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Catalysis of the photodecomposition of carbon tetrachloride in ethanol by an Amberlite anion exchange resin

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ABSTRACT

The chloride form of the polystyrene–divinylbenzene anion exchange resin Amberlite IRA-900 was found to catalyze the photodecomposition of carbon tetrachloride in ethanol at wavelengths above 350 nm. With sulfate, bromide, and perchlorate as counterions, the resin was inactive. The major products are acetaldehyde, phosgene, chloroform, and hydrogen chloride. The photoreaction is much slower under 1.0 atm O_2 than under air, while in deoxygenated solutions it is also much slower and produces no phosgene. Much of the observed behavior can be explained by a model in which the poly(styrene-co-divinylbenzene) matrix absorbs light and transfers energy to CCl_4, which undergoes photodissociation, assisted by a chloride ion to stabilize the chlorine atom as Cl_2^-. Two major reaction channels for the trichloromethyl radicals produced by photodissociation are proposed, one in which CCl_3 abstracts hydrogen from ethanol and the other involving addition of O_2 to form trichloromethylperoxy radicals.

1. Introduction

The decomposition of carbon tetrachloride in alcohols under irradiation has been the subject of several investigations. Decomposition has been carried out in water/isopropanol by means of pulse radiolysis [1], in methanol by irradiation at 254 nm [2], and in ethanol with iron porphyrins as homogeneous catalysts [3–6]. Catalysis by iron porphyrins was reported to function primarily through the ability of these species to undergo a photo-assisted oxidation–reduction cycle, reducing CCl_4 and oxidizing ethanol in the process [3,5].

As part of the ongoing interest in heterogeneous photocatalytic systems in this laboratory, we report here the photocatalysis of the decomposition of carbon tetrachloride in ethanol by Amberlite IRA-900, an anion exchange resin based on a copolymer of styrene and divinylbenzene. While polystyrene-based ion exchange resins have been used to support photocatalysts [7–11], we have found no reports of the resin itself acting in that role, even though polystyrene is known as both a good energy donor and a good electron donor [12–14]. Both types of photoactivity are thought to derive from excimers formed between excited and ground state styrene units [12].

We have focused primarily on the products formed and the mechanistic conclusions that can be reached. However, there are also implications for "green chemistry", not only for the possible degradation of waste carbon tetrachloride using sunlight, but also for the potential to convert a toxic substance, still extensively used in industry, into useful products.

2. Materials and methods

2.1. Chemicals

Ethanol (Sigma–Aldrich, HPLC grade) was used as received. Carbon tetrachloride (Erba) was purified by distillation before use.

Amberlite IRA-900 was obtained from Sigma–Aldrich in the chloride form. It is a strongly basic anion exchange resin containing quaternary ammonium groups on a poly(styrene-co-divinylbenzene) matrix, with an exchange capacity of 4.2 meq per gram of dry weight and particle sizes between 16 and 50 mesh [15]. Before use, it was soaked in water for 30 min, then washed with ethanol and air-dried. The anion was replaced in some samples by stirring the chloride form for two hours in a 1 M aqueous solution of $HClO_4$, KF, NaBr, or H_2SO_4, then washing with the same solution until the filtrate was negative to $AgNO_3$, except for the bromide, which cannot be tested in this way. Approximately 300 mL of solution was used in each case to prepare 1 g of exchanged Amberlite, and it was assumed that the exchange of Br^- was complete with the same volume of solution. Following the exchange of anion, the resin was washed with water and ethanol then air-dried.

Solutions of CCl_4 in ethanol were made fresh and discarded at the end of the day.

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2.2. Photochemical reactions

The desired amount of the Amberlite was added to 1.0 mL of a solution of CCl_4 in EtOH in a quartz spectrophotometer cuvette. The cuvette was capped, leaving 3 mL of head space, and was stirred magnetically (1000 rpm) in order to bring as much of the catalyst into the light path as possible. In some experiments, a gas balloon was attached in order to maintain a desired partial pressure of O_2. Irradiation was carried out with a 400-W Helios Italquartz Q400 medium-pressure mercury lamp (photon flux 15 mW/cm^2, as measured with a MACAM UV203X ultraviolet radiometer), with a 350-nm highpass filter to remove wavelengths below approximately 350 nm. A fan was used to maintain the temperature in the cuvette at 22 ± 1 °C.

Product analysis was carried out by removing 500 μL of the photolysate and adding 5.0 μL of a solution of xylene in EtOH as an internal standard. This was subjected to gas chromatography using an HP 6890 instrument equipped with a flame ionization detector and an Agilent DB-624 column (30 m, 0.32 mm × 1.8 μm film, consisting of 6% cyanopropylphenyl 94% dimethyl polysiloxane). A split ratio of 10:1 was employed. Quantitative analysis was accomplished by use of ethanol solutions of authentic samples.

In addition, a portion of the photolysate was removed and added to a chloroform solution of *meso*-tetraphenylporphyrin (Porphyrin Products), diluting with unreacted CCl_4/EtOH when necessary, to determine the amount of HCl produced. Protonation of tetraphenylporphyrin (H_2TPP) yields H_4TPP^{2+} in preference to H_3TPP^{+}, even at low concentrations of acid [16]. The concentration of H_4TPP^{2+} was determined from the peak at 445 nm, by use of the known extinction coefficients for H_2TPP and H_4TPP^{2+} [17,18].

Diffuse reflectance spectra were recorded with a Jasco V-570 spectrophotometer using an integrating sphere and $BaSO_4$ as the reference. The Kubelka–Munk transformation [19], $f(R)=1-R^2/2R$), was applied to the reflectance data.

3. Results and discussion

3.1. Reaction products

The major photolysis products from the irradiation of a suspension of Amberlite IRA-900 (Cl^- form) in CCl_4/EtOH can be seen in Table 1, the result of a 60-min irradiation. Under the same conditions with no Amberlite present, no significant amount of any product was found, nor were significant amounts of any product found by stirring the Amberlite for 60 min in 5% CCl_4 in the dark. All products were identified by comparison with authentic samples by means of gas chromatography on two different columns (Agilent DB-624 and DB-WAX) with dissimilar characteristics.

Table 1
Yield of principal products (in μmol) from the 60-min irradiation of 1 mL of 10% CCl_4 in ethanol with 50 mg of Amberlite IRA-900 in chloride form, in order of elution (except for HCl) in gas chromatogram.

Product	Initial	24 h
Acetaldehyde	42.3	51.7
Phosgene	28.9	19.9
Ethyl acetate	0.2	0.3
Chloroform	49.4	47.2
Ethyl chloroformate	22.2	3.7
1,1-diethoxyethane	16.8	15.0
Diethyl carbonate	3.2	24.8
1-chloroethyl chloroformate	0.1	0.2
Hexachloroethane	2.4	2.5
HCl	217.2	167.3

From these observations, it can be concluded that the major products are HCl, acetaldehyde, phosgene, and chloroform, because ethyl chloroformate and diethyl carbonate are solvolysis products of phosgene [20,21], while 1,1-diethoxyethane (acetal) is an acid-catalyzed condensation product of acetaldehyde with ethanol, Eqs. (1)–(3).

$$COCl_2 + CH_3CH_2OH \rightleftharpoons ClC(O)OCH_2CH_3 + HCl \quad (1)$$

$$ClC(O)OCH_2CH_3 + CH_3CH_2OH \rightleftharpoons OC(OCH_2CH_3)_2 + HCl \quad (2)$$

$$CH_3CHO + 2CH_3CH_2OH \xrightarrow{H^+} CH_3CH(OCH_2CH_3)_2 \quad (3)$$

When the photolysate was left overnight and reanalyzed (Table 1), it could be seen that the solvolysis equilibria shifted markedly towards diethyl carbonate. Though HCl is generated in the process, its concentration decreased after 24 h, presumably because of evaporation. Diethyl carbonate is a widely used industrial solvent that has recently received a great deal of attention as a potential fuel additive to increase octane number [22], with lower toxicity than, for example, methyl *tert*-butyl ether.

It should be noted that phosgene is normally inflammable [23] and consequently inert to flame ionization detection [24]. In fact, with our apparatus no signal was obtained for $COCl_2$ in toluene. However, in ethanol, there was a low retention-time peak, in addition to those found for the solvolysis products ethyl chloroformate and diethyl carbonate, and this signal had to be included in order to achieve mass balance for phosgene. The signal may be attributable to an association complex with ethanol. Since a satisfactory mass balance was achieved in solutions with large differences in the extent of solvolysis, it appears that very little phosgene went undetected by the flame ionization detector.

Another product, 1-chloroethyl chloroformate, is formed under certain conditions from acetaldehyde and phosgene [25] (Eq. (4)).

$$COCl_2 + CH_3CHO \rightarrow ClC(O)CHClCH_3 \quad (4)$$

Because of these reactions, product distributions involving acetaldehyde and phosgene were sensitive to the amount of time following the measurement and also to the amount of acid in solution. In order to more accurately compare product yields under different conditions, in the remainder of this article, we report only total amounts of acetaldehyde and phosgene, including all the solvolysis, condensation, and addition products. These quantities were much less variable after solutions were removed from light.

Table 2 shows the total quantities of major products formed from the 1-h irradiation described in Table 1. These can be compared with those achieved through homogeneous catalysis by iron porphyrins reported by Bartocci et al. after 20 h of irradiation, also with a 400-W medium-pressure mercury lamp and a 350-nm cutoff filter [3], whereby it can be seen, despite the inherent problems in comparing results from homogeneous catalysis with those from heterogeneous catalysis, that the efficiency of the Amberlite-catalyzed process compares very favorably, the net rate of disappearance of CCl_4 being nine times greater than that reported for the

Table 2
Comparison of reaction products from the decomposition of CCl_4 in ethanol, (a) heterogeneous catalysis by Amberlite (1 h, 10% CCl_4) and (b) homogeneous iron porphyrin-catalyzed (20 h, 10% CCl_4).

Net micromoles produced	Amberlite	Bartocci et al. [3]
Total acetaldehyde	59.2	242.0
Total phosgene	54.4	
Chloroform	49.4	240.0
Ethyl acetate	0.2	
C_2Cl_6	2.4	
HCl	217.2	246.0

TPP-catalyzed process (assuming a constant rate over the 20-h irradiation).

The different distribution of products in the two experiments implies some difference in the mechanism(s) of decomposition and the mechanism of catalysis.

3.2. Long-term irradiation and stability

A three-hour irradiation was carried out on three successive days, reusing the same sample of Amberlite. While the product distribution varied somewhat from day to day, it appears that the Amberlite did not lose substantial photocatalytic activity after nine hours of use.

It should be noted that the further oxidation of acetaldehyde to acetic acid (converted to ethyl acetate in the acidic photolysate) takes place only to a minor extent. As can be seen in Table 1, this can be held to less than 1% with irradiation times of an hour or less.

Many years ago, Kharasch and coworkers found that terminal olefins were susceptible to attack by CCl_3 radicals [26,27], one example being the direct photolysis of CCl_4 in the presence of olefins [27]. Any unpolymerized vinyl groups from the divinylbenzene crosslinker would thus be subject to attack, which could conceivably alter the properties of the resin after prolonged irradiation.

3.3. The light-absorbing species

A Kubelka–Munk transformed reflectance spectrum of the Amberlite resin is shown in Fig. 1, from which it can be concluded that there is weak, though significant, absorbance of light by the resin between 350 and 450 nm. This absorbance is enhanced by multiple reflections taking place in stirred suspensions. In this region of the spectrum, the absorbance of CCl_4 is very low, <0.002 absorbance units. Because it appears that the resin is the only part of the system that can absorb light and because the system did not undergo photodecomposition in the absence of the Amberlite, it was assumed that the Amberlite itself, that is, the poly(styrene,divinylbenzene) matrix, was the photochemically active species.

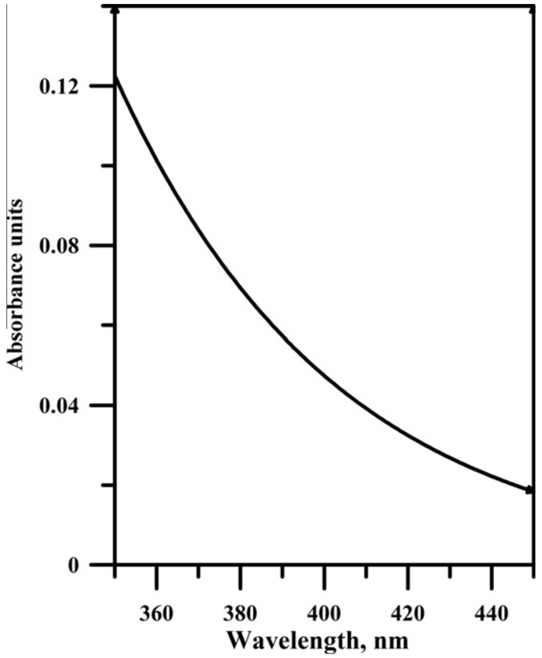

Fig. 1. Kubelka–Munk transformed reflectance spectrum of powdered Amberlite IRA-900 (Cl form). The original reflectance spectrum was recorded between 200 and 800 nm.

As control experiments for this conclusion, CCl_4/EtOH solutions were irradiated in the presence of dissolved LiCl, $CaCl_2$, Et_4NCl, and Bu_4NCl, none of which caused any significant degree of decomposition. Thus, chloride ion by itself is not photocatalytic, nor does the presence of quaternary ammonium groups in solution render Cl^- photocatalytic without the resin to absorb light.

Given that the Amberlite poly(styrene-co-divinylbenzene) backbone is the photoactive element in the decomposition process, it would be predicted that adding more Amberlite to a reaction solution would increase the rate of reaction, to a decreasing extent as the fraction of light absorbed approaches unity. In fact, it was observed that the reaction rate almost doubled when the amount of Amberlite in the 1 mL solution was increased from 10 mg to 20 mg, with a smaller increase in rate when 40 mg was used. With 60 mg of Amberlite, very little light escaped the solution and, in fact, no increase in rate was observed with larger quantities.

Table 3 The same principle should apply to particle size. A comparison was made between 15 mg of unaltered Amberlite beads (Cl^- form) with 15 mg that had been ground to a fine powder. The powder allowed very little light to escape the cuvette. The product distributions are shown in Table 4.

The general result is that reducing the particle size and thereby intercepting all of the incident radiation causes the product yield to increase to between double and triple that achieved with unaltered Amberlite. However, it should be noted that the yield of chloroform increased by almost a factor of 10, a result that may indicate a specific influence of surface area on the reaction outcome.

Additional confirmation that the Amberlite is the light-absorbing species comes from the observation that washing the resin with acetone completely inactivates it, while washing with ethanol, ether, carbon tetrachloride, or acetonitrile does not. The triplet energy of acetone lies at 330 kJ/mol [28], which corresponds to 363 nm, thus the inactivation appears to result from quenching by adsorbed acetone. It should be noted that the activity of the resin was restored by washing it with water, but not by washing with ethanol alone.

3.4. Mechanistic hypotheses

In an attempt to explain the observed products and their distribution and as an impetus for further testing, the following mechanism was considered. It was assumed that the initial photochemical event was the formation of a CCl_3 radical by energy transfer or electron transfer from the excited poly(styrene-co-divinylbenzene) matrix. Energy transfer would lead to C–Cl bond homolysis as in Eq. (6),

$$(R^+ - Cl^-) \overset{h\upsilon}{\rightleftarrows} (R^+ - Cl^-)^* \qquad (5)$$

$$(R^+ - Cl^-)^* + CCl_4 \rightarrow (R^+ - Cl^-) + \cdot CCl_3 + Cl\cdot \qquad (6)$$

while electron transfer would yield a chloride ion as in Eq. (7).

Table 3
Products (in μmol) from the 3-h irradiation ($\lambda > 350$ nm) of 1 mL of 5% CCl_4 in EtOH, reusing the same 48 mg quantity of Amberlite (Cl^- form).

	Day 1	Day 2	Day 3
Total acetaldehyde	171	199	148
Total phosgene	104	103	73
$CHCl_3$	27	55	48
Ethyl acetate	10	6	5
C_2Cl_6	3	4	3
HCl	355	345	373

Table 4
Products formed during the 20-min irradiation (λ > 350 nm) of 5% CCl_4 in EtOH with 15 g of normal (16–50 mesh) Amberlite IRA-900 (Cl^- form) and with the same amount of powdered Amberlite.

μmol produced	Normal Amberlite	Powdered Amberlite
Total acetaldehyde	8.6	20.3
Total phosgene	3.8	9.2
$CHCl_3$	0.6	5.8
Acetic acid	0.0	0.0
C_2Cl_6	0.1	0.4
HCl	18.6	37.8

$$(R^+ - Cl^-)^* + CCl_4 \rightarrow (R^+ - Cl^-)^+ + \cdot CCl_3 + Cl^- \quad (7)$$

Prior to diffusion of the products from the solvent cage or the photoactive resin site, the thermal back-reactions must also be considered.

$$\cdot CCl_3 + Cl\cdot \rightarrow CCl_4 \quad (8)$$

$$(R^+ - Cl^-)^+ + \cdot CCl_3 + Cl^- \rightarrow (R^+ - Cl^-) + CCl_4 \quad (9)$$

The primary radicals formed can each abstract hydrogen from ethanol.

$$\cdot CCl_3 + CH_3CH_2OH \rightarrow CHCl_3 + CH_3\dot{C}HOH \quad (10)$$

$$Cl \cdot + CH_3CH_2OH \rightarrow HCl + CH_3\dot{C}HOH \quad (11)$$

In principle, 1-ethoxy radicals can either disproportionate to form acetaldehyde, Eq. (12),

$$2CH_3\dot{C}HOH \rightarrow CH_3CHO + CH_3CH_2OH \quad (12)$$

or combine to form 2,3-butanediol [29]; however, the latter product was never found in photolysates.

Besides hydrogen abstraction from ethanol, we can include the consequences from the self-termination of CCl_3 and from its reaction with oxygen to produce a peroxy radical.

$$2 \cdot CCl_3 \rightarrow C_2Cl_6 \quad (13)$$

$$\cdot CCl_3 + O_2 \rightarrow CCl_3OO\cdot \quad (14)$$

In the gas phase, trichloromethylperoxy radicals decompose in a second-order process to the unstable $CCl_3O\cdot$radical [30], which decomposes rapidly to yield phosgene [31].

$$2CCl_3OO\cdot \rightarrow 2CCl_3O \cdot + O_2 \quad (15)$$

$$CCl_3O\cdot \rightarrow COCl_2 + Cl\cdot \quad (16)$$

In the absence of oxygen, CCl_3 would be predicted to react only by hydrogen abstraction from ethanol, Eq. (10). If CCl_3 is created by energy transfer, the sequence given by Eqs. (10)–(12) predicts a product ratio of 1:1:1 for $CHCl_3$, HCl, and CH_3CHO. An electron transfer cycle may be designed that would lead to the same ratio, although this is not the only possible outcome. Table 5 shows an experimental test of this hypothesis and reasonable agreement with the predicted ratios. The somewhat low value for HCl may be ascribed to evaporation.

Table 5
Products formed (in μmol) following a 2-h irradiation (λ > 350 nm) of 1 mL of 5% CCl_4 in EtOH, deoxygenated, with 47 mg Amberlite IRA-900 (Cl^- form).

Total acetaldehyde	6.3
Total phosgene	0.0
$CHCl_3$	6.5
Ethyl acetate	0.0
C_2Cl_6	0.0
HCl	5.3

3.5. The role of the anion

From the data above, it is quite likely that the Amberlite functions as the photoactive species, but it is less clear what other properties of the resin are required for photocatalysis. There may be specific sites, relative to the location of the quaternary ammonium groups or the associated anion. The chloride ion itself may be necessary. To investigate this, several samples of Amberlite were prepared by replacing the chloride with sulfate, fluoride, perchlorate, and bromide ions. A comparison of the photocatalytic performance of these samples is shown in Table 6.

It can be seen that with sulfate, perchlorate, and bromide as counterions, Amberlite IRA-900 is ineffective as a catalyst for the photodecomposition of CCl_4 in EtOH. With fluoride as the counterion, on the other hand, the photodecomposition proceeded at a rate comparable to that achieved with the chloride form. The almost negligible yield of HCl is exactly as would be expected, since fluoride ion is very effectively protonated by HCl. Because of this, it is not clear whether Amberlite-F^- is photocatalytically active in its own right, or only as a result of the substitution of chloride for fluoride as HCl is produced.

Another consequence of using Amberlite with a weak base as a counterion was that most of the phosgene product was found as diethyl carbonate, a result of a shift to the right of the equilibria in Eqs. (1) and (2) as HCl is consumed by reaction with F^-. In addition, most of the acetaldehyde was found as CH_3CHO rather than as acetal, the conversion to which is catalyzed by acid.

Since Cl^- in homogeneous solution appears to be ineffective in catalyzing the photodecomposition, we can conclude that only chloride ion associated with the cations on the surface of the resin is photocatalytic, and furthermore that Cl^- has a particular role that many other anions cannot fill. This rather specific role in the photodecomposition can be taken as evidence that the Amberlite excited state transfers energy, rather than an electron, to CCl_4. If anything, Cl^- would enhance the cage back reaction in Eq. (9), and it is difficult to imagine a means by which the presence of Cl^- would be essential for electron transfer. On the other hand, chlorine atoms are converted nearly quantitatively to Cl_2^- in the presence of an excess of Cl^- [32–35], and this stabilization may be essential to prevent the back reaction, Eq. (8).

Assuming this, the reaction steps involving chlorine atoms should be reformulated to underscore the role of the associated chloride ion.

$$(R^+ - Cl^-)^* + CCl_4 \rightarrow \cdot CCl_3 + (R^+ - Cl_2^-) \quad (17)$$

$$(R^+ - Cl_2^-) + CH_3CH_2OH \rightarrow (R^+ - Cl^-) + HCl + CH_3\dot{C}HOH \quad (18)$$

In the following, we have neglected the electron transfer mechanism, although it cannot be ruled out entirely as a contributing process.

3.6. Effect of oxygen

As is seen in Table 5 above, in the absence of oxygen, no phosgene is produced and the photodecomposition of CCl_4 in ethanol

Table 6
Product distribution (in μmol) following the 20-min irradiation (λ > 350 nm) of 1 mL of 5% CCl_4 in EtOH with 40 mg of Amberlite IRA-900 with different counterions.

	SO_4^{2-}	F^-	ClO_4^-	Br^-	Cl^-
Total acetaldehyde	2.0	18.4	0.1	0.0	16.7
Total phosgene	0.3	6.1	0.6	0.1	9.0
$CHCl_3$	0.2	3.0	0.1	0.1	1.4
Ethyl acetate	0.0	0.1	0.0	0.0	0.0
C_2Cl_6	0.0	0.1	0.0	0.0	0.1
HCl	0.1	1.0	1.5	0.1	33.3

yields CH_3CHO, $CHCl_3$, and HCl in approximately a 1:1:1 relationship. Given the additional hydroperoxide channel, Eqs. (13)–(15), in the presence of oxygen, it might be predicted that this channel would be enhanced the higher the partial pressure of O_2, producing more phosgene. Table 7 shows the results of several 20-min irradiations at different partial pressures of oxygen.

The optimum reaction rate appears to occur at an O_2 partial pressure below that in air, and the highest fraction of phosgene was achieved under the same conditions. The results show that eventually, higher partial pressures of O_2 actually retard the photodecomposition, presumably by quenching the poly(styrene-co-divinylbenzene) excited state. The much lower rate at higher concentrations of O_2 implies a quenching mechanism, which we write as

$$(R^+ - Cl^-)^* + O_2 \rightarrow (R^+ - Cl^-) + O_2^* \tag{19}$$

We have considered this to be an energy transfer, rather than an electron transfer, process, because of the assumption that if superoxide ion were formed by electron transfer to O_2, it would lead to the formation of peroxy radicals [6], which would then react as in Eqs. (15) and (16) to yield phosgene, potentially enhancing the decomposition rather than retarding it.

In the absence of oxygen, the reaction was too slow to permit an accurate assessment of the product distribution in a comparable time period, but the results of a 2-h irradiation are shown above in Section 3.4.

3.7. Dependence on the concentration of CCl_4

The product distribution from the decomposition of CCl_4 in ethanol was determined following 20-min irradiations of solutions with different concentrations of CCl_4, the results of which are shown in Fig. 2. The yield of each of the major products increases very nearly linearly with the CCl_4 concentration at low values of $[CCl_4]$, after which the rate of increase with concentration decreases steadily, the yields possibly approaching asymptotic values.

We will express the rate of absorption of light by the poly(styrene-co-divinylbenzene) matrix, the forward step in Eq. (5), as fI_o, where I_o is the incident light intensity and f the fraction of light absorbed by the active sites in Amberlite, presumably those in proximity to a chloride ion. This is a considerable approximation since it ignores the dependence of both f and I_o on wavelength, but in a given set of experiments conducted with the same quantity of Amberlite, the total rate of photon absorption may be expressed at least conceptually in this way, representing an integration over wavelength.

Table 7
Products found following 20-min irradiation ($\lambda > 350$ nm) of 5% CCl_4 with 40 mg of Amberlite IRA-900 (Cl^- form) under different partial pressures of O_2. The total pressure in the balloon was just slightly above 1 atm in each case.

µmol produced	O_2 (%)					
	0	1	8	21	35	100
Total acetaldehyde	0.0	17.3	19.6	16.9	16.9	2.3
Total phosgene	0.0	7.7	18.1	13.1	9.7	1.1
Chloroform	0.7	7.1	8.2	1.6	1.2	0.0
Ethyl acetate	0.0	0.0	0.0	0.1	0.0	0.0
C_2Cl_6	0.0	0.3	0.4	0.1	0.1	0.3
HCl	0.5	27.8	46.7	45.0	36.7	4.7

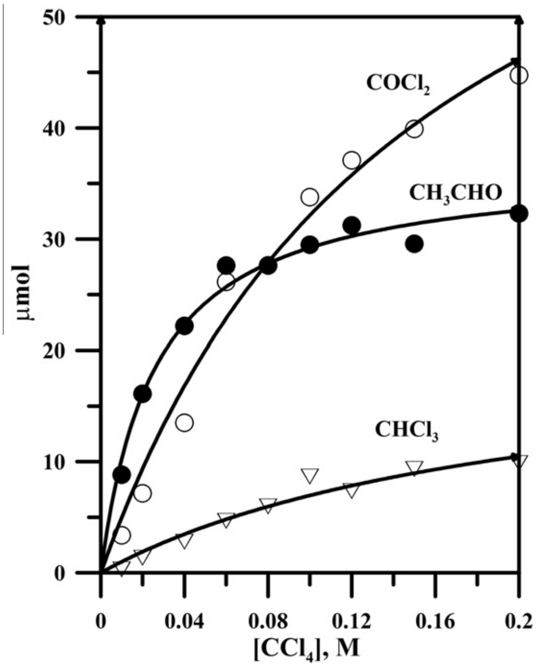

Fig. 2. Yields of acetaldehyde, phosgene, and chloroform from the 20-min irradiation ($\lambda > 350$ nm) of 1 mL of CCl_4 in EtOH with 47 mg of Amberlite IRA-900 (Cl^- form). Solid lines are fit to the function $ax/(b + x)$, with $R^2 = 0.99$ for $COCl_2$ and CH_3CHO and 0.95 for $CHCl_3$. Note that 1% CCl_4 by volume $\cong$ 0.1 *M*.

With the assumption of a photostationary state and the mechanism outlined in Section 3.2, the concentration of active excited state centers may be expressed as

$$[(R^+ - Cl^-)^*] = \frac{fI_0}{k_{-5} + k_{17}[CCl_4] + k_{19}[O_2]} \tag{20}$$

In this expression, the rate constants correspond to the equation numbers in the text. Assuming further a steady state in all radical species, and neglecting the self-termination of CCl_3 radicals, which is a reasonable approximation given the experimental product distributions, the steady-state concentration of trichloromethyl radicals is

$$[CCl_3] = \frac{k_{17}fI_0[CCl_4]}{(k_{10} + k_{14}[O_2])(k_{-5} + k_{17}[CCl_4] + k_{19}[O_2])} \tag{21}$$

At a constant concentration of O_2, this equation has the general form $a[CCl_4]/(b+[CCl_4])$, which predicts a linear relationship of the steady-state concentration of trichloromethyl radicals to the CCl_4 concentration at low values of $[CCl_4]$, with a slope of a/b, and an asymptotic maximum CCl_3 concentration a. According to the proposed mechanism, the rate of formation of each of the four major products ($COCl_2$, CH_3CHO, $CHCl_3$, and HCl) is directly proportional to the concentration of CCl_3 radicals.

It can be misleading to use product yields to model rate equations, since the integration of a rate equation results in a higher order dependence on concentrations. However, as a trial of the concept, each of the data sets of Fig. 2 was fit to the function $ax/(1 + bx)$, the results of which are shown as solid lines. In each case, the data are well fit by this function, in agreement with the predictions, which are based on the CCl_4 dependence of Eq. (21).

This apparently asymptotic behavior does not continue indefinitely as the fraction of CCl_4 is increased, and in fact, there is almost no reaction in 100% CCl_4, as is discussed further in Section 3.10.

An additional prediction from the mechanistic considerations above is that since the rate of formation of each of the four major products should be directly proportional to the steady-state CCl_3 concentration, they should be proportional to each other. This is clearly not the case, and this question is taken up next.

3.8. Mass balance

In the absence of O_2, there is a reasonably good approximation to the mass balance [CH_3CHO] = [HCl] = [$CHCl_3$] predicted from the hydrogen abstraction channel alone for CCl_3 radicals, essentially that shown above in Eqs. (10)–(12).

The reaction of CCl_3 radicals with O_2 adds the hydroperoxide channel, Eqs. (14)–(16), and leads to the generation of phosgene as an additional product. Though it is more difficult to deal with mass balance given two primary reaction channels, there are some predictions that can be made. We concentrate on the appearance and disappearance of CCl_3 radicals and consider three stages in the decomposition process initiated by energy transfer. Each 1-hydroxyethyl radical is set equal to 0.5 acetaldehydes, assuming that Eq. (12) is the only termination reaction for CH_3CHOH radicals.

1. Photohomolysis, Eq. (17), yields CCl_3 and Cl_2^- radicals. The latter yields, after hydrogen abstraction from ethanol, Eq. (18), HCl and 0.5 CH_3CHO.
2. A CCl_3 radical that reacts by hydrogen abstraction generates, from Eqs. (10) and (12), $CHCl_3$ and 0.5 CH_3CHO.
3. A CCl_3 radical that reacts by peroxy radical formation generates, from Eqs. (14)–(16) plus (11) and (12), $COCl_2$, HCl, and 0.5 CH_3CHO.

Letting *x* be the fraction of CCl_3 radicals undergoing hydrogen abstraction and $1 - x$ the fraction forming peroxy radicals, the following products are predicted to be formed from one photodissociation event:

$$\text{HCl} : 2 - x \quad \text{CHCl}_3 : x \quad \text{COCl}_2 : 1 - x \quad \text{CH}_3\text{CHO} : 1$$

The total amount of HCl will be considerably greater than this, since it is produced by the solvolysis of $COCl_2$, thus it will not be considered further. For $x = 1$, this yields the expected 1:1:1 ratio for $CHCl_3$/$COCl_2$/CH_3CHO, as observed in the deoxygenated system.

Several different mass balance predictions can be written, one of which is

$$[\text{CH}_3\text{CHO}] = [\text{COCl}_2] + [\text{CHCl}_3] \tag{22}$$

An examination of the data in Fig. 2 shows that this equation is obeyed well only near 0.5 M (5%) CCl_4. Below that concentration, acetaldehyde is in excess, relative to the prediction of Eq. (22), and above that concentration, phosgene is in excess.

Thus, we can conclude that the scheme outlined in Section 3.4, while explaining much of the observed photochemical behavior, provides an incomplete description of the system. This is not at all unusual in radical processes, but it is not yet clear what additional reaction channel(s) could be affecting the [$COCl_2$]/[CH_3CHO] ratio in the manner observed. Termination of 1-hydroxyethyl radicals other than through bimolecular disproportionation, Eq. (12), would alter this ratio; however, the low α-C–H bond energy in ethanol, 381 kJ/mol [36], makes hydrogen abstraction by CH_3CHOH from any of the species in solution improbable.

One possibility arises from the observation that the trichloromethylperoxy radical, which is known to decompose almost entirely through the bimolecular process of Eq. (15) in the gas phase, undergoes a first-order decomposition yielding phosgene [1]. In that work, the authors were unable to determine mechanistic details, except that the process involved a radical chain and a probable rearrangement of CCl_3OO.

One might also note that an increase in the solubility of O_2 at higher CCl_4 concentrations, or a preferential association of O_2 with CCl_4 would tend to favor the peroxide channel over hydrogen abstraction at higher concentrations of CCl_4. In fact, the solubility of O_2 in CCl_4 is twice that in EtOH [37], and O_2 is known to form a π–σ association complex with carbon tetrachloride [38]. However, even if all the CCl_3 radicals reacted with O_2, the mechanism above would predict that the yields of phosgene and acetaldehyde would be equal.

Another reaction that should be considered is hydrolysis. Water is produced during the condensation of acetaldehyde and ethanol to form acetal. Carbon tetrachloride undergoes slow thermal hydrolysis to phosgene [39], which itself is slowly hydrolyzed to carbon dioxide and hydrogen chloride. Though there is only scant evidence that these processes can be accelerated photochemically [40], thermal catalysis of CCl_4 hydrolysis under basic conditions by anion exchange resins has been noted [41].

3.9. Photodecomposition in the presence of water

To test the hypothesis that the hydrolysis of CCl_4 may also be taking place, we undertook experiments to assess the effect of added water on the photodecomposition process.

Table 8 indicates that the addition of 500 μmol of H_2O (ca. 0.5 M) did indeed increase the ratio of $COCl_2$ to CH_3CHO, and this result was reproduced in two additional experiments. Experiments at intermediate water concentrations did not show the same level of reproducibility, but always yielded higher ratios of phosgene to acetaldehyde. Since only 20–30 μmol of water was produced by acetal formation in typical experiments, the role of hydrolysis is still an open question.

3.10. The role of ethanol

In the foregoing, ethanol functions only as a substrate for hydrogen abstraction, Eqs. (10) and (11). The hypothesized peroxide radical channel, Eqs. (14)–(16), should not require ethanol, and in its absence, one would expect the photodecomposition to continue, with perhaps some buildup of Cl_2 as a chlorine atom termination product in place of the hydrogen abstraction from ethanol posited in Eq. (14). This was tested by adding Amberlite (Cl^- form) to neat CCl_4 and irradiating. The photolysate was then diluted 1:1 with ethanol in order to convert most of the phosgene to ethyl chloroformate, since phosgene was not detectable by flame ionization in CCl_4 alone. In fact, very little phosgene was produced, less than 1% of that produced in 5% CCl_4.

Irradiation of 5% EtOH in CCl_4 with Amberlite (Table 9) yielded the amount of acetaldehyde expected by extrapolation from Fig. 2, but considerably less phosgene and very little HCl.

From the lack of reactivity in its absence, we can infer that ethanol plays an additional role in the photodecomposition, beyond that of a source of hydrogen. Added insight into that role was sought from a qualitative comparison of the photodecomposition of CCl_4 in other primary alcohols.

Although the products were not identified, irradiation of 10% CCl_4 in 1-propanol with 50 mg of Amberlite IRA-900 (Cl^- form) yielded a number of peaks and total area in the gas chromatogram comparable to that achieved with 10% CCl_4 in ethanol, and also a similar amount of HCl formed. The same experiment done with 10% CCl_4 in 1-butanol yielded a similar number of GC product

Table 8
Products (in μmol) from 20-min irradiation ($\lambda > 350$ nm) of 1 mL of 5% CCl_4 in EtOH with 47 mg of Amberlite IRA-900 (Cl^- form) and H_2O.

Product	H_2O added (μmol)	
	0	500
Total acetaldehyde	20.0	8.4
Total phosgene	16.7	18.8
$CHCl_3$	2.1	2.7
C_2Cl_6	0.2	0.2
HCl	48.4	53.0

Table 9
Products (in μmol) from 30-min irradiation ($\lambda > 350$ nm) of 1 mL of 5% EtOH in CCl_4 with 41 mg of Amberlite IRA-900 (Cl^- form).

Total acetaldehyde	32.7
Total phosgene	18.0
$CHCl_3$	0.7
Ethyl acetate	1.0
C_2Cl_6	0.4
HCl	3.8

peaks, but only about 10–15% of the total peak area found with ethanol and 1-propanol, and likewise approximately 10% of the HCl. Moving to 1-pentanol caused another large reduction in yield, the total peak area and HCl yield being 1–2% of that found in ethanol and 1-propanol.

Based on the decrease in yield with the increase in hydrophobicity of the alcohol, we suggest that more polar alcohols solvate the ionic sites in the resin, allowing dissolved CCl_4 access to the portion of the poly(styrene-co-divinylbenzene) resin in the vicinity of chloride ions. Less polar solvents, including neat carbon tetrachloride, may be unable to approach the anions closely enough to allow the chloride ion to stabilize the chlorine atom as it dissociates from the CCl_4 molecule.

3.11. Conclusions

Amberlite IRA-900 anion exchange resin in the chloride form has been shown to be an efficient catalyst for the photodecomposition of CCl_4/EtOH solutions, yielding acetaldehyde, phosgene, and chloroform. This may be viewed as a potential means to degrade unwanted carbon tetrachloride, but also for its potential to generate useful products, diethyl carbonate, for example. From a synthetic viewpoint, the photodecomposition of CCl_4 in ethanol could be used to generate phosgene in situ, given the abundance of reactions in which $COCl_2$ is an important building block [25] but the general aversion to storing highly toxic chemicals.

Optimum efficiency of photodecomposition is achieved with a partial pressure of O_2 around half of atmospheric, under which conditions a decomposition rate over ten times that reported for homogeneous catalysis by iron porphyrins results [3]. Less resin is required to intercept the incident light if it is ground to a powder, but the bead form offers advantages in sample handling.

The experimental evidence is fairly strong that the catalysis by the chloride form of Amberlite IRA-900 of the photodecomposition of carbon tetrachloride in ethanol may be ascribed to the absorption of light by the poly(styrene-co-divinylbenzene) matrix, energy transfer to CCl_4, and its subsequent homolysis, assisted by chloride ions, which stabilize the chlorine atoms and hinder recombination. There is also evidence that ethanol facilitates the transport of CCl_4 molecules to resin sites near chloride ions.

To some extent, the data are also consistent with a partitioning of the CCl_3 radicals formed by photodissociation into two reaction channels, one in which hydrogen is abstracted from ethanol and the other in which reaction occurs with molecular oxygen to form the trichloromethylperoxy radical, which goes on to produce phosgene. Given this mechanism, the yield of phosgene should never exceed that of acetaldehyde; however, phosgene was found in excess when the concentration of CCl_4 was above 5%. Thus, there appears to be an additional reaction channel, which might involve the hydrolysis of CCl_4.

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