Slow Quenching of Triplet Ketones by Alkyl Thiols

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Summary Butanethiol quenches triplet acetophenone with a rate constant of $1\cdot4 \times 10^7$ M^{-1} s^{-1} which is slow enough to be used for trapping radical products without quenching excited states.

SINCE many photochemical reactions proceed by radical or biradical intermediates, mechanistic studies ideally require a compound which can efficiently trap such radical species without affecting excited states. This note points out the usefulness of alkyl thiols as radical traps in the photoreactions of ketones.

Traditional radical traps such as conjugated olefins, tin hydrides, and iodine quench triplet ketones with rate constants approaching that of diffusion and thus make poor trapping agents for products of triplet ketones. However, we find that butanethiol quenches the phosphorescence of acetophenone relatively slowly.

The room temperature phosphorescence intensities of degassed benzene solutions containing acetophenone (0·0056 M)[1] and various concentrations of butanethiol, [1-^{2}H]butanethiol, or 2,5-dimethylhexa-2,4-diene were measured (Table). The intensity was read directly off the microphotometer of an Aminco–Bowman spectrophotofluorometer. Excitation was at 313 nm; maximum emission intensity was at 420 nm. Each sample was opened and aerated after being measured. The residual emission intensities of the aerated samples were subtracted from the readings obtained on the degassed samples to obtain true phosphorescence intensities.† Division of Φ°/Φ values by quencher concentration yields the $k_q\tau$ values listed in the Table.

Table. *Quenching of acetophenone phosphorescence in benzene solution at* 25 °C

Quencher	Concentration (M)	I_p[a]	Φ°/Φ	$k_q\tau$(M^{-1})
None		100	1·00	—
C_4H_9SH	0·0092	58	1·72	78
	0·0110	54	1·83	75
	0·0184	41	2·46	78
	0·0276	31	3·18	80
				(av = 78 ± 1)
C_4H_9SD	0·012	59	1·86	72
	0·024	36	2·75	74
				(av = 73 ± 1)
Diene	0·000031	56	1·79	26,000
	0·000062	38	2·60	26,000
				(av = 26,000)

[a] Relative phosphorescence intensity.

Several points are clear from our results. First, there is no significant deuterium isotope effect on the quenching ability of the thiol. Therefore we conclude that triplet ketone does not attack a S–H bond but rather probably attacks the nonbonding electrons on sulphur. This conclusion agrees with the charge-transfer quenching mechanism already postulated for sulphides.[2]

Second, the conjugated diene quenches triplet acetophenone 350 times faster than does the thiol. Since k_q is generally assumed to equal 5×10^9 M^{-1} s^{-1} for diene quenching of triplet ketones,[3,4] we estimate τ to equal 5×10^{-6} s under our conditions and the rate constant for thiol quenching to equal $1{\cdot}4 \times 10^7$ M^{-1} s^{-1}. This rate constant is low enough so that low concentrations of thiols will not quench most reactive ketone triplets but can trap radical products. In fact, we have used thiols successfully to trap both the radicals produced by α-cleavage (Norrish type I) of ketones[5] and the biradicals which intervene in type II photoelimination.[6]

Even apart from the practical benefits of the relatively small k_q values for thiols toward triplet ketones, the value itself is most interesting in comparison to the comparable quenching rate constant reported for di-n-butyl sulphide toward triplet benzophenone.[2] The k_q value reported for sulphide quenching is 50 times larger than that reported here for thiol quenching. This large difference must be related to the sizeable difference in ionization potentials[7] between thiols (> 9 eV) and sulphides (<8·5 eV) and is further evidence for the charge-transfer nature of the quenching process.

The slow rate of triplet quenching by thiols suggests that the thiol inhibition of ketone photoreduction does primarily involve radical trapping, in agreement with Cohen's conclusions.[8]

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† Even short irradiation in benzene of acetophenone or other ketones with long-lived triplet states causes the rapid build-up of a fluorescent product.

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