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Carbon Atom-Initiated Degradation of Carbon Tetrachloride in the Presence of Molecular Oxygen: A Product and Mechanistic Study

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This paper reports an investigation of the gas-phase reaction of atomic carbon with carbon tetrachloride in the presence of molecular oxygen. It is demonstrated that carbon tetrachloride can be oxidatively degraded by this method. Results from FT-IR and GC/MS studies suggest that the major products from the reaction are phosgene and carbon dioxide. The initial step involves breaking the carbon−chlorine bond as a result of the reaction of atomic carbon with carbon tetrachloride. Laser-induced fluorescence studies have shown the presence of CCl as an intermediate produced from this reaction. A tentative mechanism is proposed to describe the details of the chemistry.

Introduction

This paper reports on the degradation of carbon tetrachloride with carbon atoms in the presence of oxygen. The breakdown of carbon tetrachloride is used as a model for the destruction of similar chlorinated compounds, such as chlorofluorocarbons (CFCs). Because of the structure of CCl_4, its reactivity with atomic carbon and oxygen serves as an example for other CFCs and carbon−chlorine compounds.

In light of the Montreal Protocol, which has regulated the production and emission of CFCs in industrialized countries, there is a need for safe, economical methods for destruction of the CFC stockpiles that now exist (*1*). Several methods have already been proposed (*2*−*8*). Our method, reported here, exploits the affinity of atomic carbon to cleave the carbon−chlorine bonds in CFCs. In addition, the reaction products may be collected and used in other reactions. By understanding the details of the reaction mechanism, this process may be generalized to an industrial scale as well. This research may also have implications for other CFC degradation methods. One such method involves the mineralization of CFCs using sodium oxalate (*2*). However, this method also produces atomic carbon, which cannot be accounted for in the proposed reaction scheme. It may be that the atomic carbon participates in the breakdown of CFCs via a reaction similar to the one postulated here.

Atomic carbon has been a species of interest for many years in a variety of investigations (*9*−*12*). In the past, studies have focused on the insertion reactions of atomic carbon with diatomic species, including H_2, HCl, and HBr (*13*). Carbon atoms have also been known to react with several other systems, including N_2O (*12*), chloroform (*14*), and methanol (*15*). Recent work on the reactions of chlorinated and fluorinated compounds with carbon have yielded some insight into the atomic carbon reaction process. Initial studies by Weigert (*16*) suggested that arc-generated atomic carbon inserted into fluorinated compounds. Nicoll and Francisco, investigating heterogeneous systems with activated carbon and carbon tetrachloride, proposed that carbon atoms were inserting into the C−Cl bond (*17*). This is consistent with the findings of Choi et. al. (*14*), who also concluded that C−Cl is an intermediate in the reaction pathway for the reaction of gas-phase carbon atoms with chloroform.

Of interest in recent years has been the mechanism behind these reactions. The majority of these studies have shown that the carbon prefers to insert rather than abstract in these reactions. Carbon atoms may react with these molecules via two routes: either carbon insertion, represented by reaction 1, or abstraction, represented by reaction 2. In carbon insertion, the carbon atom initially inserts into the molecule between the central carbon atom and ligand, as shown, before breaking apart into the carbon fragment and parent molecule fragment. However, in carbon abstraction, the carbon immediately pulls off the ligand from the central carbon in the molecule, forming two fragments.

$$C(^3P) + CCl_4 \rightarrow ClC{-}CCl_3 \tag{1}$$

$$C(^3P) + CCl_4 \rightarrow CCl + CCl_3 \tag{2}$$

Interestingly, the study of atomic carbon reacting with chloroform reported on the observation of both C−H and C−Cl fragments via laser-induced fluorescence (*14*). The study suggested that atomic carbon inserted into the reactant molecule. However, the study did not investigate the reaction mechanism, focusing instead on the dynamics of the insertion process.

It is the intent of this research to investigate the reaction of atomic carbon with carbon tetrachloride in the presence of oxygen using laser-ablated graphite as a source of $C(^3P)$. The oxygen is used to oxidize the trichloromethyl radical once the degradation process had been initiated by atomic carbon. In so doing, the oxygen allows the radical fragments to be further oxidized into stable products that can then be monitored via FT-IR and GC/MS techniques.

Experimental Section

There is a dearth of reports in the literature on atomic carbon reactions in general. The lack of studies of this system is mainly due to a lack of clean sources for producing atomic carbon. Sources of producing atomic carbon also inherently generate other carbon species, including C_2, C_3, larger carbon compounds, and carbon clusters. Since these other species interfere with the study of atomic carbon reactions, very few studies of the reactions of atomic carbon have been reported in the journals until recently. Several different methods of carbon production currently exist, including laser-irradiated carbon suboxide (*18*) and laser-ablated graphite as a source (*19*). Laser-ablated carbon, unlike other sources, is known to produce a relatively clean source of atomic carbon. It has been well-established that using laser irradiation above 354 nm produces $C(^3P)$ (*12*), whereas $C(^1D)$ is produced with carbon suboxide by laser photolysis at 193 nm (*20*). While

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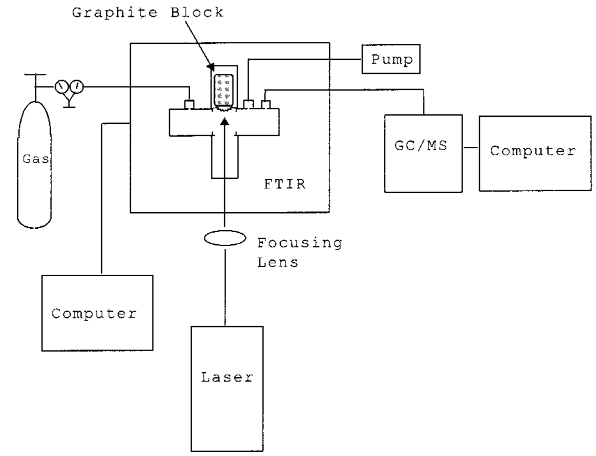

FIGURE 1. Experimental setup used to investigate the reaction of carbon atoms with carbon tetrachloride in the presence of oxygen.

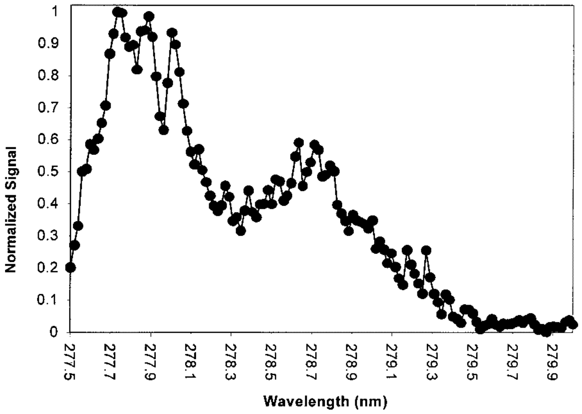

FIGURE 2. Preliminary LIF scan from 277 to 280 nm showing peaks attributed to the CCl reaction fragment. The scan, although lower resolution, agrees well with data presented by Tiee et al. (*28*).

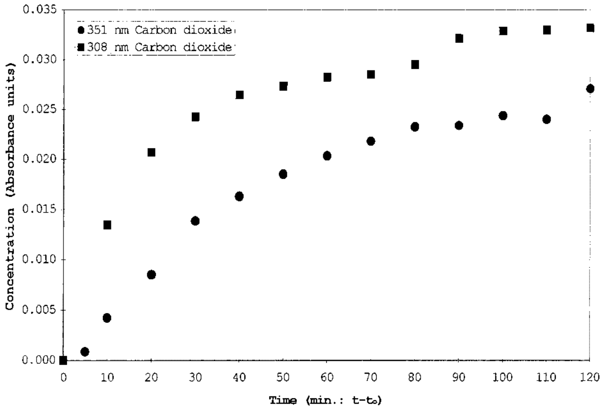

FIGURE 3. Comparison of the carbon dioxide distributions from the reaction between atomic carbon, carbon tetrachloride, and oxygen based on the wavelength used for irradiation of the graphite block. The relative proportions for phosgene were similar to the trend for carbon dioxide.

TABLE 1. Possible Reaction Mechanism for the Reaction of Atomic Carbon with Carbon Tetrachloride in the Presence of Oxygen

step	reaction	ΔH_f (kJ/mol)[a]
initiation	$C(^3P) + CCl_4 \rightarrow CCl + CCl_3$	−47
	$C(^3P) + O_2 \rightarrow CO + O(^3P)$	−578
propagation	$CCl + O(^3P) \rightarrow ClCO$	−755
	$ClCO + O(^3P) \rightarrow ClC(O)O^*$	−360
	$ClC(O)O^* \rightarrow Cl + CO_2$	−150
	$C(^3P) + CClO \rightarrow CCl + CO$	−322
	$CCl + O_2 \rightarrow Cl + CO_2$	−766
	$Cl + C(^3P) \rightarrow CCl$	−344
	$CO + Cl \rightarrow ClCO$	−22
	$CCl_3 + O \rightarrow COCl_2 + Cl$	−426
	$CCl_2O + C(^3P) \rightarrow CCl + ClCO$	−15
	$CCl_3 + O_2 \rightarrow CCl_3O_2$	−93
	$2CCl_3O_2 \rightarrow 2CCl_3O + O_2$	6
	$CCl_3O \rightarrow CCl_2O + Cl$	−87
termination	$ClCO + Cl \rightarrow COCl_2$	−336
	$CO + O(^3P) \rightarrow CO_2$	−532
	$Cl + Cl + M \rightarrow Cl_2 + M$	−242

[a] Heats of reaction were calculated from refs 26, 27, 29 and 30.

laser-ablated graphite can also produce other species, the types of carbon species generated by the laser can be controlled by the laser energy and position of the focal point (*21*). Focusing the beam to a small spot on the surface of the graphite block ensures that the maximum power is delivered to the sample, thereby breaking all the graphite bonds and ultimately producing atomic carbon.

Initially, approximately equal quantities of carbon tetrachloride and oxygen were placed in a glass reaction chamber, which was designed for the static observation of reactions. The reaction cell was placed in the path of the FT-IR beam, and an ultrahigh purity graphite rod was placed flush with the FT-IR beam, as shown in Figure 1. The laser beam entered the cell perpendicular to the FT-IR beam through a planoconvex focusing lens ($f = 5.0$ cm) and was focused down to a spot about 1 mm wide. The laser beam struck the stationary graphite block, generating atomic carbon. Both 351- and 308-nm laser radiation were used: either was sufficient to generate atomic carbon, $C(^3P)$ (*12*).

Initial studies employed 308-nm radiation from a Lambda Physik 301 EMG XeCl laser with approximately 80 mJ of power. Those studies using 351-nm radiation were conducted using a Lambda Physik Compex laser with approximately 40 mJ of power. In both cases, the laser was allowed to ablate the graphite sample for 10 min between FT-IR scans.

Prior to filling the cell, it was pumped down with a diffusion pump to less than 3×10^{-5} Torr. The cell was then consistently filled with approximately equal pressures of reactants to a total pressure of around 10 Torr. Carbon tetrachloride, because of its high vapor pressure, was introduced directly into the evacuated cell without the need for a carrier gas. The carbon tetrachloride was purified through a freeze/pump/thaw system before being placed in the cell.

Results were collected using on-line FT-IR to monitor the concentrations of reactants and products. On-line GC/MS was also available to corroborate the results obtained by FT-IR. Pressure calibrations were done using the FT-IR on carbon tetrachloride and carbon dioxide, so that the concentrations of reactants and products could subsequently be monitored in the reaction chamber. To conduct the calibrations, individual gases were placed in the cell, and the percent transmittance was monitored as a function of pressure. Calibration curves of the FT-IR absorbances were subsequently constructed versus reactant and product concentrations. Before each reaction, a background spectrum was recorded and subtracted from all scans collected by the FT-IR. Sixty-four scans were averaged for each reaction, with a spectral resolution of 2 cm^{-1}. Reproducibility and accuracy of the initial sample concentrations were found to be approximately ±1%.

For the laser-induced fluorescence studies, which were designed to probe for the presence of C−Cl fragments, a

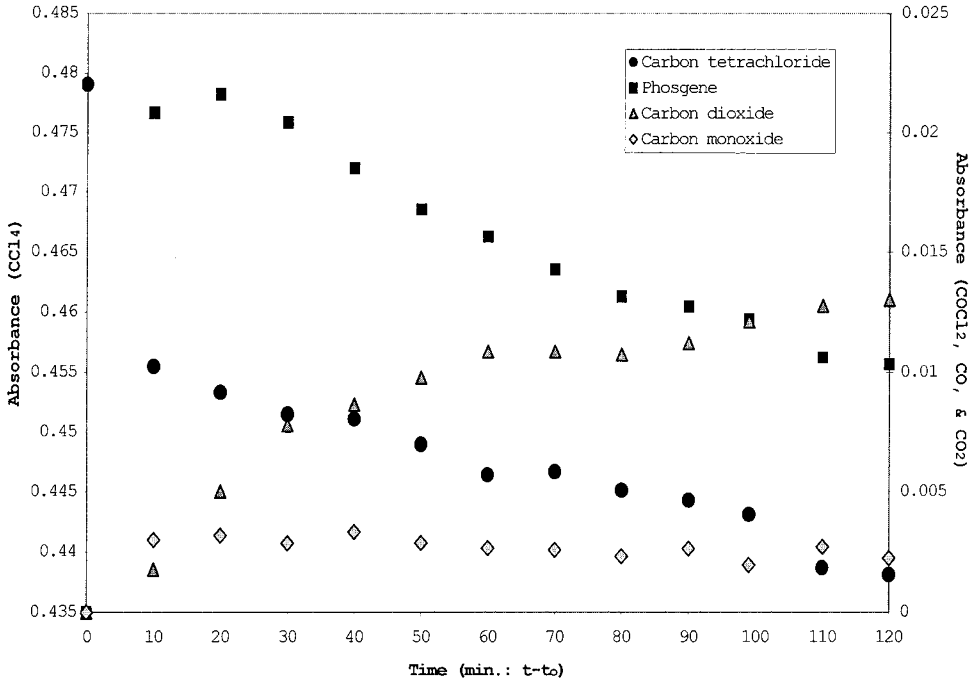

FIGURE 4. Production of carbon dioxide and phosgene as carbon tetrachloride degrades. The 308-nm laser ablated the graphite for 2 h after 4.55 Torr of oxygen and 6.01 Torr of CCl_4 were placed in the reaction vessel.

similar reaction cell was used. In this case, the cell was evacuated to less than 1×10^{-6} Torr before reactants were added to the cell. The carbon block, with the capability for rotation, was placed into the cell, and 351-nm radiation from the Lambda Physik Compex laser was focused onto the face of the block to produce carbon atoms. The probe laser, which was a Lambda Physik Dye laser with crystal doubling, scanned from 277 to 280 nm perpendicular to the pump laser beam. The resulting fluorescence was observed orthogonal to the pump/probe beams via a scanning monochromator attached to a photomultiplier tube.

Results and Discussion

Study of the Reaction of $C(^3P)$ with CCl_4 in the Absence of O_2. In experiments in which only carbon tetrachloride was used in the absence of oxygen, there was no net loss of carbon tetrachloride observed in the FT-IR. Upon repeated laser irradiation, carbon depositation on the walls of the reaction cell was observed. However, carbon deposits were not observed in the control experiments or experiments in which oxygen was present in the reaction cell. To determine if a reaction was occurring in the absence of oxygen, we performed a series of laser-induced fluorescence experiments to probe for the reaction product CCl.

The CCl radical has an $A^2\Delta - X^2\Pi$ transition in the 270–280-nm region, and the laser-induced fluorescence of the CCl radical from this transition has been previously observed by other groups (*18, 28*). A series of control experiments were initially performed. When the carbon block was ablated in the absence of CCl_4, no laser-induced fluorescence signal for CCl radical was observed. When carbon tetrachloride was present without the carbon block, no signal was observed. When carbon tetrachloride was introduced in the presence of the carbon block, signals were observed from the CCl fragment. Figure 2 shows the LIF scan showing the CCl signal, with a delay time of 2 μs between pump and probe lasers. When the probe laser was blocked, the signal was observed to disappear. The observation of a fluorescence spectrum for CCl suggests that the reaction does occur and can best be described by

$$C(^3P) + CCl_4 \rightarrow CCl + CCl_3$$

We cannot discern from these experiments if carbon atoms are inserting into the C–Cl bond of carbon tetrachloride or abstracting chlorine atoms in the reaction process. We do confirm that the product of the reaction is CCl. To explain the observation of the apparent no net loss of CCl_4 in the final product mixture, as observed by FT-IR studies, the following reaction mechanism is proposed:

$$C(^3P) + CCl_4 \rightarrow CCl + CCl_3$$

$$C(^3P) + CCl \rightarrow Cl + C_2$$

$$Cl + CCl_3 \rightarrow CCl_4$$

In this mechanism, the CCl_4 in the reaction converts $C(^3P)$ atoms into C_2 with no net loss of CCl_4. There should be a buildup of C_2 from the reaction, which is consistent with our observations that carbon deposits build up on the walls of the reaction vessel upon repeated irradiation. Moreover, we have also probed for C_2 with laser-induced fluorescence and have observed a signal consistent with C_2 observed in the literature (*19*). We also note that some C_2 is produced from the ablated graphite, so it is difficult to distinguish how much C_2 was contributed from the reaction of $C(^3P)$ with CCl. However, we note that the addition of oxygen competitively removes CCl and CCl_3 from the reaction process.

Product Study of the Reaction of $C(^3P)$ with CCl_4 and O_2. Control experiments were performed with the individual reactants to correct the data for any side reactions attributable to atomic carbon reacting with either oxygen or carbon tetrachloride separately. When oxygen and atomic carbon only were present in the cell, the only product was carbon monoxide. This is consistent with other reports in the literature, which found that carbon monoxide was produced in the presence of oxygen (*22*). When oxygen and CCl_4 were irradiated without graphite present, no reaction was observed.

When oxygen, atomic carbon, and carbon tetrachloride were all present in the reaction chamber, significant amounts of carbon dioxide and phosgene were formed. The FT-IR and GC/MS scans show the presence of unreacted carbon tetrachloride as well as carbon dioxide and phosgene. The GC/MS, which scanned up to 650 m/e, also revealed that no high mass species were present in the cell. The major peaks in the GC/MS were carbon dioxide, phosgene, and unreacted carbon tetrachloride as well as a small contribution from carbon monoxide and hydrogen chloride. Traces of water in the cell led to the production of hydrogen chloride from the decomposition of phosgene (*23*).

To account for the reactions that were proceeding inside the cell, a series of steps have been postulated to describe the chemistry. Table 1 is a step-by-step listing of the reactions proposed to characterize the reaction mechanism. It follows from the types of products formed that atomic carbon is reacting with the carbon tetrachloride. Regardless of whether atomic carbon inserts into the molecule or abstracts chlorine, CCl must be formed in the process. The CCl can then react with molecular oxygen through a series of steps to produce carbon monoxide and carbon dioxide. Similarly, CCl_3 can undergo similar reactions, giving up chlorine and reacting with oxygen to produce phosgene. It can also react with oxygen and donate chlorine, ultimately producing carbon dioxide.

The reaction was then conducted with two different types of lasers to determine if the reaction had any wavelength dependency. In both cases, it was found that phosgene and carbon monoxide were initially produced, but that these species both rapidly decayed away as the carbon dioxide grew in. Comparing the curves for 308-nm radiation versus 351-nm radiation, the product distributions were very similar to one another, although the 308-nm laser, with twice the power of the 351-nm laser, produced more phosgene and carbon dioxide than did the 351-nm laser. The increase in power implies the production of more carbon atoms from the ablation process. Figure 3 is a comparison of the product distributions of carbon dioxide from the two laser frequencies. The product distributions for phosgene are comparable to those from carbon dioxide. Therefore, the energy of the laser did not appear to affect the reaction as far as the production of any new species. Both studies resulted in the same general trends of products and reactants, although the 351-nm studies inherently produced lower volumes of products, due to the difference in power.

After 2 h of laser ablation, the 308-nm experiment resulted in 27.9% CCl_4 degradation, while the 351-nm study resulted in 9.5% degradation (*24*). The concentrations of all products were monitored with the FT-IR every 10 min over the 2 h of irradiation of the sample. The concentrations of carbon monoxide, carbon dioxide, phosgene, and unreacted carbon tetrachloride were subsequently plotted versus time to obtain some insight into the time profile of the reaction. Figure 4 is a plot of the concentrations of carbon tetrachloride degradation relative to product generation vs time, illustrating that the carbon dioxide grew in direct relationship to carbon tetrachloride degradation. Ultimately, the carbon tetrachloride is then degraded into carbon dioxide in this process. The phosgene initially grew in and then began to die away after 30 min of irradiation. This can be explained by taking into account the chemistry going on during each laser pulse: the products from the initial reaction are available for further chemistry with other species as the laser is successively fired. Therefore, the CCl generated in the first laser pulse, for instance, is available to interact with oxygen, chlorine, and carbon generated in the consecutive laser pulses.

While phosgene initially grows, it then begins to decline as it degrades into carbon dioxide. The carbon monoxide also initially grows, but is then consumed in the reaction. From the control experiments, the carbon monoxide is apparently generated from the reaction of atomic carbon with oxygen. However, it also appears to serve a useful role in the reaction mechanism, as it is then available for successive reactions, as seen in Table 1. Because of these processes, the carbon dioxide concentration continues to increase.

Product Study of the Reaction of $C(^3P)$ with $^{13}CCl_4$ and O_2. Following the time studies, experiments employing isotopically labeled $^{13}CCl_4$ were used to attempt to gain more insight into the reaction mechanism. Since the ablation of graphite would produce ^{12}C, whereas the breakdown of $^{13}CCl_4$ would produce ^{13}C, it was possible to follow some of the steps of the reaction by monitoring the concentrations of ^{12}C- and ^{13}C-containing species relative to time. Specifically, the experiments were designed to help distinguish what role atomic carbon played in the reaction mechanism. After the initiation step as shown in reaction 3, if only $^{12}CO_2$ were produced, then the laser-generated carbon atoms would be the only source of carbon-producing carbon dioxide, as shown in reaction 4. If only $^{13}CO_2$ were produced, then it could come from the oxidation of $^{13}CCl_3$, as shown in reactions 5a−5g.

$$^{12}C + {}^{13}CCl_4 \rightarrow {}^{12}CCl + {}^{13}CCl_3 \tag{3}$$

$$^{12}CCl + O_2 \rightarrow {}^{12}CO_2 + Cl \tag{4}$$

$$^{13}CCl_3 + O_2 \rightarrow {}^{13}CCl_3O_2 \tag{5a}$$

$$2\,{}^{13}CCl_3O_2 \rightarrow 2\,{}^{13}CCl_3O + O_2 \tag{5b}$$

$$^{13}CCl_3O \rightarrow {}^{13}CCl_2O + Cl \tag{5c}$$

$$^{13}CCl_2O + {}^{12}C \rightarrow {}^{12}CCl + {}^{13}CClO \tag{5d}$$

$$^{13}CClO + O_2 \rightarrow {}^{13}CCl(O)O_2 \tag{5e}$$

$$2Cl^{13}C(O)O_2 \rightarrow 2\,{}^{13}CCl(O)O + O_2 \tag{5f}$$

$$^{13}CCl(O)O \rightarrow Cl + {}^{13}CO_2 \tag{5g}$$

However, if both isotopes are produced, then both fragments must be playing a role in the reaction in order to yield equal quantities of the isotopically labeled carbon dioxide. In this case, all of the above reactions would be feasible. Reaction 5d is included because the data indicate that the phosgene decreases as more atomic carbon is generated, which is then free to react with the phosgene. Thus, as ^{13}C-containing phosgene is degraded, $^{13}CO_2$ is produced, accounting for the production of this species.

When using $^{13}CCl_4$, the general trends for all species were similar to that for the nonisotopically labeled CCl_4 studies. The percent degradation was also similar: 29% after 2 h of irradiation with 308-nm radiation. The major products of the reaction, which were identified by both GC/MS and FT-IR, were $^{12}COCl_2$, $^{13}COCl_2$, $^{12}CO_2$ and $^{13}CO_2$. The intensity of the characteristic peaks of all these species was monitored as a function of time with the FT-IR. ^{12}C-containing phosgene was identified in the FT-IR spectra through the characteristic peaks at 1827 cm^{-1} from the ν_1 mode and at 850 cm^{-1} from the ν_4 mode (*25*) while ^{13}C-containing phosgene was shifted toward lower frequencies, at 1777 and 830 cm^{-1} for the respective vibrational modes. ^{12}C-containing carbon dioxide was observed at 2349 cm^{-1} for the ν_2 mode in the FT-IR, while ^{13}C-containing carbon dioxide was present at 2331 cm^{-1}

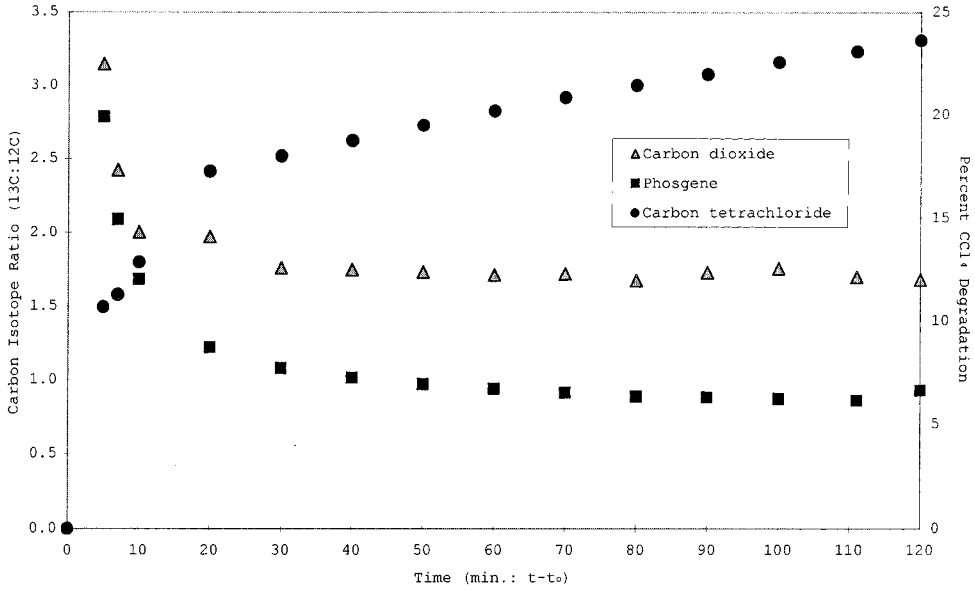

FIGURE 5. Relative ratios of the carbon-containing species as well as the degradation of carbon tetrachloride. The ratio of the production of $^{13}COCl_2$ to $^{12}COCl_2$ versus time is illustrated, showing that the ^{13}C-containing species grow rapidly as compared to the ^{12}C compounds as $^{13}CCl_4$ is degraded.

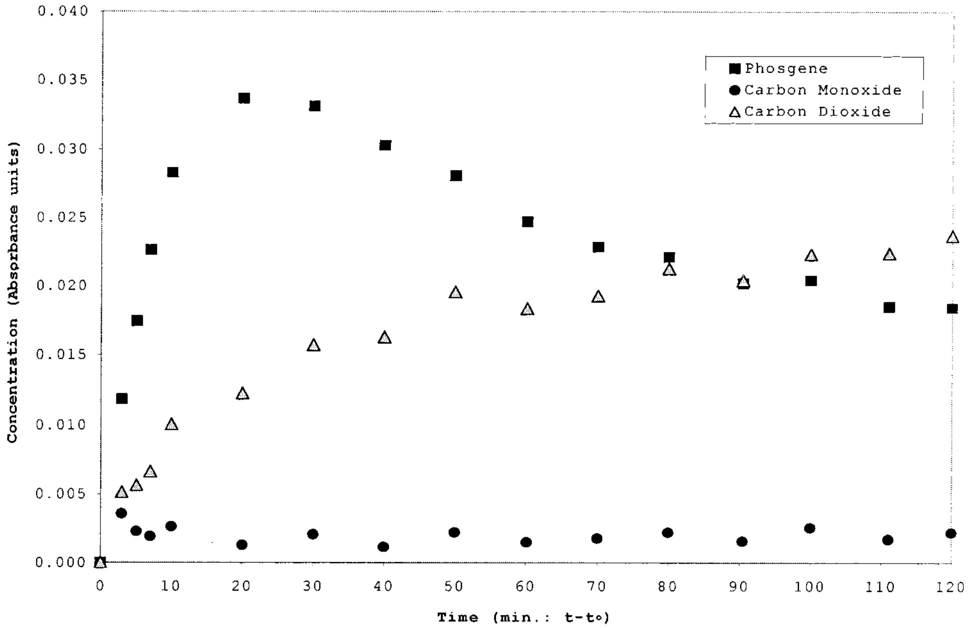

FIGURE 6. Kinetics plot of the species produced when 4.57 Torr of chlorine and 4.78 Torr of oxygen are reacted with laser-ablated carbon for 2 h. Note that the carbon dioxide continues to increase, while phosgene and carbon monoxide rapidly increase and then decay away.

(*23*). The production curves for $^{12}COCl_2$ and $^{13}COCl_2$ as well as $^{12}CO_2$ and $^{13}CO_2$ were not only similar to one another but also similar to the results obtained from the nonisotopically labeled studies. Figure 5 illustrates the relative ratio of $^{13}COCl_2$/$^{12}COCl_2$ production as a function of time when isotopically labeled carbon tetrachloride is degraded.

The ratio of ^{12}C to ^{13}C for both $COCl_2$ and CO_2 indicated that more ^{13}C species were initially created than ^{12}C. The ratio for both compounds was initially very high in ^{13}C content, but as the reaction progressed, this ratio plateaued out around 1. For instance, the ratio for $^{13}COCl_2$:$^{12}COCl_2$ was initially 2.2 after 8 min of irradiation. However, this ratio gradually declined to 1.0 after 2 h of laser irradiation, as shown in Figure 5. The $^{13}CO_2$:$^{12}CO_2$ ratio was similar. This would indicate that the ^{12}C species are growing slower than their ^{13}C counterparts, since $^{13}COCl_2$ and $^{13}CO_2$ are formed from the degradation of the original ^{13}C-containing carbon tetrachloride and $^{12}COCl_2$ and $^{12}CO_2$ are formed from the reaction of atomic carbon with the carbon tetrachloride molecule, as shown in Table 1.

On the basis of the data obtained in this study, which indicate that both phosgene and carbon monoxide are produced and consumed in the reaction process, we postulate a tentative reaction mechanism to account for these phenomena. The mechanism also takes into account the viable reactions of atomic carbon with carbon tetrachloride, oxygen, and phosgene. The proposed reaction processes are listed in Table 1. The major product formed from this mechanism, carbon dioxide, is consistent with all of the available data. Note that in this reaction scheme, the disappearance of both carbon tetrachloride and phosgene appears to be the result of the reaction of $C(^3P)$.

The reactions listed in Table 1 are thermodynamically feasible, based on the constituent species' heats of formation

(*26*). All of the reaction steps are exothermic at room temperature, not just the overall reaction. At room temperature, the exothermicity of the process will drive the reactions. Furthermore, the isotopic labeling studies show indirect evidence for the formation of the C−Cl intermediate species, which is one of the key initiating steps in the proposed reaction process. Since both $^{12}COCl_2$ and $^{13}COCl_2$ were observed in the FT-IR spectra, this leads to the conclusion that ^{12}C reaction took place to create $^{12}C{-}Cl$. This is one way in which $^{12}COCl_2$ could be formed: the $^{13}COCl_2$ originated from the degradation of the $^{13}CCl_4$ fragment. These results are consistent with the laser-induced fluorescence studies, which show the presence of CCl from unlabeled CCl_4.

Product Study of the Reaction of C(^{3}P) Atoms with Cl_2 in the Presence of O_2. One of the interesting observations from our experiments when C(^{3}P) atoms are allowed to react with CCl_4 in the presence of oxygen is the lack of Cl_2 present in the reaction mixture. It is possible that some Cl_2 present in the reaction mixture could be photolyzed with either 351- or 308-nm irradiation. However, to understand the reaction completely, it was necessary to investigate the fate of chlorine in the reaction scheme in the presence of C(^{3}P) atoms. Chlorine was placed in the reaction cell along with oxygen and irradiated graphite. The results from these studies could then be used not only to understand what role the chlorine was playing in the reaction but also to clarify the proposed reaction mechanism.

It was necessary to conduct the study of atomic carbon reacting with chlorine because there have been few reports of the reactions between atomic carbon C(^{3}P) and diatomic species. The reaction of atomic carbon C(^{1}D) with molecular hydrogen and HCl (*21*) attempted to elucidate the mechanism of reaction but did not actually propose a reaction scheme. Although Scott et al. (*21*) did find evidence of the CCl intermediate, which is strong evidence for a carbon insertion reaction, other steps in the reaction chain were not known. The reaction of C(^{3}P) with molecular hydrogen, HCl, and HBr (*13*) also found conclusive evidence of carbon−hydrogen intermediate species, but no product studies of the other halogen intermediates were reported. Assuming that some Cl_2 must be produced from the reaction of C(^{3}P) with carbon tetrachloride and oxygen, we performed a product study for the reaction of C(^{3}P) with chlorine and oxygen in order to determine the fate of any Cl_2 formed in the degradation process of carbon tetrachloride.

The same reaction cell and procedures were used for this study. Control experiments were also performed to determine if any side reactions were occurring between two of the three reactants. The reaction of oxygen with atomic carbon produced only carbon monoxide. All other combinations of two of the three reactants produced no reactions.

When 4.0 Torr of chlorine and 4.0 Torr of oxygen were placed in the cell and the laser was turned on, significant amounts of carbon dioxide and phosgene were formed. The FTIR scans showed only the presence of carbon dioxide, carbon monoxide, and phosgene. Initially, it was observed that carbon monoxide grew and then began to decay away, as is the case for phosgene. At the same time, the carbon dioxide continued to grow. It is interesting, however, that no carbon tetrachloride was formed in this reaction. The on-line GC/MS scan corroborates these data, showing only carbon monoxide, carbon dioxide, phosgene, and unreacted chlorine.

The laser was allowed to ablate the carbon in the reaction chamber for 2 h. The concentrations of all products were monitored over the duration of the study. The concentrations of carbon monoxide, carbon dioxide, and phosgene were subsequently plotted versus time to obtain some insight into the mechanism of the reaction. Figure 6 is a plot of the relative concentrations of these species, illustrating that phosgene initially grows but then begins to decline as it degrades into carbon dioxide. The carbon monoxide initially grows but is also consumed in the reaction. Because of these processes, the carbon dioxide concentration continues to increase. The general trends for carbon monoxide and phosgene are remarkably similar to the trends observed for the degradation of carbon tetrachloride. Therefore, the data obtained in this product study indicate that any Cl_2 produced in the reaction of C(^{3}P) with carbon tetrachloride will most likely be consumed and contribute to the production of both phosgene and carbon dioxide. This also suggests that another pathway to produce $^{12}COCl_2$ is via the reaction of C(^{3}P) atoms with any Cl_2 produced in the reaction mixture.

The data suggest that the carbon atom reacts with carbon tetrachloride, forming a C−Cl intermediate species. The addition of oxygen allows the conversion of the intermediates into carbon dioxide and phosgene as the major products. Carbon monoxide and phosgene are also consumed in the reaction, producing carbon dioxide. From these data, a tentative reaction mechanism has been proposed. Moreover, data from the study of the reaction of C(^{3}P) with CCl_4 in the presence of molecular oxygen suggest that it may be a model system for breaking the C−Cl bond and initiating the oxidation process using laser-generated atomic carbon. Results from this research should pave the way for future research using atomic carbon to degrade CFCs. In addition, these data may help account for the role of atomic carbon in the destruction of CFCs using sodium oxalate (*2*).

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