

# β-Scission Reactions Confound Kinetic Studies of Bimolecular Reactions of Cyclic Alkoxy Radicals



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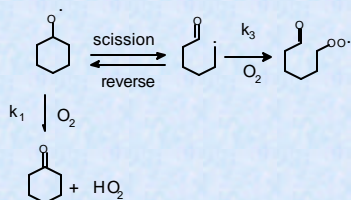
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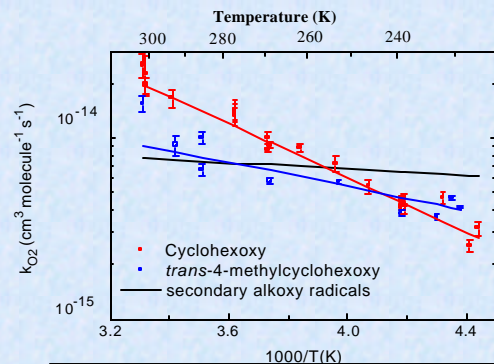
## Atmospheric Importance

Alkoxy radicals are important intermediates in the atmospheric degradation of volatile organic compounds (VOC) in polluted air. The fate of cyclic alkoxy radicals is usually determined by competition between decomposition, and reaction with O<sub>2</sub>, and the outcome of this competition affects the yield of ozone and organic aerosols in polluted air. Therefore, understanding the alkoxy radical chemistry in the atmosphere is of crucial importance for modeling smog chemistry.

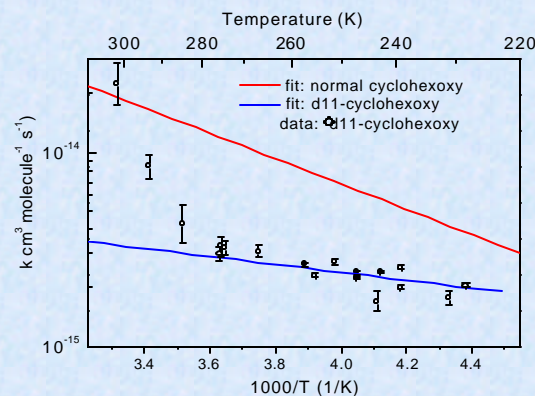
Cyclohexanes make up a non-negligible fraction of gasoline. Their six-membered ring is also a structural feature of many terpenes.



## Experimental Rate Constants and Comparison with Acyclic Alkoxy Radicals



**The Issue:**  
 As [O<sub>2</sub>] increases, the scission reaction is effectively less reversible. This affects the rate of loss of the alkoxy radical!  
 The pseudo-first order analysis of k<sub>1</sub> is invalid where the scission rate is a significant fraction of k<sub>1</sub>[O<sub>2</sub>] and k<sub>reverse</sub> is a significant fraction of k<sub>3</sub>[O<sub>2</sub>].  
 This is not an issue for acyclic alkoxy radicals, and probably not for cyclic alkoxy radicals in 1 atm of air (160 Torr of O<sub>2</sub> vs. the 1-10 Torr used here).



**Reanalysis:**

- Build kinetic model of the reaction scheme above and **compute** [alkoxy] vs. time under the full range of experimental conditions (temperature and [O<sub>2</sub>]).
- Analyze modeled concentrations just as we analyzed experimental data to "determine" the rate constant of the alkoxy + O<sub>2</sub> reaction.
- Plot modeled and experimental rate constants together.

**Results are presented below. Details of the model are at bottom left**

## Rate Constants for the Kinetic Model

- Take k<sub>1</sub> from the Arrhenius fit to the experimental data !?  
 The more precise data at low temperatures dominate the Arrhenius fit (which is why the high T data can deviate from the fit!), so the Arrhenius fit may be a good approximation to the elementary rate constant)
- Compute k<sub>scission</sub> and k<sub>reverse scission</sub> at 50 Torr for 301 K ≤ T ≤ 228 K.  
 - quantum chemistry and RRKM/Master Equation calculations.
- Assume k<sub>3</sub> (alkyl + O<sub>2</sub>) = 8 × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>
- Kinetic modeling used the KINTECUS program

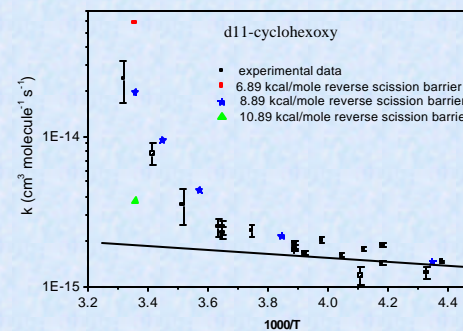
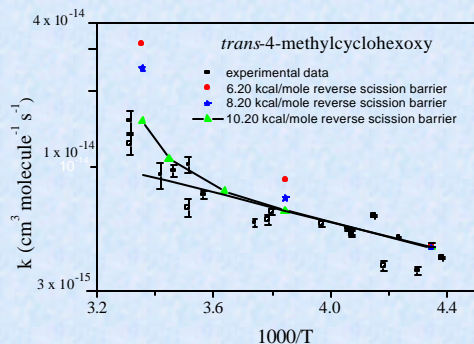
## Scission Rate Constants

Radical	A (s <sup>-1</sup> )	E <sub>a</sub> (kcal/mole)
cyclohexoxy	2.4 × 10 <sup>13</sup>	12.1
trans-4-methylcyclohexoxy	1.8 × 10 <sup>13</sup>	12.2
d11-cyclohexoxy	2.4 × 10 <sup>13</sup>	12.4

## Treatment of Reverse Scission

Radical	Barrier (kcal/mole)	6.2*	8.2	10.2
	A (s <sup>-1</sup> )	4.5 × 10 <sup>10</sup>	5.3 × 10 <sup>10</sup>	5.5 × 10 <sup>10</sup>
Ea (kcal/mole)	5.4	7.5	9.5	
	Barrier (kcal/mole)	6.9*	8.9	10.9
A (s <sup>-1</sup> )	1.6 × 10 <sup>10</sup>	1.7 × 10 <sup>10</sup>	1.8 × 10 <sup>10</sup>	
Ea (kcal/mole)	8.0	10.1	12.2	

## Modeled versus Experimental Rate Constants



Note that we are treating the barrier to reverse scission as a variable in the model. See details at right. Reasonable increases of the value of this barrier height from the value computed quantum mechanically result in good agreement between the modeled and experimental rate constants for alkoxy + O<sub>2</sub> reactions. This yields some confidence that we understand the chemistry of this system.

## Discussion and Conclusions

- The **slower** the rate constant for the alkoxy + O<sub>2</sub> reaction, the **larger** the deviation from pseudo-first order conditions at the higher temperatures studied:  
 k<sub>1</sub> is slowest for d11-cyclohexoxy radical and fastest for normal cyclohexoxy radical
- The model can reproduce the deviation of the higher temperature data from the Arrhenius fit. At the lower temperatures, scission is slow and the pseudo-first order approximation is valid for all three radicals under our experimental conditions.
- Normal cyclohexoxy radical has the highest rate constant of the three species studied and the experimental data shows no significant deviation from the Arrhenius fit.
- The computed barrier for reverse scission needs to be adjusted for the model to fit the data.