## Photodecomposition of Chloroform Catalyzed by Unmodified MCM-41 Mesoporous Silica

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## ABSTRACT

Unactivated MCM-41 mesoporous silica catalyzes the photodecomposition of chloroform to phosgene and hydrogen chloride under near-UV ( $\lambda > 360$  nm) irradiation. The rate of photodecomposition increases toward an asymptotic limit as the O<sub>2</sub> partial pressure is increased. Deuterochloroform does not decompose under the same experimental conditions. Low concentrations of both cyclohexane and ethanol quench the photodecomposition, whereas water, up to its solubility limit, does not. Dissolved tetraalkylammonium salts suppress photodecomposition. The data are consistent with a mechanism in which light absorption by an SiO<sub>2</sub> defect yields an electron-deficient oxygen atom, which then abstracts hydrogen from chloroform. The resulting CCl<sub>3</sub> radicals react with oxygen to form a peroxy radical that decomposes, eventually yielding phosgene and hydrogen chloride.

## INTRODUCTION

Mesoporous silica has been widely used as a support for a variety of catalysts (1-4); catalytic activity most often being achieved either by adsorbing a catalytic species on the silica surface (5-8) or by incorporating one or more metal oxides during the synthesis of the mesoporous silica (9-11). Mesoporous silica has also been extensively used for photocatalytic reactions (12,13), in some cases unmodified, except for activation at high temperature (14-21), but quite often by supporting the actual catalytic species (22-26) or by modifying the silica matrix (27,28).

Much of the recent work in our laboratory has been on the catalyzed decomposition of chloroalkanes (29–36); thus, we have followed with special interest the published work on the photo-decomposition of chloroalkanes and chloroarenes by modified mesoporous silica (27,37–44). These studies have incorporated a wide variety of modifications. To our knowledge, there are no reports of photodegradation of chlorinated hydrocarbons catalyzed by unmodified mesoporous silica.

Photocatalysis by unmodified mesoporous silica has generally been found to require wavelengths shorter than 370 nm (45), which corresponds quite well with the diffuse reflectance spectrum of MCM-41, which can be represented as absorbing only below approximately 370 nm (46). When irradiated at wavelengths below approximately 250 nm, chloroform absorbs light and decomposes through C–Cl bond fission, yielding phosgene and hydrogen chloride. The mechanism has been reasonably well worked out in the gas phase, and is thought to occur in substantially the same fashion in the liquid phase (47).

$$\operatorname{CHCl}_3 \xrightarrow{\operatorname{IIV}} \operatorname{CHCl}_2 + \operatorname{Cl}$$
 (1)

 $\cdot CHCl_2 + CHCl_3 \rightarrow CH_2Cl_2 + \cdot CCl_3 \tag{2}$ 

$$Cl \cdot + CHCl_3 \rightarrow HCl + \cdot CCl_3$$
 (3)

$$\cdot CCl_3 + O_2 \to CCl_3OO \cdot \tag{4}$$

$$2\operatorname{CCl}_3\operatorname{OO} \rightarrow 2\operatorname{CCl}_3\operatorname{O} + \operatorname{O}_2 \tag{5}$$

$$\operatorname{CCl}_3\operatorname{O} \to \operatorname{COCl}_2 + \operatorname{Cl}$$
 (6)

The key points are the formation of trichloromethylperoxy radicals (48–50), their self-termination (51) and the dissociation of chlorine atoms from the resulting trichloromethoxy radicals (52). The radical termination products observed in highest concentration during vapor phase decomposition are  $C_2Cl_6$  and  $C_2HCl_5$ , with lesser amounts of  $CH_2Cl_2$  and  $C_2H_2Cl_4$  and no detectable  $CCl_4$  (47). As Eqs. (3)–(6) constitute a radical chain, a photocatalyst can effect photodecomposition by generating, directly or indirectly, any of the radicals within the chain.

If unmodified MCM-41 were to catalyze the photodecomposition of chloroalkanes, this would imply that careful controls are required when specific photocatalytic species are heterogenized on MCM-41, to distinguish the relative contribution of the adsorbed species from that of the mesoporous silica itself. In fact, MCM-41 does catalyze the photodecomposition of chloroform, and this is reported herein.

## MATERIALS AND METHODS

#### Chemicals

Chloroform (J. T. Baker, ACS Grade) was washed five times with an equal volume of water to remove the ethanol stabilizer, after which 4A molecular sieves were added to remove dissolved water. Water-saturated chloroform was prepared by omitting the last step. MCM-41 mesoporous silica, with pore sizes between 2.3 and 2.7 nm, was obtained from Sigma-Aldrich and was not activated at high temperature before use.

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#### **Photochemical reactions**

A 1.0 mL portion of chloroform was added to a weighed quantity of MCM-41 in a fused silica spectrophotometer cuvette with a stirbar. The cuvette was capped loosely, leaving approximately 3 mL of head space. Light from an Oriel Q Series 100 W mercury lamp was passed through a 360-nm high-pass filter and focused on the sample. The irradiance was 0.45 mW cm<sup>-2</sup>, as measured by an Oriel Goldilux UV meter. To vary the O<sub>2</sub> partial pressure in contact with the reaction mixture, balloons were filled with predetermined amounts of air and nitrogen or air and oxygen and attached to the cuvette. A fan was used to maintain the temperature in the cuvette at  $22 \pm 2^{\circ}$ C.

#### Analytical procedures

A 500 µL portion of the final photolysate was taken, combined with 50 uL of a solution of o-xylene in ethanol as an internal standard and subjected to gas chromatography/mass spectrometry. This was carried out with a Shimadzu QP-5000 GC-MS with an Agilent DB624 column (30 m,  $0.32 \text{ mm} \times 1.8 \mu \text{m}$  cyanopropylphenyl/dimethyl polysiloxane film). The oven start temperature was 40°C and a linear temperature gradient of 20°C min<sup>-1</sup> was applied to 240°C. Injection was carried out with a 10:1 split ratio. All species were identified from their mass spectra, and peak areas were used to determine concentrations. While CCl<sub>4</sub> and C2Cl6 solutions with o-xylene were used to develop standards for their determinations, phosgene concentrations were measured by the condensation of COCl<sub>2</sub> with ethanol to make ethyl chloroformate. The ethanol in the 50 µL o-xylene solution was sufficient for complete conversion; hence, ethyl chloroformate was used as the standard. In the absence of ethanol, phosgene was readily identifiable in the gas chromatogram and its complete disappearance in favor of ethyl chloroformate was readily verified. GC-MS analysis had to be undertaken within a few hours, otherwise ethyl chloroformate began to condense further to build diethyl carbonate.

HCl production was tracked by periodically removing aliquots of the photolysate, diluting with CHCl<sub>3</sub> and adding a portion to a 3.00 mL solution of tetraphenylporphyrin (H<sub>2</sub>TPP) in CHCl<sub>3</sub>. The absorbance at 446 nm was used to determine the amount of H<sub>4</sub>TPP<sup>2+</sup> formed, by use of the extinction coefficients for H<sub>2</sub>TPP and H<sub>4</sub>TPP<sup>2+</sup> (53,54), taking note that the intermediate H<sub>3</sub>TPP<sup>+</sup> species can be neglected (55).

In addition, a chemical analysis for phosgene was conducted by taking aliquots from the photolysate during and following irradiation and mixing them with 3.00 mL solutions of approximately 0.01 M Bu<sub>4</sub>NI in CHCl<sub>3</sub> from which ethanol had been removed. After 20 min, the absorbance at 365 nm was used to determine the concentration of  $I_3^-$ , arising from the reaction (56)

$$\operatorname{COCl}_2 + 2 \operatorname{I}^- \to \operatorname{CO}(g) + \operatorname{I}_2 + 2 \operatorname{Cl}^-$$
 (7)

and the subsequent formation of  $I_3^-$  from the excess of iodide ion. Iodide also reduces  $Cl_2$ , peroxides and other oxidizing species; thus, the true concentration of  $COCl_2$  could be overestimated by this measure.

### **RESULTS AND DISCUSSION**

#### **Control experiments**

Broadband irradiation of chloroform, in the absence of mesoporous silica, at wavelengths above 360 nm produced no detectable products within 1 h. Neither did stirring a suspension of MCM-41 in chloroform for 2 h in the dark. Broadband irradiation  $(\lambda > 360 \text{ nm})$  of a suspension of ordinary silica gel in chloroform for 40 min produced no detectable decomposition products.

#### Photodecomposition products in MCM-41/CHCl<sub>3</sub> suspensions

Under broadband ( $\lambda > 360$  nm) irradiation, chloroform underwent photodecomposition in a suspension with MCM-41, yielding primarily phosgene and hydrogen chloride in a nearly one-to-one ratio, as would be expected from the stoichiometry of Eqs. (3)–(6), and the development of products with time is shown in Fig. 1. After irradiating for 50 min, the concentration of both species had risen to approximately 0.1 M. The rate of formation accelerated with time and the data in Fig. 1 were fit to an exponential growth function.

Table 1 shows concentrations of all products detected by GC-MS in a typical irradiation. The chloroalkyl termination products found were  $CCl_4$  and  $C_2Cl_6$ , the latter in much smaller amounts. None of the termination products expected from  $CHCl_2$  radicals was detected by GC-MS, i.e.  $C_2H_2Cl_4$ ,  $C_2HCl_5$  and  $CH_2Cl_2$ . This rules out radical formation by either C–Cl bond homolysis in chloroform or the reduction in chloroform to yield  $CHCl_2$  and  $Cl^-$ .

#### Mechanistic hypothesis

Because carbon–chlorine bond fission occurs during the photocatalyzed decomposition of carbon tetrachloride in ethanol (57), one might expect an analogous bond fission to occur when chloroform is photocatalytically decomposed, yet this clearly does not occur with MCM-41 as the catalyst because if it did, the termination products from CHCl<sub>2</sub> radicals would have been found (35).

Light absorption by silica, and any consequent photocatalytic activity, arises from a number of point defect sites, the optical properties of which have been extensively studied (58–63) and characterized (64). Two of these surface defect sites can be excited by radiation near 360 nm, one characterized as a nonbridging oxygen hole center (NBOHC), with an absorption maximum at approximately 260 nm, the other a surface dioxasilyrane (essentially a bidentate peroxo group on a single silicon), with a weaker absorption maximum at approximately 310 nm (64). The NBOHC may be represented as  $\equiv$ Si–O· ( $\equiv$  indicating three-single bonds to oxygen atoms) (65), and the dioxasilyrane as = Si(O<sub>2</sub>) (= indicating two-single bonds to oxygen atoms) (66). It should be noted that Inaki *et al.* have proposed, on the basis of IR evidence, that the NBOHC defect is actually a strained O–Si–O



**Figure 1.** Growth of HCl (open circles) and COCl<sub>2</sub> (filled squares) during the irradiation ( $\lambda > 360$  nm) of 1.0 mL of chloroform in which 12 mg of MCM-41 mesoporous silica was suspended. Solid (HCl) and dashed (COCl<sub>2</sub>) lines are least squares fits to the function  $y = a(e^{bt}-1)$ ; R<sup>2</sup>(HCl) = 0.97, R<sup>2</sup>(COCl<sub>2</sub>) = 0.94.

**Table 1.** Product concentrations determined by GC-MS measurements following a 20-min irradiation ( $\lambda > 360$  nm) of a suspension of 40 mg of MCM-41 mesoporous silica in 1.0 mL of CHCl<sub>3</sub>.

Product	Concentration (mM)
$COCl_2^*$	17
$CCl_4$	5.1
$C_2Cl_6$	0.2

\*After conversion to ethyl chloroformate.

linkage (45). Photoexcitation of the dioxasilyrane can be presumed to yield Si–O· units with homolysis of the weak O–O bond, while the strained siloxane bridge is proposed to break upon photoexcitation to yield adjacent Si· and Si–O· sites (45). Thus, whatever the nature of photoactive defect, it should present as an electron-deficient Si–O· unit upon excitation.

Given the oxygen-centered radical at the photoactive site, abstraction of hydrogen should be favorable, i.e.

$$\equiv Si - O^* + CHCl_3 \rightarrow \equiv Si - OH + CCl_3$$
(8)

Reaction of the trichloromethyl radical with oxygen and the self-reaction of the subsequent trichloromethylperoxy radicals, as in Eqs. (4) and (5), yield trichloromethoxy radicals. In the gas phase, the direct decay to phosgene and chlorine atoms, as in Eq. (6), is the primary fate of CCl<sub>3</sub>O· radicals (52). In the condensed phase, however, hydrogen abstraction from CHCl<sub>3</sub> may be competitive, although leading to the same products, and a fraction of the trichloromethoxy radicals may abstract hydrogen from silanol groups, regenerating the  $\equiv$  Si–O· defects.

$$CCl_3O \cdot + CHCl_3 \rightarrow CCl_3OH + \cdot CCl_3$$
 (9)

 $CCl_3O \cdot + \equiv Si - OH \rightarrow CCl_3OH + \equiv Si - O \cdot$  (10)

$$CCl_3OH \rightarrow COCl_2 + HCl$$
 (11)

The proposed sequence of steps is shown in Scheme 1.



The formation of trichloromethanol replaces a weak C–H bond (393 kJ mol<sup>-1</sup>) (67) with a strong O–H bond (calculated to be 465 kJ mol<sup>-1</sup> (68)). It should be noted that the trichloromethylhydroperoxy radical, from which CCl<sub>3</sub>O is generated, Eq. (5), would not itself be expected to abstract hydrogen from chloroform because the O–H bond energy in CCl<sub>3</sub>OOH is only 370–380 kJ mol<sup>-1</sup> (69).

The establishment of a photostationary state concentration of CCl<sub>3</sub>OH provides an answer to the puzzle of high yields of

 $CCl_4$ , which can be made by the reaction of HCl with trichloromethanol, but not with the trichloromethoxy radical.

$$CCl_3OH + HCl \rightarrow CCl_4 + H_2O$$
 (12)

The buildup of  $CCl_4$  in turn, may explain the acceleration in the rate of chloroform photodecomposition. Carbon tetrachloride may to some extent undergo dissociative adsorption on MCM-41, as it does on TiO<sub>2</sub> (70). The Cl and CCl<sub>3</sub> radicals could then, through the chain process shown in Eqs. (4) through (7), induce further chloroform decomposition.

#### Effect of oxygen

Assuming that CCl<sub>3</sub> radicals are formed as in Eq. (8), with subsequent formation of CCl<sub>3</sub>OO radicals leading to degradation products, and assuming a bimolecular termination step for trichloromethyl radicals, the decomposition rate would be expected to be directly proportional to the dioxygen concentration. This was tested by varying the atmosphere above the reaction mixture from 100% N<sub>2</sub> to 100% O<sub>2</sub>, the results from which are shown in Fig. 2. The data are not consistent with direct proportionality, suggesting that some degree of quenching by dioxygen takes place.

The data can be reasonably well fit by assuming that  $O_2$  is required to form products, as in Eq. (4), but also quenches the SiO<sub>2</sub> defect excited state. Denoting the light-absorbing mesoporous silica unit by *C*, we have for this simplified model

$$\mathbf{C} \stackrel{\mathrm{h}\nu}{\underset{k_{1}}{\rightleftharpoons}} \mathbf{C}^{*} \tag{13}$$

$$C^* + O_2 \xrightarrow{k_2} Products$$
 (14)

$$\mathbf{C}^* + \mathbf{O}_2 \xrightarrow{k_3} \mathbf{C} + \mathbf{O}_2^* \tag{15}$$

Expressing the rate of formation of the excited state as  $I_0 f/V$ , where  $I_0$  is the incident light intensity, f the fraction of light absorbed and V the sample volume, and assuming photostationary



**Figure 2.** Variation in COCl<sub>2</sub> yield with the fraction of O<sub>2</sub> in N<sub>2</sub>/O<sub>2</sub> mixtures in contact with a suspension of 12 mg of MCM-41 mesoporous silica in 1.0 mL of CHCl<sub>3</sub> after 20 min of irradiation ( $\lambda > 360$  nm). Solid line is a fit to Eq. (16), R<sup>2</sup> = 0.94.

state conditions for  $C^*$ , the rate of product formation is

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{(k_2 - k_3)I_0f}{V(k_1 + (k_2 - k_3)[\mathrm{O}_2])}[\mathrm{O}_2] = \frac{a[\mathrm{O}_2]}{1 + b[\mathrm{O}_2]}$$
(16)

The data in Fig. 2 were fit to this function, yielding a satisfactory result.

#### Rate as a function of catalyst load

The product yield varied greatly with the amount of mesoporous silica employed, passing through a maximum, as can be seen in Fig. 3. This behavior is expected from considerations of the light absorbed by a weakly absorbing suspended material, the light striking which may be transmitted through the suspension unabsorbed, reflected back from the front face, or scattered, with a particular probability of eventual absorption (71,72). This analysis predicts that the fraction of incident light absorbed by the suspension, to which the photocatalytic product yield will be proportional, can be expressed as

$$f = 1 - e^{-\beta m} - \gamma (1 - e^{-\delta m})$$
(17)

where *m* is the mass of catalyst,  $\gamma$  represents the probability that light scattered within the solution will be reflected rather than absorbed, and  $\beta$  and  $\delta$  are phenomenological constants representing the relative probabilities of transmission and reflectance (71).



**Figure 3.** COCl<sub>2</sub> yield as a function of the mass of MCM-41 mesoporous silica suspended in 1.0 mL of CHCl<sub>3</sub> after 20-min irradiation ( $\lambda > 360$  nm). Solid line is a fit to Eq. (17).

The solid line in Fig. 3 was fit to this function.

**Table 2.** Product yield (in  $\mu$ mol) as a function of bandpass filter cutoff wavelength. Exptl conditions: 10 mg MCM-41 suspended in 1.0 mL CHCl<sub>3</sub>, irradiated 30 min, 100-W Hg lamp.

Cutoff wavelength	COCl <sub>2</sub>	$CCl_4$	C <sub>2</sub> Cl <sub>6</sub>
345 nm 360 nm	90.1 89.5	2.7 3.7	0.1 0.15
375 nm	4.6	0	0

#### Product yield as a function of irradiation wavelength range

The product yields were measured with different cutoff filters (Table 2), showing a marked drop between cutoff wavelengths of 360 and 375 nm, which can be ascribed to the steep decline in absorptivity of the NBOHC defects with peak maxima at 260 and 310 nm that are implicated in the photochemical reactivity.

#### Decomposition rate in deuterochloroform

Neither HCl nor phosgene was detected in the photolysate when 10 mg of MCM-41 was suspended in 1.0 mL of deuterochloroform and irradiated ( $\lambda > 360$  nm) for 20 min. This result is compatible with the proposed mechanism in that hydrogen abstraction from chloroform at the photoactive site, Eq. (8), requires an additional 25 kJ mol<sup>-1</sup> in CDCl<sub>3</sub> (73); thus, the effect on the rate of homolysis can be very large.

# Decomposition rate in the presence of cyclohexane, ethanol and water

Following the addition of 5% cyclohexane or ethanol by volume to chloroform, no decomposition was observed to take place after irradiating a suspension (20 mg of MCM-41 in 1 mL of solution) for 20 min ( $\lambda > 360$  nm). Both cyclohexane and ethanol would be expected to retard photodecomposition by radical scavenging. Reacting with the trichloromethyl radical, as in Eq. (18), for example, would be quite effective in eliminating chain carriers.

$$C_6H_{12} + \cdot CCl_3 \rightarrow \cdot C_6H_{11} + CHCl_3$$
(18)

This would, however, generate termination products from the cyclohexyl radical in solution, particularly bicyclohexyl, but no such products were found by GC-MS. Likewise, none of the radical products from the 1-hydroxyethyl radical were found, namely acetaldehyde, acetal (57) or 2,3-butanediol (74).

We conclude, therefore, that the cyclohexyl and 1-hydroxyethyl radicals remain on the silica surface at other defect sites, and that cyclohexane and ethanol retard photodecomposition by intercepting the photoactive defect site, hindering the reaction shown in Eq. (8). The binding of cyclohexyl radicals to silica has been demonstrated (75), and there is ample experimental evidence for the dissociative addition of ROH (76) and  $RNH_2$  (45) species to silica surfaces, even in thermal reactions.

The photodecomposition rate did not change when the chloroform was saturated with water, which can be attributed to the much higher O–H bond dissociation energy in  $H_2O$ .

#### Effect of added ions

Chloroform was irradiated in suspensions of mesoporous silica with several different tetrabutylammonium salts dissolved (50 mg in 1.0 mL CHCl<sub>3</sub>). Bromide, chloride, perchlorate and hexafluorophosphate salts essentially stopped the photodecomposition. No degradation products were detected. When photodecomposition is initiated through the photodissociation of a chlorine atom (57,71), chloride ion has been shown to accelerate considerably the catalyzed photodecomposition of chlorinated hydrocarbons, stabilizing the radical as  $Cl_2^-$  and retarding recombination within the solvent cage (77–80). Thus, these experiments serve as additional evidence against a photodissociation mechanism.

The completely opposite behavior exhibited in this system cannot reasonably be ascribed to reductive quenching of the silica defect excited state, which is observed with some SiO<sub>2</sub> dopants (81), as  $PF_6^-$ , in particular, should not be oxidizable in these circumstances. This may simply be an electrostatic effect, that is, the attraction of the anions (as part of an ion pair when in chloroform) to the positively charged defects, inhibiting access by chloroform.

## CONCLUSIONS

Unmodified MCM-41 mesoporous silica acts as an effective catalyst for the photodecomposition of chloroform under near-UV light. The most likely mechanism for its photocatalytic activity is through hydrogen abstraction by excited state defect sites from chloroform and a radical chain initiated by the resulting trichloromethyl radicals ending in phosgene and hydrogen chloride. In the presence of water, which does not retard the reaction, phosgene can be converted into carbon dioxide, so this has the potential to serve as an environmentally friendly remediation process for chlorinated hydrocarbons, using sunlight and generating relatively benign final products.

An obvious question from the results obtained is why ordinary silica gel showed no photocatalytic activity while mesoporous silica was even more active than other heterogeneous catalysts for chlorocarbon photodegradation that we have studied (82,83). It is unlikely that photophysical differences are responsible for this, as the two types of silica surface should have similar photophysical properties. We suggest that the photochemical reactivity in the presence of mesoporous silica results from the small size of the pores, ca. 2.5 nm (84), so that they effectively act as reaction chambers, serving to retain CCl<sub>3</sub>O radicals near the silica surface to permit the deprotonation of silanol functionalities (Eq. 10) and the reestablishment of NBOHC sites. The faster rate of hydrogen abstraction from Si-OH groups by CCl<sub>3</sub>O compared with the rate of decomposition to COCl<sub>2</sub> and Cl, which is the primary reaction channel for COCl<sub>3</sub> in the gas-phase photodecomposition of chloroform (52), would then be responsible for the retention of catalytic activity by the mesoporous silica surface.

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