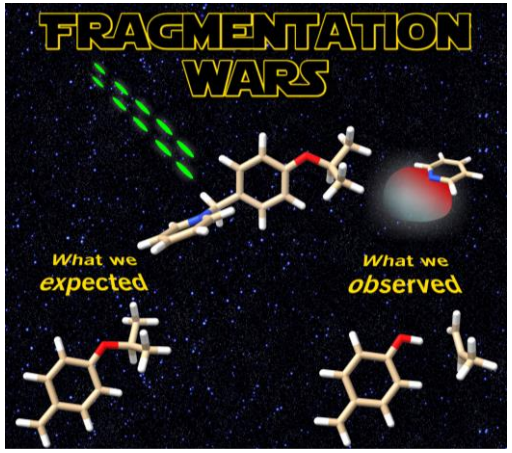
Benzylpyridinium 'Thermometer' Ions can Fragment Through an Unexpected Intramolecular Elimination: These are Not the Fragments You are Looking For

Christian Ieritano, W. Scott Hopkins

Hopkins Group

37th Annual Trent Conference for Mass Spectrometry



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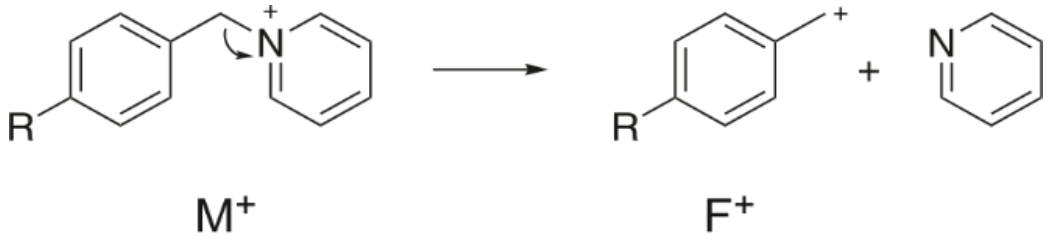
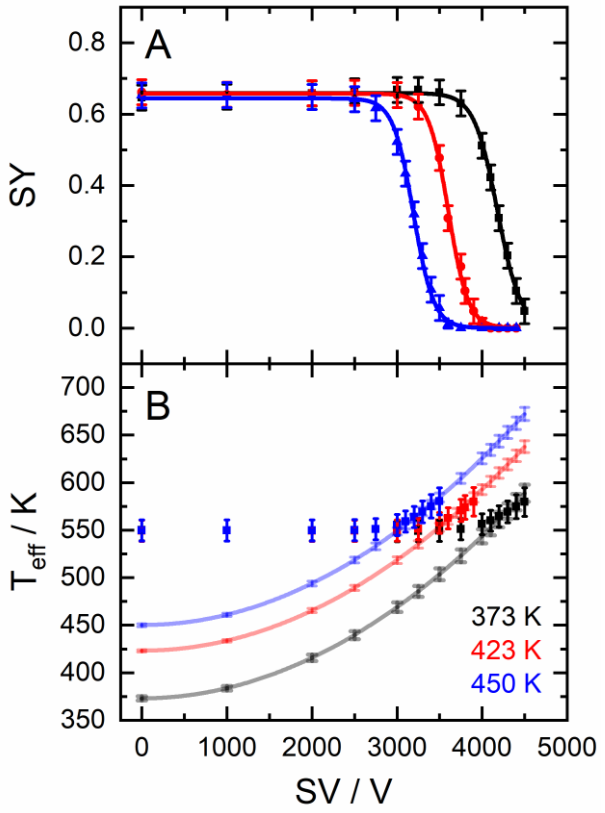
A long time ago, in a galaxy far away when COVID wasn't a thing…

We were able to characterize the effective temperature induced by the separation field in differential mobility spectrometry (DMS) using benzylpyridinium thermometer ions

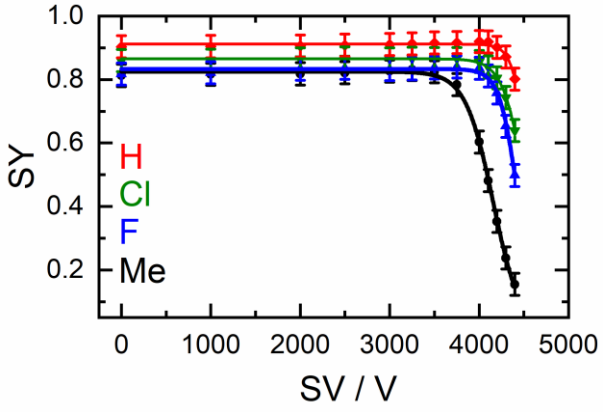


R	E_o / kJ mol^{-1}
OMe	**178.5**
Me	219.0
F	230.6
Cl	228.7
H	241.2
CN	264.4

R = OMe



R = not OMe



Requires high bath gas temp AND high SV

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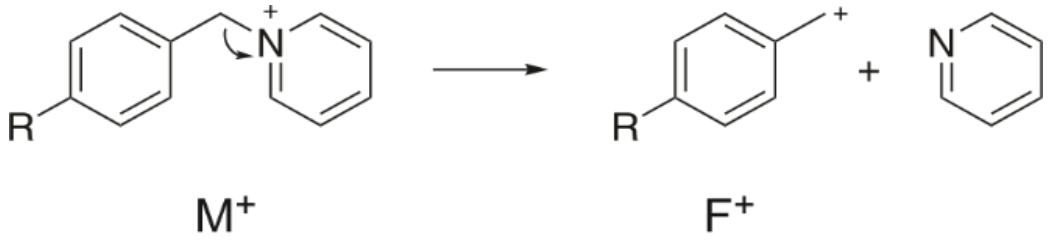

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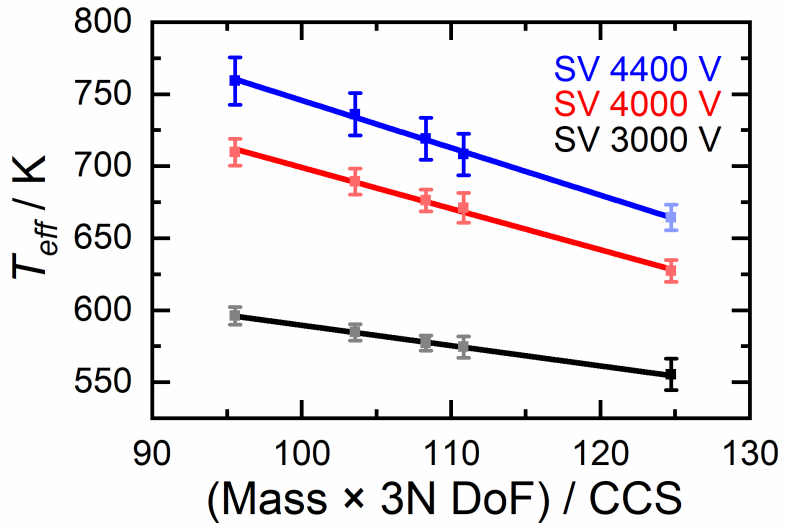
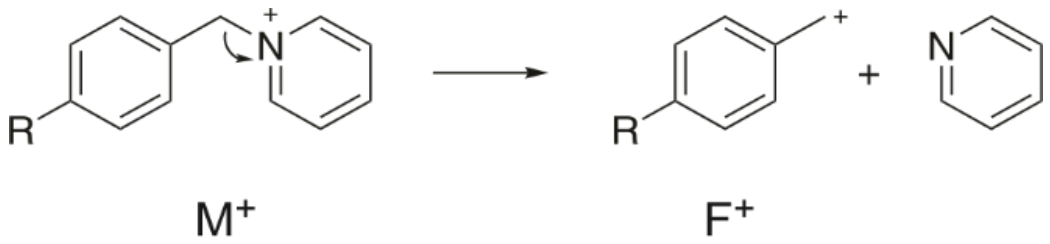
Linear relationship between ion T_{eff} and its density of states / collision probability



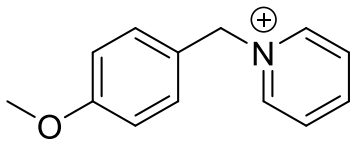
How can we extend this to lower bath gas temperatures?

A long time ago, in a galaxy far away when COVID wasn't a thing…

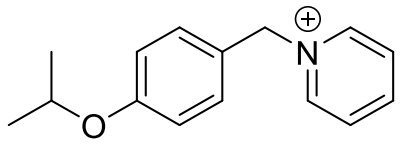
Give the methoxy BP ions more rovibrational states to funnel energy into



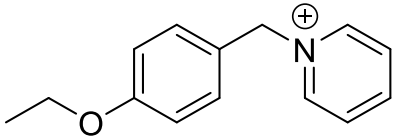
M^+ F^+



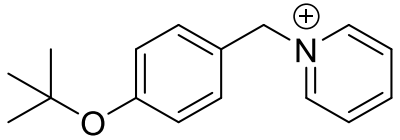
OMe
E_0 = 178.5, 87 DoF



OiPr
E_0 = 166.0, 105 DoF

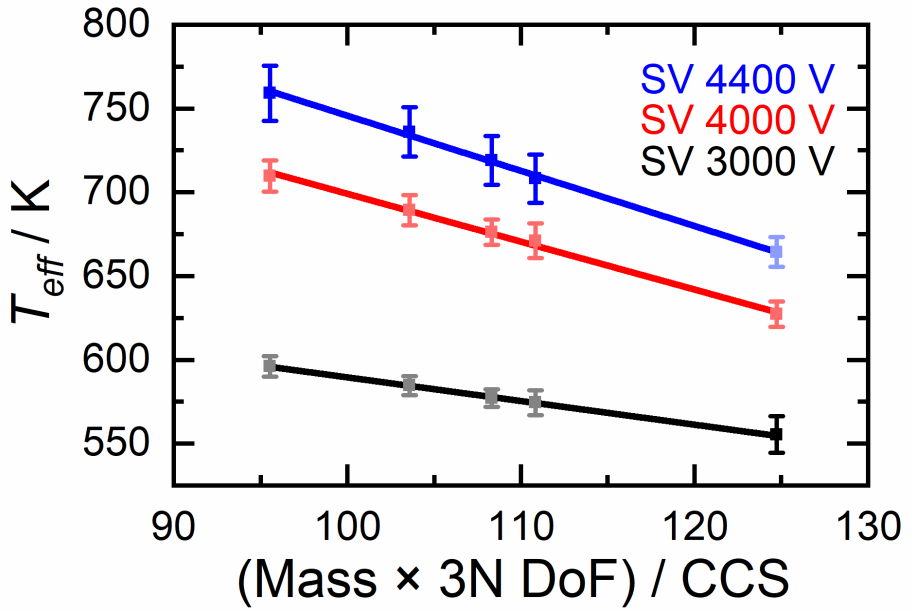


OEt
E_0 = 172.1, 96 DoF



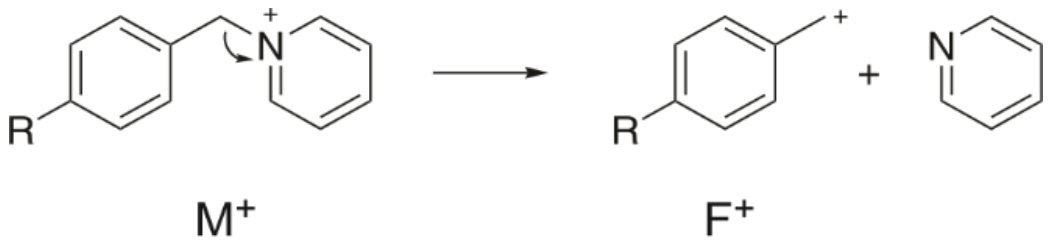
OtBu
E_0 = 160.4, 114 DoF

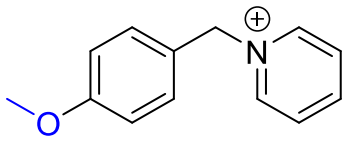
Linear relationship between ion T_{eff} and its density of states / collision probability



And that's when things go crazy

Loss of pyridine **is not the dominant fragmentation pathway**





OMe

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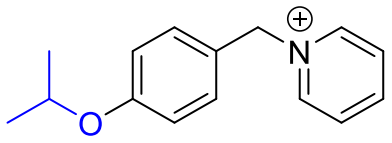

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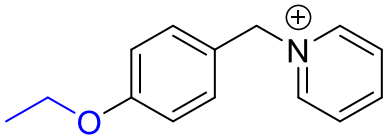

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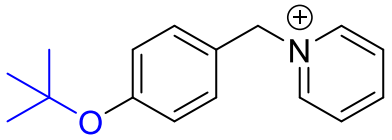

OtBu

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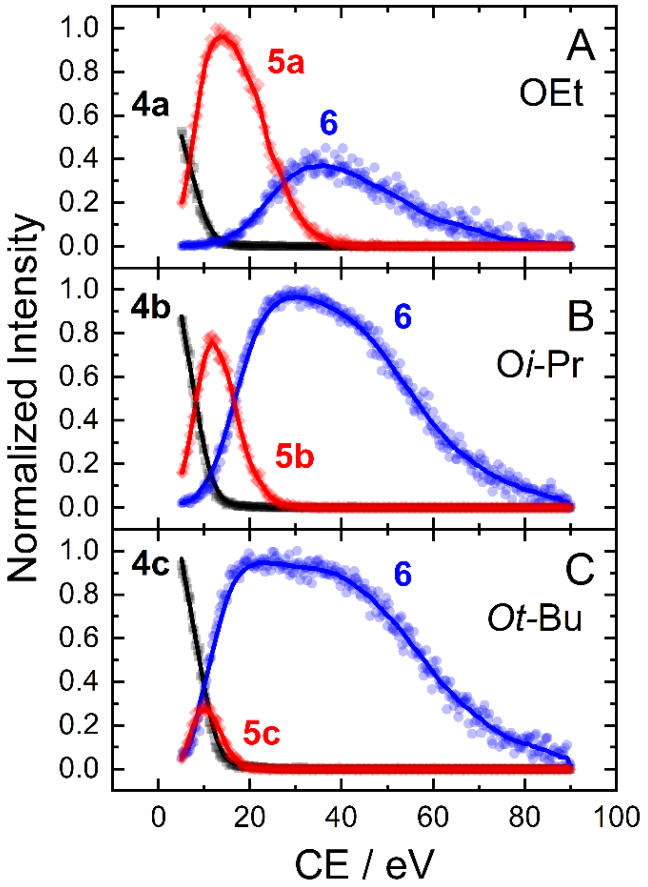

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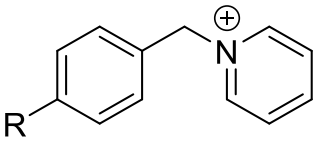

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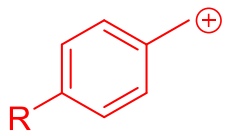
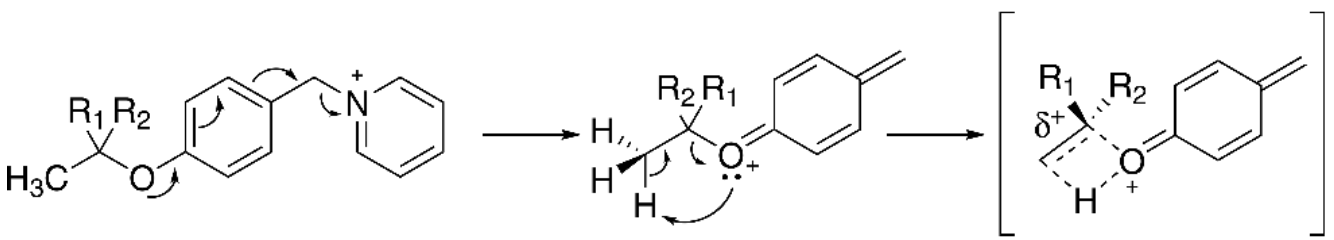


6

***m/z* 107 ???**

Breakdown behaviour gives insight into what's happening

Formation of 6 is **greater** for BP ions with bulkier side chains



4a ($R_1 = R_2 = H$)
4b ($R_1 = H$; $R_2 = Me$)
4c ($R_1 = R_2 = Me$)

5a ($R_1 = R_2 = H$)
5b ($R_1 = H$; $R_2 = Me$)
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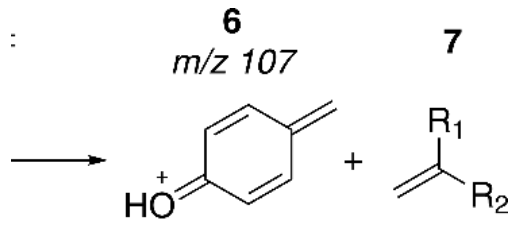

6
m/z 107

7

7a ($R_1 = R_2 = H$)
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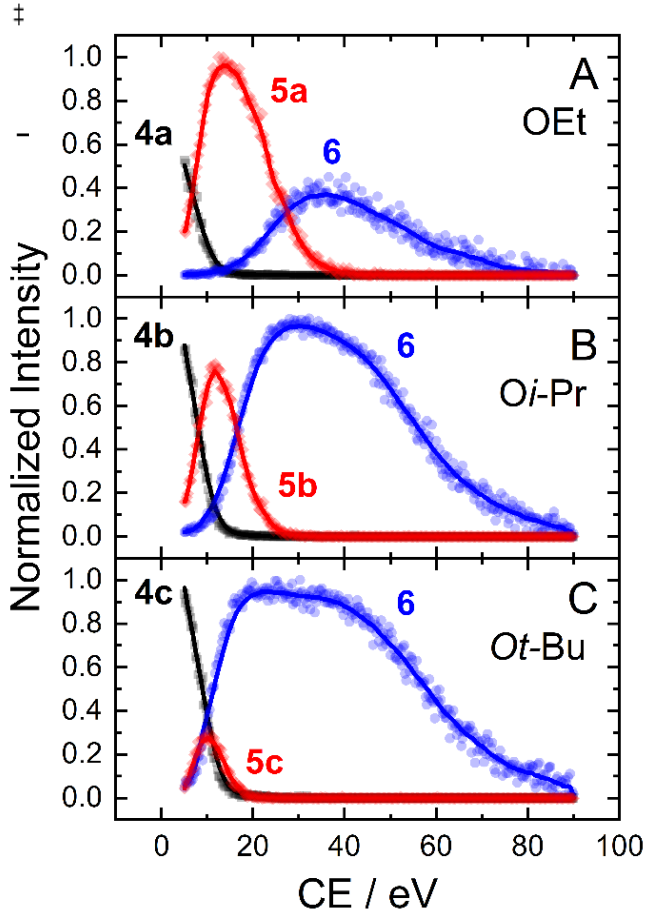

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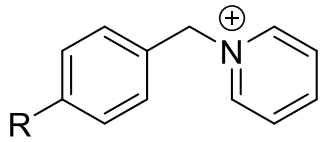

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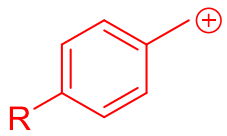
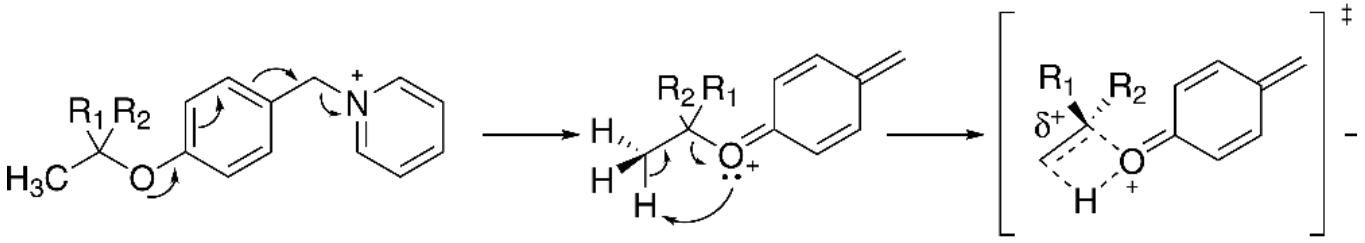


6

***m/z* 107 ???**

Figuring out wtf is going on

The only way to form 107 is via an intramolecular elimination that passes through a 4-membered ring TS.



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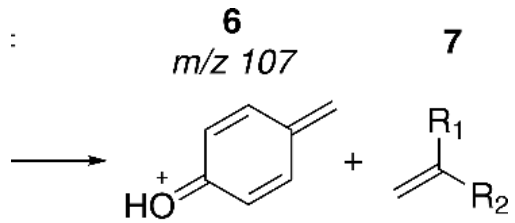

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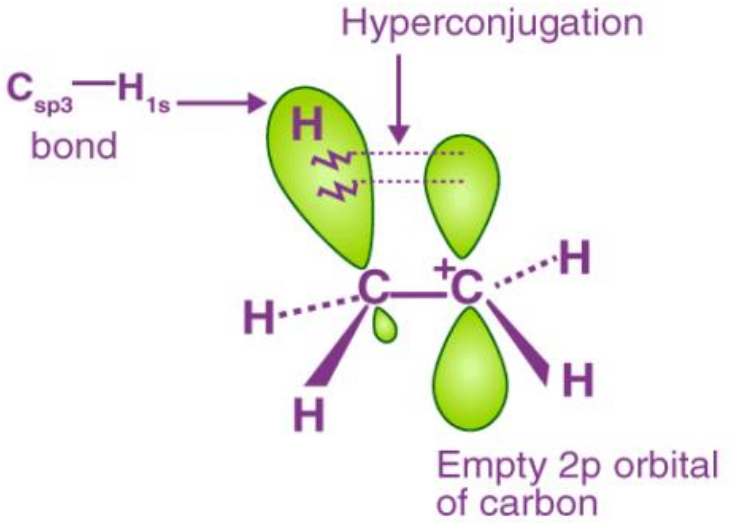
2 major implications:

1. $\Delta G^{\ddagger}$ OEt > OiPr > OtBu

Hyperconjugation effect (E_i like)



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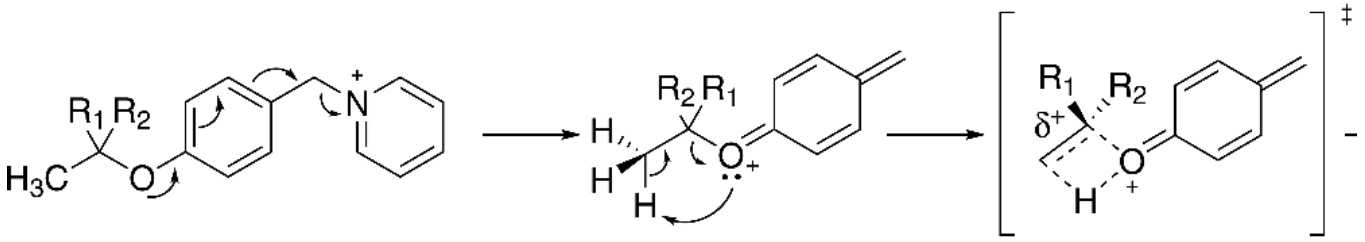

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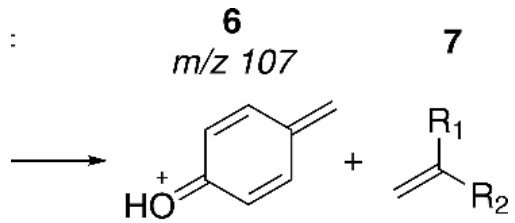

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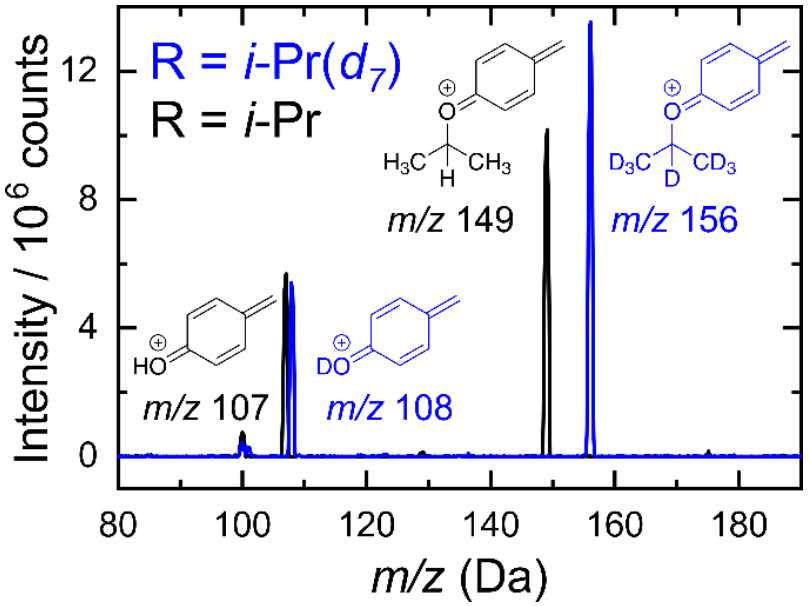
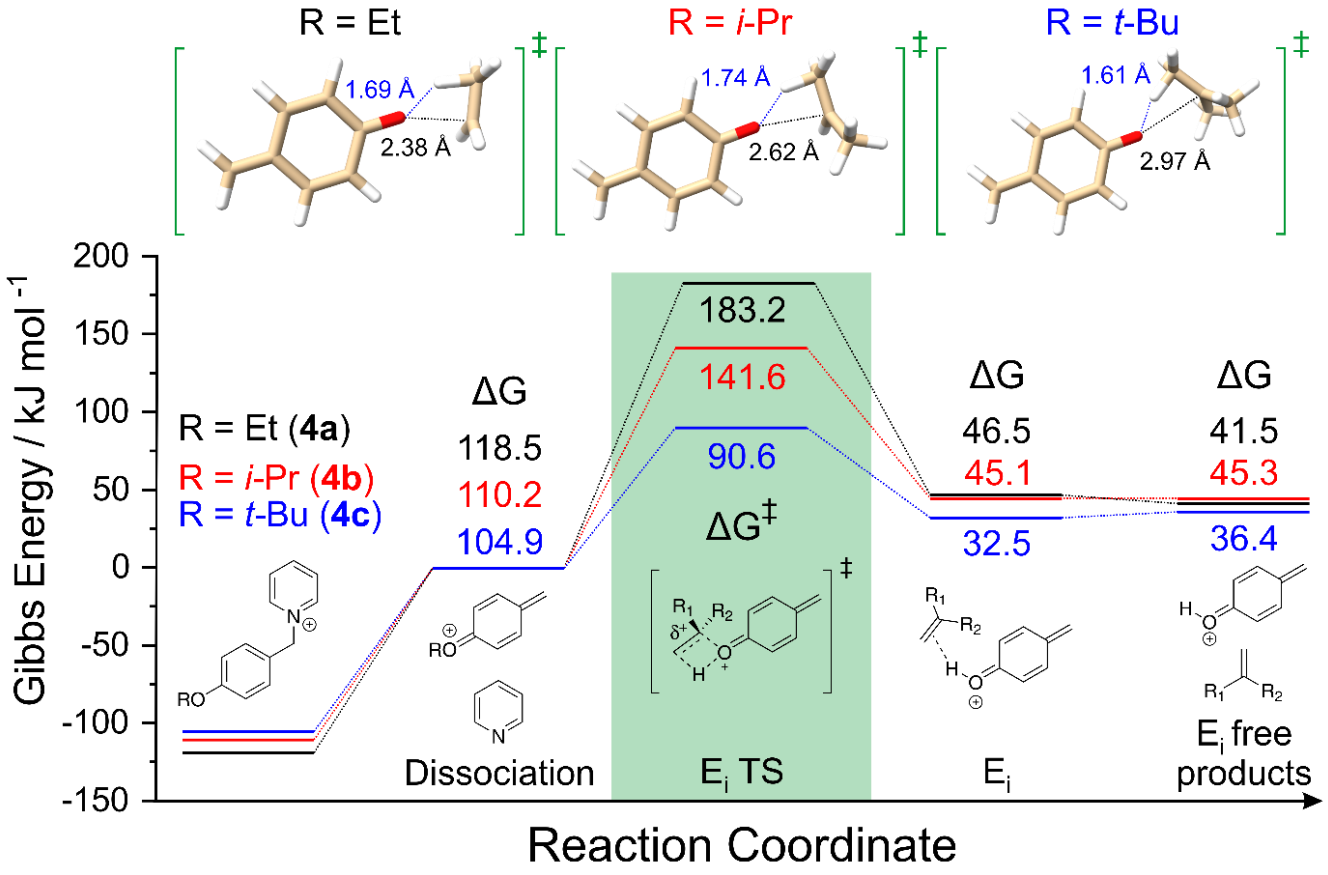
2 major implications:

2. Intramolecular elimination requires proton incorporation into the product

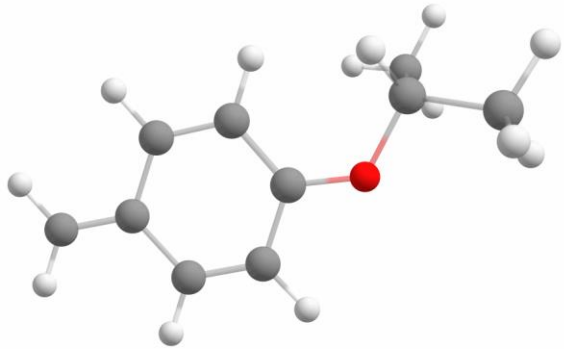


Finally understanding what was going on

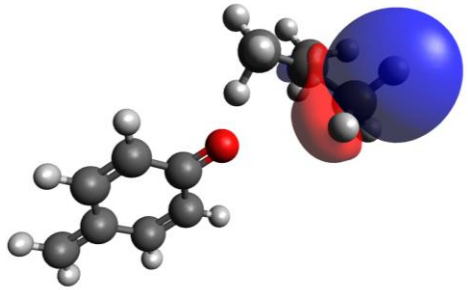
Mapping the reaction coordinate using the nudged elastic band confirms our proposed fragmentation mechanism



Reaction pathway



Hyperconjugation in the TS

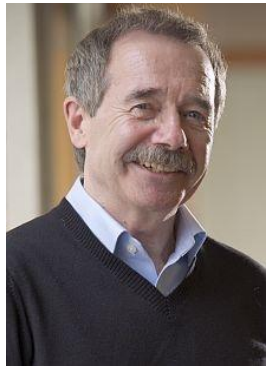


OEt: 24.0 kJ mol^{-1}
OiPr: 206.0 kJ mol^{-1}
OtBu: 759.8 kJ mol^{-1}

Acknowledgements

PhD Committee

Prof. W. Scott Hopkins



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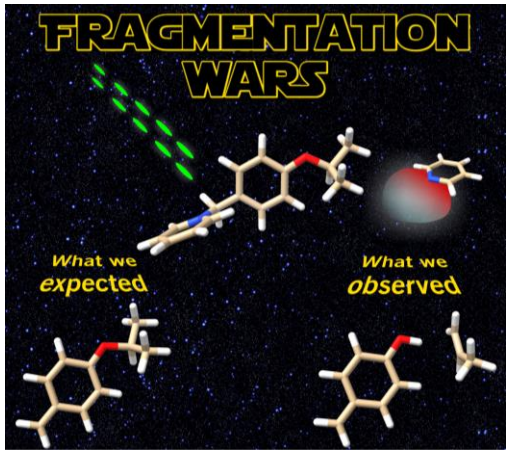

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