The University Of Sheffield.

Experimental and Modelling study of gas-phase Mercury Oxidation

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Introduction

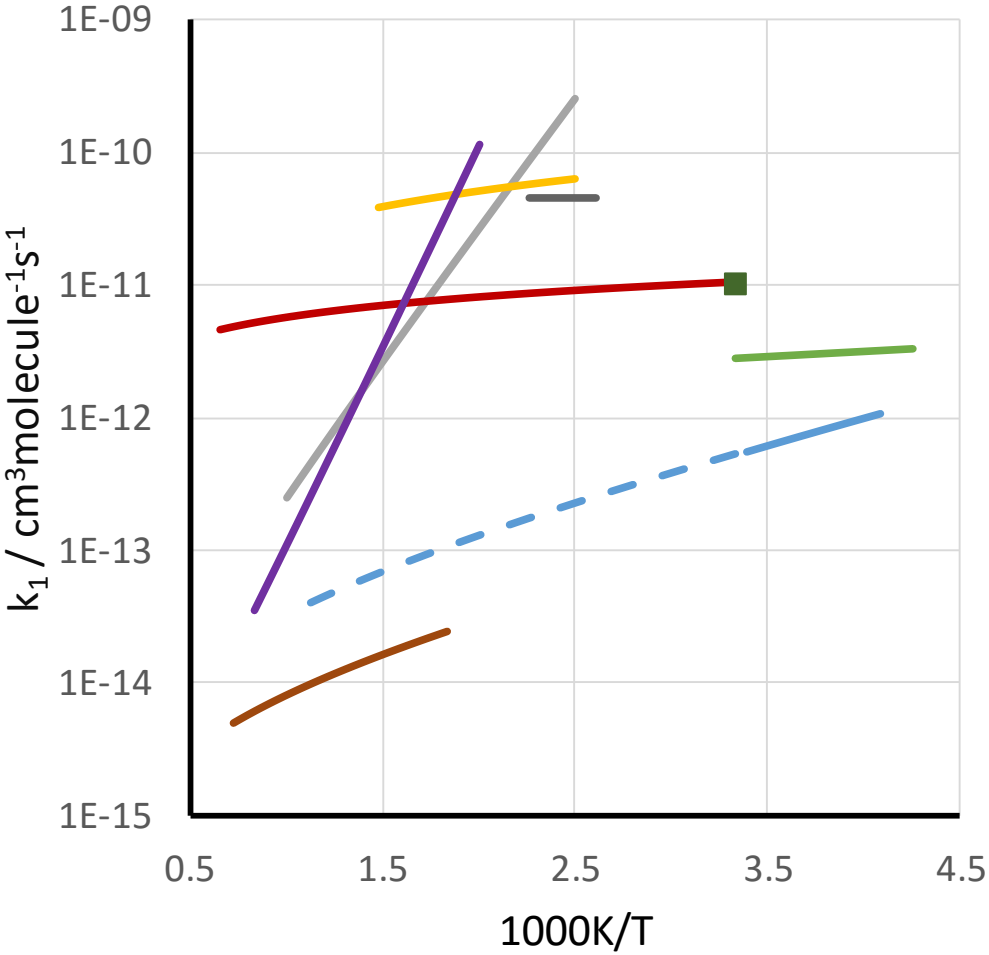
- Mercury released in its elemental state from Coal combustion
- Models of mercury oxidation in the gas phase
  - Oxygenated species not important
  - Dominated by Chlorine
- Oxyfuel Conditions
  - Elevated concentrations of minor species (Cl)
  - Elevated levels of CO_2/H_2O may affect 3rd body reactions
- Many conflicting published values of Cl + Hg rate coefficient

Aims

- Experimental measurement of Hg + Cl reaction
  - Compare to other studies
- Gas phase Kinetic Model Development of mercury oxidation
- Compare to independent lab based measurements
- Optimise model response to experiments
- Incorporate experimental measurements
  - Reoptimise model response

Hg + Cl – previous data[4]

$$Hg + Cl \xrightarrow{k_1} HgCl$$



- 9 published values, up to 2009
- Expressions calculated at 1 atm
- Experimental, theoretical, and fitted.

Experimental Method

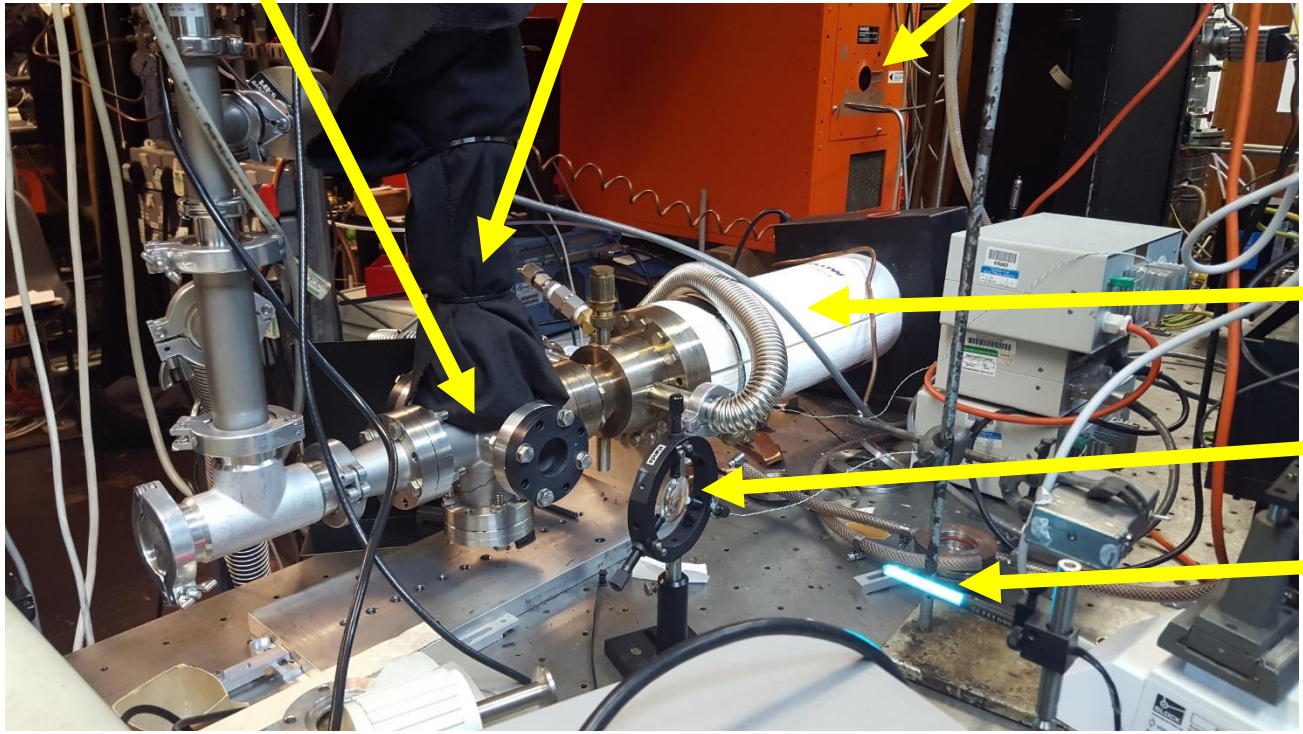
- Cl atom generation - Flash Photolysis
- Hg atom detection – resonance fluorescence
  - 253.7 nm
- Hg atom time evolution
  - Photon Counting technique
- Reaction kinetics
  - Fitting to simple 3 step mechanism

Experimental Setup

Low pressure (< 10 torr) pumped observation section

Hg interference filter, PMT, to photon counting hardware

KrF excimer laser @ 248nm
50 $mJcm^{-2}$ (5 MW peak power)

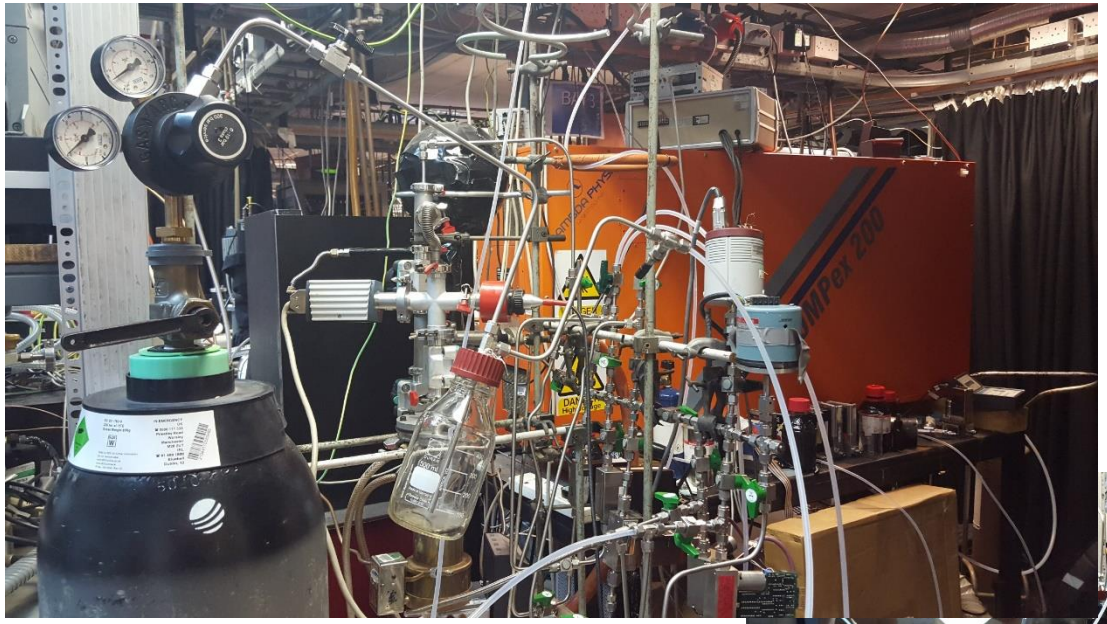


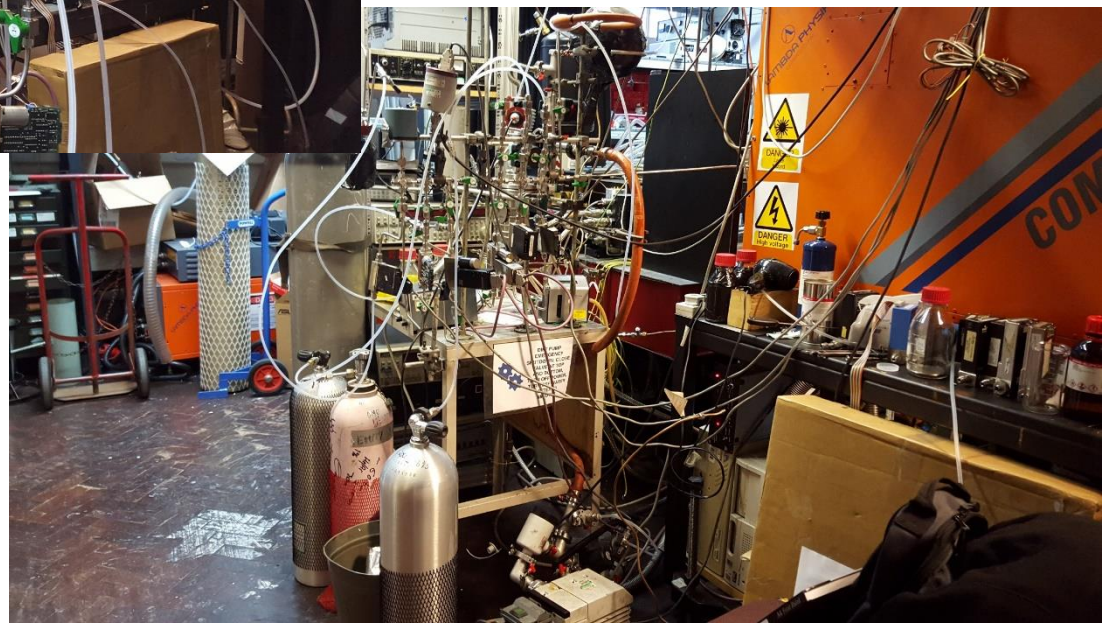
High pressure heated reaction section
Oxalyl chloride/Hg/N_2
photolysis laser @ 248 nm

Fused silica lens

Mercury lamp

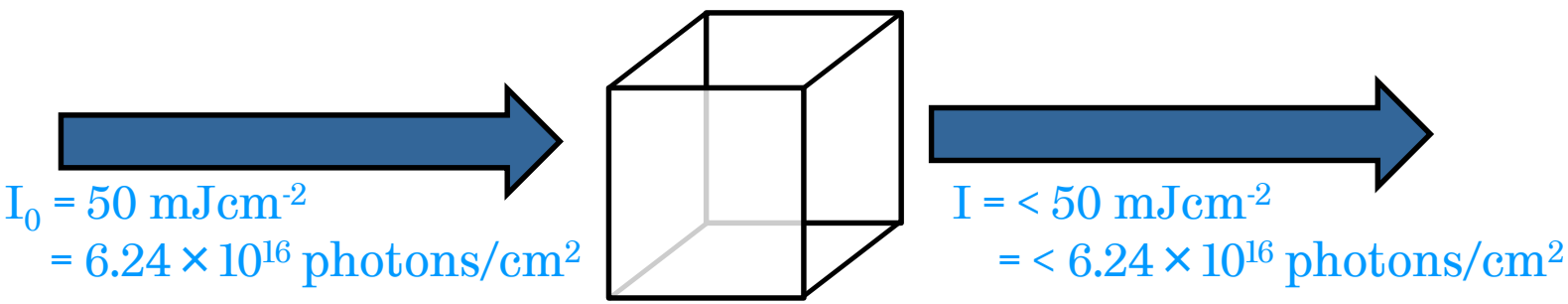
Experimental Setup





Oxalyl Chloride Photolysis

- $(ClCO)_2$
  - 1 Cl atom in direct photolysis, 2nd Cl atom in extremely rapid fragment decomposition
- Absorption Cross section, $\sigma = 2.7 \times 10^{-19}$ cm^2



- Beer-Lambert law: $I/I_0 = \exp(-\sigma c l)$ (l = 1 cm, c = oxalyl chloride concentration)
- Hence I, hence $I_0 - I$ = number of absorbed photons/cm^3
- Hence $[Cl] = 2 \times (I_0 - I)$ atoms/cm^3 (typically 1 to 2×10^{14})

Data Collection

- Ortec Photon Counting card & software (MCS-32)
  - All input over time from PMT
  - 100 (or 50) μs bin widths
  - Each photon (above a noise threshold) detected in each bin is counted
  - Run from minutes to about an hour
- Total count rate ~10^5/s in the best case
  - Still in the linear response regime

Kinetic Analysis

- Hg + Cl (+M) → HgCl (+M) (k_1)
- Cl + Cl (+M) → Cl_2 (+M) (k_2)
- Approximate first order "flow" term (Hg inflow, Cl & Hg outflow), (k_3)

If Cl >> Hg (~10^{14} vs. <10^{10})

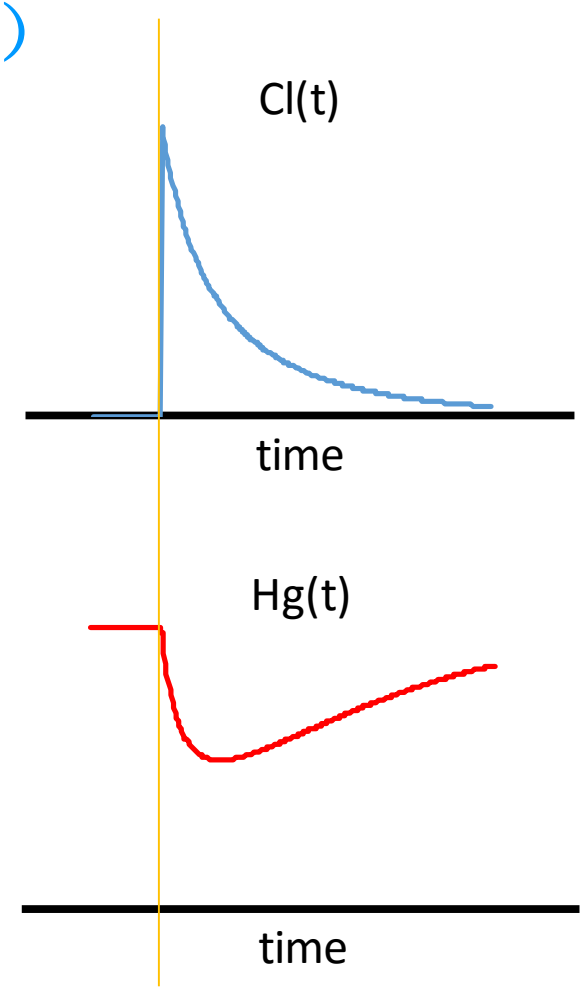
$$Cl(t) = Cl(0)\left(\frac{k_3}{2Cl(0)k_2e^{(k_3t)} - 2Cl(0)k_2 + k_3e^{k_3t}}\right)$$

$$Hg(t) = Hg(0)\left(\frac{k_3}{k_1Cl(t)+k_3} + \left(1 - \frac{k_3}{k_1Cl(t)+k_3}\right)e^{-(k_1Cl(t)+k_3)t}\right)$$

Kinetic Analysis

$Hg + Cl\ (+M) \rightarrow HgCl\ (+M)\ (k_1)$
$Cl + Cl\ (+M) \rightarrow Cl_2\ (+M)\ (k_2)$
Inflow/outflow (k_3)

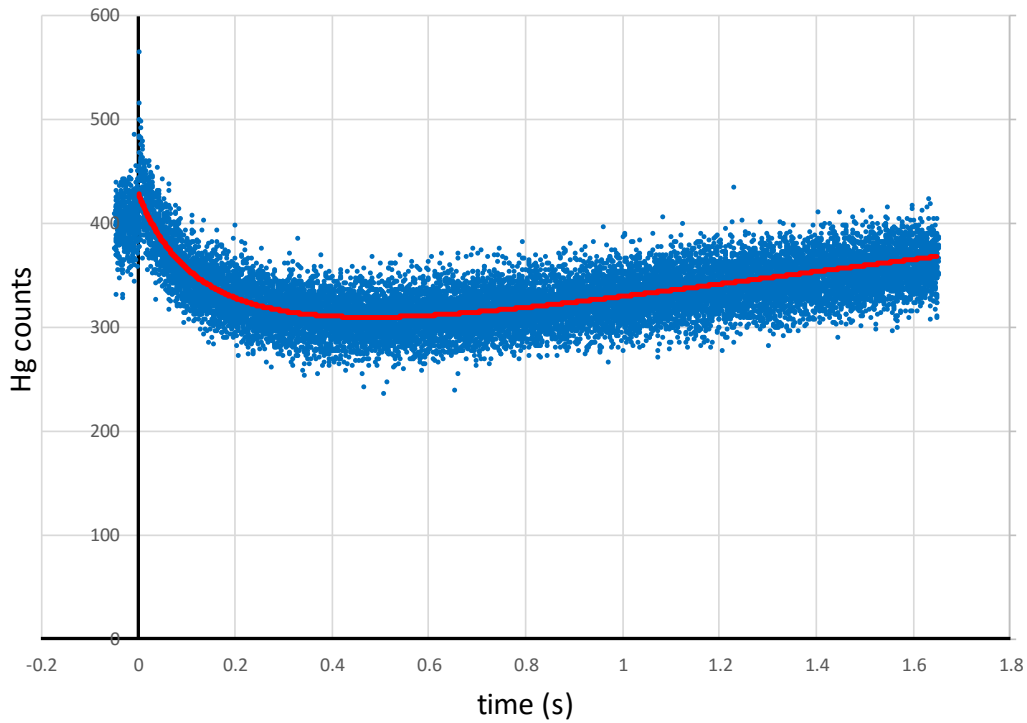
- Program into OriginPro
- k_2 – From Donohoue et al.
- Cl(0) – calculated as described <u>or</u> let it float
- Hence extract k_1



D.L. Donohoue, D. Bauer, A.J. Hynes J. Phys. Chem. A, 109 (2005) 7732-7741.

Kinetic Analysis

- An example of data & fit: 295 K, 105.2 kPa, 17,000 data points, 100 μs bin width

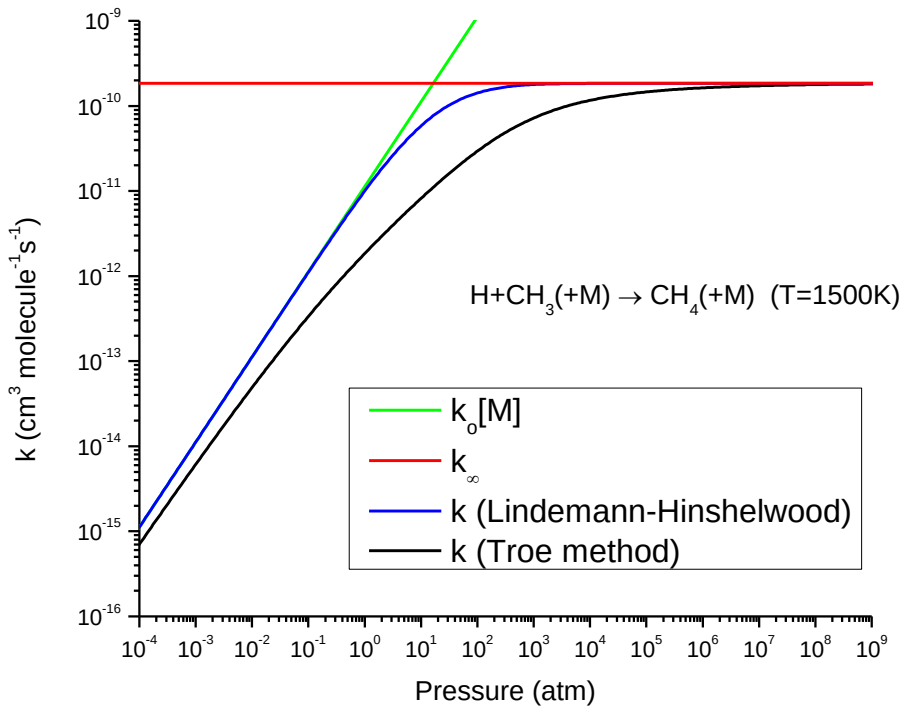


- Conditions: 295 to 497 K, 49 to 250 kPa, 39 combinations
- Factor of 7 in initial CI

Pressure Dependence

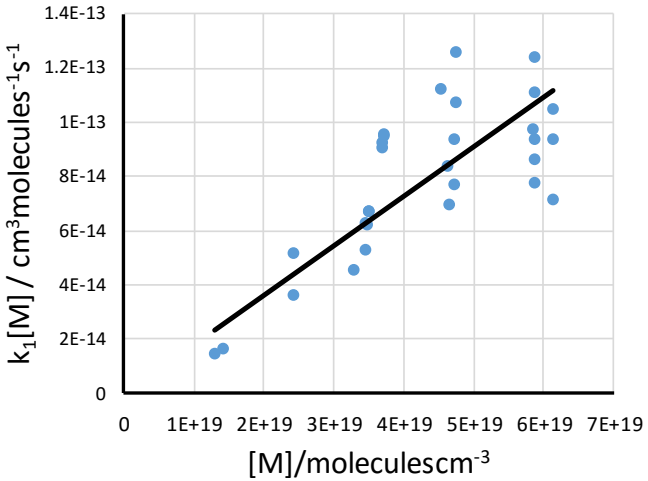
- Hg + Cl (+M) → HgCl (+M)
  - Atom + Atom recombination
  - Expect to be well in the fall-off regime
  - ie. directly proportional to pressure
  - Therefore fitted to a 3rd order rate coefficient

An illustration:

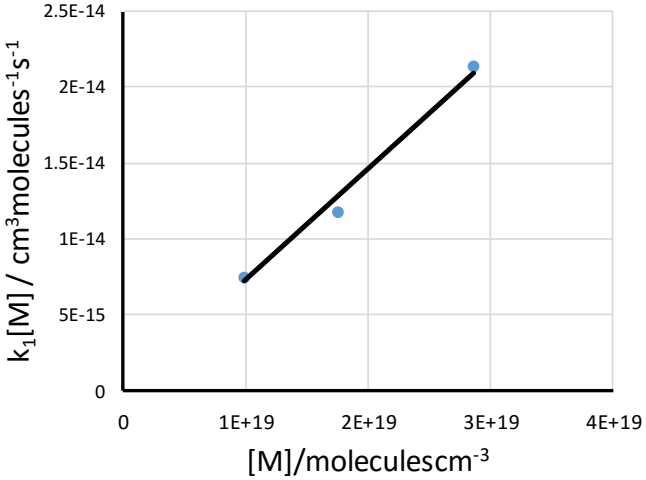


Pressure Dependence

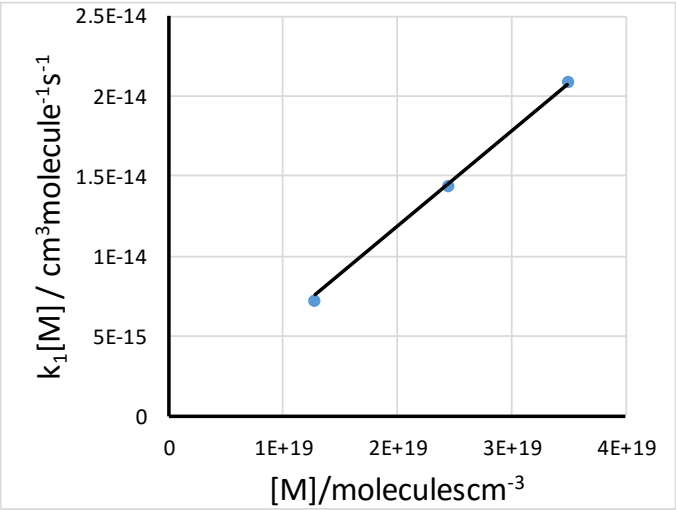
295 K



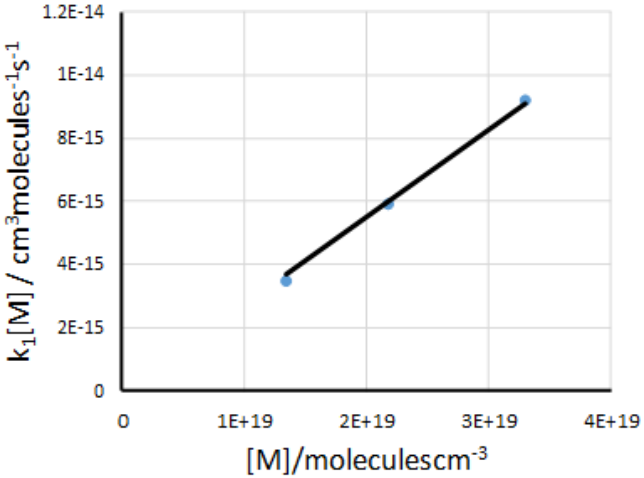
367 K



404 K



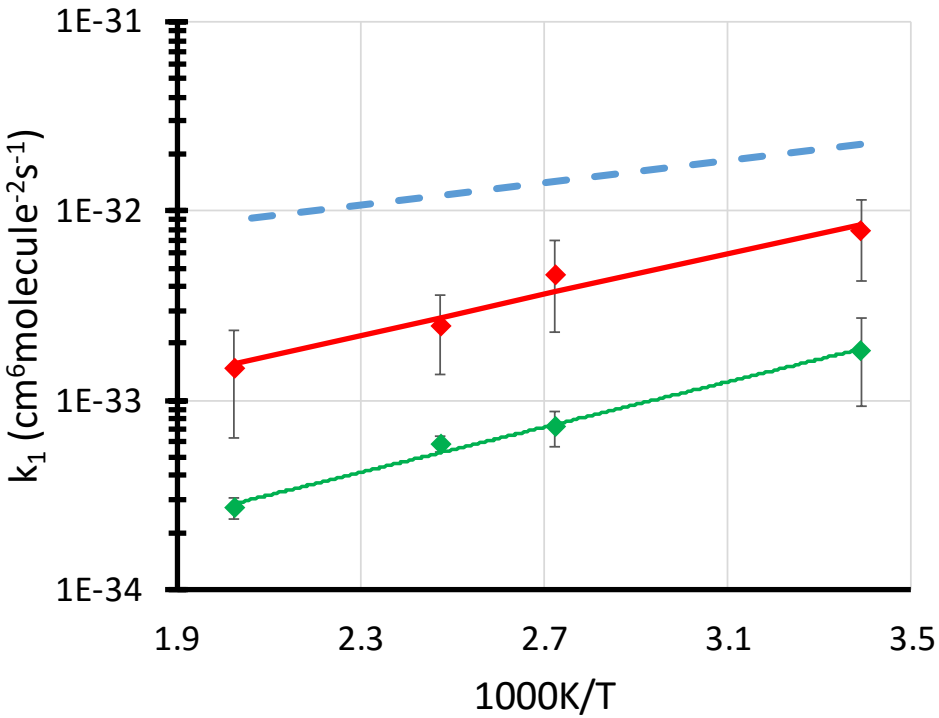
497 K



Temperature Dependence

$Hg + Cl\ (+M) \rightarrow HgCl\ (+M)$

3rd order rate coefficient, $k_1/cm^6molecule^{-2}s^{-1}$



---- Donohouhe et al., extrapolation

Floating initial Cl
$k_1(cm^6molecule^{-2}s^{-1})$
$= 1.26 \times 10^{-34} \times \exp(+1243/T)$

Fixed initial Cl
$k_1(cm^6molecule^{-2}s^{-1})$
$= 2.14 \times 10^{-35} \times \exp(+1296/T)$

Kinetic modelling

- Kinetic mechanism – based on GRI-3 C/H/N/O + Hg and Cl. (Clements et al.)
- 8 direct Hg/Cl reactions (Widmer et al.)

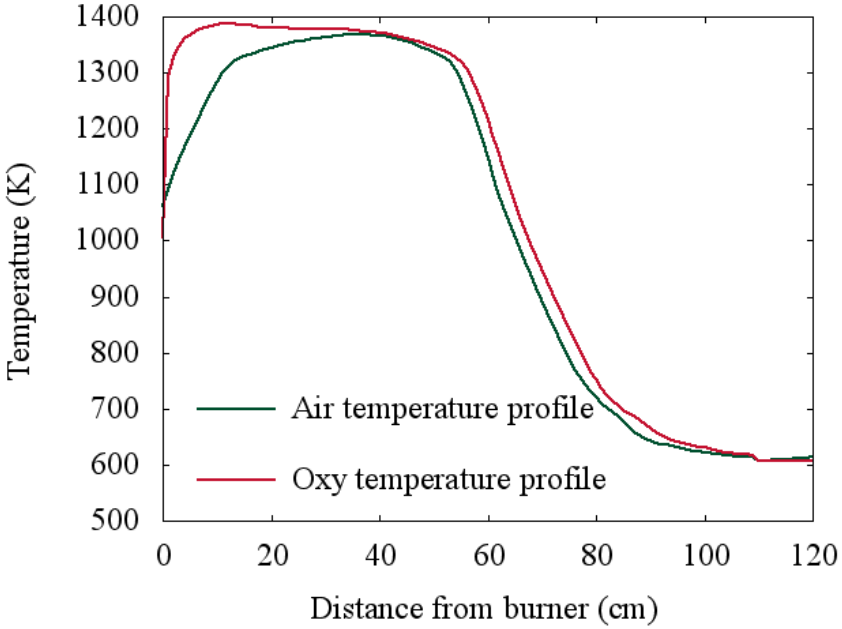
$$Hg + Cl + M \rightleftharpoons HgCl + M \quad (R1)$$
$$Hg + Cl_2 \rightleftharpoons HgCl + Cl \quad (R2)$$
$$Hg + HCl \rightleftharpoons HgCl + H \quad (R3)$$
$$Hg + HOCl \rightleftharpoons HgCl + OH \quad (R4)$$
$$HgCl + Cl + M \rightleftharpoons HgCl_2 + M \quad (R5)$$
$$HgCl + Cl_2 \rightleftharpoons HgCl_2 + Cl \quad (R6)$$
$$HgCl + HCl \rightleftharpoons HgCl_2 + H \quad (R7)$$
$$HgCl + HOCl \rightleftharpoons HgCl_2 + OH \quad (R8)$$

A.G. Clements, K.J. Hughes, R.T.J. Porter, M. Pourkashanian, *Modelling investigation into mercury oxidation under oxyfuel conditions*. 18th International IFRF Member Conference - Flexible and Clean Fuel Conversion in Industry. Freising, Germany, 1-3 June 2015

N.C. Widmer, J. West, J.A. Cole, *Thermochemical Study of Mercury Oxidation in Utility Boiler Flue Gases*, in: Proceedings of the Air & Waste Management Association Annual Conference (2000).

Experimental Dataset

- laminar methane fired, Quartz reactor (Preciado et al.)
- Doped with Hg, HCl, NO, known temperature profile and residence time



- % of Hg oxidised at exit measured

I. Preciado, T. Young, G. Silcox, *Mercury Oxidation by Halogens under Air-Fired and Oxygen-Fired Conditions*, Energy & Fuels, 28:2 (2014) 1255-1261.

Mechanism optimisation method

Mechanism optimised using a genetic algorithm

Reaction rates described by Arrhenius parameters

$$k(T) = A\left(\frac{T}{T_0}\right)^n exp\left(-\frac{E_a}{RT}\right)$$

1D flame solved with Cantera

Cost function

$$f(p) = var(p) + \sum_{c \in Cases} \frac{|M_c - P_{p,c}|}{E_c}$$

Initial Optimisation

$Hg + Cl + M \rightleftharpoons HgCl + M$

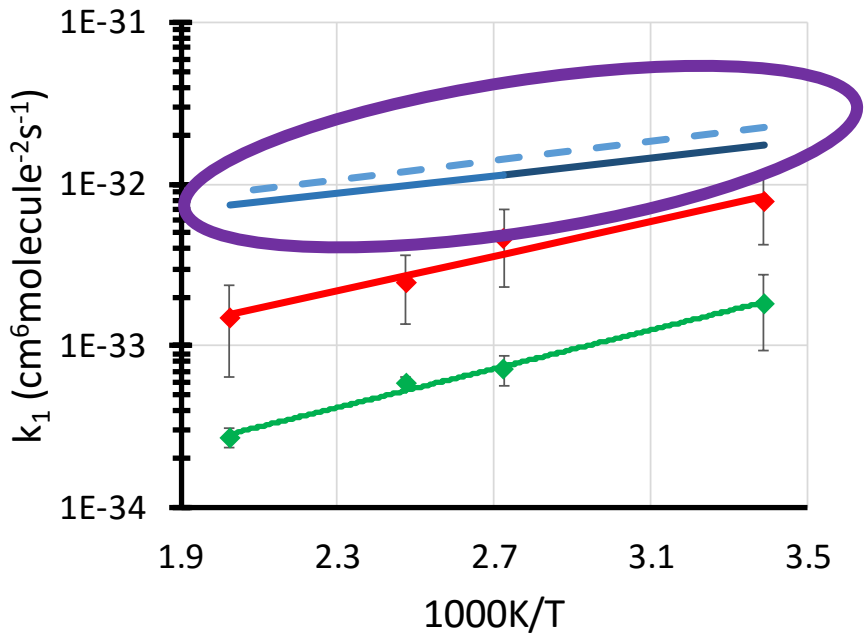
$HgCl + Cl_2 \rightleftharpoons HgCl_2 + Cl$

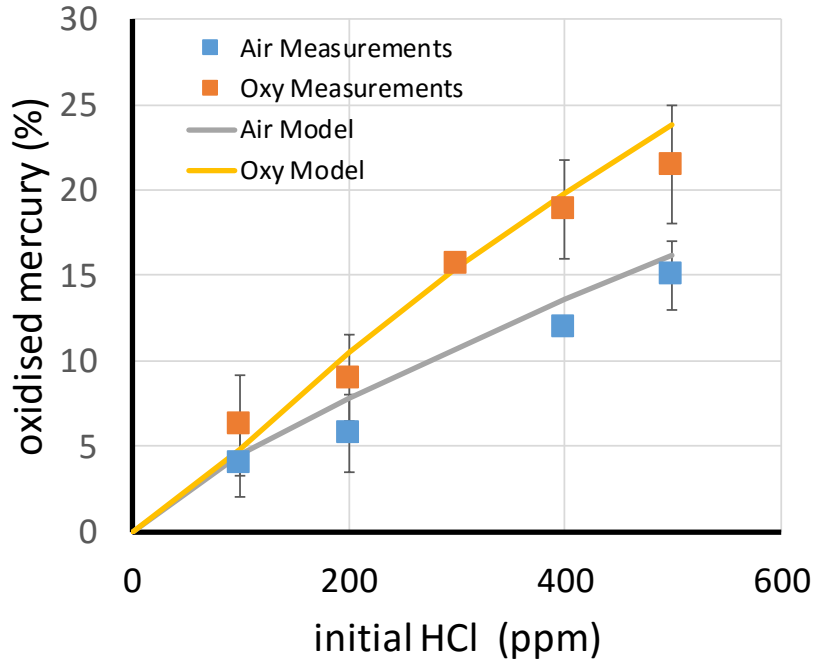
$Cl + Cl + M \rightleftharpoons Cl_2 + M$

$HOCl \rightleftharpoons OH + Cl$

$ONCl + M \rightleftharpoons NO + Cl + M$

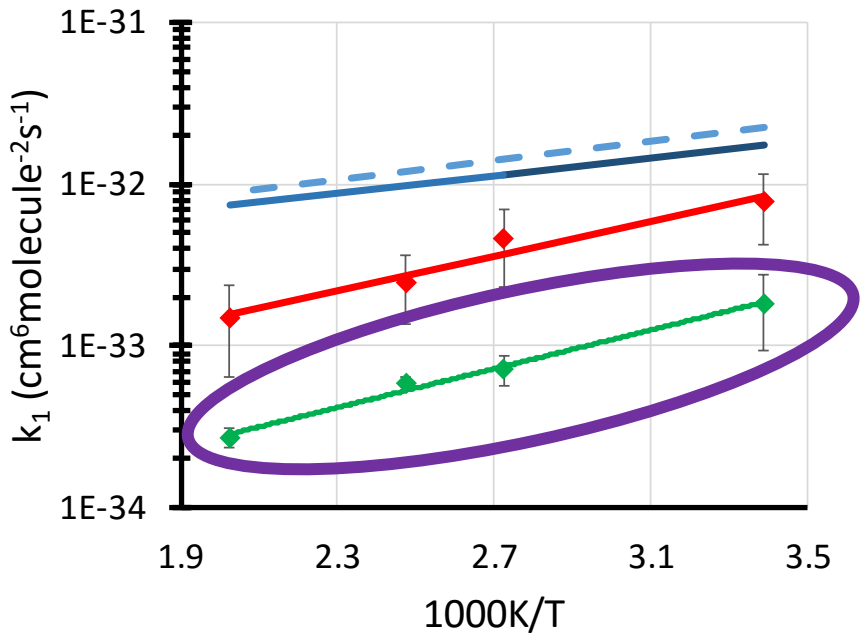
- 5 sensitive reactions
- Minor modification of k_1
- Not just Hg/Cl system
  - Other reactions perturb Cl

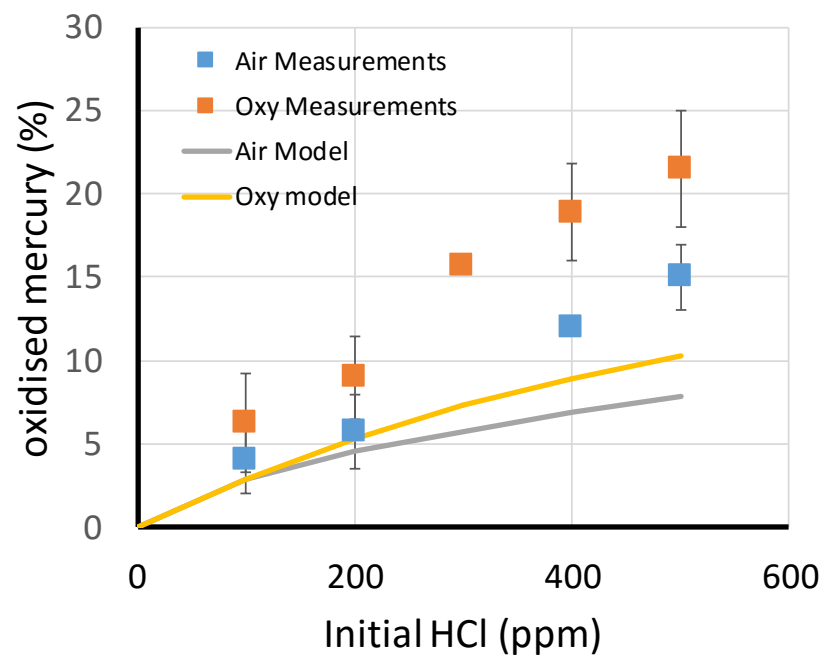




Fixed initial Cl atom

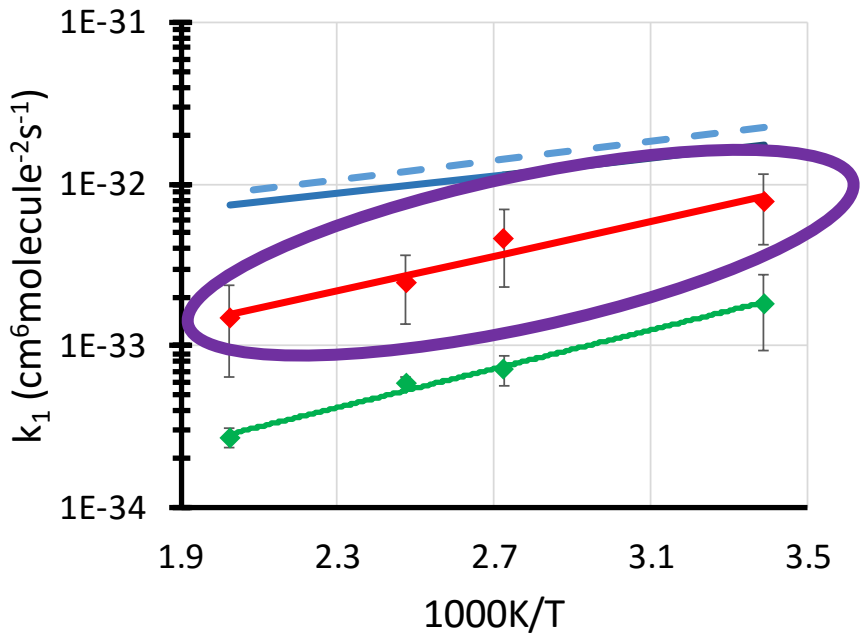
- Force k_1 to the lower expression
- No good fit possible within bounds

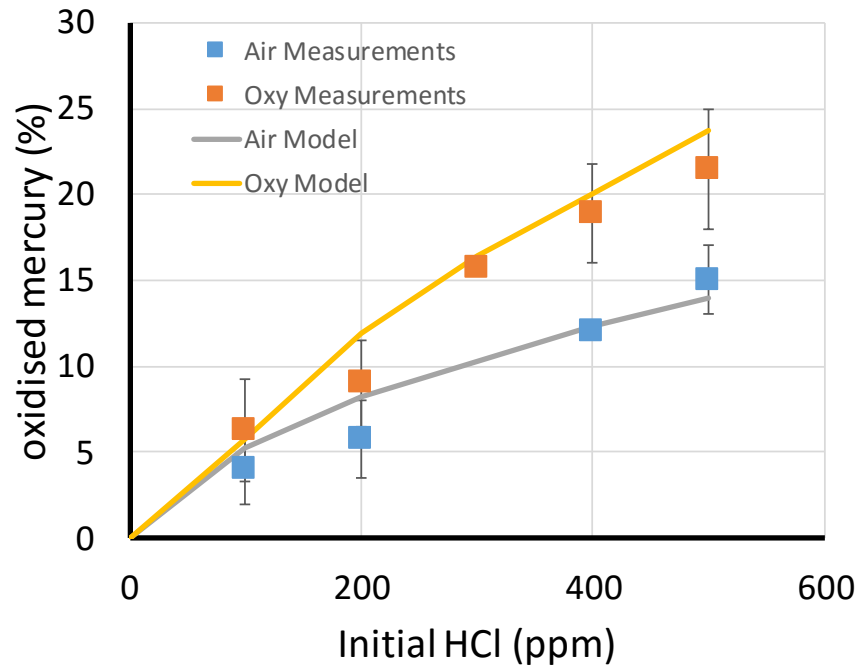




Floating initial Cl atom

- Force k_1 to the upper expression
- Reasonable fit can be obtained
- Compensating adjustments to:
  - $HgCl + Cl_2 \rightleftharpoons HgCl_2 + Cl$
  - $ONCl + M \rightleftharpoons NO + Cl + M$





Conclusions

- Hg + Cl measured experimentally
  - Dependent on an assumed Cl atom recombination rate
  - Dependent on initial Cl atom concentration
- Slower than other literature values
  - Specifically Donohoue et al. measurement
  - But, some uncertainty due to initial Cl value
- Kinetic mechanism optimization
  - Compatible with the Donohoue et al. measurement
  - Compatible with our upper bound floating Cl measurement
  - But not that at the lower bound fixed initial Cl