ß-Scission Reactions Confound Kinetic Studies of Bimolecular Reactions of Cyclic Alkoxy Radicals

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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_2, 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.
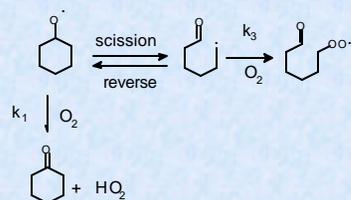
## Experimental Rate Constants and Comparison with Acyclic Alkoxy Radicals
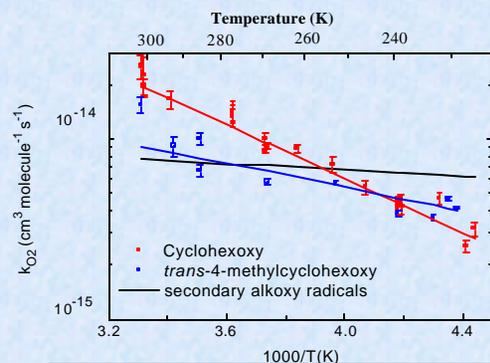
The Issue:

As $[O_2]$ 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_1 is invalid where the scission rate is a significant fraction of $k_1[O_2]$ and $k_{reverse}$ is a significant fraction of $k_3[O_2]$.

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_2 vs. the 1-10 Torr used here).
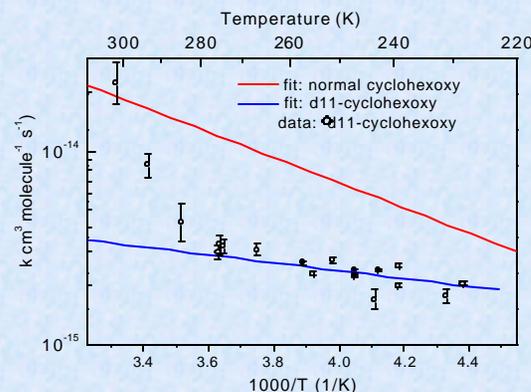
Reanalysis:

- Build kinetic model of the reaction scheme above and **compute** [alkoxy] vs. time under the full range of experimental conditions (temperature and $[O_2]$).
- Analyze modeled concentrations just as we analyzed experimental data to "determine" the rate constant of the alkoxy + O_2 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

1) Take k_1 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)
2) Compute $k_{scission}$ and $k_{reverse\ scission}$ at 50 Torr for 301 K ≤ T≤ 228 K.
   - quantum chemistry and RRKM/Master Equation calculations.
3) Assume k_3 (alkyl + O_2) = 8 x 10^{-12} cm^3 molecule^{-1} s^{-1}
4) Kinetic modeling used the KINTECUS program

Scission Rate Constants

Radical	A (s^{-1})	E$_a$ (kcal/mole)
cyclohexoxy	2.4 × 10^{13}	12.1
trans-4-methylcyclohexoxy	1.8 × 10^{13}	12.2
d11-cyclohexoxy	2.4 x 10^{13}	12.4

Treatment of Reverse Scission

Trans-4-methyl cyclohexoxy	Barrier (kcal/mole)	6.2*	8.2	10.2
	A (s^{-1})	4.5×10^{10}	5.3×10^{10}	5.5×10^{10}
	Ea (kcal/mole)	5.4	7.5	9.5
d11-cyclohexoxy	Barrier (kcal/mole)	6.9*	8.9	10.9
	A (s^{-1})	1.6×10^{10}	1.7×10^{10}	1.8×10^{10}
	Ea (kcal/mole)	8.0	10.1	12.2

Modeled versus Experimental Rate Constants
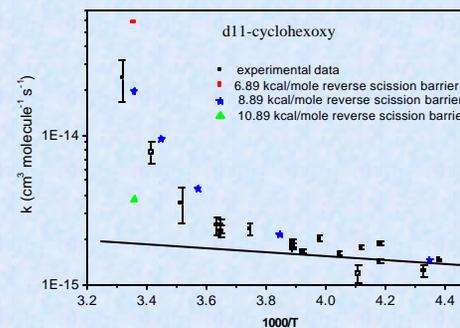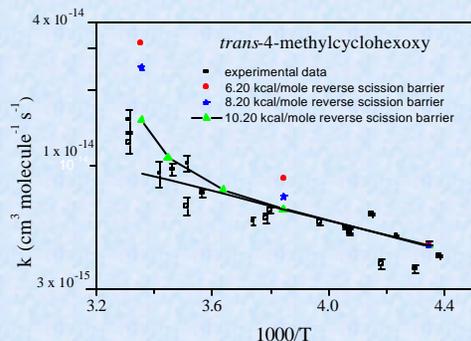
Note that we are treating the barrier to reverse scission as a variable in the model. See details at right. Reasonable increases of the value of this barrier height from the value computed quantum mechanically result in good agreement between the modeled and experimental rate constants for alkoxy + O_2 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_2 reaction, the **larger** the deviation from pseudo-first order conditions at the higher temperatures studied:
  k_1 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 adjusted for the model to fit the data.