A Reevaluation of the Carbon Bond-IV Photochemical Mechanism

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Outline

Introduction to Carbon Bond-IV

Project Statement

Tests of Past Changes

Recent Updates

Presentation and Vindication of CB-IV_99

Conclusions and Recommendations

Introduction

Utility of Photochemical Reaction Mechanism

Abstraction of the Organic Chemistry

CB-IV

- Structurally lumped mechanism
- Lumped and explicit mechanisms

CB-IV Background

Officially Released in 1989 (Gery et al., 198

- First version: 35 reactions, 5 organic species
- Release version: 81 reactions, 15 organic speci
- Current version: 95 reactions, 15 organic specie

Range of applications

Widely used in regulatory Air Quality Mod
for regulatory applications

Purpose

Significance of this project

Provide documentation for past changes

Present a new version for future regulatory modeling

Present the necessity of this type of work

Objectives

Vindicate the past changes

Review the current state of CB-IV

Provide an updated version of the CB-IV mechanism

- fully vindicated
- state-of-the-science

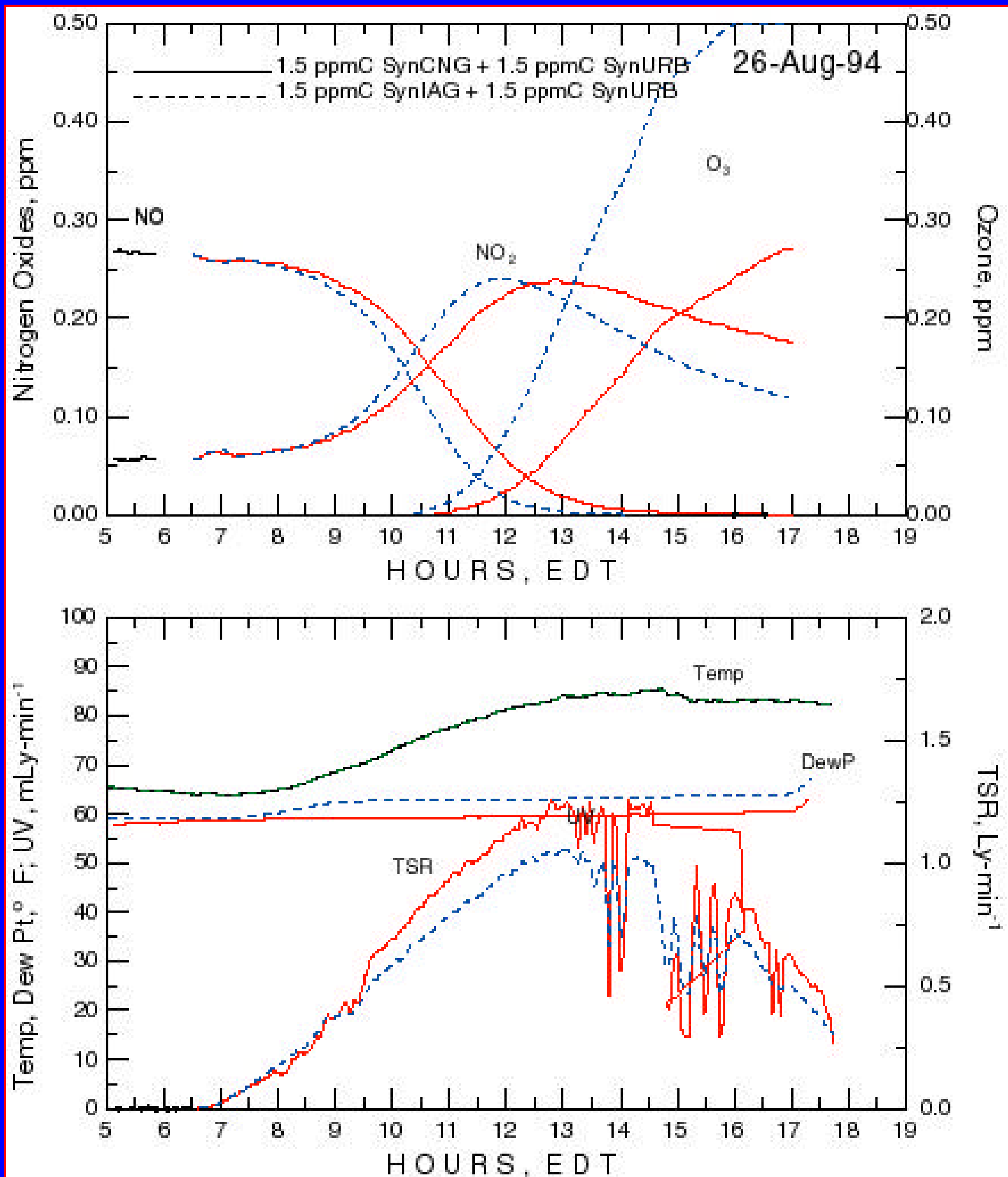
Approach and Methods

Approach:

- test the past changes for use in future applications
- present current updates and a new model

Methods:

- kinetic analyses
- smog chamber modeling
- Integrated Reaction Rates (IRR)



1.5 ppmC SynCNG + 1.5 ppmC SynURB
1.5 ppmC SynIAG + 1.5 ppmC SynURB
26-Aug-94
NO
NO2
O3
Nitrogen Oxides, ppm
Ozone, ppm
HOURS, EDT
Temp
DewP
UV
TSR
Temp, Dew Pt, °F; UV, mLy-min-1
TSR, Ly-min-1
HOURS, EDT

Testing Past Changes

PAN updates

Radical termination updates

New isoprene mechanism

Photolysis Updates

Additional modifications

PAN Updates

PAN Mechanism:

```
]C2O3 + NO    = NO2+XO2+HCHO+HO3
]C2O3 + NO2   = PAN
]PAN          = C2O3 + NO2
]C2O3 + C2O3 = 2.0[XO2+HCHO+HO2]
]C2O3 + HO2   = 0.75[C2O3+O2]+0.25[O3+C2O
```

PAN Updates

Kinetic updates

– new rate data

– pressure dependency in rates

Simplified Troe Falloff Expression

$k = k_0[M]/(1 + k_0[M]/k_{\infty}) F_c$^{1+(log$_{10}k_0[M]/k_{\infty})^2$

where $k_0 = k_0(T/300)^a$, $a = m_0$

$k_{\infty} = k_{\infty}(T/300)^b$, $b = m_{\infty}$

PAN Updates

Kinetic updates

- new rate data
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Simplified Troe Falloff Expression

$$k = k_0[M]/(1 + k_0[M]/k_\infty)\ F_c\text{^}\{1+(\log_{10} k_0[M]/k_\infty)^2]$$

where $k_0 = k_0(T/300)^a$, $a = m_0$

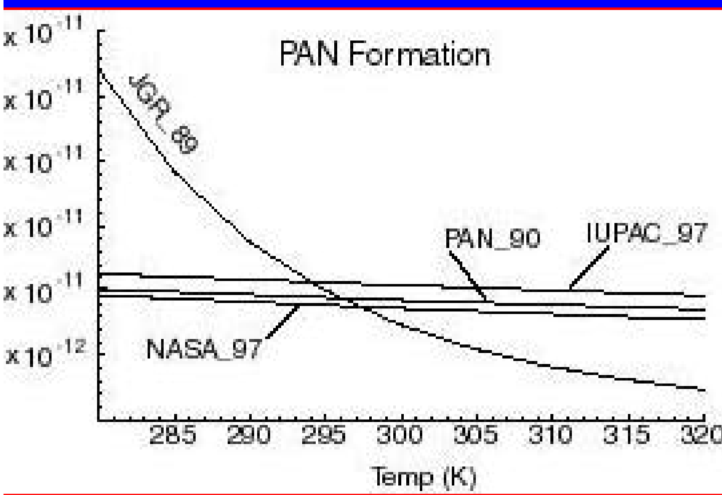
$k_\infty = k_\infty (T/300)^b$, $b = m_\infty$

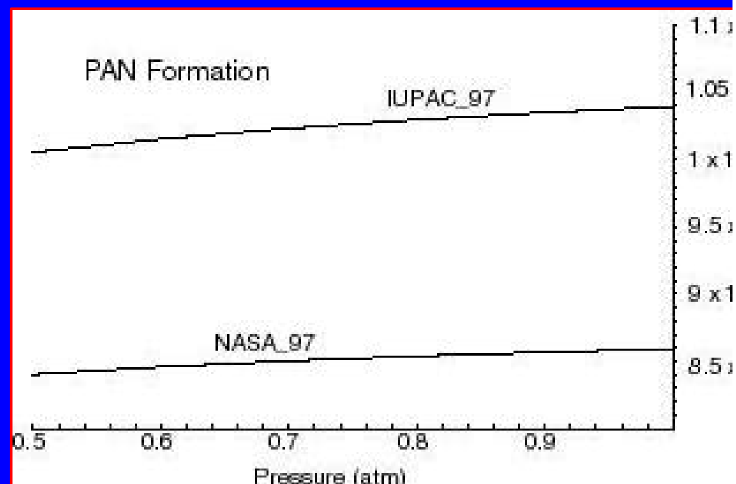
PAN Kinetic Updates

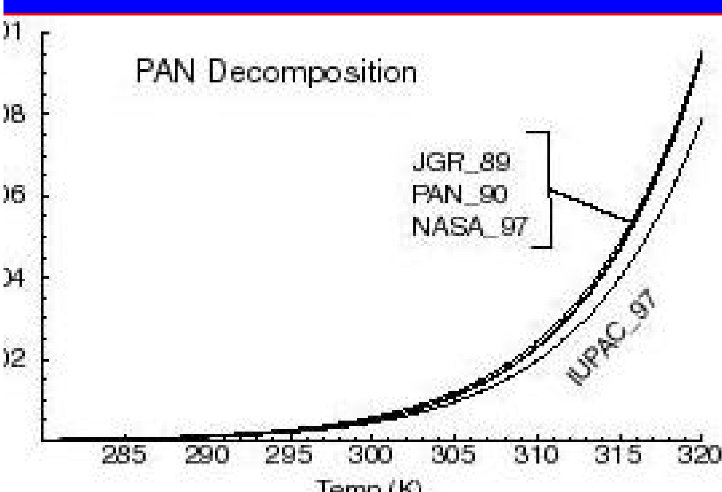
PAN rate datasets tested here:

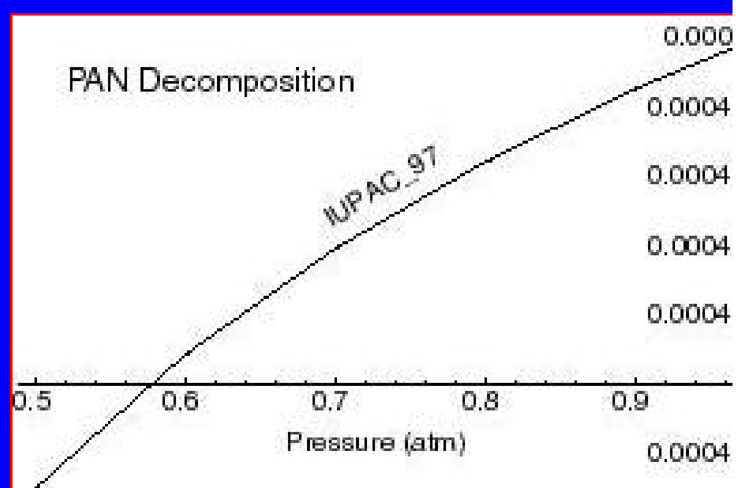
- Gery et al. (1989) - Temperature
- SAPRAC (1990) - Temperature
- IUPAC (1997) - Temperature and Pressure
- NASA (1997) - Temperature and Pressure
- This work - Temperature and Pressure

PAN Kinetic Updates







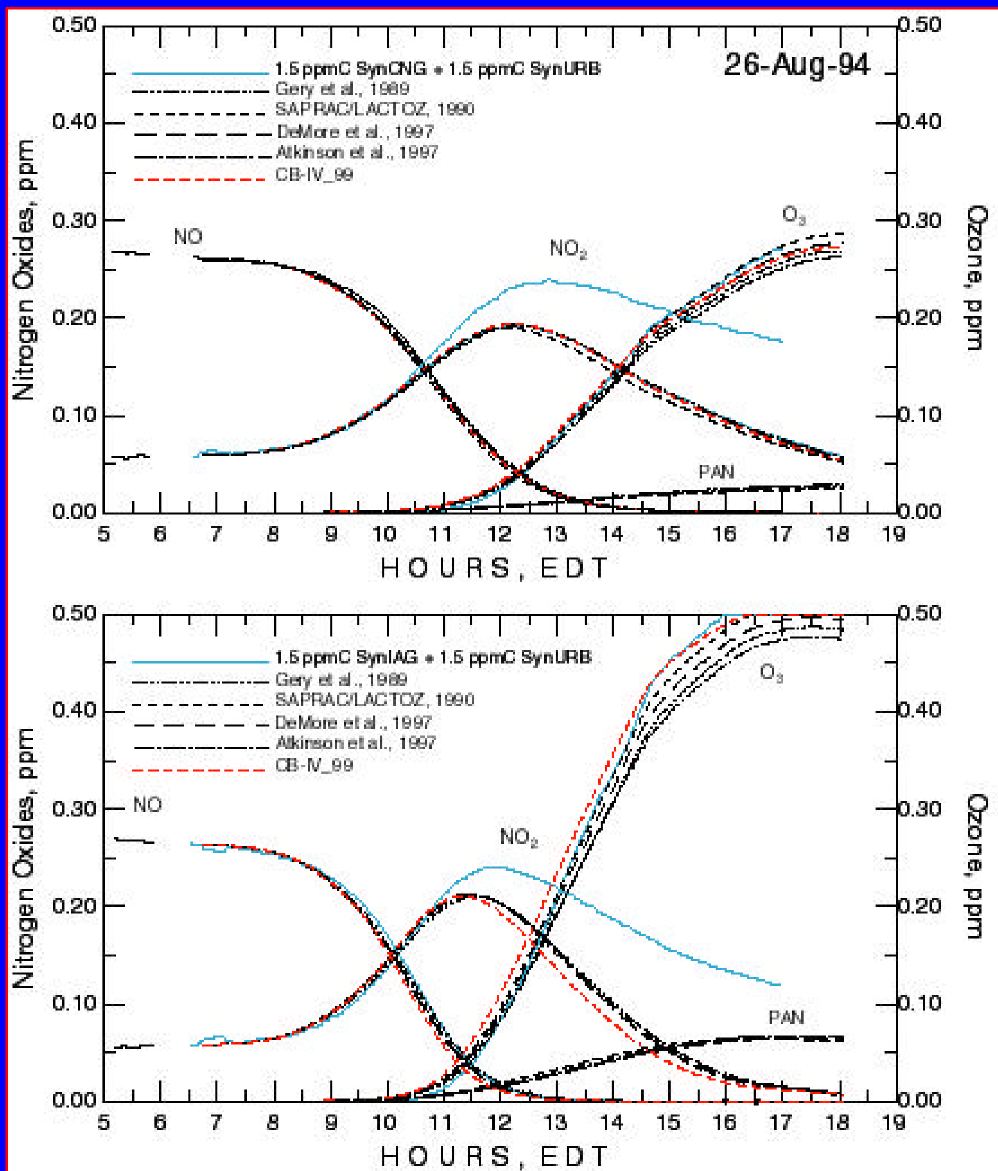


PAN Kinetic Updates

Smog chamber experiments

- Acetaldehyde
- Propene
- Urban Mix

PAN Experiments



Urban Mix/NO_x Experiment

PAN Conclusions

- In general O_3 inverse to PAN formation
- Highest IRR's through C2O3 + NO reactior always proportional to O_3 formation
  - result of lengthening NO-to-NO_2 chain length
- Basis of rate recommendations
  - credibility of rate
  - smog chamber performance

Recommended PAN Rates

Reaction:	*Kinetics Reference:*
C2O3 + NO	NASA,1997
C2O3 + NO2	IUPAC,1997
PAN	NASA,1997
C2O3 + C2O3	IUPAC,1997
C2O3 + HO2	IUPAC,1997

Radical Termination Updates

The prompt product approach

– minimize mechanism size

Needed full set of radical-radical reactions for NO_x limited conditions

Complete CB-IV Radical Set

] (XO2 + XO2N) + HO2

i] (XO2 + XO2N) + (XO2 + XO2N)

where *(i)* becomes,

XO2 + HO2

XO2N + HO2

and *(ii)* becomes,

XO2 + XO2

XO2N + XO2N

XO2 + XO2N

Complete CB-IV Radical Set

Kinetics

$$k_i = k_{(XO2+HO2)}$$

$$k_{ii} = k_{(XO2+XO2)}$$

Update old rates

$$k_{(XO2+NO)} = k_{(XO2N+NO)}$$

Effects of Radical Updates

- Increase O_3 in low NO_x conditions
  - – Demonstrated in AQSM's
- Smog chamber experiments
  - – Urban Mix
  - – Isoprene
  - – Propene

Testing the Complete Radical Se

chanism	XO2 + NO = NO2	XO2N + NO = NTR	XO2 + XO2	XO2 + HO2	XO2N + HO2	XO2N + XO2N	X
B	Throughput (ppm)						
.1f[a]	0.24048	0.01191	0.00001	-	-	-	
.1g[b]	0.24036	0.01191	0.00001	0.00008	-	-	
.1h[c]	0.24036	0.01191	0.00001	0.00008	0.00000	0.00000	0
.1f	0.37192	0.02233	0.00172	-	-	-	
.1g	0.36569	0.02209	0.00108	0.00463	-	-	
.1h	0.36566	0.02182	0.00106	0.00455	0.00031	0.00000	0
.1f	1.20732	0.18799	0.15006	-	-	-	
.1g	1.04044	0.18712	0.04915	0.30754	-	-	
.1h	1.05940	0.17640	0.04749	0.30103	0.01093	0.00036	0
.1f	1.00988	0.07651	0.02024	-	-	-	
.1g	0.93896	0.07637	0.00967	0.07774	-	-	
.1h	0.93909	0.07594	0.00964	0.07755	0.00044	0.00000	0
.1f	0.69906	0.00263	0.07708	-	-	-	
.1g	0.63681	0.00260	0.02470	0.14618	-	-	
.1h	0.63695	0.00241	0.02467	0.14603	0.00020	0.00000	0
.1f	0.77943	0.00299	0.11936	-	-	-	
.1g	0.69882	0.00295	0.03589	0.21626	-	-	
.1h	0.69908	0.00265	0.03585	0.21604	0.00031	0.00000	0

[a] Original Operator Set (Gery et al, 1989); [b] Addition of XO2+HO2 (Gery, 1994); [c] Complete Operator Set (Burton and Yarw

Conclusions on Radical Updates

- Difficult to asses in chamber because lack o low NO_x experiments
- CB-IV becomes more reactive
- More NO_x available in NO_x limited conditio
- Complete set of termination reactions

New Isoprene Mechanism

- Explict isoprene mechanism
- Impetus for mechanism update
  - BEIS2
  - New analytical techniques
- Maximum Incremental Reactivity (MIR)
- CB-IV isoprene mechanism inadequate

Carter One-Product Mechanism

- Accounts for 1° and 2 ° reactive products
- Decreased MIR
- Comparable performance to explicit mech's
- Evaluated effects in AQSM's
  - O_3 increased in NO_x limited areas
  - O_3 decreased in NO_x rich areas

Isoprene Mechanism Conclusions

- Cannot evaluate the MIR decrease
- Developed and tuned with old inorganic kinetics
- Need for an explict CB-IV isoprene mechanism
- Need for an expanded smog chamber databa

Photolysis Rate Updates

Photolysis = radical initiation

$$j = \int A_{li} \Phi_{li} \sigma_{li} \, d\, l$$

Early Assumptions

- lack of data
- species specific parameters not derived in cham
- secondary ratios

Photolysis Rate Errors

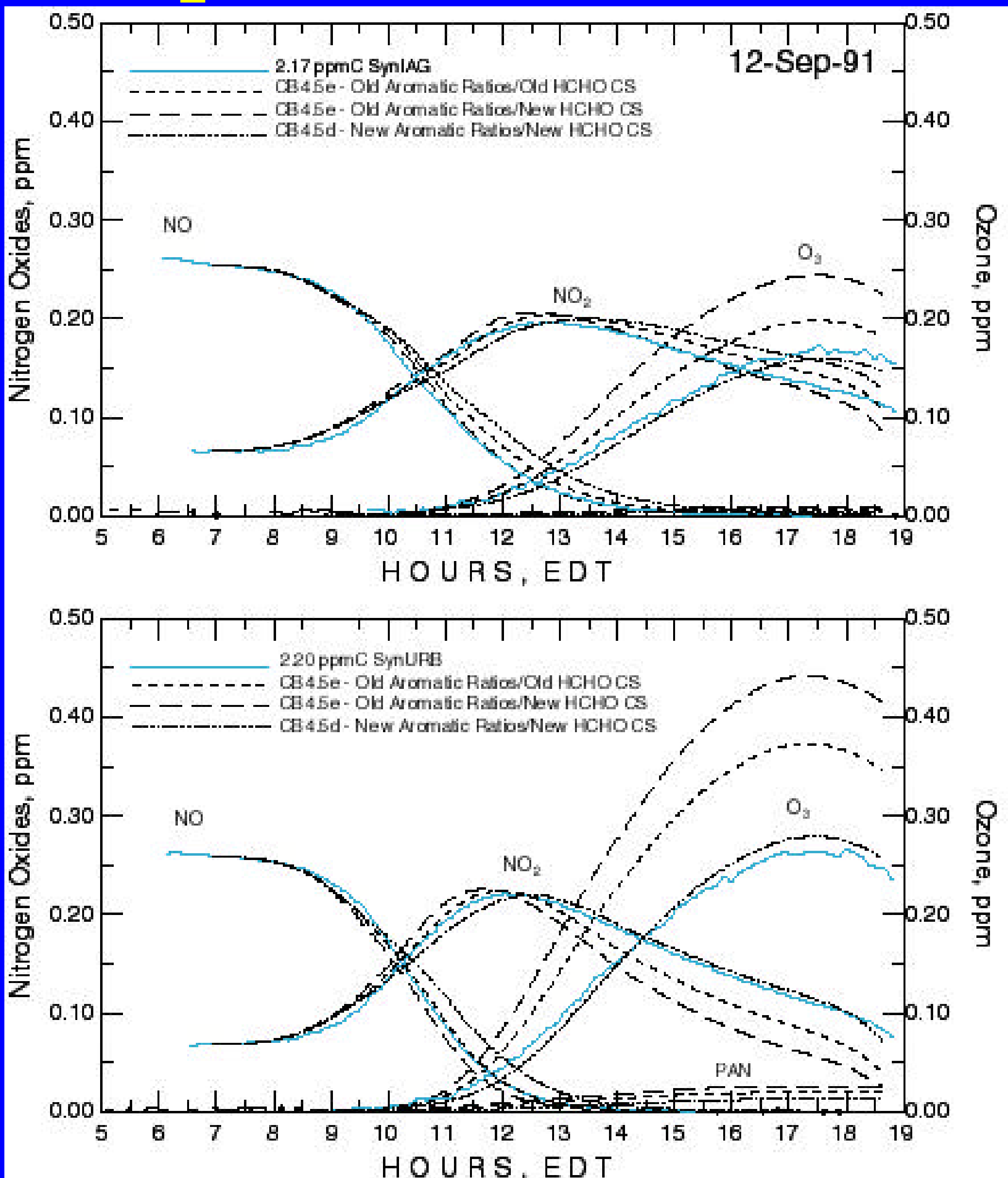
Failure to rescale = erroneous predictions

HCHO cross section updates = 30% increase in photolyis

Aromatic species (MGLY and OPEN) scaled to HCHO

Required and 22% decrease in aromatic ratios

Example of CSQY Errors



Resolving CSQY Problems

- Most current implementations of CB-IV have this error
- Literature contains sufficient data to represent all rates explicitly
- No difference between using explicit CSQY and secondary ratios
- Best implementation is to be explicit
  - OPEN and MGLY must use ratios

Additional Modifications

Alcohol chemistry

SO_x reactions

Pressure dependent rates

PNA reactions

OH + CH_4

Conclusions on Past Changes

Application of new information

Extend range of applications

Updates must be vindicated

Stage set for CB-IV_99

– complete kinetic and mechanistic reevaluation

Recent Updates to CB-IV

Requirements of photochemical mechanism

- continuous rate evaluations
- critical mechanistic reviews
- update as new data becomes available

Regulatory implications

- better predictions
- increased legal viability

Nature of Recent Updates

Application of new kinetic data

New photolysis data

Reevaluate explicit organic mechanisms

"Retuning" of lumped organic mechanisms

– coupled to inorganic mechanism

Development of new heterogeneous chamber mechanism

Development of Auxmech99

- Introduction to chamber wall mechanisms
- "Dirty Chamber" effect
  - radical source
  - NO_x source
  - organic source
- Surface catalyzed reactions

Development of Auxmech99

Literature review of relevant surface chemistry

Chamber experiments

- CH_4
- CO
- Acetaldehyde
- Ethene

IRR

Development of Auxmech99

Wall Observations

- Radical source: nitrous acid
- HNO_3 and HCHO on walls
- Deposition of O_3 and H_2O_2
- Wall water

Chamber conditions

- venting
- history

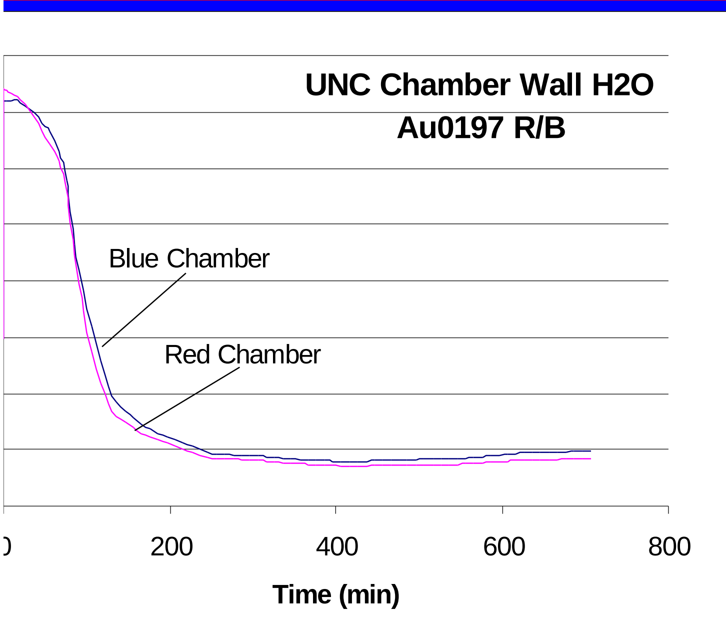
Objectives of Auxmech99

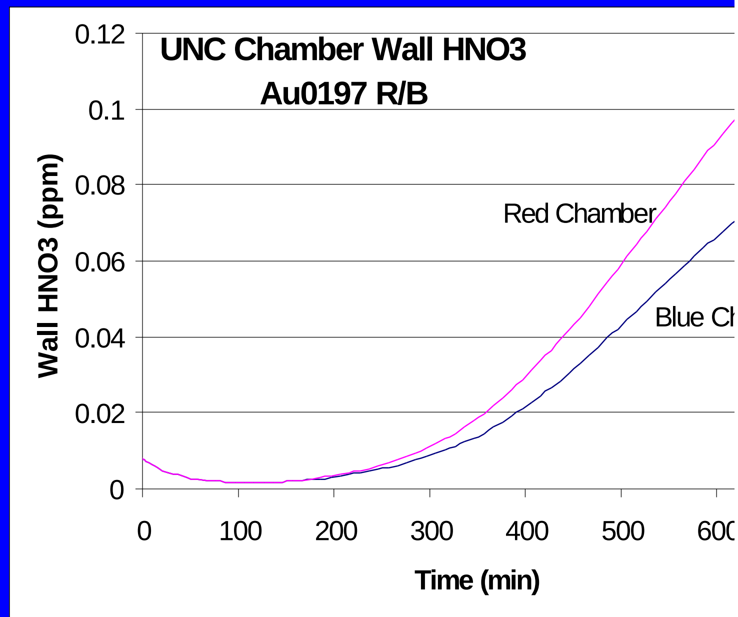
Capture observational phenomena
- deposition
- light and dark reactions

Increased temporal resolution of reactivity

Use of reasonable assumptions
- initial nitrous acid < 2.0 ppb
- intial nitric acid

Development of Auxmech99



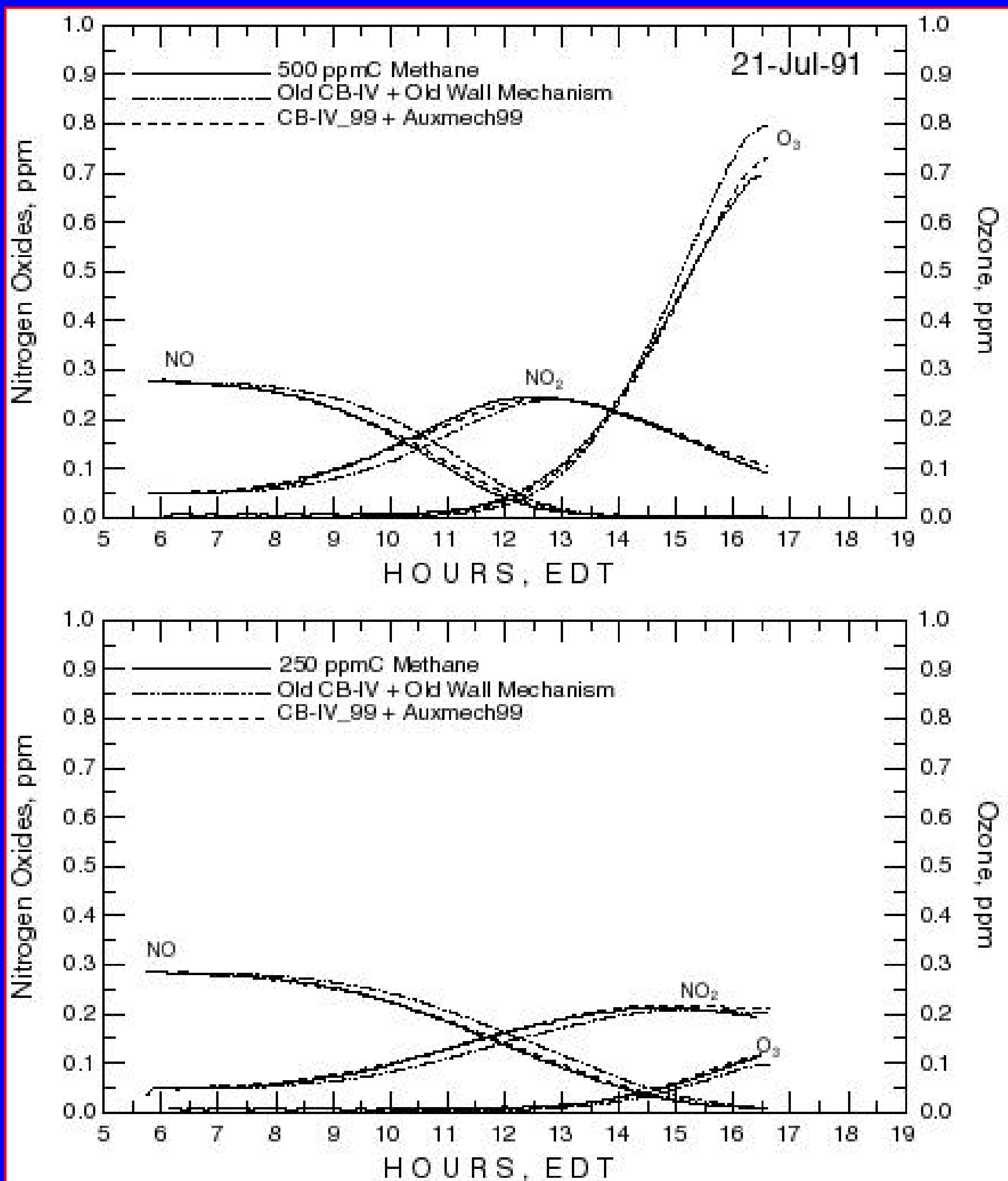


ameters used to obtain increased temporal resolution of mber wall reactivity; these parameters incorporate seaso chamber history effects.

Auxmech99

Reaction	*Rate (molec/cc sec)*
IO2 = HONO	j_{NO2} * WallOH
IO2 + WHNO3 = HONO + NO2	5.0×10^{-3}
/HNO3 = NO2	j_{NO2} * WallNO2
IO + WHNO3 = HONO + NO2	9.0×10^{-2}
IO2 + WH2O = WHNO3	1.0×10^{-8}
IO + WH2O = WHNO3	1.0×10^{-8}
I2O5 = 2*WHNO3	2.5×10^{-3}
I2O5 + WH20 = 2*WHNO3	1.0×10^{-7} exp(2000/TK
I2O2 =	4.0×10^{-2}
)3 =	1.4×10^{-4}
INO3 = WHNO3	9.0×10^{-3}

Auxmech99



21-Jul-91
500 ppmC Methane
Old CB-IV + Old Wall Mechanism
CB-IV_99 + Auxmech99
NO
NO_2
O_3
Nitrogen Oxides, ppm
Ozone, ppm
HOURS, EDT
250 ppmC Methane
Old CB-IV + Old Wall Mechanism
CB-IV_99 + Auxmech99
NO
NO_2
O_3
Nitrogen Oxides, ppm
Ozone, ppm
HOURS, EDT

Auxmech99

- Improves overall simulations
  - better simulations of HNO_2 data
- Better representation of heterogeneous chemistry
- Reflects chamber history better than old wall mechanism

Auxmech99 Conclusions

Improvement over current wall mechanisms

Necessary for vindication process

Interim mechanism

Need for empirical data

Precursor to development of CB-IV_99

Development of CB-IV_99

Organic Mechanism

Photochemical Updates

Kinetic Updates

Vindication of CB-IV_99

Organic Mechanism Updates

Mechanisms that are unchanged

- HCHO,RCHO, ISOP,PAN
- Aromatics and PAR

Modified mechanisms

- ETH and OLE

Updated Olefin Mechanisms

action		Products
3 + ETH	Old	0.12 HO2 + 0.42 CO + HCHO
	New	0.08 HO2 + 0.32 CO + 1.02 HCHO + 0.08 OH + 0.02 H2O2
+ ETH	Old	1.70 HO2 + 0.30 OH + CO + HCHO + 0.7 XO2
	New	1.55 HO2 + 0.35 OH + 0.95 CO + 0.60 XO2 + 0.95 HCHO
3 + OLE	Old	0.44 HO2 + 0.10 OH + 0.33 CO + 0.74 HCHO + 0.50 RCHO + 0.22 XO2 + -1.0 PAR
	New	0.42 HO2 + 0.30 OH + 0.39 CO + 0.86 HCHO + 0.52 RCHO + 0.45 XO2 + -1.0 PAR + 0.60 CH4 + 0.08 H2O2
+ OLE	Old	0.38 HO2 + 0.20 OH + 0.30 CO + 0.20 HCHO + 0.63 RCHO + 0.28 XO2 + 0.22 PAR + 0.02 XO2N
	New	0.29 HO2 + 0.10 OH + 0.20 CO + 0.20 HCHO + 0.49 RCHO + 0.19 XO2 + 0.61 PAR + 0.01 XO2N
H + OLE	Old	HO2 + HCHO + RCHO + XO2 + -1.0 PAR
	New	0.95 HO2 + 0.71 HCHO + 0.95 RCHO + 0.71 XO2 + -0.71 PAR

CSQY and Kinetic Updates

Sources of kinetic updates

- Inorganic:
  - NASA/JPL (DeMore et al., 1997)
  - IUPAC (Atkinson et al., 1997)
- Organic:
  - Atkinson (1997)
  - Le Bras (1997)

Sources of photolysis data updates

- NASA/JPL (DeMore et al., 1997)
- IUPAC (Atkinson et al., 1997)

Testing and Vindication

Overall impacts not incremental additions

Important reactions looked at individually

- HNO_3 formation
- PAN mechanism

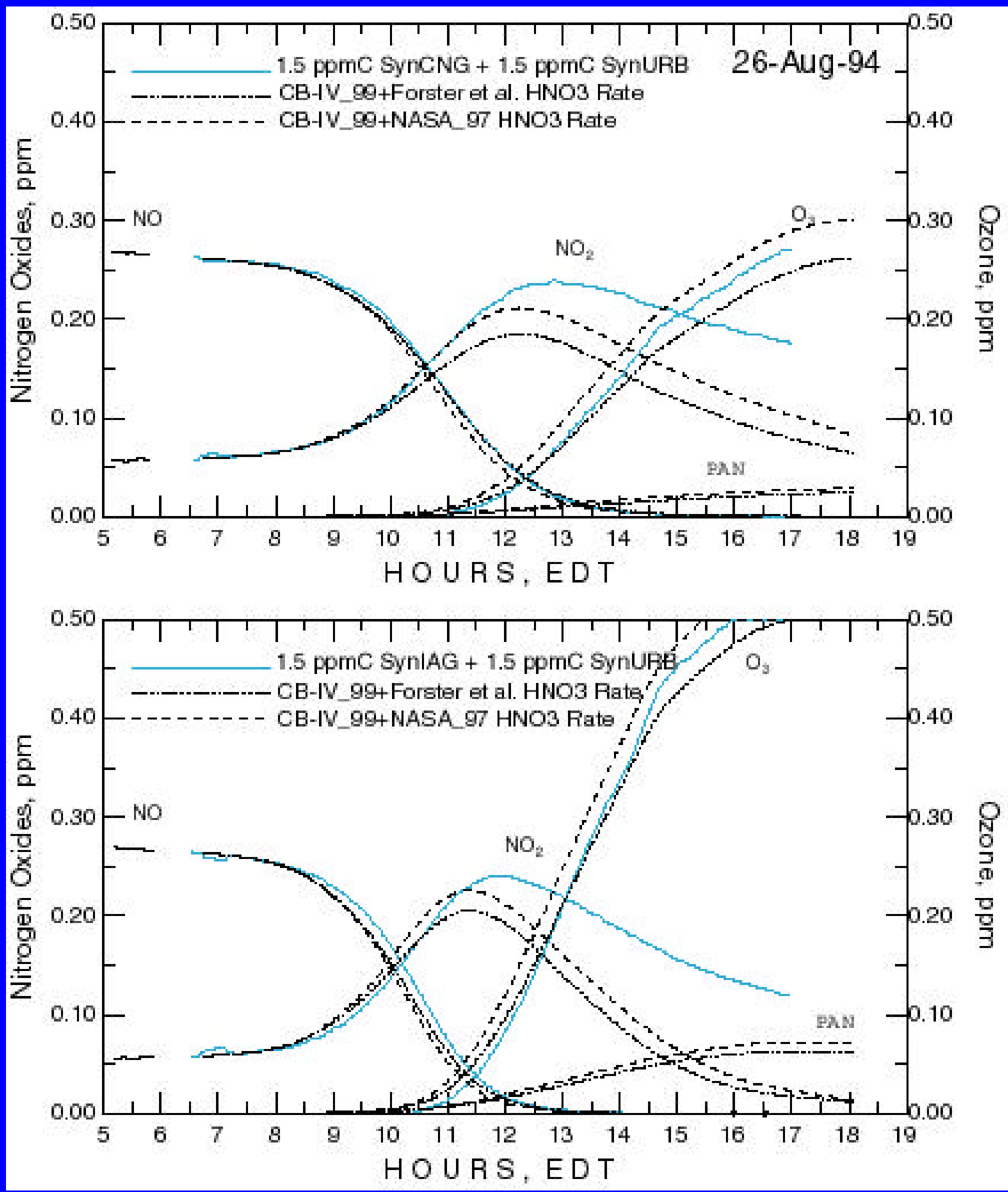
Qualitative and Quantitative Conclusions

Nitric Acid Formation

$NO_2 + OH = HNO_3$

- Several different rates in literature
  - Highest and lowest differ by 26%
- Four rates looked at
  - Forster et al., 1997
  - Dransfield et al., 1999
  - Dohahue et al., 1997
  - DeMore et al., 1997

Nitric Acid Formation



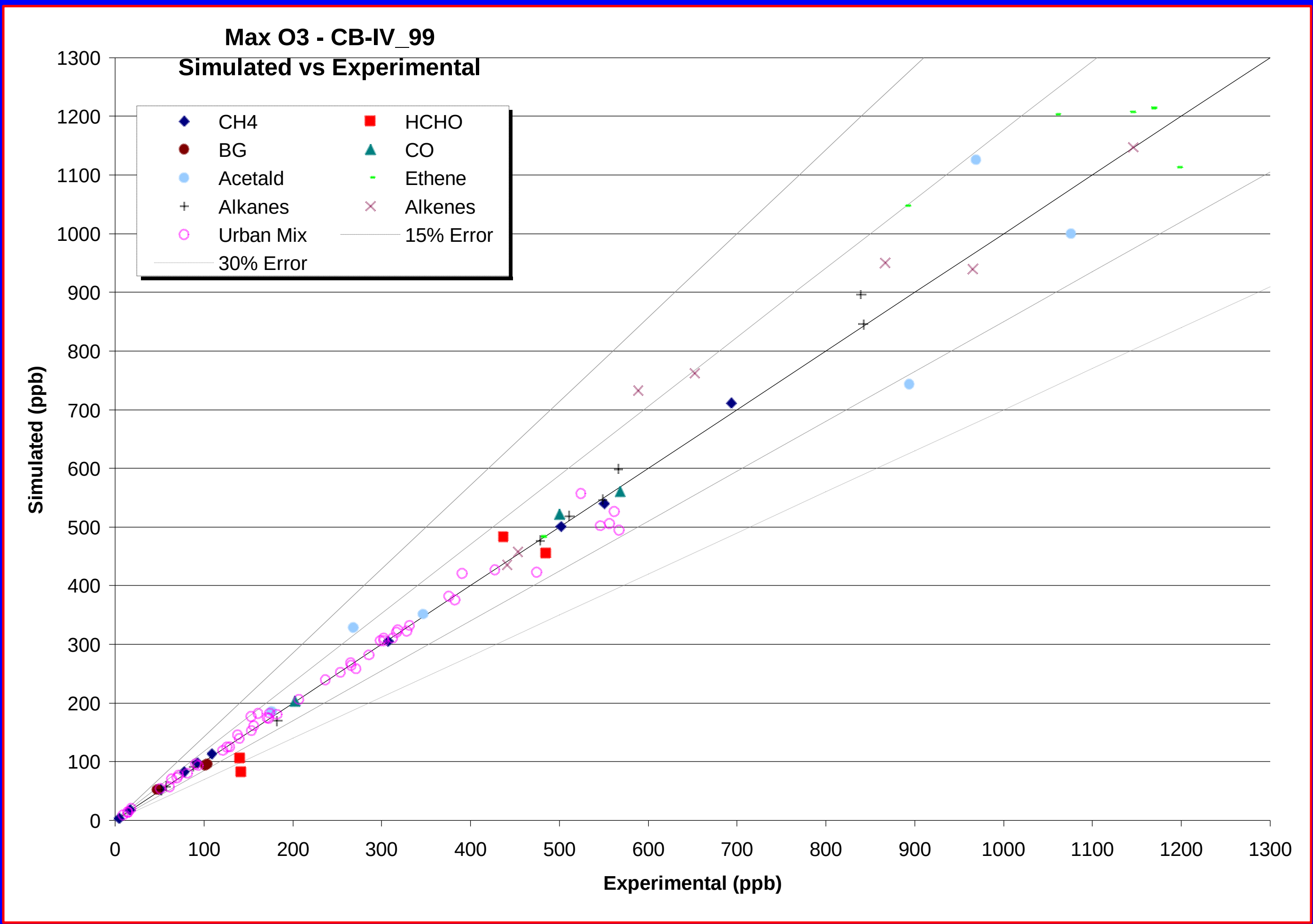
Nitric Acid Rate Recommenation

- Forster et al. rate used with CB-IV_99
  - includes new high pressure measurements
  - not enough data to disprove
  - allows historically consistent chamber assumptions
  - provides for high quality simulations of data

CB-IV_99 Vindication

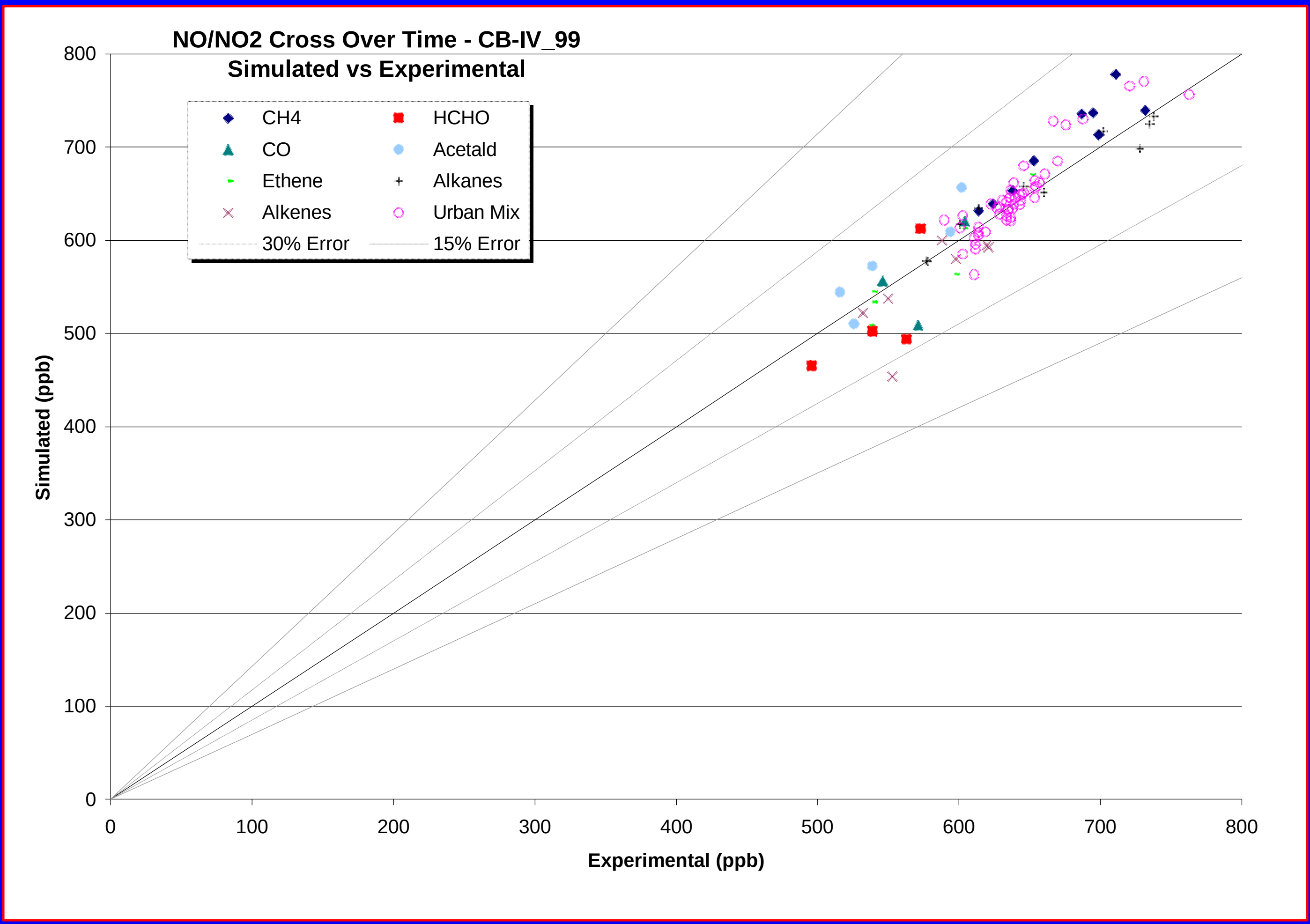
- Linear regression of several indicators
- Time series comparisons
  - UNC outdoor chamber
  - UCR-ITC
- Airshed modeling

CB-IV_99 Vindication



Simulated vs. Experimental O_3 Maximum

CB-IV_99 Vindication

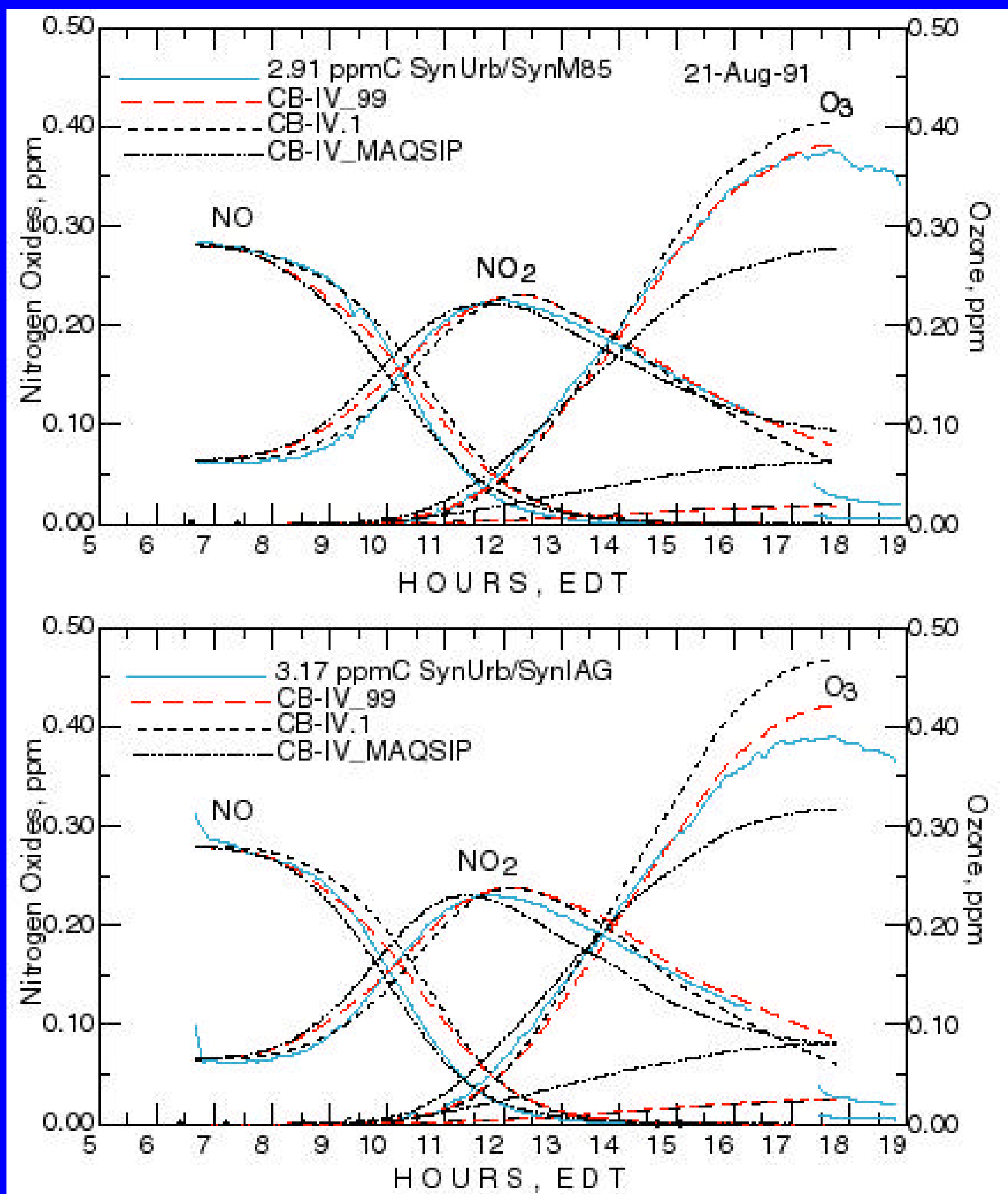


Simulated vs. Experimental NO/NO_2 X-Over Time

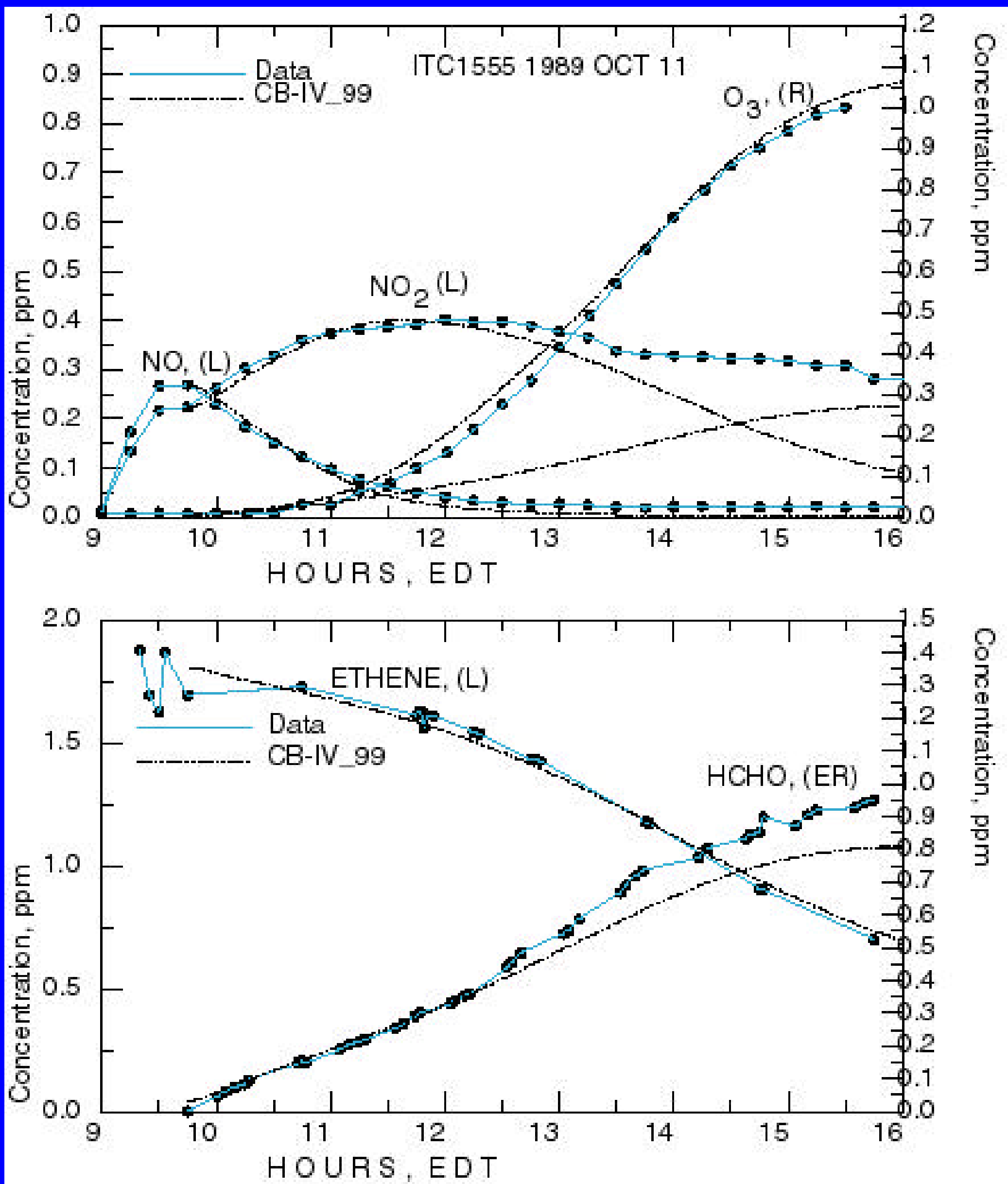
CB-IV_99 Vindication

		Error		Std.
	R^2	Avg.	Std. Dev.	Error
ax O_3 (ppb)	0.9826	9.00	±89.0	42.24
ax NO_2 (ppb)	0.9475	-56.0	±73.0	38.53
ax dO_3/dt	0.9767	-0.05	±0.28	0.45
ax dNO_2/dt	0.9572	-0.21	±0.11	0.15
ax dNO/dt	0.9456	-0.13	±0.12	0.21
O/NO_2 X-over	0.8844	6.00	±98.0	25.75
ax O_3 Time	0.2094	66.0	±104	90.08

CB-IV_99 Vindication



CB-IV_99 Vindication



Conclusions

CB-IV_99 improvements

- best features of old versions combined with current information
- fully vindicated
- fully documented
- developed with new wall mechanism

Conclusions

Importance of vindicating mechanisms

CB-IV_99 as state-of-the-science is relative

General problems with CB-IV

– NO_x and C terminated too rapidly

– needs a new biogenic mechanism

Significance of the inorganic reaction set

– CB-IV_99 inorganic reactions best available

Regulatory mechanisms require constant scrutiny

Recommendations

CB-IV_99 impacts on AQSM performance

- USEPA to test in Models 3
- UCR to test in OZIPR and asses affects on control strategies for NO_x and VOC's

Addition of reactions and pathways

- 1,2,4-TMB explicit mechanism
- CRO + HO2
- Isomerization pathway for PAR
- Full TROE falloff expression for P-dependence
- Recycling of organic nitrates back to NOx

Acknowledgements

Parents and family

Dr. Harvey Jeffries

Jeffries Research group - past and present

Dr. Don Fox and Dr. Doug Crawford-Brown

Dr. Ken Schere, Dr. Carey Jang,
Dr. Deborah Luecken, Gerry Gipson