DEVELOPMENT AND APPLICATION OF IMPROVED METHODS FOR MEASUREMENT OF OZONE FORMATION POTENTIALS OF VOLATILE ORGANIC COMPOUNDS

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Summary of Progress

During this reporting period, continued evaluating various methods for measuring direct reactivity, to find a method that gives results that are more consistent with model predictions and that give suitable data for higher molecular weight compounds. A Teflon stirred flow reactor was constructed and used to determine if the reason the model overpredicts the O_3 formation in the high concentration stirred flow experiments is because of use of glass walls on the stirred flow reactor. In addition, the effect of mechanical stirring on the data obtained using the Pyrex stirred flow reactor was investigated. The results are briefly summarized below.

The level of effort on this program was relatively limited during this reporting period because of the need for the Principal Investigator to devote most of his time on completing the SAPRC-99 mechanisms development and documentation that was needed for the CARB's regulatory programs.

Evaluation of Effects of Stirring in the Stirred Flow Experiments

The modeling of the stirred flow experiments is based on the assumption that the reactants are well mixed in the reactor. However, the stirred flow experiments reported thus far did not employ any mechanical stirring. Experiments involving injecting NO_2 and looking at the mixing of the colored gas suggested that stirring may not be adequate in the carboy experiments. A stirring method was devised based on putting Teflon vanes on a magnetic stirrer that was placed in the carboy, and viewing results of NO_2 injections suggested that this provided good stirring in the carboy. Several HONO - propane experiments were carried out using this stirrer, and the results are shown on Figure 1, where they can be compared with data obtained using the unstirred carboy and with results of model calculations.

The stirring system in the carboy turned out to be impractical to use on a routine basis because the design of the carboy caused it to fail to function if it was not closely watched. Attempts to fix this by modifying the shape of the floor of the carboy resulted in its breaking. A 50-liter Pyrex flask, with approximately the same volume as the carboy but with shape that permitted the stirrer to operate more reliably was purchased, and data was obtained using it (with mechanical stirring) in stirred flow HONO experiments with propane, n-octane, n-decane, and n-dodecane. The results of those experiments are also shown on Figure 1, where they are compared with data obtained using the unstirred carboy and with results of model calculations.

Figure 1 shows that the $\Delta([O_3]-[NO])$ tended to be somewhat lower in the experiments with the stirrer in the carboy than in the carboy experiments without the stirrer, but the data with the stirred flask was generally consistent with the data with the unstirred carboy. The data with the stirred flask was also consistent with the data with the unstirred carboy in the experiments with n-octane and n-decane. On the other hand, in the case of n-dodecane, the $\Delta([O_3]-[NO])$ data with the stirred flask tended to be somewhat lower than with the unstirred carboy, and somewhat more consistent with model predictions.

The tentative conclusion from these experiments is that stirring does not seem to have a large effect, though it is possible that it could improve the data with higher molecular weight compounds. However, more experiments are needed to determine if the difference between the stirred and unstirred experiments in the case of n-dodecane this may be due to a general reproducibility problem with higher molecular weight compounds such as n-dodecane.

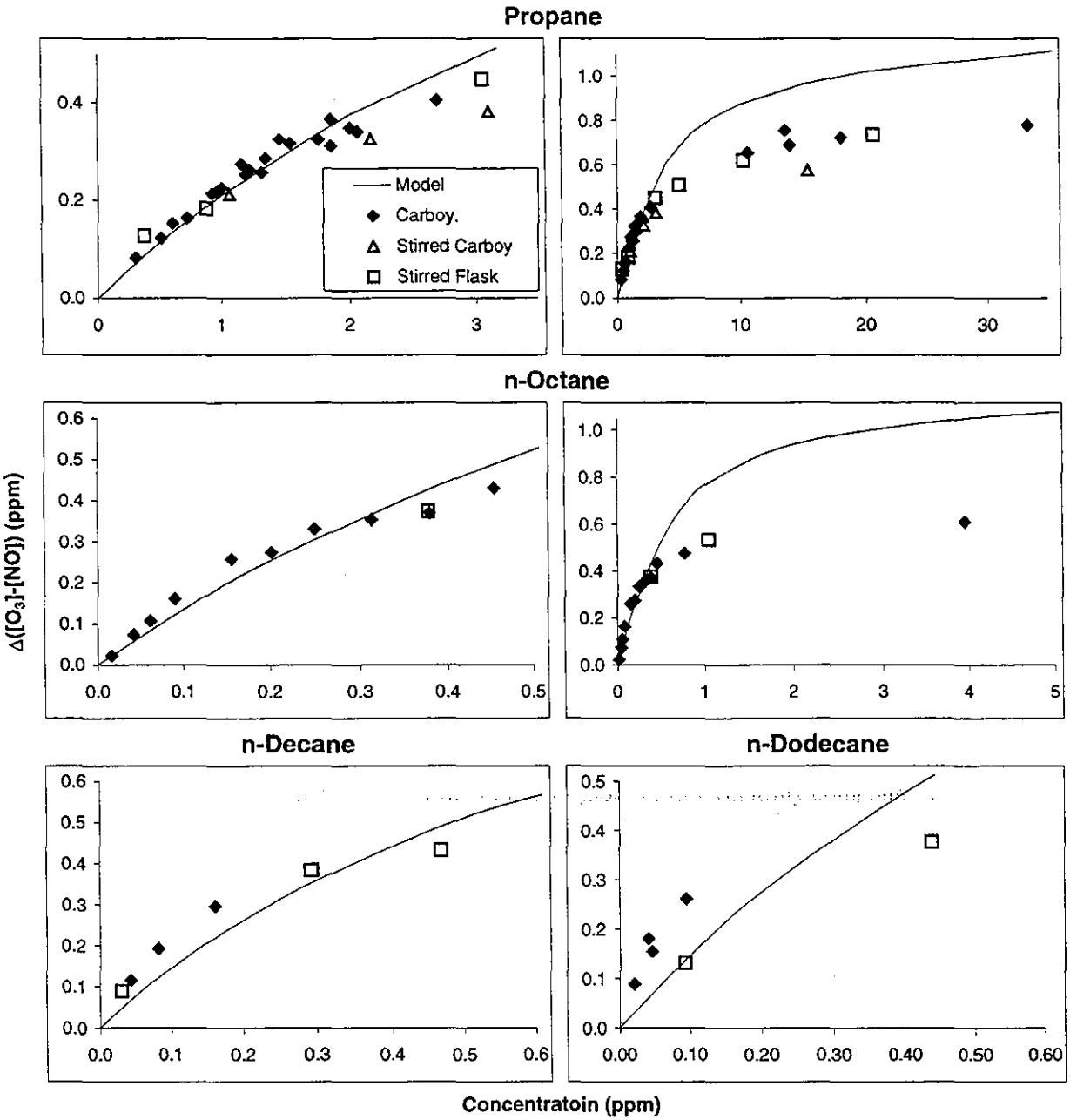

Figure 1. Plots of experimental and calculated $\Delta([O_3]-[NO])$ data for the HONO + propane, n-octane, n-decane, and n-dodecane stirred flow experiments carried out in the stirred and unstirred Pyrex reactors..

Evaluation of Effects Teflon vs Glass Reactor

To investigate whether the discrepancies between model calculation and experimental data in the HONO stirred flow experiments may be due to uncharacterized surface reactions involved with a glass reactor, the effect of using a Teflon reactor was evaluated. A ~25-liter cube-shaped reactor made of the same type of 2-mil FEP Teflon used in our chamber experiments, held rigid using an outer frame, was constructed. The reactor used the same mechanical stirring system based on a magnetic stirrer with Teflon vanes as used in the carboy and flask experiments discussed above. Several HONO - propane experiments were conducted using this reactor.

The [O_3]-[NO] data obtained in these experiments are shown on the right-side plots on Figure 2, along with results of model simulations of two of those experiments. For comparison, the left-side plots on Figure 2 show similar data for the Pyrex reactors. It can be seen that the model does not fit the data using the Teflon reactor as well as it does the data from the Pyrex reactors. For both reactors the model tends to underpredict [O_3]-[NO] at high added propane, but for the model fits the "zero propane" data for the Pyrex reactor much better than it does for the propane reactor. It is concluded that there is no advantage in using the Teflon reactor for these flow experiments; and the data may not be as well characterized because of uncertainties in the volume of that reactor.

Work Planned for Upcoming Period

Relatively little progress is expected on this project during the next quarter because of the need for the Principal Investigator to complete the development and documentation of the SAPRC-99 mechanism for the CARB's regulatory programs, and because of demands of other projects. Late in that period or early in the following quarter the investigation of the stirred flow system for higher molecular weight compounds will continue. It is expected that the initial experiments would be runs stirred flow runs using the flask with n-dodecane and higher n-alkanes. Once those data are obtained, a decision will be made as to the overall utility of this method for low volatility compounds.

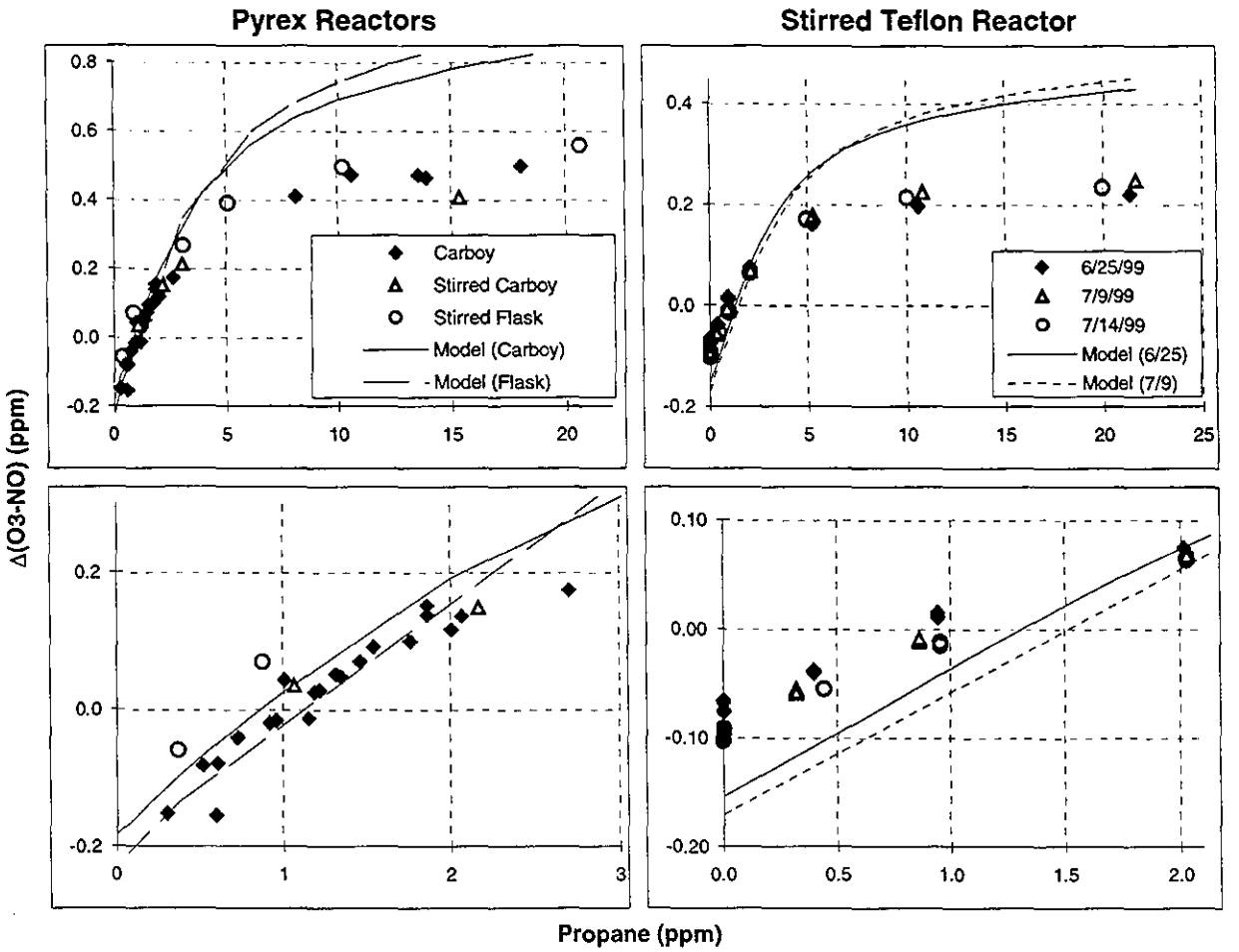

Figure 2. Experimental and calculated $[O_3]$-[NO] data for the HONO + propane experiments carried out in the stirred and unstirred Pyrex reactors and in the stirred Teflon reactor.