

Destruction mechanisms for formaldehyde in atmospheric pressure low temperature plasmas

Daniel G. Storch

University of Illinois, Department of Physics, Urbana, Illinois 61801

Mark J. Kushner^{a)}

University of Illinois, Department of Electrical and Computer Engineering, 1406 W. Green Street, Urbana, Illinois 61801

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Formaldehyde (CH_2O) is a common pollutant of indoor air in residences and commercial buildings. The removal of CH_2O 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 CH_2O results dominantly from chemical attack by OH and O radicals, with the primary end products being CO and H_2O . The predicted destruction rates for CH_2O are typically 2–8 ppm/(mJ cm^{-3}) (parts per million of CH_2O 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 outgassing² 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.^{1–5} In particular, urea foam insulation and particle boards emit formaldehyde (CH_2O) to levels of many ppm (parts per million) in new buildings, and may accumulate to higher levels.³ The ensuing health problems from unsafe levels of exposure to these indoor pollutants have raised interest in methods of cleansing contaminated indoor air streams.^{2,3} 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.⁶ New activated charcoal fibers, however, are showing promise in this regard.⁷ 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.^{8–15} Plasma based remediation techniques have recently been investigated in detail to remove SO_2 and NO_x from flue gases.^{8–12}

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).^{8,12,16,17} 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.¹⁷ 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 CH_2O are fairly efficiently converted to CO and H_2O , 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.¹⁹ 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 SO_2 from humid air, as described in Refs. 8 and 18. The important reactions and rate coefficients for the addition of CH_2O to those models are listed in Table I, and the dominant reaction pathways are shown in Fig. 1. Only heavy particle chemical reactions with CH_2O have been included in the model: electron impact processes on CH_2O have been ignored. Since the mole frac-

^{a)} Author to whom correspondence should be addressed.

TABLE I. Additional reactions included in the model for CH₂O conversion.^a

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

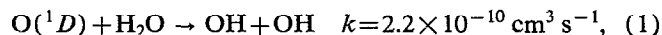
^aThis table lists a subset of the reactions used in the model which directly pertain to CH₂O removal. A more complete discussion of all of the reactions used in the model can be found in Refs. 8 and 18.

^bRate coefficients have units of cm³ s⁻¹ unless otherwise noted. Activation energies are given in K.

^cEstimated products.

tion of CH₂O is usually <0.01, the fraction of discharge power deposited in CH₂O for air plasmas is negligible, and direct electron decomposition will be small in any case.

The desired reaction pathway is to oxidize CH₂O to CO₂ and H₂O. In plasmas sustained in humid air, O and OH radicals are primarily produced by electron impact dissociation of O₂ and H₂O. Dissociative excitation of O₂ also produces OH by the abstraction reaction



where O(¹D) is generated by electron impact dissociation of O₂. (Rate coefficients *k* are evaluated at 350 K and have units of cm³ s⁻¹ unless otherwise noted.) The fragmentation of CH₂O mainly proceeds through the chemical attacks by OH and O radicals which abstract H atoms, forming HCO:

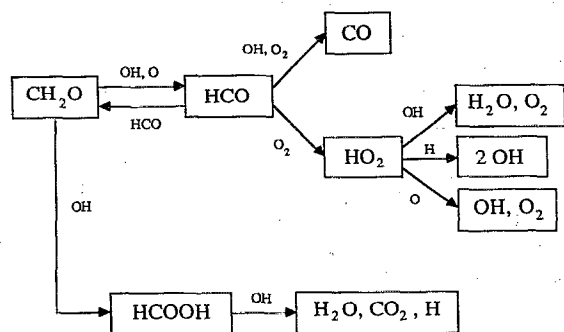
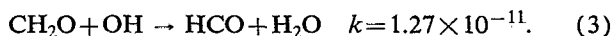
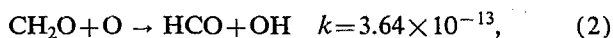
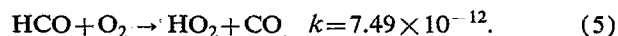
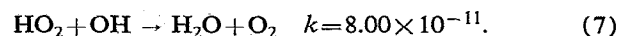
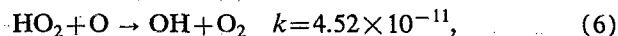


FIG. 1. Dominant reaction pathways for plasma remediation of CH₂O. The desired end products are CO₂ and H₂O. At low gas temperatures, incomplete oxidation results in conversion of CH₂O to primarily CO.

The resulting HCO either recombines to form CH₂O or reacts with O₂ to form HO₂



In both cases, CO is an end product and, at the temperatures of interest (300–450 K), is essentially stable. Reactions of HO₂ form OH, O₂, and H₂O:



The end products at low temperatures are therefore H₂O 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.²⁸ 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 η as the amount of formaldehyde converted to products/volumetric energy deposition in the plasma. The units of choice are (ppm₀)/(mJ cm⁻³), where ppm₀ is the equivalent parts per million of CH₂O in an atmospheric pressure gas stream at 300 K.

III. REMOVAL OF CH₂O 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 N₂/O₂/H₂O = 77/21/2 and an initial formaldehyde concentration of [CH₂O]₀ = 500 ppm. The DBD has a gap spacing of 0.2 cm, and a supply voltage of 40 kV. The removal efficiency scales

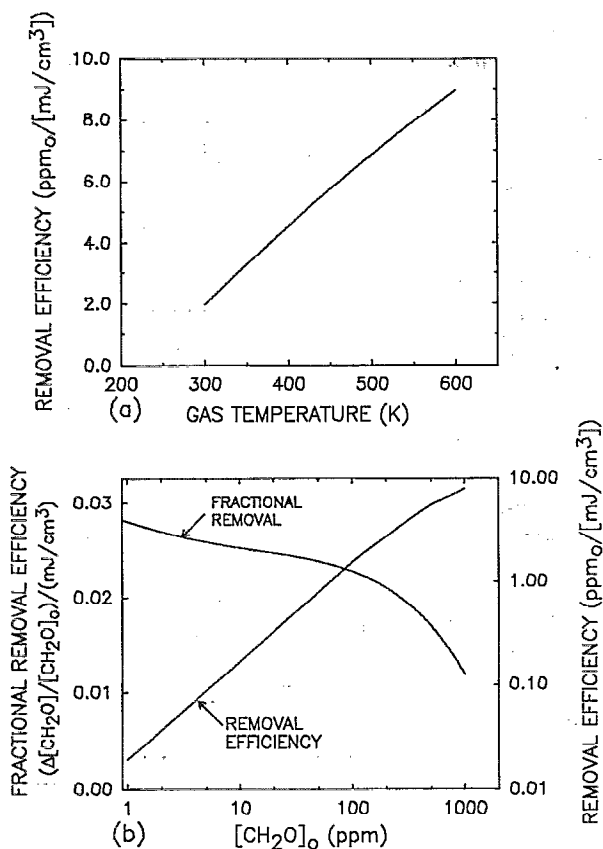


FIG. 2. Efficiencies for removal or conversion of CH₂O in dielectric barrier discharge plasmas. The gas mixture is N₂/O₂/H₂O=77/20/2. The removal efficiency is defined as amount of CH₂O converted (equivalent ppm at 1 atm, 300 K)/energy deposition in the plasma. (a) Removal efficiency as a function of gas temperature, showing improved efficiency with increasing T_g due to moderate activation energies in the oxidation of CH₂O. (b) Efficiency as a function of initial CH₂O concentration. The fractional removal efficiency is also shown.

essentially linearly with the initial gas temperature, a result of the initial oxidizing steps of CH₂O 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 [CH₂O]₀ 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 [CH₂O]₀ due primarily to a more efficient utilization of the reactant intermediates. O and OH which do not quickly react with small amounts of CH₂O will be otherwise consumed. Therefore increasing [CH₂O]₀ increases the probability that these oxidizing agents are beneficially used. The fractional removal

efficiency, defined as the fractional change in [CH₂O]/energy deposition, is relatively constant over four orders of magnitude of [CH₂O]₀, decreasing slowly with increasing [CH₂O]₀. These trends indicate that the conversion of CH₂O is not, for these conditions, limited by the production of O and OH, but by efficient utilization of those radicals.

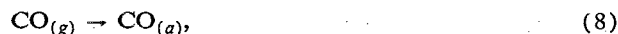
The dependence of the removal efficiency on the initial concentration of water was also investigated. Various gas mixtures were used with water mole fractions ranging from 0 to 0.1. Our results show that η does not strongly depend on water concentration, indicating that initial production of OH is not a rate limiting step. This condition results from the facts that reactions of O atoms with CH₂O produce OH as a product, and reactions of OH with CH₂O produce H₂O.

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, CH₂O, 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 CH₂O proceeds over a longer period of time as these radicals more slowly react. The densities of CH₂O, O, OH, CO, and NO are shown in Fig. 3(a) for 0.1 ms following a current pulse. The gas mixture is N₂/O₂/H₂O=77/21/2 at 450 K and [CH₂O]₀=500 ppm. Approximately 1.2×10^{15} cm⁻³ of CH₂O (75 ppm) is converted to CO and H₂O, while $\approx 2.5 \times 10^{15}$ cm⁻³ 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 CH₂O conversion during this time period are shown in Fig. 3(b). The CH₂O+OH channel accounts for about 75% of the CH₂O removed, while the CH₂O+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 H₂O, and to a lesser degree CO₂. 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.^{27–31} 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.*²⁷

The CO surface oxidation model consists of the following reactions:



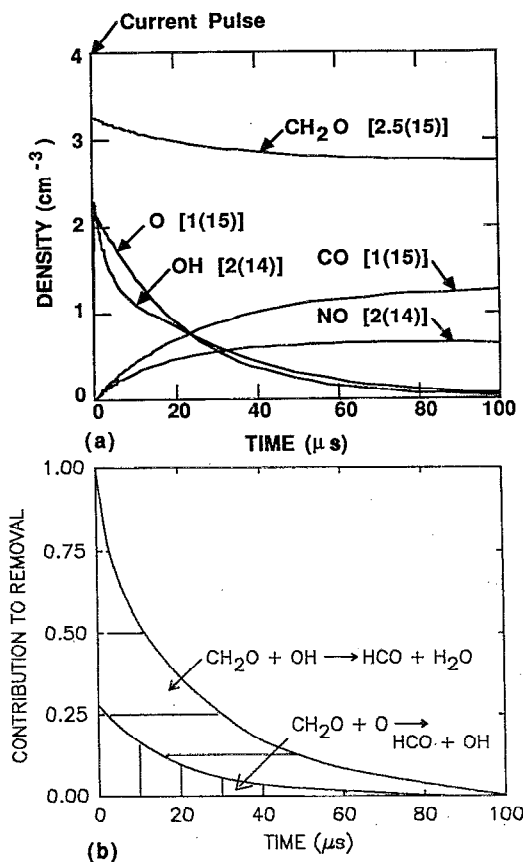
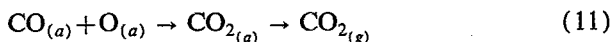


FIG. 3. Reactants and reactions following a current pulse (duration ≈ 50 ns) through a $N_2/O_2/H_2O=77/22/1$ mixture (450 K) with $[CH_2O]_0 = 500$ ppm. (a) Densities of reactants and products of oxidation of CH_2O . The densities plotted should be multiplied by the indicated values. (b) Relative contributions 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.²⁷ 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 $k_B \approx 20 \text{ s}^{-1}$, $k_C = 1.4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$.^{27,29} The sticking coefficient for carbon monoxide is essentially constant at ≈ 0.85 for fractional coverages less than 0.2, which is the regime of interest in this model.^{28,29}

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 $2\text{--}3 \times 10^{14} \text{ cm}^{-3}$ 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.²⁹

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 $\approx 5\text{--}20 \text{ W/m}^2$ 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,⁷ can be used to remove the remaining contaminant.

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