



Evaluation of Kinetic and Photochemical Data for Stratospheric Research

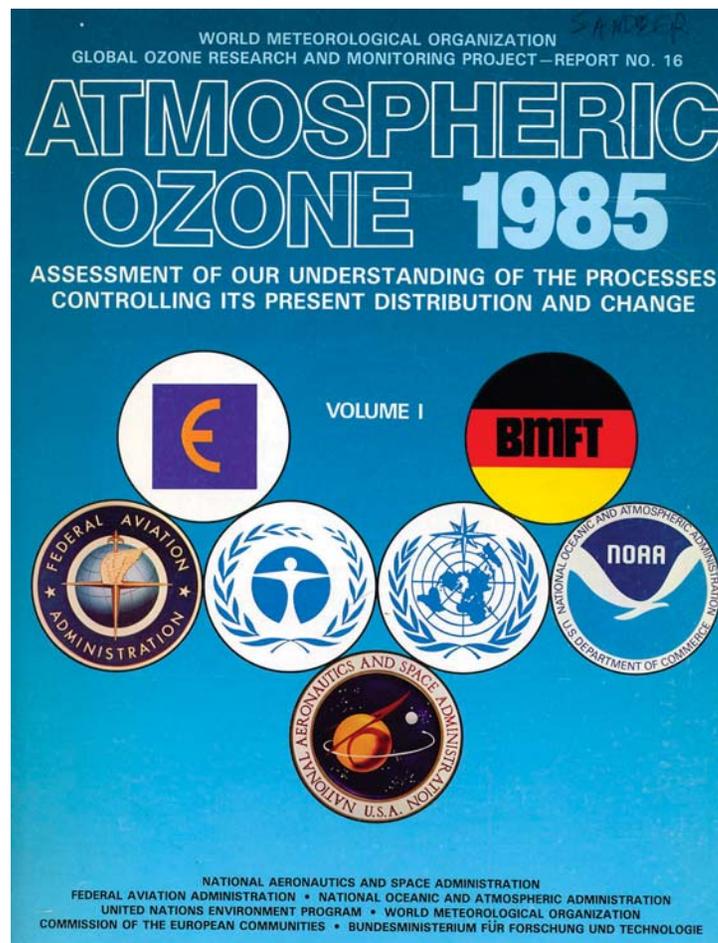
**Stanley P. Sander
NASA/Jet Propulsion Laboratory
California Institute of Technology
and
Present and Past Members of the NASA Panel for Data
Evaluation**



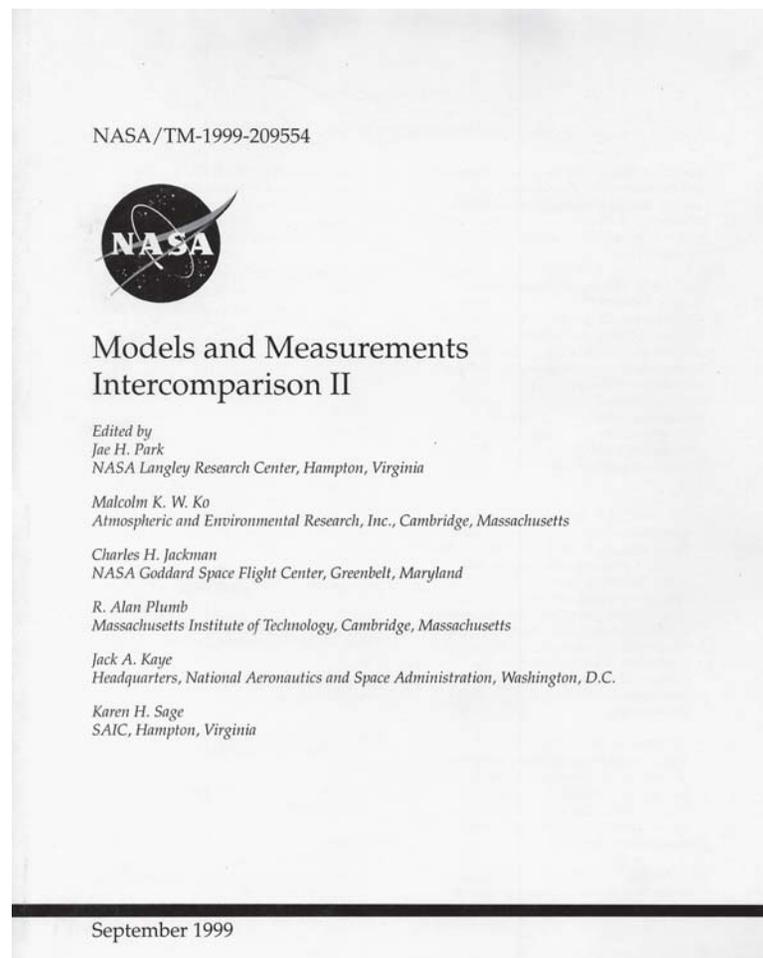
Basis of the need for critical evaluation of laboratory data



Community assessments such as WMO O₃ Evaluations



Systematic model/measurement intercomparisons





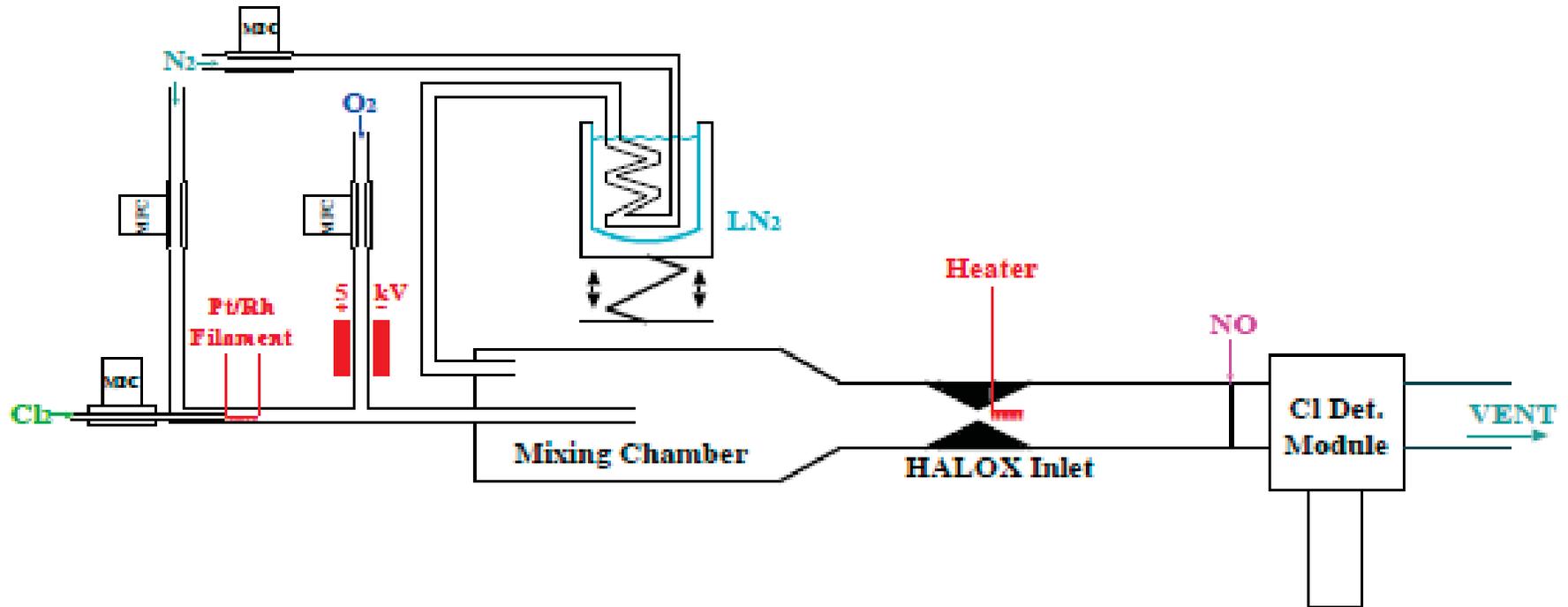
The need for critical data evaluations (cont.)



- **A starting point for chemical mechanisms used in atmospheric process models.**
 - **A “base case” for doing sensitivity analysis.**
- **Used extensively in laboratory studies to design experiments, model data.**
- **Used extensively in the design and interpretation of field measurements.**



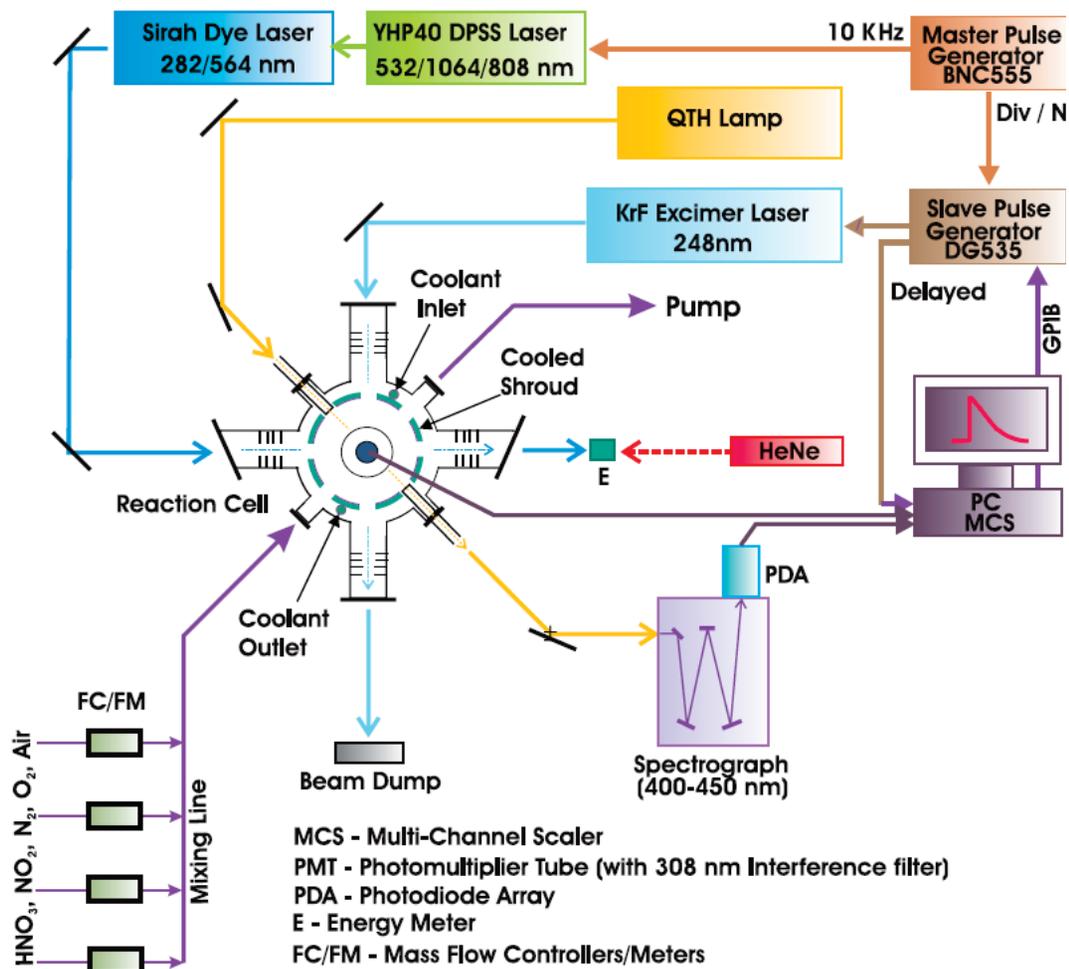
Field Instruments



- Measurement of stratospheric ClO using a fast-flow reactor in an aircraft instrument
- Anderson et al. (ER-2, WB-57), von Hobe et al. (Geophysica)



Laboratory Studies



JPL Laser Photolysis/Laser-Induced Fluorescence Apparatus



Evaluation of Kinetic and Photochemical Data for Atmospheric Modeling



- What do we mean by “critical evaluation”?

Compilations

NIST Kinetics Database
<http://kinetics.nist.gov>

Evaluations

NASA Data Evaluation
<http://jpldataeval.jpl.nasa.gov>

IUPAC Data Evaluation
<http://www.iupac-kinetic.ch.cam.ac.uk/>

It is very valuable to have two independent panels!



Starting Point for the Data Evaluation: Bob Watson's ClO_x Review (1977)



Reprint No. 101 from

Journal of
**Physical and
Chemical
Reference Data**

1977
Volume 6, No. 3, pages 871-917

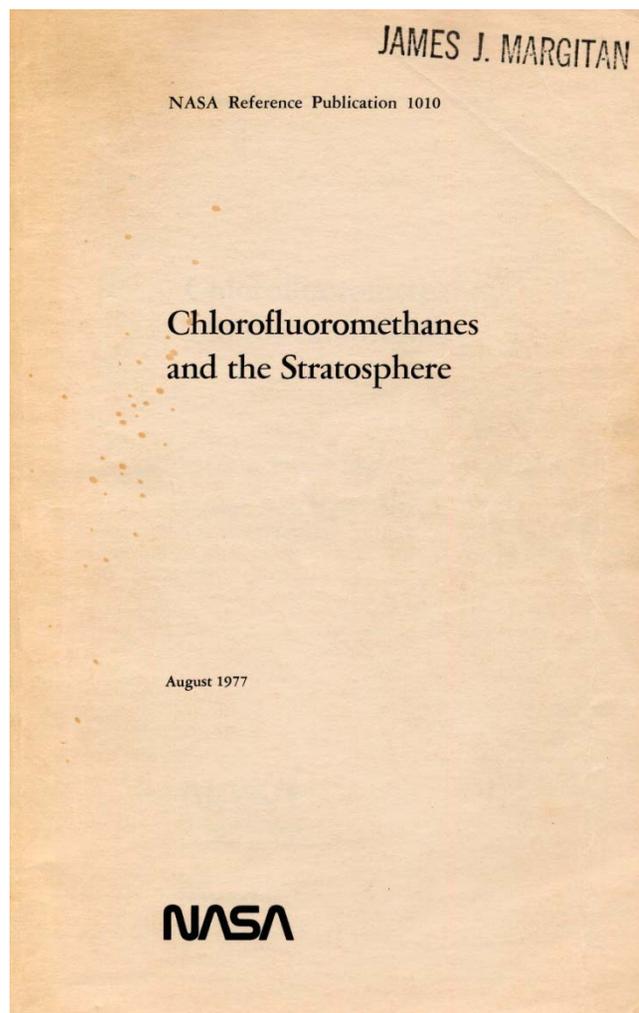
**Rate Constants for Reactions of
ClO_x of Atmospheric Interest**

R.T. Watson

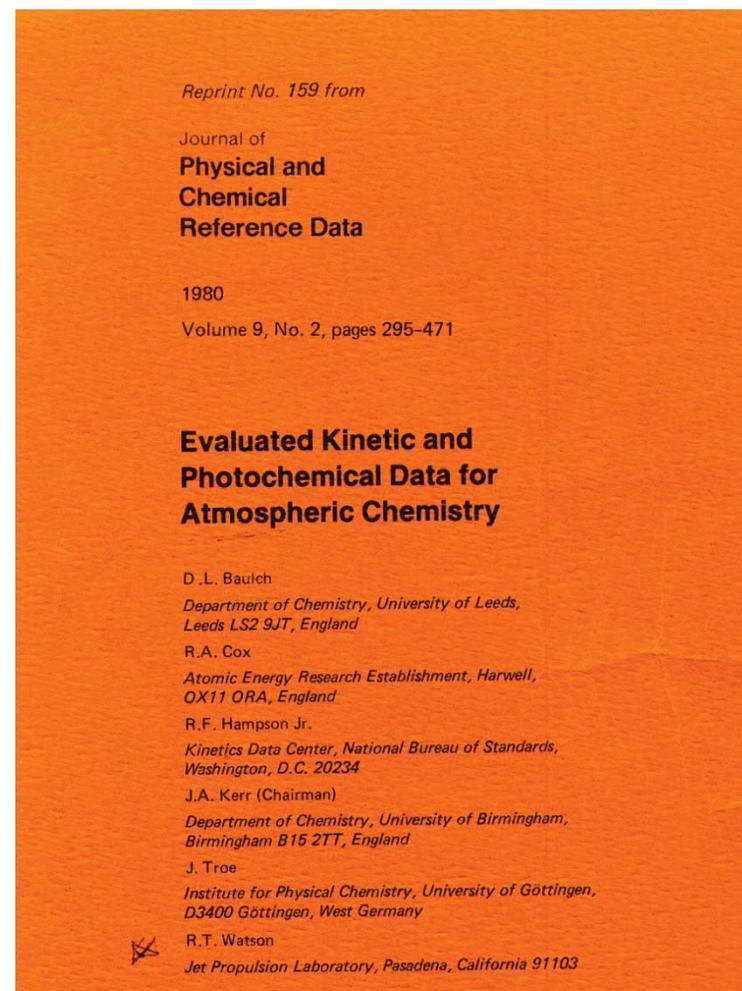
Jet Propulsion Laboratory, Pasadena, California 91103



The First NASA and IUPAC (CODATA) Evaluations



DeMore et al. (1977)



Baulch et al. (1980)



William "Moses" DeMore Founder of the NASA Data Panel





Process for Creating/Updating Recommendations



- Literature Survey: New results, community input
- One Panel member develops the recommendation
- Discussion at Panel Meetings.
- Recommendations are endorsed by the entire Panel
- Summarized as an entry in the recommendation table accompanied by an extensive note containing the rationale for the recommendation and lit. references.



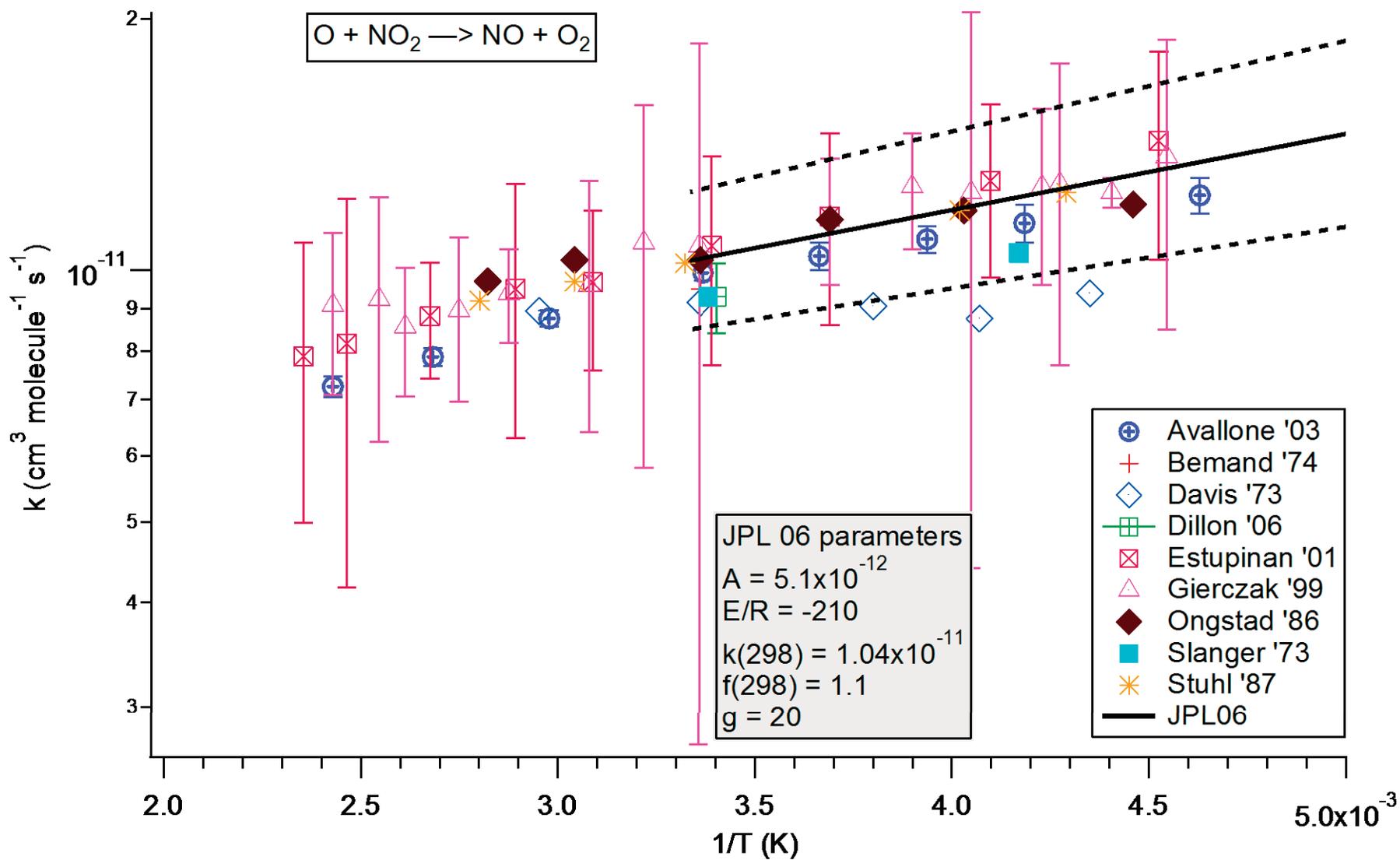
Stratospheric Ozone Sensitivity Analysis

G. Smith et al. (2001)



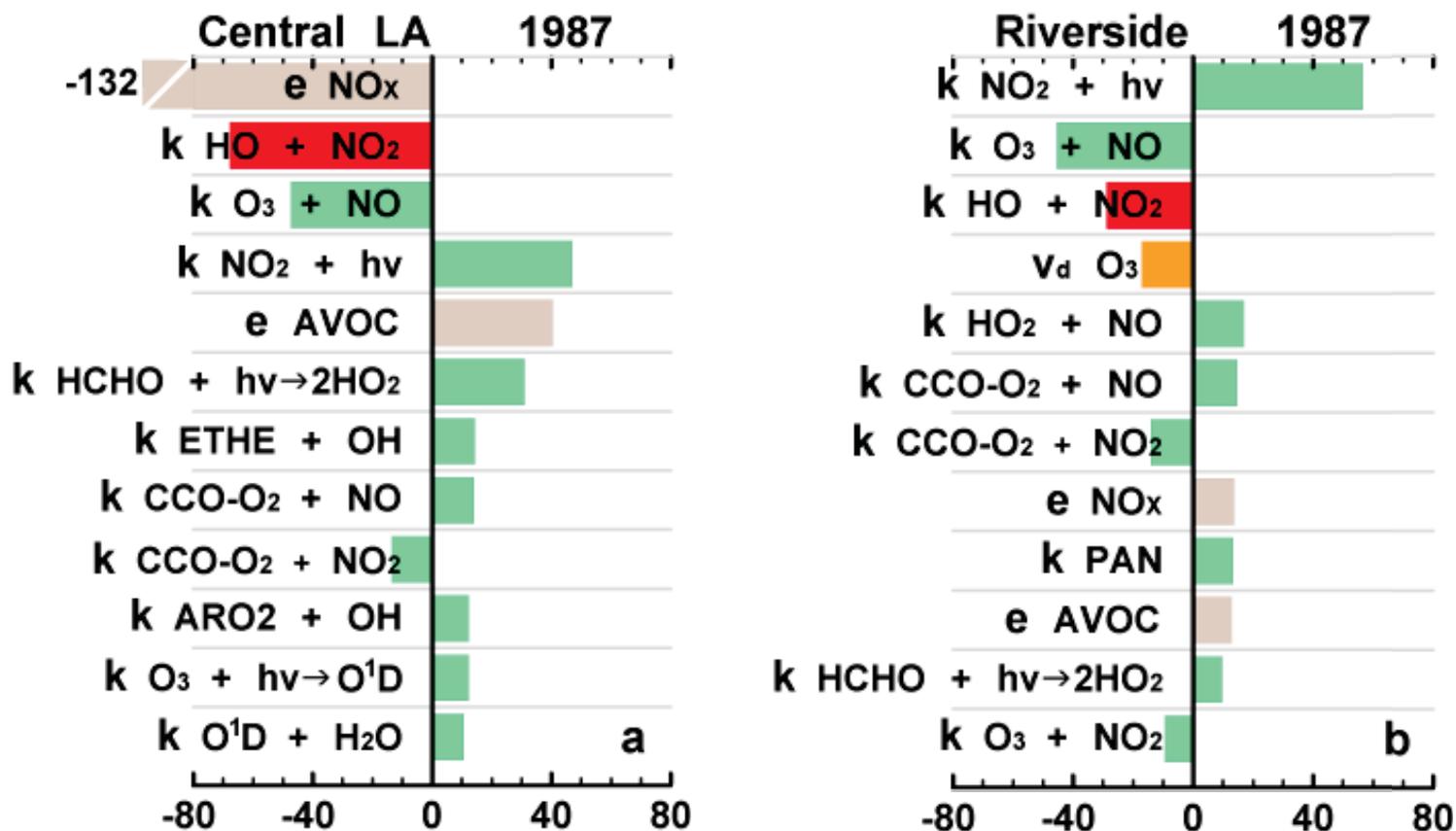
**TABLE 1: Ozone Sensitivities and Changes at 25 km 47N
Aug**

reacn	$S(O_3)$	k'/k	$\Delta O_3/O_3$
O + NO ₂	-0.327	1.129	-0.0397
OH + O ₃	-0.094	1.229	-0.0193
HO ₂ + O ₃	-0.084	0.808	0.0180
O + O ₂ = O ₃	0.471	1.031	0.0142
OH + NO ₂	0.090	0.897	-0.0098
(OH + NO ₂) ^a	0.090	(0.595)	(-0.0456)
NO + O ₃	-0.078	0.956	0.0035
HO ₂ + NO ^a	0.055	0.946	-0.0030
N ₂ O ₅ hydr	0.011	0.770	-0.0028
Cl + CH ₄	0.025	1.045	0.0011
Cl + O ₃	-0.027	1.039	-0.0010
NO ₂ + NO ₃	0.024	0.973	-0.0007
OH + HNO ₃	0.001	1.295	0.0004
total 94 to 00			-0.0391





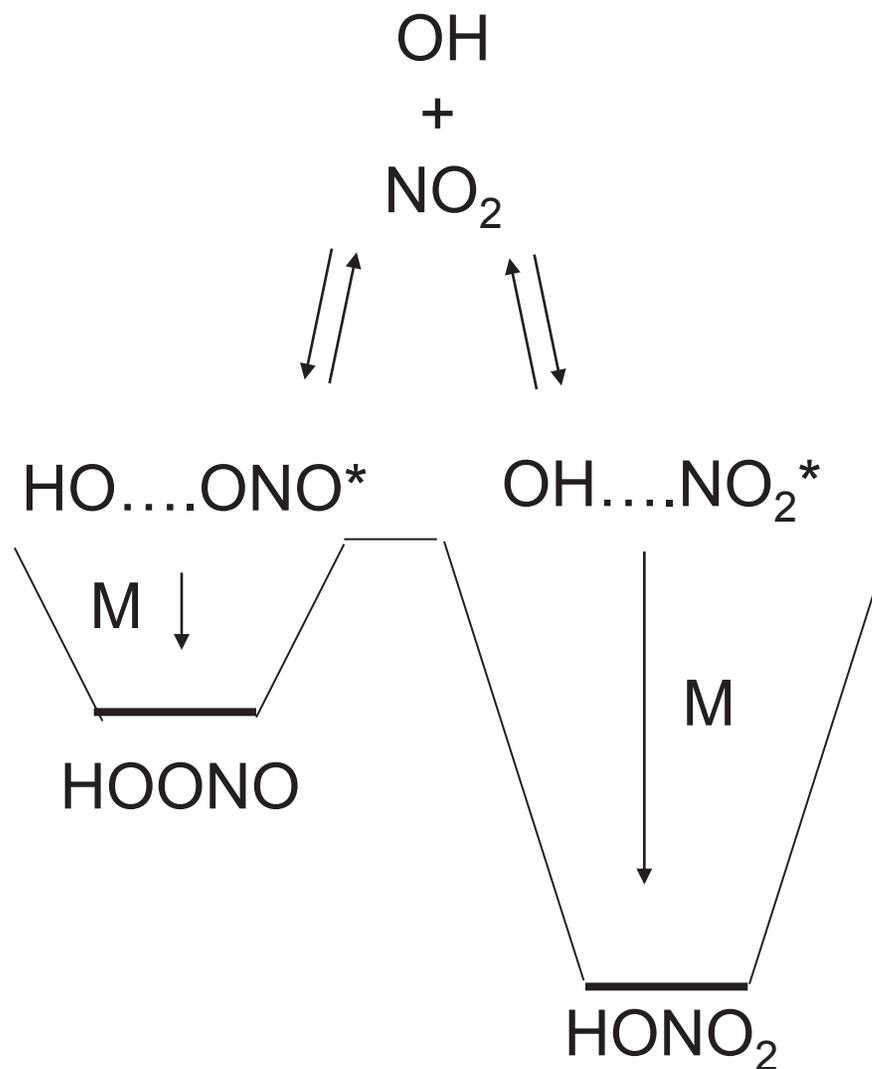
Polluted Lower Troposphere: Sensitivity Analysis Martien and Harley



Change in ozone, ppb per 100% change in parameter
 $k(\text{OH} + \text{NO}_2)$ is one of the top 5 parameters



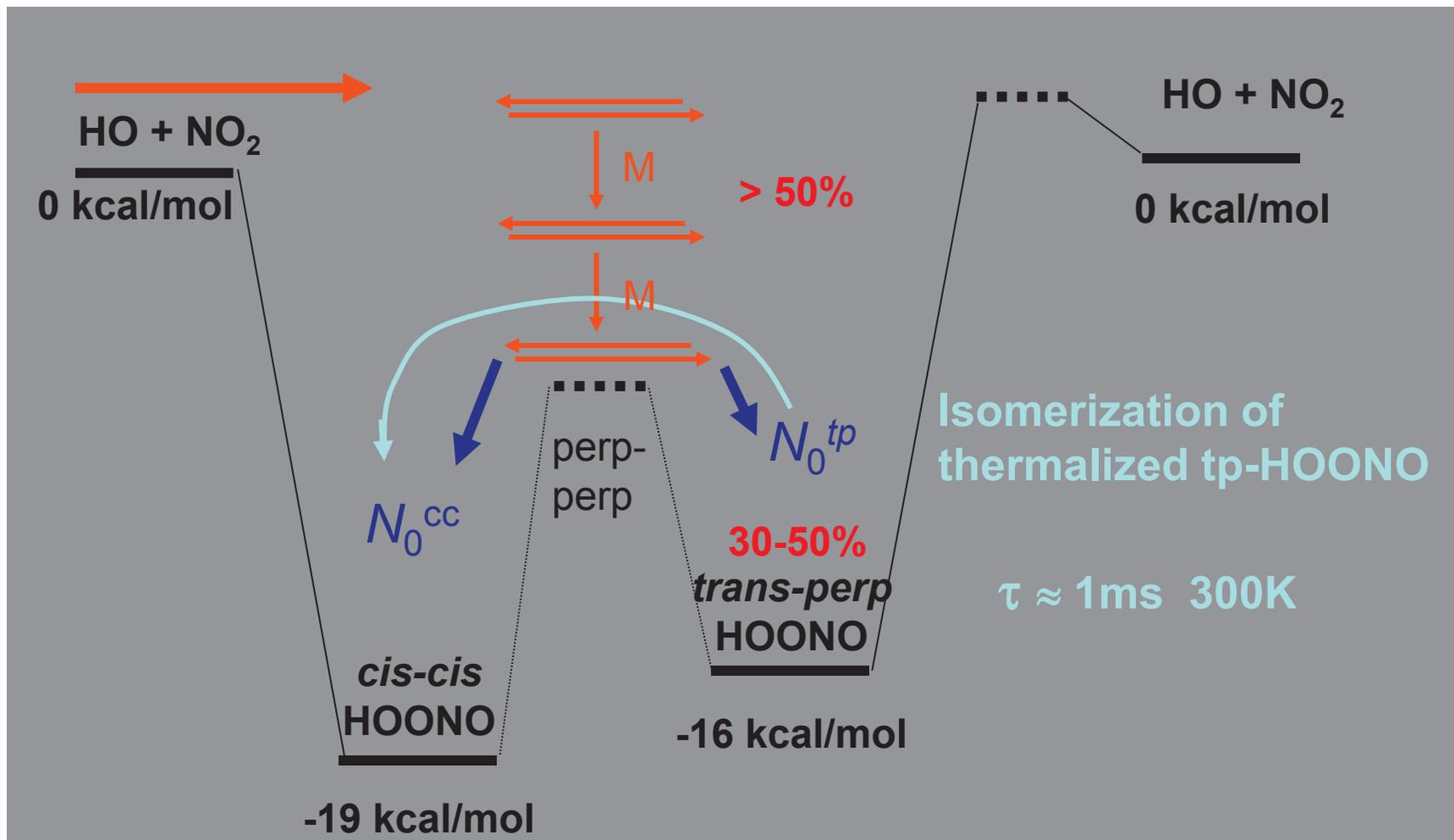
OH + NO₂ Association Mechanism





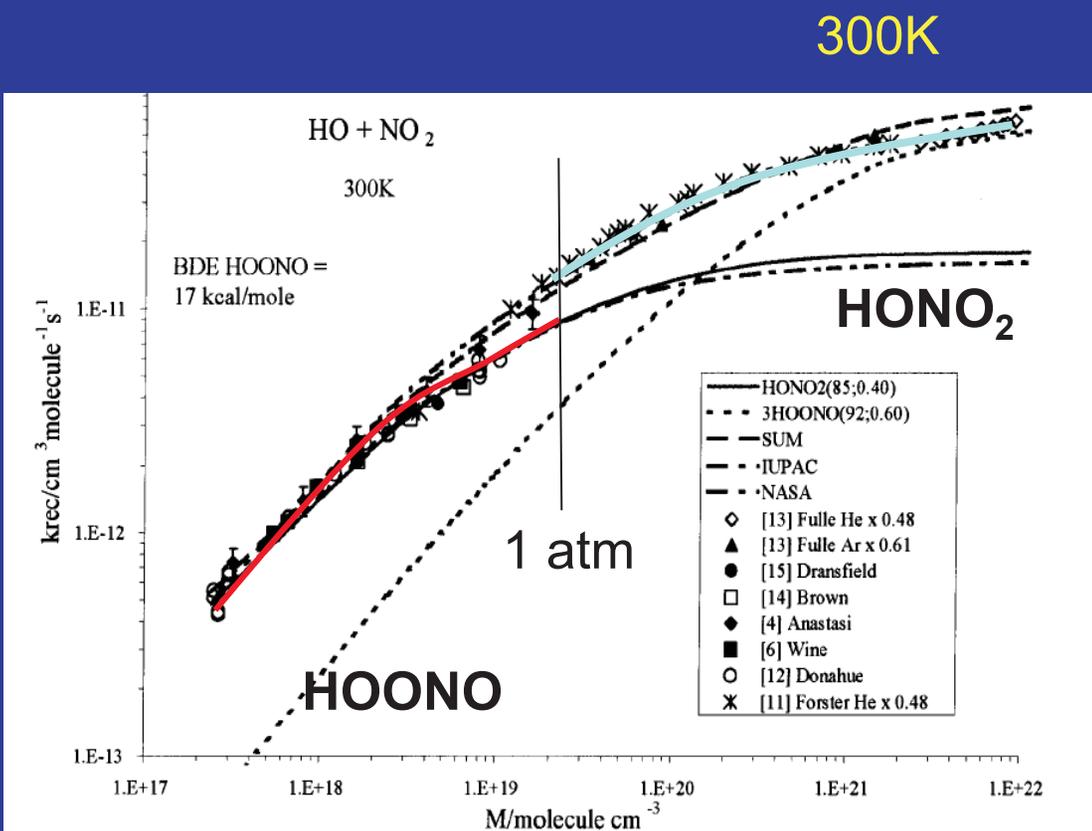
Isomerization Kinetics of HOONO

(Master Equation model of Golden, Barker, Lohr)



Master equation calculations for pressure-dependence of OH + NO₂ + M rate constants

log k, cm³ s⁻¹



log pressure

Robertshaw and Smith proposed HOONO channel to explain early inconsistencies between high and low pressure kinetics data

Golden & Smith, JPC
A 104, 3991(2000)



OH + NO₂ Reaction

Evaluated Products for the End User



Rate Constants vs. [M], T:

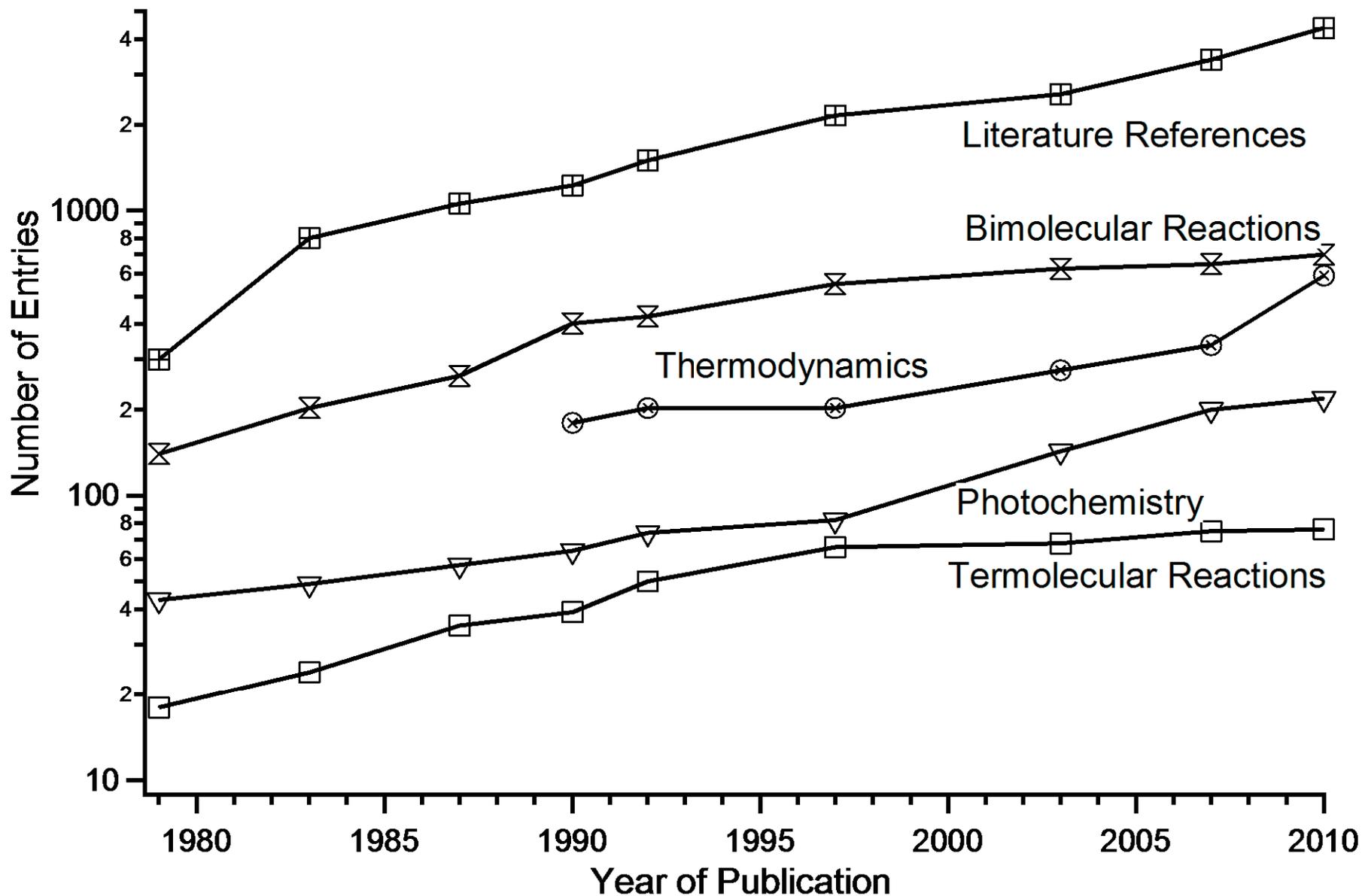


Equilibrium Constant vs. T:



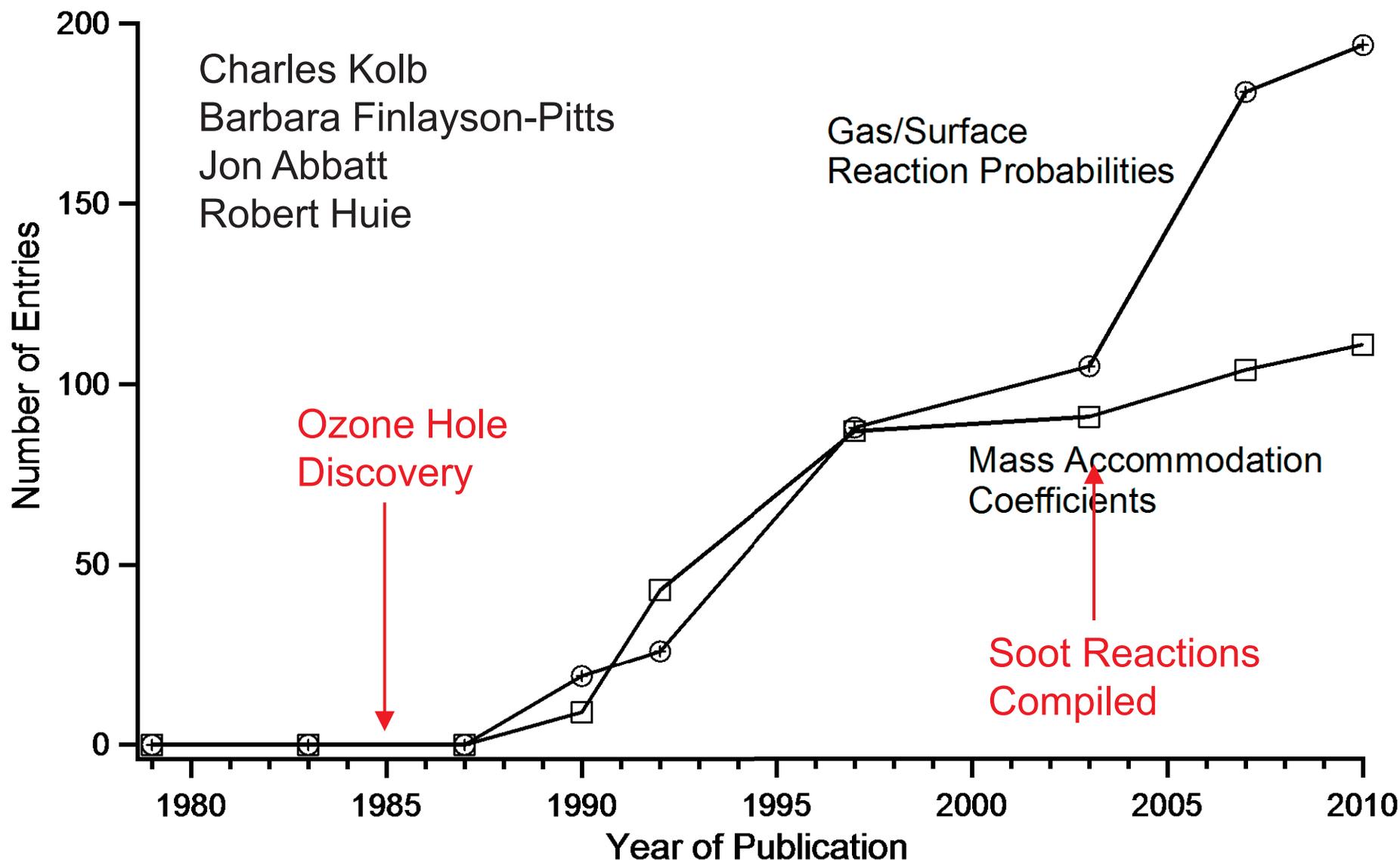


Growth in Scope and Breadth of the NASA Evaluation





Evaluation of Heterogeneous Processes: Stimulated by the Discovery of the Ozone Hole





Data Evaluation in the Future



- **More integration with other databases**
e.g. links to NIST kinetics site, NIST Webbook, spectroscopy databases
- **Quicker (hopefully) turnaround of evaluations**
(maintaining version control)
- **Other products/formats that may help meet the needs of the modeling, field measurements and laboratory communities**
- **Areas of possible expansion in the future:**
 - **Larger VOC's (currently C₄), e.g. isoprene**
 - **Kinetic Isotope Effects**

