













intermolecular nyarogen abstractions			
Some hydro	gen abstraction rate co	onstants	
(in units of 10 ⁶ M	⁻¹ s ⁻¹)		
	Benzophenone triplet	(CH ₃) ₃ CO•	
Cyclohexane	0.45	1.6	
Methanol	0.21	0.29	
Benzhydrol	7.5	7.2	
Triethylsilane	9.6	5.7	
Ph2CO* +	R-H→ Ph₂COH	+ R•	



What determines <u>rate constants</u> for hydrogen abstraction?

- Nature of the excited state: n, * states are radical-like and react faster
- Triplet energy high is better
- Strength of the R-H (frequently C-H) bond broken
- · Number of hydrogen atoms available
- Steric effects
- · Polar effects most excited carbonyl states are electrophillic
- In intramolecular examples, the ability to form an unstrained transition state 6-center is good
- · Entropic factors can be quite important in intramolecular cases
- and the usual temperature, solvent, etc.





















all rate constants in units of $10^8 \ M^{-1} s^{-1}$













Compound	k _{CT} , (Mxsec)	-1
Benzene	7.6 x 10 ⁵	
Toluene	4.2 x 10 ⁶	since the more electron rich
Pyridine	6.3 x 10 ⁶	molecules are the best queneners
o-Xylene	2.4 x 10 ⁷	
m-Xylene	3.6 x 10 ⁷	
p-Xylene	4.3 x 10 ⁷	
Durene	5.5 x 10 ⁷	
Anisole	8.4 x 10 ⁷	
Mesitylene	2.4 x 10 ⁸	







Carbonyl triplet addition to electron poor olefins Some general characteristics

- Only S₁ (n, *) forms oxetanes with cyanoethylenes
- The cis-trans isomerization is a side reaction which is not affected by quenching of the S₁ (n, *) state.
- Quenching of the T_1 (n, *) state sensitizes reactions of cyanoethylene, but it does not lead to oxetane (although the reaction does take place with electron rich*olefins).
- Oxetane formation from $S_1(n, *)$ is stereospecific.
- Oxetane formation from $S_1(n, *)$ is regiospecific.





