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POLAR SOLVENT ENHANCEMENT OF THE QUANTUM EFFICIENCY OF TYPE II PHOTOELIMINATION

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The solvent dependence of quantum yields and product distributions of photochemical reactions has become a subject of keen interest (1). Type II photoelimination, whereby ketones bearing γ C-H bonds split into enols and olefins, is remarkably inefficient (2-4) and much recent speculation about its mechanism has appeared (3-6). It has been reported that the quantum yields for photoelimination of several butyrophenones are insensitive to the nature of the solvent (3). It has also been reported that quantum yields of Type II processes in esters are depressed by polar solvents (7). It has now been found that, on the contrary, the quantum efficiency of Type II photoelimination of both aromatic and aliphatic ketones is enhanced appreciably by polar solvents. Moreover, this finding provides further strong evidence for the intermediary of biradicals in this photoreaction.

Degassed solutions of 0.2 M butyrophenone, valerophenone, or 2-octanone in various carefully purified solvents were irradiated in parallel on a merry-go-round apparatus (8). The 3130 Å line of a Hanovia 450 watt mercury arc was isolated by a 1 mm. path of 0.002 M potassium chromate in 1% aqueous potassium carbonate. Known concentrations of inert internal standards such as tetradecane permitted relative quantum yields of acetophenone formation or of ketone disappearance to be measured by glpc analysis. In the case of the phenyl ketones, absolute quantum yields were determined by parallel irradiation of benzophenone-benzhydrol actinometer solutions (9). In the case of 2-octanone, solutions containing 2M 2,5-dimethyl-2,4-hexadiene to quench all triplet reaction (6,10) were also irradiated, and light intensity was gauged by measuring the amount of acetone-sensitized isomerization of <u>trans</u>-to <u>cis</u>-piperylene (8). Table I summarizes the results.

Both butyrophenone and valerophenone react solely from their triplet states (3,6). In both cases, quantum yields for disappearance of ketone are enhanced by polar solvents, approaching unity in t-butyl alcohol. The rate at which triplet butyrophenone reacts is sufficiently slow (3,6) that hydrogen abstraction from reactive solvents would be expected

TABLE I

Solvent Effects on Quantum Yields for Ketones Undergoing Photoelimination

Ketone	Solvent	Φ-Ketone	Φ+PhCOCH$_3$
Butyrophenone	Benzene	0.40	.34
	Hexane	0.39	.27
	MeOH	0.80	.35
	t-BuOH	1.00	.86
	CH_3CN	0.90	.81
Valerophenone	Benzene	.42	.36
	Hexane	-	.40
	Hexane-1/2% t-BuOH	-	.46
	" 1% t-BuOH	-	.52
	" 2% t-BuOH	-	.57
	" 10% t-BuOH	-	.77
	" 20% t-BuOH	-	.85
	t-BuOH	1.00	.88
	CH_3CN	-	.85
	EtOH	-	.68
2-Octanone[a]	Hexane	.50	-
	Hexane + diene	.20	-
	t-BuOH	.89	-
	t-BuOH + diene	.19	-

[a] quantum yields corrected for slightly different absorbances in the two solvents,

to be competitive and to decrease acetophenone yields. This effect is particularly noticeable in methanol, and a large glpc peak with the retention time of ethylene glycol provides further evidence for competing photoreduction. It is merely a coincidence that the quantum yield for acetophenone formation is the same in both benzene and methanol.

The rate at which triplet valerophenone reacts is quite fast, on the order of $10^8 sec^{-1}$ (6), so that even in ethanol, in which the rate of photoreduction would be expected to be $\sim 10^7 sec^{-1}$(11), the quantum yield of acetophenone formation is only slightly below that found in t-butyl alcohol. In the latter solvent, glpc analysis revealed an 88% yield of acetophenone and 12% of the 1-phenyl-2-methylcyclobutanols. Griffin has reported an 85:15 ratio from the irradiation of valerophenone in acetone (12).

Aliphatic ketones such as 2-octanone have been shown to undergo Type II photoelimination from both singlet and triplet excited states (6,10). When t-butyl alcohol replaces hexane as solvent, the total quantum yield for disappearance of 2-octanone almost doubles. It is noteworthy that apparently all the enhanced reactivity involves triplet state ketone, since no solvent effect is observable for the samples containing 2 M diene in which only singlet state reaction can occur. This result suggests very strongly that the inefficiency arises solely from the triplet state.

Coulson and Yang (4) recently reported that γ-deuterium atoms increase the lifetime of triplet 2-hexanone but also increase the quantum yield of its Type II photoelimination, thus demonstrating that γ hydrogen atoms are involved in whatever radiationless decay process is responsible for the normally low quantum efficiency. The polar solvent effects are consistent only with the hypothesis that a 1,4-biradical intermediate intervenes in at least triplet state photoelimination reactions (5) and that reversible γ-hydrogen transfer provides the pathway for radiationless decay (6). Stern-Volmer plots of the quenching of valerophenone photoelimination reveal that the lifetime of the triplet ketone is twice as long in t-butyl alcohol as in hydrocarbon solvents. Consequently the polar solvent effect must involve a decrease in radiationless decay rather than an increased reactivity of the excited state. It is entirely reasonable, if not readily predictable, that the hydroxyl proton of the postulated biradical intermediate would get so involved in hydrogen bonding to a polar solvent that its otherwise efficient return to the γ-carbon would be impeded long enough for $\alpha-\beta$ bond cleavage and cyclization to occur almost exclusively.

An alternate possibility (4), which could not be ruled out by any previous evidence, would be that some particularly effective vibronic coupling with γ C-H bonds deactivated the excited triplet directly. In order to fit the observed solvent effects into this explanation, it would be necessary to postulate that polar solvents solvate the carbonyl group of ketone triplets so as to prevent thephysical interaction with the γ C-H bonds while not retarding the chemical reaction. Apart from the inherent unlikelihood of such a scheme, there is good experimental evidence against it. Krishna and Goodman (13) and Baba, Goodman, and Valenti (14) have shown that the n,π* excited states of diazines are not hydrogen bonded in alcoholic solvents. Analogous behavior would be expected for ketones, since it is well established that the carbonyl oxygen becomes electron deficient in n,π* triplets. Thus the blue shift of n,π* bands caused by polar solvents is generally ascribed to the instability

of hydrogen bonded excited states.

Several mixed t-butyl alcohol-hexane solutions of valerophenone were irradiated to determine what concentrations of alcohol are necessary to affect the quantum yield of acetophenone formation, with the rather striking results included in Table I. Even 0.5% alcohol produces a sizeable enhancement of Φ_{II}, indicating that 10% of the triplets which would not have reacted in hexane do so although only 5-10 collisions with alcohol molecules can occur in the lifetime of the triplet. Given the fact that n, π * triplets are not readily hydrogen bonded and the unlikelihood that solvation of the triplet could produce the observed solvent effects anyway, it seems that a biradical intermediate must be formed and can be protected from reverse hydrogen transfer by polar solvents.

The fact that t-butyl alcohol has no affect on the quantum yield of singlet state photoelimination in 2-octanone suggests that a different mechanism might be responsible for singlet state reaction. This possibility is being explored further.

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