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SINGLET AND TRIPLET PARTICIPATION IN THE INTRAMOLECULAR PHOTOCHEMISTRY OF SIMPLE ALKANONES

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The intramolecular photoreactions of aryl alkyl ketones proceed solely through the triplet state, and the quantum yield increases to near unity in hydroxylic solvents(1-3). This increase is attributed to the solvation of a hydroxy biradical intermediate of the type $R.\dot{C}(OH).CH_2.CH_2.\dot{C}R'R''$(I), which is the intermediate in both the product-forming reactions and the radiationless decay process by which the triplet is deactivated to the ground state. The Norrish type II reaction of alkyl ketones has been shown(2) to proceed partly through the triplet and partly through the singlet excited state, and it is of interest to know whether the singlet reaction is similarly affected by the nature of the solvent. The ketones we used were pentan-2-one ($CH_3.CO.CH_2.CH_2.CH_3$), octan-2-one ($CH_3.CO.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$), and 5-methylhexan-2-one ($CH_3.CO.CH_2.CH_2.CH(CH_3)_2$), which have respectively a primary, a secondary and a tertiary hydrogen atom involved in the ntramolecular reactions, and the rate constants for hydrogen-abstraction f the three types of hydrogen were estimated.

Solutions of the ketones (0.1 - 0.5M) were irradiated in a roundabout apparatus with light λ = 313 mµ. Analysis by v.p.c. coupled with benzophenone-benzhydrol actinometry gave the absolute quantum yields for disappearance of starting material and for the formation of cyclobutanol. The results, set out in Table I, show that the overall quantum yield for disappearance is enhanced and approaches unity in hydroxylic solvents, whereas the quantum yield which can be ascribed to singlet reaction is unaffected by a change of solvent.

TABLE I

Solvent	Pentan-2-one	Octan-2-one		5-Methylhexan-2-one	
	ϕ_{-K}	ϕ_{-K}	ϕ_{+C}	ϕ_{-K}	ϕ_{+C}
Benzene	0.43	0.47	0.045	0.49	0.059
" + diene	0.06	0.20	0.003	0.27	0.006
Cyclohexane	-	-	-	0.47	0.047
" + diene	-	-	-	0.24	0.008
Methanol	-	1.00	0.060	1.00	0.089
" + diene	0.06	0.21	0.002	0.29	0.006
t-Butanol	0.85	0.84	0.086	0.78	0.108
" + diene	0.05	0.20	0.004	0.24	0.008

ϕ_{-K} refers to the quantum yield for disappearance of starting ketone, and ϕ_{+C} to that for appearance of cyclobutanol.

The singlet reaction is observed by quenching the triplet reaction with approximately 5M 1,3-pentadiene. The mixed solvent will still efficiently solvate the hydroxy biradical intermediate (I), for Wagner (3b) has shown that a few percent of alcohol in a non-polar solvent is sufficient to enhance the triplet quantum yield considerably. Our data suggest that the triplet reaction proceeds through a hydroxy biradical intermediate (I) which is sufficiently long-lived for solvation of the hydroxyl group to occur, whereas the singlet reaction does not go through such an intermediate.

In order to determine the rate constants k_r for triplet hydrogen-abstraction, the quantum yields for ketone disappearances were determined in benzene solution with varying concentrations of 1,3-pentadiene as triplet quencher. For each of the three ketones it was found that the quantum yield for triplet reaction could be expressed as a Stern-Volmer type of equation $(\phi_o/\phi)_{triplet} = 1 + k_q [Q]/k_r$ where k_q is the quenching rate constant and [Q] is the concentration of triplet quencher. The values of k_q/k_r were found to be 5 for 5-methylhexan-2-one, 33 for octan-2-one, and 44 for pentan-2-one. The triplet quantum yield for cyclobutanol formation from the first two ketones follows the same equations, as expected, with k_q/k_r = 6 and 29 respectively. The cyclobutanol from pentan-2-one could not be accurately determined under the experimental conditions used.

The important points arising out of these results are firstly that in triplet excited states of aliphatic ketones intramolecular abstraction of a tertiary hydrogen atom is faster than that of a secondary, which in turn is faster than abstraction of a primary hydrogen. If we assume a value of 5×10^9 $1.\text{moles}^{-1}\text{sec.}^{-1}$ (footnote in ref.2) for the diffusion-controlled quenching rate constant (k_q), then the estimated values of the rate constant for hydrogen-abstraction (k_r) are 1×10^8, 2×10^8, and 1×10^9 sec.^{-1} respectively for primary, secondary and tertiary hydrogen atoms in the systems studied. This order presumably reflects the different C-H bond strengths. Secondly, the ratio of singlet to triplet reaction increases as the rate constant for triplet hydrogen-abstraction increases, suggesting that the rate constant for singlet hydrogen-abstraction also increases in the same order, if the rate constant for intersystem-crossing is assumed to be the same for these three ketones.

References

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