NO_x Formation in the Plasma Treatment of Halomethanes

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A nonthermal, atmospheric pressure plasma, made-up of a $BaTiO_3$ packed-bed reactor, has been used to study the formation of NO_x and N_2O during the plasma destruction of a range of volatile organic compounds (VOCs) and hazardous air pollutants, including chlorinated, brominated, fluorinated, and iodinated methane species, in a carrier gas of air. Using the plasma destruction of pure air as a baseline, it is found that the amount of NO_x formed is unaffected by the addition of a few hundred parts per million of a simple hydrocarbon (e.g. methane). In the case of the fluorinated, chlorinated, and brominated methanes, we find enhanced production of NO_x and a marked increase in the ratio of NO_2 to NO formed, from ∼1.1 in air and methane to ∼2.3 in halogenated species. However, iodinated additives (specifically methyl iodide and diiodomethane) have remarkably different results compared to the other halogenated additives; they show enhanced increases in the NO_2 to NO ratio (∼6−13) and reduced NO_x production. The enhanced conversion of NO to NO_2 is attributed to reactions involving halogen oxides, e.g. ClO and IO.

Introduction

Nonthermal, atmospheric pressure plasma processing is now accepted as a proven environmental cleanup technology for the removal of small concentrations of pollutants (e.g. NO_x, particulates, solvents, and chlorofluorocarbons (CFC's), etc.) from waste gas streams.[1−3] It is a viable competitor to the more established technologies of catalysis, pyrolysis, adsorption, and condensation. Plasma reactors at atmospheric pressure typically produce reactive species such as atomic oxygen and nitrogen, hydroxyl radicals, and electronically excited species which then chemically destroy the pollutants converting them into benign compounds that can be safely vented to the atmosphere or that can be safely removed and possibly recycled.

A problem encountered with destroying pollutants in gas streams containing air or smaller amounts of oxygen is that high levels of nitrogen oxides (NO, NO_2, and N_2O) may also be formed as a consequence of the processing. The perceived wisdom at present is that the mechanism of formation of these nitrogen oxides is essentially decoupled from that for the destruction of the pollutant in the plasma discharge. This paper examines this hypothesis for a wide range of halogenated methanes and additionally reports the first work carried out on the plasma destruction of iodinated additives.

We have studied the formation of NO_x and N_2O during the plasma destruction of a range of compounds including chlorinated, brominated, fluorinated, and iodinated methanes, with air as the carrier gas. Using the plasma destruction of pure air as a baseline, it is found that the amount of NO_x formed is unaffected by the addition of a few hundred parts per million of a simple hydrocarbon (e.g. methane). However, in the case of the halogenated species, we find enhanced production of NO_x and a marked increase in the ratio of NO_2 to NO produced. Iodinated additives (specifically methyl iodide and diiodomethane) have remarkably different results compared to the other halogenated additives, showing reduced NO_x production and enhanced increases in the NO_2 to NO ratio.

Futamura et al.[4] have shown how the mechanism for NO_x formation in a plasma containing air may be affected by the different pollutants that are present. Using a ferroelectric packed-bed plasma reactor, they find that hydrogen-rich pollutants do not affect the NO_x formation but that halogenated species do. Specifically, Futamura et al. studied bromomethane, CH_3Br, dichloromethane, CH_2Cl_2, and carbon tetrachloride, CCl_4. They also found that halogenated pollutants increase the selectivity for the production for NO_2 compared to NO in agreement with our work for a wider range of halogenated additives, and they attribute this to reactions involving halogen oxides. This paper will develop this argument in more detail, specifically illustrating the phenomenon with the analysis of an extensive range of halogenated pollutants, including iodinated methanes which have not been studied before.

Experimental Section

The experimental setup is the same as that used previously.[5,6] The experiments were carried out using a nonthermal, atmospheric pressure plasma, consisting of a $BaTiO_3$ dielectric packed-bed reactor, to study the destruction of various additives in a gas stream of air. An alternating current (AC) voltage between 16.5 and 17.5 kV_{pk-pk} at a frequency between 10.25 and 13.25 kHz is applied between the electrodes. Using a digital storage oscilloscope (Tektronix TDS 3012), current and voltage waveforms can be recorded for the discharge by using a calibrated high-voltage probe and measuring the current across a 1 kΩ resistor in the return earth path from the reactor. This produces an average power of 1.1 W.

The dry "air" carrier gas used is made by blending nitrogen (800 cm^3(STP)/min) and oxygen (200 cm^3(STP)/min) (BOC Gases) to give a total gas flow of 1 L min^{-1}. The flow of the additive is varied to get a concentration of 500 ppm. For the gases, methane, CH_4, CFC-12, CF_2Cl_2, and carbon tetrafluoride, CF_4 (Argo International Ltd.), the gas bottle is directly connected to the mass flow controller and the additives introduced to the air flow. For the liquids, all used as supplied, dichloromethane, CH_2Cl_2, chloroform, $CHCl_3$, carbon tetrachloride, CCl_4 (BDH

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TABLE 1: Experimental Results for the Plasma Destruction and Production of NO_x for 500 ppm of Various Species in Atmospheric Pressure Streams of Air at 1 L min^{-1a}

	species		destruction (%)	NO_2 (ppm)	NO (ppm)	N_2O (ppm)	total NOx (ppm)	NO_2/NO ratio
1	air	Air		265	240	130	505	1.1
2	methane	CH_4	1	270	240	130	510	1.1
3	dichloromethane	CH_2Cl_2	26	420	175	170	595	2.4
4	chloroform	$CHCl_3$	30	440	190	180	630	2.3
5	carbon tetrachloride	CCl_4	27	430	150	175	580	2.9
6	CFC-12	CCl_2F_2	12	365	160	185	525	2.3
7	carbon tetrafluoride	CF_4	−	320	175	170	495	1.8
8	bromoform	$CHBr_3$	29	440	185	180	625	2.4
9	iodomethane	CH_3I	7	220	35	95	255	6.5
10	diiodomethane	CH_2I_2	38	140	10	80	150	12.8

[a] No destruction is shown for carbon tetrafluoride as the concentration range used gives absorbances that are too high to be accurately measured.

Laboratory Supplies), iodomethane, CH_3I (Fisher Chemicals), diiodomethane, CH_2I_2 (Aldrich), and bromoform, $CHBr_3$ (FAS Supplies), nitrogen gas is passed through the gas bubbler at an appropriate temperature. The gas lines and the gas cell are at ambient temperature.

The gas flow is controlled by mass flow controllers (MKS Mass Flo), maintained at a pressure of 1 bar. The residence time in the plasma reactor is ~0.25 s for a total flow of 1 L min^{-1}. The identity of the end products of the plasma processing and the degree of destruction are monitored on line by infrared spectroscopy using a long-path gas cell (2.76 m Venus Series) and a Fourier transform infrared (FTIR) spectrometer (Shimadzu 8300) with a resolution of 1 cm^{-1}.

Results

The destruction, total NO_x and NO_2 to NO ratio for the additives tested are given in Table 1. The destruction of the halogenated additives lies in the range of 7−38%. This is similar to previous studies from our group.[5,6] The results show that the amount of NO_x formed is only slightly affected by the addition of simple hydrocarbons, which show similar results to air as had originally been supposed. However, for the plasma destruction of halogenated additives, we see conversion of NO to NO_2 and enhanced NO_x production when compared to a discharge in pure air (apart from the iodomethanes) as was noted by Futamura et al.[4] Destruction of the iodinated species in air is seen to be accompanied by reduced NO_x production. A marked increase in the NO_2 to NO ratio is seen for all the halogenated additives, including the iodinated additives, as shown in Table 1. CH_4 exhibits a ratio of ~1.0 similar to the ratio found for pure air discharge, whereas the ratios for most of the halogenated additives are over twice this, at ~2.3, except for the iodinated compounds, which are much higher at 6−13.

The Fourier transform infrared (FTIR) spectra of the end products of the plasma processing of CH_2I_2 and CH_3I are shown in Figures 1 and 2. The observed products are NO, NO_2, N_2O, HCOH, CO_2, CO, and a trace of HNO_3 (in the case of CH_2I_2) and CH_3OH (for CH_3I). For CH_2I_2, 85 ppm of formaldehyde, CH_2OH, and ~1 ppm of nitric acid are produced. In CH_3I, we find 29 ppm of formaldehyde and 26 ppm of methanol. No infrared-active iodine-containing end products were observed in the spectra. A possible end product is hydrogen iodide, HI, although it is not detected. In our system, our minimum measurable absorbance of only 0.05 corresponds to an HI concentration of ~820 ppm. This means that even if HI were to be present, our system would be unable to detect it. The various species that have been searched for and can be eliminated as not being present are listed in Table 2. The carbon mass balance in the destruction of CH_3I, as an example, is found to be 94%.

For the other halogenated additives, we also detect NO, NO_2, N_2O, H_2CO, and CO_2, in addition to carbonyl fluoride, COF_2, which is seen for the destruction of CF_2Cl_2 and formyl chloride, HCOCl, which is a major product in the case of CH_2Cl_2 and is also seen for CCl_4 and $CHCl_3$.

In Figures 3−5, we examine possible trends in the formation of the different nitrogen oxides, NO, NO_2, and N_2O for various systematic changes in different homologous series. For all the chlorinated methanes there is an increase in total NO_x production compared with CH_4 or air alone; this is not found to be the case when the methane is fluorinated. Figure 3 shows the effect of successive substitution of chlorine atoms in going from CH_4 to CCl_4, where there appear to be no discernible trends in the yields of the various nitrogen oxides. A distinct trend is seen as the chlorine atoms are exchanged for fluorine atoms in going from CCl_4 to CF_2Cl_2 to CF_4, as shown in Figure 4. There is a

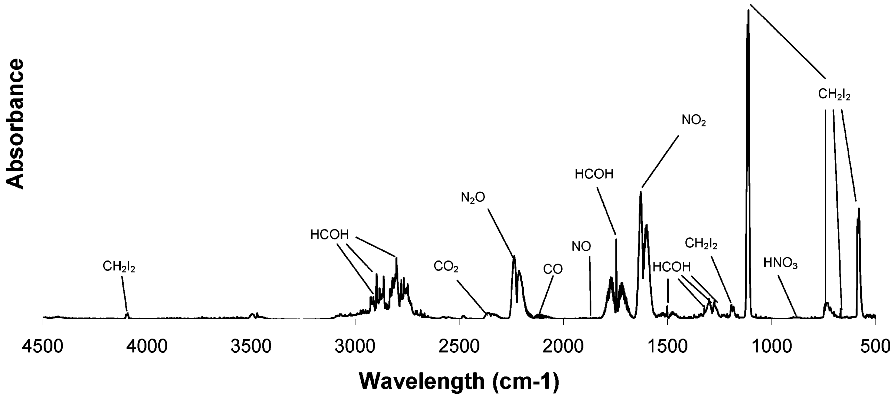

Figure 1. FTIR spectrum of the products of plasma processing in air of diiodomethane, CH_2I_2.

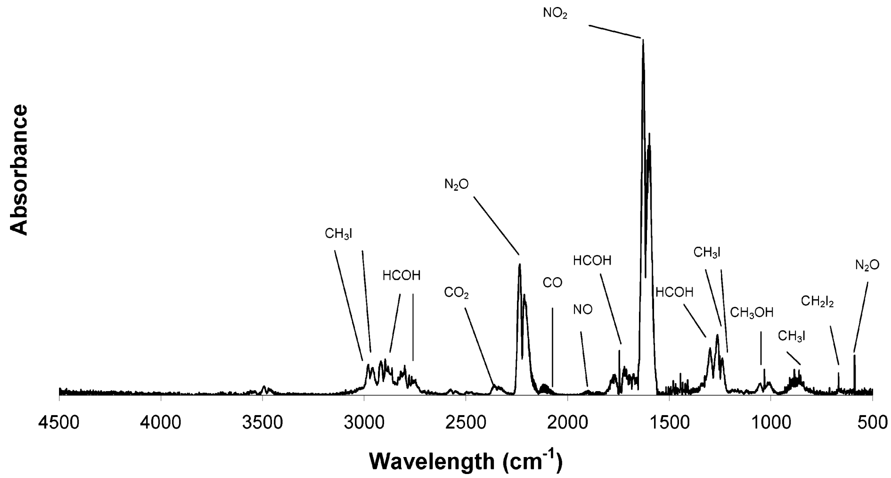

Figure 2. FTIR spectrum of the products of plasma processing in air of methyl iodide, CH_3I.

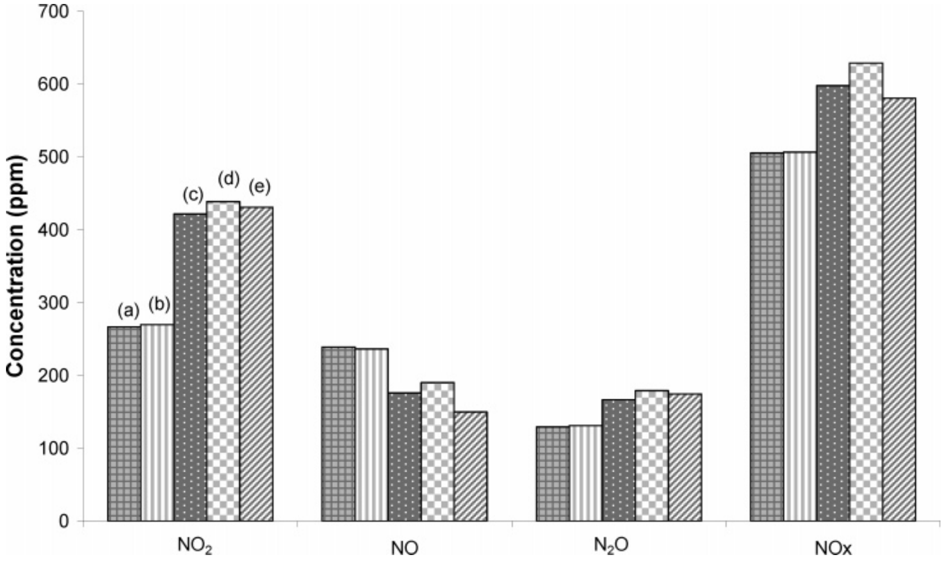

Figure 3. Effects of different levels of chlorination shown by comparison of (a) air, (b) CH_4, (c) CH_2Cl_2, (d) $CHCl_3$, and (e) CCl_4 at 500 ppm.

TABLE 2: List of Species Searched for but Not Present in the FTIR Spectra Following the Plasma Processing of CH_3I and CH_2I_2

HOI	N_2O_5	N_2O_4	HNO_2
INO	INO_2	$IONO_2$	OCHI
OCI_2	CHI_3	CI_4	CCl_2
C_2H_4	HCN	CH_4	C_2H_6

systematic decrease in the amount of NO_2, total NO_x, and the NO_2 to NO ratio (Table 1) but a small increase in NO. For N_2O, the yield is approximately constant as was also seen for the chlorinated sequence.

No distinct trend is seen across the series going from chlorinated to brominated to iodinated compounds ($CHCl_3$ to $CHBr_3$), as illustrated in Figure 5. However, the iodomethanes, CH_3I and CH_2I_2, appear distinct from the other halogenated additives in their general trend of properties, showing significantly lower NO_x yields, particularly for NO especially for CH_2I_2.

Discussion

In a nonthermal plasma, highly energetic electrons are produced which dissociate and excite the major components in the gas stream, creating ground and electronically excited oxygen and nitrogen atoms and molecules ($O(^3P$ and $^1D)$, $O_2(a^1\Delta)$, $N(^4S, {}^2D, {}^2P)$, and $N_2(A^3\Sigma_u^+)$). Excited states are generally quenched rapidly at atmospheric pressure and do not contribute significantly to reaction with the possible exception of the triplet metastable state of nitrogen, $N_2(A^3\Sigma_u^+)$ and excited nitrogen atoms, $N(^2D)$. It is these atomic and molecular species that are responsible for initiating the destruction of the various pollutants and for the production of NO_x, as we will now discuss.

The basic mechanism for NO_x formation in plasma systems is well-established[7−9] and includes the following steps, which are initiated by ground and electronically excited nitrogen atoms:

$$N(^2D) + O_2 \rightarrow NO + O \quad (1)$$

$$N(^4S) + O_2 \rightarrow NO + O \quad (2)$$

$$NO + O + M \rightarrow NO_2 + M \quad (3)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (4)$$

$$N(^4S) + NO \rightarrow N_2 + O \quad (5)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (6)$$

where the oxygen and nitrogen atoms are formed directly by electron impact processes during the discharge. The effective rate constant for the three-body reaction of N + O + M is at least 1 order of magnitude smaller (2.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1})[8] than those of eqs 1, 2, and 6 and so is not included.

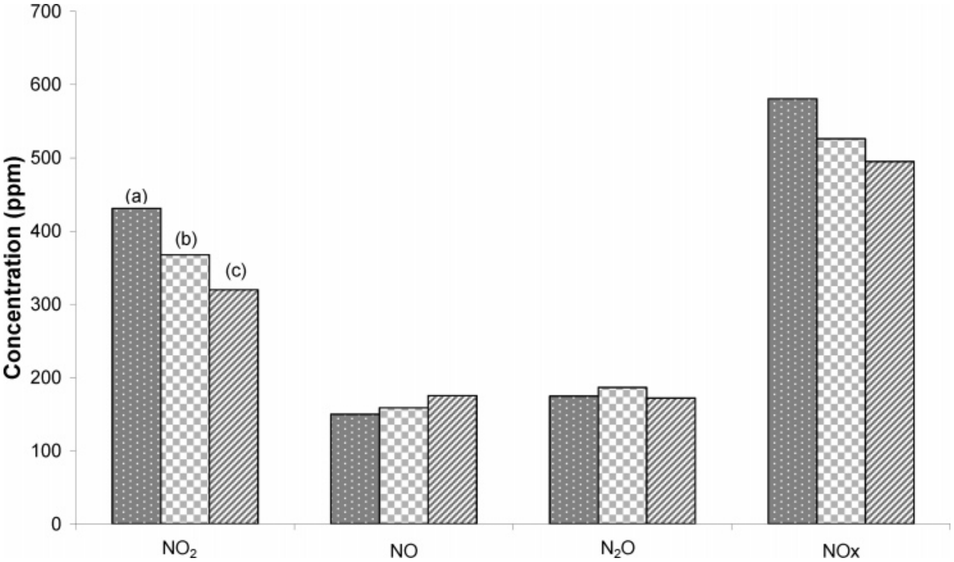

Figure 4. Effect of substituting Cl for F shown by comparison of (a) CCl_4, (b) CF_2Cl_2, and (c) CF_4 at 500 ppm.

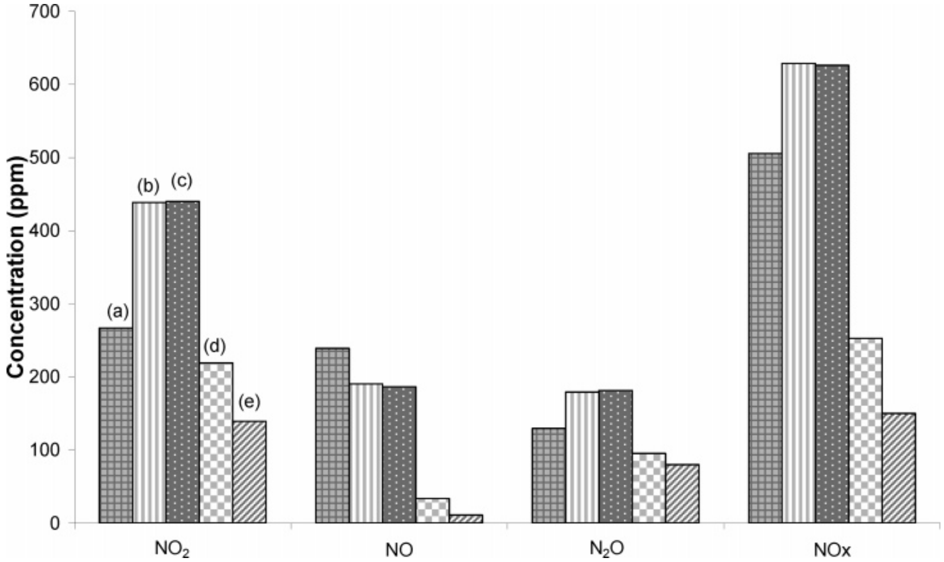

Figure 5. Homologous series of halogenated additives shown by comparison of (a) air, (b) $CHCl_3$, (c) $CHBr_3$, (d) CH_3I, and (e) CH_2I_2.

The destruction of methane or the halomethane initially proceeds via the formation of a methyl or substituted methyl radical by reaction either with an oxygen atom to form a hydroxyl radical

$$O + CH_nX_m \rightarrow OH + CH_{n-1}X_m \text{ (X} \equiv \text{halogen)} \qquad (7)$$

or by electron-impact dissociation yielding a halogen atom

$$e + CH_nX_m \rightarrow e + CH_nX_{m-1} + X \qquad (8)$$

In general, the reactions of ground-state oxygen atoms with methane and halomethanes are very slow at the temperature of our plasma experiments (~400 K) except in the case of the iodomethanes ($k = 9.69 \times 10^{-17}$, 3.69×10^{-15}, 3.7×10^{-15}, and 2.13×10^{-12} $cm^3\ s^{-1}$ for O + CH_4, CH_2Cl_2, $CHCl_3$, and CH_3I, respectively, at this temperature.)[10] In the case of O + CH_3I, the halogen abstraction channel is also open

$$O + CH_nX_m \rightarrow OX + CH_nX_{m-1} \qquad (9)$$

with a rate constant that is an order of magnitude larger than for OH production ($k = 1.86 \times 10^{-11}$ $cm^3\ s^{-1}$).[10]

The direct dissociation by electron impact (reaction 8) for the halomethanes can take place by dissociative electron attachment when an electron goes into the antibonding orbital, leading to dissociation of the molecule into a radical and a halide ion which is rapidly charge neutralized.[11] Compounds such as CCl_4[12−15] and CF_2Cl_2[5,6,16] exhibit large cross-sections for dissociative electron attachment. CCl_4 has a cross-section of 10^{-14} cm^2.[12] However some of the other pollutants studied (CH_2Cl_2, CF_4, and $CHCl_3$) have significantly lower cross-sections; there are slight variations in the literature values for their cross-sections, ranging from 10^{-19} cm^2 for CH_2Cl_2 to 10^{-16} cm^2 for $CHCl_3$.[5,6,12,15,17−20] Methyl iodide has a high dissociative attachment cross-section value of 10^{-14} cm^2.[17] While there are no reported values for the dissociative electron attachment cross-section of CH_2I_2, the addition of another iodine atom suggests a much larger cross-section than for CH_3I, making it probably the largest for the species studied here as is suggested by the relative change between CH_2Cl_2 (10^{-19} cm^2) and CH_3Cl (10^{-21} cm^2).[12] If this pattern is applied to the CH_2X_2 series, then an estimated cross-section for CH_2I_2 would be $\leq 10^{-11}$ cm^2. However, it is not possible to rationalize the observed destructions (Table 1) with these cross-sections, as has been remarked upon before,[6] implying that the destruction is governed more by the subsequent chemistry than by the initial destruction step.

The destruction of halomethanes becomes facile in the presence of a halogen atom, for example the chlorine atom oxidation of dichloromethane[21] which follows a mechanism identical to that in tropospheric chemistry[22,23]

$$Cl + CH_2Cl_2 \rightarrow CHCl_2 + HCl \quad (10)$$

Reaction of the substituted methyl radicals formed in steps with molecular oxygen forms peroxy radicals

$$CHCl_2 + O_2 \rightarrow CHCl_2O_2 \quad (11)$$

which can further react to form a substituted methoxy radical

$$CHCl_2O_2 + CHCl_2O_2 \rightarrow 2CHCl_2O + O_2 \quad (12)$$

which then decomposes to a substituted formaldehyde

$$CHCl_2O \rightarrow CHClO + Cl \quad (13)$$

and then undergoes additional reactions to yield CO and CO_2, as we have discussed previously.[6,24]

The contribution of reaction 11 is expected to be small because of the low radical concentration, and there will also be a contribution due to the hydrogen abstraction from CH_2Cl_2

$$CHCl_2O_2 + CH_2Cl_2 \rightarrow CHCl_2OOH + CHCl_2 \quad (14)$$

Further decomposition of the hydroperoxide produces aldehydes

$$CHCl_2OOH \rightarrow CHClO + HOCl \quad (15)$$

In our studies, we find a range of halogenated analogues of formaldehyde, e.g. CHClO, phosgene ($COCl_2$), and carbonyl fluoride (COF_2), due to the decay of partially halogenated peroxy radicals. This, however, is not the case for the iodinated additives where formaldehyde, H_2CO, exclusively is formed, suggesting that the destruction of CH_3I and CH_2I_2 proceeds via a CH_3O or a CH_2IO radical which decomposes to CH_2O as proposed by Cotter et al.[25]

In contrast to tropospheric chemistry, excited states of molecular nitrogen and atomic nitrogen are also present. Penetrante et al.[18] have shown that the destruction of methylene chloride, CH_2Cl_2, in nitrogen proceeds largely by reactions of atomic nitrogen and that the destruction in air is substantially reduced because the nitrogen atoms (especially $N(^2D)$) are preferentially used in the production of NO_x (reactions 1−6). In studying the low-pressure reactions of nitrogen atoms with $CHCl_3$, Jeoung et al.[26] find that ground-state nitrogen atoms, $N(^4S)$, do not react directly with chloroform but that the destruction proceeds via fast branching chain reactions of N atoms with intermediate radicals after an initial reaction of Cl atoms with CH_2Cl_2.

Futamura et al.[4] suggest that the enhanced ratio of NO_2 to NO seen in the case of halomethanes compared with the ratios seen for air, methane, and other simple organic molecules comes from the reaction of NO with halogen oxides (e.g. ClO) participating in processes such as

$$NO + ClO \rightarrow NO_2 + Cl \quad (16)$$

where the ClO comes from reaction of atomic chlorine with the intermediate ozone produced in the discharge

$$Cl + O_3 \rightarrow ClO + O_2 \quad (17)$$

TABLE 3: Comparison of Final Concentration of Species (ppm) Predicted from the Model with the Experimental Results for the Destruction of 500 ppm of CCl_4 in Air

	model	expt
CCl_4	364	365
NO	75	150
NO_2	159	431
N_2O	188	234
total NO_x	234	581
NO_2/NO	2.14	2.88

The analogue of reaction 17 is a fast reaction for all halogen oxides with a rate constant of $(1-2) \times 10^{-11}$ cm^3 s^{-1}.[10] The enhanced conversion of NO_2 in the case of the iodomethanes ($NO_2/NO = 6.5$, 12.8 for CH_3I and CH_2I_2, respectively) can be attributed to the increased amount of IO produced by the additional channel of reaction 9.

We have attempted to confirm the hypothesis that halogen oxides are responsible for the increased conversion of NO to NO_2 using kinetic modeling based on CHEMKIN-II for the case of CH_4 and CCl_4. This chemical kinetics scheme combines the input gas temperature (400 K) and pressure (1 bar) with the residence time, frequency, number of radical species produced per pulse, and the inlet gas composition, as well as a kinetic mechanism including the proposed chemical reactions (16 and 17). This has been based on our previous modeling for the plasma destruction of methane[24] and dichloromethane.[5] These models have verified that methane as an additive has no effect on the conversion of NO to NO_2[24] and show that, in the destruction of CCl_4, ClO plays a important role in the conversion of NO to NO_2 as manifest in the predicted NO_2/NO ratio, which agrees with the experimental result as shown in Table 3, even though the model underestimates the total amounts of NO_x produced. The model used is zero dimensional.[7] It is however unlikely that the gases are uniform in volume as microstreamers are formed.[27] It is possible that the NO_x is formed within these streamers and then diffuses into the plasma. It is also likely that the temperature and concentrations are not uniform throughout the gas and that instead hot spots and temperature gradients exist. The assumptions of uniformity of the gas phase seem appropriate for the oxygen chemistry[28] that is present, but it is likely that they do not match the NO_x chemistry, hence causing the differences in NO_x concentrations in the model when compared to the experimental results.

The other observation in this work is that the amount of total NO_x produced in the destruction of the halocarbons compared with an air or simple hydrocarbon discharge depends on the identity of the halogen species. For CF_4 and CF_2Cl_2, there is no real change in the NO_x levels but for Cl- or Br-containing molecules, we see an increase in the total amount of NO_x by ∼18%. However, there is a significant decrease in the amount of NO_x produced in the case of iodinated additives (CH_3I, 253 ppm; CH_2I_2, 156 ppm) when compared to the other halogenated species. Futamura et al. found that, for the destruction of CH_2Cl_2, CCl_4, C_2HCl_3, and CH_3Br, there was an increase of up to 100% in the total amount of NO_x produced.[4] They suggest that the increased yield of NO_x could result from the reaction of nitrogen atoms with the halogen oxides. However, the channel that might affect the total NO_x levels, namely, the reaction of N atoms with ClO forming NO, is very slow if it occurs at all ($k < 5 \times 10^{-14}$ cm^3 s^{-1}).[29] However, it is possible that the alternative channel that forms NCl

$$N + ClO \rightarrow NCl + O \quad (18)$$

which Freeman and Phillips[29] suggest may be $>10^{12}$ cm^3 mol^{-1}

$s^{-}1$. NCl may also be produced by other chlorine atom abstraction reactions involving nitrogen atoms. A sequence of steps involving the formation and reaction of NOCl

$$NCl + ClO \rightarrow NOCl + Cl \qquad (19)$$

($k = 2.31 \times 10^{-11}$ cm^3 s^{-1} at 298 K[10])

$$Cl + NOCl \rightarrow NO + Cl_2 \qquad (20)$$

($k = 9.20 \times 10^{-11}$ cm^3 s^{-1} at 373 K[30])

may then yield the additional NO_x.

The reason for the reduction of NO_x during the plasma destruction of iodomethanes in air is not as clear. It is possible that some iodo species present catalyze the conversion of the intermediates to nitrogen which cannot be detected by FTIR techniques. There is also the possibility that iodine specific chemistry takes place which eliminates NO_x. It is known that IO, formed as discussed above, removes NO_2 in a fast recombination reaction[31]

$$IO + NO_2 + M \rightarrow IONO_2 + M \qquad (21)$$

which would remove the NO_x levels by forming this "reservoir" compound. However, as noted in Table 3, we do not observe any $IONO_2$ (or other iodine−nitrogen oxide species) in our IR spectra. A final difference between the iodomethanes compared with the other molecules studied may come from their significantly larger electron attachment cross-sections, which may influence the gaseous electronics of the discharge shifting the electron energy distribution to less favorable conditions for the production of atomic nitrogen, which will reduce the amount of NO_x that can be produced. Further work is needed to determine which if any of these possibilities is correct.

Conclusions

We have shown that there is a high degree of coupling between the plasma chemistry responsible for the destruction of halogenated methanes and that responsible for the formation of NO_x in air streams that is not present for methane or substituted methanes that do not contain halogens. This coupling is manifest in increased conversion of NO to NO_2 compared with air or methane, and this is attributed to reactions involving halogen oxides, XO, as confirmed by modeling for the case of CCl_4. Compared with methane, total NO_x levels are similar for fluorinated methanes, increased for chlorinated and brominated methanes, but substantially reduced for iodomethanes. This aspect of the study is the least well understood, and further work is needed to elucidate the aspects of the gaseous electronics and the nature of the active species and chemistry responsible for the production of NO_x in these systems.

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