

# Destruction mechanisms for formaldehyde in atmospheric pressure low temperature plasmas

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Formaldehyde ( $\text{CH}_2\text{O}$ ) is a common pollutant of indoor air in residences and commercial buildings. The removal of  $\text{CH}_2\text{O}$  from atmospheric pressure gas streams ( $\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{CH}_2\text{O}$ ) using plasmas generated by a dielectric barrier discharge has been theoretically investigated with the goal of cleansing indoor air. The model consists of a full accounting of the electron, ion, and neutral chemical kinetics in contaminated humid air. We find that the destruction of  $\text{CH}_2\text{O}$  results dominantly from chemical attack by OH and O radicals, with the primary end products being CO and  $\text{H}_2\text{O}$ . The predicted destruction rates for  $\text{CH}_2\text{O}$  are typically 2–8 ppm/( $\text{mJ cm}^{-3}$ ) (parts per million of  $\text{CH}_2\text{O}$  in air/energy deposition). The elimination of the unwanted byproducts, CO and NO, using a platinum catalyst is discussed.

## I. INTRODUCTION

In an attempt to improve heating and cooling efficiency, commercial and residential buildings are being constructed in an almost air-tight fashion, resulting in a diminished influx of fresh air and larger fraction of recirculated air. As a consequence, internally generated pollutants from, for example, the outgassing<sup>2</sup> of building and decorative materials (drapes, carpeting, furniture, insulation), human activities (respiration, smoking, cooking, solvent fumes), and combustion accumulate in the structure, leading to the "sick house" syndrome.<sup>1–5</sup> In particular, urea foam insulation and particle boards emit formaldehyde ( $\text{CH}_2\text{O}$ ) to levels of many ppm (parts per million) in new buildings, and may accumulate to higher levels.<sup>3</sup> The ensuing health problems from unsafe levels of exposure to these indoor pollutants have raised interest in methods of cleansing contaminated indoor air streams.<sup>2,3</sup> Recirculated indoor air is most often cleansed using activated charcoal filters. Although simple, their surfaces can become saturated thereby reducing their efficiency, and conventional filters are poor at removing volatile organic compounds.<sup>6</sup> New activated charcoal fibers, however, are showing promise in this regard.<sup>7</sup> As a result, new techniques are being investigated to clean toxins from gas streams. Among these techniques are the use of plasmas, or cold combustion.<sup>8–15</sup> Plasma based remediation techniques have recently been investigated in detail to remove  $\text{SO}_2$  and  $\text{NO}_x$  from flue gases.<sup>8–12</sup>

In this context, we have theoretically investigated the removal of formaldehyde from atmospheric pressure gas streams using plasmas generated by a dielectric barrier discharge (DBD).<sup>8,12,16,17</sup> DBDs are attractive plasma generators for gas remediation applications due to their ability to operate stably at atmospheric pressures and high power deposition. They are also a mature technology as they are

common components in commercial ozonizers.<sup>17</sup> We have developed a model for DBD excited atmospheric pressure plasmas consisting of a full accounting of the electron, ion, and neutral chemical kinetics in humid air contaminated by formaldehyde ( $\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{CH}_2\text{O}$ ). We find that at near ambient temperature large amounts of  $\text{CH}_2\text{O}$  are fairly efficiently converted to CO and  $\text{H}_2\text{O}$ , with small amounts of NO also produced. The undesirable end products CO and NO can, however, be removed using Pt catalysts.

## II. DESCRIPTION OF THE MODEL AND REACTION MECHANISMS

The model is functionally similar to that described in Refs. 8 and 18. The model consists of three components: a circuit model, a solution of Boltzmann's equation for the electron energy distribution (EED), and a plasma chemistry model. The circuit model computes the applied voltage to the plasma, which is used to solve Boltzmann's equation for the EED using a two-term spherical harmonic expansion.<sup>19</sup> The EED is then used to calculate electron impact rate coefficients. The time derivatives of the plasma species' densities are calculated from the electron impact rate coefficients, gas temperature-dependent rate coefficients, and the species' densities. The conductivity of the plasma is then computed and used to calculate the resistance of the plasma for use in solving the circuit equations.

The plasma chemistry model consists of 100 species and 350 reactions. The choice of reaction mechanisms for the pristine plasma were guided by a previously developed model for the removal of  $\text{SO}_2$  from humid air, as described in Refs. 8 and 18. The important reactions and rate coefficients for the addition of  $\text{CH}_2\text{O}$  to those models are listed in Table I, and the dominant reaction pathways are shown in Fig. 1. Only heavy particle chemical reactions with  $\text{CH}_2\text{O}$  have been included in the model: electron impact processes on  $\text{CH}_2\text{O}$  have been ignored. Since the mole frac-

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TABLE I. Additional reactions included in the model for CH<sub>2</sub>O conversion.<sup>a</sup>

Process	Rate coefficient <sup>b</sup>	Ref.
CH <sub>2</sub> O + O → HCO + OH	2.99 × 10 <sup>-11</sup> exp(-1543/T)	20
CH <sub>2</sub> O + OH → HCO + H <sub>2</sub> O	1.60 × 10 <sup>-11</sup> exp(-110/T)	21
CH <sub>2</sub> O + OH → H + HCOOH	2.00 × 10 <sup>-13</sup>	22
CH <sub>2</sub> O + H → HCO + H <sub>2</sub>	3.64 × 10 <sup>-16</sup> T <sup>1.77</sup> exp(-1510/T)	23
HCOOH + OH → H <sub>2</sub> O + CO <sub>2</sub> + H	4.80 × 10 <sup>-13</sup>	24,25 <sup>c</sup>
HCO + M → H + CO + M	8.50 × 10 <sup>-3</sup> T <sup>-2.14</sup> exp(-10278/T)	26
HCO + H <sub>2</sub> → HCHO + H	3.00 × 10 <sup>-18</sup> T <sup>2.0</sup> exp(-8972/T)	15
HCO + O <sub>2</sub> → HO <sub>2</sub> + CO	8.50 × 10 <sup>-11</sup> exp(-850/T)	26
HCO + H → H <sub>2</sub> + CO	2.00 × 10 <sup>-10</sup>	26
HCO + O → H + CO <sub>2</sub>	5.00 × 10 <sup>-11</sup>	26
HCO + O → OH + CO	5.00 × 10 <sup>-11</sup>	26
HCO + OH → H <sub>2</sub> O + CO	5.00 × 10 <sup>-11</sup>	26
HCO + HO <sub>2</sub> → OH + H + CO <sub>2</sub>	5.00 × 10 <sup>-11</sup>	26
HCO + H <sub>2</sub> O <sub>2</sub> → CH <sub>2</sub> O + HO <sub>2</sub>	1.70 × 10 <sup>-13</sup> exp(-3486/T)	26
HCO + H <sub>2</sub> O → CH <sub>2</sub> O + OH	3.90 × 10 <sup>-16</sup> T <sup>1.35</sup> exp(-13146/T)	26
HCO + HCO → CH <sub>2</sub> O + CO	3.00 × 10 <sup>-11</sup>	26

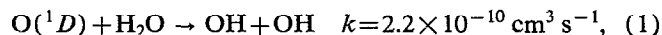
<sup>a</sup>This table lists a subset of the reactions used in the model which directly pertain to CH<sub>2</sub>O removal. A more complete discussion of all of the reactions used in the model can be found in Refs. 8 and 18.

<sup>b</sup>Rate coefficients have units of cm<sup>3</sup> s<sup>-1</sup> unless otherwise noted. Activation energies are given in K.

<sup>c</sup>Estimated products.

tion of CH<sub>2</sub>O is usually <0.01, the fraction of discharge power deposited in CH<sub>2</sub>O for air plasmas is negligible, and direct electron decomposition will be small in any case.

The desired reaction pathway is to oxidize CH<sub>2</sub>O to CO<sub>2</sub> and H<sub>2</sub>O. In plasmas sustained in humid air, O and OH radicals are primarily produced by electron impact dissociation of O<sub>2</sub> and H<sub>2</sub>O. Dissociative excitation of O<sub>2</sub> also produces OH by the abstraction reaction



where O(<sup>1</sup>D) is generated by electron impact dissociation of O<sub>2</sub>. (Rate coefficients *k* are evaluated at 350 K and have units of cm<sup>3</sup> s<sup>-1</sup> unless otherwise noted.) The fragmentation of CH<sub>2</sub>O mainly proceeds through the chemical attacks by OH and O radicals which abstract H atoms, forming HCO:

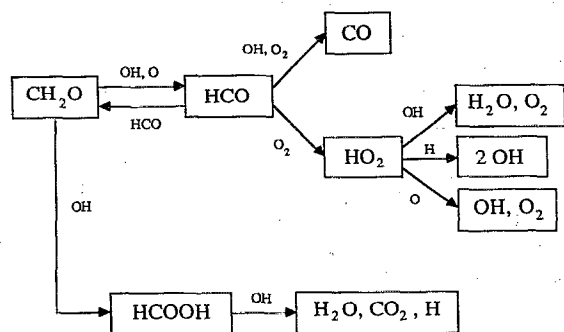
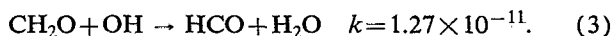
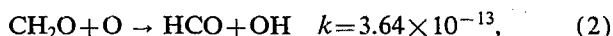
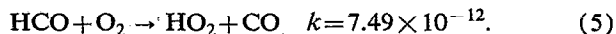
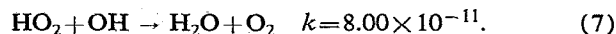
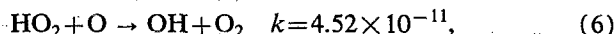


FIG. 1. Dominant reaction pathways for plasma remediation of CH<sub>2</sub>O. The desired end products are CO<sub>2</sub> and H<sub>2</sub>O. At low gas temperatures, incomplete oxidation results in conversion of CH<sub>2</sub>O to primarily CO.

The resulting HCO either recombines to form CH<sub>2</sub>O or reacts with O<sub>2</sub> to form HO<sub>2</sub>



In both cases, CO is an end product and, at the temperatures of interest (300–450 K), is essentially stable. Reactions of HO<sub>2</sub> form OH, O<sub>2</sub>, and H<sub>2</sub>O:



The end products at low temperatures are therefore H<sub>2</sub>O and CO. Since CO is itself toxic, it must be removed from the air stream via heterogeneous reactions. Fortunately, the platinum-catalyzed removal of CO as used for automobile exhausts is a mature technology.<sup>28</sup> We will consider a simplified model of this process later in this article.

Since the primary goal of this work is to ascertain the feasibility of using DBD technology in residential, commercial, and industrial settings, an appropriate quantity to parameterize is the removal efficiency. We define the removal efficiency  $\eta$  as the amount of formaldehyde converted to products/volumetric energy deposition in the plasma. The units of choice are (ppm<sub>0</sub>)/(mJ cm<sup>-3</sup>), where ppm<sub>0</sub> is the equivalent parts per million of CH<sub>2</sub>O in an atmospheric pressure gas stream at 300 K.

### III. REMOVAL OF CH<sub>2</sub>O FROM GAS STREAMS

The removal efficiency as a function of the initial gas temperature is shown in Fig. 2(a). The conditions are a pressure of 1 atm, a gas mixture of N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O = 77/21/2 and an initial formaldehyde concentration of [CH<sub>2</sub>O]<sub>0</sub> = 500 ppm. The DBD has a gap spacing of 0.2 cm, and a supply voltage of 40 kV. The removal efficiency scales

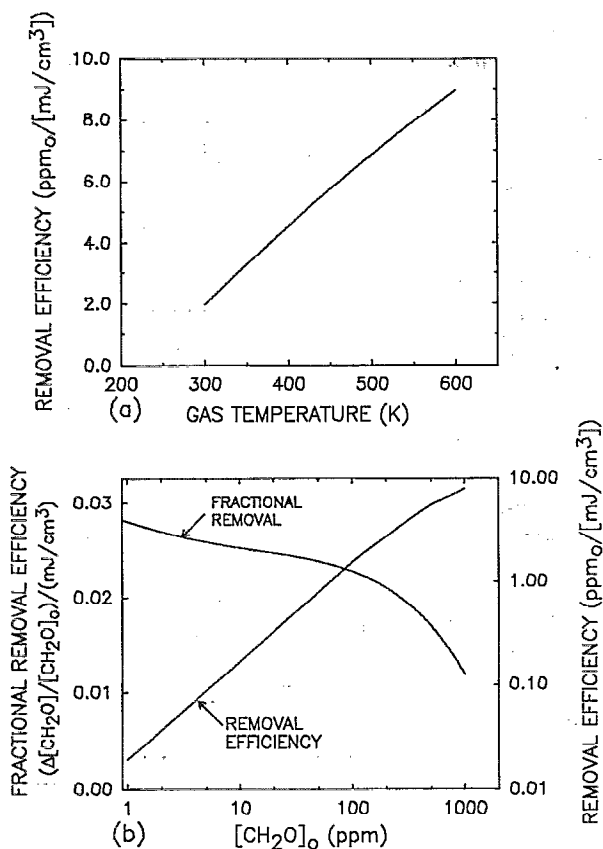


FIG. 2. Efficiencies for removal or conversion of CH<sub>2</sub>O in dielectric barrier discharge plasmas. The gas mixture is N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O=77/20/2. The removal efficiency is defined as amount of CH<sub>2</sub>O converted (equivalent ppm at 1 atm, 300 K)/energy deposition in the plasma. (a) Removal efficiency as a function of gas temperature, showing improved efficiency with increasing  $T_g$  due to moderate activation energies in the oxidation of CH<sub>2</sub>O. (b) Efficiency as a function of initial CH<sub>2</sub>O concentration. The fractional removal efficiency is also shown.

essentially linearly with the initial gas temperature, a result of the initial oxidizing steps of CH<sub>2</sub>O with O and OH having activation energies 1543 and 110 K, respectively. (Activation energies are expressed by their equivalent temperatures.) There is also an improvement which is a result of operating at higher  $E/N$  (electric field/number density) at higher gas temperatures. Due to the high activation energy for O oxidation, we should expect the efficiency to continue to improve at even higher gas temperatures. Since the intended application of this study is recirculating indoor ventilation systems, or treatment of highly contaminated air before exhaust to the atmosphere, operating the removal device at more than 100–150 K above ambient is not practical.

The removal efficiency as a function of [CH<sub>2</sub>O]<sub>0</sub> is shown in Fig. 2(b). These conditions are the same as for Fig. 2(a) but with a gas temperature of 450 K. The removal efficiency increases with increasing [CH<sub>2</sub>O]<sub>0</sub> due primarily to a more efficient utilization of the reactant intermediates. O and OH which do not quickly react with small amounts of CH<sub>2</sub>O will be otherwise consumed. Therefore increasing [CH<sub>2</sub>O]<sub>0</sub> increases the probability that these oxidizing agents are beneficially used. The fractional removal

efficiency, defined as the fractional change in [CH<sub>2</sub>O]/energy deposition, is relatively constant over four orders of magnitude of [CH<sub>2</sub>O]<sub>0</sub>, decreasing slowly with increasing [CH<sub>2</sub>O]<sub>0</sub>. These trends indicate that the conversion of CH<sub>2</sub>O is not, for these conditions, limited by the production of O and OH, but by efficient utilization of those radicals.

The dependence of the removal efficiency on the initial concentration of water was also investigated. Various gas mixtures were used with water mole fractions ranging from 0 to 0.1. Our results show that  $\eta$  does not strongly depend on water concentration, indicating that initial production of OH is not a rate limiting step. This condition results from the facts that reactions of O atoms with CH<sub>2</sub>O produce OH as a product, and reactions of OH with CH<sub>2</sub>O produce H<sub>2</sub>O.

The plasmas in DBDs consist of a collection of filaments or microstreamers, each of which has a short duration (10s–100s ns). Processing of any single volume of gas results from a series of short current pulses. Only a small fraction of, for example, CH<sub>2</sub>O, is removed as a result of any given current pulse. OH and O radicals are produced by electron impact virtually instantaneously compared to other kinetic time scales; and processing of the CH<sub>2</sub>O proceeds over a longer period of time as these radicals more slowly react. The densities of CH<sub>2</sub>O, O, OH, CO, and NO are shown in Fig. 3(a) for 0.1 ms following a current pulse. The gas mixture is N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O=77/21/2 at 450 K and [CH<sub>2</sub>O]<sub>0</sub>=500 ppm. Approximately  $1.2 \times 10^{15}$  cm<sup>-3</sup> of CH<sub>2</sub>O (75 ppm) is converted to CO and H<sub>2</sub>O, while  $\approx 2.5 \times 10^{15}$  cm<sup>-3</sup> of O and OH are produced. The net utilization of the oxidants is therefore  $\approx 50\%$ . The relative contributions of various reactions to the primary CH<sub>2</sub>O conversion during this time period are shown in Fig. 3(b). The CH<sub>2</sub>O+OH channel accounts for about 75% of the CH<sub>2</sub>O removed, while the CH<sub>2</sub>O+O mechanism accounts for most of the remainder.

#### IV. TREATMENT OF THE END PRODUCTS

Our studies indicate that the primary end products of the conversion of formaldehyde in low temperature plasmas are CO, and H<sub>2</sub>O, and to a lesser degree CO<sub>2</sub>. Additionally, NO is produced as an unwanted byproduct. Since CO is a stable, but undesirable, end product at the operating temperatures of interest, heterogeneous reactions are necessary to remove it. The oxidation of CO over a platinum catalyst has previously been studied in detail by others.<sup>27–31</sup> Here we present a simplified model of this process since we are interested only in ascertaining the feasibility of using a platinum catalyst to remove CO produced during formaldehyde removal, and not the specific CO oxidation mechanisms. These reaction mechanisms were based on the model proposed by Yeates *et al.*<sup>27</sup>

The CO surface oxidation model consists of the following reactions:



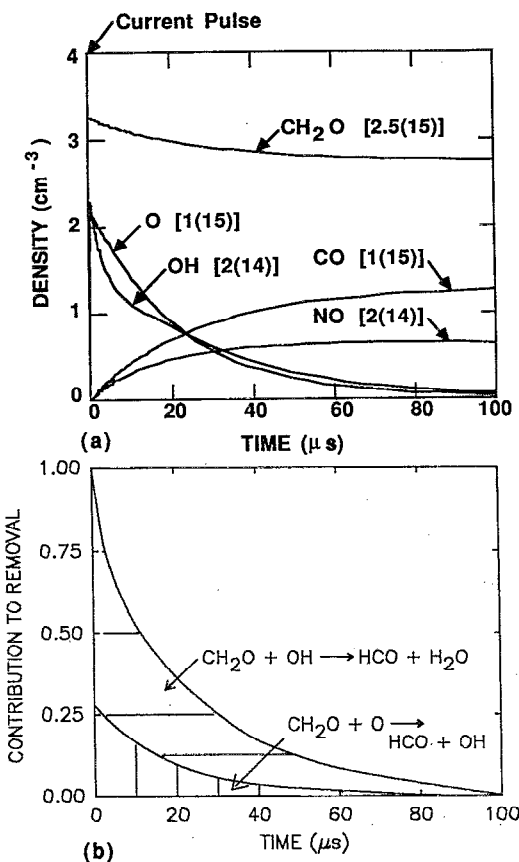
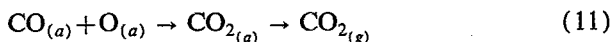


FIG. 3. Reactants and reactions following a current pulse (duration  $\approx 50$  ns) through a  $N_2/O_2/H_2O=77/22/1$  mixture (450 K) with  $[CH_2O]_0 = 500$  ppm. (a) Densities of reactants and products of oxidation of  $CH_2O$ . The densities plotted should be multiplied by the indicated values. (b) Relative contributions to the oxidation of  $CH_2O$  by OH and O.



where the subscripts (g) and (a) denote gas phase and adsorbed species on the catalyst, respectively. In accordance with previous work, we have assumed that the desorption of  $CO_2$  proceeds very quickly in comparison to the other processes.<sup>27</sup> In our model, CO and  $O_2$  adsorb on different sites. Rate equations for these processes were formulated, and integrated in time using the gas phase densities of CO and  $O_2$  calculated in the plasma chemistry model to obtain the initial fluxes of these species to the surface. For example, the rate equation for the surface density of  $CO_{(a)}$  is

$$\frac{d[CO_{(a)}]}{dt} = k_A(N_{CO}^*/N_{CO})S[CO_{(g)}] - k_B[CO_{(a)}] - k_C[CO_{(a)}][O_{(a)}], \quad (12)$$

where  $N_{CO}$  is the total surface density of CO adsorption sites,  $N_{CO}^*$  is the surface density of unfilled CO adsorption sites, and  $S$  is the sticking coefficient for CO on Pt. The coefficient  $k_A$  is the effective transport speed of  $CO_{(g)}$  to the surface which depends on the specifics of the construction

of the device. For a packed bed type of reactor, we conservatively estimated that  $k_A = 1 \text{ cm s}^{-1}$ . For a surface temperature of 450 K we have  $k_B \approx 20 \text{ s}^{-1}$ ,  $k_C = 1.4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ .<sup>27,29</sup> The sticking coefficient for carbon monoxide is essentially constant at  $\approx 0.85$  for fractional coverages less than 0.2, which is the regime of interest in this model.<sup>28,29</sup>

Results from this model show that the removal of CO from the gas stream is rate limited by its transport to the catalyst. For example, complete conversion of 500 ppm of  $CH_2O$  to CO results in a gas phase density of CO of  $1.2 \times 10^{16} \text{ cm}^{-3}$ . The processing rate of the Pt surface is  $\approx 3 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ . Complete conversion of CO to  $CO_2$  can therefore be accomplished in less than a second if the surface to volume ratio of the converter exceeds 3, which is easily accomplished.

NO and  $NO_2$  are by-products of this process, as will be true of most plasma processing activities sustained in air. For  $[CH_2O]_0$  of 10s to 100s ppm, the predicted concentrations of  $NO_x$  produced are approximately (0.03–0.1) that of the  $CH_2O$  removed,  $\Delta[CH_2O]$ . That is, concentrations of  $NO_x$  of as large as  $2-3 \times 10^{14} \text{ cm}^{-3}$  can be produced for  $\Delta[CH_2O]$  of 100s ppm.  $NO_x$  is an equally as undesirable effluent as CO, however Pt catalysts are also efficient at removing NO, and so its remediation can be handled in the same fashion as for CO.<sup>29</sup>

## V. CONCLUDING REMARKS

The fractional conversion of  $CH_2O$  to products by DBDs is fairly efficient for large concentrations of contaminants. However, the incremental energy costs to remove small amounts of  $CH_2O$  (a few ppm) most likely makes this technique impractical for applications in residences and commercial buildings. For example, to remove 5 ppm of  $CH_2O$  in 5 h, the discharge power requirements are  $\approx 5-20 \text{ W/m}^2$  of occupied space. These power requirements will always be dictated by the lower limit of removal desired. However, the power requirements to significantly reduce the  $CH_2O$  concentration in highly contaminated industrial gas streams (many 100s ppm) to a few ppm are tolerable compared to other technologies. In this respect, plasma remediation may be a viable option to reduce high concentrations of contaminant (100 s–1000 s ppm) in industrial gas streams to smaller values (a few ppm). At this point a second stage treatment technique which is more efficient at removing small amounts of contaminant, such as activated charcoal fibers,<sup>7</sup> can be used to remove the remaining contaminant.

## ACKNOWLEDGMENTS

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