

Absolute Rate Constants for the Reaction of OH with Cyclopentane and Cycloheptane from 230-350 K

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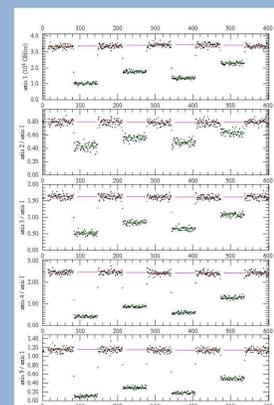
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Abstract

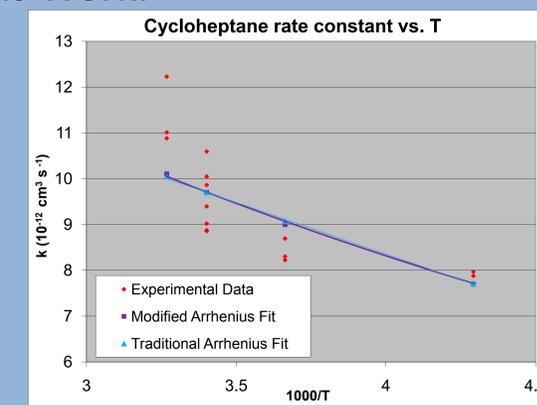
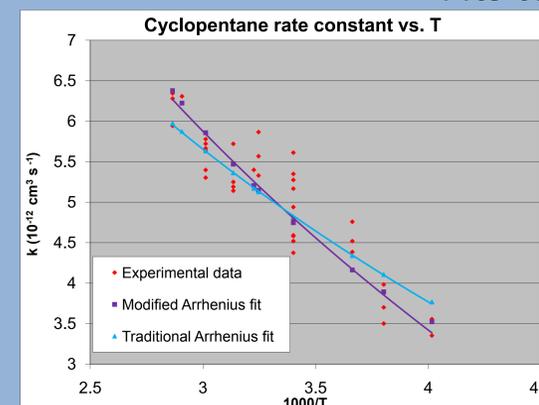
- The observed activation energy for the gas-phase reaction of OH + cyclohexane is elevated relative to other cycloalkanes, which is not predicted by our understanding of such reactions
- Little absolute rate constant data exists for OH + cyclopentane and OH + cycloheptane
- Absolute rate constants for the two title reactions were measured using Harvard's HPFS
- Experiments were conducted in 6-8 Torr of nitrogen over a temperature range of 230-350 K
- The absolute rate constant for OH + ethane was also measured as a test of system performance
- All data are fit using both a traditional Arrhenius fit and a modified fit based on transition state theory

Data Reduction:

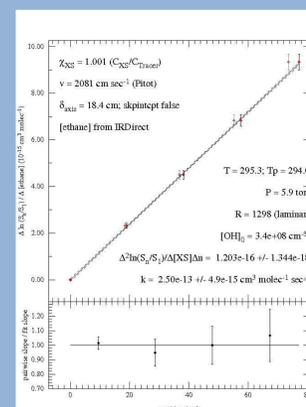
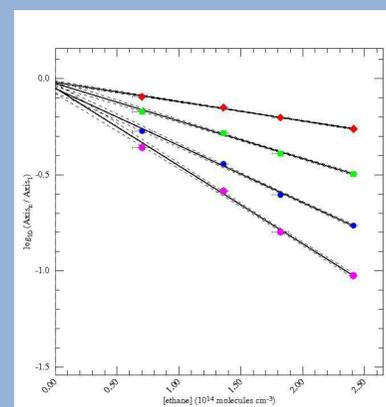
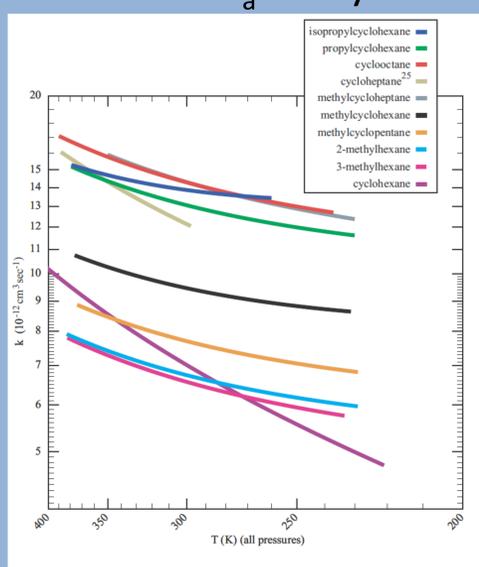


- [OH] is measured by LIF at 5 fixed detection axes.
- The signal on four of the axes is then divided by an arbitrary reference axis to normalize for laser power and fluctuations in the radical source.
- The excess reagent (XS) is cycled on and off at different concentrations.
- This allows us to determine $d \ln OH / d XS$ for each axis from a decay plot with the option of including or excluding the inferred origin from the fit.
- These derivatives are combined with velocity data to yield the rate constant: $k = -v d/dz(d \ln OH / d XS)$
- Ethane rate constants were measured simultaneously for comparison to a well-known rate constant
- Heating is produced by heating tape wrapped around the tube's exterior.
- Cooling is produced by flowing liquid nitrogen through external copper coils.
- Large temperature ranges are necessary to produce accurate barrier measurements.
- System velocities were on the order of 20 m/sec
- Reaction timescales were on the order of hundreds of milliseconds

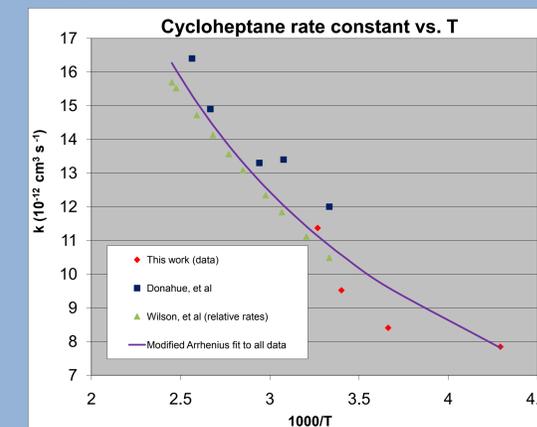
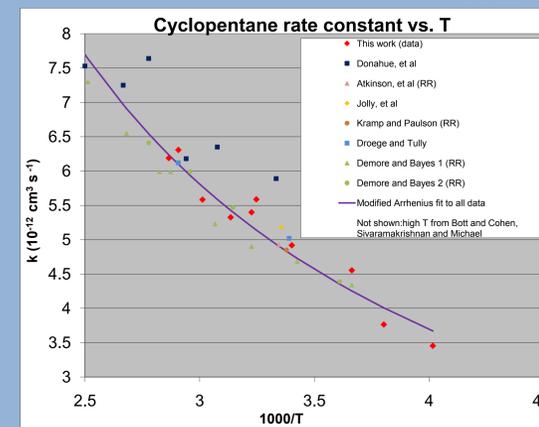
Fits to This Work:



The motivation: E_a for cyclohexane



Fits to All Data:



Fitting

Traditional Arrhenius Fit:

$$k(T) = Ae^{-E_a/T}$$

- Assumes T-independent A and E_a
- Often cannot model wide range of T

Modified Arrhenius Fit:

$$k(T) = \frac{Be^{-E_a/T}}{T(1 - e^{-1.44v_1/T})^2(1 - e^{-1.44v_2/T})}$$

- Derived from transition state theory
- Models the conversion of free rotors into vibrations at the transition state
- v₁ is a doubly-degenerate loose C-H-O bend (280 cm⁻¹)
- v₂ is a tight H-O-H bend (500 cm⁻¹)
- E_a is a true zero-point corrected activation energy

Results

Alkane	k _{fit} (298 K) 10 ⁻¹² cm ³ s ⁻¹	E _a (K)	E _a (kcal/mole)
Cyclopentane (this work)	4.82	471	0.94
Cyclopentane (fit to all)	4.88	412	0.82
Cycloheptane (this work)	9.84	250	0.50
Cycloheptane (fit to all)	10.8	332	0.66
Cyclohexane (fit to all)	6.96	326 ± 17	0.65
Cyclooctane	14.1	149 ± 26	0.30
Methylcyclopentane	7.65	109 ± 13	0.22
Methylcyclohexane	9.43	83 ± 14	0.16
Methylcycloheptane	14.4	142 ± 36	0.28
Propylcyclohexane	13	112 ± 15	0.22

References

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Conclusions

- This work represents the second temperature-dependent absolute rate constant measurement for OH + cycloheptane, and the third for OH + cyclopentane near ambient temperatures
- Room temperature rate constants are in excellent agreement with literature
- Both title reactions exhibit activation energies similar to cyclohexane, but the fit is very sensitive to outlying data
- All fits return values for E_a which are high relative to other studied cycloalkanes
- This experiment is ongoing, and extended temperature ranges will help to stabilize fits

Experimental Apparatus: the HPFS

