

Consequences of propene and propane on plasma remediation of NO_x

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Dielectric barrier discharge (DBD) reactors are being investigated for plasma remediation of NO_x from the exhaust of internal combustion engines and diesel emissions, in particular. In earlier works, it was found that unburned hydrocarbons (UHCs), inevitably present in exhausts, play a significant role in altering NO_x remediation pathways and increasing the oxidation of NO. In this study, the DBD processing of NO_x in simulated diesel exhausts with hydrocarbons [propane (C₃H₈) and propene (C₃H₆)] has been investigated. In general, the presence of UHCs improved the energy efficiency of remediation. For example, at 56 J/L, NO_x remediation improved from 12% without UHCs to 32% in the presence of 175 ppm propene. The *W*-values for NO remediation at 56 J/L decreased from 160 eV/molecule in the absence of UHCs to 96 eV/molecule with 175 ppm propene, though the majority of this improvement is a result of conversion to NO₂. Temperature dependencies of NO_x remediation were investigated and it was found that higher temperatures improve NO remediation whereas the effect on total NO_x remediation is not significant, implying that NO remediation at higher temperatures results from increased NO₂ formation. © 2000 American Institute of Physics. [S0021-8979(00)06018-7]

I. INTRODUCTION

Plasma remediation of exhaust from internal combustion engines, and diesel engines in particular, is being investigated as a means to remove nitrogen oxides (NO_x). Experimental and computational studies of corona¹⁻⁶ and dielectric barrier discharges (DBDs)^{1,2,7-10} have shown that NO remediation from atmospheric N₂/O₂/H₂O mixtures occurs primarily by conversion of NO to NO₂, and to a lesser degree by reduction by N atoms and oxidation by OH to HNO₂. The preferred channel, reduction by N atoms N+NO→N₂+O, is typically responsible for only a small fraction of NO remediation due to the difficulty of generating significant densities of N atoms using conventional pulse power. Fast rising voltage pulses capable of achieving high *E*/*N* (electric field/gas number density) are promising in this regard.¹¹

Actual diesel exhaust will inevitably contain unburned hydrocarbons (UHCs) from incomplete combustion of the fuel. Although the composition of the UHC depends on a number of factors (e.g., origin of the fuel, air-to-fuel ratio, compression ratio), it is, nevertheless, instructive to investigate the consequences of selected hydrocarbons on plasma remediation as model cases. For example, Niessen *et al.*¹⁰ showed that the *W*-value (energy/remediated molecule) for NO was reduced from 60 to 10 eV when 2000 ppmv ethene (C₂H₄) was included in a N₂/O₂/H₂O/NO/NO₂ gas mixture. The total remediation of NO_x was not significantly changed. They observed that reaction of NO with HOC₂H₄OO, the peroxy radical formed from ethene, resulted in its conversion

to NO₂. Studies have also been performed by Penetrante *et al.*¹² using propene as a representative UHC and their results show that the main fate of NO in the presence of hydrocarbons is its conversion to NO₂.

Since plasma remediation of NO using conventional discharges predominantly results in conversion to NO₂, significant NO_x remediation may require the additional use of catalysts. For example, studies were performed by Balmer *et al.*¹³ in which a catalyst-packed bed reactor was used in a surface discharge mode. They found that, with certain catalysts, the plasma-catalyst combination remediates nearly 100% of the NO with 60% going to NO₂ and 40% apparently being reduced to nitrogen. Another configuration separates the catalyst from the plasma by placing it downstream of the discharge. In experiments performed by Balmer *et al.*¹³ using such a system, they found that remediation of NO typically required less energy deposition for the same catalysts. Many catalyst systems are, however, sensitive to contamination by UHCs in the exhaust. Therefore, to optimize NO_x remediation both with and without catalysts, an improved understanding of plasma processing in the presence of UHCs is desirable.

The goal of this investigation was to computationally investigate the DBD processing of simulated diesel exhaust containing complex hydrocarbons, using as test gases propane (C₃H₈) and propene (C₃H₆). Parameterizations were performed over a wide range of power depositions, gas temperatures, and UHC concentrations. We found that with increasing energy deposition, although the NO_x remediation improved, the efficiency of the process decreased. The presence of UHCs significantly improved the remediation. In general, NO remediation improved with increasing energy

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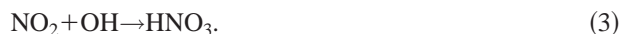
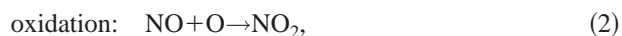
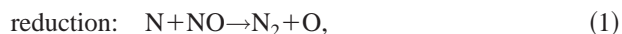
deposition, UHC concentration, and gas temperatures. NO_x remediation also improved with higher energy deposition, but remained almost unaffected with increasing hydrocarbon concentrations and gas temperatures. The model used in this study is described in Sec. II. An overview of the reaction mechanism is in Sec. III. Our results for NO plasma remediation in the presence of propane and propene are discussed in Sec. IV. Concluding remarks are in Sec. V.

II. DESCRIPTION OF THE MODEL

The model used in this study is a zero-dimensional global-kinetics simulation called GLOBAL_KIN.^{8,14} The model consists of a circuit module and a plasma chemistry module. Based on the user defined reaction mechanism, the plasma chemistry module formulates and integrates in time the differential equations which track the time evolution of charged and neutral species. The circuit module provides E/N in the plasma which is further used to obtain the rate coefficients of electron impact reactions based on the electron temperature. To facilitate this process, an offline table of electron impact rate coefficients as a function of electron temperature is initially generated by solving Boltzmann's equation for the electron energy distribution using a two-term spherical harmonic expansion over a selected range of E/N . This table is then interpolated during execution of GLOBAL_KIN. The resulting set of rate equations (including the circuit) is integrated over time using the LSODE stiff equation solver.¹⁵ The simulations reported here are of a single discharge pulse followed by a reactor residence time of 0.2 s. The gas gap in the DBD is held fixed at 2.5 mm. The energy deposition is adjusted by varying applied voltage, dielectric thickness, or dielectric permittivity. A full set of reaction rate coefficients are available in Ref. 14.

III. OVERVIEW OF THE REACTION MECHANISM

The reaction mechanism for plasma remediation of NO_x in humid air has been discussed in detail in Ref. 8. Briefly, the plasma chemistry in the NO_x -humid air system leads to NO_x remediation by two main channels, reduction by N atoms and oxidation,



The initiating radicals, N, O, and OH are produced by the electron impact reactions of N_2 , O_2 , and H_2O , respectively. They are:



HO_2 radicals also play an important role in converting NO to NO_2 as indicated by

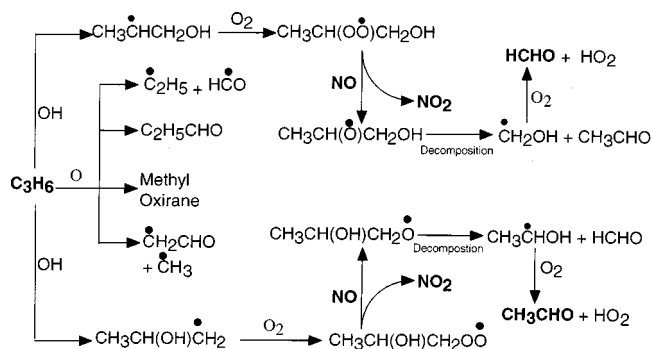


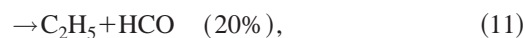
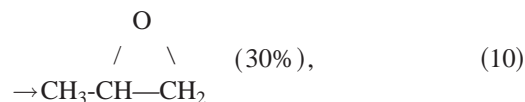
FIG. 1. Reaction mechanisms for NO_x in the presence of propene.

HO_2 radicals are primarily produced by the reaction of H with O_2 molecules;

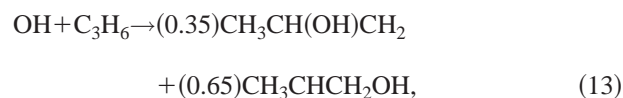


The mole fractions of UHCs in the systems of interest are typically $500\text{--}1000\text{ ppm}$. As a result, only a small fraction of the discharge energy is dissipated by collisions with the UHC. The majority of the discharge energy is dissipated by collisions with the large mole fraction species (e.g., $\text{N}_2, \text{O}_2, \text{H}_2\text{O}$) creating radicals (e.g., O, N, OH). Reactions with the UHCs are, therefore, dominated by reactions with radicals (as opposed to charged species).

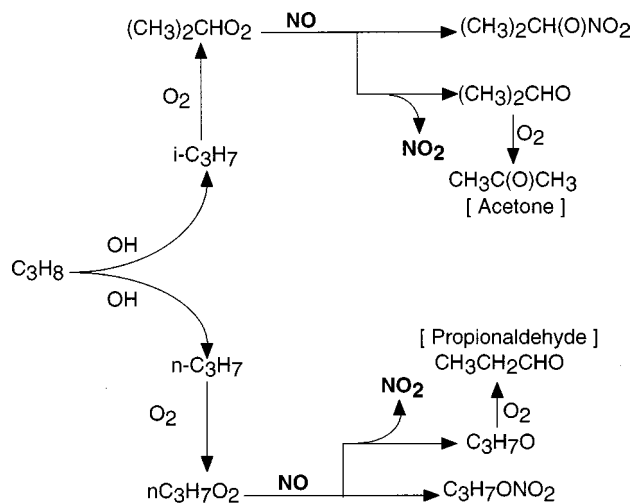
The reaction mechanism for the humid air-propene (C_3H_6)- NO_x system is summarized in Fig. 1.¹⁶ Briefly, the reaction mechanism is initiated by electron impact on O_2 and H_2O creating O and OH radicals. The reaction of O with propene proceeds along four channels,¹⁶



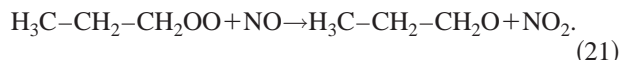
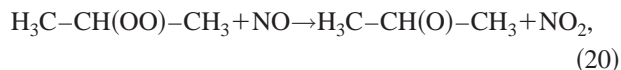
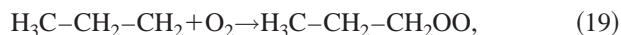
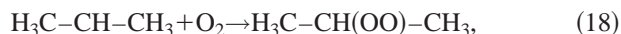
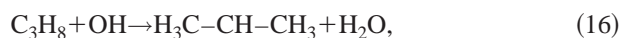
Hydroxy radicals add on to the carbon with the double bond in propene to produce hydroxyalkyl radicals. These radicals are rapidly consumed by O_2 to form the peroxy radicals which react with NO to convert it into NO_2 ,



The reaction mechanism for NO_x in the presence of propane (C_3H_8) is summarized in Fig. 2.¹⁶ The initiating reaction with propane is an abstraction reaction by OH producing alkyl radicals, as opposed to the addition reaction with pro-

FIG. 2. Reaction mechanism for NO_x in the presence of propane.

pane. The alkyl radicals then quickly react with oxygen to form peroxy radicals which then react with NO to produce NO_2 ;



The key step in this mechanism is the reaction of peroxy radicals with NO. As is the case with propene, these reactions produce NO remediation, but not NO_x removal, since the NO is largely converted to NO_2 . Propene is generally more reactive than propane because of the presence of the double bond.

IV. PLASMA REMEDIATION OF NO_x WITH PROPENE AND PROPANE

The base case for our study is a gas mixture containing 8% O_2 , 6% H_2O , 7% CO_2 , 400 ppm CO, 133 ppm H_2 , 260 ppm NO, and the remainder, N_2 , at 453 K. This mixture closely approximates that of actual exhausts and was chosen to allow comparison to experiments performed by others.¹⁷ An applied voltage of 22 kV to the DBD reactor results in an energy deposition ≈ 30 J/L. Peak electron densities for this energy deposition are approximately 10^{13} cm^{-3} and the peak electron temperature is ≈ 3 eV as shown in Fig. 3(a). The discharge pulse usually lasts around 100 ns. A typical time evolution of N, OH, O_3 , NO, and NO_2 in the absence of UHCs is shown in Fig. 3(b). In the initial stages ($t < 10 \mu\text{s}$), most of the NO remediation is by reduction by N atoms [Eq. (1)]. Later, and until 1 ms the reactions of O with NO produce NO_2 [Eq. (2)]. After this period, the remediation of NO mainly proceeds by reaction with O_3 ;

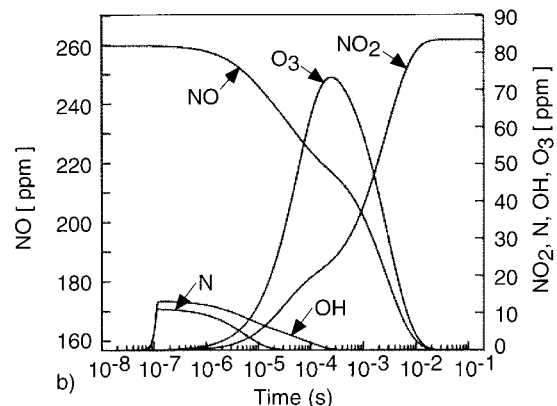
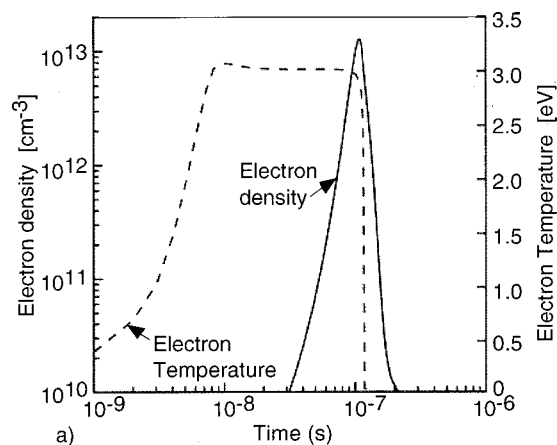


FIG. 3. Time evolution of plasma properties and NO_x chemistry initiators. (a) electron density and temperature. (b) N, OH, O_3 , NO, and NO_2 . These results are for a typical dielectric barrier discharge in the absence of hydrocarbons for an energy deposition of 30 J/L and an initial gas mixture of $\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{CO}_2 = 79/8/6/7$ with 400 ppm CO, 133 ppm H_2 and 260 ppm NO (1 atm, 453 K). The current pulse is ~ 100 ns. NO remediation proceeds primarily by the reaction with O_3 .



The exit concentrations of NO, NO_2 , NO_x , and CO as a function of energy deposition are shown in Fig. 4(a). At the highest energy deposition (56 J/L), the NO_x remediation is $\approx 12\%$. A major portion of the NO_x remediated appears in the form of HNO_2 . The additional CO is mainly produced by the electron impact dissociation of CO_2 ,



The addition of propane to the base case was investigated as an idealized UHC. The concentrations of NO, NO_2 , NO_x , and C_3H_8 as a function of energy deposition are shown in Fig. 4(b) for 175 ppm propane. In comparison to the base case, there is a small increase in the remediation of NO_x . This is attributed to the increased conversion of NO to NO_2 [by reaction products of propane with OH through the reactions in Eqs. (20) and (21)], which in turn is converted into HNO_3 ,



These reactions contribute little to the overall remediation of NO_x due to the low reactivity of propane, which is reflected by the fact that only 17 ppm of propane is consumed at 56

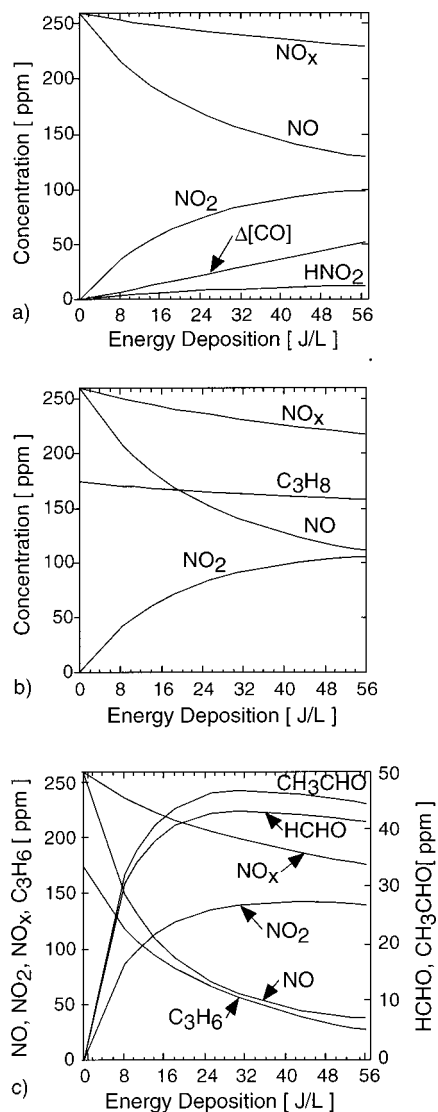
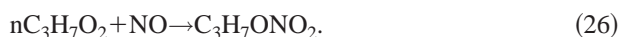


FIG. 4. Exit concentrations as a function of energy deposition. (a) NO, NO₂, NO_x, HNO₂, and increase in CO for remediation in the absence of UHCs. The conditions are same as for Fig. 3. (b) NO, NO₂, NO_x, and propane. Inlet gas conditions are same as for Fig. 3 except for the addition of 175 ppm of propane. NO_x removal improves slightly over the case with no hydrocarbons. (c) Species densities for the humid air-propene-NO_x system. Initial gas mixture is same as for Fig. 3 except for the addition of 175 ppm of propene. NO remediation improves due to the oxidation reactions, CH₃CH(OH)CH₂OO+NO→CH₃CH(OH)CH₂O+NO₂ and CH₃CH(OO)CH₂OH+NO→CH₃CH(O)CH₂OH+NO₂. Primary end products of OH initiated reactions with propene include HCHO and CH₃CHO.

J/L. Small improvements in NO_x remediation over the base case also result from the formation of (CH₃)₂CH(O)NO₂ and C₃H₇ONO₂;

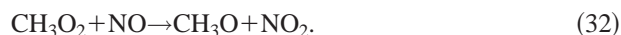


For comparison, 175 ppm of propene was added to the base mixture instead of propane. The final concentrations as a function of energy deposition are shown in Fig. 4(c). Adding propene significantly improves the remediation of NO_x. About 85 ppm of NO_x is removed at 56 J/L, an improvement

of 54 ppm over the base case. The additional NO_x remediation is mainly due to the formation of the nitrites, C₂H₅ONO and CH₃ONO;



The radicals reacting with NO are produced by



The additional reactivity of C₃H₆ results in larger rates of consumption of propene. For example, at 56 J/L, as much as 150 ppm of C₃H₆ is consumed, or 86%. The carbon from the consumed C₃H₆ is primarily converted to HCHO and CH₃CHO. These products generally increase with increasing energy deposition to ≈25 J/L. At higher energy deposition, the exit concentrations of these species decrease, as will be discussed.

The fractional remediation of NO_x without UHCs and with propane and propene addition as a function of energy deposition are compared in Fig. 5(a). With propene, a maximum remediation of 32% is obtained at an energy deposition of 56 J/L, while 16% remediation is obtained with propane and 11% without UHCs.

The energy efficiency of the remediation processes was quantified by the amount of energy required to remove one molecule of the toxin (*W*-value). Lower *W*-values are more efficient. The *W*-values for the base case without UHCs, with propane and with propene are shown in Fig. 5(b). At low energy deposition, the smallest *W*-values (highest efficiency) for NO_x removal are for propene addition, ≈130 eV/molecule and the largest (least efficient) are without UHCs, ≈470 eV/molecule. The *W*-values for NO remediation are the smallest for propene addition and largest for the base case. The smaller *W*-values for NO compared to NO_x reflect that the majority of the remediated NO is converted to NO₂. The presence of UHCs improves the efficiency of NO_x removal, lowering *W*-values to <150 eV at low energy deposition.

Experiments were performed at Ford Research Labs using a DBD reactor with inlet gas containing 175 ppm C₃H₈ and 500 ppm C₃H₆ in addition to the base case gas mixture.¹⁴ The reactor temperature was 453 K, the residence time was 0.2 s, and the energy deposition was 30 J/L. The products were measured with a chemiluminescent analyzer and a Fourier transform infrared spectrometer. Simulations were performed for these conditions and the results for the exit NO and NO₂ concentrations as a function of energy deposition are shown in Fig. 6. The presence of UHCs has a significant impact on NO and NO₂ remediation for these conditions. At high energy deposition, nearly 99% of NO is remediated. The majority of the NO is converted to NO₂. Comparison to the experimental data confirm the trend of high degrees of NO but low degrees of NO_x conversion.

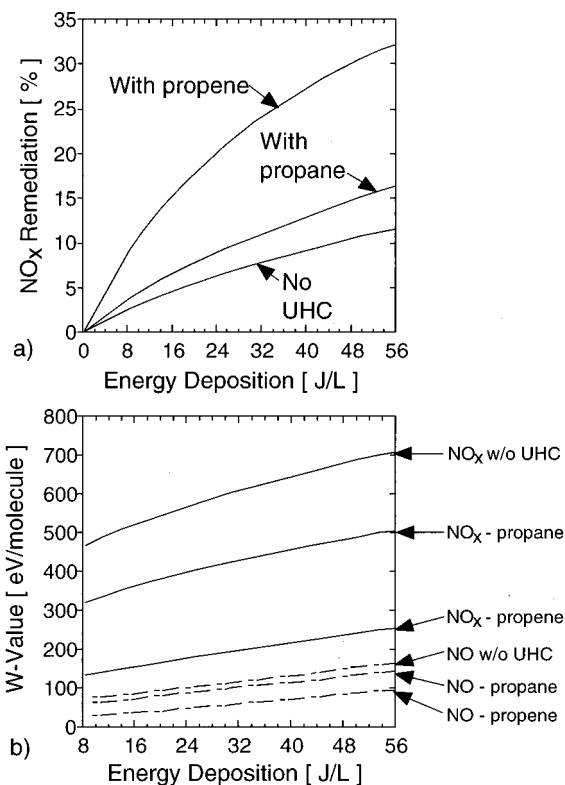


FIG. 5. Remediation metrics as a function of energy deposition. (a) NO_x remediation for the NO_x-humid air mixture with no UHCs in inlet, 175 ppm of propane in the feed, and 175 ppm of propene in the feed. Other conditions are as given in Fig. 3. NO_x remediation improves with UHCs because of the increased formation of nitrites and nitrates. (b) W-values (eV/molecule) for NO and NO_x remediation for feeds containing no UHCs, 175 ppm propane, and 175 ppm propene. Remediation of NO_x improves with the UHCs, with propene's contribution to remediation being larger than that of propane. UHCs, in general, are more effective with respect to NO remediation than NO_x remediation.

The consumption of the UHCs is shown in Fig. 7 as a function of energy deposition. When adding propane, there is a small decrease in the consumption of propene due to the increased competition from propane for radicals (principally OH and O). Propane consumption is ≈5% at an energy deposition of 56 J/L. The majority of the consumption of the

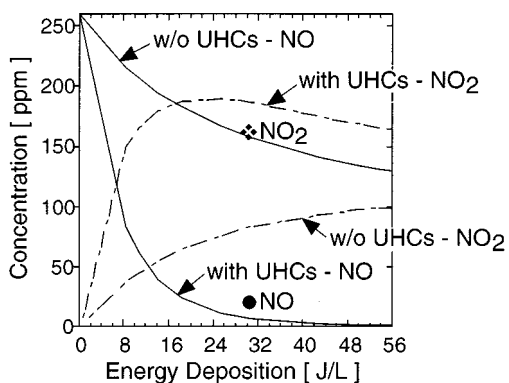


FIG. 6. Variation of NO and NO₂ as a function of energy deposition for the feed containing no hydrocarbons and the feed containing both 175 ppm propane and 500 ppm propene. Experimental values are shown for NO (circles) and NO₂ (crosses) for UHCs. Conditions of operation are as given in Fig. 3.

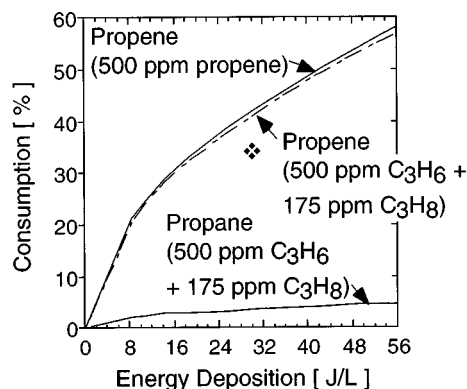


FIG. 7. Consumption of propene and propane for an initial mixture of 500 ppm propene and 175 ppm propane; and 500 ppm propene only. The experimental value (shown by the symbol) is for the feed containing 500 ppm propene and 175 ppm propane. In the presence of propane, propene conversion decreases due to the increased competition from propane for the initiating radicals (principally OH).

UHCs is a result of oxidation reactions with O and OH. CO is not directly produced by those reactions. The products of those reactions do, however, further react to produce CO. The major reactions which produce and consume CO are



One, therefore, would expect an increase in oxidation products, principally CO and CO₂, with increasing energy deposition and radical production. This is confirmed by the results shown in Fig. 8(a) where the increase in CO above the inlet value (400 ppm) is shown as a function of energy deposition. Adding propane to propene produces small decreases in CO production. This is due to the small reduction in the production of its precursors from propene, a consequence of the competition from propane for the initiating radicals, OH and O. The time-integrated contributions to the production of CO from the reactions in Eqs. (33)–(37) are shown in Fig. 8(b). The major producer of CO is the electron impact dissociation of CO₂, due to the large initial mole fraction of that species. The second largest producer is reaction of HCO with O₂, where HCO is directly generated by O reactions with propene [Eq. (11)].

Typical end products of the plasma remediation of NO with UHCs include formaldehyde (HCHO), methyl oxirane (C₃H₆O), propionaldehyde (C₂H₅CHO), glyoxal (CHO-CHO), methyl nitrate (CH₃ONO), methyl nitrate (CH₃ONO₂), and 2-nitroso ethanal (ONCH₂CHO). The outlet concentrations of these species as a function of energy deposition are shown in Fig. 9(a). These products are dominantly formed by the primary or secondary reactions of the products of OH and O with propene and propane. The primary reactions in Eqs. (9), (10), (12), and (13) generate propionaldehyde, methyl oxirane, CH₂CHO, and

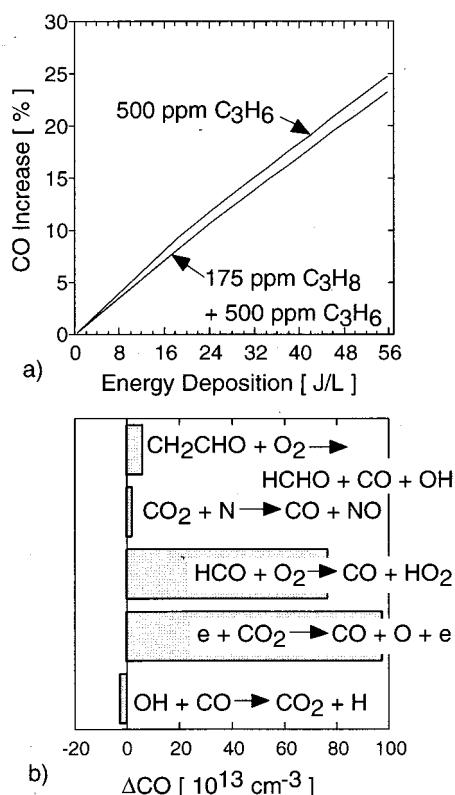
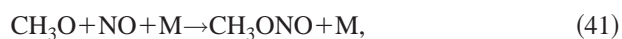
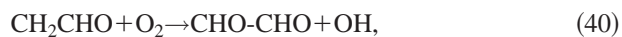
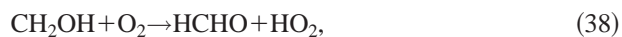


FIG. 8. Production and consumption of CO. (a) Increase in CO as a function of energy deposition in gas mixtures containing 500 ppm propene; and 500 ppm propene+175 ppm propane. (b) Time-integrated contributions for the formation and consumption of CO. Inlet gas contains 500 ppm propene and 175 ppm propane. The energy deposition is 30 J/L.

CH₃CH(OH)CH₂, respectively. The secondary reactions involve chains with the primary products resulting in CH₃O and CH₂OH;



Predictions for production of HCHO generally agree with experimental data at 30 J/L, as shown in Fig. 9(a). Note that the concentration of HCHO initially increases but, subsequently, decreases with increasing energy deposition. These trends are explained by the time integrated production of HCHO shown in Fig. 9(b). The two dominant pathways for HCHO production are the reactions in Eqs. (38) and (39). The initiating species for these reactions, CH₂OH and CH₃CH(OH)CH₂O are generated by a chain in which OH reacts with propene, producing compounds which in turn react with O₂ to form peroxy radicals [Eqs. (13)–(15)]. Reac-

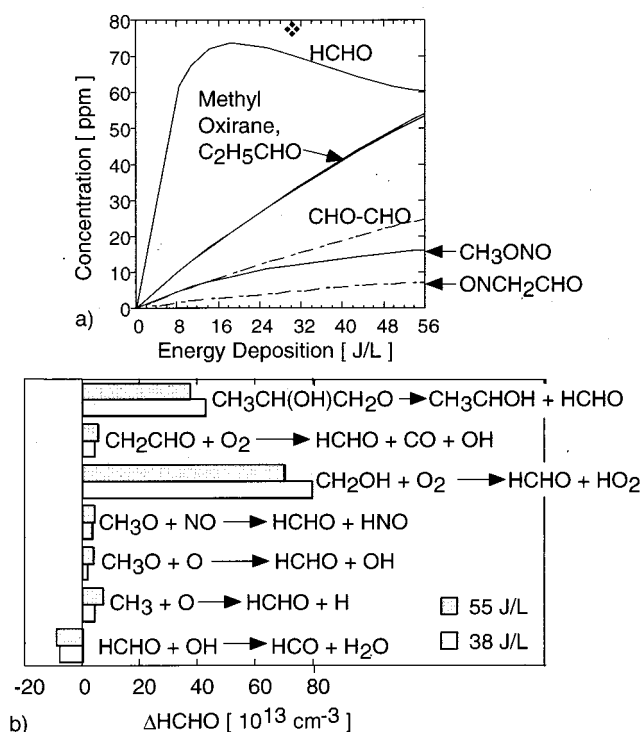
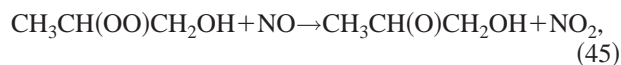
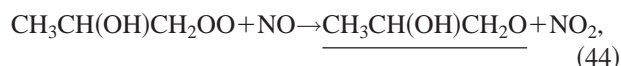


FIG. 9. Production and consumption of C_xH_yO_z products. (a) End products of propene–propane–humid air–NO_x system as a function of energy deposition. The feed consists of the base gas mixture with 500 ppm propene and 175 ppm propane. The experimental value for HCHO at 30 J/L is denoted by the symbol. (b) Time-integrated contributions for the formation and consumption of HCHO for energy depositions of 38 and 55 J/L. The feed to the DBD reactor contains 175 ppm propane and 500 ppm propene but otherwise the conditions are as given in Fig. 3.

tion of those peroxy radicals with NO produces CH₃CH(OH)CH₂O and the precursor CH₃CH(O)CH₂OH, which decomposes to produce CH₂OH;



CH₂OH then quickly reacts with O₂ to produce HCHO by the reaction in Eq. (38).

The time integrated contributions to NO production and consumption for remediation with and without UHCs are given in Fig. 10. In the presence of UHCs NO is mainly consumed by reactions in Eqs. (44) and (45), and,



With increasing energy deposition, more HO₂ is produced which then becomes the major oxidizer of NO. This decreases the amount of NO available for the reactions in Eqs. (44) and (45) and, hence, the production of CH₃CH(OH)CH₂O and CH₂OH decreases. Since the reactions in Eqs. (38) and (39) are the major precursors for HCHO production [Fig. 9(b)], the overall formation of HCHO goes down with increasing energy deposition. The

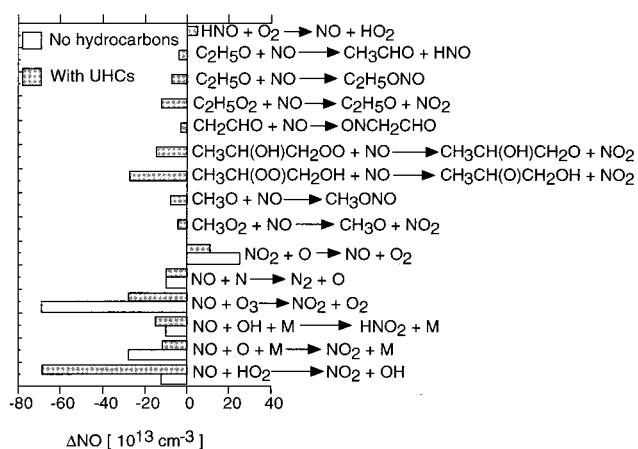
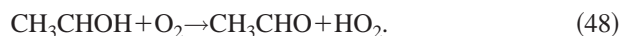


FIG. 10. Production and consumption of NO for a feed with no UHCs, and a feed with 175 ppm propane and 500 ppm propene. The background gas mixture is as given in Fig. 3.

same reasoning can be extended to explain the decrease in CH_3CHO at higher energy deposition by considering the reactions in Eqs. (46) and



Larger production of O atoms at higher energy deposition directly results in increased productions of methyl oxirane, $\text{C}_2\text{H}_5\text{CHO}$, 2-nitroso ethanal, glyoxal, and methyl nitrite because of the increased rates of the reactions in Eqs. (9)–(12). Accordingly, the W -values for NO and NO_x are shown in Fig. 11 as a function of energy deposition. With increasing energy deposition, the W -value for NO increases from 19 eV/molecule at 8 J/L to 84 eV/molecule at 56 J/L. The W -value for NO_x increased from 117 eV/molecule at 8 J/L to 221 eV/molecule at 56 J/L.

The effect of propene concentration on NO_x remediation has been addressed in detail in Ref. 18. Briefly, increasing the propene concentration increases the conversion of NO to NO_2 and so improves NO remediation. However, NO_x reme-

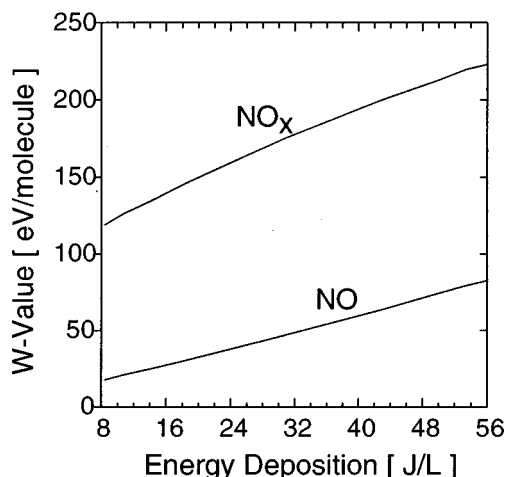


FIG. 11. W -values for NO_x and NO as a function of energy deposition. Inlet gas contains 175 ppm propane and 500 ppm propene. Other conditions are the same as given in Fig. 3. At higher energy deposition, the process become less efficient.

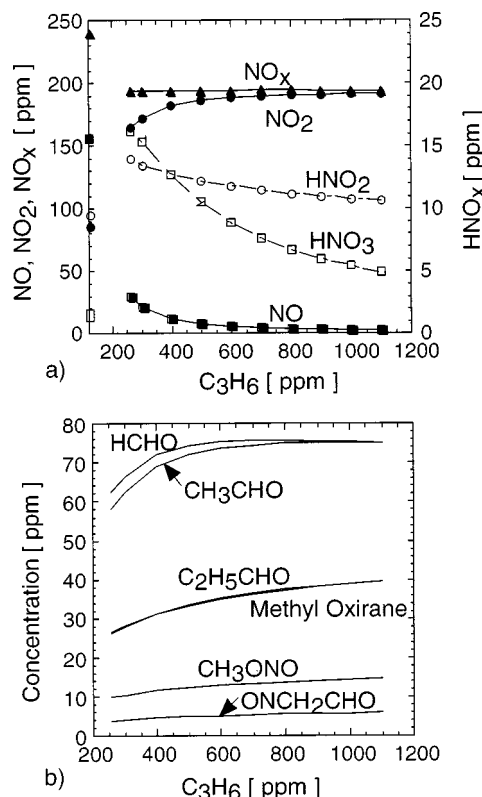


FIG. 12. Exit concentrations as a function of inlet propene. (a) NO, NO_2 , NO_x , HNO_2 and HNO_3 . Background gas composition is the same as in Fig. 3. The energy deposition is 30 J/L. Values on vertical axis are for no propene. (b) Hydrocarbon end products as a function of inlet propene.

diation remains almost unaffected. For example, the variations of NO and NO_2 as a function of inlet propene concentration are shown in Fig. 12(a). Increasing the initial concentration of propene results in a larger production of peroxy radicals [Eqs. (13)–(15)] which in turn results in an increased consumption of NO [Eqs. (44) and (45)]. With increasing propene, the number of radicals (OH, O) available for other reactions decreases and, as a result, the concentrations of HNO_3 and HNO_2 decrease. The concentrations of the C containing end products are shown in Fig. 12(b) as a function of inlet propene concentration. With increasing propene concentration, the final product concentrations also increase, though at a smaller rate than the increase in C_3H_6 . This trend is a consequence of there being a finite supply of O and OH radicals at the fixed energy deposition.

The propane concentration in the feed was varied from 50–800 ppm, holding the inlet concentrations of other species and the energy deposition, 30 J/L, constant. Due to the low reactivity of propane, increasing propane had a small effect on the NO_x remediation. For example, NO and NO_x remediation as a function of inlet propane concentration are shown in Fig. 13(a). The overall NO_x conversion remained at a constant level. Most of the NO remediated by the additional propane appeared as NO_2 due to the reactions in Eqs. (20) and (21).

Propene and propane consumption decreased with increasing inlet propane concentration as shown in Fig. 13(b). At a constant energy deposition and a constant background

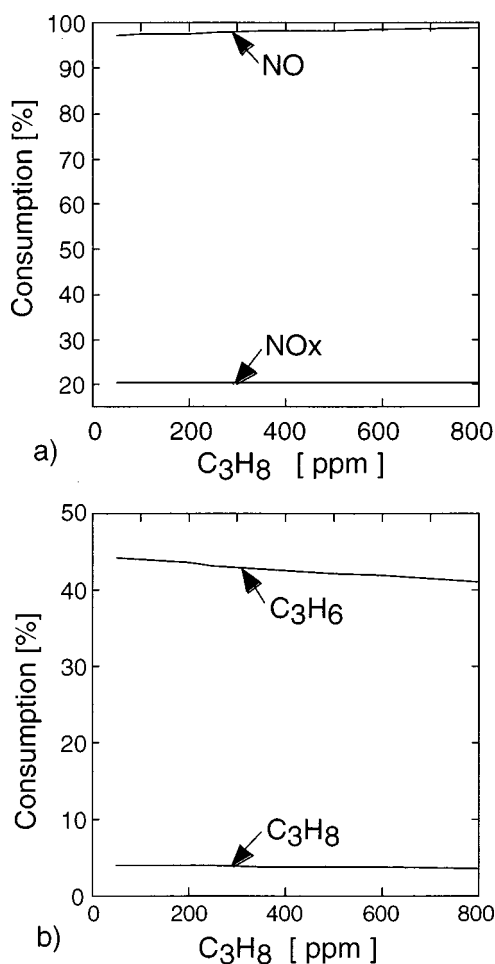
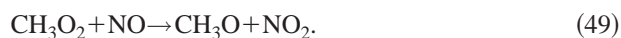


FIG. 13. Exit concentrations as a function of inlet propane for 30 J/L. (a) NO and NO_x consumption. Feed contains 500 ppm propene with the background gas composition as in Fig. 3. NO remediation improves with [C₃H₈] whereas NO_x remains almost unaffected. (b) Propane and propene consumption. Propene consumption decreases due to the increased competition from propane for the initiating radicals.

gas composition, the production of initiating radicals is approximately constant. Hence, with increasing propane, the reactions of the finite supply of radicals with propane reduces the availability of radicals for reactions with propene. However, this effect is not very pronounced due to the lower reactivity of propane compared to propene. Although a larger amount of propane is consumed at higher mole fractions, the fractional consumption is lower. The concentrations of the final N containing products are shown in Fig. 14(a) as a function of propane concentration. The concentration of ONCH₂CHO is almost unaffected by the level of C₃H₈. This is because ONCH₂CHO is largely formed from the products of the reactions of O with propene. Since propane does not react rapidly with O, the final concentration of ONCH₂CHO remains unaffected. The decrease in the concentration of CH₃ONO is due to the decreased availability of NO for reaction with CH₃O. CH₃O is mainly produced by the reaction,



The small increase in HNO₂ can be attributed to the increased rate of the reaction of HO₂ with NO₂. This results

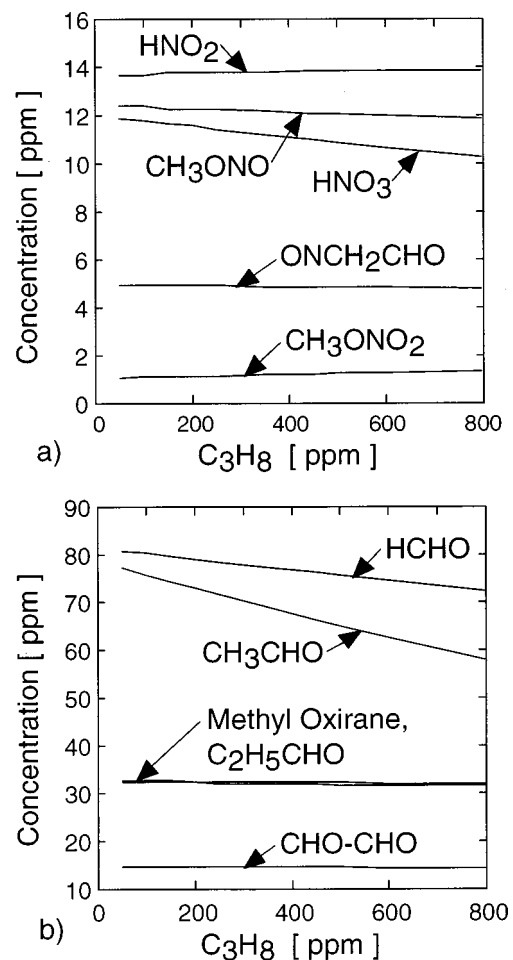


FIG. 14. End products as a function of inlet propane for an energy deposition of 30 J/L. (a) N-containing end products. CH₃ONO decreases because of the reduced availability of NO for the reaction CH₃O+NO→CH₃ONO. (b) Hydrocarbon end products. HCHO and CH₃CHO decrease with increasing [C₃H₈]. Methyl oxirane, C₂H₅CHO, and CHOCHO remain unaffected because propane does not directly influence the concentration of O atoms, which is the precursor for these compounds.

from the larger production of NO₂ from the reactions of the propane generated peroxy radicals [Eqs. (20) and (21)];



The concentration of HNO₃, however, decreases with increasing propane because of the reduction in the concentration of OH [Eq. (24)]. Since increasing propane depletes OH, the availability of OH for reaction with NO₂, which produces HNO₃, decreases. This decrease is larger than the increase in NO₂ due to the propane and so the concentration of HNO₃ decreases. Other end products are shown as a function of inlet propane concentration in Fig. 14(b). More propane produces more NO remediation by the reactions with the propane-initiated peroxies [Eqs. (20) and (21)]. As a result, smaller amounts of HCHO and CH₃CHO are produced. Methyl oxirane, CHO-CHO and C₂H₅CHO are not significantly affected by propane addition because the O atom production is not directly affected at constant energy deposition.

Species concentrations as a function of reactor temperature are shown in Fig. 15(a) for propane at 175 ppm, propene at 500 ppm, and an energy deposition of 30 J/L. NO reme-

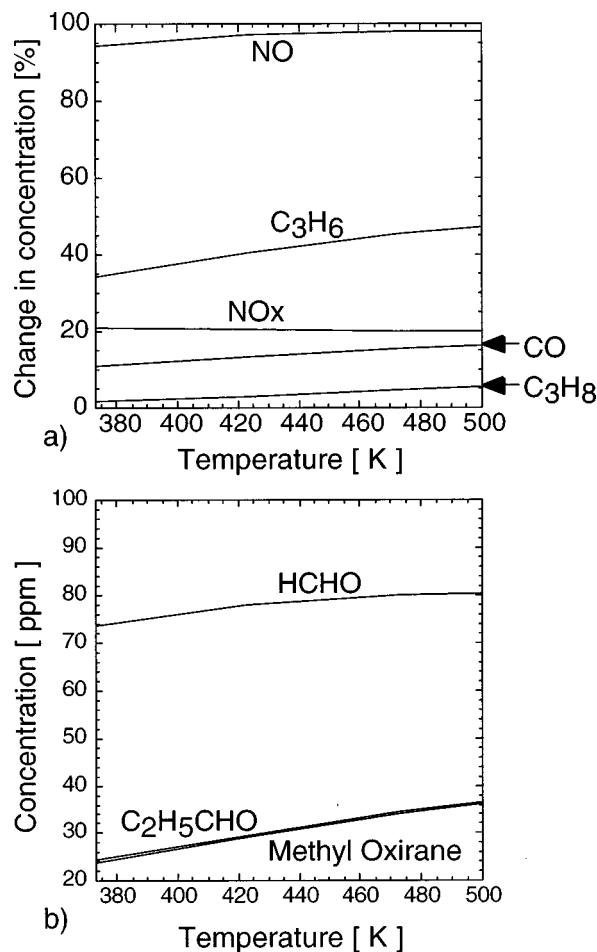


FIG. 15. Exit concentrations as a function of reactor temperature for 175 ppm propane and 500 ppm propene at an energy deposition of 30 J/L. (a) NO, C₃H₆, NO_x, CO, and C₃H₈. (b) HCHO, C₂H₅CHO, and methyl oxirane.

diation increased with temperature while NO_x conversion remained almost unchanged. Propene and propane consumption also increased with temperature. CO production increased from 10% to 22% with a temperature rise from 373 to 500 K. The rate coefficients for the reactions that lead to the formation of HCHO, methyl oxirane, and C₂H₅CHO increase with temperature and hence, there is a rise in the formation of these compounds with temperature as shown in Fig. 15(b).

V. CONCLUDING REMARKS

The combined effects of an alkene (propene) and an alkane (propane) in a simulated diesel exhaust on NO_x processing in a DBD were investigated. As much as 37% NO_x remediation was obtained at of 56 J/L with propene and propane addition corresponding to a *W*-value of 225 eV/molecule NO_x. Although NO_x remediation increased with increasing energy deposition, the efficiency of the process decreased. With propane and propene as UHCs, the major N containing end products included CH₃ONO, HNO₂, HNO₃, and C₂H₅ONO. The extra NO_x remediation resulting from adding UHCs came from the direct formation of these or-

ganic nitrites and nitrates and the indirect acceleration of HNO₃ formation because of the increase in the concentration of NO₂. Propane made a small contribution to the overall NO_x remediation, although its effect on NO remediation was appreciable. Increasing temperature increased NO remediation while NO_x remediation was nearly unaffected.

In this study, the term “NO_x remediation” has been used to describe the total removal of nitrogen oxides from the exhaust stream with no value judgement made concerning the ultimate fate of the products of the remediation process in the atmosphere. It is possible that the final products in the remediated exhaust (e.g., organic nitrates, nitrites, nitrous, and nitric acids) could participate in photolytically initiated reactions resulting in the regeneration of NO_x. For example, the deep ultraviolet photolysis of organic nitrites and nitrates, nitrous, and nitric acids results in the formation of NO₂, NO, alkoxy radicals, and OH, the end result of which can also increase ozone production.¹⁹ Products such as formaldehyde, acetaldehyde, and other organic nitrates and nitrites could also pose health risks. Although an assessment of the final disposition in the atmosphere of these remediation products is beyond the scope of this study, their predicted production does emphasize the need to perform a global analysis as to the benefits of any given remediation technology.

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- B. M. Penetrante, M. C. Hsiao, B. T. Merritt, G. E. Vogtlin, P. H. Wallman, M. Neiger, O. Wolf, T. Hammer, and S. Broer, *Appl. Phys. Lett.* **68**, 3719 (1996).
- B. M. Penetrante, M. C. Hsiao, and B. T. Merritt, *IEEE Trans. Plasma Sci.* **23**, 679 (1995).
- R. H. Amirov, E. I. Asinovsky, I. S. Samoilov, and A. V. Shepelin, *Plasma Sources Sci. Technol.* **2**, 289 (1993).
- Y. S. Mok and I.-S. Nam, *IEEE Trans. Plasma Sci.* **27**, 1188 (1999).
- Y. S. Mok, S. W. Ham, and I.-S. Nam, *IEEE Trans. Plasma Sci.* **26**, 1566 (1998).
- J. Y. Park, I. Tomicic, G. F. Round, and J. S. Chang, *J. Phys. D: Appl. Phys.* **32**, 1006 (1999).
- R. Wegst, M. Neiger, H. Russ, and S. Liu, *International Fall Fuels & Lubricants Meeting and Exposition, Toronto, Canada, 1999* (Society of Automotive Engineers, Warrendale, PA, 1999).
- A. C. Gentile and M. J. Kushner, *J. Appl. Phys.* **78**, 2074 (1995).
- K. Takaki, M. A. Jani, and T. Fujiwara, *IEEE Trans. Plasma Sci.* **27**, 1137 (1999).
- W. Niessen, O. Wolf, R. Schruft, and M. Neiger, *J. Phys. D: Appl. Phys.* **31**, 542 (1998).
- P. A. Vitello, B. M. Penetrante, and J. N. Bardsley, *Phys. Rev. E* **49**, 5574 (1994).
- B. M. Penetrante *et al.*, SAE Technical Paper No. 982508, 1998.
- M. L. Balmer, R. Tonkyn, S. Yoon, A. Kolwaite, S. Barlow, G. Maupin, T. Orlando, and J. Hoard, in Ref. 7.
- R. Dorai, M. S. thesis, 2000 (<http://uigelz.ece.uiuc.edu/theses.html>).
- A. C. Hindmarsh, Lawrence Livermore Laboratories, 1987 (unpublished).
- Roger Atkinson, *J. Phys. Chem. Ref. Data* **26**, 215 (1997).
- John Hoard (private correspondence).
- R. Dorai and M. J. Kushner, in Ref. 7.
- B. J. Finlayson-Pitts and J. N. Pitts, *Atmospheric Chemistry: Fundamentals and Experimental Techniques* (Wiley, New York, 1994).