The Nature of the Triplet State in βγ-Unsaturated Ketones

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Summary The phosphorescence spectra and lifetimes of representative *βγ*-unsaturated ketones at 77 K are indicative of *π*–*π** triplet excited states.

We report a systematic examination of the phosphorescence spectra and lifetimes of some representative *βγ*-unsaturated ketones,[1] and present evidence suggesting that *π*–*π**, not *n*–*π**, triplet states are the photochemically reactive species.

The Table summarizes the triplet energies (0–0 band values), phosphorescent emission maxima, and mean lifetimes for eleven typical $\beta\gamma$-unsaturated ketones of varying stereochemistry and reaction course. The phosphorescence spectra were recorded at 77 K in both ethanol and isopentane glasses, with no sizeable energy or lifetime differences except where noted. The authenticity of the emission spectra was ensured by careful sample purification and was verified by comparison of phosphorescence, excitation, and absorption spectra.

Table

	Compound	Triplet energy[a] (kcal mol^{-1})	Emission maximum (nm)	Mean lifetime[d] (ms)	Acyl shift	Ref.
(1)	3-Methylene-2,2,5,5-tetramethylcyclohexanone	70·7	427[b]	205	[1, 3]	1(c)
(2)	3-Ethylidene-2,2,5,5-tetramethylcyclohexanone	68·9	446	156	[1, 3][f]	1(d)
(3)	Bicyclo[2,2,1]hept-5-en-2-one	69·5	449	190[c]	[1, 2] [1, 3]	6
(4)	Cyclo-oct-3-en-1-one	68·4[b] 68·8[c]	442[b] 480[c]	95[b] 5·4[c]	[1, 3]	5
(5)	2,2-Dimethylcyclohept-3-en-1-one	68·8	445	44	[1, 3]	7
(6)	Chrysanthenone	69·2	465	34	[1, 3]	8
(7)	2,4,4-Trimethyl-6-phenylhex-5-en-3-one	68·8[b]	442[b]	49	[1, 2] [1, 3]	9
(8)	17β-Acetoxy-4β,19-oxidoandrost-5-en-3-one	73·7	440[c]	55[c]	[1, 2]	10
(9)	4,4-Dimethyl-17β-acetoxyandrost-5-ene-3,7-dione	68·9	441	28[e]	[1, 2]	3, 11
(10)	17β-Acetoxy-4,4-dimethyl-19-norandrost-5-en-3-one	68·9	468	48	[1, 2]	10
(11)	Benzobicyclo[2,2,2]octadienone	60·9	504	210	[1, 2] [1, 3]	1(a), 12

[a] From 0–0 phosphorescence band, ±1·5 kcal mol^{-1}, in both ethanol and isopentane glasses at 77 K. [b] In ethanol. [c] In isopentane. [d] Excitation within n–π^* absorption band, experimental uncertainty estimated at 10—15%. [e] Compares with lit[3] value of 32 ms. [f] The triplet reaction is geometrical isomerization.[1d]

The observed range of mean lifetimes suggests π–π^* configurations for all of the emitting triplet states. Although solvent shifts and vibrational spacing in phosphorescence spectra would not in themselves be definitive criteria for the π–π^* configuration, those observed were consistent with this assignment. Shifts of the 0–0 phosphorescence band to longer wavelength by 2—5 nm when ethanol replaced isopentane as the medium were observed for most of the ketones, as expected for emission from triplets of the π–π^* variety. Also, compounds (**1**), (**3**), (**5**), (**7**), (**8**), (**9**), (**10**), and (**11**)† had spectra with typical π–π^* vibrational band progressions averaging between 800—1400 cm^{-1}, whereas n–π^* ketonic triplets generally have vibrational spacing patterns corresponding to carbonyl or olefinic stretching frequencies.[2] The shortest lifetime in this series was the 28 ms observed for compound (**9**), whose π–π^* configuration might therefore seem most in doubt. However, the π–π^* triplet configuration in (**9**) has been confirmed[3] by polarized phosphorescence excitation studies. Thus, although some configuration interaction mixing of n–π^* and π–π^* states is reasonable, the emitting triplet must be regarded as largely π–π^* in nature.

One exception to the long emission lifetimes is compound (**4**). Although the triplet state lifetime in ethanol is consistent with a π–π^* configuration, the lifetime in isopentane is only 5·4 ms. The phosphorescence spectrum shows a different maximum in isopentane, and the vibrational spacing averages 1500 cm^{-1}, perhaps suggesting that an n–π^* triplet now lies lowest. Such a solvent-induced inversion in ordering between nearly degenerate n–π^* and π–π^* levels has been noted to have photochemical reactivity consequences in $\alpha\beta$-unsaturated ketones.[4] In (**4**), however, any possible reordering of lowest triplets from π–π^* in ethanol to n–π^* in isopentane apparently does not materially affect the photoreactivity of (**4**), which rearranges to 2-vinylcyclohexanone in both polar and non-polar solvents.[5]

From the assumption that the reactive triplet in solution phase photochemistry has the same configuration as the lowest triplet in a rigid glass at 77 K, it may be deduced that the dichotomous reactivity of $\beta\gamma$-unsaturated ketones does not derive from either the n–π^* *vs.* π–π^* configuration or the energy of the lowest triplet state.‡ The triplet energies were all closely grouped, [excepting that of (**11**)], between 68—74 kcal mol^{-1}, and all except (**4**) in isopentane were

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† The remaining spectra were too diffuse to permit accurate determination of vibrational band positions.

‡ Alternatively, the photo-sensitized reaction may involve a nonspectroscopic triplet state.

clearly π–π^* triplets, despite the diverging photoreactivities that have been reported.[1]

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