Figure A-34. Plots of experimental and calculated reactivity results for Octamethylcyclotetrasiloxane.
Figure A-35. Plots of experimental and calculated reactivity results for Decamethylcyclopentasiloxane.
Figure A-36. Plots of experimental reactivity results for Pentamethyldi-siloxanol.
Figure A-37. Plots of experimental and calculated reactivity results for Carbon Monoxide.
This Appendix provides an illustration of how all the experimentally derived quantities were calculated for a selected added test VOC experiment. This includes calculations of the 6-hour $d(O_3-NO)$, IntOH, amount of test VOC reacted, base case results, the incremental and mechanistic $d(O_3-NO)$, IntOH, and direct reactivities, and the estimated uncertainties in all these quantities. This appendix was generated using the Mathcad 3.1 computer program (MathSoft, 1992). The example run chosen was added propane run ETC-226, where the amount reacted was estimated using the IntOH method.

The format of this appendix is as follows: Text in **bold font** are comments which are ignored by the Mathcad program. Expressions of the form

\[ \text{function(var1,var2,...):=expression} \]

give definitions of functions. Expressions of the form

\[ \text{variable:=expression} \]

assign a variable the value which is the result of the mathematical operations and/or function evaluations in the expression. Expressions of the form

\[ \text{variable=value} \]

give the current value of the variable. The numerical value on the right of the "=" is output by the program, and can be compared with the results for this run in the data tabulations. Slight differences may be due to roundoff error — the Mathcad program is used for illustrative purposes only; the actual data were processed using FORTRAN programs.

The names of the variables could not be the same as used in the text to avoid confusion of subscripts and superscripts with exponentiation. However, they should be reasonably self-explanatory, or obvious from the comments preceding them. The prefix "u" is used to indicate the uncertainty of the variable.
Constants For Set 3 Runs

- \( \text{Dt} := .029 \) Dilution x Time (6 hrs x 0.48%/hr)
- \( \text{uDt} := .0150 \) Uncertainty in Dt (6 hrs x 0.26%/hr)
- \( \text{kOHxyl} := 3.46 \times 10^4 \) kOH for tracer (m-xylene) (ppm-1 min-1 units)
- \( \text{kOHvoc} := 1.71 \times 10^3 \) kOH for Propane
- \( \text{Xyl0avg} := .0999 \) Average Initial m-Xylene (ppm)
- \( \text{Hex0avg} := .387 \) Average Initial n-Hexane (ppm)
- \( \text{NO0avg} := .391 \) Average Initial NO (ppm)
- \( \text{k1avg} := .320 \) Average of Assigned NO2 photolysis rate (min-1)
- \( \text{avgTavg} := 301.4 \) Average of Run's Average Temperatures

Initial Concentrations and Run Conditions

- \( \text{VOC0} := 11.57 \) Initial propane (ppm)
- \( \text{uVOC0} := .23 \) Uncertainty in initial propane (precision only)
- \( \text{Xyl0} := .1017 \) Initial m-Xylene (ppm)
- \( \text{Hex0} := .403 \) Initial n-Hexane (ppm)
- \( \text{NO0} := .372 \) Initial NO (ppm)
- \( \text{k1} := .315 \) Assigned NO2 photolysis rate (min-1)
- \( \text{avgT} := 300.0 \) Average Temperature
- \( \text{lnXyl0} := 2.29 \) Initial -ln[m-Xylene (ppm)] (from fit to data using eq. (XXVI)
- \( \text{ulnXyl0} := 0.02 \) Uncertainty in initial ln[m-Xylene] (from fit to eq. XXVI)

Final (t = 6 hour) Concentrations

- \( \text{VOC6} := 11.112 \) Final propane (ppm)
- \( \text{uVOC6} := .304 \) Uncertainty in final propane (ppm)
- \( \text{lnXyl6} := 2.735 \) Final -ln[m-Xylene] (from fit to eq. XXVI)
- \( \text{ulnXyl6} := 0.02 \) Uncertainty in final -ln[m-Xylene]
- \( \text{dO3NOtest} := 0.736 \) Final d(O3-NO) (ppm)

Computation of IntOH.

\[
\begin{align*}
\text{dlnXyl} & := \ln Xyl6 - \ln Xyl0 \\
\text{udlnXyl} & := \sqrt{\text{ulnXyl0}^2 + \text{ulnXyl6}^2} \\
\text{IntOH} (\text{dlnXyl}, \text{Dt}) & := \frac{\text{dlnXyl} - \text{Dt}}{\text{kOHxyl}} \\
\text{uIntOH} & := \sqrt{\text{ulnXyl6}^2 + \text{ulnXyl0}^2 + \text{uDt}^2} \\
\text{dlnXyl} & = 0.445 \\
\text{udlnXyl} & = 0.028
\end{align*}
\]
Determine amount of propane reacted: Direct method

\[
\text{TstRedD} := VOC0 - VOC6 - \frac{VOC0 + VOC6}{2} \quad \text{TstRedD} = 0.129
\]

\[
\text{uTstRedD} := \sqrt{\text{uVOC0}^2 + \text{uVOC6}^2 + \left(\text{uDt} \cdot \frac{VOC0 + VOC6}{2}\right)^2} \quad \text{uTstRedD} = 0.417
\]

Determine amount of propane reacted: IntOH method (Eq. XXIX):

\[
\text{TstRedI}(\ VOC0, \ d\ln Xyl, \ Dt, \ kOHvoc) := \frac{VOC0 \cdot kOHvoc \cdot \text{IntOH}(\ d\ln Xyl, \ Dt)}{kOHvoc \cdot \text{IntOH}(\ d\ln Xyl, \ Dt) + \text{Dt}} \cdot \left(1 - e^{kOHvoc \cdot \text{IntOH}(\ d\ln Xyl, \ Dt) - \text{Dt}}\right)
\]

\[
\text{TstRedI}(\ VOC0, \ d\ln Xyl, \ Dt, \ kOHvoc) = 0.232
\]

\[
\text{uTstRedI} := \sqrt{\text{uVOC0} \frac{d}{d\ln Xyl} \text{TstRedI}(\ VOC0, \ d\ln Xyl, \ Dt, \ kOHvoc)^2 + \left(\text{udlnXyl} \frac{d}{d\ln Xyl} \text{TstRedI}(\ VOC0, \ d\ln Xyl, \ Dt, \ kOHvoc)^2 + \left(\text{uDt} \frac{d}{d\ln Xyl} \text{TstRedI}(\ VOC0, \ d\ln Xyl, \ Dt, \ kOHvoc)^2\right)\}
\]

\[
\text{uTstRedI} = 0.019
\]

Use least uncertain estimate for amount reacted. But add 20% uncertainty in kOHvoc to uTstRcd for the purposes of comparison.

\[
\text{uTstRedIchk} := \sqrt{\text{uTstRedI}^2 + \left(0.2 \cdot kOHvoc \frac{d}{dkOHvoc} \text{TstRedI}(\ VOC0, \ d\ln Xyl, \Dt, \ kOHvoc))^2\}
\]

\[
\text{uTstRedIchk} = 0.05 \quad \text{Uncertainty in IntOH method}
\]

\[
\text{uTstRedD} = 0.417 \quad \text{Uncertainty in direct method}
\]

IntOH method has least uncertainty, so amount propane reacted and its uncertainty are:

\[
\text{TstRed} := \text{TstRedI}(\ VOC0, \ d\ln Xyl, \ Dt, \ kOHvoc) \quad \text{TstRed} = 0.232
\]

\[
\text{uTstRed} := \text{uTstRedI} \quad \text{uTstRed} = 0.019
\]
Base case estimates for t=6 (Regression coefficients from Table 4.)

\[
dO3NO_{\text{base}} = 0.658 \quad \text{(ppm)}
\]

\[
udO3NO_{\text{base}} = 0.047 \quad \text{Uncertainty of regression estimate}
\]

\[
\text{IntOH}_{\text{base}} = 22.26 + 84.13 \cdot (Xyl0 - Xyl0\text{avg}) - 16.04 \cdot (NO0 - NO0\text{avg}) + 1.56 \cdot (\text{avgT} - \text{avgTavg})
\]

\[
\text{IntOH}_{\text{base}} = 20.532 \quad \text{(ppb-min)}
\]

\[
u\text{IntOH}_{\text{base}} = 1.9 \quad \text{Uncertainty of regression estimate}
\]

\[
\text{ConvR}_{\text{base}} = 17.08 - (NO0 - NO0\text{avg}) + 33.18
\]

\[
\text{ConvR}_{\text{base}} = 32.855 \quad (10^3 \text{ min}^{-1})
\]

\[
u\text{ConvR}_{\text{base}} = 3.0 \quad \text{Uncertainty of regression estimate}
\]

Computation of \(d(O3-NO)\) incremental and mechanistic reactivities

\[
\text{Change} := dO3NO_{\text{test}} - dO3NO_{\text{base}} \quad \text{Test run \(d(O3-NO)\) uncertainty estimated from variability in base case runs}
\]

\[
\text{udO3NO}_{\text{test}} := udO3NO_{\text{base}}
\]

\[
u\text{Change} := \sqrt{udO3NO_{\text{test}}^2 + udO3NO_{\text{base}}^2} \quad u\text{Change} = 0.066
\]

**Incremental Reactivity (mol O3-NO/mol VOC added)**

\[
\text{IR}_{O3NO} := \frac{\text{Change}}{\text{VOC0}} \quad \text{IR}_{O3NO} = 0.007
\]

\[
u\text{IR}_{O3NO} := \sqrt{\frac{u\text{Change}}{\text{Change}}}\left(\frac{u\text{VOC0}}{\text{VOC0}}\right) \quad u\text{IR}_{O3NO} = 0.006
\]

**Mechanistic Reactivity (mol O3-NO/mol VOC reacted)**

\[
\text{MR}_{O3NO} := \frac{\text{Change}}{\text{TstRcd}} \quad \text{MR}_{O3NO} = 0.334
\]

\[
u\text{MR}_{O3NO} := \sqrt{\frac{u\text{Change}}{\text{Change}}}\left(\frac{u\text{TstRcd}}{\text{TstRcd}}\right) \quad u\text{MR}_{O3NO} = 0.288
\]
Convert to ppt-min units

\[
\text{IntOH} \text{test} := 10^6 \cdot \text{IntOH} (\text{dlnXyl}, D_t) \quad \text{IntOH} \text{test} = 12.023
\]

\[
\text{uIntOH} \text{test} := 10^6 \cdot \text{uIntOH} \quad \text{uIntOH} \text{test} = 0.925
\]

Computation of IntOH Reactivities

Test run uncertainty must be at least as great as base run estimate, to account for uncertainty due to run to run variability. So set uIntOHtest to larger of uIntOHbase and uIntOHtest.

\[
\text{uIntOH} \text{test} := \text{if} (\text{uIntOH} \text{test} > \text{uIntOH} \text{base}, \text{uIntOH} \text{test}, \text{uIntOH} \text{base}) \quad \text{uIntOH} \text{test} = 1.9
\]

\[
\text{Change} := \text{IntOH} \text{test} - \text{IntOH} \text{base} \quad \text{Change} = -8.509
\]

\[
\text{uChange} := \sqrt{\text{uIntOH} \text{test}^2 + \text{uIntOH} \text{base}^2} \quad \text{uChange} = 2.687
\]

Incremental Reactivity (ppt-min IntOH/ppm VOC added)

\[
\text{IRIntOH} := \frac{\text{Change}}{\text{VOC}0} \quad \text{IRIntOH} = -0.735
\]

\[
\text{uIRIntOH} := \sqrt{\left(\frac{\text{uChange}}{\text{Change}}\right)^2 + \left(\frac{\text{uVOC}0}{\text{VOC}0}\right)^2} \quad \text{uIRIntOH} = 0.233
\]

Mechanistic Reactivity (ppt-min IntOH/ppm VOC reacted)

\[
\text{MRIntOH} := \frac{\text{Change}}{\text{TstRcd}} \quad \text{MRIntOH} = -36.665
\]

\[
\text{uMRIntOH} := \sqrt{\left(\frac{\text{uChange}}{\text{Change}}\right)^2 + \left(\frac{\text{uTstRcd}}{\text{TstRcd}}\right)^2} \quad \text{uMRIntOH} = 11.966
\]
Computation of Direct Reactivity

O₃-NO due to reactions of base ROG in test run (Eq. XIV)
(10⁻³ converts units back to ppm, since IntOH is in ppt-min, and ConvR is in 10⁻³ min⁻¹)

\[
dO₃NO_{baseROGtest} := ConvRbase\cdot IntOH_{test}\cdot 10^{-3}
\]
\[dO₃NO_{baseROGtest} = 0.395\]

\[
udO₃NO_{baseROGtest} := dO₃NO_{baseROGtest}\sqrt{\left(\frac{uConvRbase}{ConvRbase}\right)^2 + \left(\frac{uIntOH_{test}}{IntOH_{test}}\right)^2}
\]
\[udO₃NO_{baseROGtest} = 0.072\]

**Direct Incremental Reactivity (mol O₃-NO/mol VOC added)**

\[
IR_{direct} := \frac{dO₃NO_{test} - dO₃NO_{baseROGtest}}{VOC_{0}}
\]
\[IR_{direct} = 0.029\]

\[
uIR_{direct} := IR_{direct}\sqrt{\left(\frac{udO₃NO_{baseROGtest}}{dO₃NO_{test} - dO₃NO_{baseROGtest}}\right)^2 + \left(\frac{uVOC_{0}}{VOC_{0}}\right)^2}
\]
\[uIR_{direct} = 0.006\]

**Direct Mechanistic Reactivity, ConvF (mol O₃-NO/mol VOC reacted)**

\[
ConvF := \frac{dO₃NO_{test} - dO₃NO_{baseROGtest}}{TstRcd}
\]
\[ConvF = 1.469\]

\[
uConvF := ConvF\sqrt{\left(\frac{udO₃NO_{baseROGtest}}{dO₃NO_{test} - dO₃NO_{baseROGtest}}\right)^2 + \left(\frac{uVOC_{0}}{VOC_{0}}\right)^2}
\]
\[uConvF = 0.312\]