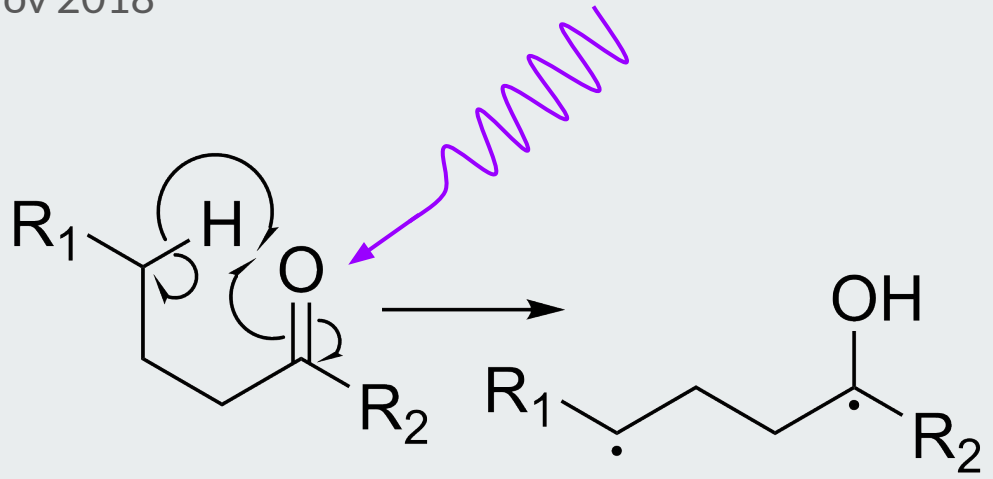
The Norrish Type II reaction

(γ-H abstraction)

Keiran Rowell - Group Meeting - 30th Nov 2018



Carbonyls in the atmosphere

Jenkin M., Saunders S., Pilling M., *Atmospheric Environment*, **1997**, *31*, 81-104

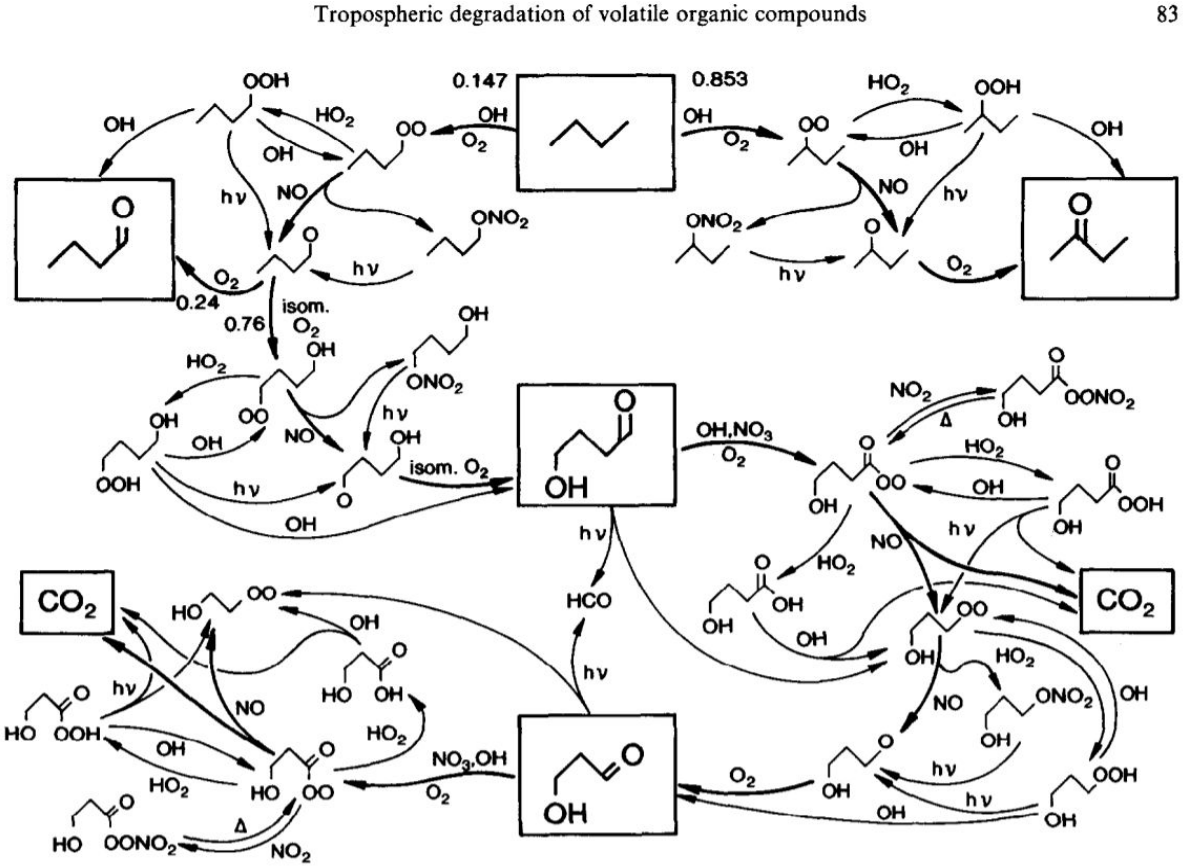
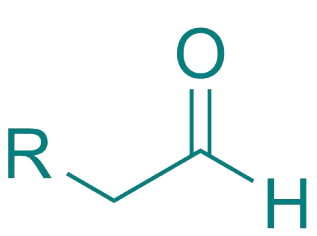
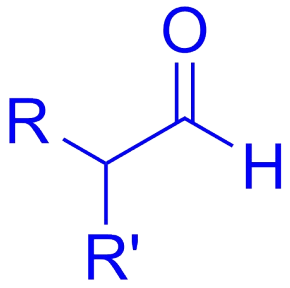


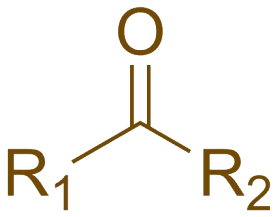
Fig. 1. Schematic representation of the degradation of butane, showing most of the chemistry which makes up the mechanism for this compound.



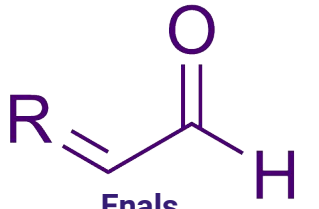
Linear aldehydes



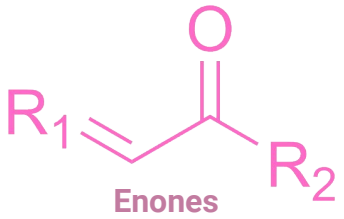
Branched aldehydes



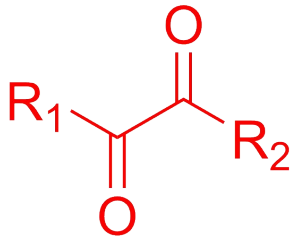
Ketones



Enals



Enones

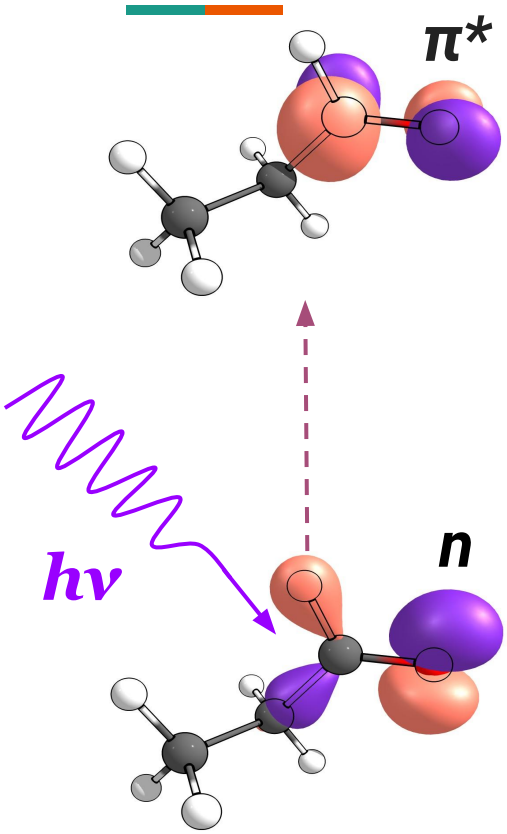


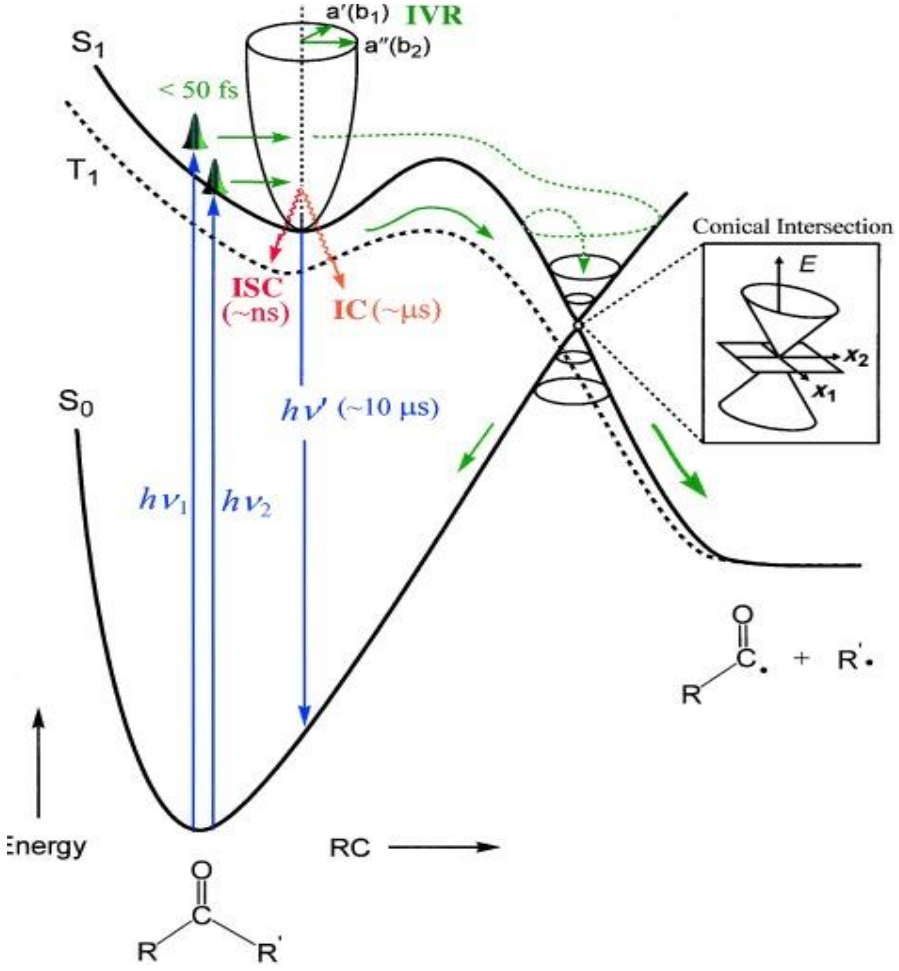
Dicarbonyls

Corrigan M. **"Modelling the photochemistry of acetaldehyde" 2015** [*Honours Thesis*]

Heicklen J., *J. Am. Chem. Soc.* **1959**, *81*, 3863–3866
Diau E. W-G., Kötting C., Zewail A., *CHEMPHYSCHEM*, **2001**, *2*, 273-293

NTI photochemistry

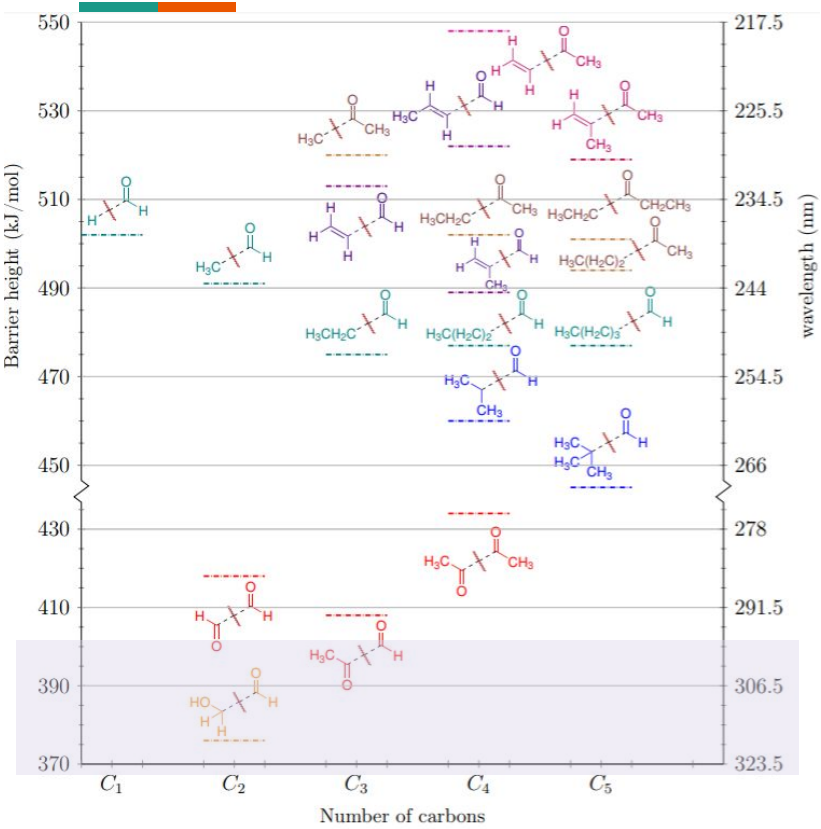


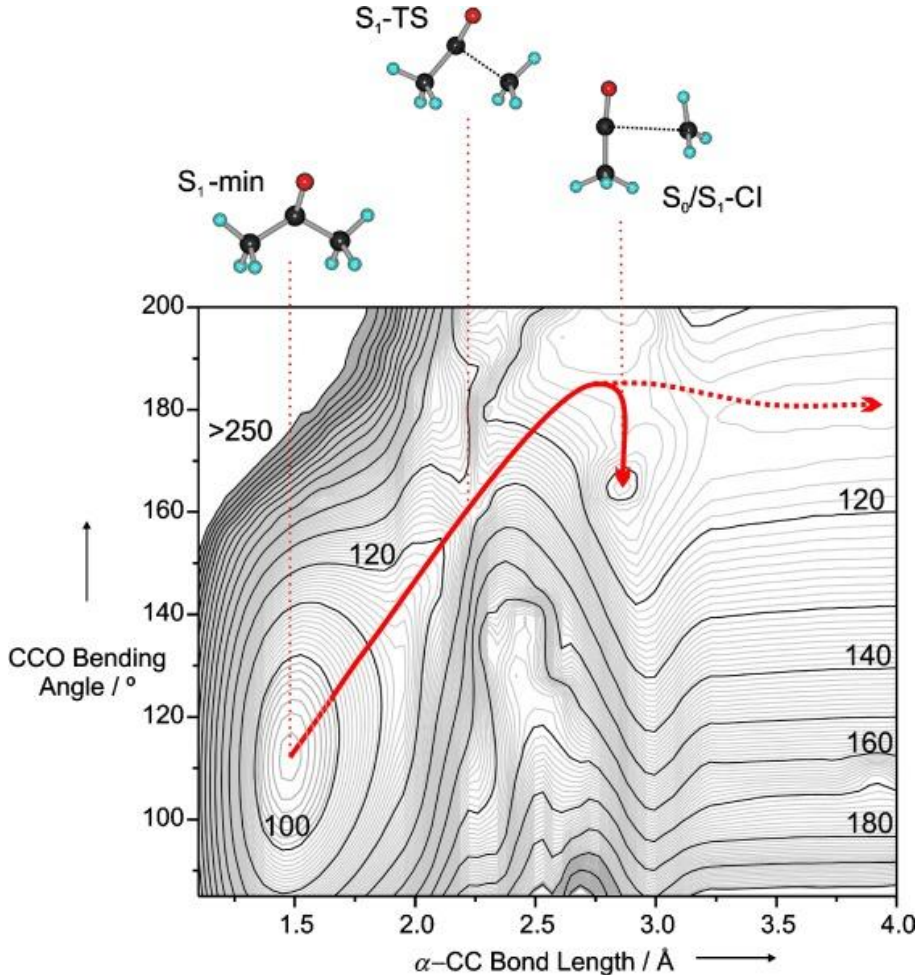


Rowell K., Kable S., Jordan M., **"Substituent effects on the α-bond cleavage of photochemically important carbonyls"**, [*in preparation*]

Diau E. W-G., Kötting C., Zewail A., *CHEMPHYSCHEM*, **2001**, *2*, 273-293

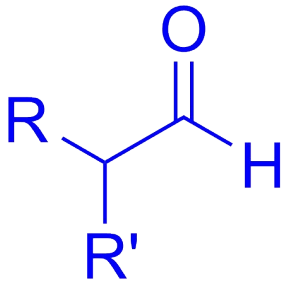
S_1 and NTI

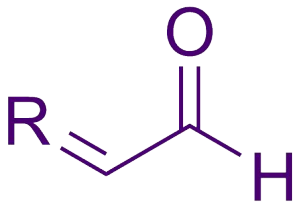




What factors affect NTI?

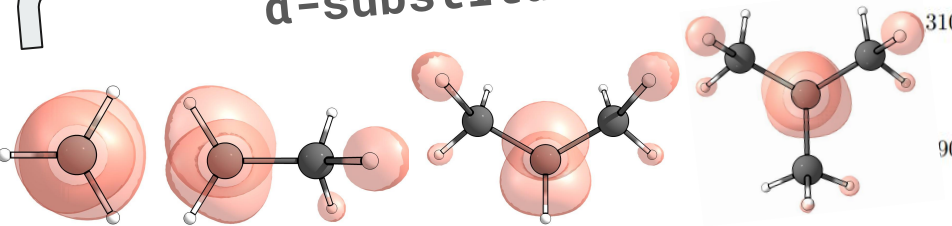
Branching *vs* **Conjugation**

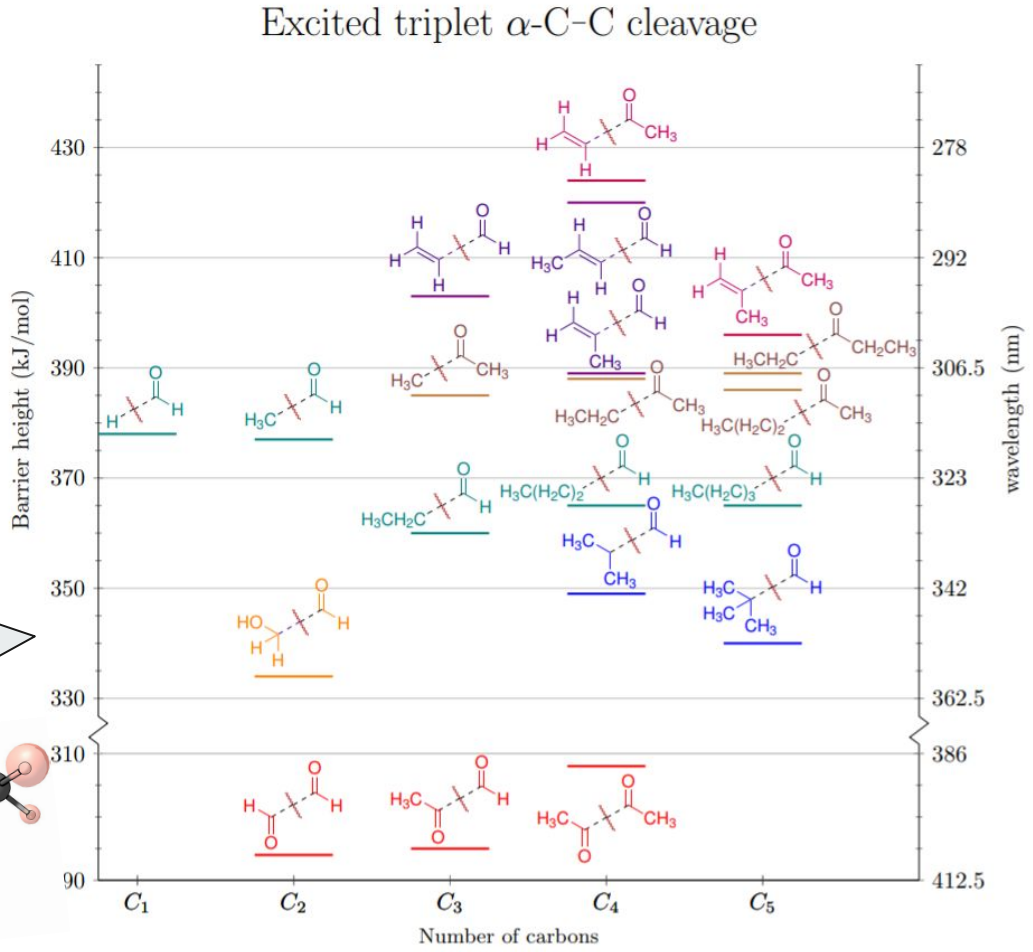




Hyperconjugation

α-substitution

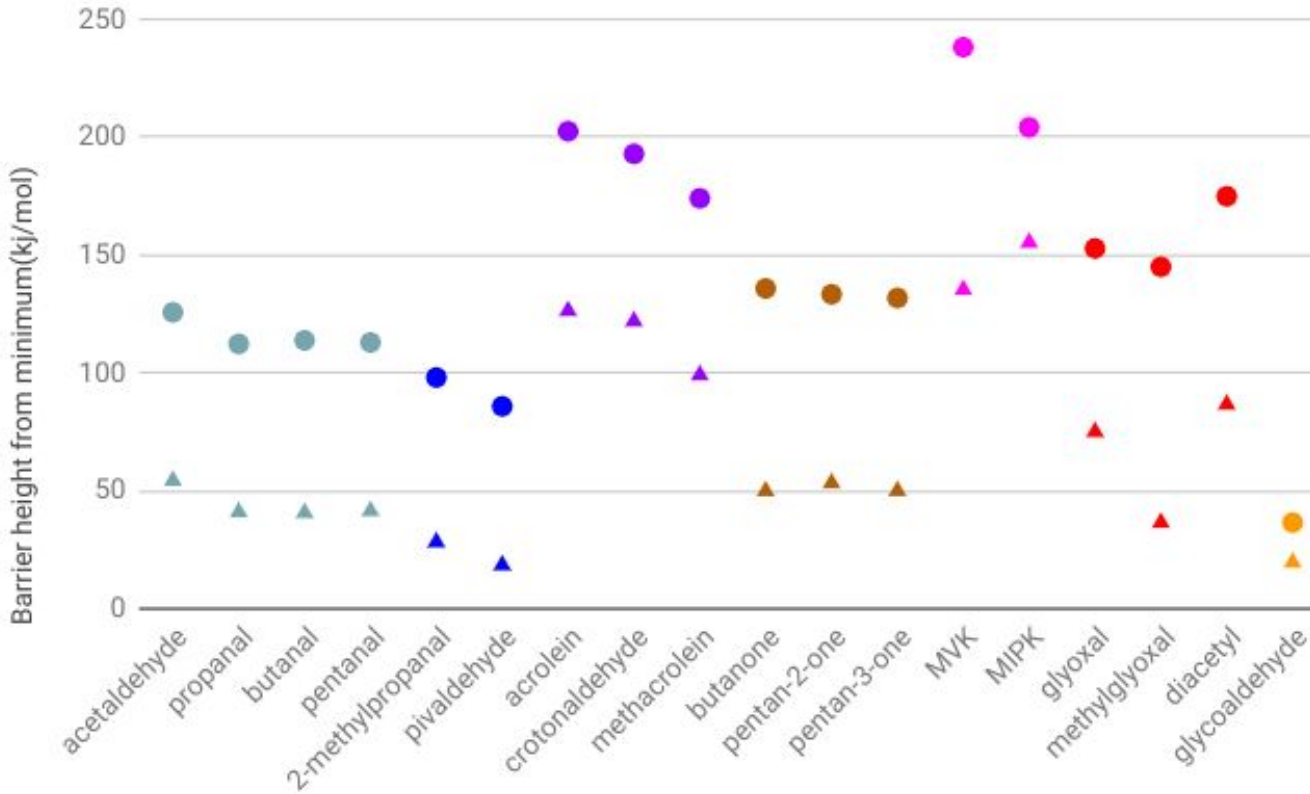




Intrinsic barriers

- ▶ S_1 & T_1 show same trends
- ▶ S_1 shifted higher ~50 kj/mol
- ▶ '0-0' excitation energy diff.
- ▶ •H & •CH_3 NTI*b* basically flat
- ▶ SARs describe all surfaces!

NTI*a* on S_1 (●) *vs* T_1 (▲)

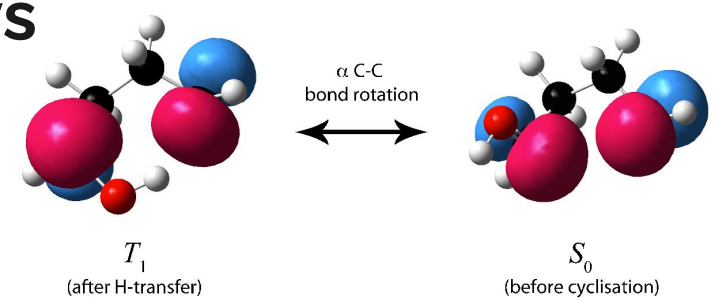


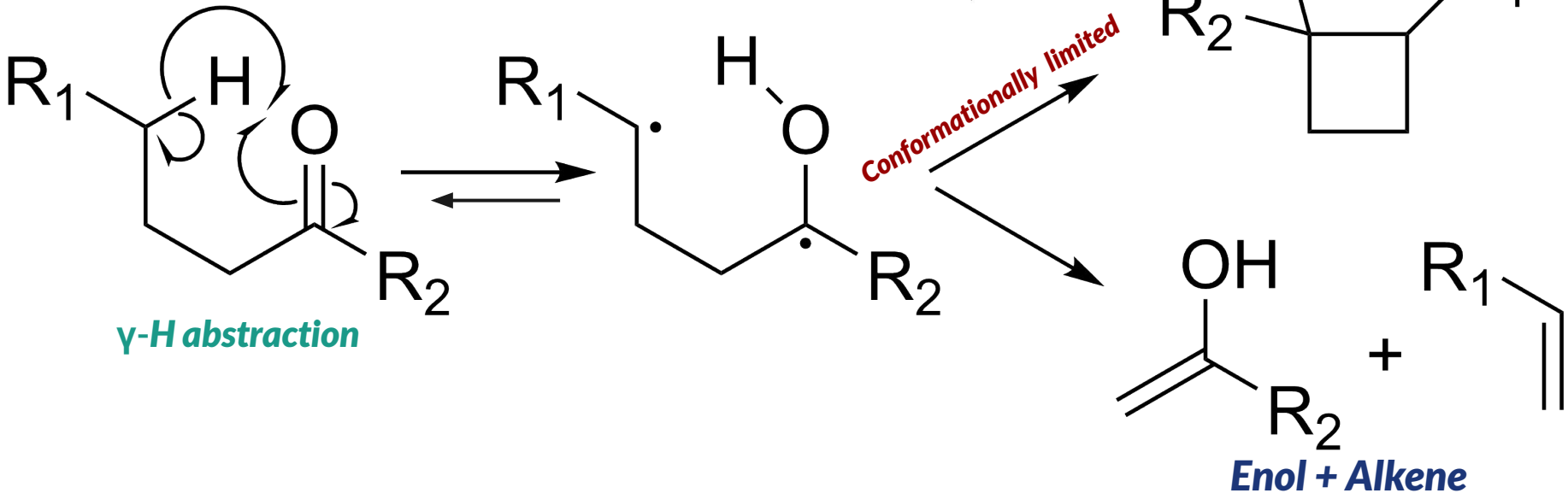
De Feyter S., Diau E. W.-G., Zewail A., *Angewandte Chemie*, **2000**, *39*, 260-263

Shaw M. **"Photochemical Formation of enols from carboyls" 2017** [*PhD Thesis*]

IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: http://goldbook.iupac.org (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.

The NTII pathways





Michael J., Noyes W., *JACS*, **1963**, *85*, 1027-1032
Tolgyesi M., Nacsa A., *J. Photochem.*, **1979**, *11*, 333-345
Shaw M. **"Photochemical Formation of enols from carboyls" 2017** [*PhD Thesis*]
O'Neal H., Miller G., Gunderson E., *JACS*, **1974**, *96*, 3351-3357
Wagner P., Hammond G., **1965**, *87*, 4009-4011
Stephenson L., Cavigli P., Parlett J., *JACS*, **1971**, *93*, 1984-1988
Chen B., Fang W., *Chem. Phys. Lett.*, **2002**, *361*, 472-482
De Feyter S., Dia E. W.-G., Zewial A., *Angewandte Chemie*, **2000**, *39*, 260-263

Surface(s) of NTII?

- Quenching studies used to distinguish between S_1 & T_1 reactivity
  - Experiments conducted at 380-385 kJ/mol
- Different species showed different quenching sensitivity:
  - hexan-2-one: singlet
  - pentan-2-one: triplet
  - butanal: equal parts singlet & triplet
- The triplet biradical has a μs lifetime and can be trapped.

Surface is molecule-dependent

- Tertiary or secondary γ-H stabilised by hyperconjugation.
  - Rapid S_1 ∴ unquenchable.
  - C-H bond strength, deuteration
  - Femtosecond-MS & DFT
  - α-C radical stabilisation
  - ISC same, diff. is chemical
- Triplet scrambles stereochemistry
- Singlet has some scrambling

Rationalising NTII

PHOTOCHEMISTRY OF ALKYL KETONES BEARING γ-HYDROGENS

M. V. ENCINA and E. A. LISSI
Departamento de Quimica, Universidad Técnica del Estado, Santiago (Chile)

(Received May 20, 1976)

TABLE 4

Values of β_s and β_T obtained at 20 °C and apparent activation energies

Ketone	β_S	$E\beta_s$ (kcal)	β_T	$E\beta_T$ (kcal)
2-pentanone	0.14	—	0.24	—
4-methyl-2-pentanone	0.14	0	0.23	0.6
3-heptanone	0.11	1.0	0.21	0.6
2-hexanone	0.15	0.8	0.28	—0.15
2-heptanone	0.13	0.7	0.36	0.4
2-octanone	0.11	—	0.39	—
5-methyl-3-heptanone	0.08	1.7	0.20	1.5
5-methyl-2-hexanone	0.13	1.5	0.38	—0.6

The preceding discussion shows that the factors which determine the value of β_S are so numerous that any attempt to rationalize the data shown in Table 4 is meaningless. The most remarkable characteristic of these data is the small range of β_S values covered by all the ketones considered in the present work, and the small values of the apparent activation energies. We can only conclude that the factors which determine the singlet behaviour are extremely insensitive to both temperature and ketone structure.

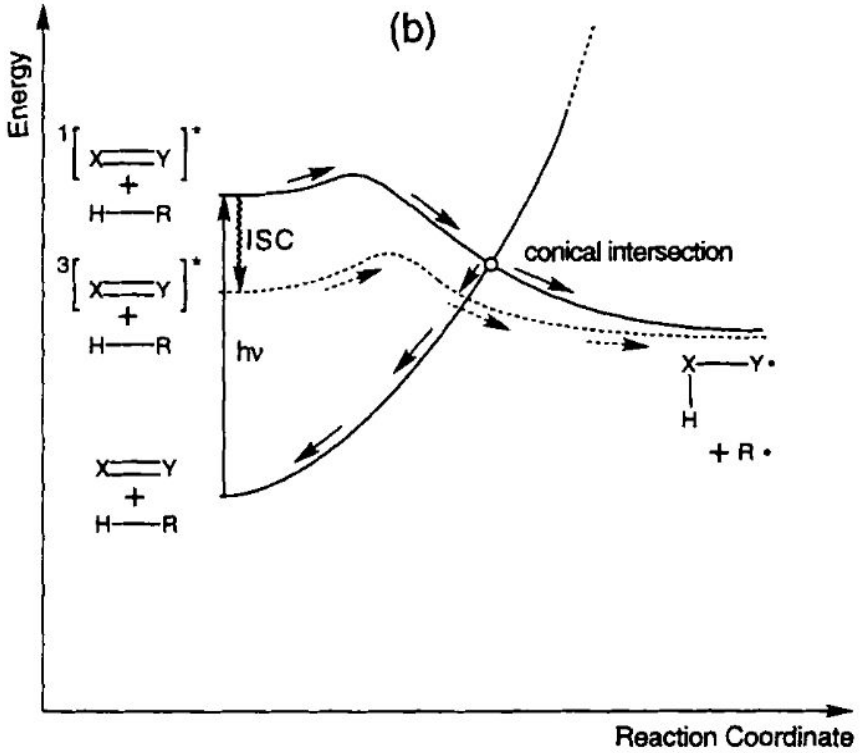
The Mechanism of Photochemistry of Alkanones with γ Hydrogens

N. C. Yang,[11] Steven P. Elliott,[12] Bongsub Kim
Department of Chemistry, The University of Chicago Chicago, Illinois 60637

Received October 3, 1969

The results of this investigation and our earlier work constitute a complete analysis of the behavior of photoexcited 2-alkanones with γ hydrogens.[10a]

The NTII conical intersection



► 'Absolute reactivity of S_1 exceeds T_1, but S_1 is chemically less efficient due to radiationless deactivation'

► S_1 deactivation > 80%

► CI competitive with dissociation, H-back transfer, ISC

► Conical intersection following the TS — common to a range of H-abstraction reactions

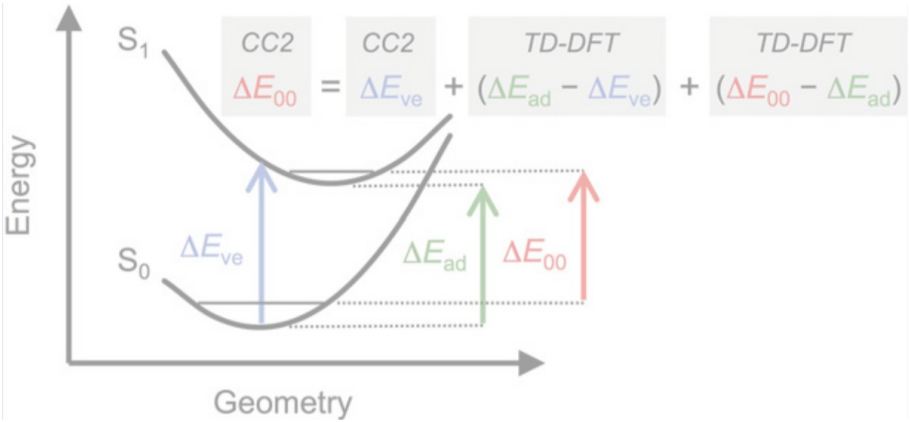
► Requires a CAS calculation (multistate optimisation)

S_1 calculations

Excited state calculations are a pain

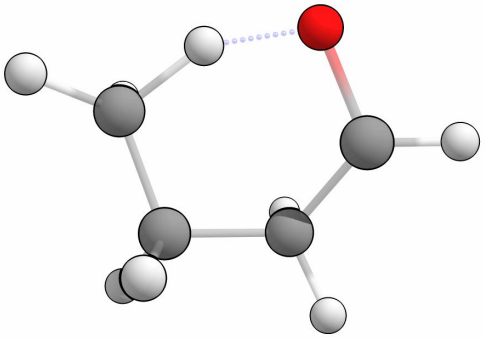
T_1 is lowest spin-unpaired solution — can use unrestricted

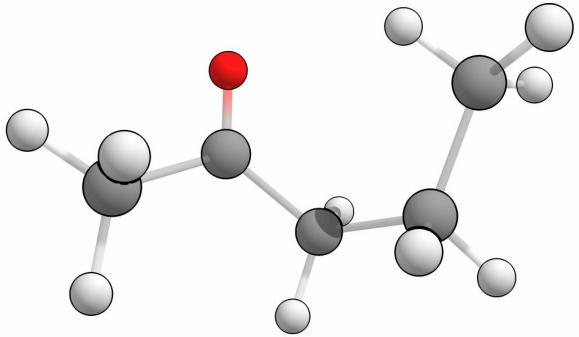
TD-DFT is inaccurate (~$^1/_{10}$ eV) — use composite procedure

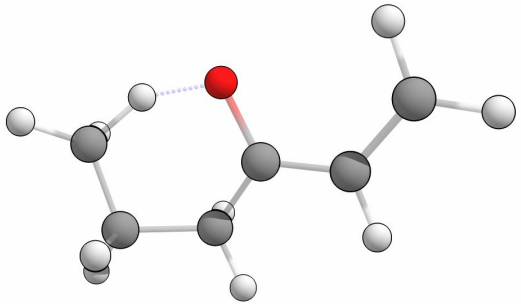


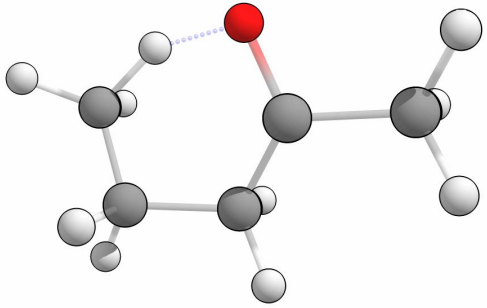
Issues with S_1 and NTII

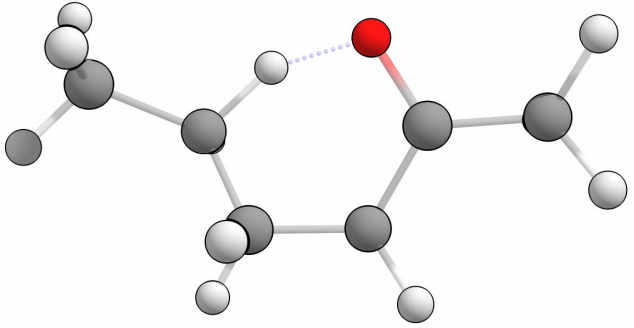
- Needs to distinguish close S_1 & T_1 barriers
- NTII process has involved CI — TD-DFT can fail
- NTII molecules C_4+ — EOM-CC scales badly!
- H-transfer reaction — need high E_x^{HF} exchange
  - BH&HLYP bumps E_x^{HF} up to 50% — still fails
  - Meta-functionals (M06-2X) expensive for TD
  - Use range-separated hybrids (CAM-B3LYP)
    - ✓ TSs found! Need to use same ZPVE in all



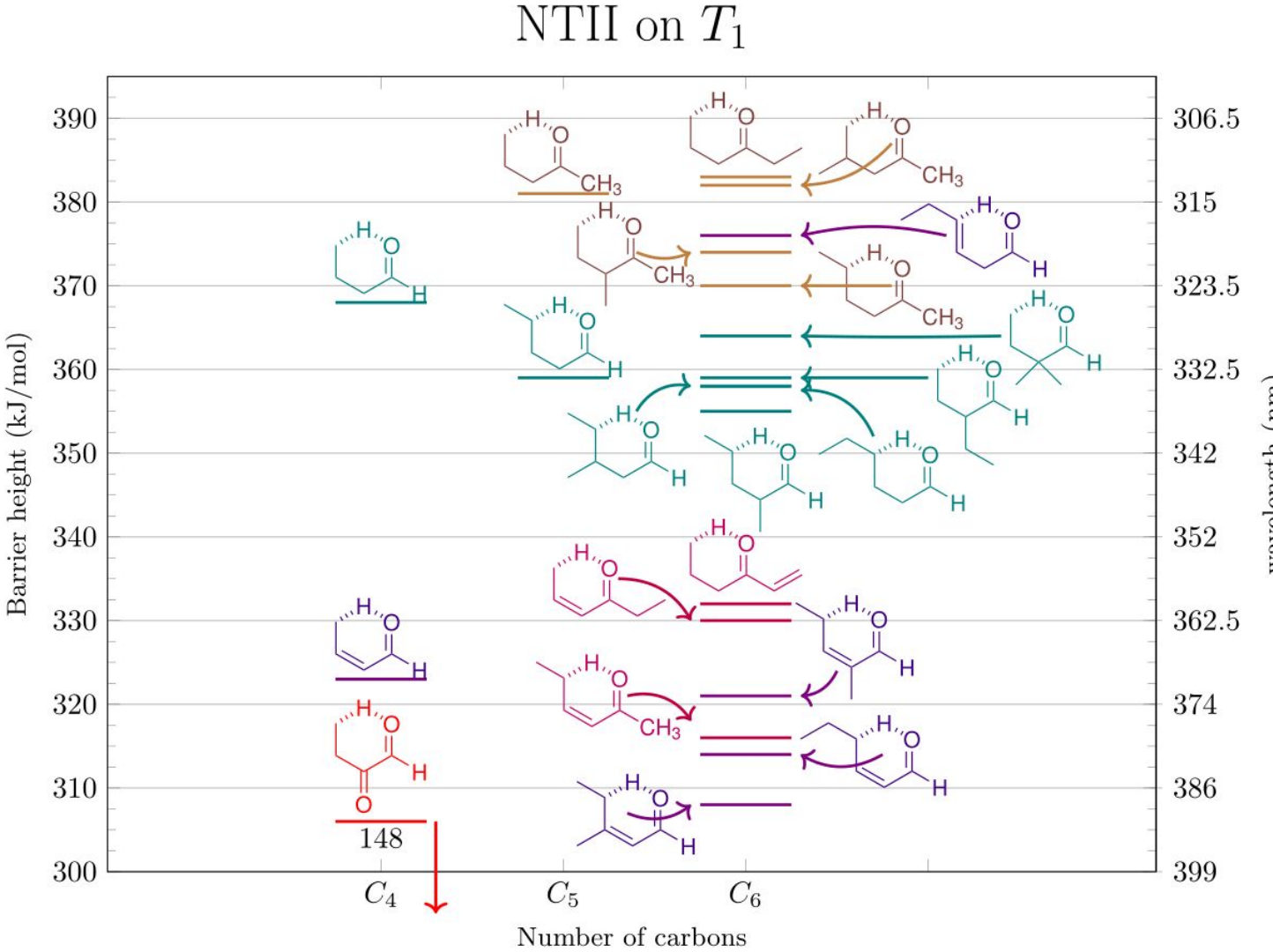








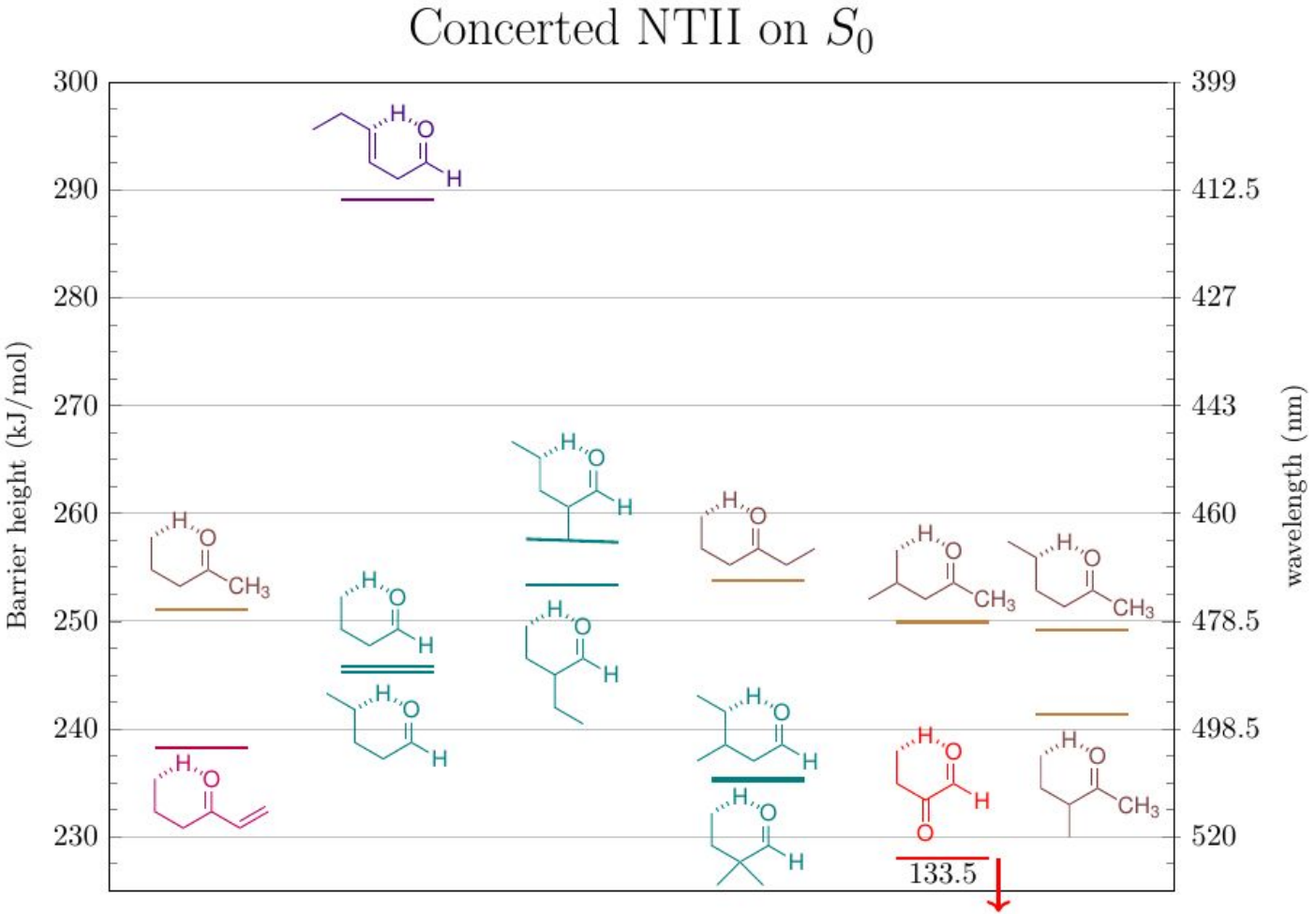
SARs of NTII


NTII on T_1
Barrier height (kJ/mol)
390
380
370
360
350
340
330
320
310
300
306.5
315
323.5
332.5
342
352
362.5
374
386
399
148
C_4
C_5
C_6
Number of carbons

NTII barriers from S_1 min

- Still waiting on EOM-CC calcs — don't have absolute energies
- S_1 intrinsic barriers are very low, > 30 kJ/mol — ~20 kj/mol lower than T_1
- In absolute energy terms, conjugation should lower the excitation energy
  - primary γ-C ketones and aldehydes should be highest barriers
  - enones and enals should have low absolute barriers, secondary & tertiary even more so

S_0 reaction?


Concerted NTII on S_0
Barrier height (kJ/mol)
wavelength (nm)
300
290
280
270
260
250
240
230
399
412.5
427
443
460
478.5
498.5
520
133.5

Thank you!

State correlation diagrams