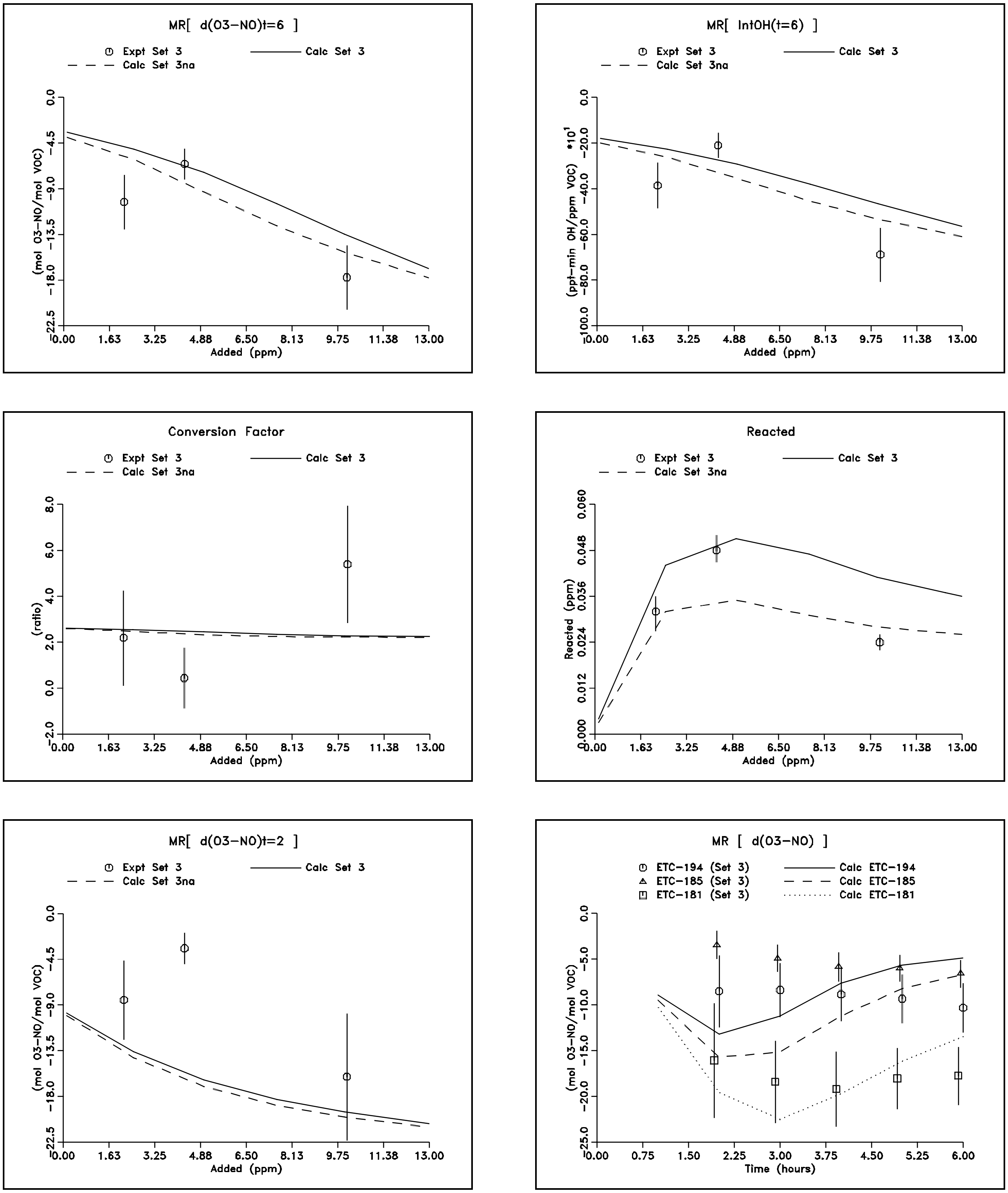

Figure A-34. Plots of experimental and calculated reactivity results for **Octamethylcyclotetrasiloxane.**

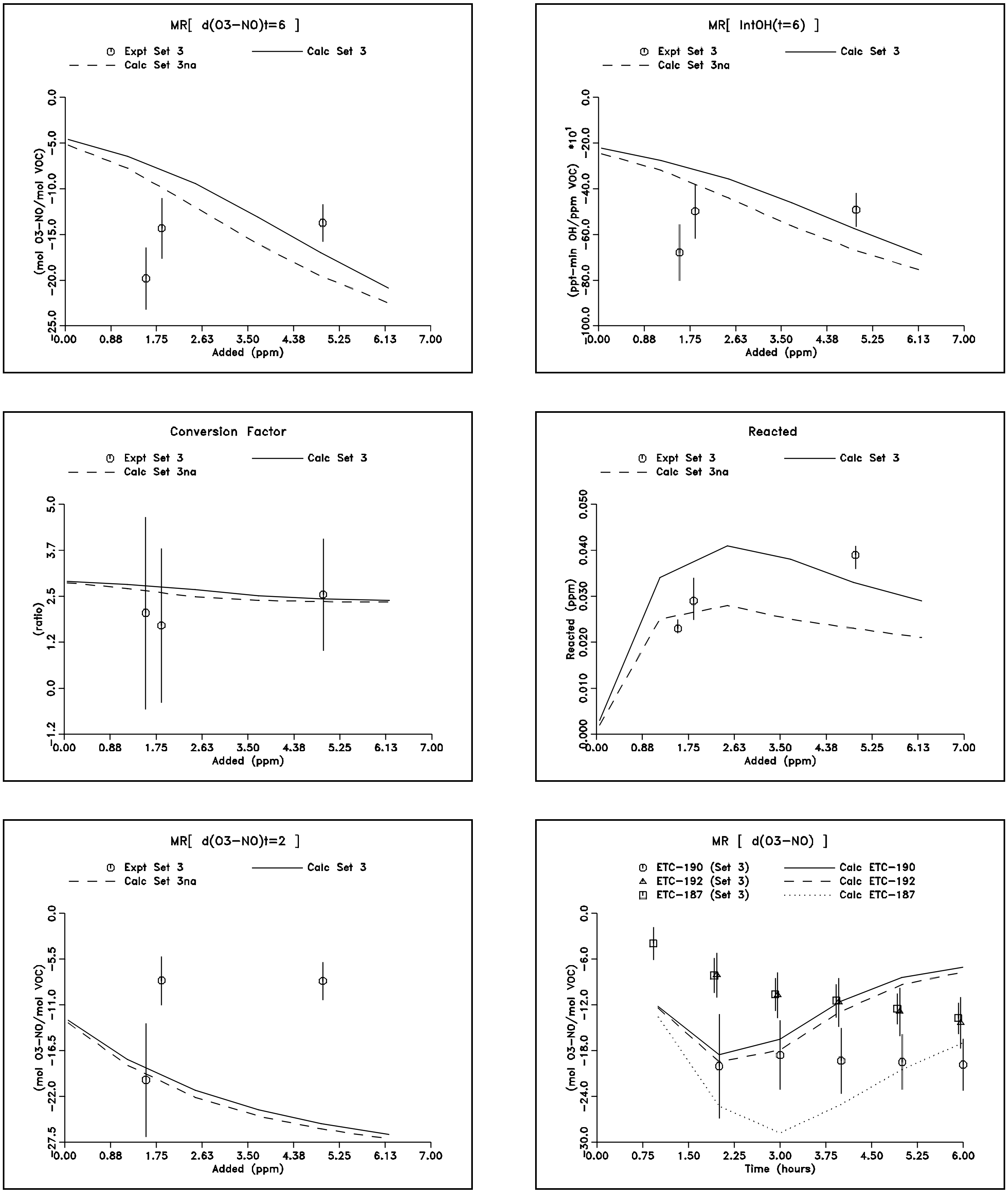

Figure A-35. Plots of experimental and calculated reactivity results for **Decamethylcyclopentasiloxane.**

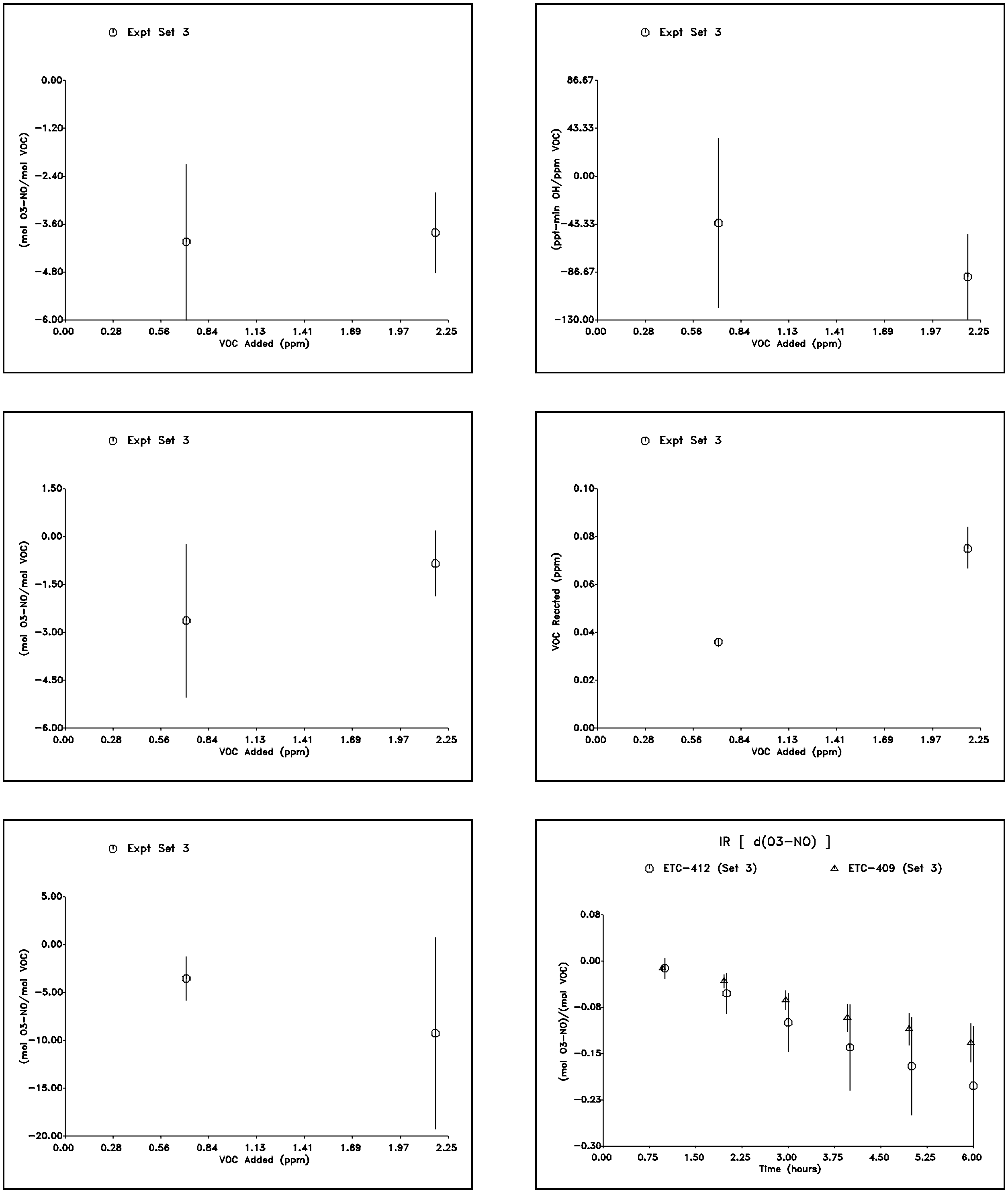

Figure A-36. Plots of experimental reactivity results for **Pentamethyldisiloxanol.**

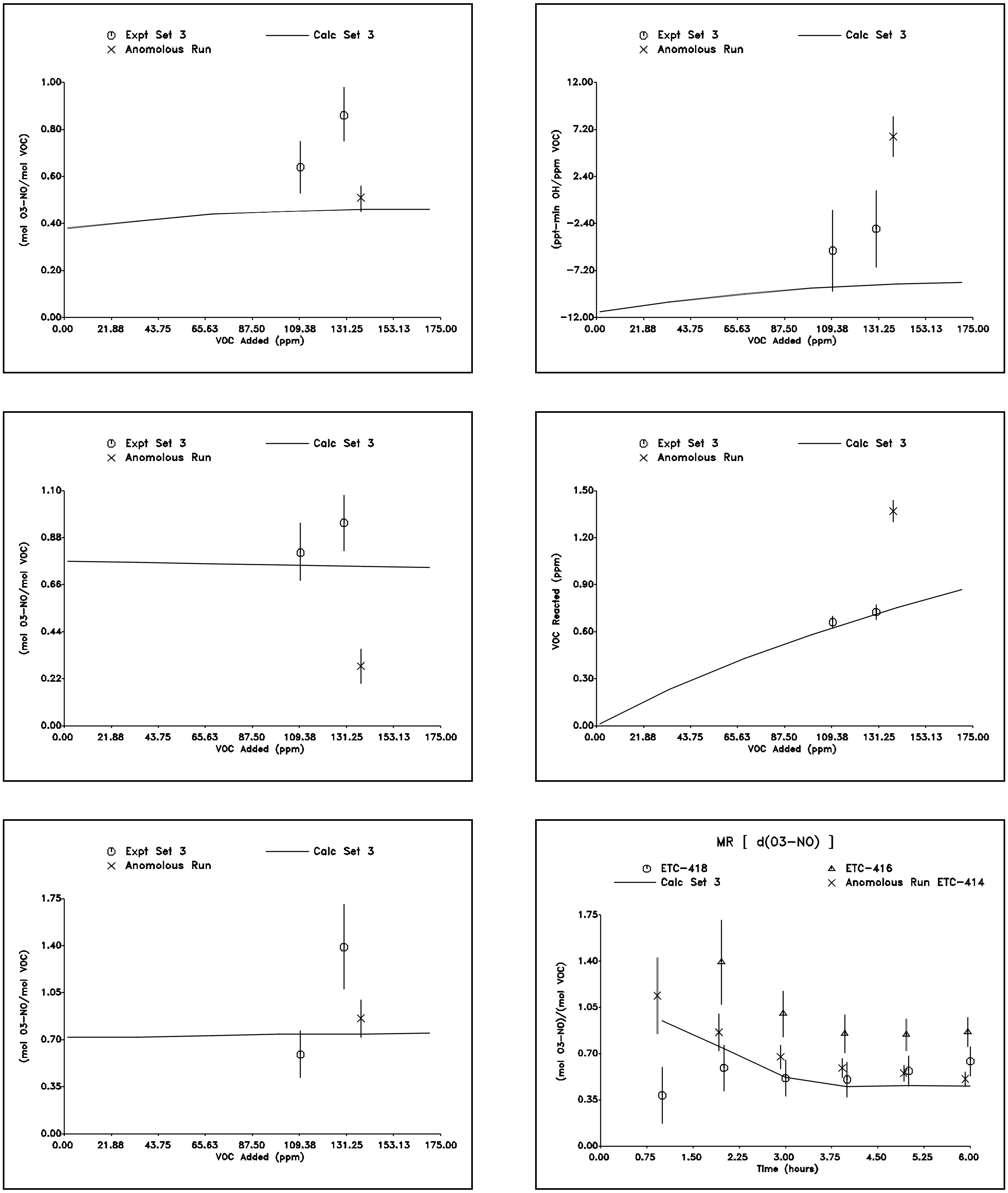

Figure A-37. Plots of experimental and calculated reactivity results for **Carbon Monoxide.**

APPENDIX B

EXAMPLE OF DATA CALCULATIONS: ETC-226

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

function(var1,var2,...):=expression

give definitions of functions. Expressions of the form

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

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

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

Initial Concentrations and Run Conditions

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

Final (t = 6 hour) Concentrations

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

Computation of IntOH.

$$dlnXyl := lnXyl6 - lnXyl0$$

$$dlnXyl = 0.445$$

$$udlnXyl := \sqrt{ulnXyl0^2 + ulnXyl6^2}$$

$$udlnXyl = 0.028$$

$$IntOH(dlnXyl, Dt) := \frac{dlnXyl - Dt}{kOHxyl}$$

$$uIntOH := \frac{\sqrt{ulnXyl6^2 + ulnXyl0^2 + uDt^2}}{kOHxyl}$$

Determine amount of propane reacted: Direct method

$$TstRcdD := VOC0 - VOC6 - Dt\cdot\frac{VOC0 + VOC6}{2} \qquad TstRcdD = 0.129$$

$$uTstRcdD := \sqrt{uVOC0^2 + uVOC6^2 + \left(uDt\cdot\frac{VOC0 + VOC6}{2}\right)^2} \qquad uTstRcdD = 0.417$$

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

$$TstRcdI(VOC0, dlnXyl, Dt, kOHvoc) := \frac{VOC0\cdot kOHvoc\cdot IntOH(dlnXyl, Dt)}{kOHvoc\cdot IntOH(dlnXyl, Dt) + Dt}\cdot\left(1 - e^{-kOHvoc\cdot IntOH(dlnXyl, Dt) - Dt}\right)$$

$$TstRcdI(VOC0, dlnXyl, Dt, kOHvoc) = 0.232$$

$$uTstRcdI := \sqrt{\left(uVOC0\cdot\frac{d}{dVOC0}TstRcdI(VOC0, dlnXyl, Dt, kOHvoc)\right)^2 \ldots + \left(udlnXyl\cdot\frac{d}{ddlnXyl}TstRcdI(VOC0, dlnXyl, Dt, kOHvoc)\right)^2 \ldots + \left(uDt\cdot\frac{d}{dDt}TstRcdI(VOC0, dlnXyl, Dt, kOHvoc)\right)^2}$$

$$uTstRcdI = 0.019$$

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

$$uTstRcdIchk := \sqrt{uTstRcdI^2 + \left(0.2\cdot kOHvoc\cdot\frac{d}{dkOHvoc}TstRcdI(VOC0, dlnXyl, Dt, kOHvoc)\right)^2}$$

$uTstRcdIchk = 0.05$ **Uncertainty in IntOH method**

$uTstRcdD = 0.417$ **Uncertainty in direct method**

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

$$TstRcd := TstRcdI(VOC0, dlnXyl, Dt, kOHvoc) \qquad TstRcd = 0.232$$

$$uTstRcd := uTstRcdI \qquad uTstRcd = 0.019$$

Base case estimates for t=6 (Regression coefficients from Table 4.)

$$dO3NObase := .7356 + .0558\cdot(avgT - avgTavg) + 2.90\cdot(Xyl0 - Xyl0avg) \ldots + 1.26\cdot(k1 - k1avg) - 0.42\cdot(NO0 - NO0avg) - 0.37\cdot(Hex0 - Hex0avg)$$

$dO3NObase = 0.658$ **(ppm)**

$udO3NObase := .047$ **Uncertainty of regression estimate**

$$IntOHbase := 22.26 + 84.13\cdot(Xyl0 - Xyl0avg) - 16.04\cdot(NO0 - NO0avg) + 1.56\cdot(avgT - avgTavg)$$

$IntOHbase = 20.532$ **(ppb-min)**

$uIntOHbase := 1.9$ **Uncertainty of regression estimate**

$ConvRbase := 17.08\cdot(NO0 - NO0avg) + 33.18$

$ConvRbase = 32.855$ **(10^3 min^-1)**

$uConvRbase := 3.0$ **Uncertainty of regression estimate**

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

$Change := dO3NOtest - dO3NObase$ $Change = 0.078$

$udO3NOtest := udO3NObase$ **Test run d(O3-NO) uncertainty estimated from variability in base case runs**

$uChange := \sqrt{udO3NOtest^2 + udO3NObase^2}$ $uChange = 0.066$

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

$IRdO3NO := \frac{Change}{VOC0}$ $IRdO3NO = 0.007$

$$uIRdO3NO := \left| IRdO3NO\cdot\sqrt{\left(\frac{uChange}{Change}\right)^2 + \left(\frac{uVOC0}{VOC0}\right)^2} \right|$$ $uIRdO3NO = 0.006$

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

$MRdO3NO := \frac{Change}{TstRcd}$ $MRdO3NO = 0.334$

$$uMRdO3NO := \left| MRdO3NO\cdot\sqrt{\left(\frac{uChange}{Change}\right)^2 + \left(\frac{uTstRcd}{TstRcd}\right)^2} \right|$$ $uMRdO3NO = 0.288$

Convert to ppt-min units

$IntOHtest := 10^6 \cdot IntOH(dlnXyl, Dt)$ $IntOHtest = 12.023$

$uIntOHtest := 10^6 \cdot uIntOH$ $uIntOHtest = 0.925$

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 uIntOHtest..

$uIntOHtest := if(uIntOHtest > uIntOHbase, uIntOHtest, uIntOHbase)$

$uIntOHtest = 1.9$

$Change := IntOHtest - IntOHbase$ $Change = -8.509$

$uChange := \sqrt{uIntOHtest^2 + uIntOHbase^2}$ $uChange = 2.687$

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

$IRIntOH := \frac{Change}{VOC0}$ $IRIntOH = -0.735$

$uIRIntOH := \left| IRIntOH \cdot \sqrt{\left(\frac{uChange}{Change}\right)^2 + \left(\frac{uVOC0}{VOC0}\right)^2} \right|$ $uIRIntOH = 0.233$

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

$MRIntOH := \frac{Change}{TstRcd}$ $MRIntOH = -36.665$

$uMRIntOH := \left| MRIntOH \cdot \sqrt{\left(\frac{uChange}{Change}\right)^2 + \left(\frac{uTstRcd}{TstRcd}\right)^2} \right|$ $uMRIntOH = 11.966$

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)

$$dO3NObaseROGtest := ConvRbase \cdot IntOHtest \cdot 10^{-3}$$

$$dO3NObaseROGtest = 0.395$$

$$udO3NObaseROGtest := dO3NObaseROGtest \cdot \sqrt{\left(\frac{uConvRbase}{ConvRbase}\right)^2 + \left(\frac{uIntOHtest}{IntOHtest}\right)^2}$$

$$udO3NObaseROGtest = 0.072$$

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

$$IRdirect := \frac{dO3NOtest - dO3NObaseROGtest}{VOC0}$$

$$IRdirect = 0.029$$

$$uIRdirect := \left| IRdirect \cdot \sqrt{\left(\frac{udO3NObaseROGtest}{dO3NOtest - dO3NObaseROGtest}\right)^2 + \left(\frac{uVOC0}{VOC0}\right)^2} \right|$$

$$uIRdirect = 0.006$$

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

$$ConvF := \frac{dO3NOtest - dO3NObaseROGtest}{TstRcd}$$

$$ConvF = 1.469$$

$$uConvF := \left| ConvF \cdot \sqrt{\left(\frac{udO3NObaseROGtest}{dO3NOtest - dO3NObaseROGtest}\right)^2 + \left(\frac{uVOC0}{VOC0}\right)^2} \right|$$

$$uConvF = 0.312$$