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Rapid Gas-Phase Radical Rearrangement in Ketones

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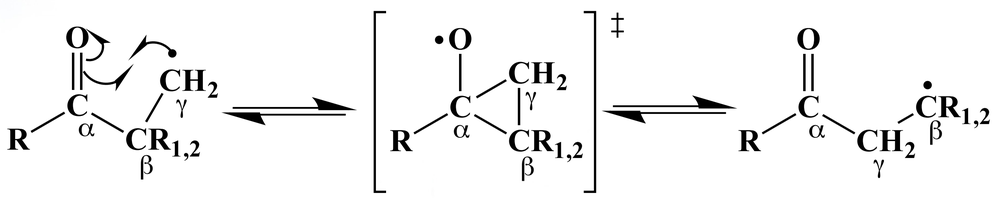
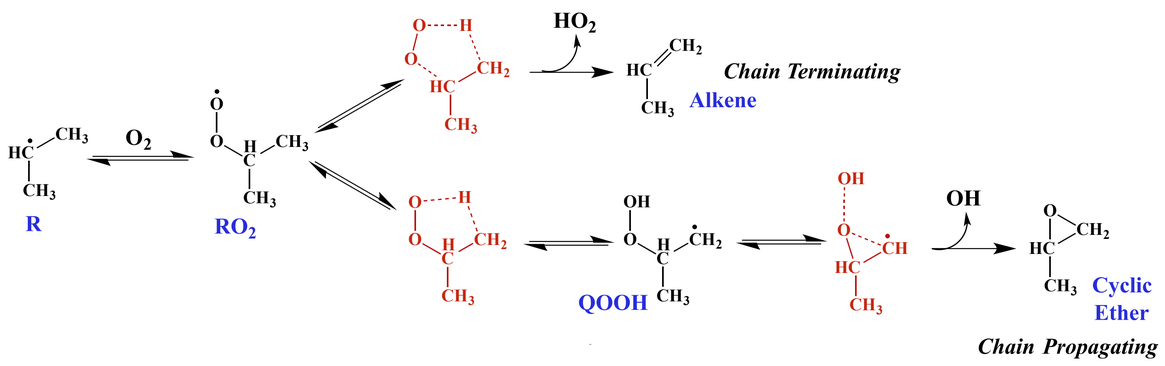
Introduction and Experiment

Rapid Radical Rearrangement (1,2-acyl group migration[1]) is observed for β ketone radicals.



Chain-Propagating Oxidation Channels via resonance-stabilized QOOH are highly favored in open-chain ketones.

Background: Isopropyl Radical Oxidation[2]



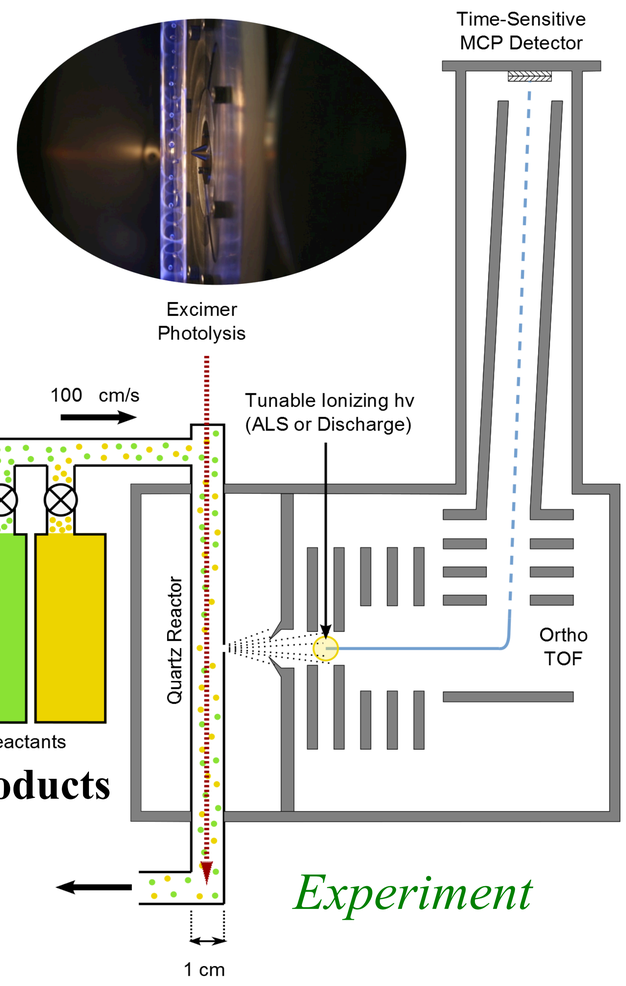
- **Multiplexed Photoionization TOF Mass Spectrometry** with tunable synchrotron light generates three-dimensional data in the mass, energy and time domains.
- **Photoionization Spectra (PI)** help determine products and branching.
- **Photolysis** generates Cl•, which abstract H, leaving a radical (R) that can add O_2.

$$Cl_2 \xrightarrow{h\nu\ (351\ nm)} 2\,\dot{Cl}$$

$$\dot{Cl} + R\text{-}H \longrightarrow R + HCl$$

$$R + O_2 \rightleftharpoons RO_2 \longrightarrow \text{Products}$$

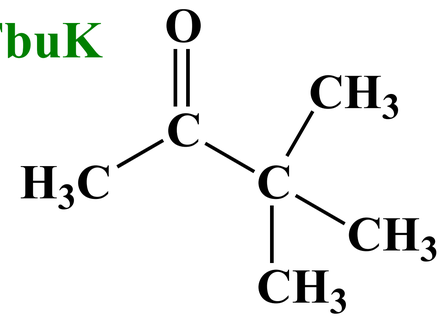
T = 300 – 700 K; P = 2 – 10 Torr

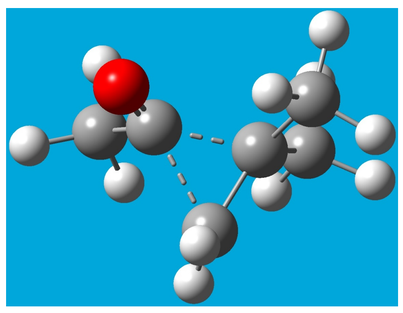


Oxidation of Methyl-Tert-butyl Ketone (MTbuK)

All MTbuK carbons are either quaternary or terminating methyl groups. Thus HO_2 + alkene channels analogous to propane are not possible.

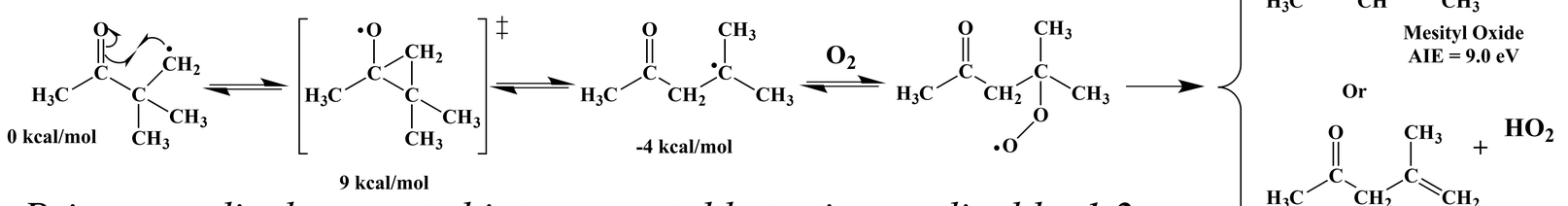
MTbuK



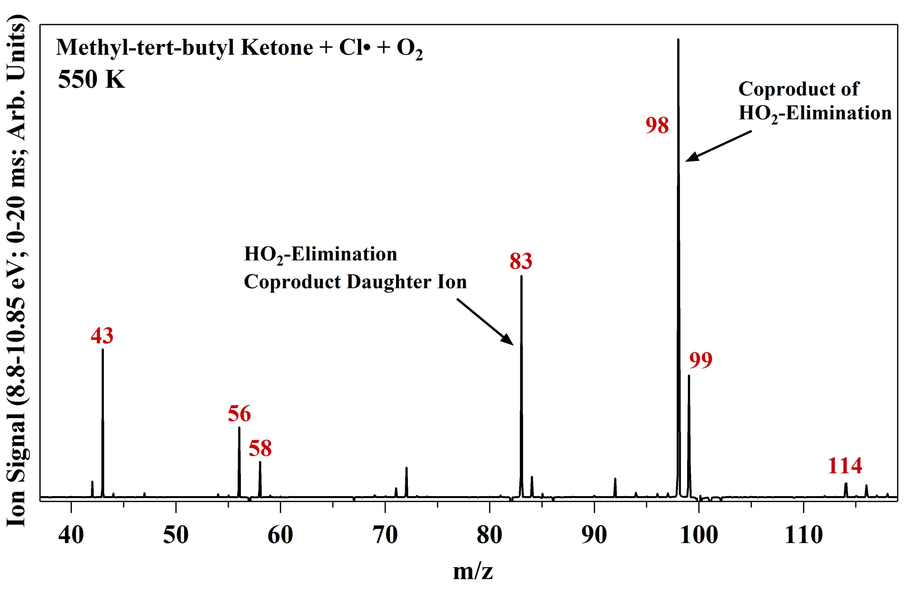


Rearrangement TS

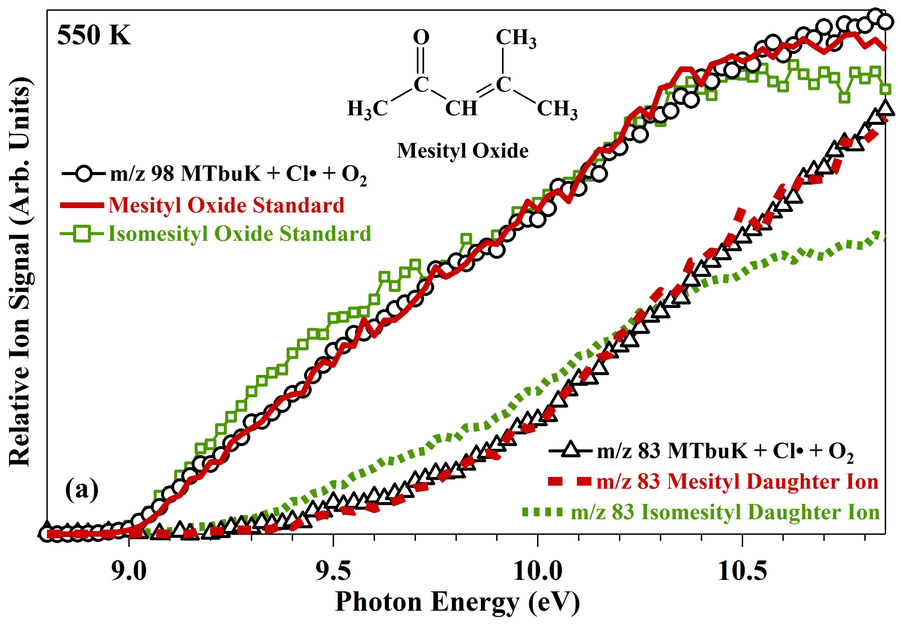
Yet the m/z 98 HO_2-elimination coproduct is ***dominant*** and results from radical rearrangement that enables formation of a double bond:



Primary radical converted into more stable tertiary radical by 1,2-acyl group migration



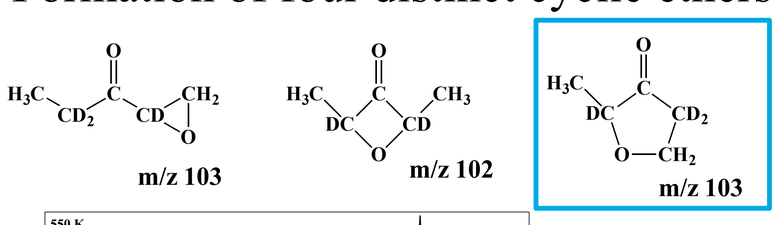
PI spectra show mesityl oxide is m/z 98 product.

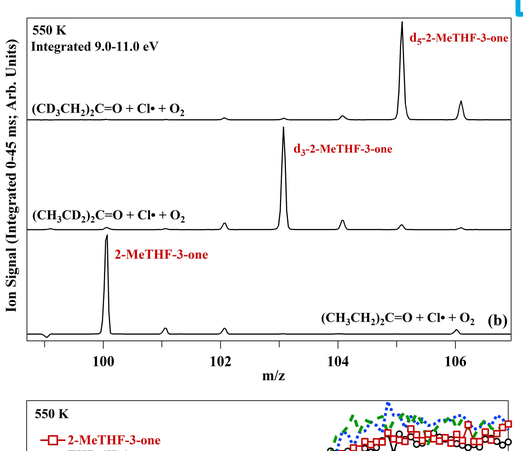


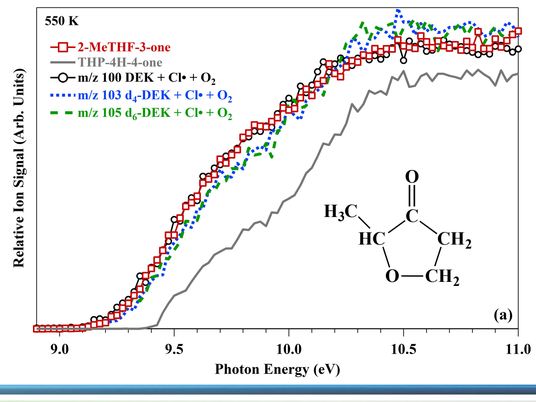
Rearrangement is fast relative to O_2-addition under our conditions (550 K, 8.0 Torr; $[O_2] = 3 \times 10^{16}$ cm^{-3})

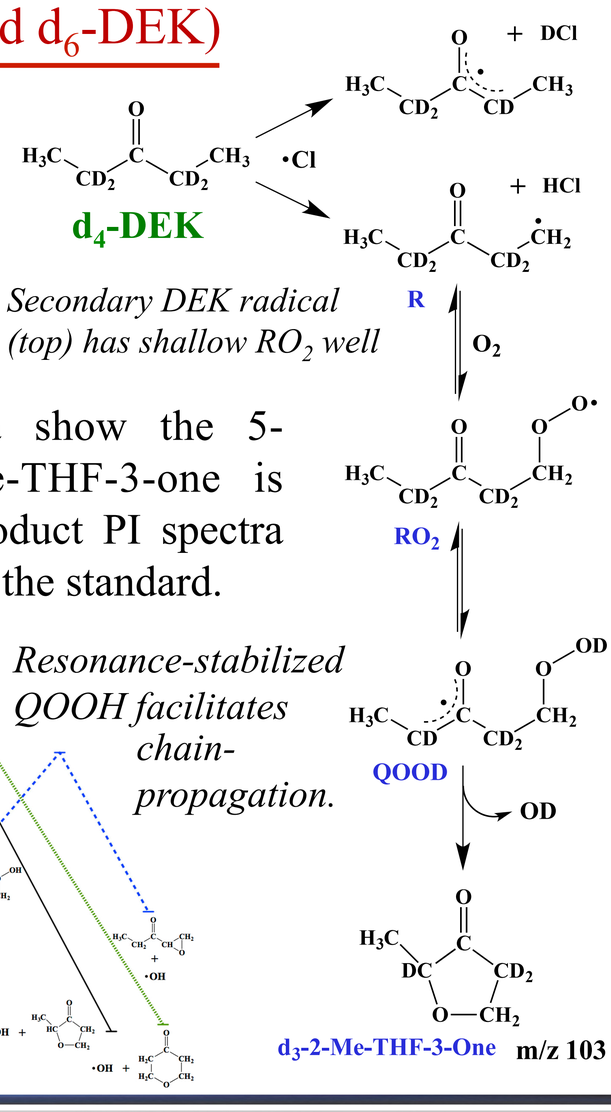
Oxidation of Diethyl Ketone (DEK; d_4-DEK and d_6-DEK)

Formation of four distinct cyclic ethers is possible.



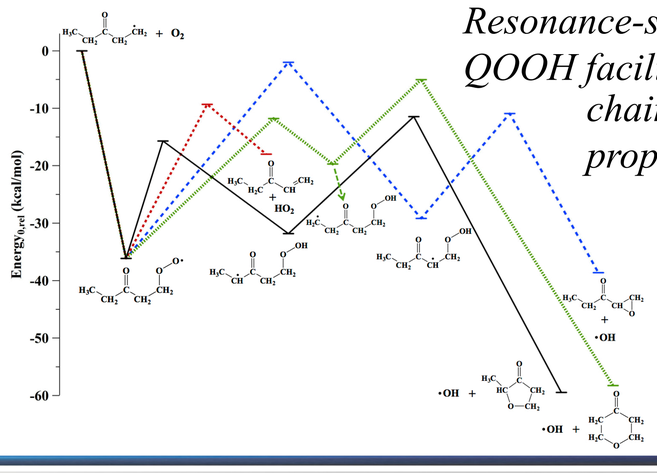






Secondary DEK radical (top) has shallow RO_2 well

d_4- and d_6-DEK data show the 5-membered ring, 2-Me-THF-3-one is highly favored. The product PI spectra are nearly identical with the standard.



Resonance-stabilized QOOH facilitates chain-propagation.

[1]. e.g. Karl et al. *JOC*, **37**, 2834 (1972).
[2]. DeSain et al. *JPCA,* **107**, 4415 (2003).

COMBUSTION RESEARCH FACILITY

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