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Atmospheric Chemistry Studies of Exhaust from Vehicles Operating with Reformulated Fuel

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Introduction

In many areas of the United States, ozone concentrations continue to be higher than that specified by the NAAQS. In spite of substantial improvements, automobile exhaust still remains one of the major sources of ozone precursors, reactive organic gases and oxides of nitrogen. One strategy for dealing with this emission source is to use fuels that have lower reactivity than conventional gasoline. The degree of ozone reduction expected from these fuels has only been estimated using reactivity scales which are largely based on modeling results.

The U.S. Congress, in the 1990 Clean Air Act Amendments [1] has required further reduction of emissions from new motor vehicles, introduction of environmentally favorable reformulations of conventional diesel and gasoline fuels, and introduction of alternative fuels such as methanol, ethanol, and natural gas with associated vehicle technologies. Gasoline reformulation is designed to result in mass (and reactivity) reductions of both ozone-forming volatile organic compounds (VOCs) and toxic compounds (formaldehyde, acetaldehyde, polycyclic organic matter, benzene, and 1,3-butadiene). The Alternative Motor Fuels Act of 1988 (AMFA) also mandated the introduction of alternatives to conventional vehicle and fuel technologies. In addition to changes and improvements in fuels, considerable efforts have been made by automotive manufacturers to produce vehicles that generate lower levels of exhaust and evaporative emissions. Many of these new technology vehicles are specifically designed to use alternatives to conventional fuels. As new fuels and vehicle technologies are introduced, the distribution of compounds introduced into the atmosphere, particularly, the urban atmosphere, could change considerably.

With lower levels of exhaust and evaporative emissions from new vehicles, their associated reactivity (i.e., their ability to produce ozone) has been found to be lower than that from present-day vehicles, according to computer models. Whereas kinetic and mechanistic experiments have been conducted on individual fuel components of both reformulated and alternative fuels, little effort has been expended to examine effects from the entire exhaust. Information on the photochemical transformations of these emissions is vital for determining tropospheric lifetimes, effects on ozone formation, and possible

generation of toxic and genotoxic reaction products in the atmosphere.

The formation of ozone and other toxic compounds is frequently studied in the laboratory using smog chambers. Research in studying reactivities of complex mixtures typically uses surrogate mixtures to represent automotive exhaust and/or evaporative emissions. This approach permits controlled additions of the initial reactant mixtures to the chamber. However, there are two potential shortcomings to this approach. First, there is no guarantee that the surrogate mixture adequately represents the distribution of reactive constituents present in the exhaust. Second, the formulation of a realistic surrogate mixture is not necessarily straightforward for fuels having a complex composition. For fuels, such as compressed natural gas (CNG), having a few major constituents, surrogates which represent vast majority of the reactivity can be produced by mixing one to two dozen organic constituents in the proper ratio in a high pressure cylinder. However, for gasoline-based fuels more sophisticated approaches for surrogate development must be undertaken.

We have recently assembled a facility for conducting direct irradiations of exhaust from vehicles operated on a dynamometer. The approach has permitted a direct measure of reactivity parameters (related to the maximum incremental reactivity) for complex exhaust mixtures. Controlled irradiations of these mixtures has shown remarkable reproducibility, much better than originally anticipated. This high degree of experimental reproducibility has permitted us to examine in detail direct comparisons between surrogate mixtures designed to represent automotive exhaust and automotive exhaust itself. The reported study describes experiments that have been conducted to examine the reactivity and major product constituents from direct irradiations of complex exhaust mixtures. These experiments will serve as the basis for producing realistic surrogates for automotive exhaust. The approach is demonstrated with exhaust generated with a reformulated gasoline (RFG). A complex surrogate representing this exhaust was designed and formulated to allow the initial conditions to be generated reproducibly. A series of irradiations were then undertaken to compare reaction profiles for the adjusted exhaust mixtures.

Experimental Section

The dynamometer/photochemistry chamber system used in this study was previously developed to examine the reactivity of exhaust from vehicles operating on alternative fuels. While the main features of the apparatus have been previously described, some of the salient and additional aspects of the experimental design are included below.

Apparatus

A schematic diagram for the experimental apparatus required to conduct these studies is shown in Figure 1. The primary components for this system are the dynamometer (not shown) for generating the required exhaust emissions, the photochemical chamber with associated apparatus for reactant introduction and product sampling, and the analytical instrumentation for making chemical and physical measurements.

Automobile exhaust was generated in an adjoining area from vehicles operated on a chassis dynamometer. The dynamometer used in these studies was a twin-roll, electric chassis dynamometer manufactured by Burke-Porter (Grand Rapids, MI). The entire exhaust from the automobile was transferred through a heated, stainless-steel line to the dilution tunnel. The exhaust was diluted at $20 \text{ m}^3 \text{ min}^{-1}$ with a constant volume sampler (CVS) using ambient air to reduce exhaust concentrations and to

equilibrate the hot exhaust gases. Exhaust samples for injection into the chamber were collected from the dilution tunnel with the use of five Metal Bellows pumps (Sharon, MA; Models MB-302 and MB-151) operating in parallel. Exhaust was collected in 200 L Teflon bags for transfer to the photochemical chamber.

The reaction chamber is an 9,000-L rectangular chamber constructed of 2-mil Teflon film. Samples are taken from fittings mounted on a Teflon plate at the bottom of the chamber. A fan was installed to achieve active mixing of the reactants and pure compounds injected into the chamber. Ultrazero air was used in the chamber as the base air matrix and for as dilution during the irradiations. The air was produced in-house with an Aadco pure air generator (Aadco, Inc., Model 737). This air typically had NO_x levels less than 1 ppbv and hydrocarbon levels less than 50 ppbC. The irradiation chamber is typically operated with 2-3 L min^{-1} dilution air to compensate the volume loss due to sampling.

The irradiation source for indoor experiments was based on a system of 122-cm fluorescent bulbs. Radiation in the range 300–350 nm was generated with UVA-340 (Q-Panel, Cleveland, OH) fluorescent blacklight bulbs; radiation at wavelengths 350–400 nm was generated with standard UV bulbs (F40-BL). The mixture of bulbs was designed to match, to the extent possible, the distribution of solar radiation between 300 and 400 nm. In most cases, the distribution of bulbs were 50% UVA-340 and 50% F40-BL. It has been found that different lots of the UV-340 bulbs can yield different absolute radiation intensities and therefore each lot is checked with a spectral radiometer. The spectral distribution of the light setting was measured with a portable spectroradiometer (LI-COR, Inc., Model LI-1800). During the experiment, the light intensity was continuously monitored with an integrating radiometer (Eppley Laboratory, Inc. Newport, RI) that measured radiation between 300 and 385 nm.

Materials and Surrogate Formulation

Exhaust was generated from a Dodge Caravan with a V-6, 3.3 L engine. This vehicle was selected based on other program requirements. The vehicle was fueled with California Phase II reformulated fuel. The major physical characteristics of this fuel are given in Table 1. Hydrocarbons and NO_x for this study were derived from collected automobile exhaust generated during the first two cycles (i.e., the first 124 s) of Bag 1 of the FTP. This mixture was relatively hydrocarbon rich compared to exhaust mixtures obtained from other gasoline based vehicles. These exhaust characteristics provided a unique opportunity to measure exhaust reactivity without a substantial addition of hydrocarbon to bring the mixture into a photochemically active regime, that is having a sufficiently high reactive organic gas (ROG)/ NO_x ratio initially present. In some cases, NO from a 100 ppmv in air cylinder mixture (National Specialty Gases, Raleigh, NC) was required to produce equivalent photochemical starting conditions. This cylinder was also used in irradiations of the hydrocarbon surrogate mixture.

The hydrocarbon surrogate was formulated to match the hydrocarbon composition of the RFG exhaust mixture described above. The exhaust and associated surrogate comprised 4 major components important to ozone formation - the fuel itself, the major combustion-derived alkenes (C_2 - C_4), C_7 - C_9 aromatic hydrocarbons, and C_1 - C_2 carbonyl compounds. Calculations were initially performed to establish the reactivity of the RFG exhaust using principles of incremental reactivity [2]. The reactivity-weighted compositional difference between the fuel and the exhaust was then determined. Appropriate amounts of pure organic compounds were then used to make adjustments to the hydrocarbon mixture to better represent the reactivity of the exhaust. According to the calculations, better than 95% of the

reactivity was represented by the resultant surrogate mixture. To produce the experimental mixture the whole fuel and appropriate levels of 16 individual organic components were added to an evacuated vessel. The vessel was then filled with ultrazero air to produce a mixture in the high part-per-million level. Table 2 provides overall characteristics of the surrogate mixture produced and includes the identity of the 25 most abundant compounds along with the distribution of the surrogate according to hydrocarbon class and number. The contents of the vessel could then be used for reproducible chamber experiments with the addition of formaldehyde, carbon monoxide, NO_x, and water vapor. When this RFG hydrocarbon surrogate is irradiated in the chamber in the presence of NO_x, it was found that the mixture produced 99% of the ozone found in the exhaust after a similar 12 h irradiation.

Sampling and Instrumentation

Gas-phase samples were taken through a 200-mL Teflon manifold that was connected to the chamber with 6.4-mm Teflon tubing. The sampling line was inserted 45 cm above the chamber floor to ensure that a well-mixed and representative sample was obtained from the chamber. Nitric oxide (NO), total NO_x, and ozone were measured with continuous monitors and techniques as previously described [3, 4]. Temperature and relative humidity (RH) were measured with an Omega digital Thermo-Hydrometer (Model RH411). The temperature-humidity sensor was placed in an insulated Teflon tube that was in-line with samples taken from the manifold. Air samples drawn past the temperature and RH sensor were in close proximity to the irradiation chamber but shielded from the UV lights. This approach permitted the air temperature of the chamber samples to be accurately measured while avoiding radiative heating from fluorescent bulbs. To prevent excessive chamber heating from the fluorescent bulbs, cooled air from an auxiliary air conditioner in the laboratory was circulated in the ballast cavity, as well as between the lights and the chamber walls. This configuration allowed the temperature of the mixture in the chamber to be maintained between 25 and 27 °C during the irradiation.

Direct concentrations of vapor-phase water in the chamber were measured continuously by using a fast response water analyzer (LICOR Corp., Lincoln, NE; Model LI6262). This analyzer could provide more accurate and precise measurements of the water level in the chamber than could be achieved with the combination of temperature and relative humidity indicated above. The instrument operates by IR absorption and concentrations above 500 ppmv can be accurately determined. For these measurements, a sample flow of 0.5 L/min was used and dry nitrogen was used as the reference cell gas.

Measurements of organic precursors and reaction products were obtained from the chamber as a function of irradiation time. Speciated hydrocarbons were measured by GC with detection by flame ionization (FID), electron capture (ECD), or mass spectrometry (MS) [5]. Samples were cryogenically collected and separated on a methyl silicone column (Restek Corp. RTx-1, 60 m × 0.32 mm, 1-μm film thickness) which was connected serially to a Carbowax column (Restek Corp. Stabilwax, 30 m × 0.32 mm, 0.5-μm film thickness). This approach substantially improves the peak shape of polar compounds produced during the irradiation and permitted separation of methanol from C₄ hydrocarbons.

Peroxyacetyl nitrate (PAN) and other peroxyacyl nitrates were measured by GC/ECD. The column used for analysis was of moderate polarity, trifluoropropyl methyl silicone (Restek RT_x-200; 30 m × 0.53 mm, 1-μm film thickness) giving an elution order similar to those obtained with a standard Carbowax column. The column, operated at room temperature, provided baseline separation for PAN and peroxypropionyl nitrate (PPN) and mitigated moisture problems. The carrier gas for the analytical column was ultrahigh purity hydrogen with detection using a ⁶³Ni ECD.

Measurements for carbonyl compounds were obtained by bubbling the effluent through a solution of 2,4-dinitrophenylhydrazine (DNPH) in acidified acetonitrile. The derivatization reactions produce carbonyl hydrazones which were separated and quantified by HPLC (Milton Roy, Model CM4000). The column used in the analysis was a Zorbax ODS-1 column with detection of the separated hydrazones by UV absorption at 360 nm. A ternary gradient, composed of acetonitrile, methanol and water, was used to provide reasonable separation of intermediate-weight carbonyl compounds [6].

Absolute concentrations of nitric acid were obtained through nylon filter technique. Approximately 100 L of the chamber effluent was drawn through a 47-mm, 1- μ m nylon membrane filter (Gelman Sciences, Inc., Ann Arbor, MI) at a flow rate of 5 L/min. Filters were extracted in 15 mL of 0.01 mM perchloric acid solution. The extract was analyzed by ion chromatography (Dionex, Inc., Sunnyvale, CA) for nitrate ion. The analysis used a standard anion column (AS4) with a $\text{HCO}_3^-/\text{CO}_3^{2-}$ eluent and conductivity detection.

Identifications of *t*-butyl formate were performed principally by GC/MS. The instrument (Hewlett-Packard Model 5970) was tuned with perfluorotributylamine (PFTBA, or FC-43). An initial library search of the mass spectrum for TBF was conducted using the Wiley/NBS Mass Spectra Library. Pure samples of TBF were procured for matching spectra and chromatographic retention time. Full-scan electron impact (EI) spectra (70 eV) were then collected for mass units 35–250 to validate the standard spectrum, particularly with respect to the principal mass ratios.

Characteristic ions were selected from the mass spectra for TBF for the quantitative SIM runs. No problems were associated with this process because each of the components was chromatographically well resolved. With the cryogenic sampling system, 100 mL gas samples were collected, then flash injected into the GC/MS. Each ion was integrated for 150 ms. Standard bags containing known quantities of TBF were run each day usually at the beginning and end of each set of experiments to determine calibration factors and check the instrument performance. For the SIM mode, the TBF ions used for analysis were $m/e = 59$ and 87. In most cases, concentrations were quantified with the 59 ion and the 87 ion was used for confirmation. Thus, the presence of these ions (in the correct ratio) at the appropriate retention time served as the criteria for validating the presence of TBF. Due to the presence of water in the photochemical system, the full 100 mL sample could not be collected in many instances. However, sample collection volumes of 25 mL also yielded an excellent signal-to-noise ratio for typically measured sample concentrations detected during the irradiation (1-5 ppbv). An examination of the instrumental noise indicated a detection limit of 0.03 ppbv ($S/N=3$) for the full 100 mL collection volume.

Procedures

Exhaust from test vehicles was generated using a conventional dynamometer operated under the Federal Test Procedure (FTP). The exhaust samples were injected into a smog chamber and irradiated under conditions which simulate ambient urban atmospheres. The experimental procedures generally followed those previously described [4]. Prior to irradiations, the chamber was typically flushed with ultrazero air for 48 h. Background samples for detailed hydrocarbons and carbonyl compounds verified negligible levels of these compounds prior to reactant addition.

Automobile exhaust samples were collected into 200-L Teflon bags during the first two cycles of the FTP, that is, the first 124 s of Bag 1. During this period, there is a substantially higher hydrocarbon emissions before the catalyst becomes operative. After collection, the exhaust content of the Teflon bags were immediately injected into the irradiation chamber using a metal bellows pump. The initial chamber mixture was targeted at an ROG/NO_x ratio of 5.5. The volume of exhaust injected into the chamber was

typically limited by the level of NO_x present in the exhaust sample. Exhaust was injected to bring the initial chamber concentration of NO_x to the target value of 400 ppbv. If the ROG/ NO_x ratio was below the target ratio of 5.5, surrogate was added to raise the mixture to this target ratio. If the ROG/ NO_x ratio was greater than 5.5, NO was added to the chamber to lower the ratio to the appropriate level. In either case, this approach rendered an initial ROG concentration of 2.2 ppmC.

Once the reactant mixture had been added to the chamber, initial samples (i.e., time zero irradiation samples and parameters) were taken and the irradiation source was turned on. Physical parameters and inorganic concentrations (i.e., NO, NO_x , O_3) were monitored continuously during the irradiation. Samples for peroxyacyl nitrates were taken at 1-h intervals. Detailed NMHC, carbonyl, and nitric acid samples required direct operator intervention and were taken at 2 h intervals. GC/MS measurements for TBF were made at the beginning, midpoint, and at the end of the irradiation. The total irradiation time was typically 12 h or the time required to reach a peak in the ozone concentration.

Results

The results are given for three experiments (referred to as IR109, IR110, and IR111) where RFG exhaust was irradiated. For two of the experiments, greater than 89% of the hydrocarbon was derived from the exhaust mixture. In IR111, all of the hydrocarbon initially present in the chamber was derived from the exhaust. As noted, experiments were conducted at an initial ROG/ NO_x ratio of 5.5. The ratio was selected to accentuate differences in reactivity from the composition of the hydrocarbon mixture. At substantially lower ratios (e.g., <3), these mixtures have unacceptably low reactivity for radiation levels that can be achieved in the chamber. At substantially higher reactivities, the system becomes NO_x -limited and the rate of oxidant formation becomes far less dependent on the ROG distribution.

Table 2 provides the overall initial chamber conditions for each of the experiments. In each experiment, the target conditions (ROG and NO_x) were largely achieved. IR111 shows a slightly higher ROG/ NO_x ratio than the other two experiments. In each of these runs water was added to the initial mixture through a humidification system. At the temperature of the irradiations, these added water concentrations correspond to approximately 50% relative humidity. The distributions of the major hydrocarbon classes are given and show nearly equivalent paraffin and aromatic abundances, which are approximately twice that of the olefin. The oxygenate (i.e., MTBE) and carbonyl abundances together are less than 10% of the total ROG.

As indicated in Table 3, IR109 required a 0.117 ppmC (5.4%) increase of the hydrocarbon surrogate to give the desired initial ROG/ NO_x ratio; Experiment IR110 required a 0.230 ppmC (10.9%) increase of the surrogate. Major features for the composition of the hydrocarbon surrogate representing RFG exhaust are given in Table 2. The surrogate shows excellent conformity to the exhaust in both composition and reactivity. However, there were some compositional differences between the surrogate and the exhaust. Alkynes, which are generated exclusively in the combustion process (particularly acetylene), were not added to the surrogate mixture due to their negligible effect on the reactivity. By contrast, MTBE was substantially higher in the surrogate than in the exhaust, since it is removed during the combustion process. In the exhaust, MTBE represents approximately 2% of the total emitted carbon in the 124 s bag. As in the case of the alkynes, MTBE has a minor influence on the total reactivity. Finally, the exhaust produced approximately 50% greater carbonyl mass than found in the surrogate. Total carbonyl abundance in the exhaust was never larger than 3%, however. Thus, for purposes of these irradiations the hydrocarbon surrogate is considered to be an excellent representation of the exhaust,

particularly given the low levels of surrogate required to adjust the initial ratio.

Figure 2 presents time series profiles for the major inorganic species in the photochemical system which include nitric oxide, nitrogen dioxide, and ozone. The photochemical reactions are typically initiated by the photolysis of compounds such as formaldehyde or nitrous acid. Both compounds can serve as a primary source of OH which oxidizes organic compounds present. Nitrous acid can be formed at the chamber walls from a heterogeneous reaction between NO_2 and water and photolyses to give OH directly. The conversion of NO to NO_2 is clearly seen in the figure. Once NO is removed from the system ozone increases until its formation rate is equivalent to the loss rate. The overlaid data shows the excellent agreement for the family of profiles for the three experiments.

The major set of reactive compounds formed in photochemical systems are carbonyl compounds, especially the aldehydes, formaldehyde and acetaldehyde. Time series profiles for these compounds are given in Figures 3(a) and 3(b), respectively. For both compounds, the rate of formation exceeds the rate of removal due to OH reaction and/or photolysis until an irradiation time of 4 h and leads to the observed peaks in concentration. The acetaldehyde data shows high experimental consistency for the 3 experiments. By contrast, the formaldehyde is considerably more scattered and is probably more sensitive to difference in the distribution of precursors. Figure 3c gives the data for acetone, which next to formaldehyde is the second most abundant carbonyl compound formed in these irradiations. Again in this case, the run-to-run consistency for this compound is remarkably good. Acetone is formed from precursor hydrocarbons which have two methyl groups in the alpha position with respect to alkoxy radical intermediate, such as the alkoxy radical formed from the oxidation of isobutylene.

Termination reactions form inorganic and organic nitrates which are found as stable products in most photochemical systems. Figure 4 shows the time-series profiles for the two major nitrogen containing products, nitric acid and peroxyacetyl nitrate (PAN). These are also the major NO_y compounds found in the troposphere. Both plots show excellent agreement among the experiments for the first six hours of irradiation with moderate divergences toward the end of the radiation period.

The major product for the oxidation of MTBE (the major oxygenated component of RFG) is *tertiary*-butyl formate (TBF). From previous studies [7], this compound has been found to form with a reported yield ranging between 0.6 - 0.7 and thus was examined during this study. During these experiments, measurements for TBF were made for the preirradiation mixture, at the midpoint of the irradiation, and at the ozone peak. TBF concentrations for all preirradiation samples were below the detection limit of approximately 0.03 ppbv. Table 4 gives both the reactive losses for MTBE and formation yield for TBF. IR110 and IR111 were quite consistent with previous kinetic results even given the substantial uncertainties from these measurements. The 11 h sample from run IR110 was lost due to an excessive injection of water onto the GC column. In these measurements, the major uncertainties for the MTBE loss included the low level of MTBE present initially in the mixture (ca. 10 ppbv), its relatively slow rate of reaction with OH, and corrections for required for dilution. TBF measurement uncertainties included difficulties in producing an accurate calibration at the 10 ppbv level and calibration reproducibility in the mass spectrometer.

Discussion

The photooxidation of RFG exhaust results in oxidation of NO to NO_2 , followed by the formation of ozone once the NO level is sufficiently low to render the NO + ozone reaction as unimportant. The rate

of NO removal in the system is an excellent indicator of the reactivity of the system. This value generally ranges from 1 ppbv/min for slowly reacting mixtures to greater than 5 ppbv/min for mixtures that show high reactivity. In these experiments, the values ranged between 2.4 and 2.9 ppbv/min. These values have the most meaning in comparison with the reactivity from other systems.

Several features typify the composition of RFG exhaust, the two main features being relatively high abundance of MTBE and its major combustion product, isobutylene. At present, the photochemistry of MTBE is thought to be fairly well understood [7, 8, 9]. MTBE is removed from the atmosphere mainly by its reaction with the hydroxyl radical (OH). However, the removal rate is relatively slow with an OH + MTBE rate constant of $3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This value leads to an atmospheric lifetime of approximately 3 days, assuming an average OH concentration of 0.05 pptv. The mechanism for OH reaction with MTBE is through hydrogen atom abstraction from the methyl or *t*-butyl group of MTBE with abstraction from the methyl group favored by a factor of three. Abstraction from the methyl group leads to the formation of TBF. The preponderance of evidence from mechanistic studies suggest that the yield from the reaction is 67%. The experiments in this study have yielded measurable quantities of TBF as expected from prior studies. However, given extremely low initial concentrations of 10 ppbv MTBE and the slow removal rate relatively little conversion of MTBE was found to occur. Notwithstanding this situation, positive identification for TBF was made by mass spectrometry in the selected ion mode. TBF yields in this study were consistent with previous measurements of 68%, although the precision here is substantially poorer than previous reported measurements, particularly for the amount of MTBE removed during photooxidation upon which the yield measurements rely.

The MS-SIM measurements provided excellent precision for TBF, as noted earlier 0.03 ppbv under the sampling conditions for this study. Measurements of the initial chamber composition thus provided a sensitive measure of the amount of TBF present in the combustion mixture. For the initial ROG concentration of 2.2 ppmC and the previously stated detection limit, less than 0.008% of the exhaust mixture would consist of TBF. Moreover, some additional GC/MS measurements were made from the undiluted exhaust which also does not show the presence of TBF in the nonirradiated exhaust. Thus, it is highly unlikely that TBF observed in environmental samples result directly from the combustion of RFG fuel.

Isobutylene (2-methylpropene) is a highly reactive compound formed from the combustion of MTBE. Detailed hydrocarbon measurements indicates that the compound comprises approximately 5% of the total ROG and approximately 25% of the olefin component in the exhaust. This compound reacts with OH radicals with a rate constant of $5.2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and thus having an atmospheric lifetime of 7 h under the conditions previously specified. OH reacts with isobutylene by adding to the double bond of the molecule. While reaction to the most substituted carbon is preferred, addition at either site will lead to the same products. Following normal photooxidation mechanisms and by analogy with ethylene and propylene, the alkoxy radical formed following OH addition is expected to decompose to give equimolar quantities of acetone and formaldehyde. Since acetone is substantially less reactive than either formaldehyde or acetaldehyde, isobutylene is expected to be less reactive than either ethylene and propylene which each form 2 aldehydic molecules for each reacted molecule. The relatively high acetone levels observed during the photooxidation suggests that isobutylene is an important yet not sole precursor to this compound.

The initial isobutylene concentrations for the exhaust irradiations were 37.1, 41.4, and 35.5 ppbv for IR109, IR110, and IR111, respectively. Figure 3c shows corresponding time series profiles for the formation of acetone. This plot shows a rapid rise in the acetone concentration over 4–6 h which is most

likely due mainly to reaction from one or more olefins, with isobutylene being the most reasonable contributor given its high initial concentration. Since isobutylene is completely removed by 6 h, further increase in the acetone concentration is probably due to the oxidation of moderate molecular weight alkanes such as isopentane or 2,2,4-trimethylpentane which has tertiary carbons.

Secondary reactions of acetaldehyde leads to the formation of PAN. Compounds, such as methyl glyoxal or biacetyl, can also formed acetyl radicals following photolysis or reaction with OH. Thus, these molecules can also serve as a precursor for PAN. Methyl glyoxal and biacetyl are typically generated following reaction of OH with aromatic compounds. As Table 3 indicates, aromatic hydrocarbons (particularly toluene, xylenes and the trimethylbenzenes) are present at yields approaching 40% of the total carbon. Product distributions from aromatic compound reactions with OH are poorly understood. However, their rapid reactions with OH (for $>C_7$ aromatics) and the potential for products to form radicals make these compounds highly reactive. However, these compounds also have a propensity for reacting with NO_2 to remove NO_x from the system and careful studies under a broad range of conditions must be undertaken to evaluate the reactivity of aromatic compounds.

As seen from the initial conditions in Table 3, moderate variability is present even under highly controlled conditions. Even with such variability, compensating factors appear to render the inorganic parameters largely invariant to the specific conditions provided that the initial levels of NO_x and total ROG are consistent. For example, the peak ozone level in the three experiments are all within 3%. The agreement is even closer when the values are normalized to the initial NO_x present. Reactivity factors (e.g., $-d[NO]/dt$ and $d[O_3]/dt$) can also be calculated from the inorganic profiles. These factors allow comparisons in the reactivity of different real-world exhaust mixtures. Further consideration of these issues will be left for a separate forum.

Conclusions

This study has been conducted to examine the atmospheric chemistry and reactivity of real-world exhaust mixtures. Considerable effort has been expended in establishing an accurate representation of the initial conditions for these experiments. Use of exhaust from the first 124 s of the FTP for the vehicle utilized permitted irradiations of the exhaust mixture without the substantial addition of a surrogate compound. Even with the moderate variability observed in these experiments, the formation of oxidant compounds such as ozone and PAN are quite reproducible. Reactive intermediates, particularly formaldehyde, are considerably less reproducible in their time-series profile. A major differences between RFG exhaust and that produced with standard 1990 industry average gasoline is the presence of MTBE and isobutylene. The oxidation of MTBE produces a high yield of TBF which have been reconciled on a semiquantitative basis in this study. However, the conversion of MTBE was extremely slow in the chamber, as it is in the ambient atmosphere. Likewise, isobutylene produces acetone as a major product for which their is reasonably good mass balance between the reactive removal of isobutylene and the formation of acetone. Since acetone reacts extremely slowly with OH in the ambient atmosphere, it could distribute widely over the upper troposphere and serve as an additional source of radicals following photolysis.

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Table 1. Fuel specification for RFG used in the study.

Specification	Value	Specification	Value
Specific Gravity	0.7385	Distillation, °C.	
RVP, psi	7.06	IBP	39
Sulfur, wt %	0.0036	10%	56
MTBE, v %	12.4	50%	93
Alkane, v %	56.0	90%	148
Alkene, v %	5.8	EP	191
Aromatic, v %	25.8	Lower Heating Value, BTU/gal	112,240

Table 2. Results of hydrocarbon analysis for the RFG hydrocarbon surrogate; (left) top 25 compounds by carbon abundance, (right) generic distribution according to carbon number.

Hydrocarbon	Surrog Conc ^a for 2.2 ppmC	Distribution	% of Total Hydrocarbon
Toluene	0.1800	Alkanes: C4	1.07
Methyl <i>t</i> -butyl ether	0.1636	C5	7.92
<i>m</i> + <i>p</i> -Xylene	0.1621	C6	7.12
Isopentane	0.1463	C7	10.21
2,2,4-Trimethylpentane	0.1302	C8	12.30
Ethylene	0.1113	C9	1.65
Isobutylene	0.0972	>C9	0.48
2,3-Dimethylpentane	0.0790	Alkenes: C2	5.06
Ethylbenzene	0.0675	C3	2.94
Propylene	0.0646	C4	5.05
<i>o</i> -Xylene	0.0613	C5	1.45
2-Methylpentane	0.0521	C6	1.29
1,2,4-Trimethylbenzene	0.0471	C7	0.84
1-Methyl-3-ethylbenzene	0.0437	>C7	0.95
2,3,4-Trimethylpentane	0.0416	Aromatics: C6	0.98
2,4-Dimethylpentane	0.0384	C7	8.18
3-Methylpentane	0.0343	C8	13.36
3-Methylhexane	0.0316	C9	7.56
2-Methylhexane	0.0296	>C9	2.35
2,3-Dimethylbutane	0.0260	Total Alkanes:	40.8
<i>n</i> -Pentane	0.0259	Total Alkenes:	17.6
1,3,5-Trimethylbenzene	0.0226	Total Aromatics:	32.4
Benzene	0.0215	Total Oxygenates:	7.9
<i>n</i> -Butane	0.0214	Total Carbonyls:	1.2
1-Methyl-4-ethylbenzene	0.0194	Unknowns:	0.1

Table 3. Initial conditions for RFG exhaust irradiations. RFG surrogate additions indicated.

Parameter	IR109	IR110	IR111
NO, ppbv	402	396	397
NO _x , ppbv	234	342	360
ROG, ppmC	2.17	2.11	2.22
Surrogate, %	5.4	10.9	0
ROG/NO _x	5.39	5.33	5.59
Water, ppmv	16,300	15,200	15,300
HCHO, ppbv	14.2	18.7	10.3
CH ₃ CHO, ppbv	3.3	4.2	2.8
CO, ppmv	8	8	10
Sum Alkanes, %C	32.4	33.6	36.0
Sum Alkenes, %C	19.3	21.5	20.1
Sum Alkynes, %C	3.6	4.1	6.7
Sum Aromatics, %C	39.7	36.1	32.3
Sum Oxygenate, %C	2.4	4.1	6.7
Sum Carbonyl, %C	2.4	2.9	2.6

Table 4. Concentrations (ppbv) of *t*-butyl formate (TBF) for measured reactive losses of MTBE. TBF concentrations from selected ion mass spectrometry ($m/e=59$) and initial concentrations were below the detection limit of approximately 50 pptv. MTBE concentrations were based on a per carbon response factor from propane and its losses were corrected for dilution.

Experiment	MTBE loss (6 h)	MTBE loss (11 h)	TBF formed (6 h)	TBF formed (11 h)
IR109	2.0	4.2	1.8	4.9
IR110	2.4	3.9	1.9	---
IR111	3.2	6.2	2.2	4.1

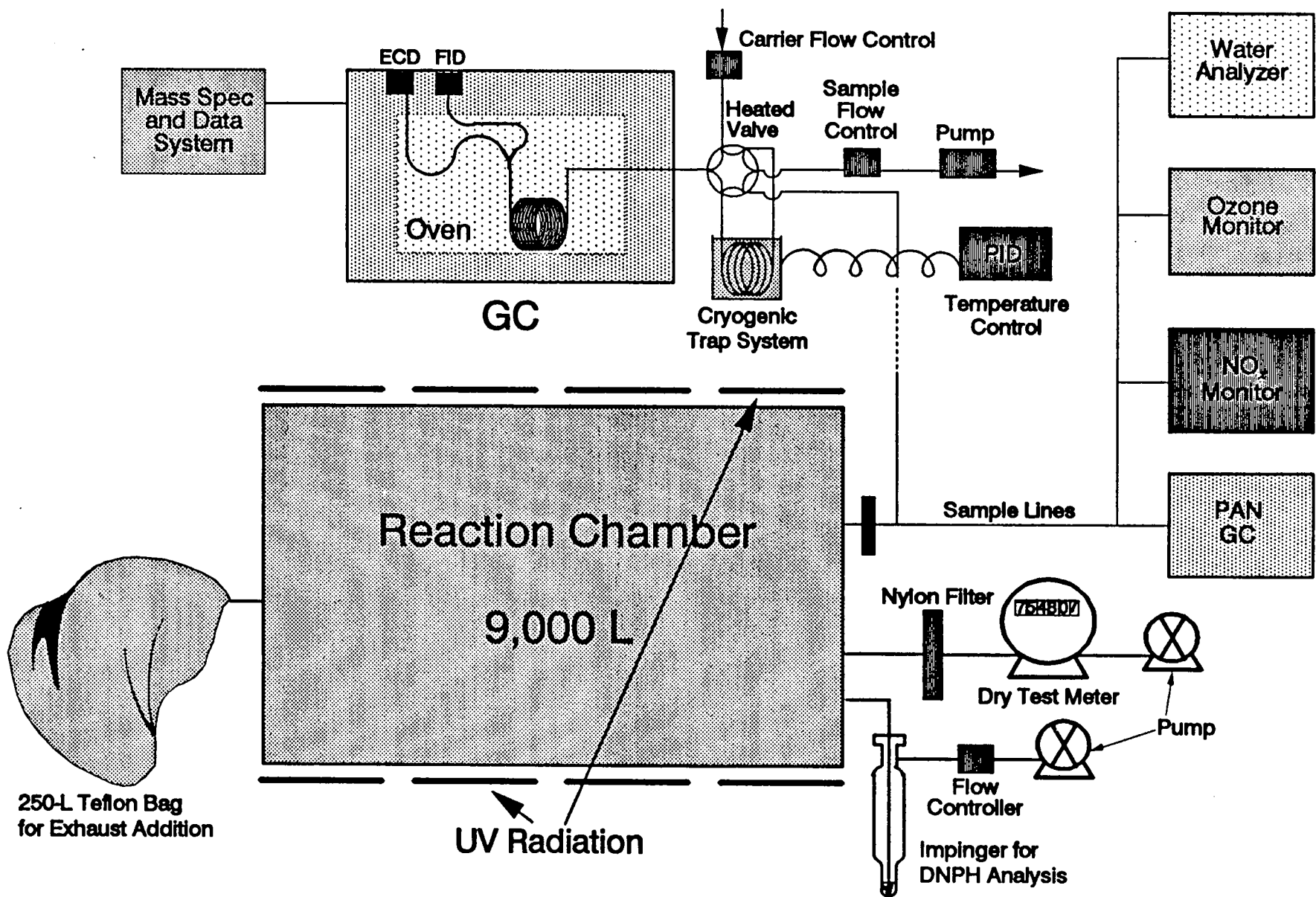


Figure 1. Schematic of chamber irradiation system for alternative-fuel automobile exhaust.

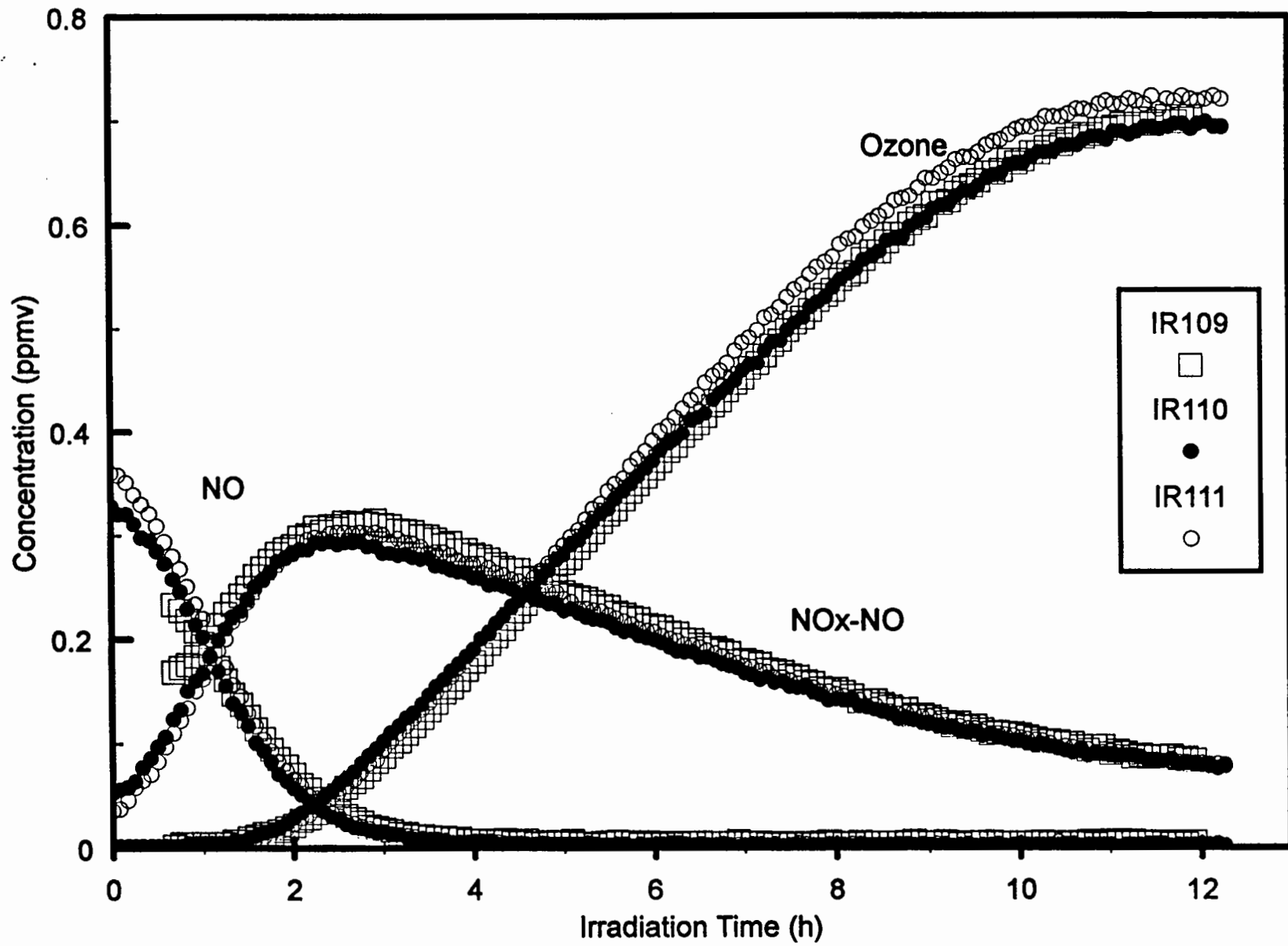


Figure 2. Time series profiles for the major inorganic components ozone, NO, and NO_x-NO.

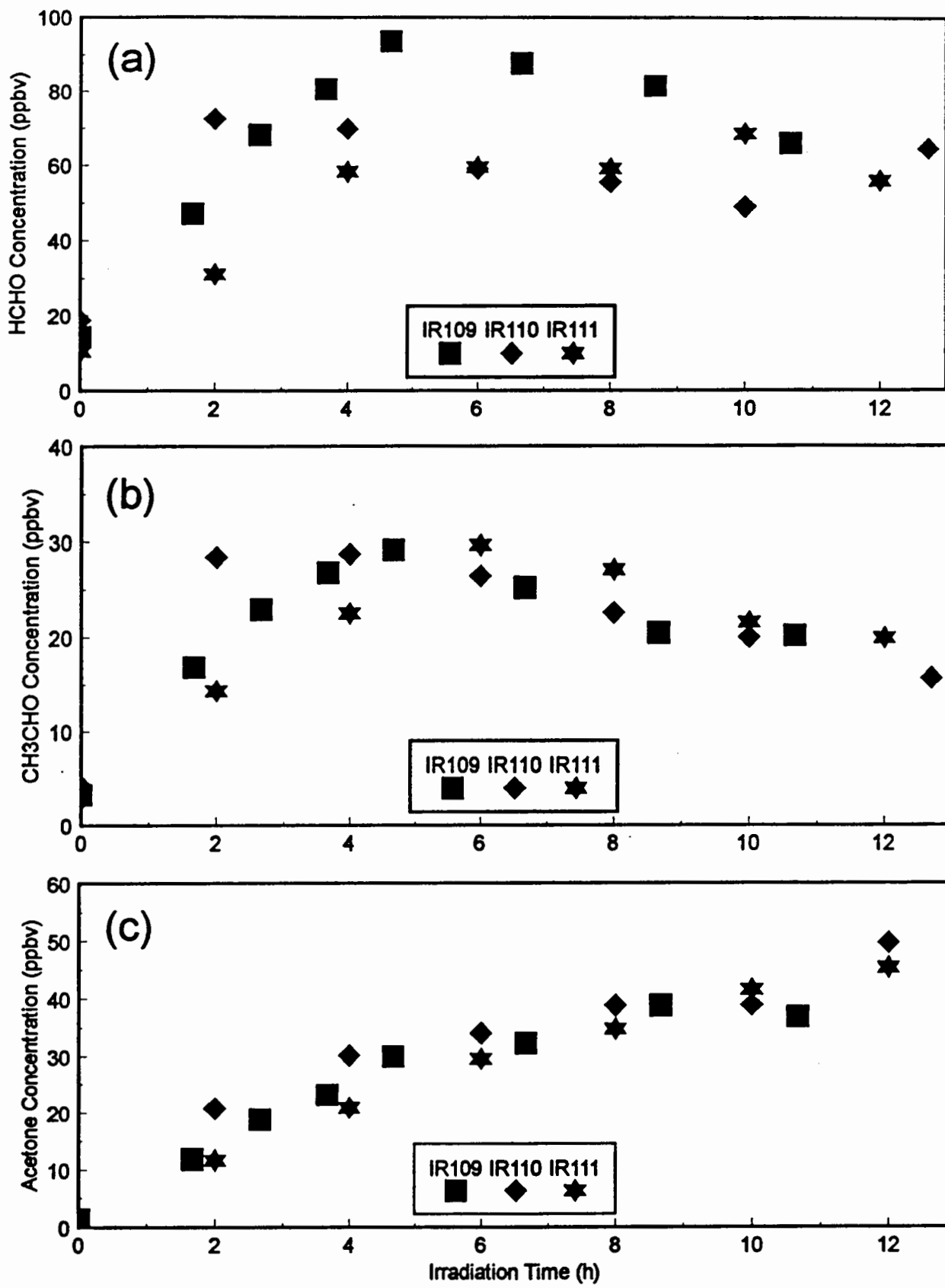


Figure 3. Time series profiles for selected carbonyl compounds formed through termination reactions during the irradiations (a) formaldehyde, (b) acetaldehyde, and (c) acetone.

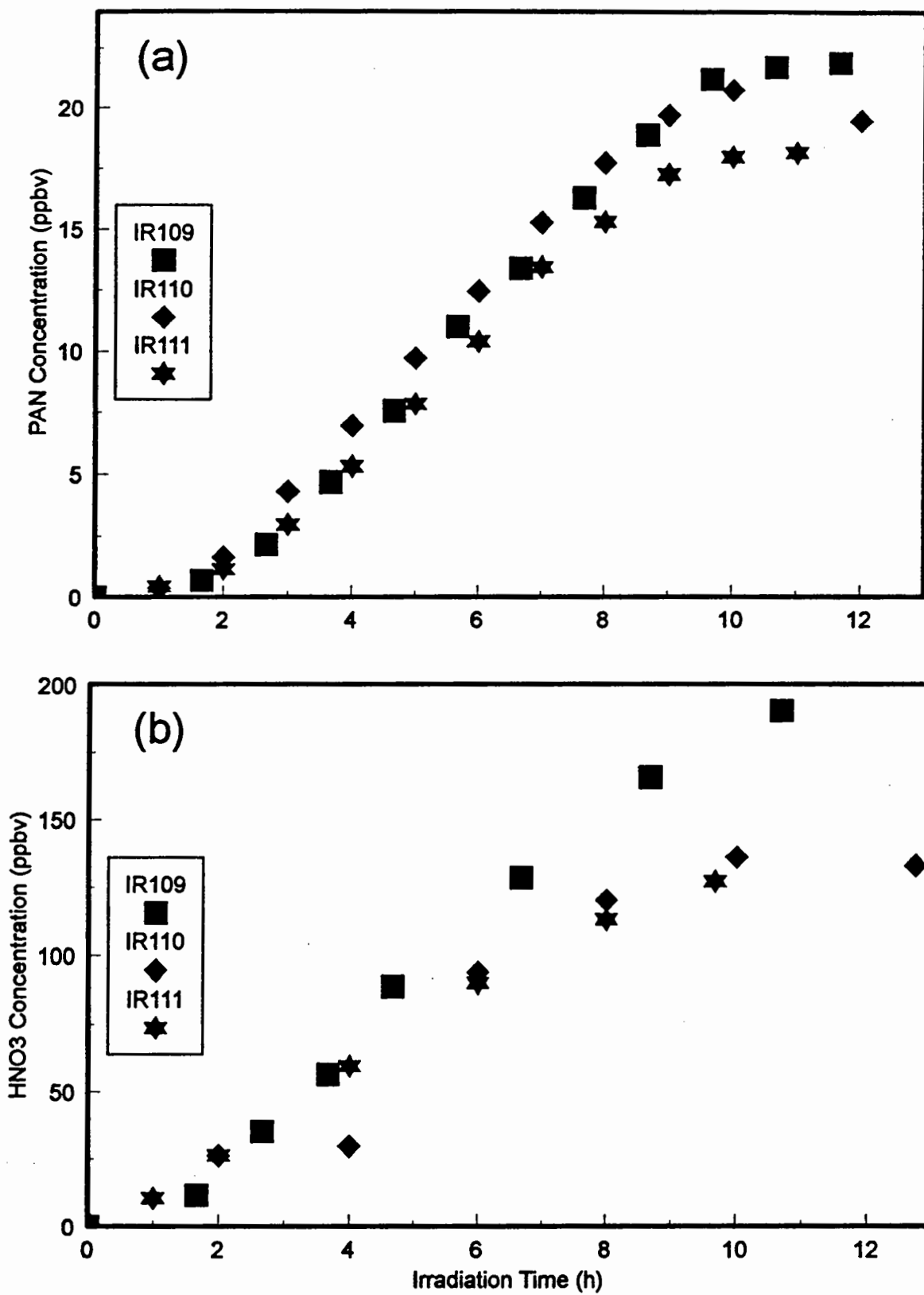


Figure 4. Time series profiles for the major NO_y compounds formed through termination reactions during the irradiations (a) peroxyacetyl nitrate; PAN, (b) nitric acid; HNO₃.

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16. ABSTRACT The Alternative Motor Fuels Act (AMFA) of 1988 requires the Department of Energy (DOE) to purchase alternative fuel motor vehicles for use in government fleets, and further requires DOE to cooperate with the Environmental Protection Agency (EPA) and the National Highway Traffic Administration to evaluate potential safety, fuel economy, and emissions implications of these alternative technologies. EPA and DOE initiated cooperative study of alternative fuel vehicle emissions and their implications for air quality in 1991. This paper describes studies of the atmospheric photochemistry of motor vehicle exhaust emissions with reformulated gasoline fuel. Alternative fuel (e.g., methanol, ethanol, and natural gas) benefits must be contrasted with those of reformulated gasoline. The results of indoor (using an array of fluorescent lights to simulate sunlight) chamber irradiations of vehicle exhaust are reported. Time profiles of NOx, ozone, PAN, nitric acid, and aldehydes are reported. Tertiary butylformate, a transformation product of MTBE emissions, is also examined.			
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