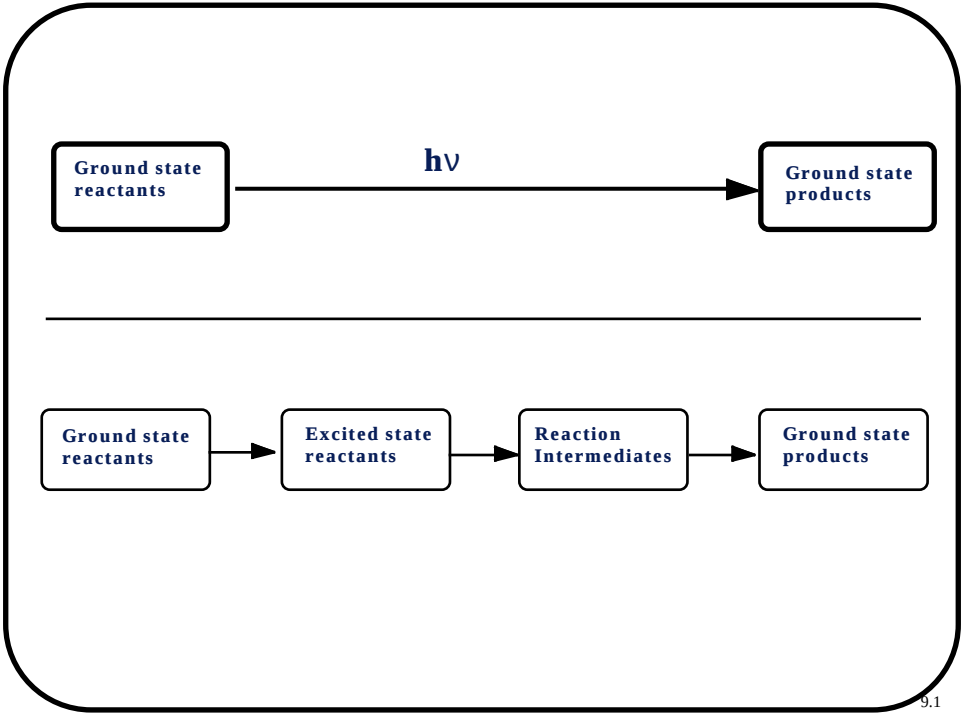

Ground state reactants
hν
Ground state products
Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products

Criteria to establish reasonable mechanistic options

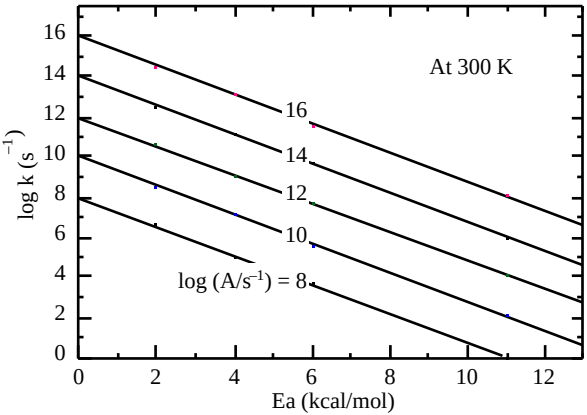
In determining a plausible from a possible mechanistic set, we may first apply criteria relating to:

1. **Energetics**
2. **Dynamics**
3. **Structure**
4. **Electronics**

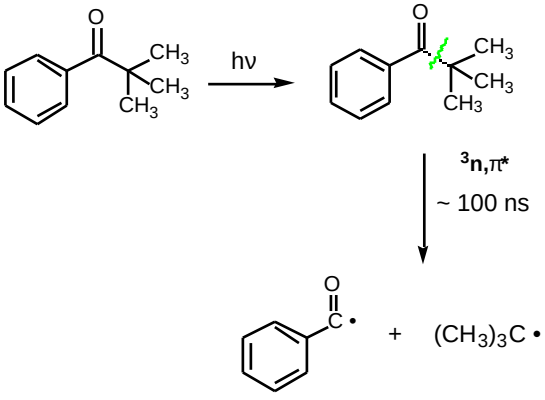
Additional criteria to select from among plausible mechanisms the most *probable* one

- **1. Reactant and Product structure**
- **2. Structure of intermediates on the pathway from reactant to product**
- **3. Kinetic rate law**
- **4. Labeling experiments**
- **5. Structure-reactivity relationships**

Calculated rate constants at 300 K for various pre-exponential factors and variable activation energies.



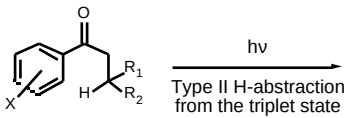
Norrish Type I reaction



The triplet lifetime is around 100 ns at room temperature. We assume that for this chemical reaction to contribute significantly to triplet decay, its rate constant will have to be at least 10^5 s^{-1} for the Norrish Type I cleavage. We calculate that the maximum activation energy is ~ 11 kcal/mol.

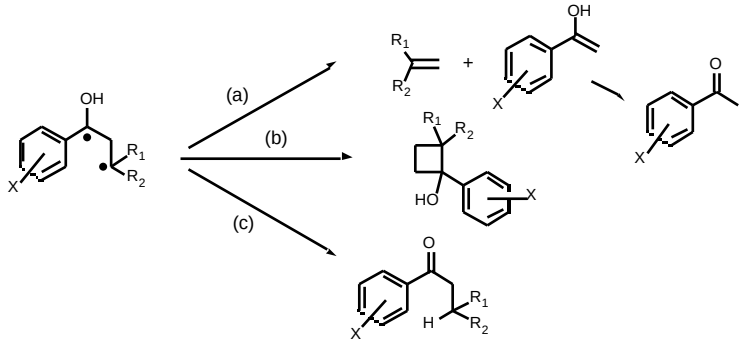
Experimentally the measured values are A = 2 x 10^{12} s^{-1} and Ea = 7.3 kcal/mol and the cleavage occurs with a high quantum yield.

The Norrish Type II reaction

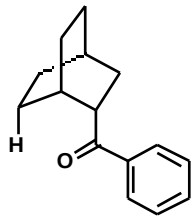


Type II 1,4-biradical typical lifetimes are around 30-100 ns

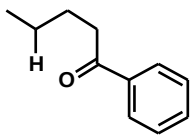
Ea (kcal/mol)	
primary	7
secondary	5
tertiary	4.5



Norrish Type II reaction
Pre-exponential factors



$A = 10^{13}\ s^{-1}$



$A = 10^{12}\ s^{-1}$

Entropic factors are important in determining A factors

Quantum yield and state efficiency

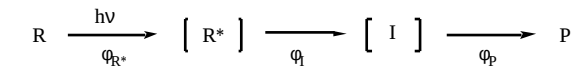
Quantum yield:

$$\Phi = \frac{\text{moles of a given species formed or destroyed}}{\text{moles of photons absorbed by the system}}$$

A mole of photons is also called an Einstein

State efficiency :

$$\varphi = \frac{\text{moles of a given species formed or destroyed}}{\text{moles of a given state formed by absorption of an Einstein}}$$



Reactants Products

$$\Phi_p = \Phi_{R^*} \times \varphi_I \times \varphi_p$$

Some mechanistic tools and criteria

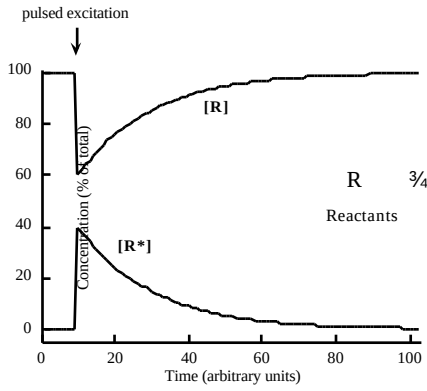
1. **Does the overall reaction correspond to a standard reaction type or to a sequence of standard reaction types?**
2. **How does the product atomic composition and connectivity relate to the reactant atomic composition and connectivity?**
3. **How does the product stereochemistry relate to the reactant stereochemistry?**

Reactions can be classified in terms of mechanistic types, and for any given class of reactions only a small set of mechanistic types is likely to be required for a detailed analysis

Hammond postulate

If a transition state and an intermediate possess comparable energies and occur consecutively along a reaction coordinate, the chemical composition, the chemical constitution (structures) and chemical properties of the transition state will be similar to those of the intermediate

Excitation-decay of R*



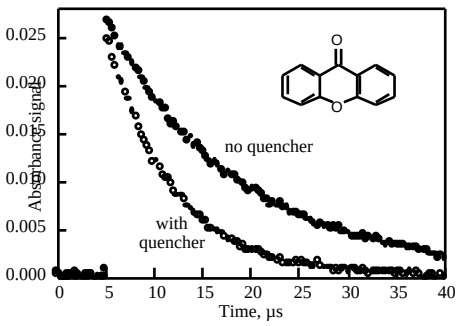
$$R \xrightarrow{h\nu} [R^*] \xrightarrow{\tau_R} R$$

Reactants — Products = Reactants

Pulsed excitation at t = 10 excites 40% of the R molecules, Reading to an excited state (R*) that decays with $\tau_R = 20$. Excited decay is accompanied by the concurrent regeneration of R.

Decay of triplet xanthone following pulsed laser excitation

Decay of triplet xanthone monitored at 600 nm following 355 nm laser excitation in acetonitrile. The faster decay process is in the presence of 9 mM pyridine. Quenching is due to charge-transfer interactions



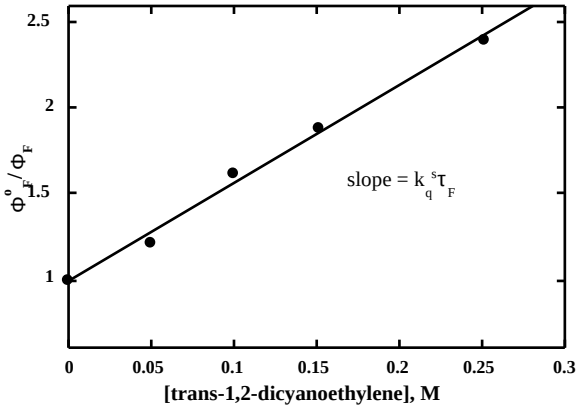
Lifetime of R*, *no quencher*

$$1/\tau_1 = k_1$$

Lifetime of R*, *quencher present*

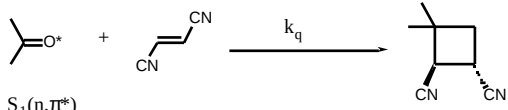
$$1/\tau_2 = k_1 + k_q[Q] = 1/\tau_1 + k_q[Q]$$

Stern-Volmer plot based on fluorescence



Experimental plot of $\Phi_0{}^F/f\,\Phi^F$ vs. [trans-1,2-dicyanoethylene] for the cycloaddition of acetone singlets to the ethylene.

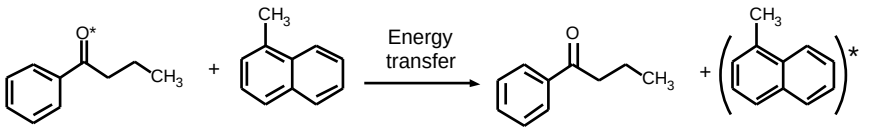
The intercept is 1.0 and the slope is 7 $M^{-1} = k_q\tau$.



$S_1(n,\pi^*)$

1

Stern-Volmer plots in laser photolysis

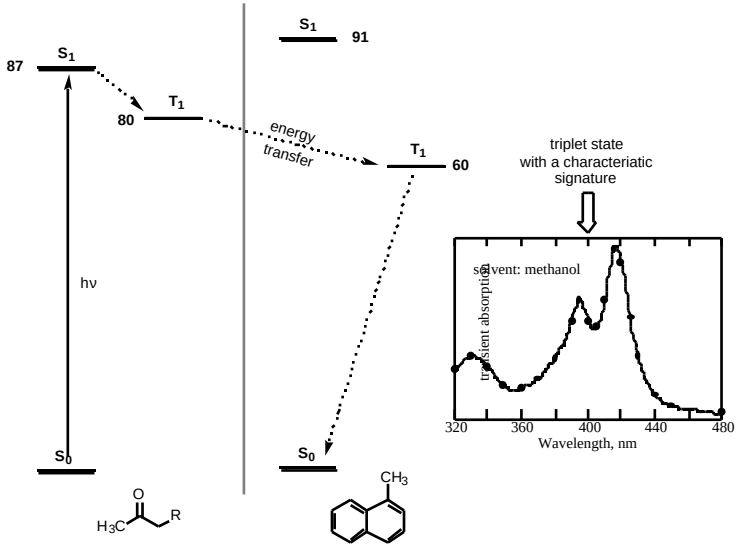


Butyrophenone triplet | 1-Methylnaphthalene ground state | Butyrophenone ground state | 1-Methylnaphthalene triplet (~420 nm absorption)

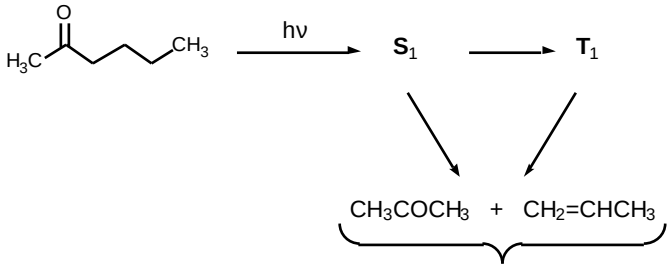
$$\left[MeN^*\right]_\infty = \frac{k_q\left[MeN\right]}{\tau_o^{-1} + k_q\left[MeN\right]}\left[BTP^*\right]_o$$

$$\frac{1}{\Delta OD_\infty} = a + \frac{a}{k_q\,\tau_0\left[MeN\right]}$$

Detecting the excited quencher



Kinetics of Reactions Involving More than One Excited State



Relative efficiencies

$$\frac{\varphi_q^S}{\varphi_q^T} = \frac{k_q^S \tau_S}{k_q^T \tau_T}$$

Relative rates

$$\frac{\text{rate of } S_1 \text{ quenching}}{\text{rate of } T_1 \text{ quenching}} = \frac{k_q^S[\text{diene}]}{k_q^T[\text{diene}]} = \frac{k_q^S}{k_q^T}$$

Possible forms of Stern-Volmer plots

Plot type	Cause
A) Linear	1) Only one excited state reacts
	2) Two rapidly equilibrating excited states with either or both quenched
	3) Two non-interconverting states coincidentally quenched with the same value of kq Z
	4) The first of two consecutively formed states is quenched, with either one reacting
B) Downward curvature	1) Reaches a zero slope. Two reactive excited states, but only one quenched
	2) Reaches a positive asymptotic slope. (a) Two non-interconvertin excited states quenched with different kq values, or (b) Two interconverting excited states with the shorter lived or both reacti the quencher disrupts the interconversion equilibrium. Final slo corresponds to initial shorter state
C) Upward curvature	1) Two consecutive excited states are quenched, but only the secon one is reactive
	2) Two non-interconverting excited states are both reactive and quenched with different kq2 values
	3) Two interconverting excited states, with only the lower one react and with the quencher disrupting the interconversion equilibrium
	4) Same as B2
	5) A sensitized reaction with both sensitizers and substrate states quenched
	6) Static or time dependent quenching.

Two different approaches to the study of short lived reaction intermediates

- **By making the technique sufficiently fast that it can access the time scale in which the intermediate naturally lives.**
- **By isolating the intermediate under conditions where its lifetime is long enough for the technique of choice, such as in matrix isolation.**

Sensitization: why and how

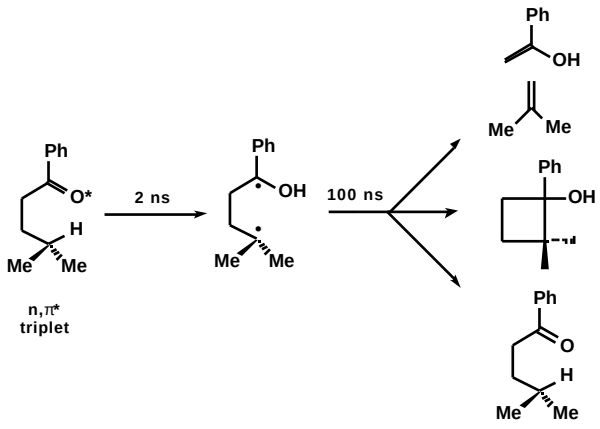
The idea of triplet sensitization is to test if a given triplet reaction can be induced while completely bypassing the singlet manifold of that compound. Thus, for efficient and selective sensitization, the sensitizer should have the following characteristics:

(1) Triplet energy higher than that of the molecule to be sensitized.

(2) An absorption in a region where the molecule under study is transparent, so that selective excitation can be readily achieved.

(3) Either a very short singlet lifetime, or a sufficiently large S-T energy gap to place the sensitizer S1 level significantly above the S1 level of the sensitized molecule.

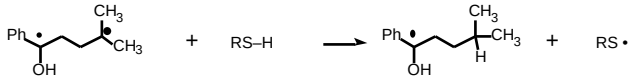
The Norrish Type II reaction
An example of intramolecular hydrogen abstraction



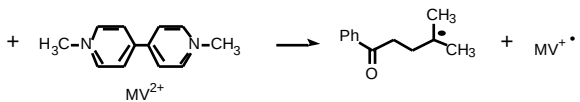
γMeVLP —hν→ Acetophenone (ACP)

Experimental tests for the involvement of biradicals in the Norrish Type II reaction

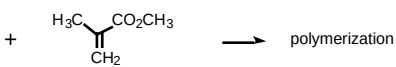
Hydrogen abstraction



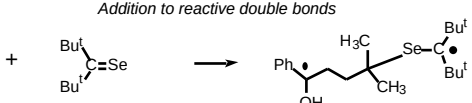
Electron transfer



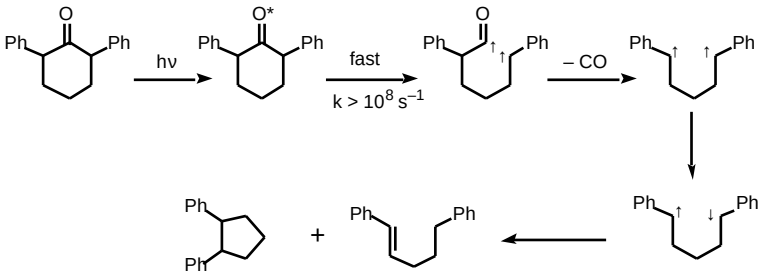
Initiation of polymerization



Addition to reactive double bonds



The Norrish Type I reaction of cyclic ketones



The Norrish Type I reaction of 2,6-diphenylcyclohexane involves the fragmentation of a triplet biradical to another triplet biradical following rapid decarbonylation.

The paradigm for biradical reactions

RULES	Biradical paradigm concepts
Rule # 1	^{1}BR will only yield singlet products
Rule # 2	^{3}BR will only yield triplet products. These reactions are uncommon, unless another biradical is produced (see the example of Scheme nn.11)
Rule # 3	Biradicals undergo monoradical-like reactions with essentially the same rate constants a typical monoradicals. Whether or not these processes dominate will largely depend on the dynamics of biradical-specific reactions (see rule # 4)
Rule # 4	^{3}BR will undergo biradical-specific reactions when they interact with paramagnetic species, such as oxygen, nitroxides and certain transition metal ions
Rule # 5	Intersystem crossing (^{3}BR $\leftrightarrow$ ^{1}BR) plays an important role in biradical reactions. Equilibration is rarely achieved. For triplet biradicals intersystem crossing is frequentl irreversible and determines their lifetime
Rule # 6	The decay of ^{1}BR to molecular products can be fast enough to compete with bond rotations. As a result the partition anong different biradical products may depend on th conformation at which intersystem crossing occurs
Rule # 7	The lifetime of ^{3}BR will depend on the factors that control spin-spin interactions, such as distance, S-T energy gap, and spin-orbit coupleing interactions (these effects will be covered in detail in Chapter zz)
Rule # 8	Structures in which odd electrons are of the same spin are more stable the fusther apart are the location of the unpaired electrons