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Destructive Adsorption of Chlorinated Hydrocarbons on Ultrafine (Nanoscale) Particles of Calcium Oxide. 3. Chloroform, Trichloroethene, and Tetrachloroethene

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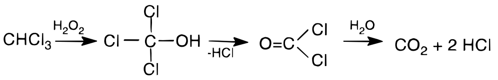
As a one-step approach to the safe destruction of chlorocarbons, the reactions of trichloroethene, chloroform, and tetrachloroethene with ultrafine particles of calcium oxide have been studied. Calcium oxide prepared by an aerogel/hypercritical drying method (AP-CaO) is generally superior to conventionally prepared (CP-CaO) and vastly superior to commercially available (CM-CaO) samples, although in higher temperature reactions with C_2Cl_4 CP-CaO exhibited higher capacity but slower reaction kinetics. The main reaction products of CaO with C_2HCl_3 were $CaCl_2$, H_2O, CO and C; with $CHCl_3$ were $CaCl_2$, H_2O and CO and with C_2Cl_4 were $CaCl_2$, $CaCO_3$, and C. Reaction temperatures were 300−500 °C, and optimum temperatures were found. If temperatures were too low, reaction efficiencies were low and if too high, efficiencies could also go down due to graphite formation which could block reactive sites.

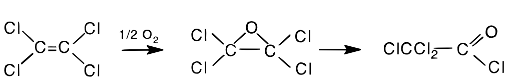
Introduction

There are about 15 000 compounds containing chlorine available in commerce, of which 18% are chlorinated solvents.[1] There have been many studies concerning the toxicity of these compounds. Particularly, the reactions of chlorocarbons with enzymes have been studied extensively.[2] For example, chloroform can react with cytochrome P450 with the formation of trichloromethanol that eliminates hydrogen chloride to form phosgene, which undergoes water attack to form carbon dioxide and hydrogen chloride.



(1)

In a similar reaction with cytochrome P450-dependent monooxygenases, the chlorinated ethene derivatives are converted to reactive oxiranes, which can alkylate, or acylate essential biomolecules. In such a manner tetrachloroethene is converted into trichloroacetyl chloride (reaction 2), and trichloroethene can either form trichloroacetylaldehyde (thermodynamically favorable), or dichloroacetyl chloride.



(2)

New approaches to the safe degradation of chlorocarbons have come under investigation. For example, interactions between tetrachloroethene and the Fe (110) surface have been investigated by several groups.[3] It was found that at low temperatures (about 100 K) C_2Cl_4 adsorbs on the surface, without cleavage of C−Cl bonds. At 325 K cleavage of these bonds occurs with formation of $FeCl_2$ and carbon which diffuses into the bulk. However, no formation of radical species, such as $:CCl_2$ and $\cdot CCl_3$, was observed. The decomposition of tetrachloroethene on metal oxide/porous catalysts, with the production of HCl and CO_2 was studied by Drago and co-workers,[4a] and at 250 °C moderate decomposition efficiency was realized. In addition, chlorocarbon decomposition on zeolites has been studied by Krawietz and co-workers.[4b]

Herein, ultrafine calcium oxide particles were employed as destructive adsorbents (high surface area solids that dissociatively chemisorb and immobilize all or fragments of incoming adsorbates) for three of the most common solvents: trichloroethene (TCE), chloroform, and tetrachloroethene. As was the case for carbon tetrachloride decomposition,[5] the destructive adsorption on aerogel (autoclave) prepared (AP-CaO), conventionally prepared (CP-CaO) and commercially available (CM-CaO) is described.

Experimental Section

Calcium Oxide Samples. Sample preparation and properties have been described previously.[5] Briefly: CM-CaO was purchased from Fisher Sci., surface area = 10 m^2/g, crystallite size = 39 nm; CP-CaO, 100 m^2/g, 14 nm; AP-CaO, 120 m^2/g, 7 nm.

Gas Chromatography. A U-tube pulsed reactor system was employed as previously described for CCl_4 studies.[5] Usually 0.1 g samples of CaO were used, and 1 μL pulses of chlorocarbon were injected. To better analyze the decomposition products and amount of destroyed chlorocarbon, calibration of the GC instrument with respect to carbon dioxide (one of the decomposition products) and chlorocarbon under study was carried out. Aerogel prepared (AP-CaO), conventionally prepared (CP-CaO), and commercial calcium oxides (CM-CaO) were used in these experiments. The number of injections was either 50 or 65. Similar studies were used with GC-MS to help identify the decomposition products.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) Hileman, B. *C&EN* **1993**, April 19, 11.

(2) Henschler, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33,* 1920.

(3) Smentkowski, V. S.; Cheng, C. C.; Yates, J. T., Jr. *Surf. Sci.* **1989**, *220,* 307, and references therein.

(4) (a) Petrosius, S. C.; Drago, R. S.; Young, V.; Grunewald, G. C. *J. Am. Chem. Soc.* **1993**, *115,* 6131. (b) Krawietz, T. R.; Goguen, P.; Haw, J. F. *Catal. Lett.* **1996**, *42,* 41.

(5) (a) Koper, O.; Lagadic, I.; Klabunde, K. J. *Chem. Mater.* **1997**, *9,* 838−848 and references therein. (b) Koper, O.; Li, Y. X.; Klabunde, K. J. *Chem. Mater.* **1993**, *5,* 500 and references therein.

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Thermal decomposition studies were also carried out for the three chlorocarbons. An empty stainless steel reactor, packed with alumina wool, was used, and the chlorocarbon was injected. The range of temperatures studied was from 200 to 650 °C. In the case of chloroform decomposition, deuterated chloroform, $CDCl_3$, was used to confirm the identity of the decomposition products.

Infrared spectroscopy was used to analyze gaseous products and unreacted chlorocarbon in a batch-type reactor. For example, CP-$Ca(OH)_2$ (0.774 g, 1.38×10^{-2} moles) was placed in a Schlenk tube and activated at 500 °C overnight. The final weight of CaO was 0.624 g (1.12×10^{-2} mol). After cooling the sample to room temperature, 0.1 mL of liquid trichloroethylene (freeze-thaw degassed) was introduced, to achieve a ratio of 10 mol of CaO to 1 mol of TCE. The Schlenk tube was closed and slowly (1 h) heated to 450 °C and kept under these conditions for 4 h. During this time the gases in the Schlenk tube turned brownish and a small deposit of carbon film was observed on the walls of the tube. After 4 h the furnace was taken off and the gaseous products were cryogenically transferred to a gas IR cell and an FT-IR spectrum was taken at room temperature. Similar experiments were conducted with CaO to TCE molar ratios of 5:1 and 2:1. Also, a blank experiment was carried out (without calcium oxide) to study the thermal decomposition of TCE under such conditions.

For chloroform decomposition, with a 10:1 ratio of calcium oxide to chlorocarbon, 1.73 g (3.09×10^{-2} mol) of calcium hydroxide and 0.2 mL of $CHCl_3$ was used. The temperatures employed were 400 and 500 °C. For tetrachloroethene decomposition the amount of CaO, for a 10:1 ratio was 1.37 g (2.45×10^{-2} mol) of CaO and 0.2 mL of C_2Cl_4. The reactions were carried out at 400 and 500 °C.

Gain in mass during destructive adsorption reactions was studied using a spring balance.[5] Chlorocarbon vapor (under its vapor pressure) was inlet and exposed to a known mass of CaO at a desired temperature, and mass change monitored. For the destructive adsorption of trichloroethene the temperatures used were 350, 400, 450, and 500 °C, and the amount of adsorbed TCE was based on the weight gain of the oxide. However, only comparative data are useful since the solid product was a mixture of calcium chloride, calcium chlorite, carbon, and calcium carbonate. After the oxide was exposed to chlorocarbon vapors, the first reading was taken after 30 s and then every 5 min up to 30 min, and then every half an hour to 2 h and every hour to 4 h. The last reading was taken after a 10 h exposure.

For adsorption studies of chloroform and tetrachloroethene, the amount of conversion of calcium oxide into calcium chloride was calculated, assuming that the only solid product was $CaCl_2$. The readings for adsorption were taken in a similar manner as for TCE; however, the last reading was taken after overnight exposure (16 h) to the chlorocarbon.

Powder X-ray Diffraction (XRD). Samples were analyzed on a Scintag-XDS-2000 instrument, set at a voltage of 40 kV and current 40 mA. The scans were from 20 to 85° with a scanning rate of 2°/min. Hygroscopic samples were protected by mixing with mineral oil.

Results

A. Trichloroethene (TCE). Gravimetric adsorption studies were carried out at various temperatures, to compare the amount of C_2HCl_3 adsorbed/decomposed per one mole of calcium oxide. Figures 1 and 2 show the adsorption/decomposition curves (up to 4 h) for CP- and AP-CaO, respectively. With increasing temperature, adsorption on AP-CaO proceeded faster; however, at 450 and 500 °C the final amount of adsorbed chlorocarbon on AP-CaO was almost the same. The adsorption on CP-CaO followed the same pattern, but the amount of adsorbed chlorocarbon was smaller at every temperature, compared with AP-CaO. The solid products from these reations were studied by IR and XRD which indicated a mixture of CaClOH (XRD) or $CaOCl_2 \cdot xH_2O$ (IR), $CaCl_2$, $CaCl_2 \cdot 2H_2O$ and graphite.

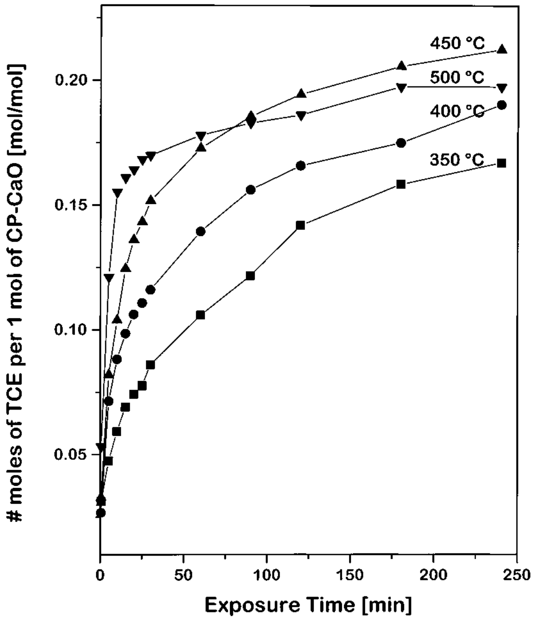

Figure 1. Adsorption/decomposition of trichloroethene on CP-CaO, preactivated at 500 °C.

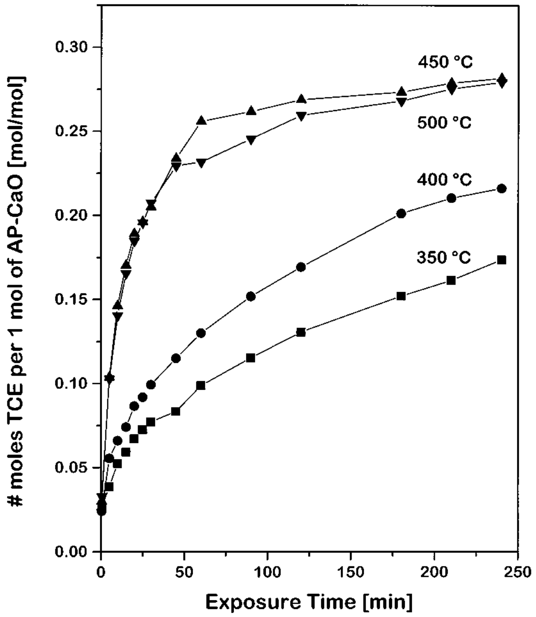

Figure 2. Adsorption/decomposition of trichloroethene on AP-CaO, preactivated at 500 °C.

To determine the amount of calcium oxide that was necessary for complete adsorption/decomposition of TCE, infrared spectroscopy was employed. With 10:1 ratio of conventionally prepared calcium oxide to trichloroethene (Figure 3), no gaseous product was observed. The solid product was a black powder probably due to the formation of carbon. XRD revealed a mixture of unreacted CaO, CaClOH (or hydrated $CaOCl_2$ as seen by IR), and traces of $CaCO_3$ as shown in Figure 4. Carbon was not seen in the XRD spectrum, most probably due to its amorphous state. When the CaO to TCE ratio was decreased to 5:1 the gaseous products were carbon monoxide and water (FT-IR studies). The solid product was again a black powder, and according to XRD it was a mixture of CaClOH or $CaOCl_2 \cdot H_2O$ (major product), unreacted CaO, $CaCl_2 \cdot 2H_2O$, and a small amount of

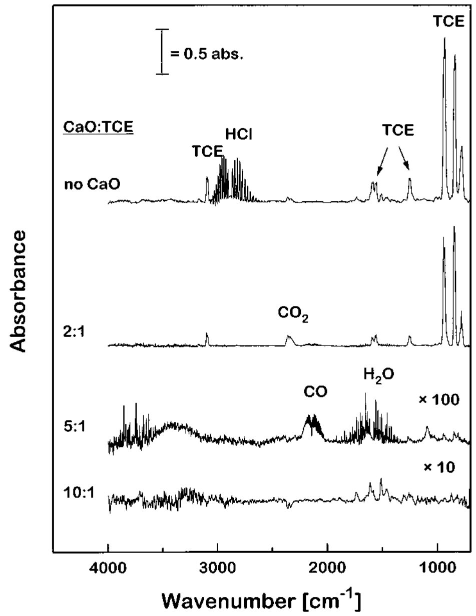

Figure 3. IR spectra of the gaseous products after decomposition of trichloroethene on CP-CaO (preactivated at 500 °C) at 450 °C. The top spectrum was taken after thermal decomposition at this temperature (no CaO).

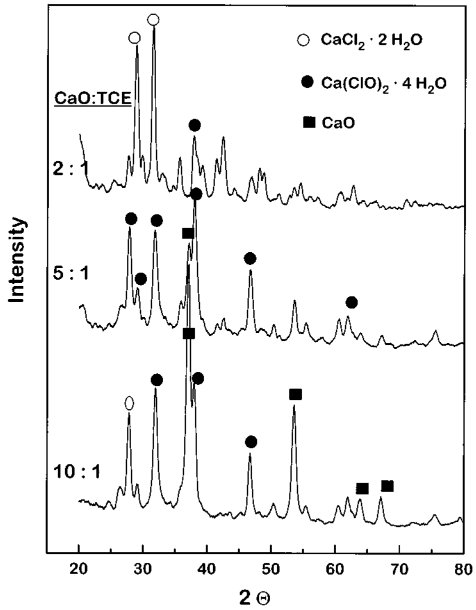

Figure 4. XRD spectra after decomposition of TCE on CP-CaO, at 450 °C, with different calcium oxide to chlorocarbon ratios.

$CaCO_3$. With a 2:1 ratio TCE was not completely destroyed; however, its concentration was smaller compared with when CaO was not present. Carbon monoxide was the gaseous product, and hydrated $CaCl_2$ was the solid product. When the same experiment was conducted without calcium oxide (blank experiment) some thermal decomposition of trichloroethene took place and HCl was observed by IR as the only gaseous product.

Decomposition of trichloroethene was also studied in a U-tube pulse reactor employing GC and GC-MS for product analyses.[5] First, a blank experiment (no CaO) was carried out using a stainless steel U-tube. Up to 300 °C no decomposition was observed. At 300 °C small amounts of CO and CO_2 were observed, but even as high as 450 °C very little C_2HCl_3 was decomposed. At 650 °C, CO and CO_2 production increased, but C_2HCl_3 was still largely undecomposed. No evidence for C_2Cl_4, $C_2H_2Cl_2$, or HCl was found.

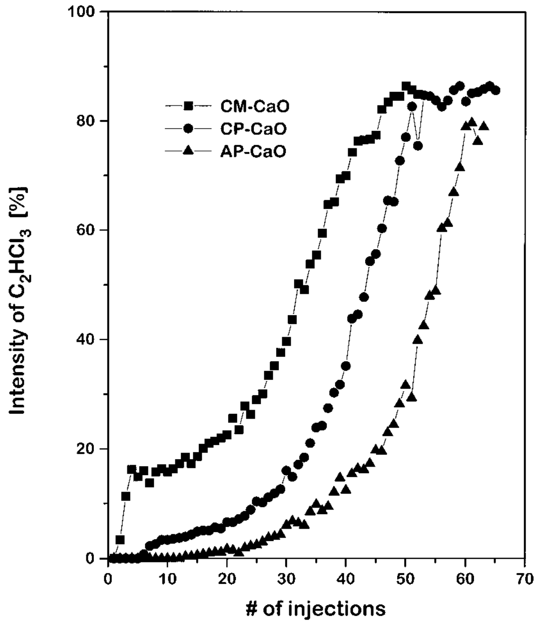

Figure 5. Comparison of reaction efficiencies for AP, CP and CM-CaO with injections of trichloroethene (0.1 g CaO and 1 μL injections of TCE).

When CaO was placed in the U-tube, very different results were obtained. Temperature of C_2HCl_3 decomposition was dramatically lowered; however, destructive adsorption capacity was heavily dependent on the CaO sample employed.

Using CM-CaO, studies at 450, 500, 550, and 600 °C were carried out. As 1 μL samples were injected over the CaO bed, breakthrough was noted on the first injection at the lower temperatures. However, at 450 °C acetylene, mono- and dichloroacetylene along with H_2O, CO, and CO_2 were detected by GC-MS after the first injection. After the third injection, only unreacted C_2HCl_3 was observed. At 600° all of the first μL of C_2HCl_3 was decomposed, and CO_2 was the major product. However, CM-CaO exhibited a very low capacity for C_2HCl_3 destructive adsorption and after two or three injections, the bed was nearly exhausted.

Using CP-CaO with a decomposition temperature of 450 °C, 1 μL of chlorocarbon was completely destroyed. When the temperature was increased to 500 °C, the amount of completely decomposed trichloroethylene increased to 6 μL. Further improvements were noted with AP-CaO. At 450 °C 12 μL of C_2HCl_3 were completely decomposed per 0.1 g of AP-CaO, as observed by gas chromatography, and the major decomposition product was carbon monoxide. The MS spectra of the gaseous products on the 1 injection, at 450 °C, indicated the presence of CO, CH_4, H_2O, CO_2, C_2HCl, and C_2Cl_2.

Figure 5 summarizes decomposition ability of CM, CP and AP-CaO for trichloroethene. The reactions for CM and CP-CaO were carried out at 500 °C and for AP-CaO at 450 °C. Even at lower temperature the AP-CaO decomposed twice as much TCE compared with CP-CaO and more than 10 times as much as CM-CaO.

B. Chloroform. In a similar way, $CHCl_3$ was studied. From the thermogravimetric studies of $CHCl_3$ adsorption on CP and AP-CaO,[5b] it was found that chloroform was quite sensitive to reaction temperature.

Table 1. Conversion of CaO into $CaCl_2$ at Different Temperatures of Adsorption of Chloroform

	$CaCl_2$/CP-CaO[a]		$CaCl_2$/AP-CaO[a]
temp (°C)	4 h	overnight	4 h
200	0.19	0.27	0.07
300	0.29	0.37	0.49
400	0.38	0.52	0.40
500	0.31	0.43	0.37

[a] Moles of $CaCl_2$ formed/mole of CaO.

In the case of AP-CaO even at 400 °C the decomposition was less efficient than at 300 °C. Autoclave prepared oxide seemed to be more affected by higher temperature, compared to conventionally prepared. The amount of adsorbed/decomposed $CHCl_3$ was higher for every temperature on AP-CaO compared with CM and CP-samples, although not as high as for the decomposition of carbon tetrachloride. Table 1 gives the amount of conversion of CaO into $CaCl_2$ after 4 h and overnight exposure to the chlorocarbon. For the AP-CaO the highest conversion after 4 h occurred at 400 °C, and the lowest at 200 °C. The solid products were studied by XRD and showed that for CP-CaO the largest amount of calcium chloride was formed at 400 °C, and the smallest at 200 °C. For the AP-CaO sample, at lower temperatures mainly CaClOH was formed that converted into $CaCl_2$ at higher temperatures. The best results (smallest CaO peak) were obtained at 300 °C.

For identification of the gaseous products of decomposition infrared spectroscopy was employed. Two different ratios of calcium oxide to chloroform were used. When the adsorption/decomposition was carried out at 500 °C, with a calcium oxide to chloroform ratio of 10:1, almost no decomposition was observed. The only gaseous product observed by IR was a small amount of carbon dioxide. The major species present was undecomposed chloroform. The sample was completely black after reaction at 500 °C. Probably, chloroform thermally decomposed with graphite formation, that covered the surface of the oxide inhibiting further decomposition, as it was observed in the gravimetric studies. After lowering the decomposition temperature to 400 °C, the results were much better. The gaseous products from a 400 °C reaction over AP-CaO (CaO:$CHCl_3$ = 5:1) were CO, H_2O, and a small amount of CO_2. At a ratio of 10:1 only CO and H_2O were detected. The solid product after the reaction was studied by power X-ray diffraction spectroscopy and it was found to be calcium chloride. A major reaction pathway at 300−400 °C appears to be CO and H_2O formation. A minor pathway is graphite formation, which becomes more important at higher temperature.

Pulsed U-tube reaction studies at 400 °C showed that up to 12 μL $CHCl_3$/0.1 g AP-CaO could be completely decomposed and that the only gaseous product was carbon monoxide. With addition of larger amounts of $CHCl_3$, tetrachloroethene, carbon dioxide, and hydrogen chloride appeared in the mass spectrum (assignments supported by $CDCl_3$ studies). When this reaction was conducted in the presence of preadsorbed water on the surface of calcium oxide, after injecting 6 μL of chloroform, tetrachloroethene and phosgene were observed.[6]

Table 2. Conversion of CaO into $CaCl_2$ at Different Temperatures upon Adsorption of Tetrachloroethene

	$CaCl_2$/CP-CaO[a]		$CaCl_2$/AP-CaO[a]
temp (°C)	4 h	overnight	4 h
200	0.03	0.05	0.03
300	0.06	0.10	0.05
400	0.30	0.50	0.11
500	0.80	0.97	0.40

[a] Moles of $CaCl_2$ formed/mole of CaO.

C. Tetrachloroethene. This compound does not thermally decompose below 650 °C. When calcium oxide was present this temperature was lowered to 500 °C. The major products were graphite, calcium chloride, and calcium carbonate, as observed by powder XRD. Table 2 gives the amount of conversion for CP and AP calcium oxides. At 200 and 300 °C, almost no adsorption was observed even after overnight exposure. Interestingly, in this case AP-CaO did not perform as well as CP-CaO regarding overall capacity, although reaction kinetics were more favorable for AP.

The infrared spectrum of the head gas after reaction (500 °C) of C_2Cl_4 with CP-CaO (CaO:C_2Cl_4 ratios of 10:1 or 15:1) showed that C_2Cl_4 had been completely destroyed and the only gas present was a trace of CH_4 (due to ethanol stabilizer present in C_2Cl_4).

Discussion

A. CaO Reactivity. Calcium oxide is capable of destructively adsorbing C_2HCl_3, $CHCl_3$, and C_2Cl_4. However, none react as cleanly or efficiently as CCl_4,[5] but of these three C_2HCl_3 is the most reactive. Generally the order of reactivity of the oxide samples is AP-CaO > CP-CaO ≫ CM-CaO. For example, the U-tube reaction studies showed breakthrough numbers (μL C_2HCl_3 injected before C_2HCl_3 was observed in the effluent) of 1 for CM-CaO, 6 for CP-CaO, and 12 for AP-CaO even with AP-CaO operating at lower temperature (450 vs 500 °C).

B. Reaction Products. From C_2HCl_3, the products C_2H_2, C_2HCl, and C_2Cl_2 were detected in pulsed U-tube reaction studies and appear to be important intermediates enroute to formation of final products H_2O, CO, CO_2, and solids, perhaps by the stoichiometries shown below:

$$\text{initial}\quad CaO + C_2HCl_3 \rightarrow CaOCl_2 + C_2HCl \tag{3}$$

$$\text{overall}\quad 3CaO + 2C_2HCl_3 \rightarrow 3CaCl_2 + 2C(3C) + H_2O + 2CO(CO_2) \tag{4}$$

$$\Delta H^\circ_{rxn} = -901\ \text{kJ}\ (-1074\ \text{kJ})$$

Scheme 1 is an attempt to show how the initial reactions may take place and involves base abstraction of proton and chloride elimination sequences. However, complex events involving oxygen transfer to carbon are not shown. For choroform, the following stoichiometry is evident:

$$3CaO + 2CHCl_3 \rightarrow 3CaCl_2 + 2CO + H_2O \tag{5}$$

$$\Delta H^\circ_{rxn} = -719\ \text{kJ}$$

Above 300 °C

$$3CaO + 2CHCl_3 \rightarrow 3CaCl_2 + CO_2 + C + H_2O \tag{6}$$

$$\Delta H^\circ_{rxn} = -892\ \text{kJ}$$

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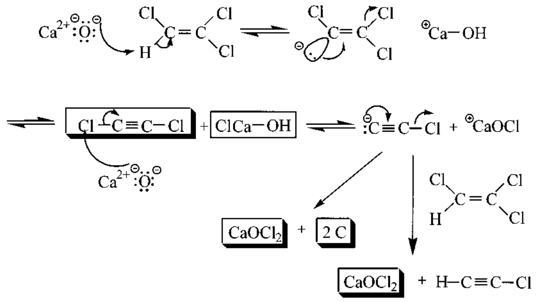
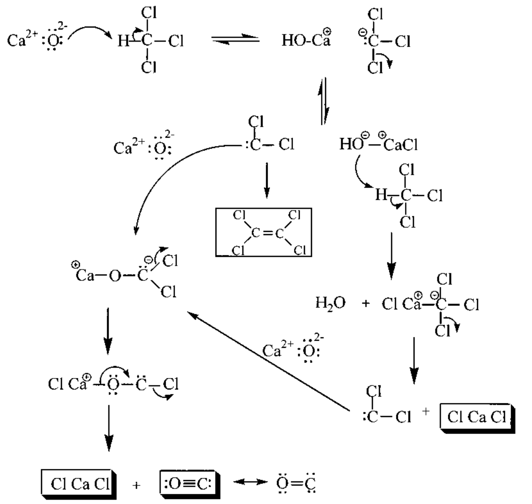
[6] Zhou, X. L.; Cowin, J. P. *J. Phys. Chem.* **1996**, *100*, 1055. They have studied photoinduced CCl_4 reactions on MgO−H_2O systems and have also observed phosgene; water appears to encourage its formation.

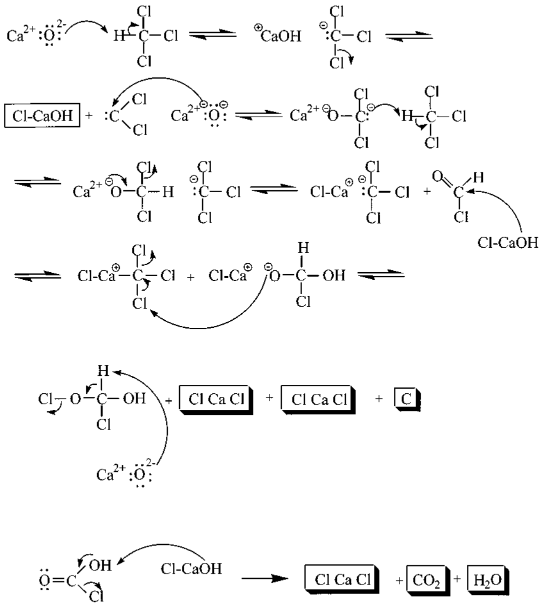
Scheme 1. Possible Reaction Scheme for Decomposition of Trichloroethene with the Production of Chlorinated Acetylene, $CaOCl_2$, and Carbon



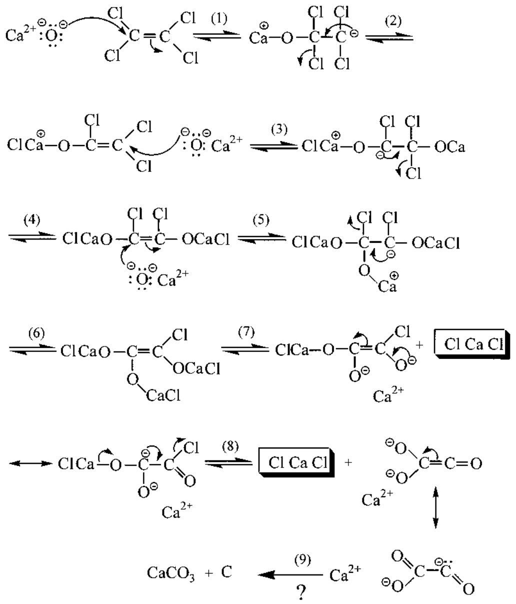
Scheme 2. Possible Reaction Scheme for Decomposition of Chloroform with the Formation of Carbon Monoxide and Calcium Chloride



Scheme 3. Possible Reaction Scheme for Decomposition of Chloroform with the Formation of Carbon Dioxide, Carbon, and Calcium Chloride and Water



Scheme 4. Possible Reaction Scheme for Decomposition of Tetrachloroethylene with the Formation of Calcium Carbonate, Carbon, and Calcium Chloride



Schemes 2 and 3 suggest how these products could be formed. Again, proton abstraction is probably the first step followed by chloride elimination, so that $:CCl_2$ can be trapped by more CaO or (in a minor pathway) dimerize to C_2Cl_4.

Tetrachloroethene is the most thermally stable and least reactive toward CaO. However, at 500 °C it can be completely decomposed if excess fine particles of CaO are present. The major reaction pathway is carbon formation along with CO_2 that forms $CaCO_3$ solid. In the case of CCl_4 destructive adsorption, $CaCO_3$ is also a product but reacts further with more CCl_4.[5] This does not seem to be the case with C_2Cl_4 and the $CaCO_3$ remains as unreactive in the solid product. The probable stoichiometry is shown below, and Scheme 4 shows reaction pathways that may be operating.

$$3CaO + C_2Cl_4 \rightarrow 2CaCl_2 + CaCO_3 + C \qquad (7)$$

$$\Delta H^\circ_{rxn} = -842 \text{ kJ}$$

The likely first step is attack on carbon by CaO, which sets off a chain of Cl^- elimination and carbon−oxygen bond formation steps.

Summary of Results

1. Calcium oxide is a good choice as a decomposing agent for trichloroethene, chloroform, and tetrachloroethene.

2. At low temperatures AP-CaO works much better as a destructive adsorbent; however, at higher temperatures conventionally prepared CaO seems to be a better choice, at least with C_2Cl_4. In addition, commercially available CaO is vastly inferior to either CP or AP-CaO.

3. The products, which are nontoxic, depend on the type of chlorocarbon being decomposed as well as on the ratio between calcium oxide and chlorocarbon. Complex surface reactions are involved which are currently not well understood.

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