DEVELOPMENT AND APPLICATION OF AN UPDATED PHOTOCHEMICAL MECHANISM FOR VOC REACTIVITY ASSESSMENT

Quarterly Report

to the

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Summary of Progress

During this reporting period, we extended the reoptimization of the aromatics to ethylbenzene and all the di- and tri-methylbenzene isomers, using the results of the environmental chamber experiments carried out under the separate ARB and CRC-funded chamber program. These results will be described in more detail below. In addition, we have started the process of updating the mechanism to incorporate the newer kinetic information.

Effects of Aromatic Mechanism Updates

As indicated in the previous report, it was found that by adding a second type of unknown aromatic photooxidation product model species, which could be represented in the model by increasing the methylglyoxal yield, then significantly improved fits to the new xenon-arc teflon chamber runs, without degrading the fits to the runs in the blacklight chambers. This finding was based on simulations of toluene and m-xylene experiments. During this period, this approach was used in reoptimizing the mechanisms for all the other aromatic isomers for which we have chamber data. The effects of these changes in the aromatic mechanisms in the simulations of ozone formation and NO oxidation in the chamber data are shown on Figures 1-8, which gives experimental and calculated concentration time plots of NO oxidized + ozone formed (as measured by $d(O_3\text{-NO})$, the change in $[O_3]\text{-}[NO]$ during the experiment) for all the usable single aromatic - NO_x runs carried out in the ARB and CRC-funded chamber program. The model calculations show the performance of the new mechanism relative to that of the "SAPRC-93" mechanism which was used in the analysis of the reactivity experiments which have been reported previously (Carter et al., 1993, 1995a; Carter, 1996), as well as in our report on the effects of chamber and light source on mechanism evaluation results (Carter et al., 1995b). Figures 9a and 9b show the effects of the changes in the aromatic mechanism in the simulations of the previous aromatic experiments in the chamber data which were modeled in the chamber and light source effects report (Carter et al., 1995b).

The figures show that although the previous mechanism performed reasonably in simulating the EC and blacklight chamber experiments for toluene, o- and m-xylene, and 1,3,5- and 1,2,3-trimethyl-benzene, it performed poorly in simulating the experiments for these compounds in the teflon chamber experiments using the xenon arc light source (the XTC and CTC runs), and tended to consistently overpredict ozone formation and NO oxidation rates in the reactivity in the experiments using ethylbenzene, p-xylene and 1,2,4-trimethylbenzene. The new mechanism performs much better in simulating the experiments in the xenon arc teflon chambers while still simulating experiments in the blacklight chambers, and the independent optimization for each isomer significantly improves the model simulations of the experiments using the compounds whose reactivities were overpredicted previously.

To show the effects of these changes on reactivity scales, the new mechanism was used to calculate incremental reactivities for selected compounds and TLEV exhaust mixtures, for MIR and MOIR averaged conditions scenarios. The results of these calculations, shown as reactivities relative to the base ROG mixture for the selected individual calculations, and as reactivity adjustment factors relative to RFA for the TLEV exhaust mixtures, are summarized on Table 1. The calculations in the columns labeled "1990" and "1993" were using the SAPRC-90 and SAPRC-93 mechanisms, respectively, while in the columns labeled "new" were conducted using the new, reoptimized mechanisms for the aromatics, and the SAPRC-93 mechanism for all other species. The "change" columns are the differences between the new mechanism relative to SAPRC-93, and thus show the effect of the aromatic mechanism change only.

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Note that the "SAPRC-90" relative reactivities may not be exactly the same as used in the ARB CF/LEV regulation because each set were derived for a single "averaged conditions" scenario, rather than averages of the 39 MIR or MOIR scenarios for the individual cities as employed previously (Carter, 1994). However, the "averaged conditions" MIR or MOIR calculations give fairly good approximations of the full calculations using all 39 scenarios (Carter, 1993, 1994), and thus these data give a good indication of how a complete reactivity scale recalculation would be affected by these mechanism modifications.

The table shows that the changes in the aromatic mechanism cause substantial changes in the reactivities of some of the aromatic species, with the reactivities of toluene, m-xylene and (to a lesser extent) 1,2,3-trimethylbenzene increasing significantly, while those of ethylbenzene, p-xylene, and 1,2,4-trimethylbenznene substantially decreasing. These changes also cause the relative reactivities of all the non-aromatic compounds shown to decrease; presumably due to the fact that the aromatics in the base ROG mixture are dominated by those whose reactivities substantially increase, making the other compounds less reactive by comparison. On the other hand, the effect of the mechanism changes on the exhaust RAF's are relatively small, though the RAF's tend to decrease on a fairly consistent basis (by ~6% for MIR and ~3% for MOIR) for all the alternative fuels except for Phase 2 gasoline, whose RAF is almost unchanged.

This mechanism, and the reactivities derived from it, must still be considered to be highly preliminary, and are still undergoing refinement. As indicated above, we are just starting the process of updating the base mechanism to be consistent with the latest evaluations of new laboratory data, and thus some rate constants and perhaps some reaction schemes will almost certainly change. The new aromatics mechanism is not totally satisfactory in all respects, especially for p-xylene where the optimized fits are not particularly good, and where the adjusted methylglyoxal yield, which is intended to represent formation of methylglyoxal + products which are assumed to react like methylglyozal, is lower than the experimental yield of methylglyozal alone. There is some preliminary indication that the new mechanism may overpredict ozone formation rates in surrogate - NO_x experiments in the blacklight chamber, though it gives good fits to surrogate experiments using the xenon arc light source. Therefore, development of these mechanisms is continuing.

Future Schedule

During the next reporting period, we expect to further examine the aromatic optimization approach to see if some of the problems noted above can be addressed, as well as making more progress on implementing the results of the new data evaluation in the mechanism. Roger Atkinson will assist in the latter effort. We will also explore the feasibility of enhancing the computer program we have used to generate alkane mechanisms so it can be applied to broader classes of compounds such as alcohols, ethers, and perhaps other classes, and to be consistent with the revised estimation methods for alkoxy radical reactions developed by Atkinson and Carter (1992). We will also be implementing the new condensed isoprene mechanism into the general updated SAPRC mechanism, initially into the SAPRC-93 mechanism which otherwise is considered to be a finished product which is now being implemented into a number of models, including the UAM as part of our related ARB contract ((3-716) on the effects of mechanism uncertainty on airshed model results.

References

Atkinson, R. and W. P. L. Carter (1992): "Reactions of Alkoxy Radicals under Atmospheric Conditions: The Relative Importance of Decomposition versus Reaction with O_2," J. Atm. Chem., 13, 195-210.

Carter, W. P. L. (1993): "Development and Application of an Up-To-Date Photochemical Mechanism for Airshed Modeling and Reactivity Assessment," Draft final report for California Air Resources Board Contract No. A934-094, April 26.

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Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1995b): "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying Chamber and Light Source," Final report to National Renewable Energy Laboratory, Contract XZ-2-12075, Coordinating Research Council, Inc., Project M-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323, March 26.

Carter, W. P. L. (1994): "Development of Ozone Reactivity Scales for Volatile Organic Compounds," J. Air & Waste Manage. Assoc., 44, 881-899.

Carter, W. P. L. (1995): "Computer Modeling of Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds," Atmos. Environ., 29, 2513-2527.

Table 1.   Comparisons of relative reactivities of selected compounds and reactivity adjustment factors for selected TLEV exhaust mixtures, calculated for the MIR and MOIR "averaged conditions" scenarios using the SAPRC-90, SAPRC-93, and the preliminary updated mechanisms. (Reactivities are calculated on a mass basis).

| Compound or Mixture	Averaged Conditions (MIR)				Averaged Conditions (MOIR)			
	1990	1993	New	Change	1990	1993	New	Change
Incremental Reactivities Relative to Base ROG								
CO	0.018	0.017	0.016	-8%	0.033	0.029	0.028	-4%
ETHANE	0.08	0.08	0.08	-8%	0.14	0.15	0.15	-4%
N-C4	0.33	0.35	0.32	-8%	0.57	0.62	0.59	-4%
N-C8	0.20	0.22	0.21	-6%	0.34	0.41	0.41	-1%
N-C15	0.10	0.13	0.12	-6%	0.17	0.24	0.24	-1%
TOLUENE	0.87	0.87	1.27	47%	0.51	0.47	0.86	80%
C2-BENZ	0.86	0.85	0.55	-35%	0.50	0.48	0.22	-53%
O-XYLENE	2.10	1.90	1.90	-3%	1.60	1.48	1.44	-3%
M-XYLENE	2.60	2.40	3.60	51%	2.10	1.80	2.80	54%
P-XYLENE	2.10	2.00	0.60	-70%	1.70	1.50	0.35	-77%
123-TMB	2.80	2.70	3.00	8%	2.30	2.10	2.30	10%
124-TMB	2.80	2.70	1.27	-53%	2.30	2.10	0.91	-56%
135-TMB	3.20	3.10	3.10	2%	2.60	2.30	2.40	3%
ETHENE	2.40	2.30	2.00	-10%	2.70	2.50	2.30	-8%
PROPENE	3.00	3.10	2.70	-11%	3.20	3.10	2.80	-9%
T-2-BUTE	3.20	3.70	3.30	-12%	3.30	3.50	3.10	-10%
1-HEXENE	1.42	1.60	1.40	-10%	1.49	1.70	1.60	-8%
FORMALD	2.30	1.90	1.70	-13%	1.80	1.35	1.18	-13%
ACETALD	1.80	1.70	1.50	-11%	1.90	1.80	1.60	-10%
ACETONE	0.18	0.13	0.12	-11%	0.17	0.14	0.13	-8%
BENZALD	-0.17	-0.06	-0.05	-21%	-1.10	-1.08	-1.01	-7%
MEOH	0.18	0.17	0.16	-9%	0.23	0.21	0.20	-6%
ETOH	0.43	0.45	0.41	-8%	0.62	0.67	0.64	-5%
CRESOL	0.74	0.71	0.63	-12%	-0.55	-0.49	-0.45	-8%
Exhaust RAFs Relative to RFA								
RFA	1.00	1.00	1.00		1.00	1.00	1.00	
M85	0.37	0.35	0.33	-6%	0.39	0.35	0.34	-3%
CNG	0.18	0.17	0.16	-6%	0.23	0.23	0.22	-4%
LPG	0.51	0.50	0.47	-6%	0.61	0.60	0.58	-3%
E85	0.63	0.64	0.60	-6%	0.79	0.82	0.79	-4%
PH2	0.97	0.99	0.97	-2%	0.99	1.00	0.99	-1%

Toluene
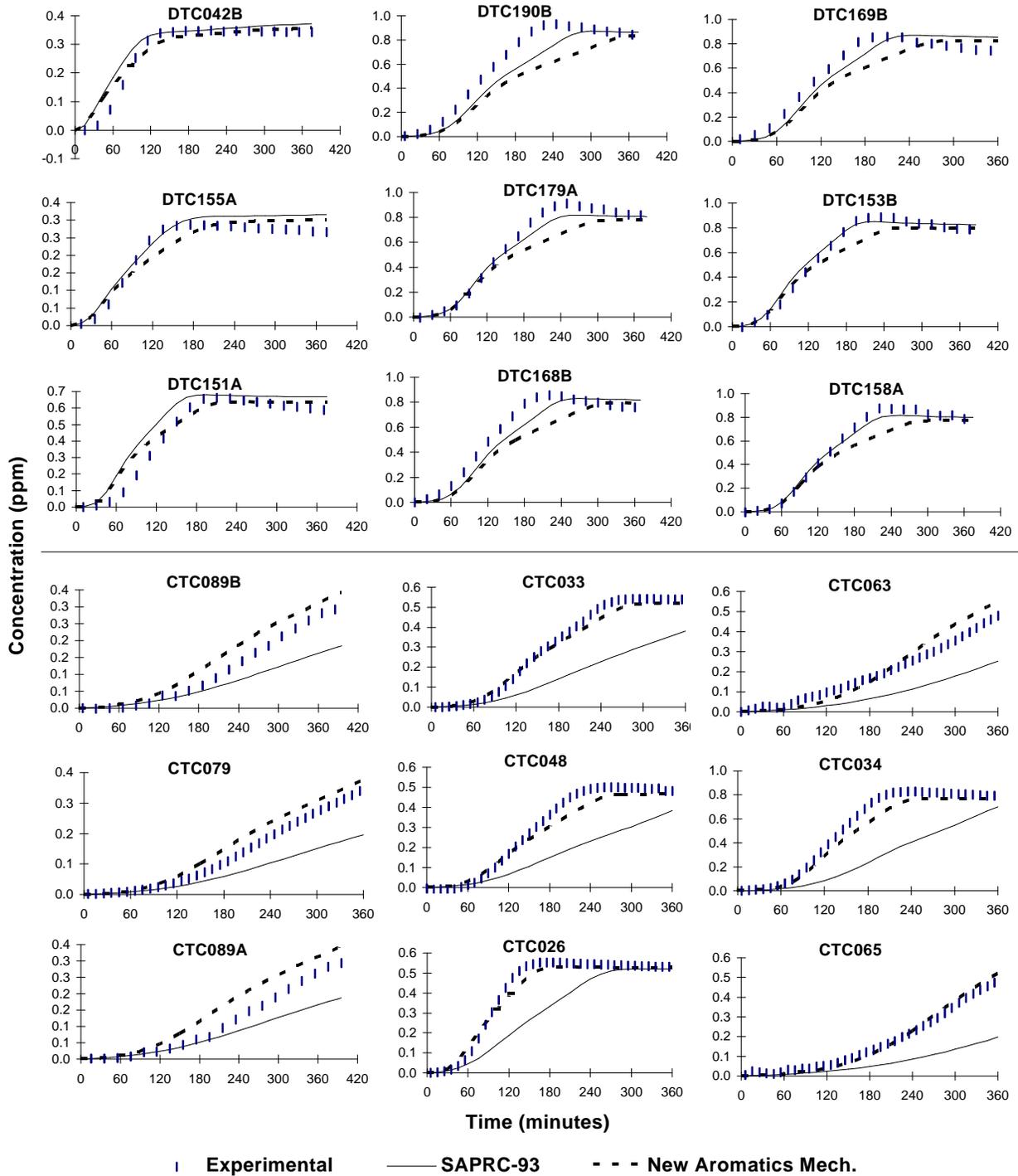
Figure 1.   Plots of experimental and calculated d(O$_3$-NO) in the new toluene - NO$_x$ - air environmental chamber experiments. CTC = Xenon-arc light source; DTC = blacklight light source.
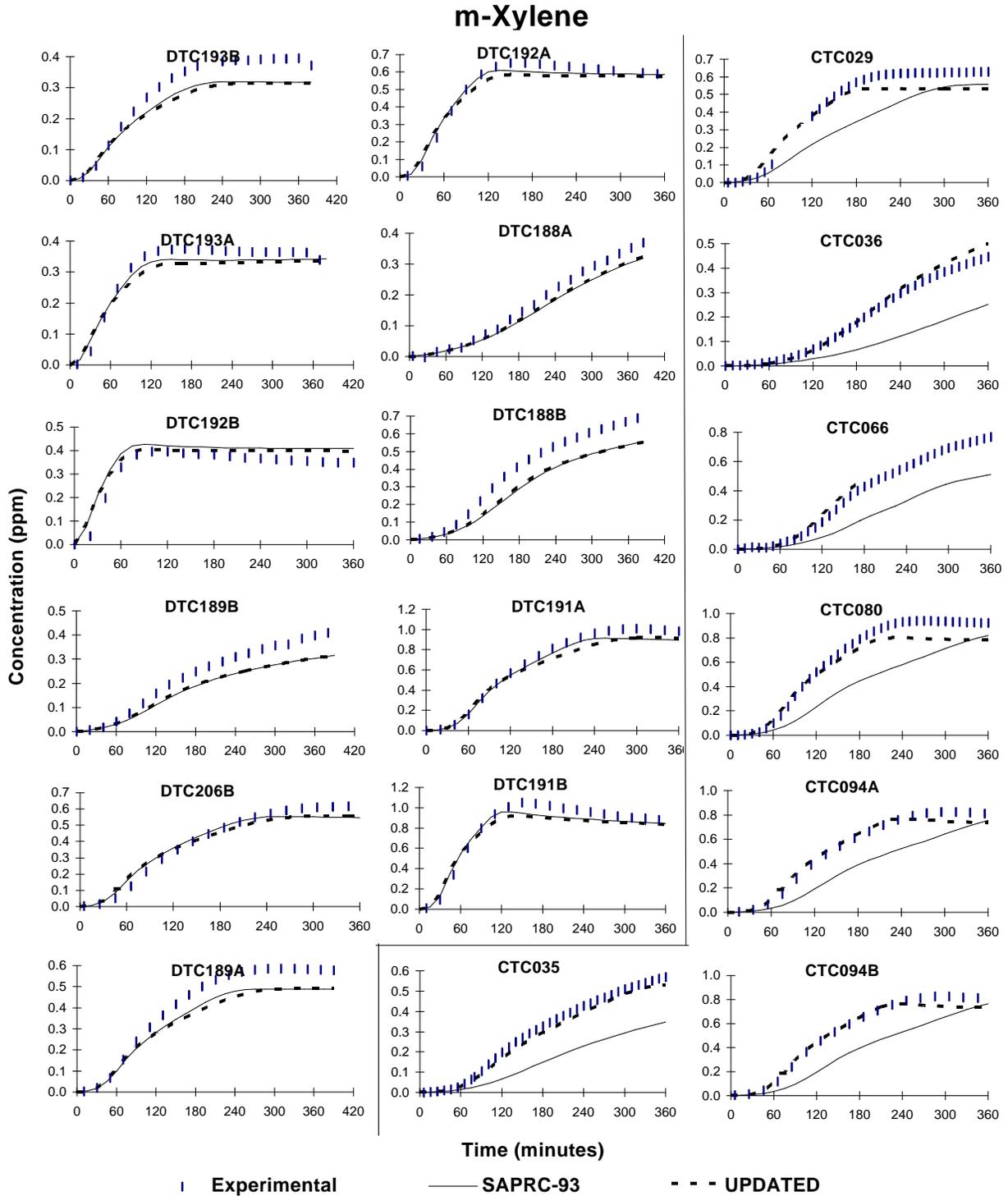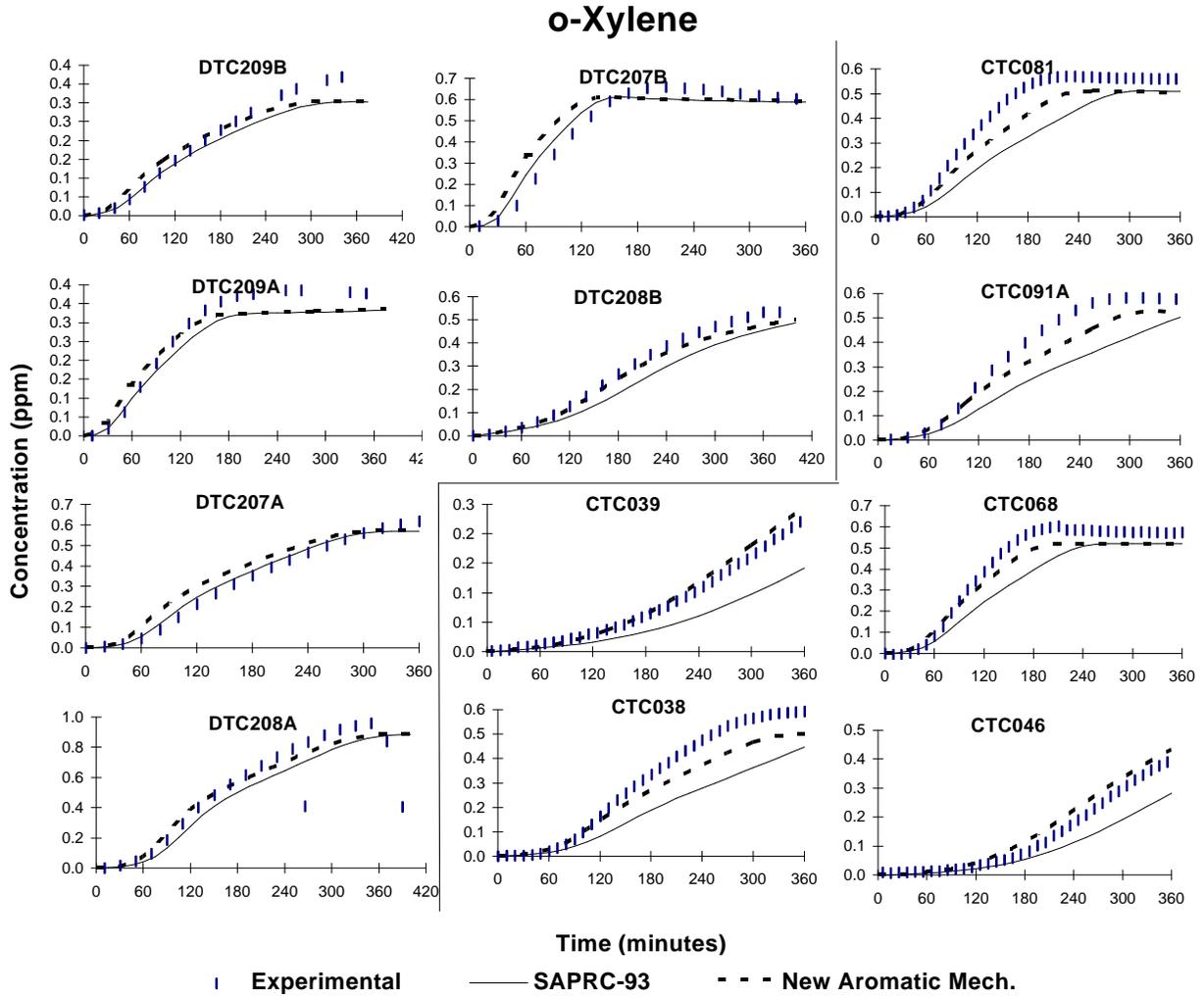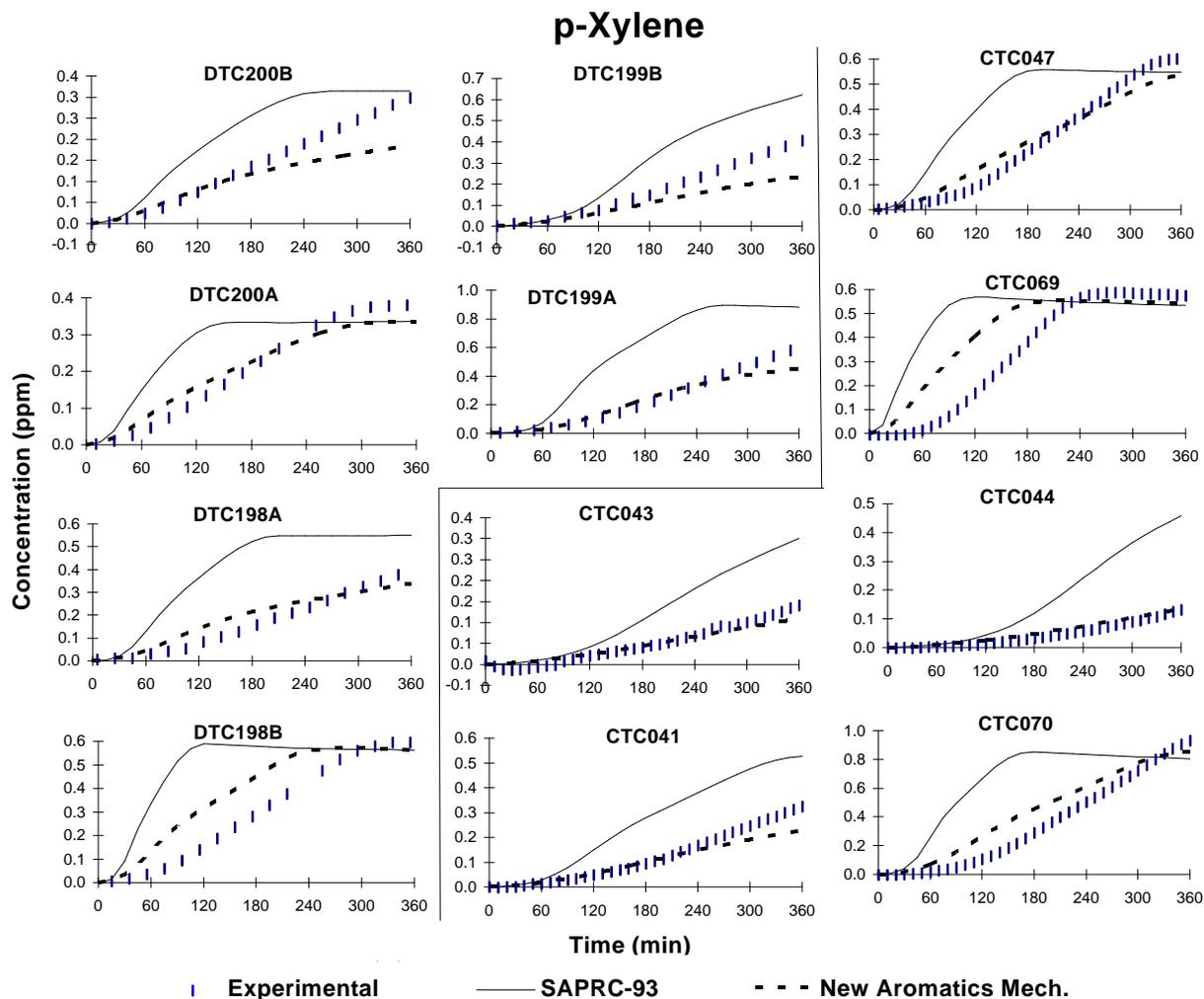
m-Xylene

Figure 2. Plots of experimental and calculated d(O₃-NO) in the new m-xylene - NOₓ - air environmental chamber experiments. CTC = Xenon-arc light source; DTC = blacklight light source.

o-Xylene

Figure 3. Plots of experimental and calculated d(O$_3$-NO) in the new o-xylene - NO$_x$ - air environmental chamber experiments. CTC = Xenon-arc light source; DTC = blacklight light source.

p-Xylene

Figure 4. Plots of experimental and calculated d(O₃-NO) in the new p-xylene - NOₓ - air environmental chamber experiments. CTC = Xenon-arc light source; DTC = blacklight light source.
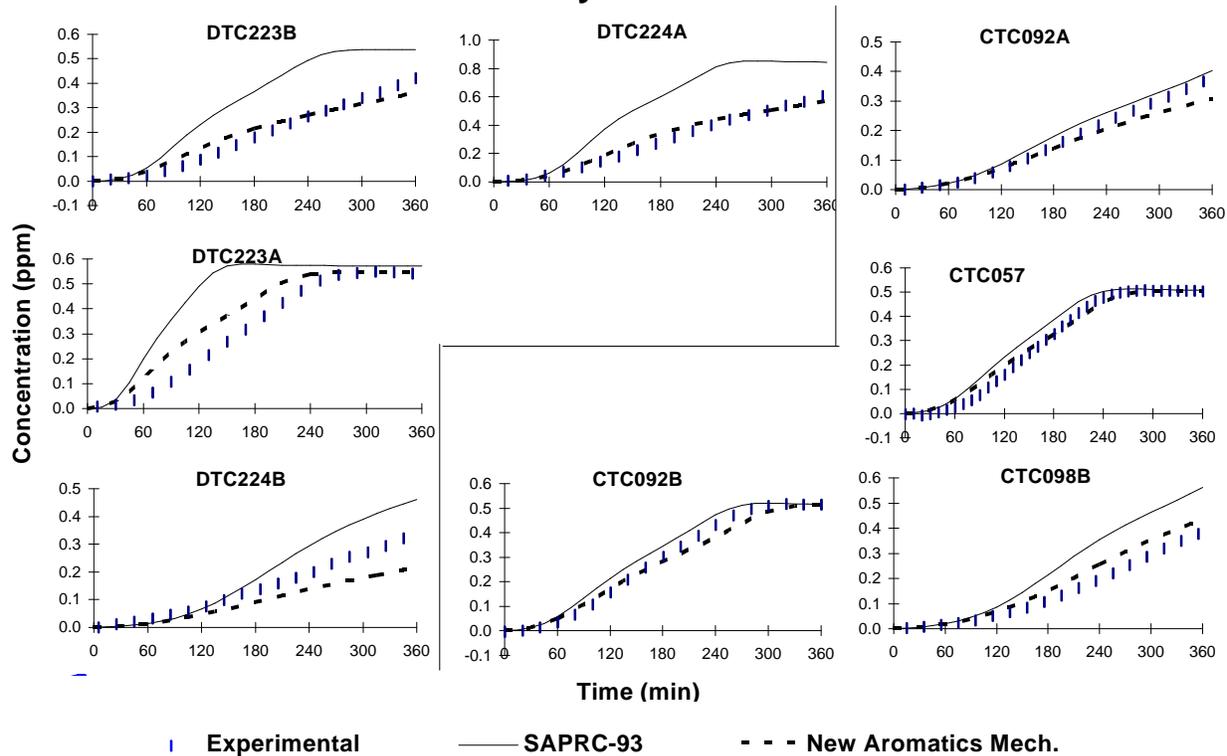
Ethylbenzene

Figure 5. Plots of experimental and calculated d(O_3-NO) in the new ethylbenzene - NO_x - air environmental chamber experiments. CTC = Xenon-arc light source; DTC = blacklight light source.
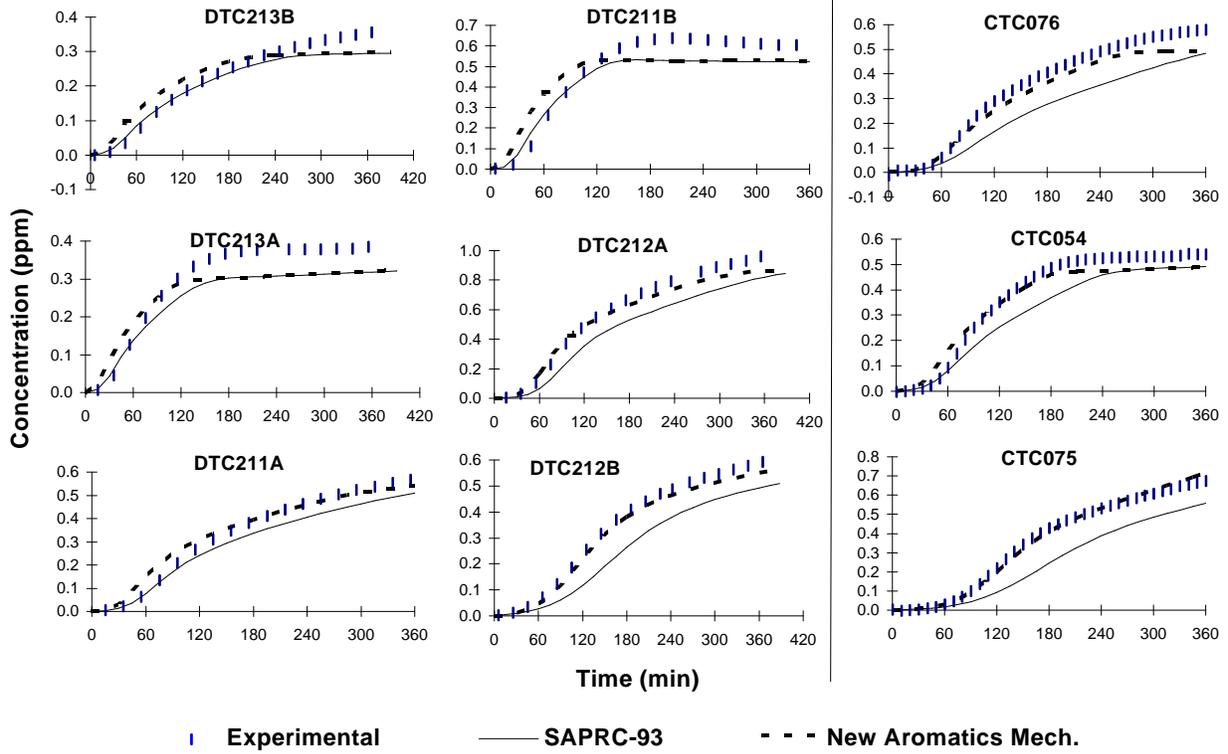
1,2,3-Trimethylbenzene

Figure 6.   Plots of experimental and calculated d(O₃-NO) in the new 1,2,3-trimethylbenzene - NOₓ - air environmental chamber experiments. CTC = Xenon-arc light source; DTC = blacklight light source.
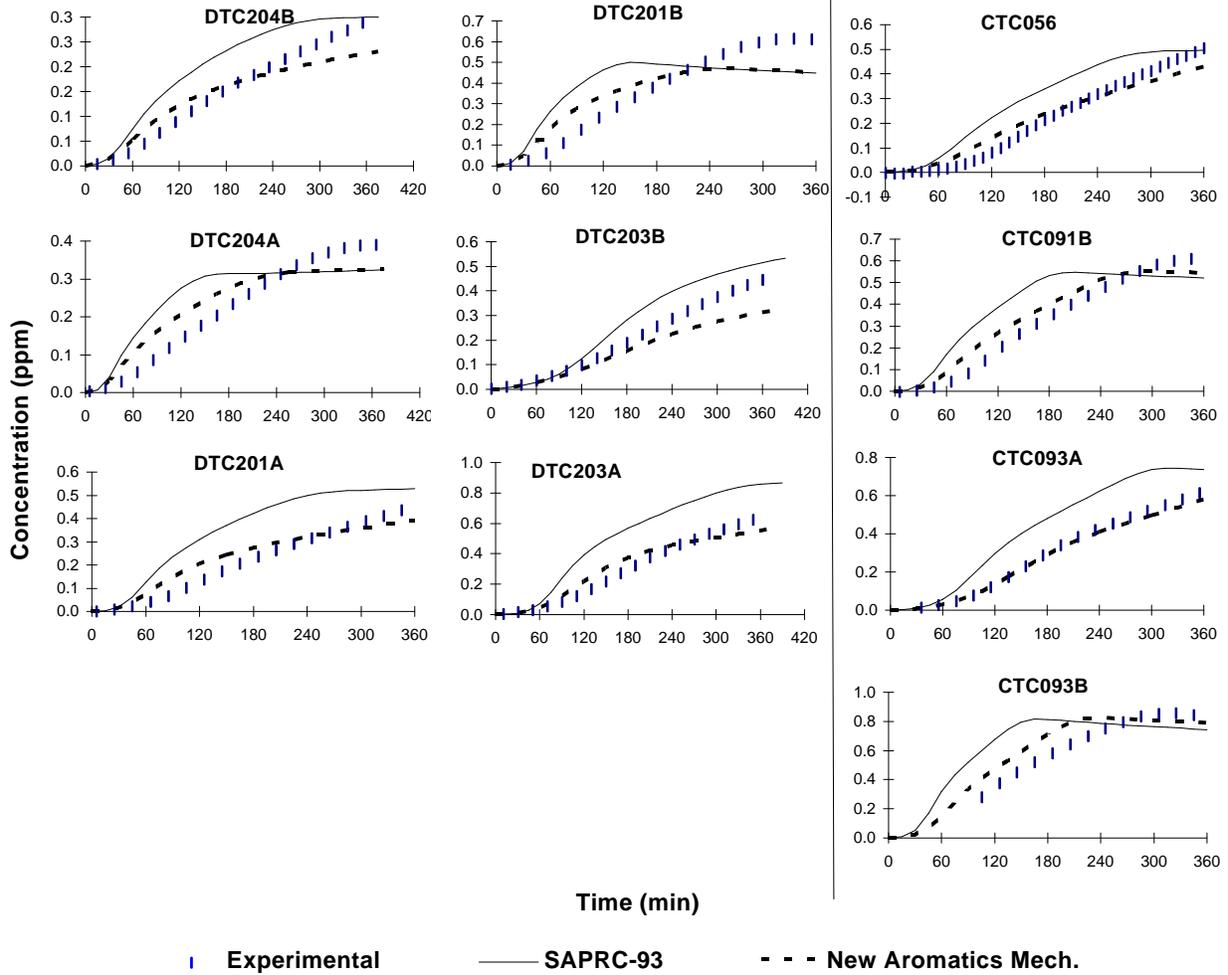
1,2,4-Trimethylbenzene

Figure 7. Plots of experimental and calculated d(O₃-NO) in the new 1,2,4-trimethylbenzene - NOₓ - air environmental chamber experiments. CTC = Xenon-arc light source; DTC = blacklight light source.
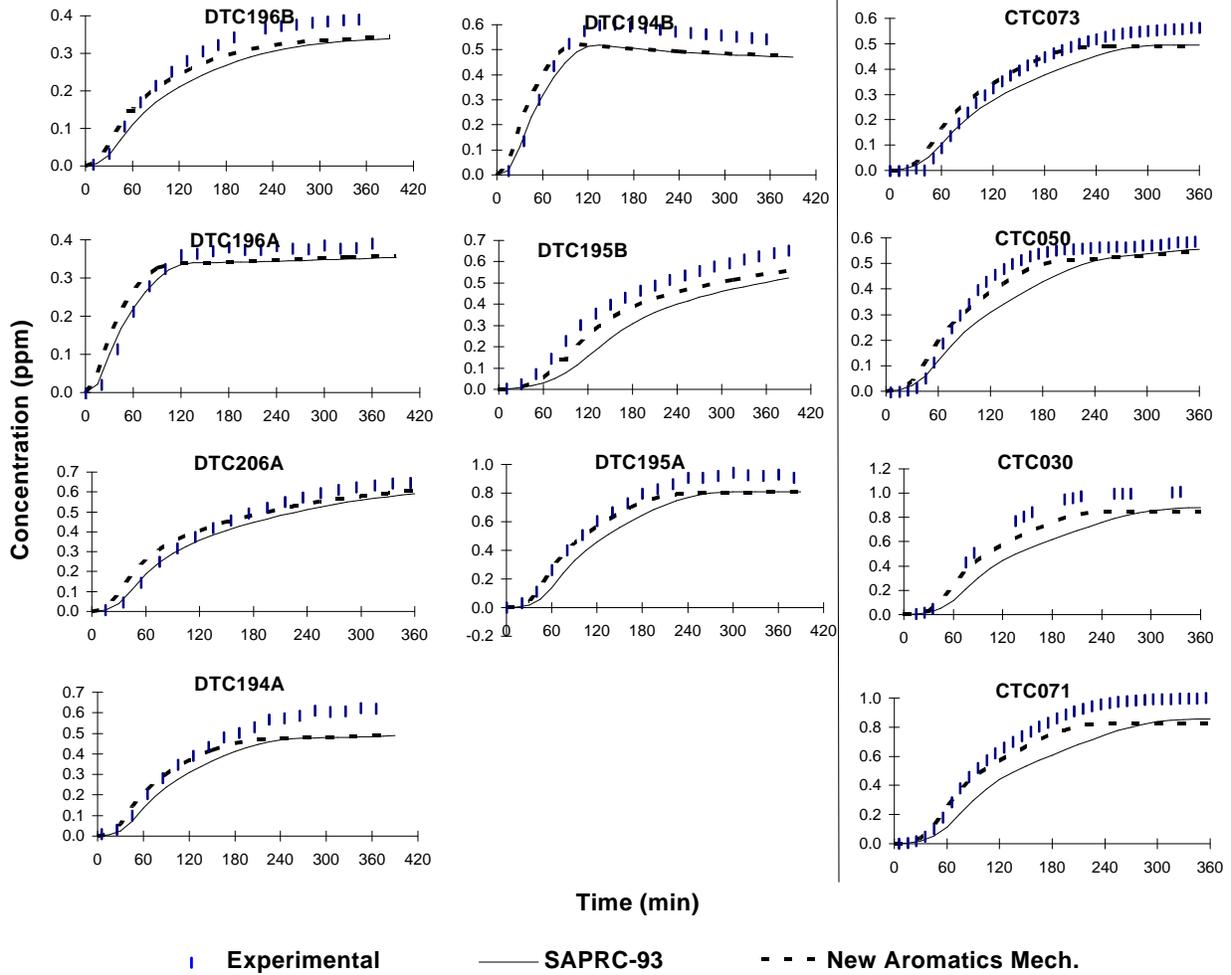
1,3,5-Trimethylbenzene

Figure 8.   Plots of experimental and calculated d(O₃-NO) in the new 1,3,5-trimethylbenzene - NOₓ - air environmental chamber experiments. CTC = Xenon-arc light source; DTC = blacklight light source.
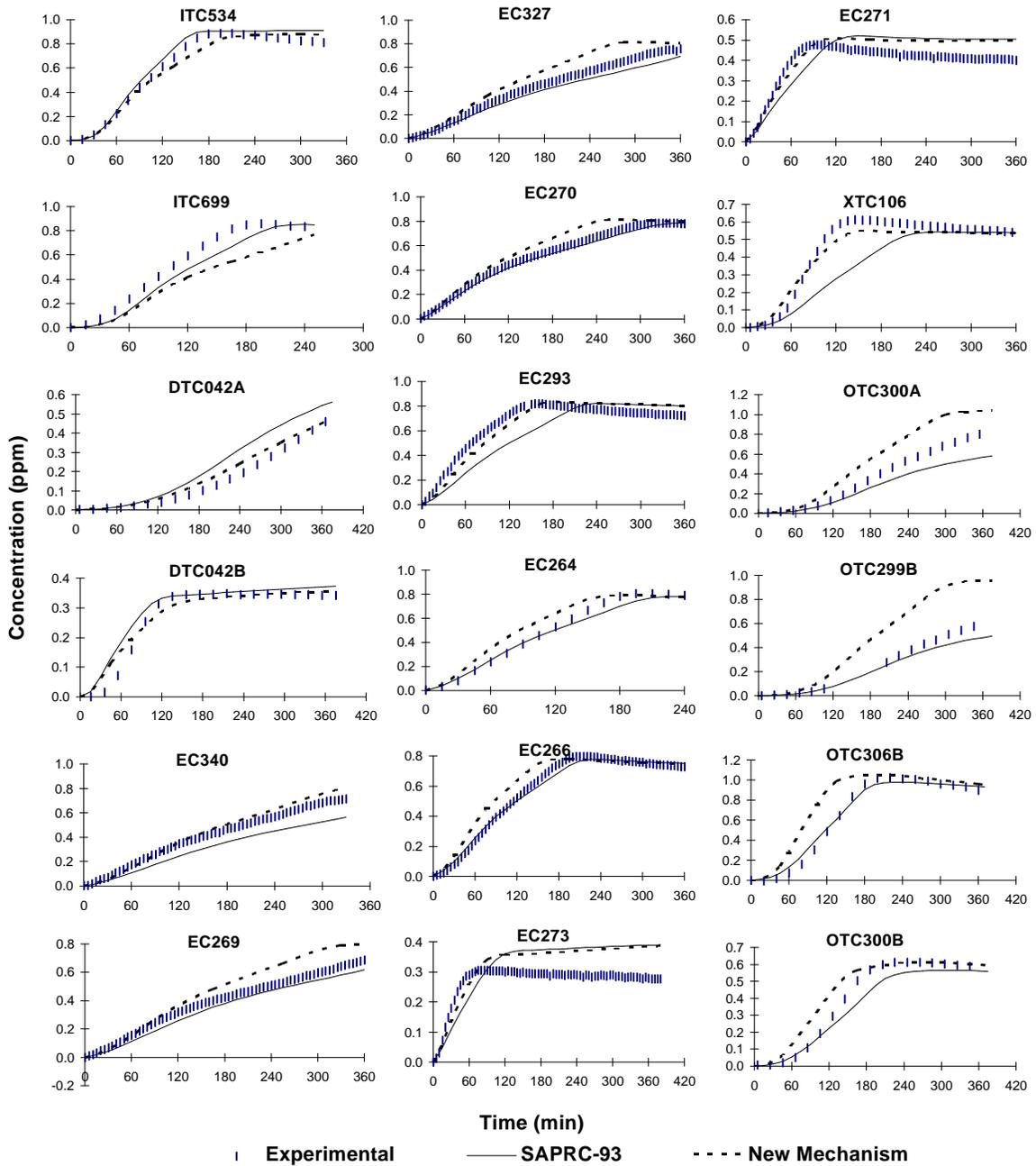
Toluene

Figure 9a.   Plots of experimental and calculated d(O$_3$-NO) in the aromatic - NOx - air chamber runs in the previous chamber data base. EC - SAPRC Evacuable chamber with xenon arc light source; ITC, ETC, DTC = blacklight teflon chamber, XTC = xenon arc teflon chamber; OTC = outdoor teflon chamber. Part 1 of 2.

Toluene

M-Xylene

OTC299A

EC344

OTC308B

OTC306A

EC345

ITC709

ITC702

XTC107

ITC706

135-TMB

ETC222

OTC315A

ITC703

DTC073A

OTC315B

EC903

DTC076B

OTC308A

EC901

Concentration (ppm)

Time (min)

ı **Experimental** —— **SAPRC-93** - - - - **New Mechanism**

Figure 9b.   Plots of experimental and calculated d(O$_3$-NO) in the aromatic - NOx - air chamber runs in the previous chamber data base. EC - SAPRC Evacuable chamber with xenon arc light source; ITC, ETC, DTC = blacklight teflon chamber, XTC = xenon arc tefl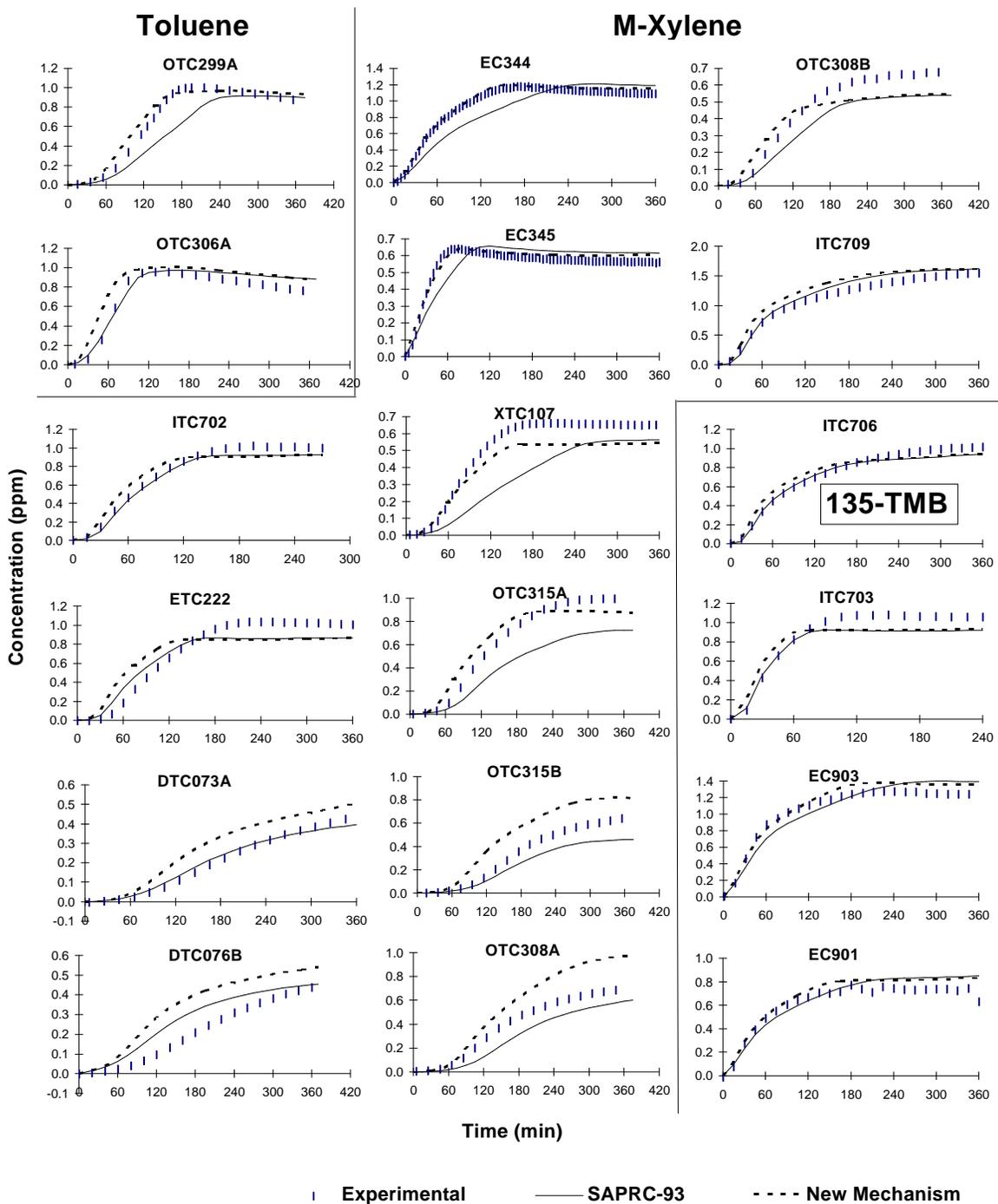on chamber; OTC = outdoor teflon chamber. Part 2 of 2.