alcohol, 70 °C, 16 h}]{\text{PTC, toluene}} \underset{\text{85\% conversion,100\% selectivity}}{4NaCl + Na_2CO_3 + 3H_2O} \tag{3}$$

Reaction 3 achieved 85% conversion after 16 h. When isopropanol was used in excess in the above experiment, in the presence of solid sodium hydroxide and 5 mol% TBAC at ambient temperature, a rapid autothermal reaction developed (reaching 75 °C) with a different stoichiometry: (eq 4)

$$CCl_4 + 4NaOH_{(aq)} \xrightarrow[\text{isopropanol, 20 – 75 °C, 3 h}]{\text{PTC}} \underset{\text{98\% conversion, 100\% selectivity}}{4NaCl + CO_2 + 2H_2O} \tag{4}$$

In the latter faster reaction, 4 equiv of sodium hydroxide was sufficient to almost completely convert the CT into carbon dioxide. The latter was formed so rapidly that it did not have the time to react with the base to form sodium carbonate. The enthalpy change in the latter reaction was calculated to be −778 kJ/mol CT. A very slow reaction was observed in this case even in the absence of the phase transfer catalyst.

One can actually direct the process either to reaction 3, in the presence of toluene as a solvent, or to reaction 4 when isopropanol was used as the solvent.

In both reactions, assay of CCl_4(by gas chromatography), of OH^-, Cl^-, CO_3^{-2} (by titration) and of CO_2 (volumetric analysis and capture with $Ba(OH)_2$ followed by titration) in the

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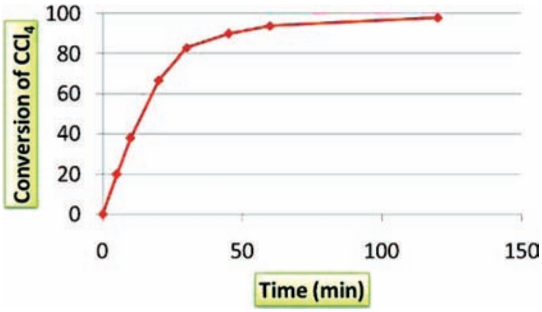

***Figure* 2. Reaction profile (eq 4). Experimental conditions CCl_4 - 10.4 mmol, NaOH - 62.4 mmol, TBAC - 5 mol%, IPA - 50 mmol, magnetically stirred open flask. Initial temperature: 25 °C.**

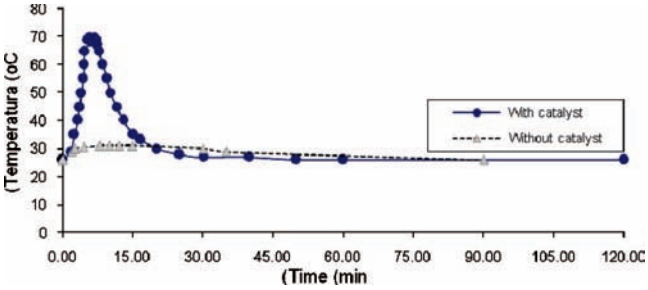

***Figure 3.* Temperature profile of catalytic and noncatalytic reaction 4. Experimental conditions for catalytic system: CCl_4 - 10.4 mmol, NaOH - 62.4 mmol, TBAC - 0.52 mmol, 5 mol% relative to CT, IPA - 50 mmol, magnetically stirred open flask. Initial temperature: 25 °C. Noncatalytic system: same conditions, but without TBAC.**

course and at the end of each process, confirmed the stoichiometry and the mass balance of reactions 3 and 4. We established that both the consumption of NaOH and the formation of NaCl, as functions of time, are linear with the rate of destruction of CT.

IR spectroscopy of both reaction mixtures, at various levels of CT conversion, unequivocally rejects the presence of any oxidation products such as aldehydes or ketones, thus eliminating the possibility of a redox reaction taking place in these systems.

A typical nonisothermal reaction profile (eq 4) is shown in Figure **2**. Figure 3 presents the temperature profile of reaction 4 in the presence and in the absence of the phase transfer catalyst.

At the end of reaction 4 the mixture was filtered, the aqueous, concentrated brine phase was separated from the mother liquor, and the remaining organic phase was analyzed to contain all the initial isopropanol, the phase transfer catalyst, and the nonreacted CT. After addition of a fresh batch of CT this mixture could be recycled as-is for a second reaction batch without any loss in activity.

In a series of experiments we have assessed the effect of some critical parameters on the rate of the isothermal reaction (eq 3). We found that the reaction rate was strongly influenced by the concentration of the alkali, the characteristics and concentration of the quaternary ammonium phase transfer catalyst, and the nature and concentration of the alcohol cocatalyst. Interestingly, the mixing rate had only a negligible effect on the reaction rate.

Effect of the Base Concentration. Table 1 displays the conversion of CT after 80 min (reaction 3) and 30 min (reaction 4) as function of the initial aqueous sodium hydroxide concentration. Figure 4 presents the measured initial rates in reaction 4 as function of the initial aqueous NaOH concentration (weight %). Practically no reaction was observed, in both cases, when the aqueous NaOH concentration was below 10%. The rate sharply increased above 50% w/w concentration up to 100% concentration (solid NaOH). Phase transfer systems in the presence of bases are known to be strongly dependent on the base concentration.[25] Weaker bases such as potassium carbonate or potassium phosphate were totally inactive in reaction 4. Application of molar excess of sodium hydroxide beyond 50% excess (up to 12:1 NaOH/CT molar ratio) had only a negligible effect on the reaction rate and the final conversion.

Nature and Concentration of the Phase Transfer Catalyst. Figure 5 displays the activity of several phase transfer catalysts in reaction 3 in the presence of 1-hexanol (conversion achieved after 1 h). It is clear that the chloride and hydrogen sulfate catalysts are superior to the bromide catalysts. This lower activity of bromide salts can be attributed to partial "poisoning" of the catalyst by the bromide anion which has a relatively high extraction coefficient.[26] Tetrabutylammonium catalysts are more active than tetraethyl- and tetrahexylammonium catalysts, probably due to the most favorable balance between lipophilicity and accessibility of the catalyst's cation.[27] Polyethylene glycol (PEG) 600 has shown some activity as well.

The effect of the catalyst concentration on the rate of reaction 3 is shown in Figure 6. The rate is increasing linearly up to 3 mol% of catalyst and then levels off to reach saturation above 10 mol % of catalyst. This can be rationalized by the limited interfacial area in the system that can transfer only certain amount of anions per unit time. Above a particular concentration of catalyst, further addition would not increase the reaction rate further.

Structure and Concentration of the Cocatalyst. Figure 7 compares the impact of different alcohols as cocatalysts on reaction 3. Evidently phenol acts as a catalyst poison, giving a lower rate than the blank experiment. Aliphatic primary alcohols and diols had a clear cocatalytic effect on the process, with 1-hexanol showing the highest activity. Increasing the concentration of the added alcohol in reaction 3 augmented the reaction rate almost linearly. The obvious conclusion has been to apply the cocatalyst as a solvent in order to achieve maximum rate. In a series of experiments where various alcohols were used as solvents we concluded that isopropanol is by far the best cocatalyst in these systems. This is shown in Figure 8 where the cocatalytic effect of isopropanol is compared with the effects of 1-hexanol, benzyl alcohol, and 1-propanol. These results suggest that the cocatalytic effect of the alcohol is governed

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Table 1. **Effect of the initial NaOH concentration on the reaction rate (eqs 3 and 4)**

	[NaOH] w/w %						
	40	50	60	70	80	90	100
reaction 3 CT conversion (%)after 80 min[a]	3.7	7.4	19	35.1	48.3	58.7	64.8
reaction 4CT conversion (%)after 30 min[b]	15.0	23.0	35.0	48.5	72.0	76.6	84.8

[a] Reaction conditions: reaction 3: CT 6.25 mmol, toluene 3.5 mL, 1-hexanol 2.94 mmol, Aliquat 336 0.312 mmol in a sealed tube. 80 min at 60 °C, magnetic stirring. [b] Reaction conditions: reaction 4: CT, 10.4 mmol; NaOH, 41.6 mmol; isopropanol, 85 mmol; TBAC, 0.52 mmol. In an open flask equipped with a reflux condenser; 25 °C initial temperature; magnetic stirring for 30 min.

by its acidity and by the extractability and nucleophilicity of the corresponding alkoxide anion. Finally, Figure 9 presents the effect of the concentration of 1-hexanol on the rate (conversion after 1 h) of reaction 3. Some conversion is observed even in the absence of the alcohol cocatalyst (15% conversion), but evidently the cocatalytic effect is strongly dependent on the 1-hexanol concentration, thus substantiating the conclusion to use the alcohol as a solvent in this process.

Proposed Reaction Mechanism. The destruction processes 3 and 4 can proceed via one of the following three mechanisms formerly proposed by Sawyer:[28]

[1] A single electron transfer (SET) from hydroxide or alkoxide anion to CT to form a radical anion:

$$\mathrm{OH^- + CCl_4 \rightarrow {\bullet}OH + CCl_4^{-\bullet}}$$

$$\mathrm{OR^- + CCl_4 \rightarrow {\bullet}OR + CCl_4^{-\bullet}}$$

[2] A nucleophilic attack of hydroxide or alkoxide on the carbon of CT:

$$\mathrm{RO^- + CCl_4 \rightarrow RO + CCl_3^-}$$

where R = H, alkyl.

[3] A nucleophilic attack of alkoxide on chlorine:

$$\mathrm{OR^- + CCl_4 \rightarrow ROCl + CCl_3^-}$$

where R = H, alkyl.

Both routes 1 and 3 would result in formation of alcohol oxidation products such as aldehyde or ketone. These could not be detected in any of the reaction mixtures that we have studied. In addition, mechanism 5 would be strongly influenced by the presence of radical scavengers such as *p*-dinitrobenzene.[29] Addition of the latter to reactions 3 and 4 had no perceptible effect on the measured rate. The possible presence of hydroxyl radical was excluded in view of our failure to trap it with salicylic acid.[30] We thus conclude that the destruction processes 2 and 3 proceed via a four-step consecutive nucleophilic substitution reactions. Since no intermediate could be identified in our process, we presumed that all the intermediary products decompose faster than their formation rate. This probably includes the putative ortho carbonate ester formed by substitution of all the chlorine atoms in CT with alkoxides. The ortho carbonates instantly decompose under our reaction conditions to yield carbon dioxide and release the original alcohol which enters a new catalytic cycle (eq 5):

$$\mathrm{C(OR)_4 + 4NaOH \rightarrow CO_2 + 4RONa + 2H_2O} \qquad (5)$$

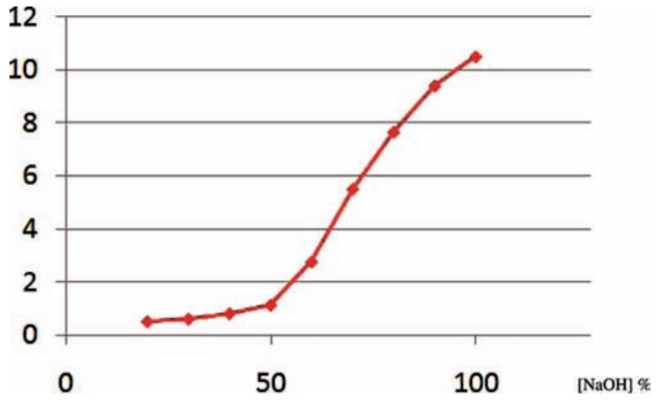

Figure 4. **Initial rates of reaction3 as function of initial NaOH concentration; CT, 6.25 mmol; toluene, 3.5 mL; 1-hexanol, 2.95 mL; Aliquat 336, 5 mol % relative to CT; NaOH, 37.5 mmol at different concentrations in water; 60 °C in a magnetically stirred, sealed tube.**

On the basis of our results we propose the following conceptual flowchart for the continuous destruction of CT to carbon dioxide with consumption of only sodium hydroxide (Figure 10). One equivalent of fresh CT and four equivalents of solid sodium hydroxide are fed into an adiabatic reactor maintained at 75 °C and mixed with recycled isopropanol solvent and Aliquat 336 catalyst. The reactor has a residence time of 1 h in which CT and NaOH are converted to CO_2 and NaCl. The reaction is sufficiently fast to prevent the neutralization of the $CO_2$by the base as was demonstrated on the laboratory scale. At the following stage the mixture is transferred to a settler where the aqueous and solid sodium chloride are separated from the organic phase containing the isopropanol and the Aliquat 336 catalyst. The latter mixture is recycled to the reactor and the sodium chloride is discarded.

In a similar manner we were able to decompose hexachloroethane, tetrachloroethylene and trichloroethylene although at a slower rate. We thus propose this method as a general technique for the destruction of polyhalomethanes, -ethanes and -ethylenes.

Conclusions

We explored and developed a simple, novel and autothermal method for the total destruction of bulk carbon tetrachloride under remarkably mild conditions using solid sodium hydroxide

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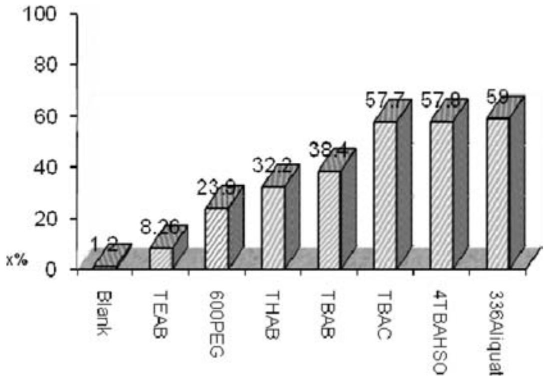

Figure 5. **Effect of different phase transfer catalysts on the conversion of reaction 3. Experimental conditions: CT, 6.25 mmol; solid NaOH, 37.5 mmol; toluene, 3.5 mL; 1-hexanol, 2.95 mmol; catalyst 5 mol% relative to CT; 60 °C in a magnetically stirred, sealed tube; 1 h.**

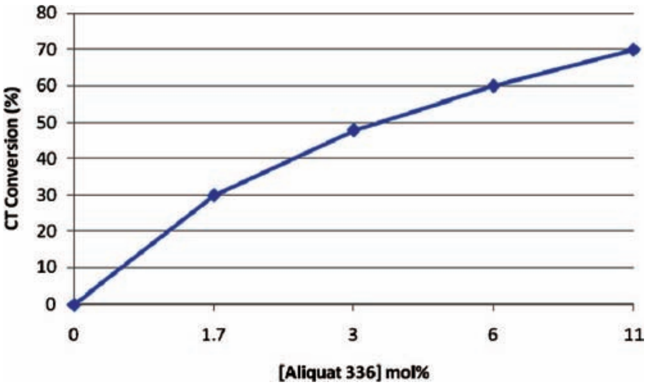

Figure 6. **Conversion of reaction 3 after 1 h as function of the phase transfer catalyst concentration. Experimental conditions: CT, 6.25 mmol; solid NaOH, 37.5 mmol; toluene, 3.5 mL; 1-hexanol, 2.95 mmol; 60 °C in a magnetically stirred, sealed tube; 1 h.**

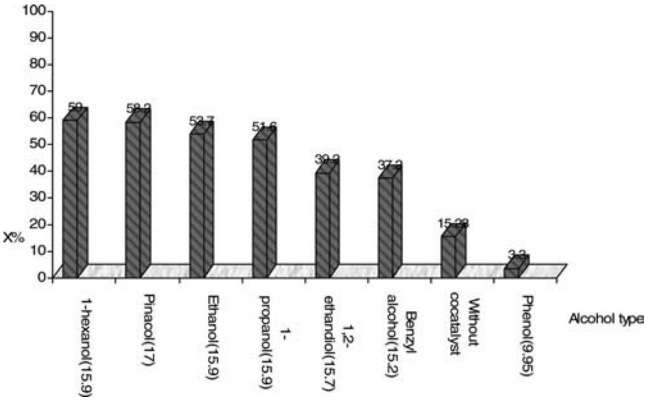

Figure 7. **Effect of the nature of the alcohol cocatalyst on conversion of reaction 3. Experimental conditions: CT, 6.25 mmol; solid NaOH, 37.5 mmol; alcohol, 2.95 mmol; Aliquat 336, 5 mol %; toluene, 3.5 mL;. 60 °C in a magnetically stirred, sealed tube, 1 h. pK_a's of each alcohol in parentheses.**

as sacrificial reagent. The system is based on a synergic combination of a quaternary ammonium phase transfer catalyst and a secondary alcohol which are both uncomplicatedly recyclable.

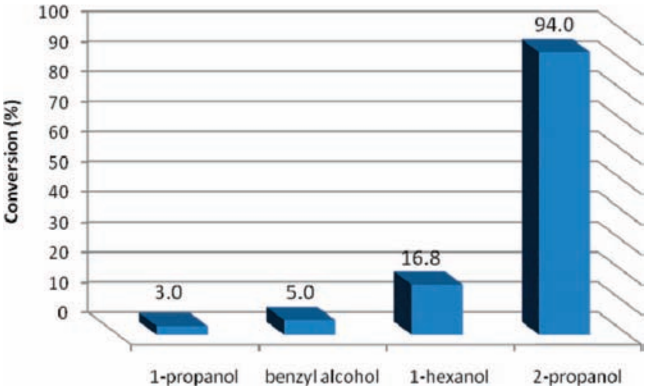

Figure 8. **Effect of the nature of the alcohol cocatalyst on the conversion of reaction 4. Experimental conditions: CT, 10.4 mmol; solid NaOH, 62.4 mmol; TBAC, 5 mol%; alcohol 50 mmol; 25 °C initial temperature in a stirred, open flask; 1 h.**

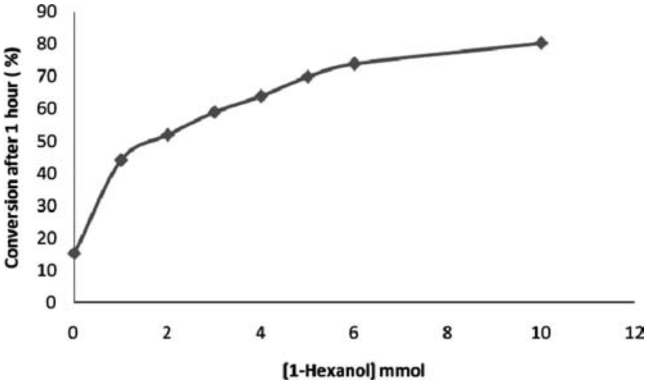

Figure 9. **Dependence of reaction 3 rate on 1-hexanol concentration. Experimental conditions: CT, 6.25 mmol; solid NaOH, 37.5 mmol; toluene, 3.5 mL; Aliquat 336, 5 mol % relative to CT; 60 °C in a magnetically stirred, sealed tube; 1 h.**

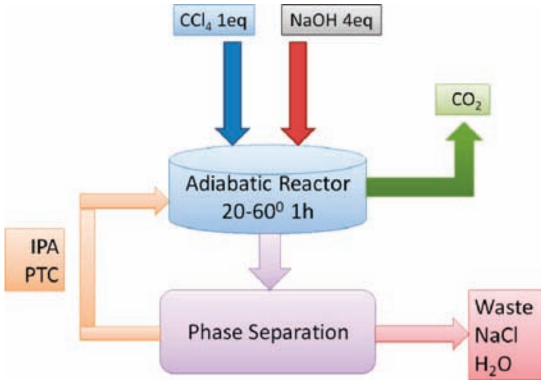

Figure 10. **Conceptual design for a CT destruction unit based on this study.**

Experimental Section

Materials. All the materials, solvents and catalysts were purchased from Aldich and were used without further purification.

Destruction of CT Using Isopropanol as Solvent (eq 4). A mixture of 10.4 mmol of CT (1.6 g), 85 mmol isopropanol (5 g, IPA solvent and cocatalyst), 62.4 mmol sodium hydroxide (2.5 g of solid, granulated) and 5 mol % tetra-*n*-butylammonium chloride (TBAC, 0.145 g), was stirred at room temperature in an adiabatic glass reactor equipped with a reflux condenser. The reaction started instantly, reaching reflux temperature within minutes and started to cool down after 12 min. The stirring was continued for 3 h. The progress of the reaction was monitored by volumetric analysis of the released carbon dioxide. The released carbon dioxide was captured in an aqueous barium hyrdroxide trap. The precipitated barium carbonate was filtered, dried and weighed to confirm the overall mass balance. After completion of the reaction, 100 mL of water was added. The phases were separated, and the aqueous solution was analyzed for Cl^- and OH^- content by volumetric titration (HCl, 0.01 N for titrating OH^- using 0.5 w/w % phenolphthalein as indicator; $AgNO_3$, 0.1 N, for titrating chloride ions, using 5 w/w % K_2CrO_4 as indicator). A quantity of 9.8 mmol of carbon dioxide was trapped as barium carbonate; 39.1 mmol chloride and 23 mmol hydroxide were assayed in the aqueous phase. The final organic phase was found to contain 4.6 g of isopropanol and 0.138 g of TBAC.

Destruction of CT Using Toluene/1-Hexanol System (eq 3). A mixture of 6.25 mmol of CT (0.95 g), 3.5 mL of toluene, 37.5 mmol sodium hydroxide (1.5 g of solid, granulated), 2.94 mmol 1-hexanol (0.3 g) and 5 mol % methyl-tricaprylammonium chloride (Aliquat 336, 0.31 mmol, 0.126 g), was stirred in a sealed tube at 60 °C for 1 h. Water (100 mL) was added to the mixture. The phases were separated, and the aqueous solution was analyzed for Cl^- content by argentometric titration ($AgNO_3$, 0.1 N for titrating chloride ions, using 5 w/w % K_2CrO_4 as indicator). The carbonate anion was assayed by gravimetric analysis of the barium carbonate obtained by the addition of barium hydroxide. Conversion of 59% of CT was measured. Practically all the original 1-hexanol, Aliquat 336, and toluene and the remaining CT were found in the organic phase.

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