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DIFFERENCES BETWEEN SINGLET AND TRIPLET STATE TYPE II PHOTOELIMINATION OF ALIPHATIC KETONES

Peter J. Wagner

Chemistry Department, Michigan State University,
East Lansing, Michigan 48823

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Ever since it was discovered that both singlet and triplet states of aliphatic ketones participate in Type II photoelimination processes (1), there has been speculation about the relative reactivities of the two excited states. In the original report of polar solvent effects on photoelimination (2), one experiment was described which indicated that t-butyl alcohol enhances the quantum efficiency of only the triplet state of 2-octanone. Barltrop and Coyle have recently confirmed this effect for three aliphatic ketones containing primary, secondary, and tertiary γ C-H bonds (3). This paper describes some results which further differentiate between the behavior of excited singlets and triplets.

In the experiments to be described, degassed solutions 0.4 M in 2-hexanone or 4-octanone were irradiated at 3130 Å and 25° on a merry-go-round apparatus. Yields of product formation were determined by vpc analysis. Quantum yields were measured by parallel irradiation of pentane solutions containing 0.8 M acetone and 0.2 M cis-1,3-pentadiene. The quantum yield of the sensitized cis-to-trans isomerization was taken as 0.555 (4).

Since 4-octanone contains both a primary and a secondary γ site, the relative yields of 2-pentanone and of 2-hexanone obtained upon irradiation provide a measure of the selectivity of the ketone's excited states under a variety of conditions. Table I lists the quantum yields of these two products which were measured in both hexane and t-butyl alcohol solvents with and without added triplet quenchers. Two product peaks corresponding in retention time to the expected cyclobutanols were observed on the vpc traces of the irradiated samples. Rough estimates of the quantum yields of their appearance are also included in Table I. Four of the experiments were run with an excess of triplet quencher present. In each, the same quantum yields of product formation and the same product ratio, within experimental error, were observed. The following facts can be concluded from the results in Table I.

Singlet state: (1) In hexane, 30% of the total photoelimination comes from the singlet

TABLE I. QUANTUM YIELDS OF PRODUCTS FROM 4-OCTANONE

SOLVENT	2-pentanone[a]	2-hexanone[a]	CB[b]	2-P/2-H
hexane	0.164	0.0106	0.035	15.5
" + 2 M dienol[c]	.044	.0037	.0054	12.0
" + 6 M N[d]	.048	-	.0055	-
dichloroethylene	.049	.0041	.007	12.0
t-butyl alcohol	.232	.0127	.043	18.3
" + 2 M dienol[c]	.042	.0034	-	12.4

[a] quantum yields ± 5%. [b] rough estimates based on areas of vpc peaks presumed to be cyclobutanols, accuracy ~ ± 25%. [c] 2,4-hexadienol absorbs some light, therefore quantum yields may be low. [d] singlet reaction sensitized by 1-methylnaphthalene.

state. (2) In hexane, the ratio of photoelimination products resulting from attack on secondary versus primary hydrogens is 12:1 in the singlet state. (3) Both the quantum efficiency and the selectivity of the singlet state are unaffected by t-butyl alcohol.

Triplet state: (1) In hexane, 70% of the total photoelimination comes from the triplet state. (2) In hexane, the secondary/primary selectivity of the triplet state is 17:1. (3) In t-butyl alcohol, the selectivity rises to 20:1 and the quantum efficiency of the triplet state is increased by 67%.

In summary, the triplet state of 4-octanone differs in at least two respects from the singlet: (1) it shows a greater selectivity even in inert solvents, and (2) both its selectivity and quantum efficiency are altered by a polar solvent.

It is worth note that the intramolecular secondary/primary selectivity displayed by both excited states of 4-octanone is higher than might have been predicted from studies of 2-pentanone and 2-hexanone (5). The gas phase behavior of 4-octanone also indicates a high selectivity (6). The fact that the singlet state selectivity is less than that of the triplet state is consistent with the smaller deuterium isotope effect reported for the singlet state of 2-hexanone-5-d (7). The smaller apparent yield of cyclization products from the singlet state compared to the triplet is also consistent with previous studies (7).

Table II contains the quantum yields of acetone obtained from irradiation of 2-hexanone

TABLE II. QUANTUM YIELDS OF PRODUCTS FROM 2-HEXANONE

SOLVENT	acetone[a]	2-hexanol
hexane	0.22 (0.25)	0
hexane + 4M isoprene	0.08 (0.10)	0
hexane + 0.38 M Bu_3SnH	0.12	0.29
hexane + 0.38 M Bu_3SnH + 4M isoprene	0.07	0
t-butyl alcohol	0.37	0
t-butyl alcohol + 4M isoprene	0.08	0

[a] Values in parentheses are those reported in ref. 7.

under various conditions. Again, substitution of *t*-butyl alcohol for hexane as solvent doubles the quantum yield of triplet state photoelimination but has no effect on the singlet yield. The intersystem crossing yield of 2-hexanone is 0.60, so that half the triplet state undergoes photoelimination in *t*-butyl alcohol. Addition of tri-*n*-butylstannane produces only a slight decrease in singlet state yield but a substantial decrease in the triplet yield. The decrease in triplet state photoelimination is attended by formation of the photoreduction product 2-hexanol (8). It is very significant that no photoreduction takes place from the singlet state and that the amount which takes place from the triplet is double the amount of triplet photoelimination which takes place in the absence of the stannane. The latter phenomenon is another manifestation of the low efficiency inherent in photoelimination processes (9).

The polar solvent effects on triplet state photoelimination most likely reflect solvation of a reasonably long-lived hydroxybiradical intermediate (10). The lack of such solvent effects on singlet state photoelimination indicates either (1) that no such biradical intermediate is involved or (2) that any biradical intermediate is extremely short-lived. The lower selectivity of the singlet compared to the triplet indicates that either (1) the singlet state is somewhat more reactive, if both states react by simple hydrogen abstraction to yield a biradical, or (2) the singlet state reacts by another, probably concerted, mechanism. Previously estimated rate constants for triplet state photoelimination (5) and photoreduction by stannane (8) suggested that the two processes should be competitive, as has now been observed. Singlet state photoreduction is so slow that it does not compete with photoelimination or with intersystem crossing. If the rate of intersystem crossing of 2-hexanone is the same as that of acetone, around 2×10^8 sec^{-1} (8, 11), the rate of its singlet state photoelimination is $0.3\text{-}1.3 \times 10^8$ sec^{-1}. Yang also has estimated that the value lies near 10^8 sec^{-1} (12). Since at least half the triplets of 2-

hexanone react, the minimum rate constant for triplet state reaction is 5×10^8 sec^{-1} (5), a somewhat larger value than Yang estimated (12). More exact values cannot be assigned because the extent to which the singlet and triplet state photoeliminations of aliphatic ketones involve reversible processes is not yet known. In any event, it is probable that the triplet state reaction is 3-10 times more rapid than the singlet state reaction, a conclusion which Wettack and Noyes have also reached (13). If singlet state photoelimination does proceed by hydrogen atom abstraction to yield a 1,4-biradical, it is remarkable that the singlet state reaction is both slower and less selective than the triplet state reaction and even more remarkable that the intramolecular/intermolecular hydrogen abstraction competition should be so different for the two states. All these facts taken together suggest that photoelimination occurs by different mechanisms in the singlet and triplet manifolds.

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