Formation of Methyl Nitrite and Methyl Nitrate during Plasma Treatment of Diesel Exhaust

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FTIR spectroscopy was used to identify CH₃ONO and CH₃ONO₂ as products of the nonthermal plasma treatment of simulated diesel exhaust. This is the first observation of CH₃ONO formation in such systems. The yield of CH₃-ONO relative to CH₃ONO₂ scaled linearly with the average [NO]/ [NO₂] ratio in the system. A plot of [CH₃ONO]/[CH₃ONO₂] versus [NO]/[NO₂] gives a slope of 1.81 ± 0.30 . This result is indistinguishable from the literature value of the rate constant ratio $k(CH_3O + NO)/k(CH_3O + NO_2) = (2.6 \times 10^{-11})/$ $(1.5 \times 10^{-11}) = 1.73 \pm 0.37$. The experimental observations suggest that reactions of CH₃O radicals with NO and NO₂ are the sources of CH₃ONO and CH₃ONO₂ in such systems. The linear relationship between the yields of CH₃-ONO and CH₃ONO₂ provides a means of estimating the yield of these compounds during nonthermal plasma treatment of diesel exhaust.

Introduction

Concerns about global climate change have increased the pressure on automobile manufacturers to increase vehicle fuel efficiency. Diesel vehicles have superior fuel economy and approximately 20-30% lower CO₂ emissions than their gasoline counterparts. Unfortunately, NO_x emissions from diesel engines are difficult to control to proposed future emissions standards. Modern spark-ignition engines operate at stoichiometry, and NO_x emissions are controlled by a three-way catalytic converter. In contrast, diesel engines operate fuel lean, and the exhaust contains substantial amounts of O₂ (typically 6–10%). The reduction of NO_x by a three-way catalyst in such oxidizing environments is difficult (1).

Nonthermal plasma discharge combined with a downstream catalyst is a technology under evaluation for use in the removal of NO_x from diesel exhaust (2-8). The details of the gas-phase chemistry occurring in the plasma discharge of exhaust gas are unclear. It is believed that O(³P) atoms and, to a lesser extent, OH radicals are the dominant species responsible for initiating hydrocarbon oxidation in such systems (9). However, the subsequent chemistry occurring during nonthermal plasma treatment of diesel exhaust is not fully understood. Optimization of the efficiency of plasma exhaust treatment devices and assessment of their utility in controlling NO_x emissions from diesel vehicles requires an understanding of the gas-phase chemistry in such devices. Methyl nitrate, CH₃ONO₂, is produced during the nonthermal plasma treatment of simulated diesel exhaust (*10*). CH₃ONO₂ is believed to be formed via the association reaction between CH₃O radicals and NO₂ (*10*):

$$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$$
 (1)

If reaction 1 is indeed the source of CH_3ONO_2 , then there should also be significant formation of methyl nitrite, CH_3 -ONO, by the analogous reaction with NO:

$$CH_3O + NO + M \rightarrow CH_3ONO + M$$
 (2)

CH₃ONO photolyzes rapidly in the sunlit atmosphere, releasing NO_x and generating OH radicals which can promote the formation of urban smog. An understanding of the possible formation of CH₃ONO in vehicle exhaust is clearly of interest. While its presence has been predicted by kinetic models (*11, 12*), the observation of CH₃ONO in plasma treatment systems has not been reported. As part of a collaborative research effort in our laboratories to elucidate the chemistry in nonthermal plasma devices, an investigation of the formation of CH₃ONO was undertaken. The aim of the present work was to determine if, and how, CH₃ONO is formed in such systems.

Experimental Section

The experimental system used in the present work is described in detail elsewhere (10). Figure 1 is a schematic of the apparatus. NO, NO₂, CO, CO₂, O₂, C₃H₆, and C₃H₈ gases can be mixed in N2 carrier. Liquid water can be injected into the gas in heated lines. For the experiments here, a simplified gas blend was used, consisting of C₃H₆, O₂, NO, and NO₂. Previous experiments have shown little or no impact of the other components listed above on the chemistry occurring in the system (9, 10), and their presence (especially H₂O) complicates the FTIR measurements. The test plasma was in an oven which was maintained at either 30 or 180 °C. The effluent was mixed with extra N₂ at a ratio of 2.5:1 dilution, to match flow rates to the analytical equipment, and passed through measurement instrumentation. The principal analytical instrument is a Mattson Nova Cygni FTIR spectrometer operated at room temperature with a spectral resolution of 0.25 cm^{-1} and equipped with a long-path-length (20.7 m) Foxboro sampling cell. A Horiba FIA-220 flame ionization detector, a MPA-220 magnetopneumatic oxygen analyzer, a CLA-220 chemiluminescent NO_x analyzer, and AIA-220 NDIR CO and CO₂ analyzers were also used.

The present study is an extension of our previous work in which FTIR spectroscopy was used to identify CH₃ONO₂ formation (10). In our previous work we did not observe the presence of CH₃ONO. The IR features of CH₃ONO are significantly weaker than those of CH₃ONO₂ in the 700–900 cm⁻¹ region of the spectrum where the FTIR analysis is performed. CH₃ONO may have been present in the previous experiments, but we would not have been able to detect it. To improve the detection sensitivity in the present experiments, three changes to the experimental protocol were made. First, we employed 512 (rather than 32) co-added interferograms, giving IR spectra with 4-fold better S/N at the cost of a 16-fold (768 s versus 48 s) increase in data acquisition time. Second, instead of diluting the sample gas with N₂ 10:1 prior to passing through the FTIR cell to minimize exposure of the moisture-sensitive optical components to

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FIGURE 1. Schematic of the test lab configuration (FTIR, Fourier transform infrared spectrometer; FID, flame ionization detector for hydrocarbons; CLA, chemiluminescence NO_x analyzer). A schematic of the plasma is shown in the oven.

 H_2O vapor, the exhaust gas was diluted only 2.5:1. Third, a simplified gas blend was used as mentioned above. The detection limits for CH₃ONO and CH₃ONO₂ in the present experiments were 2.0 and 0.3 ppm, respectively.

In the tests reported here, the gas composition was 500-740 ppm C_3H_6 , 8% O_2 , and 0–420 ppm both NO and NO₂ in 1 atm of N₂ diluent. A sketch of the dielectric barrier discharge device used to generate a plasma is shown (in the oven) in Figure 1. It consists of two 24×100 mm sheets of alumina. Each sheet has a conductive electrode embedded in it. The two sheets are bonded together with a ceramic adhesive, leaving a gap of 1.3 mm between the sheets (13). The assembly is mounted in a quartz tube such that all the gas must flow through the gap between sheets. The two electrodes are connected to a Trek 10/10 high-voltage amplifier driven by an HP33120A function generator. For these tests, the excitation wave was a 250 Hz triangle wave with peak voltage between 5 and 6 kV, adjusted so that the energy density is 30 J of energy/L of gas flow (typical of that which may be used in passenger car applications) when the plasma is turned on. The gas residence time in the oven was approximately 10 s.

Methyl nitrite, CH₃ONO, was synthesized by the dropwise addition of concentrated H_2SO_4 to a saturated solution of NaNO₂ in methanol using the method of Taylor et al. (*14*). The CH₃ONO sample was devoid of any detectable impurities using FTIR analysis. A small sample (4–5 cm³) was transferred to an evacuated metal gas cylinder (size 300) and pressurized to 200 psi with pure nitrogen gas. The final concentration of CH₃ONO in the steel cylinder was measured to be 601 ppm by FTIR. Control experiments were performed to determine the stability of CH₃ONO/N₂ mixtures; there was no observable (<1%) change in the CH₃ONO concentration after standing for 2 months.

Results

CH₃ONO is a reactive compound which is prone to decomposition (particularly at elevated temperatures (15)). The first question was whether it would survive the flow through the apparatus consisting of stainless steel lines, glass lines, stainless steel couplings, and the ceramic plasma device which was located in an oven maintained at either 30 or 180 °C. To answer this question, control experiments were performed in which mixtures containing 20 ppm CH₃ONO diluted in N₂ flowed through the plasma treatment system under various conditions.

Table 1 shows the results of these control experiments. First, 20 ppm CH₃ONO in N₂ flowed through the system with the oven maintained at 30 °C and the plasma off. There was a 6% difference between the nominal composition and the FTIR measured value. Turning the plasma discharge on (30 J/L) increased the difference to 12%. Adding NO, O₂, and propylene to the flow with the plasma off caused an 11% loss of CH₃ONO. When exposed to the plasma discharge, the CH₃-ONO concentration in this gas blend increased (not shown

TABLE	1. CH ₃ C	NO	Survival	through	the	Experimental	Apparatus
under	Various	Co	nditions ^a	Ű		•	

[CH₃ONO]₀, ppm	[NO]₀, ppm	[O ₂]₀, %	[C₃H₀]₀, ppm	temp, °C	plasma discharge, J/L	CH₃ONO Ioss, %
20	0	0	0	30	0	6
20	0	0	0	30	30	12
20	260	8	510	30	0	11
20	0	0	0	180	0	60
20	0	0	0	180	30	85
20	260	8	510	180	0	75
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^a All experiments were performed in 1 atm of N₂ diluent.

in this table, but discussed below in the main experiment). With the gas lines held at 90-120 °C and the oven at 180 °C, CH_3ONO loss was 60% in $N_2.$ This increased to 85% when the plasma was on. Adding NO, O₂, and C₃H₆ without the plasma caused a 75% loss of CH₃ONO. These control experiments show that when the apparatus is maintained at 30 °C, there is only a minor loss of CH₃ONO on passage through the system. With the oven at 180 °C and transfer lines at 90-120 °C there is a substantial loss of CH₃ONO on flowing through the system. Although not shown here, the primary decomposition products are HCHO and NO. In subsequent experiments at 30 °C the observed concentration of CH₃ONO was corrected by multiplication by 1/0.89 to account for decomposition losses. As discussed previously (10), there are no discernible losses of CH₃ONO₂ on passage through the experimental system. No corrections were applied to the CH3-ONO2 data.

Figure 2 shows spectra taken before (A) and after (B) passage of a mixture of 8% O₂, 739 ppm C₃H₆, 419 ppm NO, and 371 ppm NO₂, in 1 bar of N₂ diluent, through the plasma treatment device. After passage through the plasma the FTIR analysis gave $347 \text{ ppm } C_3H_6$, 356 ppm NO, and $393 \text{ ppm } NO_2$. Subtraction of features attributable to C₃H₆, NO₂, HNO₂, and HNO₃ from panel B in Figure 2 gives the product spectrum shown in panel C. Comparison of panel C with reference spectra for CH₃ONO and CH₃ONO₂ clearly shows the formation of these species. The concentrations of CH₃ONO and CH₃ONO₂ in panel C were 8.7 and 4.6 ppm, respectively. Comparison with a reference spectrum of propylene oxide shows the formation of a 15 ppm concentration of this species. Propylene oxide is formed by reaction of O atoms with propene and demonstrates the importance of O atom chemistry in the system (9). The goal of the present experiments was to investigate the formation of CH₃ONO. A detailed analysis of the propene oxidation products was not performed.

It is important to consider potential gas-phase losses of CH_3ONO and CH_3ONO_2 in the system. $O(^3P)$ atoms, and to a lesser extent OH radicals, are the dominant species responsible for initiation of the oxidation of organic compounds in nonthermal plasma of simulated diesel exhaust



FIGURE 2. IR spectra of a mixture of $[O_2] = 8\%$, [NO] = 419 ppm, $[NO_2] = 371$ ppm, and $[C_3H_6] = 738$ ppm in 1 bar of N₂ diluent at 30 °C with the plasma turned off (A) and on (B) with 30 J/L of energy deposition. Panel C is the product spectrum obtained by stripping IR features attributable to C_3H_6 , NO_2 , HNO_2 , and HNO_3 from panel B. Panels D–F are reference spectra of CH₃ONO₂, CH₃ONO, and propylene oxide (CH₃CHOCH₂, methyl oxirane).

(9). O(³P) atoms and OH radicals react at least 100 times more rapidly with C₃H₆ than with either CH₃ONO or CH₃-ONO₂ (*16*). Given that the consumptions of C₃H₆ on passage through the plasma were 5–60%, it can be concluded that loss of CH₃ONO or CH₃ONO₂ via reaction with O(³P) atoms and OH radicals will be of negligible importance. Gas-phase processes within the plasma are unlikely to be a significant loss of either CH₃ONO and CH₃ONO₂ in the present experiments.

Experiments were performed at 30 °C using a variety of initial [NO] and [NO₂] in the range 0-420 ppm. Observed concentrations of CH₃ONO and CH₃ONO₂ in the plasma exhaust were 7-13 and 5-9 ppm, respectively. Figure 3 shows a plot of [CH₃ONO]/[CH₃ONO₂] observed in the plasma exhaust versus the ratio of the average [NO] and [NO₂] in the gas stream passing through the plasma. The average [NO] and [NO₂] values were computed from the average concentration values with the plasma on and off (all other parameters held constant). As seen from Figure 3 there is a linear relationship between [CH₃ONO]/[CH₃ONO₂] and [NO₂]. The line through the data is a linear least-squares fit which gives a slope of 1.81 ± 0.30 . Quoted errors are 2 standard deviations from the regression analysis.

It is of interest to compare this result with the ratio of the rate constants for the association reactions 1 and 2.

$$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$$
 (1)

$$CH_3O + NO + M \rightarrow CH_3ONO + M$$
 (2)

In 1 bar of N₂ at 298 K, the IUPAC Committee recommends $k_1 = 1.5 \times 10^{-11}$ and $k_2 = 2.6 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (17). Assuming an uncertainty of 15% for these rate constants, which seems reasonable on the basis of the agreement in the literature data (17), we arrive at $k_2/k_1 = 1.73 \pm 0.37$. The slope of the line through the data in Figure 3 is indistin-



FIGURE 3. [CH₃ONO]/[CH₃ONO₂] ratio present in plasma-treated exhaust versus the average [NO]/[NO₂] ratio in the gas passing through the plasma for experiments conducted at 30 $^{\circ}$ C.



FIGURE 4. IR spectra of a mixture of $[O_2] = 8\%$, [NO] = 240 ppm, and $[C_3H_6] = 537$ ppm in 1 bar of N₂ diluent at 180 °C with the plasma turned off (A) and on (B) with 30 J/L of energy deposition (B). Panel C is the product spectrum obtained by stripping IR features attributable to C₃H₆, NO₂, HNO₂, and HNO₃ from panel B. Panels D and E are reference spectra of CH₃ONO₂ and CH₃ONO.

guishable from the rate constant ratio k_2/k_1 , suggesting that the origin of CH₃ONO_x is reaction of CH₃O radicals with NO_x.

The data presented in Figure 3 were obtained in experiments conducted at 30 °C. CH₃ONO formation was also observed in experiments conducted at 180 °C. For example, Figure 4 shows spectra taken when a mixture of $8\% O_2$, 537 ppm C₃H₆, and 240 ppm NO in 1 bar of N₂ diluent was passed through the system with the oven at 180 °C and the plasma treatment device turned off (A) and on (B). With the plasma turned on the FTIR analysis gave 399 ppm C₃H₆, 98 ppm NO, and 131 ppm NO₂. Subtraction of features attributable to $C_{3}H_{6}$, NO₂, HNO₂, and HNO₃ from panel B in Figure 4 gives the product spectrum shown in panel C. Comparison of panel C with reference spectra for CH₃ONO and CH₃ONO₂ clearly shows the formation of these species. As discussed above, control experiments established that there is significant loss of CH₃ONO on flowing through the heated experimental system. The computation of suitable corrections to account

for decomposition of CH₃ONO in the apparatus at high temperature prior to reaching the FTIR detection apparatus is problematical, and experiments at high temperature were not pursued in detail. It is clear from Figure 4 that CH₃ONO is formed in the plasma at high temperatures. This finding is reasonable given the observation of CH₃ONO in the lowtemperature experiments and the fact that the rate constant ratio k_2/k_1 does not change substantially over the temperature range 30-180 °C (17).

Discussion

Two conclusions can be drawn from the present work. First, CH₃ONO and CH₃ONO₂ are formed in the nonthermal plasma treatment of simulated diesel exhaust. Second, the source of CH₃ONO_x is the association reaction of CH₃O radicals with NO_x. The source of CH₃O radicals in the present study is oxidation of propene, which produces CH₃ radicals which, in turn, are oxidized to CH₃O radicals. Essentially all hydrocarbon fuels contain substantial amounts of chemicals containing CH₃ groups, and it should be expected that CH₃-ONO and CH₃ONO₂ will be common products formed during plasma treatment of exhaust from vehicles powered using a variety of fuels.

The goal of the present work was to determine if, and how, CH₃ONO is formed during nonthermal plasma treatment of diesel exhaust. We show that CH₃ONO is formed in such systems and that reaction of CH₃O radicals with NO is the likely source. At elevated temperature (180 °C) it was observed that a significant fraction (60-85%) of the CH₃-ONO decomposed upon flowing through the experimental apparatus. It seems likely that thermal decomposition of CH3-ONO would also be significant in real world applications. In real world applications it is envisioned that, after passage through the plasma treatment device, the exhaust would flow over a catalyst designed to facilitate reduction of NO₂ into N₂ (9). Given the reactive nature of CH₃ONO, it seems very likely that most, if not all, of the CH₃ONO produced in the plasma would be removed by reactions on the catalyst surface. A detailed study of the fate of CH₃ONO on passage over a catalyst was not within the scope of the present study. The present work demonstrates unambiguously that CH₃-ONO is formed during the passage of simulated diesel exhaust through a nonthermal plasma. If the plasma-treated exhaust is not passed over a catalyst, or if the catalyst is deactivated, then it is likely that CH₃ONO will be emitted into the atmosphere. CH₃ONO is not a desirable vehicle emission. The control of CH₃ONO emissions should be a design

consideration for future commercial diesel exhaust treatment systems which incorporate nonthermal plasma devices.

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