

# Experimental Evaluation of Ozone Forming Potentials of Motor Vehicle Emissions

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## ABSTRACT

Evaluations of air quality impacts from vehicle emissions are based on the assumptions that all the important reactive species in the exhaust have been identified and quantified and that they are accurately represented in airshed models. To test this, environmental chamber experiments were carried out with exhaust from vehicles fueled by LPG, M100, M85, CNG, diesel, and Phase 2 reformulated gasoline (RFG), with the latter including vehicles representing a range of mileages, types, and pollution levels. Baseline FTP tests and speciation analyses were carried out for all vehicles studied but diesel. The chamber experiments consisted of irradiations of the exhausts themselves, "incremental reactivity" experiments with the exhaust added to two different surrogate VOC - NO<sub>x</sub> mixtures simulating conditions of photochemical smog, and irradiations of synthetic exhaust mixtures based on the results of the exhaust analyses. Computer model simulations of the experiments were also carried out. The results of most of the experiments were consistent with results of experiments using synthetic exhausts derived to represent them, and were generally consistent with model predictions. This indicates that the major constituents contributing to their ozone impacts have probably been identified, and that a current chemical mechanism is reasonably successful in predicting these impacts. The major exception to this was the one experiment with diesel exhaust, where a complete analysis was not conducted. There was some evidence, albeit inconclusive, that the model may be underpredicting the ozone impacts of some of the constituents of exhausts from the two highest mileage RFG-fueled vehicles in some experiments, but the model gave reasonably good simulations of effects of adding these to realistic ambient VOC - NO<sub>x</sub> mixtures, as was the case for all the other exhausts for which complete analyses were conducted.

## INTRODUCTION

Over the past two decades, there has been a considerable effort in the United States to develop and introduce alternatives to gasoline and diesel as transportation fuels. The introduction of alternative fuels is considered by many to be an important component in the implementation of air quality improvement plans. The benefits of alternative fuel vehicles for air quality are related both to an anticipated decrease in the mass emission rate and a decrease in the atmospheric reactivity of the exhaust gas components. To account for the lower reactivity of alternative fuel exhaust, the California Air Resources Board has established reactivity-based emission standards. Such standards use "reactivity adjustment factors" to adjust the non-methane organic carbon gas (NMOG) mass emission rate for the different ozone formation potentials of the chemical species in the exhaust.<sup>1</sup> Reactivity factors have been developed over the years on the basis of chemical

mechanisms for volatile organic carbon (VOC) and nitrogen oxides (NO<sub>x</sub>). These mechanisms are used in airshed models and are the primary means for assessing the effects of alternative fuels on air quality. The validity of such evaluations rest on the assumptions that all the important reactive species in the exhaust have been identified and quantified, and that the chemical mechanisms used in the model accurately represent how their atmospheric reactions affect ozone production.

There is a need for further validation of these assumptions. Conducting environmental chamber experiments involving irradiation of actual vehicle emissions and determining whether the formation of ozone and other secondary pollutants is consistent with model predictions is one way of testing these assumptions. A limited number of environmental chamber experiments involving automobile exhaust have been carried out,<sup>2-6</sup> and some have been used to a limited extent for model evaluation.<sup>7,8</sup> However, most of the previous experiments involving automobile exhaust have not been sufficiently well characterized for model evaluation, or have not used current state-of-the-art methods for speciated vehicle emissions analysis. In addition, if the model is not successful in simulating the results of an irradiated exhaust experiment, one does not know whether the problem is with the identification and quantification of the reactive species present, the gas-phase chemical mechanism for the species, or with the representation in the model of important chamber and light source characteristics. Furthermore, a successful model simulation of such an experiment does not by itself provide convincing evidence that we adequately understand the system, since there is always the possibility that errors in the exhaust speciation might be masked by compensating errors in the chemical mechanism or the model for chamber conditions.

To address these issues, this project was carried out is to provide data to test whether all of the important reactive species in vehicle exhausts using selected fuels have been identified, and to test whether current chemical models can predict the amount of ozone and other oxidants formed when the exhaust is irradiated. The approach involved conducting environmental chamber experiments using diluted exhaust from conventional and alternative fueled vehicles, and also with known mixtures designed to represent the compounds identified in these exhaust samples. The experiments were conducted under sufficiently well characterized conditions to allow model testing, and in conjunction with the array of control and characterization experiments to characterize chamber and light source effects. A comparison of the results of synthetic and “actual” exhaust experiments can then be used to assess whether the important reactive species in the exhaust have been identified. Comparison of the ozone and other oxidants formed in the chamber experiments with those predicted by the model can be used to evaluate the level of understanding of which exhaust components are contributing to the reactivity.

## **METHODS**

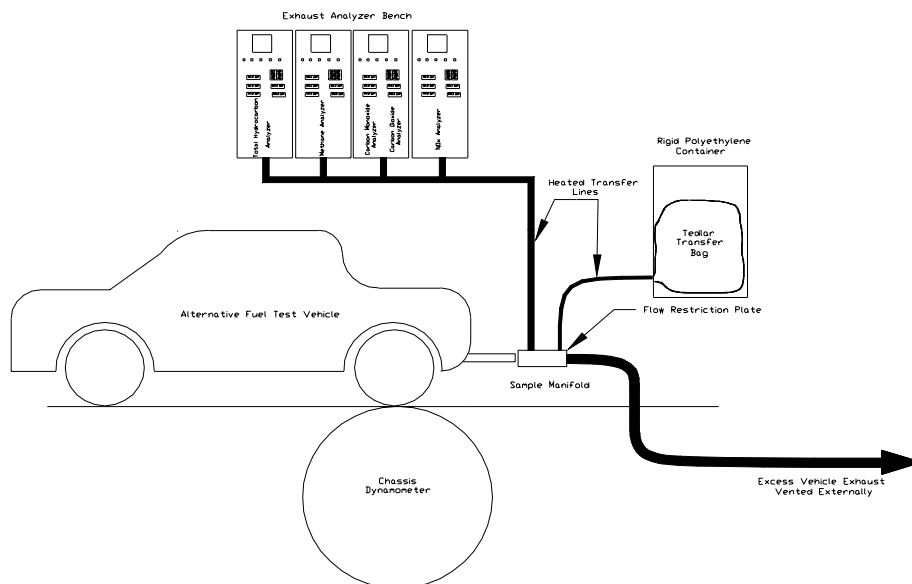
The vehicle emissions testing and exhaust sampling was carried out in the College of Engineering Center for Environmental Research and Technology (CE-CERT)'s Vehicle Emissions Research Laboratory (VERL). The VERL utilizes a Burke E. Porter 48-inch single-roll, electric chassis dynamometer coupled with a Pierburg CVS and analytical system. Speciated analyses of the hydrocarbons and oxygenates in the exhausts were

carried out according to the Auto/Oil Phase II protocol<sup>9</sup> using GC/FID and HPLC analysis. The Federal Test Procedure (FTP) tests were carried out using the protocol in the Code of Federal Regulations.<sup>10</sup>

The tests used to produce and collect the exhausts for the chamber experiments were carried out separately from the FTP tests. To obtain a useful measure of the effects of the VOCs present in the exhaust mixtures on ozone formation and other measures of air pollution, it is necessary to introduce a sufficient amount of exhaust VOCs in the chamber to yield a measurable effect. Therefore, most chamber experiments utilized cold-start exhausts to provide the largest amount of exhaust VOC for chamber testing. The typical procedure was to gradually accelerate the vehicle to 40 mph from a cold start condition, followed immediately by sampling for ~30 seconds once steady state operation was achieved.

Two different procedures were used to transfer the exhaust from the vehicle to the chamber during the course of this program. During the first phase, a mini-diluter system was used to dilute the exhaust and transfer it to the chamber laboratory, with the dilution being such that the humidity was no more than 50% RH at ambient temperature. Tests with a M100 vehicle indicated that there may be loss of formaldehyde on the sample line during this procedure, so this was not used for the second phase. (For that reason, M100 data from the first phase of this program are not discussed in this paper.) During the second phase the exhaust was injected into a Teflon transfer bag (again diluted so the humidity was less than 50% at ambient temperature), which was then moved to the chamber laboratory for injection into the chamber. The vehicle exhaust sampling system used in the second phase is shown in Figure 1.

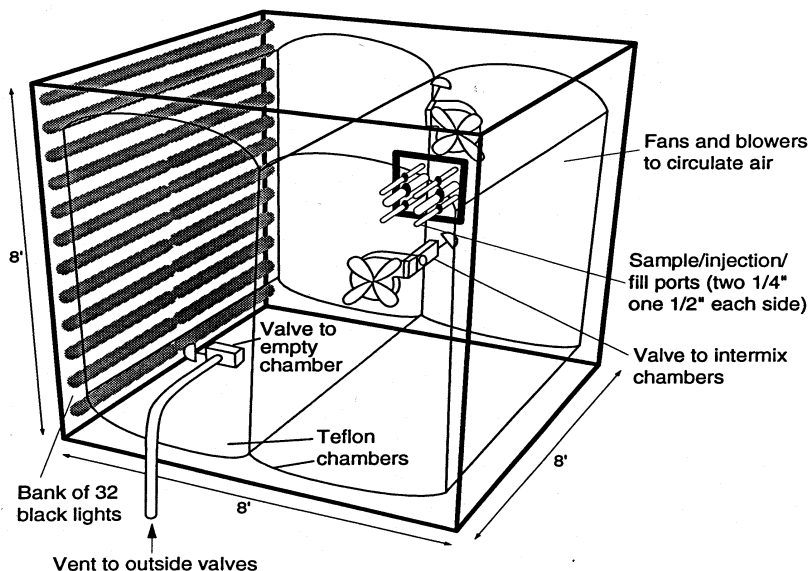
**Figure 1.** Schematic of vehicle exhaust sampling system for the Phase 2 environmental chamber experiments.



In both cases, analyses were made both of the raw exhaust, and of the diluted exhaust in the transfer line or the transfer bag prior to injecting the exhaust into the chamber.

The chamber experiments were carried out using CE-CERT's dual-mode Dividable Teflon Chamber (DTC). This, which is described in detail elsewhere,<sup>11, 12</sup> consists of two ~5000-liter FEP Teflon reaction bags surrounded by blacklights. A schematic of the chamber employed is shown in Figure 2.

**Figure 2** Schematic of the environmental chamber used in this study.



Two types of experiments were carried out using exhausts or synthetic exhaust mixtures: one where the exhaust (or the mixture of VOCs and  $\text{NO}_x$  designed to simulate the exhaust) was irradiated by itself, and the other where the exhausts or synthetic exhausts were evaluated in "incremental reactivity" experiments. In those experiments, the exhaust was added to a "surrogate" reactive organic gas (ROG) -  $\text{NO}_x$  mixture, to measure the incremental effect of the exhaust (or synthetic exhaust) addition. Two types of ROG surrogates were used to simulate the effects of ambient VOCs in the incremental reactivity experiments. A simple 3-component "mini-surrogate" was employed because it was found to be highly sensitive to the effects of added VOCs, and in particular their effects on the overall radical levels (an important factor affecting a compound's Maximum Incremental Reactivity [MIR]).<sup>12</sup> In addition, a more complex 8-component "full surrogate" designed to represent more closely the VOCs present in polluted urban atmospheres, was also employed.<sup>12</sup> Experiments with mechanism evaluation and VOC reactivity assessment indicate that experiments with these two surrogates provide good tests of different aspects of a VOC's mechanism which affect ozone formation.<sup>12, 13</sup> The incremental reactivity experiments were carried out with the  $\text{NO}_x$  levels the same in both the "base case" and the added exhaust reaction mixtures, to assess the effects of the exhaust VOCs only.

The results of the experiments were compared with the predictions of model calculations using an updated version of the Statewide Air Pollution Research Center (SAPRC) chemical mechanism.<sup>13, 14</sup> An earlier version of this mechanism<sup>15</sup> was utilized to calculate the MIR scale that was used to derive the RAFs in the California vehicle regulations.<sup>16</sup> The updates incorporate improvements to mechanisms for aromatics, alkenes, and other VOCs resulting from more recent laboratory and environmental chamber studies.<sup>13</sup> Note that the mechanism employed in this study is not the latest version of the SAPRC mechanism,<sup>17</sup> but the recent updates to the mechanism are not expected to significantly affect results of simulations of the actual or synthetic exhaust mixtures used in this study.<sup>17</sup>

## **Vehicles Studied**

The ten fuel-vehicle combinations studied in this program are summarized in Table 1. The results of the FTP tests are also summarized for those vehicles that were tested. The table shows that the vehicle test matrix employed in this study includes a diverse cross section of late model and intermediate age alternative fuel and conventional fuel vehicles. These vehicles are all equipped with closed loop feedback and catalytic converters (except for the diesel vehicle) and show a range of restorative and preventative maintenance. The mass emission rates are similarly diverse with transitional low-emissions vehicle (TLEV) certified vehicles tested with older malfunctioning super emitters. Therefore, they provide a varied set of exhaust types for reactivity evaluation in the environmental chamber experiments.

## **RESULTS**

### **LPG Reactivity**

The major reactive VOC species measured in the cold-start exhaust from the LPG vehicle were found to be CO, propane, isobutane, n-butane, ethylene, and propene. Experiments were carried out using LPG exhaust and a surrogate LPG mixtures which was prepared based on the assumption that these are the only species accounting for LPG's reactivity. Results of selected experiments are shown on Figure 3 and Figure 4, where Figure 3 shows data from the experiments with the exhaust (or surrogate exhaust) alone, and Figure 4 shows data from incremental reactivity experiments with the actual and surrogate LPG exhausts. Results of model simulations are also shown on both figures.

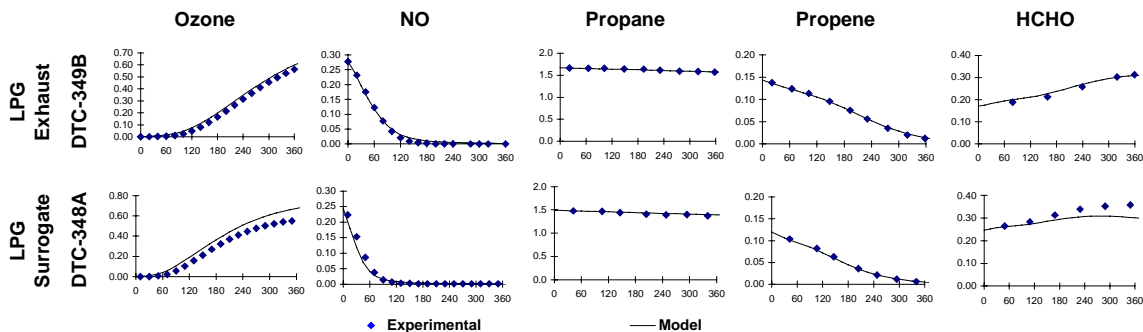
There are apparently no undetected compounds significantly affecting the reactivity of the cold-start LPG exhaust, because, as shown on the figures, experiments with synthetic exhausts made up with the measured compounds in the appropriate proportions with NO<sub>x</sub> gave essentially the same results as the experiments with the actual exhausts. The model performed reasonably well in simulating the results of both the actual and the surrogate LPG experiments. This is expected, because the main contributors to LPG reactivity are simple compounds whose mechanisms are believed to be reasonably well understood, and which have been individually evaluated previously using chamber data. The slight differences between the actual and surrogate LPG experiments can be accounted for by differences in initial reactant concentrations, which are taken into account in the model simulations.

**Table 1.** Summary of fuel-vehicle combinations studied and FTP results.

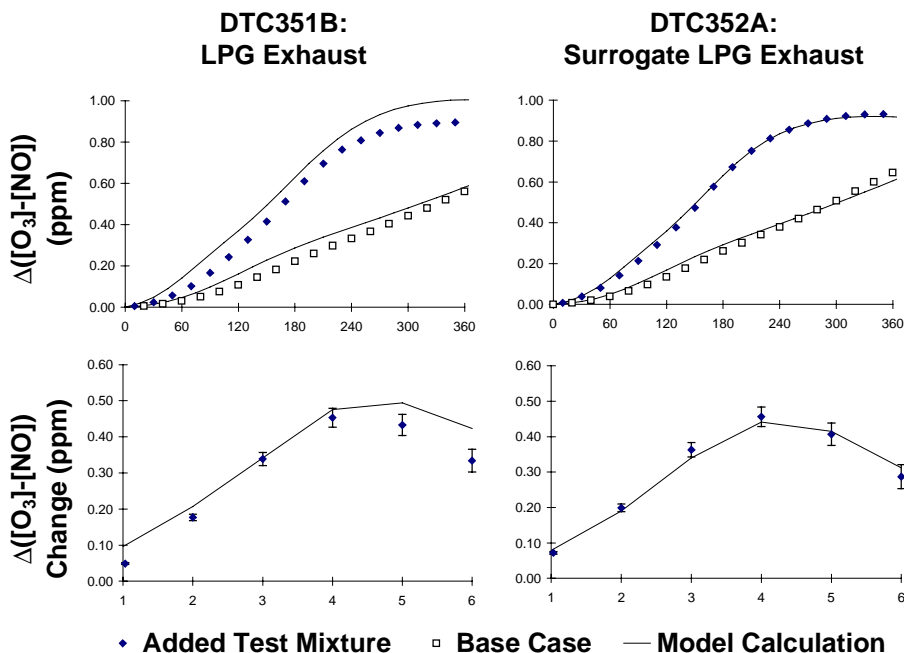
Vehicle Description	Fuel	Odometer at start	FTP Emissions (mg/mile)				
			NMHC	MeOH	HCHO	CO	NO <sub>x</sub>
Retrofitted 1989 Plymouth Reliant. 2.2-liter, 4-cylinder engine.	LPG	29,600	1,080	-	-	18,170	163
1993 Ford Taurus Flexible Fuel Vehicle. 3.0-liter, 6-cylinder engine.	M100	38,100	181	335	21	1,793	206
1997 Ford Taurus OEM Flexible Fuel Vehicle. 3.0-liter, 6-cylinder engine.	M85	6,890	71	247	17	1,149	103
1991 Ford Ranger PU. Dedicated retrofit CNG.	CNG	17,800	42	0	5	3,591	498
1997 Ford Taurus OEM Flexible Fuel Vehicle. 3.0-liter, 6-cylinder engine.	RFG	13,600	(Not tested. Lowest VOC, NO <sub>x</sub> and CO in chamber experiments than all the other vehicles tested.)				
1991 Dodge Spirit. OEM Flexible Fuel Vehicle. 2.5-liter 4 cylinder engine	RFG	14,300	107	11	3	2,373	184
1994 Chevrolet Suburban C1500 2 wheel drive. 5.7-liter V8 engine	RFG	58,000	350	0	3	7,930	540
1984 Toyota PU. 2.4-liter engine.	RFG	227,000	2,080	-	-	6,220	1,670
1988 Accord 2.0-liter 4 cylinder engine	RFG	150,000	190	-	-	5,900	740
1984 Mercedes Benz 300D. 3.0-liter, 5 cylinder turbocharged diesel	RFD	170,000	(Not tested)				

Based on these results, we can conclude that we understand the compounds and mechanisms accounting for the ozone impacts of the cold-start exhaust from this type of LPG-fueled vehicle. Although the mass emission rates of the LPG vehicle tested were higher than the appropriate emission standard would indicate, the hydrocarbon profiles found in this study are consistent with previous work and indicate the results should be representative of LPG vehicles in general.

**Figure 3.** Experimental and calculated concentration-time profiles for selected species in selected LPG exhaust and surrogate LPG exhaust experiments. Time units are minutes.



**Figure 4.** Experimental and calculated results with selected incremental reactivity experiments with actual and surrogate LPG exhaust.  $\Delta([\text{O}_3]-[\text{NO}])$  is the sum of  $\text{O}_3$  formed and  $\text{NO}$  oxidized. The “ $\Delta([\text{O}_3]-[\text{NO}])$  change” is the difference between this quantity measured in the added exhaust or surrogate exhaust experiment and that measured in the experiment without the added mixture. Time units are minutes on the  $\Delta([\text{O}_3]-[\text{NO}])$  plots and hours on the  $\Delta([\text{O}_3]-[\text{NO}])$  change plots.

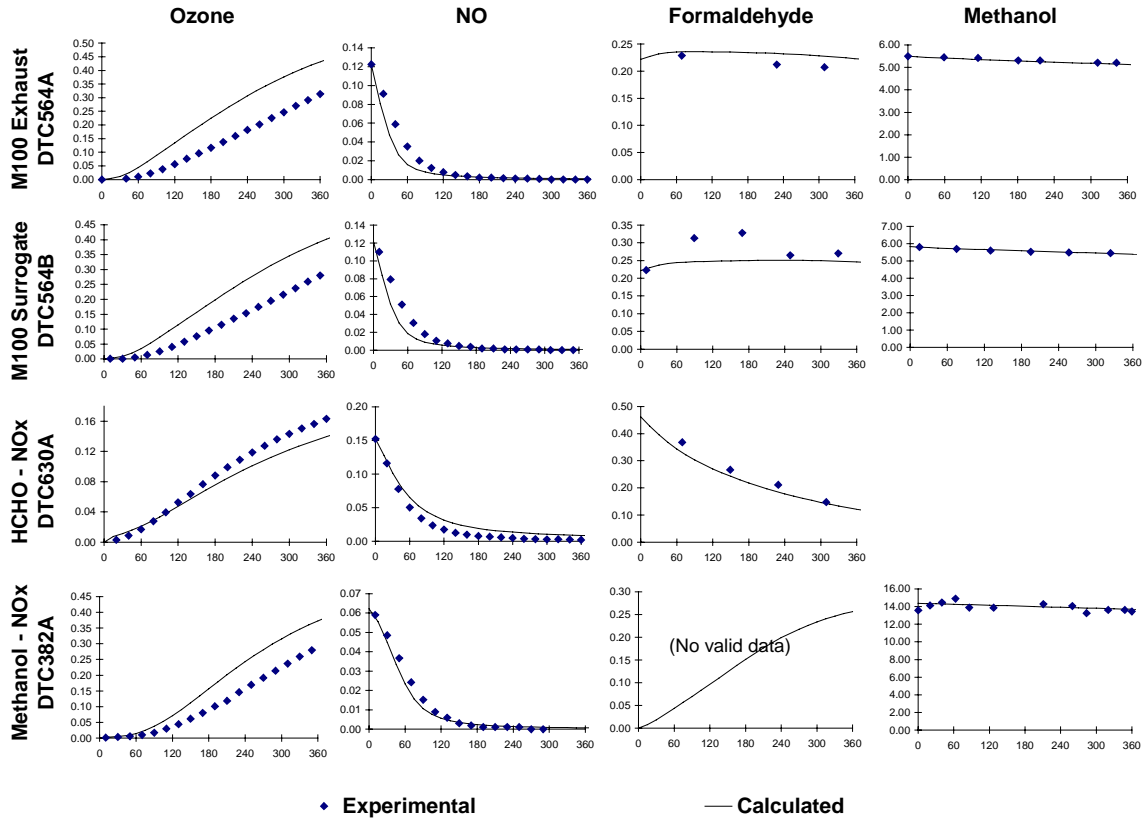


## M100 and M85 Reactivity

The species accounting for the reactivity of the cold-start M100 emissions were, as expected, methanol and formaldehyde. Methanol and formaldehyde were also found to be the only species measured in high enough levels to contribute significantly to the reactivity of the cold-start M85 exhausts as well. Therefore, the surrogate M100 and M85 exhausts were made using only methanol and formaldehyde.

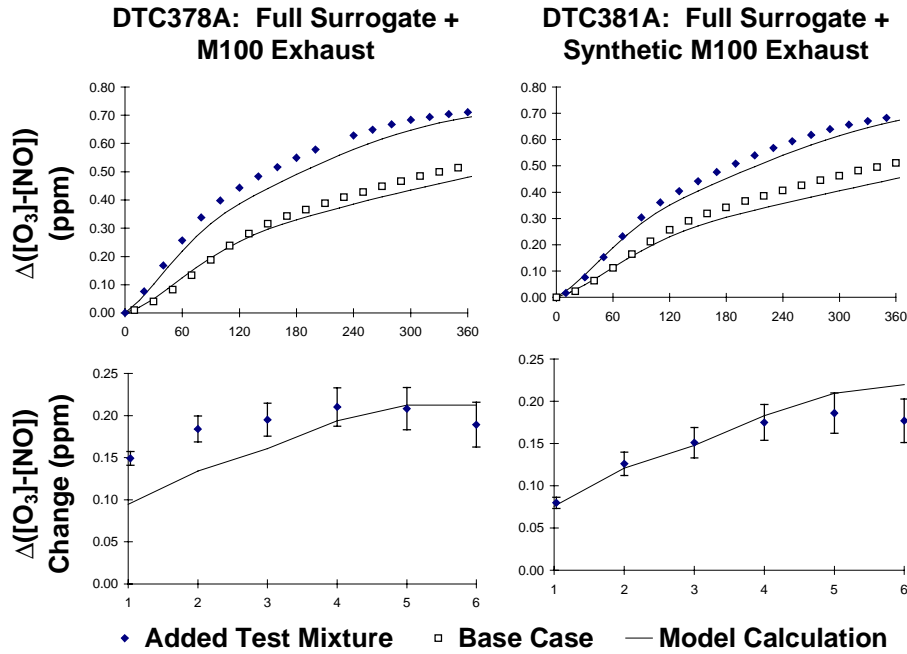
The results of selected experiments with actual and surrogate M100 alone in the presence of  $\text{NO}_x$  are shown on Figure 5. (Results with M85 alone are not shown because relatively little reactivity was observed due to the low VOC levels.) The results of selected incremental reactivity experiments with the actual and surrogate exhausts are shown on Figure 6 for M100 and on Figure 7 for M85. Note that experiments with both the mini-surrogate and the full surrogate were carried out for both types of exhausts; the data shown on these figures are representative.

**Figure 5.** Experimental and calculated concentration-time plots for selected species in selected M100 exhaust, surrogate M100, formaldehyde -  $\text{NO}_x$  and methanol -  $\text{NO}_x$  experiments.

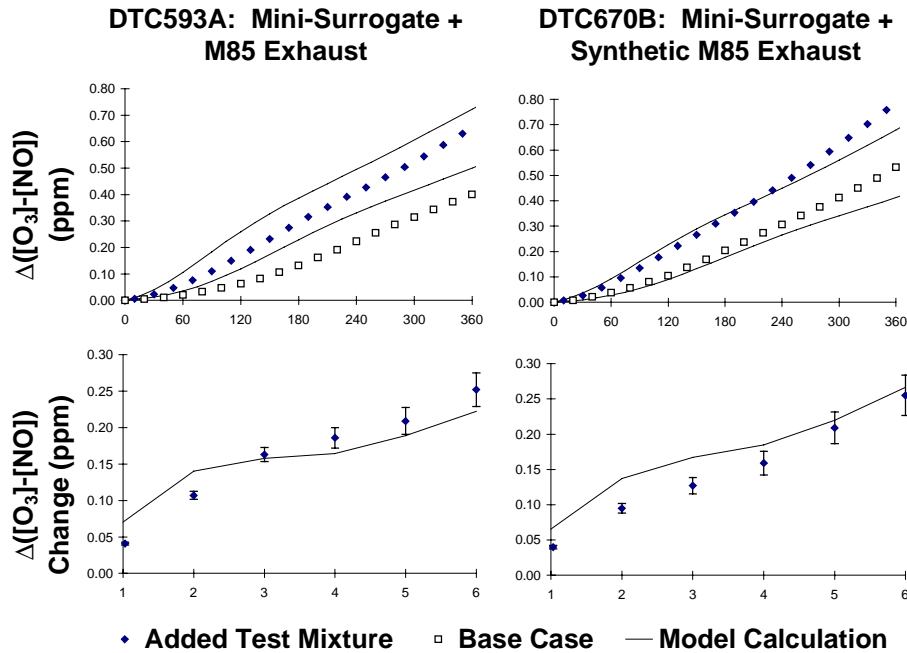




**Figure 6.** Experimental and calculated results with selected incremental reactivity experiments with actual and surrogate M100 exhaust.



**Figure 7.** Experimental and calculated results with selected incremental reactivity experiments with actual and surrogate M85 exhaust.



As shown on the figures, no significant differences were observed in incremental reactivity experiments between actual cold-start M100 and M85 exhaust and the methanol/formaldehyde/ $\text{NO}_x$  mixtures designed to simulate them. This indicates that there are

probably no significant contributors to M100 and M85's reactivity which are not being detected, and that the hydrocarbons from at least the M85 vehicle used in this study do not contribute measurably to the cold-start exhaust reactivity. In no case was there any evidence for any contribution of methyl nitrite to M100's reactivity, which, if it were significant, would be apparent in the initial NO oxidation rate.

The results of the model simulations are also shown on the figures. Similar results were obtained in the simulations with the actual and synthetic exhausts for both types of fuels, and generally the model gave good simulations of the incremental effects of adding the actual or synthetic methanol fuels to the surrogate mixtures. This provides further support to our conclusion that the observed methanol and formaldehyde are the main contributors to M100's reactivity, and that undetected compounds do not play a significant role.

However, as shown on Figure 5, some inconsistencies were observed in the simulations of the experiments with the actual or synthetic exhausts when injected into the chamber in the presence of NO<sub>x</sub> alone. These inconsistencies appeared to be due to problems with the model's ability to simulate any experiments with formaldehyde or methanol, regardless of whether they are in synthetic mixtures or in actual exhausts. In particular, the model had a slight but consistent bias towards underprediction of reactivity of formaldehyde in this chamber, and overprediction of reactivity of methanol or methanol with formaldehyde when irradiated in the absence of other VOCs. (Note that this overprediction in the simulations of the methanol-containing systems cannot be attributed to formation of methyl nitrite, since the presence of methyl nitrite in the model simulation would make the overprediction even worse.) These biases were essentially the same when simulating actual M100 or M85 exhausts as when simulating synthetic methanol with formaldehyde - NO<sub>x</sub> mixtures.

On the other hand, the model simulated the incremental effects of adding the exhausts or methanol with formaldehyde mixtures to photochemical smog surrogate mixtures without any apparent consistent biases. The reasons for these biases in the simulations of experiments with methanol and/or formaldehyde in the absence of other pollutants is unknown and may be due to problems with chamber characterization, since the atmospheric reactions of these compounds are believed to be reasonably well established. If this is the case, the experiments with the more realistic mixtures appear to be less sensitive to this characterization problem. In any case, the results of the reactivity experiments suggest that the model will probably perform reasonably well in simulating the reactivities of methanol exhausts in the atmosphere.

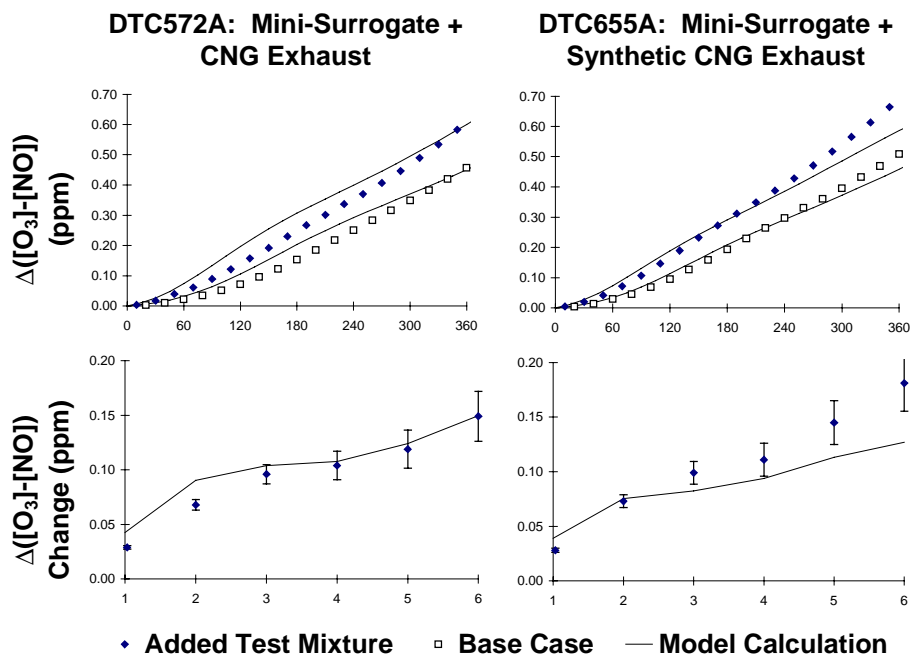
## **CNG Reactivity**

The only species detected in the cold-start CNG exhausts studied in this program at levels sufficient to affect ozone formation were NO<sub>x</sub>, CO, and formaldehyde. The levels of methane and other hydrocarbons detected in these exhausts were insufficient to significantly affect predicted reactivity. Therefore, only CO and formaldehyde were used to synthesize the surrogate CNG exhaust for this study.

Although essentially no O<sub>3</sub> formation occurs when the exhaust is irradiated by itself, the CO and formaldehyde levels in the cold start CNG exhausts were sufficient to have a measurable (and positive) effect on NO oxidation and O<sub>3</sub> formation when added to smog surrogate VOC - NO<sub>x</sub> mixtures. Essentially the same results were obtained in experiments using CO and formaldehyde mixtures at the same levels as measured in the CNG exhaust experiments, and the results were consistent with model predictions. This is shown on Figure 8, which results from representative incremental reactivity experiments. This indicates that CO and formaldehyde are indeed the major species accounting for CNG reactivity. Significantly less reactivity was observed when formaldehyde was omitted from the synthetic CNG mixtures, indicating that the formaldehyde in CNG exhaust makes a non-negligible contribution to its reactivity, at least in the chamber experiments.

The results of model simulations of the selected CNG incremental reactivity experiments are also shown on Figure 8. As expected given the simple mixture of compounds affecting CNG reactivity, the model performs reasonably well in simulating the effect of adding the actual or surrogate exhaust.

**Figure 8.** Experimental and calculated results with selected incremental reactivity experiments with actual and surrogate CNG exhaust.



## RFG Reactivity

As shown on Table 1, the five RFG-fueled vehicles used in this program represented a variety of vehicle types, mileages, and NO<sub>x</sub> and VOC pollutant levels, and thus provided a good survey of cold-start exhausts from gasoline-fueled vehicles. The results of selected experiments irradiating the actual or surrogate RFG exhausts only in the presence of NO<sub>x</sub> are shown on Figure 9, and selected incremental reactivity experiments

for actual or synthetic exhausts for each of the vehicles are shown on Figure 11 through Figure 13. Results of model simulations are also shown.

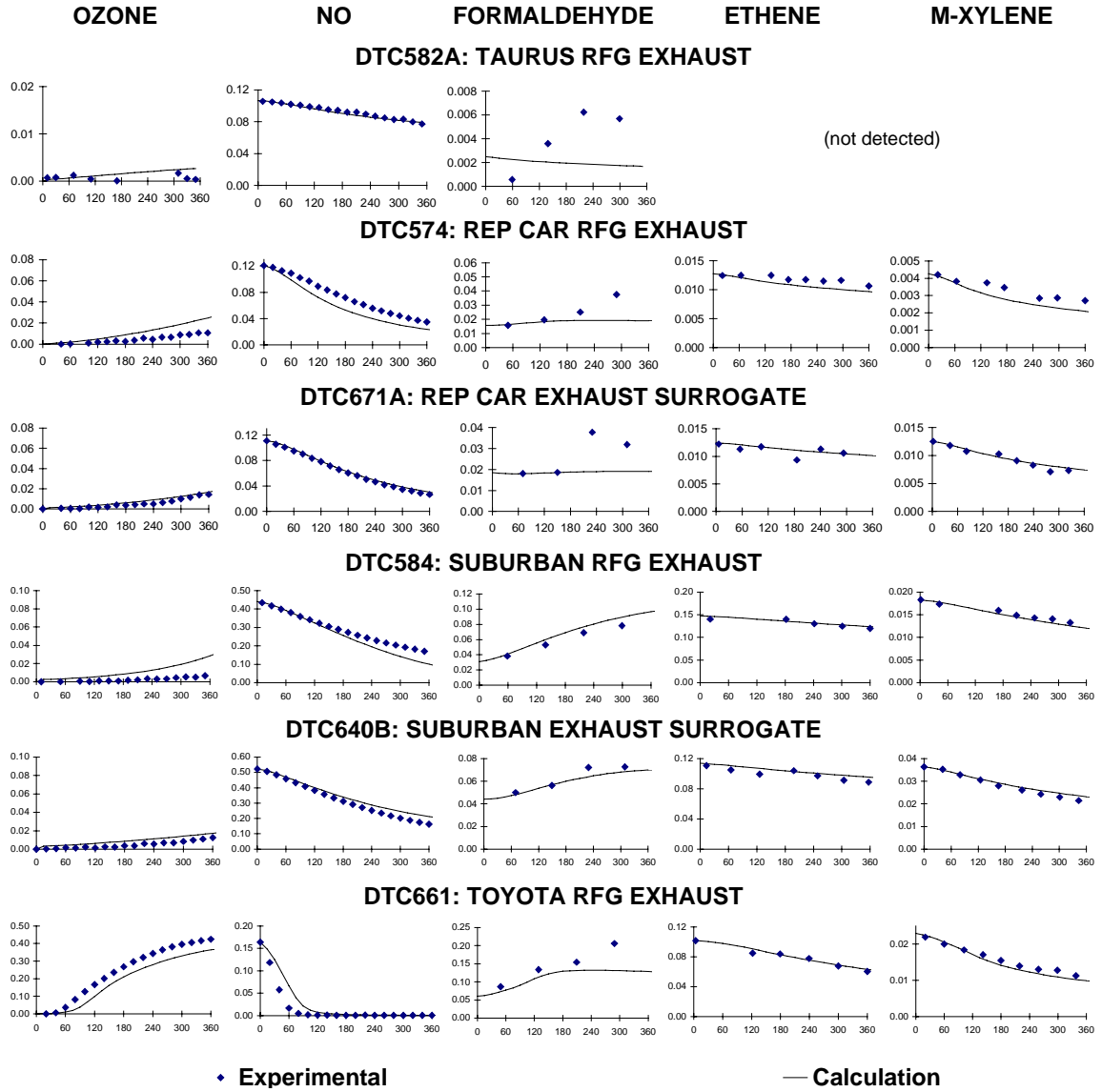
The VOC levels in the cold-start exhaust of the cleanest of the vehicles studied, a low-mileage 1997 Ford Taurus, were too low for the chamber experiments to provide a very precise measurement of the VOC reactivity, but the chamber data were useful in confirming that the overall reactivity was indeed as low as indicated by the exhaust analysis and the model predictions. In particular, the experiments with the 1997 Ford Taurus indicated there were no unmeasured species in the cold-start exhaust contributing significantly to its reactivity. Because of the low levels of VOCs in that exhaust, no attempt was made to formulate a surrogate exhaust representing it. However, although the NO oxidation rate in the exhaust only + NO<sub>x</sub> experiment showed NO oxidation rates only slightly above background (see Figure 9), as shown on Figure 10 the VOCs in the exhaust were sufficient to cause a measurable effect on O<sub>3</sub> when added to the surrogate - NO<sub>x</sub> experiment.

Experiments using synthetic RFG exhaust mixtures, derived by lumping VOCs of similar types and reactivities together and using a single compound to represent each VOC type, gave very similar results as the experiments with the actual exhausts. This is shown on the figures referenced above. This indicates that representing the complex exhaust mixtures by simpler synthetic mixtures, with reactivity weighting based on relative MIR values to account for differences among individual VOCs of the various types, gives reasonably good approximations of the overall effects of the exhausts on NO oxidation, ozone formation, and overall radical levels in the environmental chamber experiments. More significantly, this also indicates that, as with the LPG, methanol-containing and CNG exhausts discussed above, there is no significant contribution to reactivity caused by undetected compounds in the exhaust, and that the exhaust analyses methods currently employed for RFG exhausts are accounting for the major components causing their reactivities.

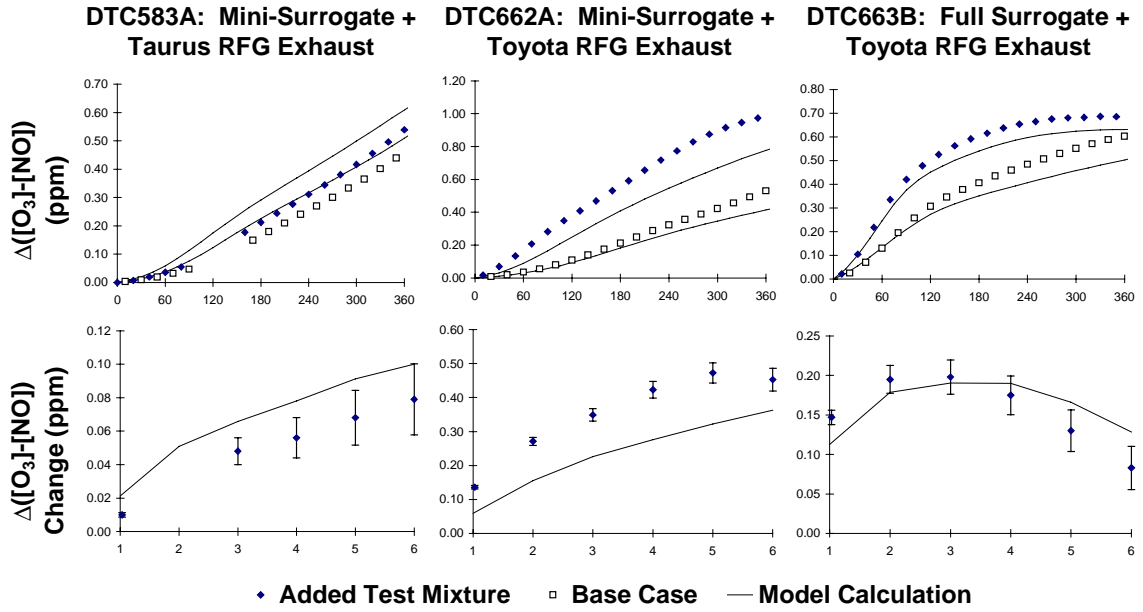
As is also shown on the figures referenced above, the model performed reasonably well in simulating most of the actual and synthetic RFG exhaust experiments. The results of all the synthetic exhaust experiments were simulated without significant consistent bias, as were the results of the experiments using the actual exhausts from the moderately low VOC 1991 Dodge Spirit used for reproducibility studies in our laboratories, and from the relatively high VOC Chevrolet Suburban. Thus for these two vehicles (and also for the 1997 Taurus, where both the model and the experiment indicated low reactivity), the model is able to satisfactorily account for the reactivities of their cold-start exhausts.

The other four vehicles studied had sufficiently high VOC levels to permit quantitative reactivity measurements to be obtained from the environmental chamber data. The cold-start exhausts from these other four vehicles were found to significantly enhance rates of NO oxidation and O<sub>3</sub> formation when added to ambient surrogate - NO<sub>x</sub> mixtures, and to measurably increase integrated OH radical levels. Data from selected experiments are shown on Figure 9 through Figure 13.

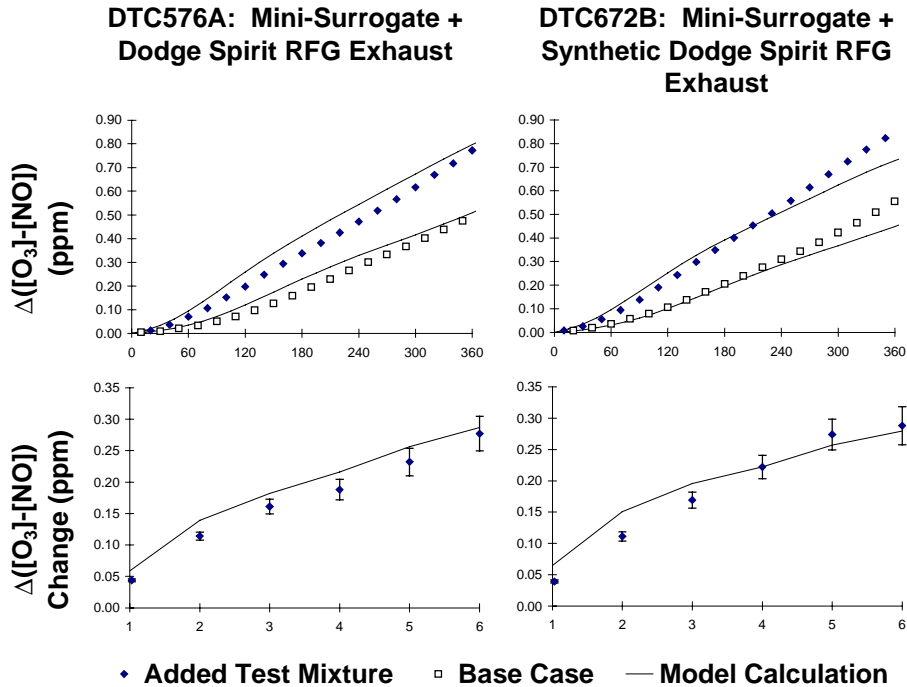
**Figure 9.** Experimental and calculated concentration-time plots for selected species in selected actual and synthetic RFG exhaust - NO<sub>x</sub> experiments.



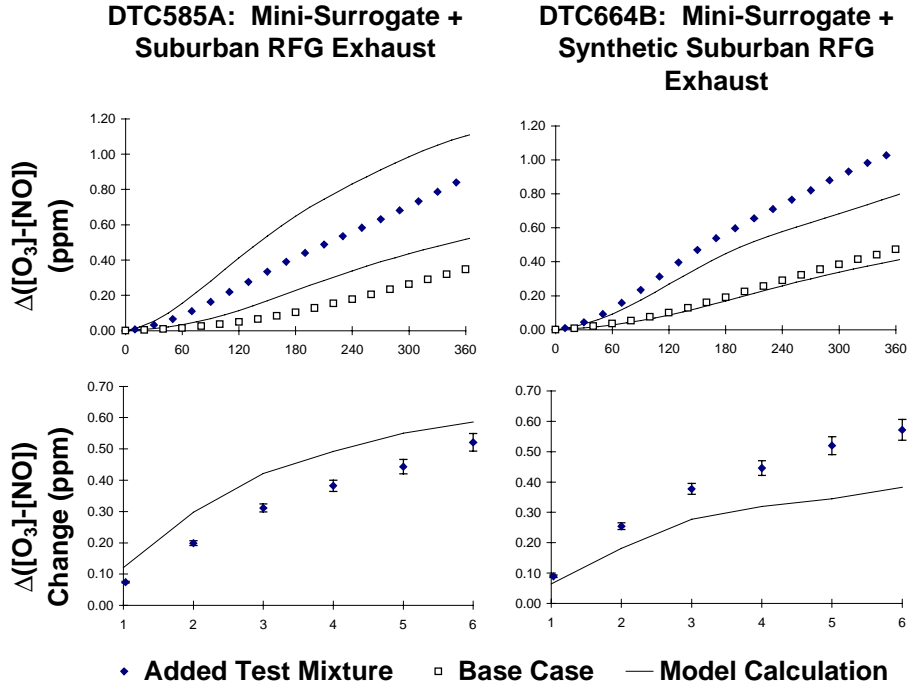
**Figure 10.** Experimental and calculated results with selected incremental reactivity experiments with RFG exhaust from the Ford Taurus and the Toyota pickup.



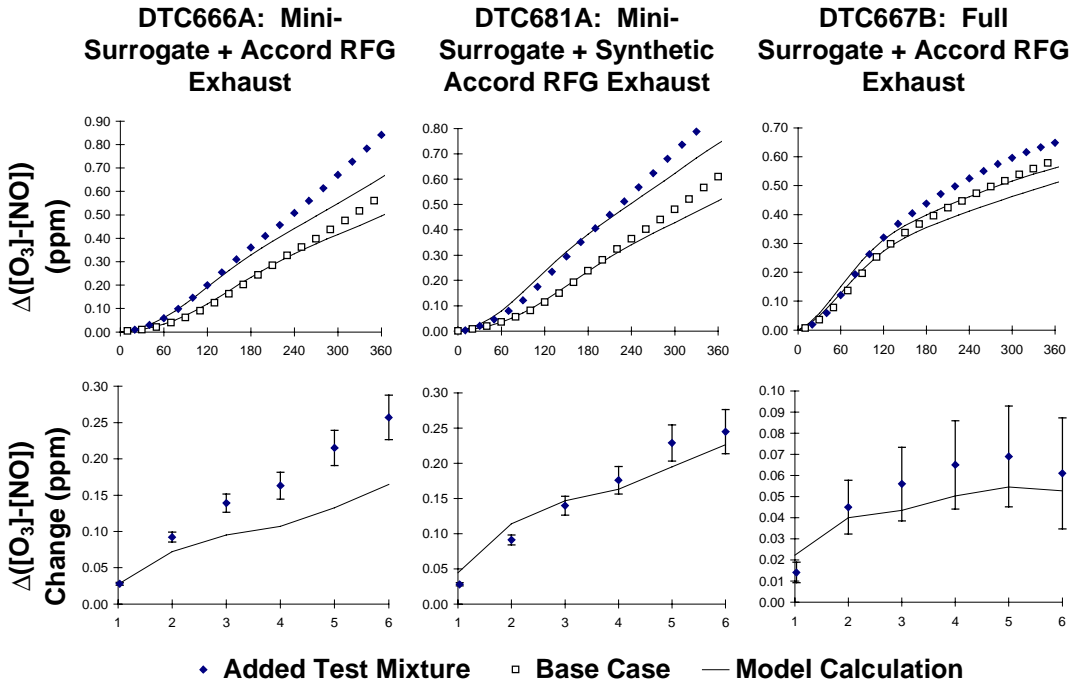
**Figure 11.** Experimental and calculated results with selected incremental reactivity experiments with actual and surrogate RFG exhaust from the Dodge Spirit.



**Figure 12.** Experimental and calculated results with selected incremental reactivity experiments with actual and surrogate RFG exhaust from the Chevrolet Suburban.



**Figure 13.** Experimental and calculated results with selected incremental reactivity experiments with actual and surrogate RFG exhaust from the Honda Accord.



For the older, higher mileage 1988 Honda Accord and 1984 Toyota pickup, the model performed reasonably well in simulating the experiments with the exhausts alone or when the exhaust was added to a mixture representative to VOCs measured in ambient air. However, the model somewhat underpredicted the effect of the exhaust on NO oxidation and O<sub>3</sub> formation when added to a simpler mini-surrogate - NO<sub>x</sub> mixture. For example, Figure 9 and Figure 10 show experiments for the Toyota pickup, and Figure 13 shows surrogate experiments for the Honda Accord. This is despite the fact that, for the Accord at least, the synthetic exhaust had about the same effect on the mini-surrogate as the actual exhaust, and the model simulated the mini-surrogate with synthetic Accord exhaust run reasonably well. It may be that there is a constituent of these exhausts which is not well represented by the model and is better represented by the model for the compound used in the synthetic exhaust to represent it. However, more replicate experiments with these vehicles, and experiments with other relatively high mileage, in-use vehicles would be needed to determine if this is a consistent problem, or just a problem with the characterization of the two experiments involved, which were not replicated. However, even for these vehicles the model performs in simulating the exhaust reactivity in the experiments with the more realistic surrogate, indicating that it probably will also in simulating the effects of these and the other RFG exhausts in the atmosphere.

## **Diesel Reactivity**

One exploratory experiment was carried out with a high-mileage 1984 diesel sedan, and selected results of that experiment are shown on Figure 14. The data indicate that the cold-start exhaust from this vehicle can significantly enhance NO oxidation and O<sub>3</sub> formation rates and also measurably increase integrated OH radical levels. However, as indicated by the results of the model simulations that are also given on the figure, the species accounting for this reactivity have not been accounted for. It is clearly not due to light hydrocarbons such as C<sub>≤10</sub> alkenes, olefins, or aromatics, or C<sub>≤3</sub> oxygenates such as formaldehyde and acetaldehyde, levels of these compounds in the chamber was either below the detection limits or too small to significantly affect the results. It is clear that chamber experiments need to be carried out with more comprehensive analyses before we can assess whether we can understand the factors accounting for the reactivities of diesel exhausts.

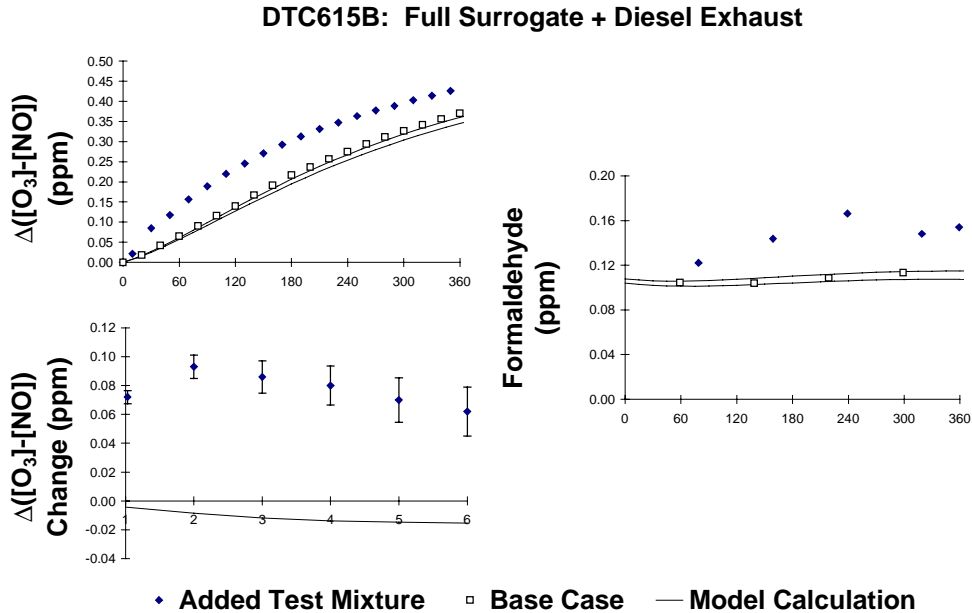
## **CONCLUSIONS**

Although some experimental and model evaluation problems were encountered as indicated above, we believe that overall this program has been successful in achieving its objective. Environmental chamber data which are sufficiently well characterized for model evaluation were obtained using exhausts from a variety of fuels and vehicle types. Incremental reactivity experiments were found to be particularly useful in providing reactivity evaluation data, especially for the lower reactivity exhausts or exhausts with low ROG/NO<sub>x</sub> ratios. In most cases the results of the experiments with the exhausts were consistent with model predictions, and consistent with results of experiments using synthetic exhausts derived from mixtures of compounds measured in the actual exhausts. This indicates that in most cases the major exhaust constituents which contributes to the



ozone impacts of these exhausts have probably been identified, and that current chemical mechanisms are reasonably successful in predicting the impacts of these species on ozone.

**Figure 14.**



The major exception noted in this study was diesel, where it was clear that the major reactive species have not been identified. There was also some evidence, albeit inconclusive, that the model is underpredicting the ozone impacts of some of the constituents of exhausts from the two high-mileage, in-use RFG-fueled vehicles that were studied. In addition, problems were encountered in the model's ability to simulate experiments containing formaldehyde or formaldehyde with methanol that affected the evaluation of the model for the methanol-containing fuels. However, the model successfully predicted the incremental effects of methanol-containing exhausts to surrogate mixtures simulating ambient environments. This was the case for most of the other exhaust studied as well.

## ACKNOWLEDGEMENTS

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