Electron Beam Atmospheric Pressure Cold Plasma Decomposition of Carbon Tetrachloride and Trichloroethylene

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FIGURE 1. Electron attachment reaction rates, adapted from refs 1 and 6.

The cold plasma decomposition of carbon tetrachloride (CCl_4) and trichloroethylene (C_2HCl_3) at dilute concentrations in dry and wet air of atmospheric pressure was investigated. The cold plasma was generated in a tunable plasma reactor, where the electron concentration is controlled by an electron beam and the average electron energy is controlled by a superimposed sub-breakdown electric field. The energy expense for decomposition, i.e., the electron beam energy per molecule decomposed, as well as the intermediate and final decomposition products were determined. Moreover, likely reaction mechanisms for the decomposition of CCl_4 and C_2HCl_3 are presented. These mechanisms are based on bimolecular dissociative electron attachment for both CCl_4 and C_2HCl_3 and additionally a chlorine chain reaction for C_2HCl_3. The present work provides a reference for the development of an advanced oxidation process on the basis of a tunable plasma reactor. Such a process would be especially suitable for the treatment of air contaminated with chemical compounds that dissociatively attach electrons.

Introduction and Background

The decomposition of chemical compounds by means of a flame, hot plasma, or cold plasma is initiated primarily by rapid gas-phase reactions of radicals, ions, and electrons. These are produced by electronic excitation and ionization rather than by vibrational and rotational excitation. In comparison to a flame or a hot plasma, a cold plasma exhibits a substantially higher ratio of electronic excitation and ionization to vibrational and rotational excitation.

Moreover, in contrast to radicals, ions and electrons frequently react more selectively with chemical compounds.
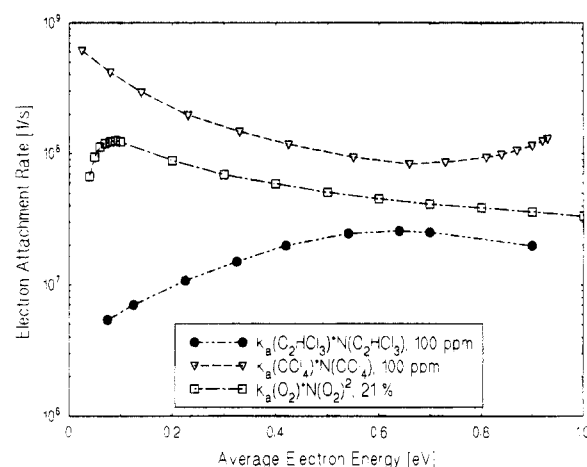
Thus, decomposition by means of a cold plasma, in contrast to a flame or hot plasma, has the potential of being more energy efficient. The energy stored in "useless" vibrational and rotational excitation is reduced, and the energy stored in "useful" electronic excitation and ionization is channeled selectively to the chemical compounds.

The present work explores the utilization of a tunable plasma reactor for the selective decomposition of chlorinated hydrocarbons via dissociative electron attachment. In particular, the energy expense for the decomposition, i.e., the electron beam energy per molecule decomposed, and the decomposition products of CCl_4 and C_2HCl_3 in dry and wet air were the subject of an experimental investigation.

It is well known that high reaction rate constants are exhibited by CCl_4 and C_2HCl_3 for bimolecular dissociative electron attachment (*1–5*) and by O_2 for termolecular nondissociative electron attachment (*6–9*). The electron attachment reaction rates for CCl_4, C_2HCl_3, and O_2 are shown in Figure 1 as a function of the average electron energy. The ideal gas law is assumed at 1.01325×10^5 Pa and 298.15 K. The concentrations of CCl_4, C_2HCl_3, and O_2 are taken to be 100 ppm, 100 ppm, and 21%, respectively, in air.

The concentrations of CCl_4, C_2HCl_3, and O_2 in air are such that the electron attachment reaction rate for O_2 is lower than that for CCl_4 and higher than that for C_2HCl_3. Therefore, O_2 represents a competition for C_2HCl_3 but not for CCl_4 with respect to electron attachment. Hence, it may be expected that a variation of the average electron energy shows a noticeable effect on the decomposition of C_2HCl_3 but not on that of CCl_4.

Experimental Section

Setup. The experimental setup consists of the gas mixing system, the tunable plasma reactor, and the gas analysis system. The gas mixing system comprises several compressed gas cylinders; rotameter volume flowmeters; vapor generators for CCl_4, C_2HCl_3, and H_2O; and 0.25-in. electropolished stainless steel tubing. A wide range of concentrations of CCl_4 or C_2HCl_3 in dry or wet air can be generated by this system.

The tunable plasma reactor comprises the reaction chamber, the electron beam, and the electric field. The

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reaction chamber consists of two parallel titanium plates that are separated by a Pyrex glass frame. One titanium plate has a 1×1 in.^{2} opening for the electron beam. The other titanium plate serves as the electron beam dump and is therefore water-cooled.

The electron beam is generated at an energy of 110 keV with a vacuum of 10^{-6} Torr. The electron beam energy loss is approximately 50 keV upon passage through a 1 mil (25.4 μm) aluminum foil that separates the electron beam vacuum from the reaction chamber atmosphere. The aluminum foil is supported on the vacuum side by a water-cooled copper support grid for mechanical and thermal reasons. The cross section of the electron beam is approximately 1×1 in.^{2}, and the depth of the reaction chamber along the direction of the electron beam is approximately 5/8 in. The electron beam energy loss is approximately 20 keV upon passage through the reaction chamber.

The results of electron beam dosimetry through facsimile paper radiography, Monte-Carlo simulation, and N$_2$O chemical dosimetry indicate a power deposition in the reaction chamber of 6.3 W/1 mA of electron beam current, incorporating an observed electron beam spreading within the vacuum (10). This power deposition corresponds to an electron beam dose of 3.2 Mrad at an air volume flow rate of 10 000 cm^3/min. Note that 1 Mrad = 10 kJ/kg and that a mass heat capacity of air of 1000 J kg^{-1} K^{-1} corresponds to an adiabatic air temperature rise of 10 K. However, since the reaction chamber is water-cooled, i.e., nonadiabatic, this air temperature rise is only partially realized.

The electric field is applied across the two titanium plates, including the aluminum foil visible through the opening of one titanium plate. The electron energy distribution in an electron beam cold plasma is determined by the reduced electric field and elastic and inelastic collision cross sections for low to medium energy electrons (eV) as well as for high energy electrons (keV). At high electron energies, the electron beam serves as a source of fast electrons, while at low electron energies, electron attachment serves as a sink for slow electrons.

Therefore, the electron energy distribution in an electron beam cold plasma may be expected to be somewhat different from that in an electric field breakdown cold plasma. However, an estimate for the average electron energy may be obtained on the basis of the latter type of cold plasma. The average electron energy as a function of the reduced electric field in N$_2$, O$_2$, and air is given, for example, in refs 2, 11, and 12.

Simple curve-fitting to the data provided in these references shows that, for a reduced electric field of 0.1 Td < E/N < 10 Td, the average electron energy is very approximately given as $\epsilon = 1/4(E/N)^{2/3}$, where ϵ is in eV and E/N is in Td. In the present work, the pressure was approximately $p = 1.01325 \times 10^5$ Pa, and the temperature was approximately $T = 300$ K, so that $N \approx 2.5 \times 10^{25}$ m^{-3}. With an electric field limited by breakdown of the electron beam generated plasma to a maximum of $E = 2$ kV/cm, the maximum reduced electric field results as $E/N = 8$ Td, and the maximum average electron energy results as $\epsilon = 1$ eV.

The results of measurements of the electric field current as a function of the electric field voltage and the electron beam current indicate a plasma resistance of approximately 250, 160, and 110 kΩ at an electron beam current of 1, 2, and 3 mA, respectively. This corresponds to a power deposition in the reaction chamber of approximately 4,

6.25, and 9 W, respectively, at an electric field voltage of 1000 V. Therefore, the electric field "dose" is on the order of, and up to a few times higher than, the electron beam dose.

The gas analysis system comprises a gas chromatograph (GC) with electron capture detector (ECD), thermal conductivity detector (TCD), and mass selective detector (MSD) and a customized mass spectrometer (MS) based on the MSD (13). The intake and the exhaust of the tunable plasma reactor can be analzyed.

The calibration of the GC and the MS was accomplished via calibration standards in compressed gas cylinders as obtained from Matheson Gas Products. The calibration standards were CO, CO$_2$, HCl, Cl$_2$, CCl$_4$, and C$_2$HCl$_3$ in air or nitrogen at certified concentrations between 500 and 2500 ppm.

With two exceptions, the calibration standards proved extraordinarily stable. The HCl and Cl$_2$ calibration standards were unstable in that their certified concentrations, as confirmed by Matheson Gas Products, dropped by a factor of up to 2 within a period of up to 3 months (10). Also, due to Environmental, Safety & Health (ES&H) restrictions associated with the use of carbonyl chloride (phosgene, COCl$_2$) and dichloroacetyl chloride (C$_2$HCl$_3$O) and due to the relative instability of COCl$_2$ and C$_2$HCl$_3$O, no calibration standards were obtained for these chemical compounds.

Procedure. For given reactor intake concentrations of CCl$_4$ or C$_2$HCl$_3$ in air and for given air volume flow rates and relative humidities, the reactor exhaust concentrations of CCl$_4$, C$_2$HCl$_3$, CO, CO$_2$, HCl, Cl$_2$, COCl$_2$, and/or C$_2$HCl$_3$O were measured as a function of the electron beam current, i.e., electron beam dose, and the electric field voltage.

The concentrations of CCl$_4$ (CCl$_3$, M/Z = 117 g/mol) were measured by GC/ECD and MS/MSD; those of C$_2$HCl$_3$ (M/Z = 130 g/mol) were measured by MS/MSD only. The concentrations of CO and CO$_2$ were measured by GC/TCD; those of HCl (M/Z = 36 g/mol), Cl$_2$ (M/Z = 70 g/mol), COCl$_2$ (COCl, M/Z = 63 g/mol), and C$_2$HCl$_3$O (CHCl$_2$, M/Z = 83 g/mol) were measured by MS/MSD. For a more detailed description of the MS/MSD measurements, see ref 13.

The calibration standards of CCl$_4$, C$_2$HCl$_3$, CO, and CO$_2$ were stable, and the measured concentrations may be estimated to be accurate within 5% of the true value. The calibration standards of HCl and Cl$_2$ were unstable, and the measured concentrations may be estimated to be accurate within 50% of the true value, even though it was attempted to take into account the drop in the certified concentrations of the calibration standards.

Also, the calibration standards of COCl$_2$ and C$_2$HCl$_3$O were not available, and the concentrations are thus shown as abundances measured by the MS/MSD rather than concentrations. Also, preliminary experiments indicated that chemical compounds other than those named were not present or present only at very low levels. Therefore, the experimental investigations focused on the above chemical compounds.

The concentrations for a given condition were typically measured twice in order to monitor and ensure reproducibility. This is indicated in the subsequent figures through a solid line with symbols for the original measurement and a dashed line without symbols for the repeat measurement. Also, the subsequent figures will show concentrations for dry air only. The differences to wet air are mentioned in
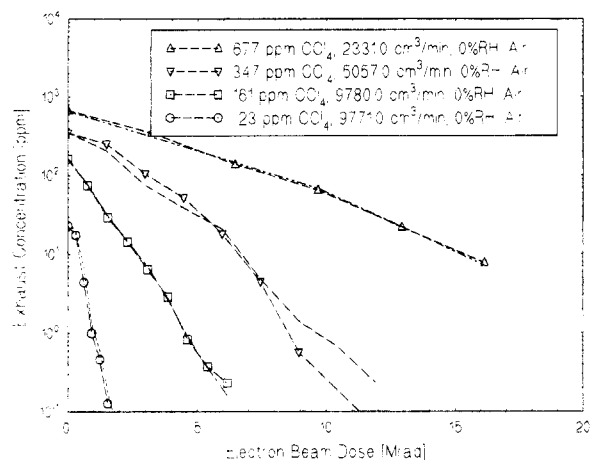
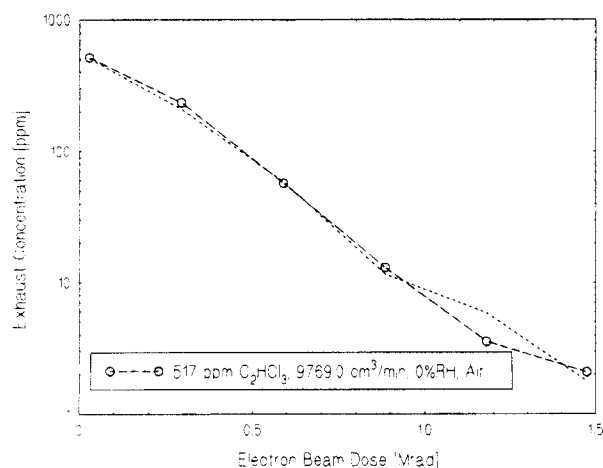**FIGURE 2.** CCl₄ exhaust concentration as function of electron beam dose.

FIGURE 3. C₂HCl₃ exhaust concentration as function of electron beam dose.
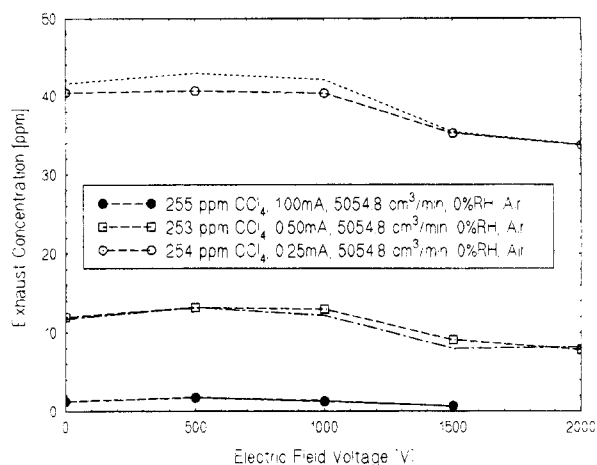

FIGURE 4. CCl₄ exhaust concentration as function of electric field voltage.
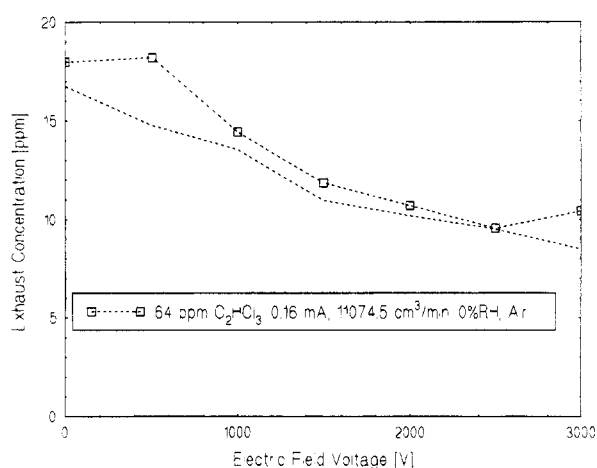
FIGURE 5. C₂HCl₃ exhaust concentration as function of electric field voltage.

TABLE 1
Energy Expense for CCl₄ and C₂HCl₃

intake concn (ppm)	destruction and removal efficiency (%)	energy expense (eV)
23 (CCl₄)	95.72 (95.16)	124.25 (107.58)
161 (CCl₄)	99.49 (99.45)	85.83 (83.45)
347 (CCl₄)	99.84 (99.60)	77.08 (75.78)
677 (CCl₄)	98.86 (98.92)	72.16 (73.75)
517 (C₂HCl₃)	99.60 (99.65)	8.38 (8.52)
490 (C₂HCl₃)	99.85 (99.91)	8.83 (9.20)

subsequent paragraphs and in the description accompanying each figure where applicable.

Results

Electron Beam Dose. Figures 2 and 3 show the exhaust concentrations as a function of different intake concentrations and electron beam doses for the decomposition of CCl₄ and C₂HCl₃, respectively.

The energy expense at the end points of the curves in these figures is given in Table 1. Here, the numbers without parentheses represent the values for the original measurement, and the numbers with parentheses represent the values for the repeat measurement.

For comparable conditions, the energy expense in dry air was found to be more than 10 times lower for C₂HCl₃ than for CCl₄. Moreover, for comparable conditions, the

energy expense for CCl₄ was found to be up to 5 times lower in dry air than in wet air. In contrast, the energy expense for C₂HCl₃ was found to be comparable in dry air and in wet air. The electron beam cold plasma decomposition of C₂HCl₃ in air at similarly low electron beam doses has been observed elsewhere (14). These observations support the argument for propagation of the decomposition by a chlorine chain reaction, which is present for C₂HCl₃ but absent for CCl₄.

Electric Field Voltage. Figures 4 and 5 show the exhaust concentrations as a function of different electron beam doses and electric field voltages for the decomposition of CCl₄ and C₂HCl₃, respectively. The expected lack of effect of the electric field on the CCl₄ exhaust concentration and the expected effect of the electric field on the C₂HCl₃ exhaust concentration are observed experimentally. In fact, the dependence of the exhaust concentration on the electric field is consistent with the dependence of the bimolecular dissociative electron attachment reaction rate on the average electron energy. These observations support the argument for initiation of the decomposition by bimolecular dissociative electron attachment, which is present for both C₂HCl₃ and CCl₄.

Decomposition Products. Figure 6 shows the CO, CO₂, and N₂O exhaust concentrations as a function of different electron beam doses for the decomposition of CCl₄.

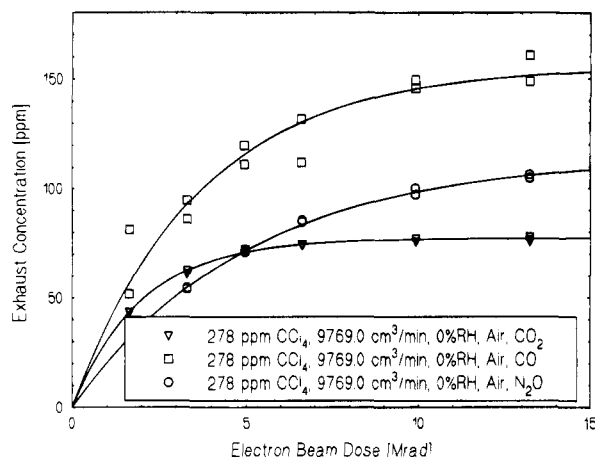At a sufficiently high electron beam dose, CO and CO₂ account for more than 95% of the carbon balance and,

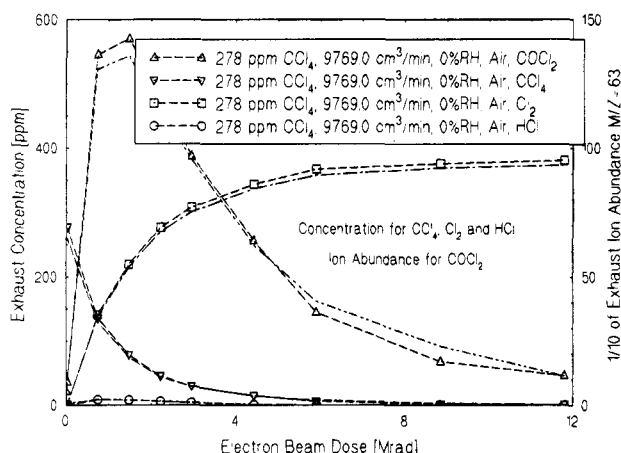**FIGURE 6.** CO, CO_2, and N_2O exhaust concentration as function of electron beam dose.

FIGURE 7. HCl, Cl_2, and $COCl_2$ exhaust concentration as function of electron beam dose.

FIGURE 8. HCl, Cl_2, $COCl_2$, and C_2HCl_3O exhaust concentration as function of electron beam dose.

therefore, indicate a near-complete conversion of the CCl_4 to CO and CO_2. This observation was made for dry as well as wet air.

Figure 7 shows the HCl, Cl_2, and $COCl_2$ exhaust concentrations and abundances, respectively, as a function of different electron beam doses for the decomposition of CCl_4. Although the Cl_2 concentration is only accurate within 50%, the leveling off of the Cl_2 exhaust concentration and the disappearance of the $COCl_2$ abundance at a sufficiently high electron beam does support a near-complete conversion of the CCl_4 to Cl_2.

Figure 8 shows the HCl, Cl_2, $COCl_2$, and C_2HCl_3O exhaust concentrations and abundances, respectively, as a function of different electron beam doses for the decomposition of C_2HCl_3. Although the $COCl_2$ and C_2HCl_3O concentrations were only measured as abundances, both appear to be correlated in that they have similar shapes. This could indicate a conversion of C_2HCl_3O into $COCl_2$.

Supported by Figures 6 and 7, the dominant intermediate decomposition product of CCl_4 was found to be $COCl_2$. Also, the dominant final decomposition products of CCl_4 were found to be CO, CO_2, and Cl_2 in dry air and additionally HCl in wet air.

Supported by Figure 8, the dominant intermediate decomposition products of C_2HCl_3 were found to be C_2-HCl_3O and $COCl_2$, where the latter results from decom-

position of the former. The dominant final decomposition products of C_2HCl_3 were found to be Cl_2 and HCl, where the ratio of Cl_2 to HCl was higher in dry air than in wet air. The final decomposition products CO and CO_2 are anticipated but were not analyzed for.
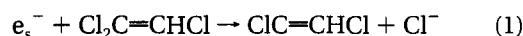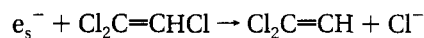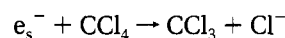
For the CCl_4 decomposition, $COCl_2$ was found to disappear at a comparable electron beam dose to that at which CCl_4 was found to disappear. For the C_2HCl_3 decomposition, C_2HCl_3O and $COCl_2$ were found to disappear only at a much higher electron beam dose than that at which C_2HCl_3 was found to disappear. Although wet air contains a sufficient concentration of H_2O to enable the complete conversion of Cl_2 to HCl, this was not observed for CCl_4 or C_2HCl_3 in wet air.

Discussion

The reaction mechanisms for the decomposition of CCl_4 and C_2HCl_3 in dry air are presented here. They are based on a literature review and are in qualitative agreement with the experimental observations.

For both CCl_4 and C_2HCl_3, the reaction mechanism is consistent with the experimentally observed formation of carbonyl chloride ($COCl_2$) and/or dichloroacetyl chloride (C_2HCl_3O) as intermediate decomposition products and CO, CO_2, HCl, and Cl_2 as final decomposition products.
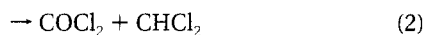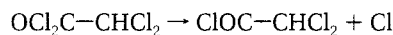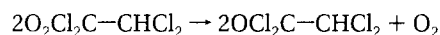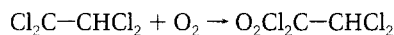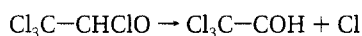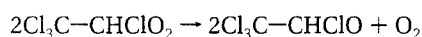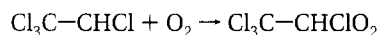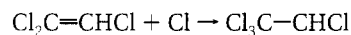
Bimolecular Dissociative Electron Attachment. The decomposition of both CCl_4 and C_2HCl_3 is initiated via bimolecular dissociative electron attachment as described in refs 1, 2, 5, 15, and 16. However, since C_2HCl_3 contains two carbon atoms and a carbon double bond, it shall be necessary to indicate the location of this double bond through a "$=$" sign. Thus, for example, C_2HCl_3 is represented as $Cl_2C=CHCl$:

$$e_s^- + CCl_4 \rightarrow CCl_3 + Cl^-$$

$$e_s^- + Cl_2C=CHCl \rightarrow Cl_2C=CH + Cl^-$$

$$e_s^- + Cl_2C=CHCl \rightarrow ClC=CHCl + Cl^- \qquad (1)$$

While the decomposition of CCl_4 is propagated in this way also, that of C_2HCl_3 is propagated via a chlorine chain reaction. It is currently not known whether $Cl_2C=CH$ or $ClC=CHCl$ is the main product of the electron attachment reaction and how the decomposition of $Cl_2C=CH$ and
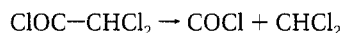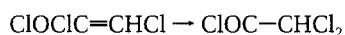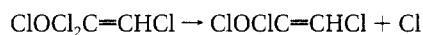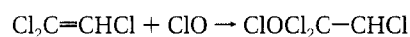
ClC=CHCl is effected. However, this reaction is significant only for the decomposition of a minor fraction of C_2HCl_3 in which it releases Cl. These are then multiplied in the Cl chain reaction, which effects the decomposition of the major fraction of C_2HCl_3.

Chlorine Chain Reaction. The Cl chain reaction becomes possible through the carbon double bond and involves the chemical compounds dichloroacetyl chloride, represented as $ClOC-CHCl_2$ and trichloroacetaldehyde, represented as Cl_3C-COH. According to ref 17, radical attack on C_2HCl_3 through Cl can occur at the more heavily chlorinated carbon atom or the less heavily chlorinated carbon atom:

$$Cl_2C=CHCl + Cl \rightarrow Cl_3C-CHCl$$

$$Cl_3C-CHCl + O_2 \rightarrow Cl_3C-CHClO_2$$

$$2Cl_3C-CHClO_2 \rightarrow 2Cl_3C-CHClO + O_2$$

$$Cl_3C-CHClO \rightarrow Cl_3C-COH + Cl$$

$$\rightarrow CCl_3 + COHCl$$

$$Cl_2C=CHCl + Cl \rightarrow Cl_2C-CHCl_2$$

$$Cl_2C-CHCl_2 + O_2 \rightarrow O_2Cl_2C-CHCl_2$$

$$2O_2Cl_2C-CHCl_2 \rightarrow 2OCl_2C-CHCl_2 + O_2$$

$$OCl_2C-CHCl_2 \rightarrow ClOC-CHCl_2 + Cl$$

$$\rightarrow COCl_2 + CHCl_2 \qquad (2)$$
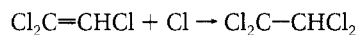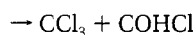
Since $ClOC-CHCl_2$ rather than Cl_3C-COH is observed as the intermediate decomposition product, attack on the less heavily chlorinated carbon atom is assumed to be dominant.

The decomposition of C_2HCl_3 via radical attack on the carbon double bond through Cl may be enhanced by additional radical attack through ClO (*18*). This chlorine oxide is expected to form as part of the chlorine–oxygen cycle, which is well known from atmospheric chemistry and which is described, for example, in refs 19–21:
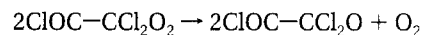
$$Cl_2C=CHCl + ClO \rightarrow ClOCl_2C-CHCl$$

$$ClOCl_2C=CHCl \rightarrow ClOClC=CHCl + Cl$$

$$ClOClC=CHCl \rightarrow ClOC-CHCl_2$$

$$ClOC-CHCl_2 \rightarrow COCl + CHCl_2$$
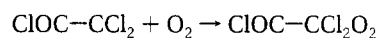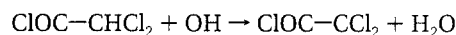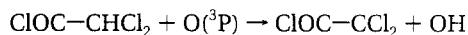
$$\rightarrow CO + CHCl_3 \qquad (3)$$

The chloroform ($CHCl_3$) formed in this reaction mechanism is also subject to decomposition by bimolecular dissociative electron attachment as described in refs 1, 2, 5, and 15.

In all reaction mechanisms, the Cl is recovered and thus continues to effect the decomposition of C_2HCl_3. However, the intermediate decomposition products in these reaction mechanisms are subject to further decomposition, which, as shown subsequently, releases additional Cl. Therefore a multiplication of Cl is achieved that is thought to give rise to the substantially complete decomposition of C_2HCl_3 at a low electron beam dose.
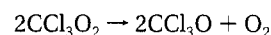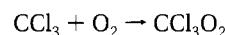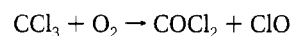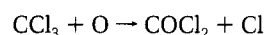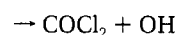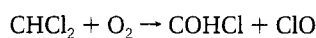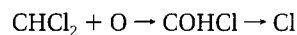
Dichloroacetyl Chloride Decomposition. Although the $O(^3P)$ and OH radicals are insignificant with respect to the decomposition of C_2HCl_3, they nevertheless are thought to be important to the decomposition of $ClOC-CHCl_2$ ac-

cording to refs 17 and 22:

$$ClOC-CHCl_2 + O(^3P) \rightarrow ClOC-CCl_2 + OH$$

$$ClOC-CHCl_2 + OH \rightarrow ClOC-CCl_2 + H_2O$$

$$ClOC-CCl_2 + O_2 \rightarrow ClOC-CCl_2O_2$$

$$2ClOC-CCl_2O_2 \rightarrow 2ClOC-CCl_2O + O_2$$

$$ClOC-CCl_2O \rightarrow COCl + COCl_2 \qquad (4)$$

The importance of OH and $O(^3P)$ in this reaction mechanism is supported by the rather high electron beam dose required for significant decomposition of $ClOC-CHCl_2$, i.e., a chain reaction is very likely not involved.
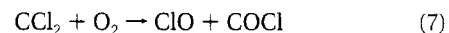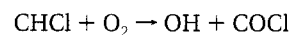
Radical Decomposition. In the presence of O_2, the radicals trichloromethyl (CCl_3) and dichloromethyl ($CHCl_2$) decompose to carbonyl chloride (phosgene, $COCl_2$) and formyl chloride (COHCl) (*17*):

$$CHCl_2 + O \rightarrow COHCl \rightarrow Cl$$

$$CHCl_2 + O_2 \rightarrow COHCl + ClO$$

$$\rightarrow COCl_2 + OH$$

$$CCl_3 + O \rightarrow COCl_2 + Cl$$

$$CCl_3 + O_2 \rightarrow COCl_2 + ClO$$

$$CCl_3 + O_2 \rightarrow CCl_3O_2$$

$$2CCl_3O_2 \rightarrow 2CCl_3O + O_2$$

$$CCl_3O \rightarrow COCl_2 + Cl \qquad (5)$$

Moreover, in the presence of Cl_2, the radicals CCl_3 and $CHCl_2$ may initiate the following reverse chemical reactions, which would increase the electron beam dose required for the decomposition of CCl_4 and $CHCl_3$:

$$CCl_3 + Cl_2 \rightarrow CCl_4 + Cl$$

$$CHCl_2 + Cl_2 \rightarrow CHCl_3 + Cl \qquad (6)$$
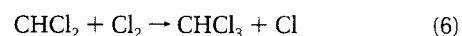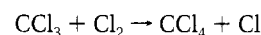
In the presence of O_2, the radicals dichloromethylene (CCl_2) and chloromethylene (CHCl) decompose to COCl (*17*):

$$CHCl + O_2 \rightarrow OH + COCl$$

$$CCl_2 + O_2 \rightarrow ClO + COCl \qquad (7)$$

In the presence of Cl_2, the chemical compounds carbonyl chloride (phosgene, $COCl_2$) and formyl chloride (COHCl) decompose to COCl (*17*):

$$COHCl + Cl \rightarrow COCl + HCl$$

$$COCl_2 + Cl \rightarrow COCl + Cl_2$$

$$COCl_2 + e_s^- \rightarrow COCl + Cl^-$$
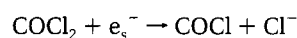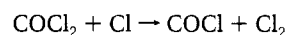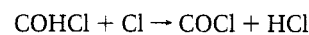
$$\rightarrow CO + Cl_2^- \qquad (8)$$

Note that just the same as CCl_4, $CHCl_3$, and C_2HCl_3, $COCl_2$ is subject to decomposition by bimolecular dissociative electron attachment, described as well in ref 5. Moreover, both COHCl and $COCl_2$ are expected to dissociate upon dissolution in (liquid) water.

Finally, in the presence of O_2 and Cl_2, the chemical compound $COCl$ decomposes to CO and Cl (17):

$$COCl \rightarrow CO + Cl$$

$$COCl + O \rightarrow CO_2 + Cl$$

$$\rightarrow CO + ClO$$

$$COCl + O_2 \rightarrow CO_2 + ClO$$

$$COCl + Cl \rightarrow CO + Cl_2 \qquad (9)$$
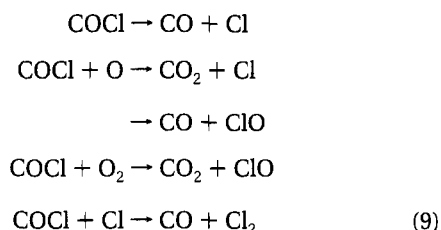
Effect of Water on Decomposition. While the above reaction mechanisms reflect a fairly complete understanding of the decomposition of CCl_4 and C_2HCl_3 in dry air, the understanding of such decomposition in wet air is much less complete. However, the following considerations offer possible explanations for the strong effect of H_2O on the decomposition of CCl_4 and the negligible effect on the decomposition of C_2HCl_3. These considerations are consistent with the assumption of bimolecular dissociative electron attachment and a Cl chain reaction, respectively.

In contrast to CCl_4, $CHCl_3$, C_2HCl_3, O_2, and $COCl_2$, electron attachment to H_2O is negligible. However, it is well known that H_2O forms positive and negative cluster ions. Of particular interest in this context are the cluster ions with negative oxygen ions, e.g., $O_2^-H_2O$. These ions may be more stable than the negative oxygen ions themselves, which may result in a decreased electron concentration, and thus a decreased CCl_4 decomposition, via two mechanisms.

First, the electron concentration in wet air decreases compared to that in dry air since the negative charge is not exclusively carried by electrons and negative oxygen ions anymore, but additionally by negative cluster ions. Second, if the negative charge concentration increases through such negative cluster ions, the positive charge concentration increases as well, which means that the electron concentration decreases even further due to increased electron to positive ion recombination.

Moreover, CCl_4 may not only decompose through bimolecular dissociative electron attachment but also through ion molecule reaction with negative oxygen ions. The formation of negative cluster ions between negative oxygen ions and H_2O results in a decreased negative oxygen ion concentration and thus a decreased CCl_4 decomposition.

Finally, in the presence of H_2O, the N_2 contained in air forms nitric acid (HNO_3) under electron beam irradiation. It is well known that HNO_3 has a large reaction rate constant for bimolecular dissociative electron attachment (23). Therefore, even small concentrations of N_2 in the presence of H_2O could result in strong competition for electrons between CCl_4 and HNO_3. The CCl_4 decomposition would then decrease correspondingly.

The H_2O in wet air may cause a decreased decomposition of C_2HCl_3 via two mechanisms. First, as assumed for the decomposition of CCl_4, the H_2O may result in a decreased electron concentration. Second, the fragmentation products of H_2O may scavenge Cl and thus result in a decreased Cl concentration. Additionally, the fragmentation products of H_2O may also cause an increased decomposition of C_2HCl_3, so that this latter effect would counteract the two former effects.

With respect to a decreased electron concentration, the decomposition of C_2HCl_3 is a function of the electron attachment reaction rate, which is the product of the electron attachment reaction rate constant and the electron concentration. The electron attachment reaction rate constant increases by approximately 1 order of magnitude from an average electron energy of 0.025 eV to an average electron energy of 0.8 eV. Assuming that in dry air the electron concentration is controlled by O_2 rather than by C_2HCl_3, this concentration remains constant with a variation of the electron attachment reaction rate constant. Therefore, the electron attachment reaction rate increases by an order of magnitude as well. This results in a decrease of the C_2HCl_3 exhaust concentration by a factor of not quite 2. Obviously, the response to the variation of the electron attachment reaction rate is nonlinear and also quite flat.

Assuming that, in the absence of an electric field, the electron concentration in wet air decreases by not more than a factor of 2 compared to that in dry air, the electron attachment reaction rate also decreases by a factor of 2. Because of the above nonlinear and quite flat response, the C_2HCl_3 exhaust concentration may then increase by a factor that is within the error margin of the measurement of this concentration, and therefore an effect of H_2O is not experimentally observed.

With respect to a decreased Cl concentration, the H_2O is subject to fragmentation in the tunable plasma reactor. Cl may react with the fragmentation products, e.g., H, H_2, OH, or HO_2. It therefore may be lost from the Cl chain reaction. However, such loss may be considered insignificant if the reaction rate constants for reaction of Cl with fragmentation products are much lower than that for reaction of Cl with C_2HCl_3. In this case, H_2O would become effective only after the decomposition of C_2HCl_3 is virtually complete. Also, the reaction rate constants for reaction of fragmentation products with other chemical compounds may be much higher than that for reaction of fragmentation products with Cl, leaving the Cl concentration virtually unaffected.

Engineering Consequences

Optimization of the decomposition of CCl_4 with respect to the electron beam dose appears to be independent of the electric field but very strongly dependent on the relative humidity. In order to minimize the electron beam dose, the air containing CCl_4 requires dehumidification.

Optimization of the decomposition of C_2HCl_3 with respect to the electron beam dose appears to be independent of the relative humidity but slightly dependent on the electric field. In order to minimize the (more expensive) electron beam dose, application of an (less expensive) electric field may be considered.

The $COCl_2$ readily reacts with H_2O to form CO and HCl, while the C_2HCl_3O readily reacts with sodium hydroxide (NaOH) in H_2O to form sodium dichloroacetate ($C_2HCl_2O_2$-Na) (24). Cl_2 and HCl readily react with NaOH in H_2O to form NaCl. In contrast to CCl_4 and C_2HCl_3, the decomposition products CO, CO_2, Cl_2, HCl, NaCl, and $C_2HCl_2O_2$-Na are considered less hazardous or nonhazardous. Consequently, $COCl_2$ and C_2HCl_3O may not require complete decomposition in the tunable plasma reactor when a "scrubber" system is installed in the exhaust of the reactor. In particular, the more than 10-fold electron beam dose advantage of C_2HCl_3 decomposition over CCl_4 decomposition may be fully utilized for this reason.

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