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Decomposition of 1,1-Dichloroethane and 1,1-Dichloroethene in an electron beam generated plasma reactor

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An electron beam generated plasma reactor is used to decompose low concentrations (100–3000 ppm) of 1,1-dichloroethane and 1,1-dichloroethene in atmospheric pressure air streams. The energy requirements for 90% and 99% decomposition of each compound are reported as a function of inlet concentration. Dichloroethene decomposition is enhanced by a chlorine radical propagated chain reaction. The chain length of the dichloroethene reaction is estimated to increase with dichloroethene concentration from 10 at 100 ppm initial dichloroethene concentration to 30 at 3000 ppm. Both the dichloroethane and dichloroethene reactions seem to be inhibited by electron scavenging decomposition products. A simple analytic expression is proposed for fitting decomposition data where inhibition effects are important and simple first order kinetics are not observed. © *1997 American Institute of Physics.* [S0021-8979(97)04506-4]

INTRODUCTION

The use of plasma reactors to decompose dilute concentrations of volatile organic compounds (VOCs) in waste streams is an emerging technology. However, it has become evident that there is a lack of understanding of the fundamental processes which occur inside plasma reactors. To add to the understanding of plasma induced decomposition of VOCs, the authors are conducting a study of chlorinated compound decomposition in an electron beam generated plasma reactor. The aim of this study is to examine the energy requirements for decomposition of these compounds, as well as to propose simple descriptions of the decomposition pathways and kinetics.

An electron beam generated plasma reactor is very efficient at creating a nonequilibrium plasma in the reaction chamber. Electron beam reactors are well suited to studies of VOC reactions, since the energy deposited in the plasma is easily controlled by the electron beam current and the gas flow rates. It is the most energy efficient, high throughput atmospheric pressure plasma reactor for decomposing low concentrations (100–3000 ppm) of chlorinated VOCs. This is because the energy from the beam is directed preferentially toward the VOC molecules, due to their low ionization potential and high electron capture cross sections.[1–4] Energy is not wasted in heating the carrier gas molecules. The final decomposition products from plasma treatment of these chemicals, such as CO_2, HCl, CO, and $COCl_2$, are easily treated in an aqueous sodium hydroxide scrubber to yield environmentally benign end products.

The present article reports on the decomposition of two compounds in an electron beam reactor: 1,1-dichloroethane (DCA) and 1,1-dichloroethene (DCE). Previously, Borger[5] modeled decomposition of dichloroethane in a plasmatron, and Schultz[6] studied the reaction of dichloroethane with hydrogen in an rf plasma. To the authors' knowledge, there has been no study of dichloroethene decomposition in a plasma reactor. These two compounds are very similar in most of their physical properties, though dichloroethene has a carbon–carbon double bond, whereas dichloroethane does not. Both compounds are susceptible to radical abstraction and substitution reactions, but only dichloroethene is susceptible to radical addition to the double bond. It is shown here that this radical addition mechanism enhances the rate of dichloroethene decomposition by a chain reaction mechanism not available to dichloroethane. As a result, dichloroethene requires much less energy for decomposition than dichloroethane.

EXPERIMENT

The electron beam generated plasma reactor has been described in detail previously,[3,4] though the present study was conducted using a modified reaction chamber. The gas enters the reactor at atmospheric pressure and ambient temperature. The gas flow rate to the reactor was varied from 1 to 5 standard liters per minute. Inlet streams to the reactor were from two calibrated gas cylinders from BOC gases: 5019 ppm dichloroethene in air and 4912 ppm dichloroethane in air. The gas from the calibrated cylinders was mixed with a high purity air stream to achieve the desired dichloroethane or dichloroethene inlet concentration. The inlet concentration to the reactor was varied from 100 to 3000 ppm on a mol/mol basis. No water was added to the gas streams, so the gas is considered to be essentially dry. The flow rates of the streams were measured by digital mass flow meters, which have a stated accuracy of 2%.

The exhaust gas from the reactor was analyzed using a Hewlett Packard 5890 gas chromatograph and a HP-5971-A mass spectrometer. The mass spectrometer was calibrated using the certified calibration cylinders. The mass spectrometer was recalibrated every few days to ensure that there was no change in the system. Based on the reproducibility of the results, the error in the measurement of dichloroethane or dichloroethene concentration is estimated to be ±10%.

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The electron beam generated plasma reactor itself consists of a triode arrangement. The electrons are generated in a vacuum chamber by thermionic emission from a directly heated tungsten filament. The electrons pass through a control grid, which may be biased up to -100 V with respect to the filament. The bias on the grid allows control over how many electrons pass through the grid, thus allowing control of the beam current. The electrons are then accelerated by an applied voltage of 100 kV from the control grid, through a 25-μm-thick aluminum foil window, into the reaction chamber through which the VOC contaminated air stream flows at atmospheric pressure. The reaction chamber is an alumina cylinder, 44 mm inside diameter and 100 mm long. The electrons enter the front of the cylinder, and the VOC contaminated gas enters from the rear. The contaminated gas thus flows countercurrent to the electron beam. The gas exists through a small hole in the reaction chamber near the source of the electron beam. Each electron enters the reaction chamber with approximately 50 keV of energy, of which approximately 19 keV is deposited into the air stream before being dumped onto a titanium plate opposite the electron beam window.[7] Electron beam dosimetry calculations were performed using a Monte Carlo electron code from the ITS series.[8] The maximum electron beam power to the plasma is approximately 30 W. The fast electrons from the beam ionize and dissociate the nitrogen and oxygen molecules in the carrier gas, creating many secondary electrons. The electrons slow down quickly by collisions with the VOC and carrier gas molecules. Slow electrons are then thought to initiate the decomposition of the VOC molecules through dissociative electron attachment.

FIG. 1. Concentration of (a) 1,1-dichloroethane and (b) 1,1-dichloroethene vs electron beam dose to the plasma for decomposition in an electron beam generated plasma reactor. Continuous curves are best fits of the data to Eq. (30). Note that 1 Mrad$=10^4$ J/kg.
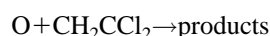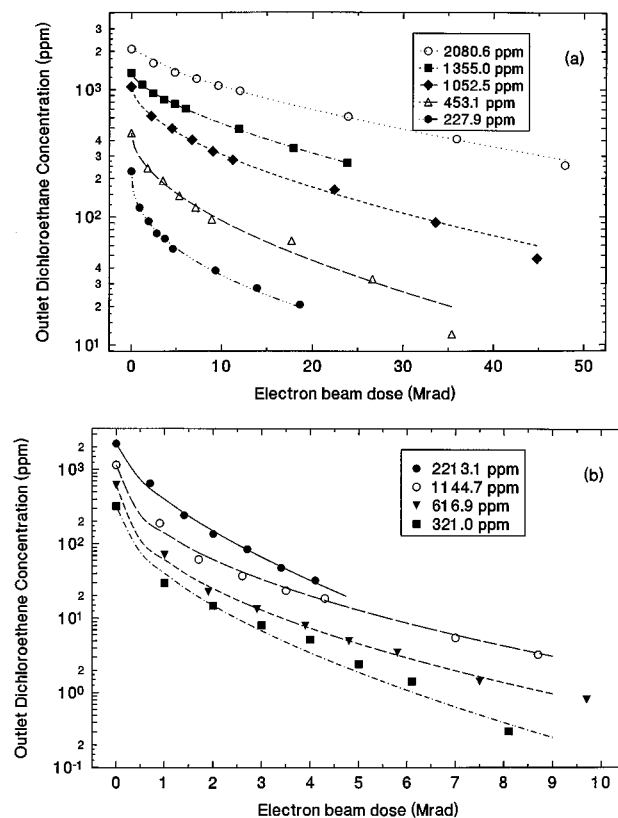
PATHWAYS OF DICHLOROETHANE AND DICHLOROETHENE DECOMPOSITION

Graphs of dichloroethane and dichloroethene outlet stream concentration as a function of electron beam dose are given in Figs. 1(a) and 1(b), respectively. It is evident from these graphs that dichloroethane requires a much higher electron beam dose to the plasma to achieve the same fractional decomposition as dichloroethene. The difference in the energy required for decomposition arises from the difference in decomposition pathways of the ethene and the ethane.

The decomposition of dichloroethene may be initiated by either electrons or oxygen radicals formed in the plasma (all rate constants for neutral species reactions are evaluated at 298 K, and electron-molecule reaction rate constants are given in ranges for electrons from 0.1 to 1.0 eV),

$$e + CH_2CCl_2 \rightarrow CH_2CCl + Cl^-$$
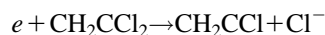
$$k = 1 \times 10^{-10} - 1 \times 10^{-9} \quad cm^3/s \quad (Ref.\ 9) \tag{1}$$

$$O + CH_2CCl_2 \rightarrow products$$

$$k = 9.8 \times 10^{-13} \quad cm^3/s \quad (Ref.\ 10). \tag{2}$$

The electron and oxygen radical concentrations in the plasma were not measured. However, Koch has shown[11] that in an attachment controlled cold plasma, such as the one in this study, the oxygen radical concentration is approximately 100 times higher than the electron concentration. An attach-

ment controlled plasma is one in which the attachment rate of electron to neutral species is faster than the recombination rate with ions. The authors have calculated the approximate concentrations of reactive species in the plasma based on steady state generation and loss balances.[12] For a typical electron beam power to the plasma of 30 W, the electron concentration was calculated to be approximately 8×10^9 cm^{-3} and the oxygen radical concentration to be approximately 1×10^{12} cm^{-3}. Thus the calculated rates of reactions (1) and (2) are of the same order of magnitude, and both reaction pathways are considered below.

If the decomposition is initiated by dissociative electron attachment to dichloroethene, a chlorine ion and a chloroethyl radical will be formed. Upon collision with other species in the gas, the radical will most likely lose a chlorine atom to form a carbene radical. The carbene radical will either polymerize with other carbene radicals, or oxidize in the air to form carbon monoxide and water. The chloride ion produced in reaction (1) will most likely neutralize through charge exchange or through positive-negative ion recombination.[13,14] The neutral chlorine radical can proceed to attack another dichloroethene molecule. The fastest reaction for a chlorine radical with dichloroethene is addition to the double bond,

$$Cl + CH_2CCl_2 \rightarrow CH_2ClCCl_2$$
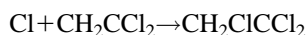
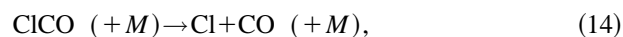$$k = 5 \times 10^{-11} - 1.3 \times 10^{-10} \text{ cm}^3/\text{s (Refs. 15–17).} \quad (3)$$

Here the radical adds to the less substituted carbon, since it is more sterically favorable. This species may decompose by reaction with oxygen molecules in the carrier gas, following a mechanism outlined by Sanhueza:[18]

$$CH_2ClCCl_2 + O_2 \rightarrow CH_2ClCCl_2OO \quad (4)$$

$$2CH_2ClCCl_2OO \rightarrow 2CH_2ClCCl_2O + O_2 \quad (5)$$

$$CClH_2CCl_2O \ (+M) \rightarrow CClH_2CClO + Cl \ (+M) \quad (6a)$$

$$CH_2ClCCl_2O \ (+M) \rightarrow COCl_2 + CH_2Cl \ (+M), \quad (6b)$$

where M is a molecule in the gas that provides the energy for the unimolecular decomposition through collisions. The reactions (6a) and (6b) produce chloroacetyl chloride and phosgene, respectively. Since hydrogen chloride and phosgene account for much more of the observed products than chloroacetyl chloride, the authors propose that the chloroacetyl chloride decomposes rapidly by reacting with chlorine radicals to form carbon monoxide, hydrogen chloride, and more phosgene,

$$COClCH_2Cl + Cl \rightarrow COClCHCl + HCl \quad (7)$$

$$COClCHCl + O_2 \rightarrow COClCHClOO \quad (8)$$

$$2COClCHClOO \rightarrow 2COClCHClO + O_2 \quad (9)$$

$$COClCHClO \ (+M) \rightarrow CHO + COCl_2 \ (+M) \quad (10)$$

$$CHO + O_2 \rightarrow CO + HO_2. \quad (11)$$

The abundance of oxygen radicals in the plasma leads one to consider a mechanism of dichloroethene decomposition based on $O(^3P)$ sensitized oxidation. Sanhueza[18] examined this reaction, and determined that the following two pathways are the most important:

$$O(^3P) + CCl_2CH_2 \rightarrow CO + HCl + CHCl \quad (12a)$$

$$O(^3P) + CCl_2CH_2 \rightarrow CCl_2CH_2O^* \quad (12b)$$

$$CHCl + O_2 \rightarrow HO + ClCO \quad (13)$$

$$ClCO \ (+M) \rightarrow Cl + CO \ (+M), \quad (14)$$

where the asterix indicates an excited species. The product of reaction (12b) leads to polymer. Although solid polymer was not actually observed in the reactor, if it was formed, it is likely to have been swept out of the continuously flowing system without being detected. Reaction (14) produces a free chlorine radical, which may then react with a dichloroethene molecule by reaction (3). This will produce more chlorine radicals, and thus a chain reaction takes place. Neither chloroacetyl chloride nor phosgene are produced directly by $O(^3P)$ sensitized oxidation. Thus, in order to account for the formation of these products, a chlorine radical reaction with dichloroethene must take place. However, both the dissociative electron attachment and the $O(^3P)$ sensitized oxidation mechanisms produce chlorine radicals, and it cannot be determined from this study whether the initation step is dissociative electron attachment as was assumed in the first mechanism, or through the $O(^3P)$ sensitized oxidation mechanism.

For dichloroethene decomposition, dissociative electron attachment is the predominant reaction pathway, since the rate constant for oxygen radical reaction is 10^5 times smaller,

$$e + CH_3CHCl_2 \rightarrow CH_3CHCl + Cl^-$$
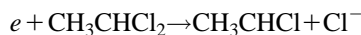
$$k = 2 \times 10^{-11} - 1 \times 10^{-9} \text{ cm}^3/\text{s (Ref. 19)} \quad (15)$$
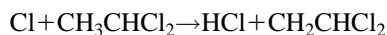
$$O + CH_3CHCl_2 \rightarrow \text{products}$$

$$k = 1.3 \times 10^{-15} \text{ cm}^3/\text{s (Ref. 20).} \quad (16)$$

The only observed products of dichloroethene decomposition were hydrogen chloride, carbon monoxide, and small amounts of vinyl chloride. Other studies of dichloroethane decomposition reactions have also found HCl, CO, and vinyl chloride as the major reaction products.[21,22] The vinyl chloride is formed from dichloroethane through dehydrochlorination, which is similar to a commercial high temperature process in which dichloroethane is converted to vinyl chloride monomer.[23] In the present work, the reaction is initiated by dissociative electron attachment rather than thermal processes. It is then possible for the chlorine radical produced to abstract a hydrogen atom from the resultant radical, the net result being dehydrochlorination:

$$Cl + CH_3CHCl \rightarrow CH_2CHCl + HCl. \quad (17)$$
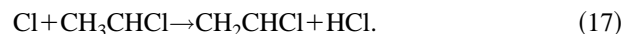
Alternatively, the chlorine radical produced in reaction (15) may abstract a hydrogen atom from another dichloroethane molecule rather than a radical,

$$Cl + CH_3CHCl_2 \rightarrow HCl + CH_2CHCl_2$$

$$k = 1.2 \times 10^{-12} \text{ cm}^3/\text{s (Ref. 24)} \quad (18)$$

$$CH_2CHCl_2 + M \rightarrow Cl + CH_2CHCl + M \quad (19)$$

and the product is again vinyl chloride. The vinyl chloride produced by either of these mechanisms will decompose in the plasma by reaction with electrons and oxygen atoms or molecules in the plasma, to form carbon monoxide and HCl. The details of vinyl chloride decomposition in the electron beam generated plasma reactor have been given by the authors in another article.[25]

COMPARISON OF THE DECOMPOSITION PATHWAYS

The concentration of electrons and oxygen radicals is not affected by the presence of low concentrations of dichloroethane or dichloroethene, so the difference in reactivity observed between the two compounds must be due to the difference in reaction kinetics. Dichloroethene decomposes using much less energy than dichloroethane, thus either (1) the rate of electron attachment to dichloroethene is much faster, (2) the oxygen radical reaction pathway available to dichloroethene is much faster than the electron attachment reaction to dichloroethane, or (3) more than one dichloroethene molecule is decomposed per electron attachment reaction. Comparing the reaction rates of reactions (1–3) show that possibilities (1) and (2) are unlikely. A chlorine radical propagated chain reaction for dichloroethene decomposition

FIG. 3. Apparent chain length of the chlorine radical propagated dichloro-ethene decomposition mechanism, determined by taking the ratio of the energy requirements for dichloroethane and dichloroethene decomposition in Fig. 2(a).
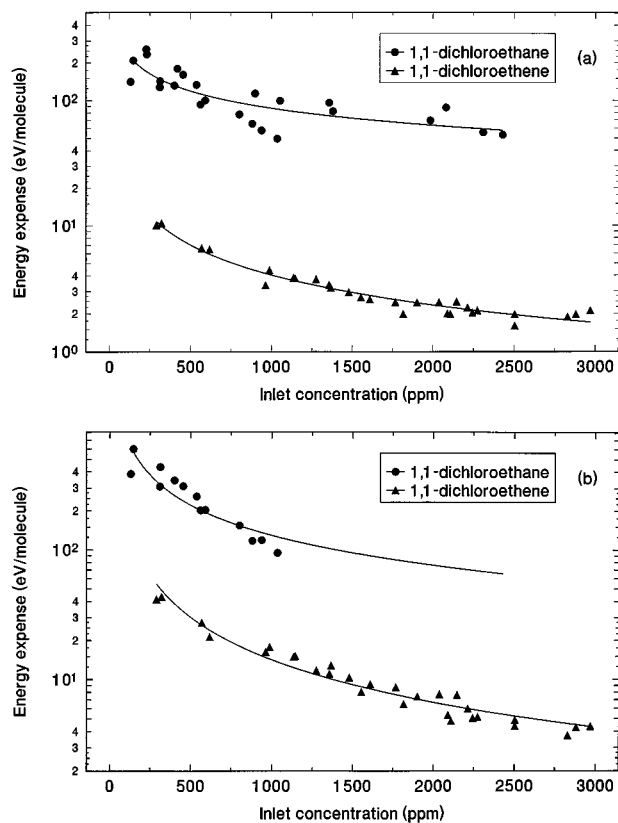
FIG. 2. Energy requirements per molecule for decomposition of 1,1-dichloroethane and 1,1-dichloroethene in an electron beam generated plasma reactor: (a) 90% decomposition, (b) 99% decomposition. The continuous curves are simple nonlinear regressions of the data. Dichloroethane does not achieve 99% decomposition at higher concentrations due to the limited power of the electron beam.

is possible, however. The overall stoichiometry of the dichloroethane molecule would inhibit a chlorine radical propagated chain, since there is an excess of hydrogen available to form a very thermodynamically stable chloride radical sink, HCl.

An estimate of the chain length of the dichloroethene reaction is obtained by comparing the energy required for decomposition to that required for the nonchain dichloroethane decomposition. Since the electron attachment rate constants for dichloroethane and dichloroethene are similar, the number of chlorine radicals produced by dissociative electron attachment per unit energy absorbed by the molecules will be approximately equal for both molecules. Thus the difference in the number of molecules decomposed per unit energy will be due to the difference in chain length between the two reaction mechanisms. VOC decomposition in a plasma reactor can be characterized by the energy required per molecule decomposed in the plasma, or energy expense, ε. The results for 90% and 99% decomposition are given in Figs. 2(a) and 2(b).

The apparent chain length of the dichloroethene decomposition mechanism was estimated by comparing the energy required per molecule of dichloroethane decomposed to that required for dichloroethene decomposition. Over the range of concentrations studied, dichloroethane requires 10 to 30
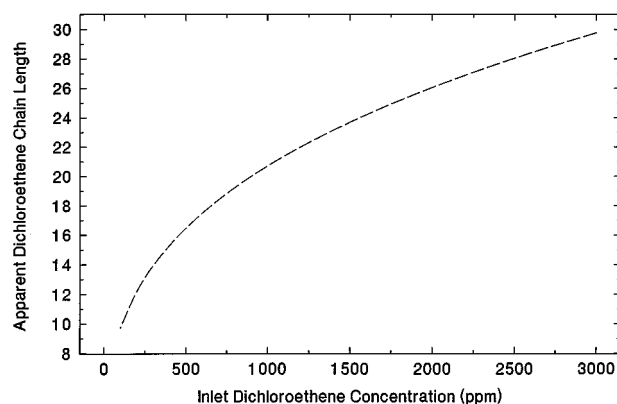
times as much energy for decomposition as dichloroethene. Assuming dichloroethane decomposition is not a chain reaction, this gives an estimate of the chain length of the dichloroethene reaction mechanism of 10 to 30. By taking the ratio of the two best fit curves in Fig. 2(a), the chain length, ϕ, is given approximately by:

$$\phi = \frac{\epsilon_{90,DCA}}{\epsilon_{90,DCE}} = 2.1[V_0]^{0.33}. \qquad (20)$$

This function is graphed in Fig. 3. It seems reasonable that the length of the dichloroethene chain reaction should increase as the dichloroethene concentration increases. At higher dichloroethene concentrations, it will be more likely that a free chlorine radical will react with a dichloroethene molecule to continue the chain reaction, rather than be lost through some sort of radical scavenging reaction. The dependence of ϕ on the cube root of the concentration supports this suggestion, since the average distance between dichloroethene molecules is proportional to the cube root of the concentration.

REACTION INHIBITION

In the concentration versus electron beam dose plots in Figs. 1(a) and 1(b), the lines are not linear on the semilog plot, indicating that the decomposition kinetics are not exactly first order. As the decomposition of dichloroethene or dichloroethane increases with electron beam dose, the concentration begins to level off; in other words, the reaction rate decreases faster than would be expected from first-order kinetics. This may mean that the reaction is being inhibited by decomposition products at high conversions of reactant. Since the rate of decomposition of both molecules depends on the initial dissociative electron attachment reaction, and since both molecules appear to exhibit inhibited kinetics, the inhibitor species are most likely reaction products which scavenge electrons. This situation has been treated by the authors previously for trichloroethylene[26] and 1,1,1-trichloroethane[1] decomposition in an electron beam generated plasma reactor. There are several reaction products

for each compound which could act as electron scavengers. For example, a possible inhibitor species of dichloroethane decomposition is vinyl chloride:

$$e + CH_2CHCl \rightarrow CH_2CH + Cl^-$$
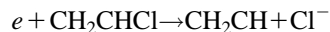
$$k = 1 \times 10^{-10} \ cm^3/s \ (Ref. \ 27). \tag{21}$$

For dichloroethene, phosgene could be an inhibitor species:

$$e + COCl_2 \rightarrow COCl + Cl^-$$
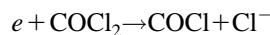
$$k = 5 \times 10^{-8} \ cm^3/s \ (Ref. \ 28). \tag{22}$$

Other species in the plasma could also be electron scavengers. Other possibilities for which electron attachment data could not be found include chlorine radicals, chloroacetyl chloride, or any of the chlorinated intermediates in the decomposition mechanisms. The dissociative electron attachment rate constant of phosgene is three orders of magnitude higher than that for dichloroethene. Thus even small concentrations of phosgene product could severely inhibit further dichloroethene decomposition. This may account for the very rapid fall off in reaction rate seen in Fig. 1(b). It has also been suggested that electrons attach rapidly to hydrogen chloride.[29] Thus HCl is also a possible inhibitor species of dichloroethane and dichloroethene decomposition.

A very simplified treatment of inhibited kinetics is given by considering two reactions occurring in parallel. This treatment is based on one provided by Slater for vinyl chloride decomposition,[3] in which it was assumed that the rate constant for the inhibition reaction was equal to the rate constant for the decomposition reaction, and that the conversion of reactant was small. In this limiting case, the reaction follows first order behavior; that is the concentration of reactant falls off exactly exponentially with electron beam dose. The model predicts that the rate constant of decomposition will decrease with increasing inlet reactant concentration.

In the present study, the limiting case of low conversion is not applicable, because the interesting effects of inhibition become important at high conversion. It is also not at all clear that the rate constants of the inhibition and decomposition reactions are similar. The data was fit instead to a simple expression to describe the global decomposition kinetics which exhibit inhibited behavior,

$$[V] = [V_0]\exp(-kD^b). \tag{23}$$

If $b = 1$, then first order, uninhibited kinetics are recovered. If $b < 1$, then the reaction appears to be inhibited by products. As demonstrated first by Slater,[3] and confirmed by the present authors in studies of trichloroethane and trichloroethylene decomposition, the rate constant, k, can be a decreasing function of inlet concentration. The rate constant decreases with inlet concentration because high concentrations favor the formation of the inhibitor species, which in turn causes the reaction rate to decrease.

The curves of dichloroethane and dichloroethene concentration versus electron beam dose are fit very well by this expression, as shown by the continuous curves in Figs. 1(a) and 1(b). By fitting Eq. (23) to sixty curves similar to those in the figures, values of k and b were determined for dichloroethane and dichloroethene, and are given in Table I. The

TABLE I. Parameters for the equation $[V] = [V_0]\exp(-kD^b)$ describing the VOC concentration as a function of electron beam dose. Parameters were determined by fitting the dichloroethane and dichloroethene decomposition data. $[V_0]$ is the inlet concentration, in units of ppm.

	Dichloroethane	Dichloroethene
Rate constant, k [Mrad^{-b}]	$-6.96 \times 10^{-4}\,[V_0] + 0.62$	$-0.89 \times 10^{-4}\,[V_0] + 2.44$
Inhibition parameter, b	$1.92 \times 10^{-4}\,[V_0] + 0.49$	$1.31 \times 10^{-4}\,[V_0] + 0.41$

lower value of b for dichloroethene indicates that inhibition is more important for dichloroethene decomposition than dichloroethane decomposition. This is consistent with the supposition that the main inhibitor of dichloroethene decomposition is phosgene which has a high electron attachment coefficient and is thus a good electron scavenger.

CONCLUSION

An electron beam generated plasma reactor was used to decompose low concentrations (100–3000 ppm) of 1,1-dichloroethane and 1,1-dichloroethene in atmospheric pressure air streams. Both compounds are believed to decompose by dissociative electron attachment. The energy requirements for 90% and 99% decomposition of each compound were reported as a function of inlet concentration. Dichloroethene requires much less energy for decomposition than dichloroethane. This enhancement in the dichloroethene decomposition rate may be explained by a chlorine radical propagated chain reaction in the dichloroethene decomposition mechanism. The chain length of the dichloroethene reaction was estimated to increase with increasing concentration, from 10 at 100 ppm dichloroethene to 30 at 3000 ppm. Both dichloroethane and dichloroethene decomposition seem to be inhibited by decomposition products which may scavenge electrons that would otherwise initiate the decomposition of the reactants. Phosgene has a very high dissociative electron attachment cross section, thus it is an effective inhibitor of dichloroethene decomposition. Dichloroethane may be inhibited by vinyl chloride, HCl, chlorine radicals, or undetected chlorinated intermediates. A simple analytic expression was proposed for fitting decomposition data where inhibition effects are important and simple first order kinetics are not observed.

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