

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/226087575>

# The effect of a carbon-carbon double bond on electron beam-generated plasma decomposition of trichloroethylene and 1,1,1-trichloroethane

ARTICLE *in* PLASMA CHEMISTRY AND PLASMA PROCESSING · JANUARY 1997

Impact Factor: 2.06 · DOI: 10.1007/BF02766822

---

CITATIONS

20

---

READS

12

## 4 AUTHORS, INCLUDING:



Steven Vitale

Massachusetts Institute of Technology

52 PUBLICATIONS 556 CITATIONS

SEE PROFILE



Kamal Hadidi

University of Connecticut

44 PUBLICATIONS 334 CITATIONS

SEE PROFILE

## The Effect of a Carbon–Carbon Double Bond on Electron Beam-Generated Plasma Decomposition of Trichloroethylene and 1,1,1-Trichloroethane<sup>1</sup>

S. A. Vitale,<sup>2,3</sup> K. Hadidi,<sup>2,\*</sup> D. R. Cohn,<sup>2,3</sup>  
and P. Falkos<sup>2</sup>

Received September 16, 1995; revised March 18, 1996

---

*The effect of a carbon–carbon double bond on the energy required for decomposition in an electron beam-generated plasma reactor is studied by comparing the decomposition of trichloroethylene and 1,1,1-trichloroethane. A reaction mechanism for TCE decomposition based on a chlorine radical chain reaction is presented which accounts for the formation of all of the experimentally observed reaction products. TCE decomposition is autocatalyzed by reaction products, whereas TCA decomposition is inhibited. The rate expression for the decomposition of TCE in the reactor is determined to be  $r = -[T](15.07[T_0]^{-0.40} + 0.006\{[T_0] - [T]\})$ , where  $[T]$  and  $[T_0]$  are both in ppm, and  $r$  is in ppm Mrad<sup>-1</sup>. The energy expense  $\varepsilon$  for TCE decomposition is determined as a function of inlet concentration. For 99% decomposition of 100 ppm TCE in air,  $\varepsilon = 28$  eV/molecule, and  $\varepsilon = 2.5$  eV/molecule at 3000 ppm. This is only 2.5–5% of the amount of energy required to decompose a similar amount of TCA as reported by the authors in a previous study. By comparing the energy requirements for TCE decomposition to those for TCA decomposition, the TCE reaction chain length is determined to increase from approximately 20 at 100 ppm initial TCE concentration, to 40 at 3000 ppm.*

---

**KEY WORDS:** Plasma-assisted decomposition; electron beam; plasma reactor; 1,1,1-trichloroethane; trichloroethylene.

### 1. INTRODUCTION

Chlorinated ethylenes and ethanes are some of the most common solvents used in the metal machining industries, and they are now found in hazardous concentrations at many government cleanup sites.<sup>(1)</sup> Cost-effective technology to decompose chlorinated VOCs is being sought both

<sup>1</sup>This work was supported by the Contaminant Plume Containment and Remediation Focus Area, Office of Environmental Management, U.S. Department of Energy.

<sup>2</sup>Massachusetts Institute of Technology Plasma Fusion Center, Cambridge, Massachusetts 02139.

<sup>3</sup>Also affiliated with the Department of Nuclear Engineering.

\* E-mail address: hadidi@PFC.mit.edu

by government and by industry. In order to optimize existing technology and to develop new technologies, there is a need to obtain reliable data concerning the decomposition mechanisms and kinetics associated with these compounds. Further, it is desirable to have the ability to predict the behavior of other chlorinated species from the data known for a few representative chemicals. As a step toward achieving this goal, this paper investigates the effect of a carbon-carbon double bond on the energy required for chlorinated VOC decomposition. An electron beam-generated plasma reactor is used to decompose low concentrations of trichloroethylene in air streams at atmospheric pressure, and these results are then compared with those for 1,1,1-trichloroethane decomposition given by the authors in a previous paper.<sup>(2)</sup> An electron beam-generated plasma reactor is well suited to this type of quantitative study, since the electron beam dose to the plasma is easily controlled, and a large range of atmospheric pressure reactant flow rates can be used. A wide range of inlet concentrations may be studied, and the effective reactor residence time may be easily varied by changing the electron beam dose. This allows the kinetics of the reaction mechanism to be studied. This paper expands upon previously reported results on TCE decomposition in plasma reactors, by examining the mechanism and kinetics of decomposition, estimating the chain length of the mechanism, as well as determining the energy requirements for decomposition as a function of inlet concentration from 100 to 3000 ppm.

Several different types of plasma reactors have been used previously to decompose TCE and TCA, including: silent discharge,<sup>(3,4)</sup> pulsed corona discharge,<sup>(3,5)</sup> and microwave discharge.<sup>(6,7)</sup> TCE decomposition using electron beams has been reported by Penetrante<sup>(5)</sup> and Koch.<sup>(8)</sup> However, in these studies TCE decomposition was studied under a limited range of inlet concentrations, and thus the energy requirements for decomposition were assumed to be independent of inlet concentration. This paper will expand upon the previous efforts by showing that the energy required for decomposition is a function of the inlet concentration, and by providing a chemical kinetic treatment of the data.

The electron beam-generated plasma reactor is the most energy-efficient, high-throughput atmospheric-pressure plasma reactor for decomposing low concentrations (1–3000 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.<sup>(2,8–10)</sup> Energy is not wasted in heating the carrier gas molecules, as in thermal processes such as microwave pyrolysis or incineration. The decomposition products from plasma treatment of these chemicals (CO<sub>2</sub>, HCl, CO, Cl<sub>2</sub>, COCl<sub>2</sub>, and chloroacetyl chlorides) are easily treated further in a sodium hydroxide scrubber solution to yield environmentally benign end products.

**Table I.** Comparison of the Physical and Chemical Properties of 1,1,1-Trichloroethane (TCA) and Trichloroethylene (TCE)<sup>a</sup>

Properties	TCA	TCE
Formula	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	C <sub>2</sub> HCl <sub>3</sub>
Molecular weight	133.41	131.29
Boiling point	74.1°C	87°C
Density	1.3390 g/ml	1.4642 g/ml
Ionization potential	11.25 eV <sup>(26)</sup>	9.68 eV <sup>(26)</sup>
<i>e</i> <sup>-</sup> attachment rate	$5 \times 10^{-9}$ cm <sup>3</sup> /sec <sup>(27)</sup>	$2 \times 10^{-9}$ cm <sup>3</sup> /sec <sup>(28)</sup>

<sup>a</sup>The electron attachment rates of these two compounds are very similar, thus the production rate of chlorine radicals by this mechanism should be the same for both TCA and TCE.

To isolate the effect of a carbon-carbon double bond on the energy required for decomposition in the electron beam-generated plasma reactor, this study examines two very similar compounds, which differ only by the presence or absence of a double bond. TCA and TCE have very similar physical properties, as shown in Table I: both compounds are triply chlorinated C<sub>2</sub> molecules, with similar molecular weights, vapor pressures, boiling points, and ionization potentials. Of particular importance to the present work, TCA and TCE have very similar electron attachment rate constants; thus the rate of decomposition by dissociative electron attachment is expected to be the same for both compounds. Therefore the difference in the energy required for decomposition of the two compounds is due only to the difference in the number of TCE or TCA molecules decomposed per initial dissociative electron attachment reaction. The number of TCE or TCA molecules decomposed per chlorine radical produced by dissociative electron attachment is the apparent chain length of the chlorine radical reaction mechanism. TCA decomposes primarily through hydrogen abstraction by chlorine and oxygen radicals, which does not lead to a chain reaction. TCE, on the other hand, has an unsaturated bond which is susceptible to chlorine radical addition reactions, as proposed by Sanheuz<sup>(11)</sup> and Blystone.<sup>(12)</sup> This chlorine radical addition mechanism leads to a chain reaction, which allows chlorinated ethylenes to be decomposed using less energy than for similar chlorinated ethanes.

## 2. EXPERIMENTAL APPARATUS

The electron beam-generated plasma reactor has been described in detail previously.<sup>(8,10,13)</sup> The gas enters the reactor at atmospheric pressure and ambient temperature. The gas flowrate to the reactor used in this study was varied from 1 to 10 standard liters per minute. Cylinders of Matheson ultrahigh purity air (99.999%) were used to generate TCE inlet streams by

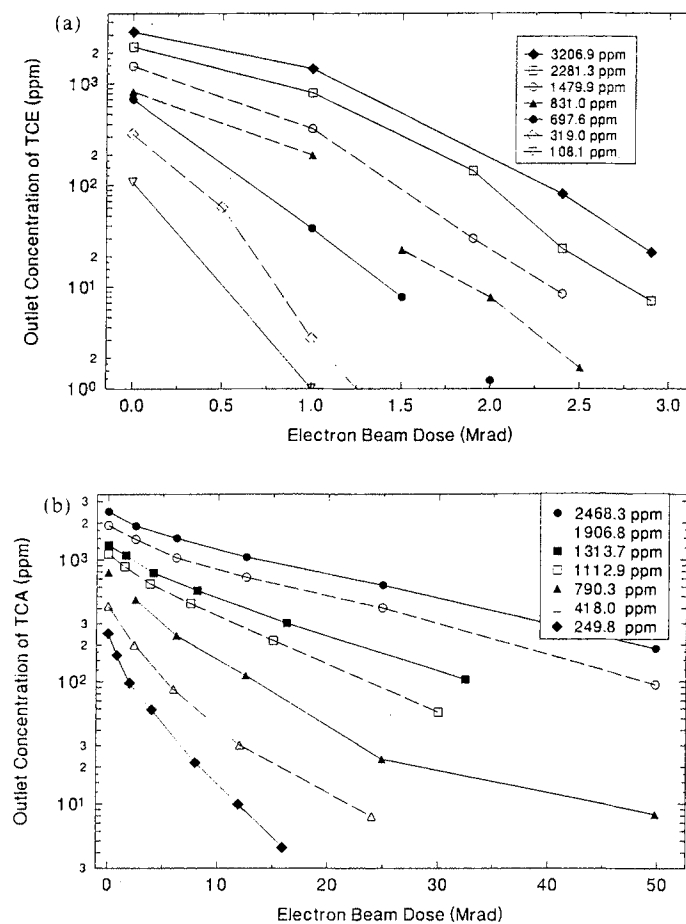
passing the air through bubblers containing liquid TCE. This stream was then mixed with another air stream to achieve the desired TCE inlet concentration, which was varied from 100 to 3000 ppm on a mole/mole basis. No water was added to the gas streams, so the gas is considered to be essentially dry. The flowrates of the streams were measured by rotameters calibrated with soap film flow meters.

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 a certified calibration cylinder of 3628 ppm TCE in air produced by Matheson. 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 TCE concentration is estimated to be  $\pm 10\%$ .

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- $\mu$ m aluminum foil window, into the reaction chamber through which the VOC contaminated air stream flows at atmospheric pressure. Each electron enters the reaction chamber with approximately 50 keV of energy, of which approximately 17 keV is deposited into the air stream before being dumped onto a titanium plate opposite the electron beam window.<sup>(13)</sup> Electron beam dosimetry calculations were performed using a Monte Carlo electron code from the ITS series.<sup>(14)</sup> The maximum electron beam power to the plasma is approximately 25 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.

### 3. EXPERIMENTAL RESULTS

Several decomposition products of TCE and TCA were observed experimentally. The products of TCA decomposition were given in a previous paper.<sup>(2)</sup> The primary decomposition products from TCE decomposition are found in this study to be carbon dioxide, carbon monoxide, phosgene, dichloroacetyl chloride and hydrogen chloride, in agreement with the results found by Koch.<sup>(8)</sup> The minor decomposition products, which in total account



**Fig. 1.** Exhaust VOC concentration from the electron beam-generated plasma reactor as a function of electron beam dose to the plasma for (a) trichloroethylene and (b) 1,1,1-trichloroethane. Total flowrates for the TCE experiments were 6.4–6.5 liters/min, and 3–5 liters/min for TCA.

for less than 10% of the reacted carbon, are trichloroacetyl chloride and chloroform. The reaction mechanism proposed below accounts for the experimental observation of all of the major and minor reaction products.

A graph of exhaust stream TCE concentration versus electron beam dose is shown in Fig. 1a for several VOC inlet concentrations. The uncertainty in the electron beam dose is estimated to be  $\pm 5\%$ , due to the uncertainty in the flow rates of the gases. Greater than 99% removal of TCE is achieved for flow rates up to 7 liters/min. A decomposition of 99% could

also be achieved for higher flow rates if the total reactor power were increased. For comparison, a graph of TCA decomposition versus electron beam dose is also given in Fig. 1b. It is evident that TCE requires a much lower electron beam dose than TCA to achieve the same decomposition.

There is another important comparison to be made between the decomposition of TCE and TCA as shown in Fig. 1. Neither TCE nor TCA show exact first-order reaction kinetics; that is, the reactant concentrations do not fall off exactly linearly with electron beam dose on these semilog graphs. The TCE concentration seems to fall off more rapidly as the reaction proceeds, thus causing the downward curvature in the curves. For TCA, however, the opposite appears to be true, since the concentration falls off less rapidly as the electron beam dose increases.

#### 4. DISCUSSION OF RESULTS

The TCA results may be easier to explain than the TCE results, since this unusually rapid fall-off in reaction rate as the reaction proceeds is common in complex reaction systems such as the one in this study. As the TCA decomposes, reaction products are formed which inhibit the decomposition reaction. These inhibitors cause the rate of TCA decomposition to decrease. As the reaction proceeds further, the inhibitor concentration continues to increase and the TCA decomposition rate continues to fall off. Thus the TCA concentration versus electron beam dose curves tend to level off at high levels of decomposition, as shown in Fig. 1b.

Inhibited kinetics have been well studied experimentally and theoretically, and an analytic solution to the TCA decomposition rate equations was presented by the authors previously.<sup>(2)</sup> The decomposition of TCE does not seem to follow inhibited kinetics; in fact, since the rate of TCA decomposition seems to fall off less rapidly than would be predicted by first-order kinetics, it is possible that the decomposition reaction is actually autocatalytic. Although autocatalytic reactions have been studied for some time (see, for example, Ref. 15), this behavior is somewhat unusual, and a brief discussion of autocatalysis will be presented here.

In an autocatalytic reaction, some reaction product is formed which increases the rate of the reaction. Consider, for example, the pseudo-first-order decomposition of a reactant A to product P:



$$r_1 = -\frac{d[A]}{dt} = k_1[A][P] \quad (2)$$

where the autocatalytic reaction (1) has a rate equation given by Eq. (2). The rate is seen to depend upon the concentration of product. Since the rate

equation does not correspond to the stoichiometry of reaction (1), the latter cannot be a simple reaction. The actual reaction pathway must proceed through a number of steps, some of which must depend on the presence of the product. Autocatalytic reactions are never simple reactions, and the reaction mechanism is often rather complicated. Complicated rate equations are often expressed in terms of the extent of reaction  $x$ , defined as

$$x = \frac{[A_0] - [A]}{[A_0]} \quad (3)$$

where  $[A_0]$  is the initial concentration of reactant. According to reaction (1), one molecule of product P is formed for every molecule of A decomposed; thus,

$$[A_0] = [A] + [P] \quad (4)$$

and the rate equation can be written

$$\frac{dx}{dt} = k_1 \cdot x(1 - x) \quad (5)$$

Note that Eq. (5) does not predict the initial stages of the reaction well, since initially  $x = 0$ , and thus the reaction will never start. If one assumes that there is some initial relative concentration of product,  $x_0$ , Eq. (5) becomes

$$\frac{dx}{dt} = k_1 \cdot (x_0 + x)(1 - x) \quad (6)$$

However, in the present study there is no product initially present, so  $x_0 = 0$ . Oswald<sup>(16)</sup> first resolved this problem by assuming that in addition to reaction (1), the reactant could also decompose by another pathway which did not require the presence of the product, and which follows a first-order rate expression,

$$r_2 = -\frac{d[A]}{dt} = k_2[A] \quad (7)$$

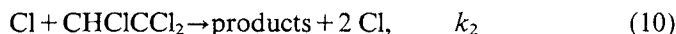
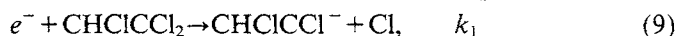
This second reaction pathway may be faster or slower than the autocatalytic pathway. If the rates of these two reaction pathways are added, the total rate becomes

$$\frac{dx}{dt} = (k_1 + k_2[A_0] \cdot x)(1 - x) \quad (8)$$

Equation (8) is equivalent to Eq. (6) with the substitutions  $k = k_2[A_0]$ , and  $x_0 = k_1/k$ . The reaction rate represented by Eqs. (5), (6), or (8) was referred to by Kondrat'ev<sup>(17)</sup> as the basic law of autocatalysis.



Applying the autocatalytic principle to the decomposition of TCE, the first-order and autocatalytic reactions are the dissociative electron attachment and the reaction of TCE with a chlorine radical, respectively:



It is important to note that reaction (10) produces two chlorine radicals for every TCE decomposition reaction. This is necessary for an autocatalytic reaction, since the Cl concentration must increase with time in order to cause an autocatalytic effect. If only one chlorine atom were produced in reaction (10), the net production of Cl radicals by this mechanism would be zero, and autocatalytic behavior would not be observed. However, the production of just one chlorine atom in reaction (10) would still allow a chain reaction to occur, which is the primary cause for the very low energy required for TCE decomposition when compared to TCA decomposition. The reaction mechanism proposed below accounts for the formation of two chlorine radicals for every TCE molecule decomposed by reaction (10).

Since reactions (9) and (10) both result in the net formation of one chlorine radical for each TCE molecule decomposed, Eq. (4) is still valid, and the rate of TCE decomposition is still given by Eq. (8). Replacing the conversion with the concentration of TCE, one obtains

$$-\frac{d[T]}{dt} = [T] \cdot (k_1 + k_2 \cdot ([T_0] - [T])) \quad (11)$$

where  $[T_0]$  is the initial concentration of TCE. In the electron beam-generated plasma reactor, it is the dose to the plasma which controls the extent of the VOC decomposition. The electron beam dose  $D$  is equivalent to the residence time  $\tau$  in a traditional chemical reactor. Thus,  $D$  can be substituted for  $t$  in Eq. (11) without any loss of generality; only the units of the rate constants  $k_1$  and  $k_2$  need to be changed,

$$-\frac{d[T]}{dD} = [T] \cdot (k_1 + k_2 \cdot ([T_0] - [T])) \quad (12)$$

In this form, the rate constants  $k_1$  and  $k_2$  relate the decomposition of TCE to the electron beam dose. These constants are measured empirically from the TCE concentration versus electron beam dose data, and are expected to be dependent on the characteristics of the electron energy distribution in the plasma reactor. Since most reactor designs of this type currently being studied produce relatively similar electron energies, it is expected that these rate constants will be valid for most electron beam reactor designs. The rate constant  $k_1$  is related to the dissociative electron attachment rate constant for TCE given in Table I, but it should be noted that the value in Table I was determined for a monoenergetic beam of electrons at 0.1 eV, whereas in an electron beam

reactor, there is a wide distribution of electron energies, and the energy distribution itself is a function of position in the reactor. To determine the dissociative electron attachment rate in a reactor from the cross sections for attachment and the electron energy distribution functions in the reactor is a formidable task, since these distribution functions must be measured as a function of space. In this study, the overall rate constants for decomposition determined experimentally in this study are a simplification of this problem, and should be considered only for electron beam-generated plasma reactor design.

Equation (12) can be integrated, giving

$$[T] = [T_0] \left( 1 - x_0 \frac{1 - \exp(-K \cdot D)}{x_0 + \exp(-K \cdot D)} \right) \quad (13)$$

where

$$x_0 = \frac{k_1}{k_2[T_0]} \quad (14)$$

$$K = k_1 + k_2[T_0] \quad (15)$$

Equation (13) predicts that the concentration will fall off with increasing rate up to a certain point, and then the reaction rate will slow to zero as the reactant concentration becomes very low. Note that the TCE concentration will not fall to zero unless  $D \rightarrow \infty$ .

In the limit  $k_2 \rightarrow 0$ , that is, if the autocatalytic reaction does not occur, first-order decay is recovered from Eq. (13),

$$[T] = [T_0] \exp(-k_1 D) \quad (16)$$

This simple first-order decay is the form used by Rosocha<sup>(4)</sup> and Penetrante<sup>(3,5)</sup> to model TCE decomposition in corona and electron beam reactors. Rosocha<sup>(4)</sup> defines a parameter  $\beta$  such that

$$[T] = [T_0] \exp\left(-\frac{D}{\beta}\right) \quad (17)$$

Thus by comparison to Eq. (16), it is evident that  $\beta$  is equivalent to  $1/k_1$ .

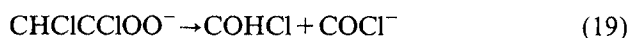
The simple reactions given here as reactions (9) and (10) are undoubtedly simplifications of a complex mechanism. However, Semenov<sup>(14)</sup> showed that the basic law of autocatalysis expresses fairly accurately the rate of branched-chain reactions. With this in mind, in the next section reaction pathways are presented for a branched-chain TCE reaction, which also account for the formation of the observed products of reaction.

## 5. REACTION PATHWAYS

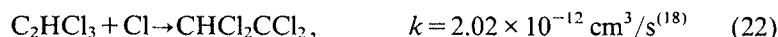
The reaction mechanisms of any VOC with oxygen in a plasma reactor are very complicated, and only a cursory treatment of the reaction pathways

are presented here. The objective of the following discussion of the TCE and TCA reaction pathways is twofold: to provide possible pathways to account for the formation of the observed reaction products based on mechanisms described in the literature, and to account for the formation of chlorine radicals which are necessary to explain the autocatalytic behavior observed in TCE decomposition.

Based on the high electron capture cross sections of the VOCs of interest in this study, it is believed that dissociative electron attachment is the primary initiation step in the VOC reactions, not positive ion chemistry reactions. Thus, in this paper, two main reaction pathways will be considered for both TCE and TCA decomposition. First, a molecule of TCA or TCE is decomposed through dissociative electron attachment with a slow electron in the plasma, producing a chlorine radical and a doubly chlorinated ethylene anion, as shown in reaction (9). The anion will likely decompose by direct oxidation, as shown here for TCE,



Second, the free chlorine radicals produced in reactions (9) or (20), and the ion produced in reaction (21), can go on to decompose other TCA or TCE molecules in the plasma through radical reactions. However, there is an important difference in the TCA and TCE radical reactions in the presence of atomic chlorine. A chlorinated ethane such as TCA will most likely decompose through hydrogen abstraction, followed by chlorine elimination, producing 1,1-dichloroethylene and hydrogen chloride, as proposed by the authors previously.<sup>(2)</sup> On the other hand, a chlorinated ethylene such as TCE can decompose by both hydrogen abstraction and by chlorine or oxygen radical addition to the double bond. As shown below, the Cl addition to TCE is faster than the hydrogen abstraction reaction from either TCE or TCA, with the rate constants evaluated at 298 K,



Oxygen radical reaction addition to TCE is also possible, but this reaction is slow compared to Cl radical addition and is believed to be negligible when compared to the Cl radical chain reaction mechanism. Thus, the reaction pathways proposed below for the secondary autocatalytic radical reaction are based on reaction (22).

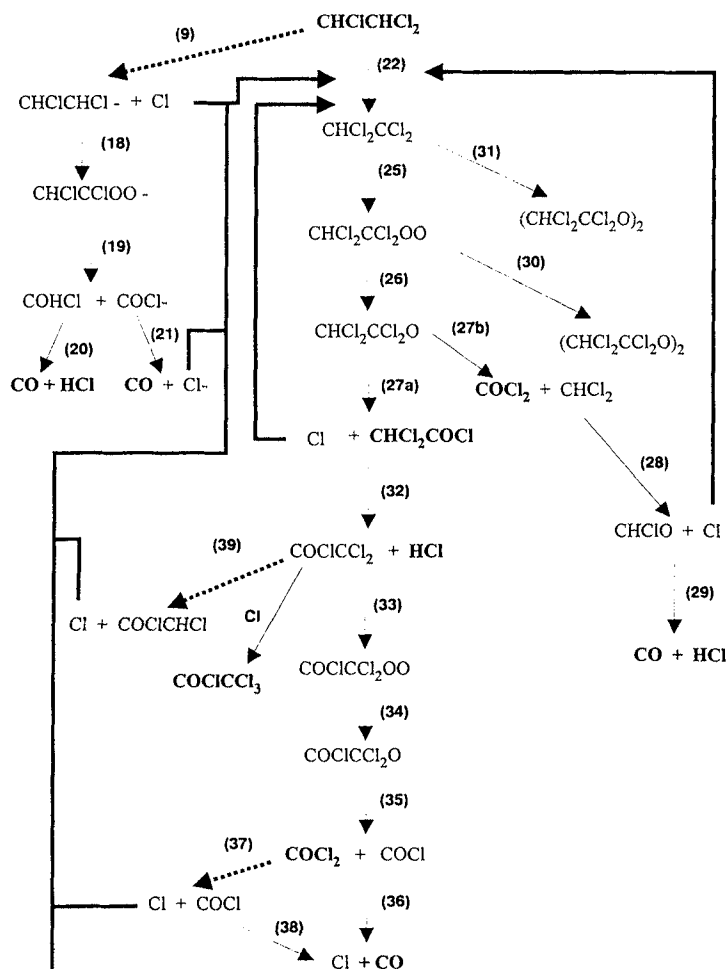
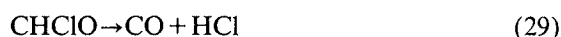
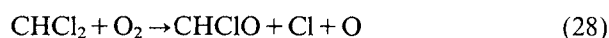


Fig. 2. Schematic diagram of the trichloroethylene decomposition mechanism in the electron beam-generated plasma reactor. Numbers in parenthesis refer to reactions in the text. Thick lines show possible mechanisms for chlorine chain reaction, dashed lines show dissociative electron reactions.

Reaction mechanisms for the decomposition of chlorinated ethylenes such as TCE have been proposed extensively in the literature,<sup>(12,13,20,21)</sup> and through a combination of these reaction pathways, all of the decomposition products found in this study can be accounted for. The reaction pathways presented in this paper are illustrated schematically in Fig. 2.

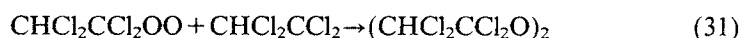
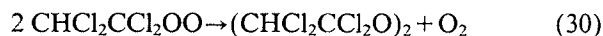
Note that in reaction (22) the chlorine radical adds preferentially to the least substituted carbon atom. Addition to the more chlorinated carbon

atom is also possible, but this is less likely to occur. Further, addition at the more chlorinated carbon would lead to the formation of trichloroacetaldehyde, which is not observed experimentally. Sanheuzza<sup>(11)</sup> suggests that addition at the least chlorinated site is favored over addition at the more chlorinated site by a factor of 8. A possible mechanism for the favored addition reaction is as follows:



The chlorine radical used in reaction (22) is regenerated in reactions (27a) or (28) and a chain reaction may occur. Chang<sup>(20)</sup> estimated that reaction (27a) is favored over reaction (27b) by a factor of 6. This is consistent with the large amount of dichloroacetyl chloride formed as a reaction product.

Chain termination can occur in at least two ways:



This product, tetrachloroethanol anhydride, was not seen experimentally. The long chain length would indicate that this termination-step product is present only in very low concentrations.

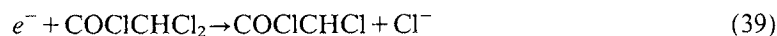
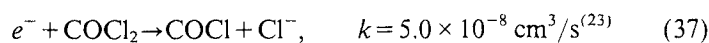
The dichloroacetyl chloride formed in reaction (27a) decomposes in the plasma to form HCl, phosgene, and chlorinated radicals:



The phosgene thus formed may decompose through Cl abstraction in the plasma by chlorine, oxygen, or other radicals, to form carbon monoxide and molecular chlorine or chlorine radicals.<sup>(13,22)</sup>

Both phosgene and dichloroacetyl chloride may also decompose by another mechanism. Given enough residence time in the plasma, either of

these compounds may collide with an electron from the electron beam and dissociate:



and the ion formed in reaction (39) may be oxidized via a pathway analogous to reaction (33) above. The dissociation of phosgene or dichloroacetyl chloride by an electron creates one or two more chlorine radicals. Therefore, in total this mechanism predicts the formation of one to four free Cl radicals from every Cl + TCE reaction. If the dichloroacetyl chloride formed does not decompose, only one Cl radical will be produced, which will allow a chain reaction. If the dichloroacetyl chloride does decompose, and if the phosgene thus formed further decomposes, it is possible to produce up to four free chlorine radicals. Thus, it is possible to satisfy the requirement in reaction (10), and an autocatalytic reaction may proceed. This reaction mechanism also accounts for the formation of all of the observed reaction products.

Reactions (37) and (39) are actually inhibition reactions of the initiation step of the TCE decomposition mechanism, dissociative electron attachment. The phosgene and dichloroacetyl chloride scavenge electrons in the plasma which could otherwise be used to initiate more TCE decomposition reactions. The reaction rate constant for dissociative electron attachment in reaction (37) is seen to be greater than the rate constant for TCE or TCA decomposition given in Table I; thus, phosgene is an effective inhibitor of the electron attachment process. The reaction rate for electron attachment to dichloroacetyl chloride could not be found in the literature. It has been suggested that hydrogen chloride also captures electrons very rapidly,<sup>(29)</sup> making it a possible inhibitor species as well. The TCE removal rate is reduced by the presence of reaction products, and the reaction is inhibited. This behavior has been seen previously in electron beam-generated plasma decomposition of TCA<sup>(2)</sup> and vinyl chloride,<sup>(9)</sup> and is accounted for in the data analysis section below.

Note that the inhibition of the initiation step (dissociative electron attachment) does not necessarily contradict the observed autocatalytic behavior. If the TCE radical reaction chain length is long, that is, if many TCE molecules are decomposed for each dissociative electron attachment initiation step, then the observed kinetics will be dominated by the autocatalytic nature of the decomposition reaction.

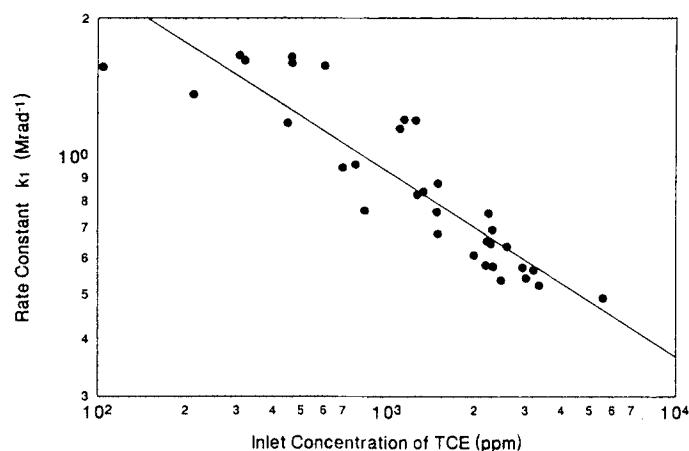


Fig. 3. Rate constant for dissociative electron attachment to TCE in an electron beam-generated plasma reactor as a function of inlet concentration.

## 6. ANALYSIS OF DATA

The rate constants  $k_1$  and  $k_2$  are determined from the data in Fig. 1a and from 31 other curves similar to these. The rate constants are found from the rate equation (13). At very low electron beam dose,  $[T] \approx [T_0]$ , and the initial rate is related to the rate constant  $k_1$ ,

$$-\frac{d[T]}{dD} = k_1[T] \quad (40)$$

Thus, if the initial rate is plotted against the initial concentration of TCE, the slope of this line will give  $k_1$ . It was found that this relation does not give a straight line; in fact,  $k_1$  was found to depend on inlet concentration according to the relation

$$k_1 = \frac{15.07}{[T_0]^{0.40}} \text{ Mrad}^{-1} \quad (41)$$

with  $[T_0]$  in units of ppm. The data points and best-fit curve are shown in Fig. 3. This dependence of  $k_1$  on the inlet concentration was not unexpected, as the authors found a  $1/[T_0]$  dependence of the first-order decay rate on inlet concentration for TCA decomposition.<sup>(2)</sup> In addition, Slater<sup>(9)</sup> derived an analytic relation for the first-order rate constant for vinyl chloride decomposition in an electron beam which expressly predicted that  $k_1$  would be inversely related to the inlet concentration. This kinetic model was derived assuming that some inhibitor species in the plasma competed with vinyl

chloride for the initial “removal agent,” which in this case is believed to be electrons. The inhibition reactions for TCE decomposition are given above as reactions (37) and (39).

The second rate constant  $k_2$  can be found from a simple rearrangement of Eq. (13),

$$\frac{1}{[T]} \frac{d[T]}{dD} = k_2[T] - (k_1 - k_2[T_0]) \quad (42)$$

Plotting the left-hand side of Eq. (42) vs.  $[T]$  for each curve of concentration vs. electron beam dose should give a straight line of slope  $k_2$ . Unfortunately, the scatter in the data did not allow a very accurate determination of this rate constant; however, from best-fit curves to the data shown in Fig. 1a,  $k_2 \approx 0.006 \pm 0.003 \text{ ppm}^{-1} \text{ Mrad}^{-1}$ .

From Eq. (13), it is seen that the rate of TCE decomposition is the sum of the rate of the initial decomposition by dissociative electron attachment and the rate of decomposition by the secondary autocatalytic reaction. By taking the ratio of these two rates, one can determine which process is dominant,

$$\frac{r_1}{r_2} = \frac{k_1}{k_2([T_0] - [T])} = \frac{15.07/[T_0]^{0.40}}{0.006([T_0] - [T])} = \frac{25,100}{x \cdot [T_0]^{1.40}} \quad (43)$$

This ratio decreases as the extent of the reaction and the TCE inlet concentration increases. As more TCE is decomposed, and thus  $x$  increases, the Cl radical concentration increases and the autocatalytic reaction becomes significant compared to the dissociative electron attachment reaction. Similarly, for higher inlet TCE concentrations, more chlorine radicals will be produced, thus increasing the rate of the autocatalytic reaction with respect to the electron attachment reaction.

It is useful to determine the  $\beta$  value for TCE decomposition in this study for comparison with literature values (see Fig. 4). Theoretically,  $\beta$  should be the inverse of  $k_1$  according to Eq. (17). However, previous studies<sup>(4,5)</sup> have determined  $\beta$  by fitting the data to Eq. (17), whereas in this study  $k_1$  was determined by a differential method by examining the initial rate of reaction, according to Eq. (40). These two methods will give the same value for  $\beta$  only if the concentration versus electron beam dose data falls off exactly exponentially as predicted by Eq. (17). The data shown in Fig. 1a do not support a purely first-order reaction; instead, it was shown above to exhibit a sort of autocatalytic behavior. Nevertheless, at low fractional decomposition (less than  $\approx 90\%$ ), the linear approximation is not bad and the data may be fit to an exponential decay fairly accurately. The data presented by previous researchers did not exceed 90% decomposition, and thus their data were well fit by the first-order model. By nonlinear regression



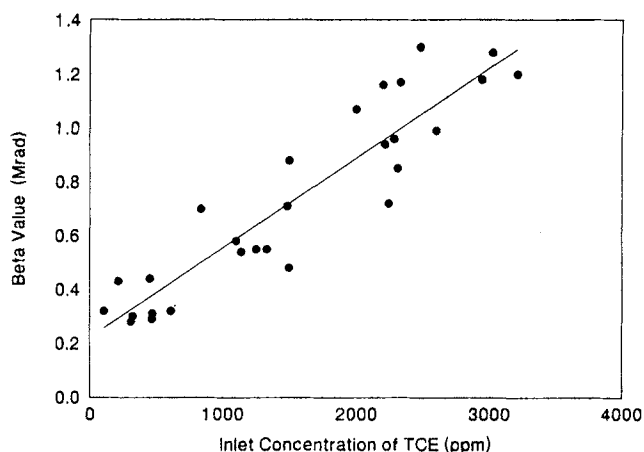


Fig. 4. Specific energy  $e$ -folding parameter  $\beta$  as a function of inlet concentration for TCE decomposition in the electron beam-generated plasma reactor. The line is a linear regression of the data.

of the TCE concentration vs. electron beam dose curves, the following relation for  $\beta$  was obtained:

$$\beta = 0.00033[T_0] + 0.22 \text{ Mrad} \quad (44)$$

with  $T_0$  in ppm. Penetrante<sup>(5)</sup> reports  $\beta = 0.23$  Mrad for the decomposition of 100 ppm TCE in an electron beam reactor, which agrees very well with the value of  $\beta = 0.253$  Mrad calculated by Eq. (44).<sup>4</sup> In contrast, for TCE decomposition in a pulsed corona reactor, Penetrante<sup>(5)</sup> reports  $\beta = 1.24$  Mrad at 100 ppm inlet concentration. From the data of Lerner<sup>(24)</sup> for TCE decomposition in a dielectric barrier discharge, at 300 ppm inlet concentration,  $\beta = 7.1$  Mrad. This shows that the electron beam-generated plasma reactor is more energy efficient than the pulsed corona or the dielectric barrier discharge for TCE decomposition. Rosocha<sup>(4)</sup> reports  $\beta = 0.9$  Mrad in a dielectric barrier discharge, though the inlet concentration was not specified, so it is difficult to make a comparison between these results and the results of this study.

For comparison, the  $\beta$  value for TCA decomposition in the electron beam-generated reactor was shown by the authors previously to be 2.54 Mrad.<sup>(2)</sup> TCE has a lower specific energy for decomposition than TCA due to the chlorine radical chain reaction mechanism available to chlorinated ethylenes such as TCE.

<sup>4</sup>Note that 1 J/standard liter as reported in the references is equal to 0.0776 Mrad.

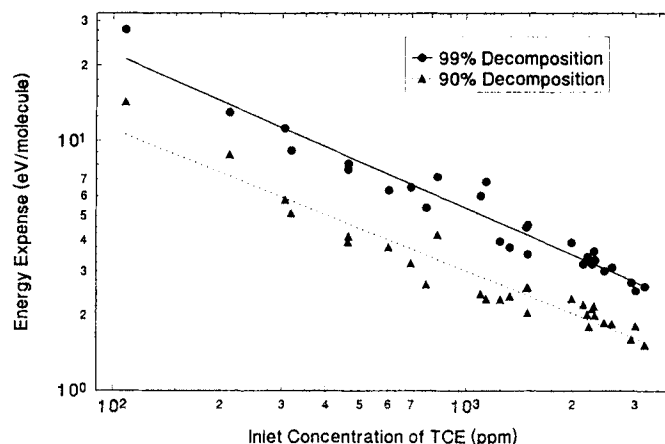


Fig. 5. Energy requirements for trichloroethylene decomposition in the electron beam-generated plasma reactor as a function of inlet concentration and extent of reaction.

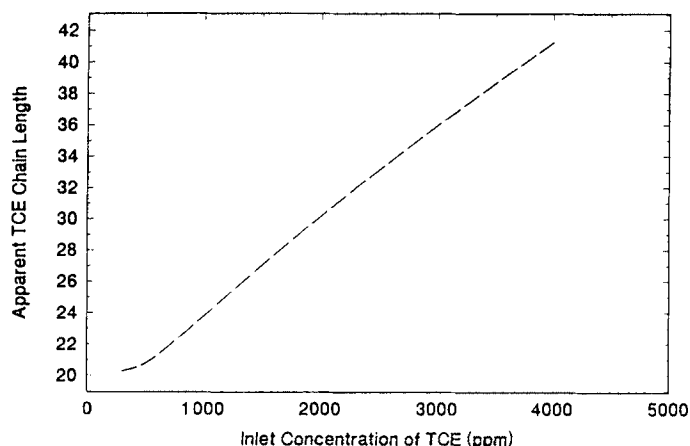
To compare the chain length of the TCE reaction to the nonchain TCA reaction, it is necessary to know how many molecules are decomposed on average per chlorine radical produced in the plasma. Since the electron attachment rate constants for TCA and TCE are similar, the rate of chlorine radical production will be approximately equal for the two molecules. Thus, the difference in the number of molecules decomposed will be due to the difference in chain length between the two reaction mechanisms. A useful expression for VOC decomposition in a plasma reactor is the *specific energy* or *energy expense*  $\varepsilon$  per molecule decomposed. The energy expense was related to the electron beam dose by Koch<sup>(13,25)</sup>:

$$\varepsilon = \frac{Q}{N_0 - N} = \frac{1}{x} \frac{Q}{T_0 \cdot N} = \frac{1}{x \cdot T_0} \frac{M_c}{N_A} D \quad (45)$$

where  $Q$  is the electron beam energy deposited in the plasma,  $N$  is the number of molecules of species  $T$  being decomposed,  $N_A$  is Avogadro's number, and  $M_c$  is the molecular weight of the gas stream. Using Eq. (45), we calculated the energy expense from the data for each of the concentration vs. electron beam dose curves obtained. The results for  $x=0.90$  and  $x=0.99$  are given in Fig. 5. The best-fit lines in these figures are given by

$$\text{for } x=0.90, \quad \varepsilon = \frac{182}{[T_0]^{0.6}} \text{ eV/molecule} \quad (46)$$

$$\text{for } x=0.99, \quad \varepsilon = \frac{380}{[T_0]^{0.6}} \text{ eV/molecule} \quad (47)$$



**Fig. 6.** Chlorine radical reaction chain length as a function of inlet trichloroethylene concentration in the electron beam-generated plasma reactor. Chain length was determined by comparing the energy required for trichloroethylene decomposition to that required for 1,1,1-trichloroethane decomposition, which is not a chain reaction.

The apparent chain length of the TCE decomposition mechanism was determined by comparing the energy required per molecule of TCA decomposed, given previously by the authors,<sup>(2)</sup> to that required for TCE decomposition. The apparent chain length is shown in Fig. 6. Over the range of concentrations studied, TCA requires 20 to 40 times as much energy for decomposition as TCE. Assuming TCA decomposition is not a chain reaction, this gives an estimate of the chain length of the TCE reaction mechanism of 20–40. This agrees with the results reported by Blystone<sup>(12)</sup> using a xenon flashlamp, where the apparent quantum efficiency of TCE decomposition was found to be 42 times greater than for TCA decomposition, although the concentration of the reactants was not reported. It seems reasonable that the length of the TCE chain reaction should increase as the TCE concentration increases, since at higher concentrations there will be more nearby TCE molecules to continue the chain reaction.

## 7. CONCLUSION

The effect of a carbon–carbon double bond on the energy required for decomposition was determined by comparing the energy required for TCE decomposition in an electron beam-generated plasma reactor to the energy required for decomposition of a very similar molecule without a double bond: 1,1,1-trichloroethane. By choosing two molecules for study which

have similar electron attachment cross sections and similar properties, the effect of the carbon-carbon double bond was isolated. Decomposition of TCE requires only 2.5–5% of the energy required to decompose the same amount of TCA. A chain reaction mechanism based on chlorine radical substitution to the double bond was presented for TCE decomposition. This mechanism accounts for the formation of all of the reaction products, and accounts for the low energy required for TCE decomposition. Since the number of chlorine radicals produced per unit of energy absorbed is expected to be the same for both molecules, the low energy requirement for TCE decomposition is due to the long chain length of the reaction mechanism. The chain length of the TCE reaction mechanism was determined to increase with increasing TCE concentration, from 20 at 300 ppm TCE to 40 at 4000 ppm. For less than 90% decomposition, the specific energy  $\beta$  for decomposition of TCE was determined as a function of inlet concentration. These results agree well with previous literature results given for only one inlet concentration. For greater than 90% decomposition, the specific-energy model does not account for the curvature in the plots, so a simple kinetic model was used to study the effects of reaction products on TCE and TCA decomposition. TCE decomposition was determined to be autocatalyzed by radical products, whereas TCA decomposition is inhibited by chlorine radical scavenging by reaction products.

## REFERENCES

1. National Research Council, *Alternatives for Groundwater Cleanup*, National Academy Press, Washington DC (1994).
2. S. A. Vitale, K. Hadidi, D. R. Cohn, P. Falkos and L. Bromberg, *Plasma Chem. Plasma Process.* **16**, 651 (1996).
3. M. C. Hsiao, B. T. Merritt, B. M. Penetrante, G. E. Vogtlin, and P. H. Wallman, *J. Appl. Phys.* **78**, 3451 (1995).
4. L. A. Rosocha and J. J. Coogan, "Processing of pollutants in dielectric-barrier plasma reactors," *Proceedings of the 12th International Symposium on Plasma Chemistry*, Minneapolis, Minnesota (1995), pp. 665–676.
5. B. M. Penetrante, M. C. Hsiao, J. N. Bardsley, B. T. Merritt, G. E. Vogtlin, P. H. Wallman, A. Kuthi, C. P. Burkhardt, and J. R. Bayless, *Pure Appl. Chem.* **68**, 1083 (1996).
6. J. W. Bozzelli and R. B. Barat, *Plasma Chem. Plasma Process.* **8**, 293–314 (1988).
7. T. R. Krause and J. E. Helt, "Chemical detoxification of trichloroethylene and 1,1,1-trichloroethane in a microwave discharge plasma reactor at atmospheric pressure," Chapter 19 in *Emerging Technologies in Hazardous Waste Management III*, W. D. Tedder and F. G. Pohland, eds., ACS, Washington, DC (1993).
8. M. Koch, D. R. Cohn, R. M. Patrick, M. P. Scheutze, L. Bromberg, D. Reilly, K. Hadidi, P. Thomas and P. Falkos, *Environ. Sci. Technol.* **29**, 2946 (1995).
9. R. C. Slater and D. H. Douglas-Hamilton, *J. Appl. Phys.* **52**, 5820–5828 (1991).
10. M. Koch, D. R. Cohn, R. M. Patrick, M. P. Scheutze, L. Bromberg, D. Reilly and P. Thomas, *Phys. Lett. A* **184**, 109 (1993).

11. E. Sanhueza, I. C. Hisatsune, and J. Heicklen, *Chem. Rev.* **76**, 801 (1976).
12. P. G. Blystone, M. D. Johnson, R. H. Werner and P. F. Daley, "Advanced ultraviolet flash lamps for the destruction of organic contaminants in air," Chapter 18 in *Emerging Technologies in Hazardous Waste Management III*, W. D. Tedder and F. G. Pohland, eds., ACS, Washington, DC (1993).
13. M. Koch, "Decomposition of chlorinated organic compounds in gaseous hazardous waste using a tunable plasma reactor," Ph.D. Thesis, MIT, Department of Nuclear Engineering, 1994.
14. See V. N. Kondrat'ev, *Kinetics of Chemical Gas Reactions*, Academy of Sciences, USSR, Moscow (1958), pp. 40-54, 616-701.
15. D. P. Kononov, *Zh. Eksp. Teor. Fiz. (J. Exp. Theor. Phys.)* **1**, 62 (1887).
16. W. Ostwald, *Lehrbuch der Allgemeinen Chemie*, Bd. II, Leipzig (1887), p. 635; or see V. N. Kondrat'ev, *Kinetics of Chemical Gas Reactions*, Academy of Sciences, USSR, Moscow (1958), p. 50.
17. V. N. Kondrat'ev, *Kinetics of Chemical Gas Reactions*, Academy of Sciences, USSR, Moscow (1958), p. 51.
18. P. B. Ayscough, A. J. Cochen, F. S. Dainton, S. Hirst and M. Weston, *Proc. Chem. Soc.* 244 (1961).
19. E. Tschuikow, J. Niedzielski and F. Faraji, *Can. J. Chem.* **63**, 1093 (1985).
20. J. S. Chang and F. Kaufman *J. Chem. Phys.* **66**, 4989-4994 (1977).
21. C. J. Howard, *J. Chem. Phys.* **65**, 4771-4777 (1976).
22. M. J. Thomson, D. Lucas, C. P. Koshland, R. F. Sawyer, Y. Wu, and J. W. Bozzelli, *Combust. Flame* **98**, 155-169 (1994).
23. E. Schultes, A. A. Christodoulides, and R. N. Schindler, *J. Chem. Phys.* **8**, 354-365 (1975).
24. B. Lerner, J. Biringham, R. Tonkyn, S. Barlow and T. Orlando, "Decomposition of trichloroethylene by a large-scale, high-flow packed-bed gas phase corona reactor," *Proceedings of the 12th International Symposium on Plasma Chemistry*, Vol. 2, Minneapolis, Minnesota (1995), pp. 697-702.
25. M. Koch, *Radiat. Phys. Chem.* **46**, 359 (1995).
26. K. Kimura, S. Satsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Halsted Press, New York (1981).
27. L. G. Christophorou, *Electron-Molecule Interactions and Their Applications*, Vol. 1, Academic Press, New York, (1984) p. 543.
28. L. G. Christophorou, *Atomic and Molecular Radiation Physics*, Wiley-Interscience (1972), p. 483.
29. M. J. Rossi, H. Helm, and D. C. Lorents, *Appl. Phys. Lett.* **47**, 576-578 (1985).