Determination of the Reactivity of First Excited Singlet States of Organic Compounds toward Unimolecular Primary Photochemical Processes from Molecular Fluorescence Characteristics. Application to Intramolecular γ-Hydrogen Abstraction Reactions of Alkyl Ketones[1a,b]

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Abstract: An experimental test is given of the often-cited theoretical formula (eq 3) relating the inherent fluorescence lifetime to the integrated intensity of the absorption band. The photochemical results of Yang and coworkers provide a totally independent check of our results. The good agreement between rates based solely on our spectroscopic results and the photochemical data of Yang demonstrates the utility and validity of molecular fluorescence characteristics as a probe for photochemical mechanisms.

Considerable information on the reactivity of the first excited singlet state (S_1) of organic molecules toward unimolecular primary photoprocesses can be obtained from a study of molecular fluorescence properties. The key to this application is the fact that a unimolecular primary photochemical process occurring from S_1, with a rate constant $k_r{}^s$, will normally compete with the primary photophysical processes of intersystem crossing (k_{st}), fluorescence (k_f), and internal conversion to the ground state (k_s) for deactivation of excited singlet states. Thus, the introduction of a photochemical process in a molecule will result in a decrease in both the excited-singlet-state lifetime (τ_s) and the fluorescence quantum yield (ϕ_f), relative to a suitable model compound in which the photochemical process is absent. This can be seen readily from eq 1 and 2, which give expressions for τ_s and ϕ_f, respectively.

$$\tau_s = \frac{1}{k_f + k_{st} + k_s + k_r{}^s} \qquad (1)$$

$$\phi_f = \frac{k_f}{k_f + k_{st} + k_s + k_r{}^s} = k_f\tau_s \qquad (2)$$

Clearly, τ_s will be longer and ϕ_f larger for the model compound in which the primary photochemical process of interest is absent (*i.e.*, $k_r{}^s \ll$ other k's). Quantitatively, if the sum of k_f, k_{st}, and k_s is constant, then the increase in the decay rate ($1/\tau_s$) of S_1 can be equated with the rate constant for the primary photochemical process.

In the absence of a direct measurement of the excited-singlet-state lifetime an approximate τ_s value can be calculated (eq 2) from the measured fluorescence quantum yield and the rate constant for fluorescence (k_f). For a symmetrical band, the value of k_f can be estimated[2] from the ultraviolet absorption spectrum using

$$k_f = \nu_m{}^2\epsilon_{max}\Delta\nu_{1/2}/(3.5 \times 10^8) \qquad (3)$$

where $\gamma_m{}^2$ is the mean frequency (cm^{-1}) for the absorption band, ϵ_{max} is the maximum extinction coefficient for the absorption band, and $\Delta\nu_{1/2}$ is the half-width of the absorption band (cm^{-1}). In cases where the compound of interest and the model compound have very similar uv spectra (ν_m, ϵ_{max}, $\Delta\nu_{1/2}$), the k_f values will clearly be similar and τ_s will be directly proportional to ϕ_f. Thus, although it is preferable to measure excited-singlet-state lifetimes, information on the reactivity toward unimolecular primary photochemical processes can also be obtained from relative quantum yields of fluorescence.

Results and Discussion

As a test of the validity of this technique, we have used the fluorescence characteristics of a series of acyclic alkyl ketones to determine the reactivity ($k_r{}^s$) of their S_1 states toward the intramolecular γ-hydrogen abstraction process. Our results are compared to those of Yang and coworkers[3] who have recently measured the $k_r{}^s$ values for several of these ketones by chemical-quenching techniques.

The measured relative quantum yields of fluorescence for 2-butanone (**1**), 2-pentanone (**2**), 2-hexanone (**3**), 5-methyl-2-hexanone (**4**), and 5,5-dimethyl-2-hexanone (**5**) are given in Table I. It is apparent that the introduction of a photochemical pathway, intramolecular γ-hydrogen abstraction (or interaction with the γ hydrogens), for deactivation of the first excited singlet state of these alkanones leads to substantial reductions in the fluorescence quantum yields. As we would expect,[3] the relative fluorescence quantum yields decrease with decreasing γ-C–H bond strength as the γ hydrogen goes from primary to tertiary. Significantly, when the γ hydrogens are all replaced with

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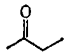
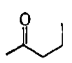
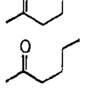
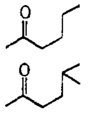
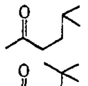
(1) (a) Molecular Photochemistry. XL. Paper XLI: K. Dawes, J. C. Dalton, and N. J. Turro, *J. Amer. Chem. Soc.*, submitted for publication. (b) The authors wish to thank the Air Force Office of Scientific Research (Grants No. 68-1381 and 70-1848) for its generous support of this work. In addition, acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. (c) NIH Predoctoral Fellow, Columbia University, 1967–1970; Chemistry Department, University of Rochester, Rochester, N. Y. 14627.

(2) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 48.

(3) N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, 91, 7551 (1969).

Table I. Comparison of Photochemical and Spectroscopic Calculations for Type II Photoreactions[a]

Molecule		ϕ_f^{rel}	τ_s^{rel}	τ_s, nsec	k_r^s(this work), sec^{-1}	k_r^s(Yang), sec^{-1}
	(1)	1.00	1.00	2.5		
	(2)	0.82	0.72	1.8	1.5×10^8	1.8×10^8
	(3)	0.39	0.32	0.81	8.4×10^8	9.9×10^8
	(4)	0.17	0.14	0.35	2.5×10^9	2.1×10^9
	(5)	1.02				

[a] Relative quantum yields of fluorescence for the ketones were obtained in *n*-hexane solution (~0.1 *M*) using an Aminco–Bowman spectrofluorometer. Correction was made for small differences in absorbance at the excitation wavelength, 313 nm.

methyls (**5**), the relative fluorescence quantum yield undergoes a large increase to a value near unity. This implies that intramolecular abstraction of δ hydrogens does not compete favorably with intersystem crossing in the S_1 state of **5**. Irradiation of **5** has been reported to result only in intermolecular photoreduction.[4]

Although the position and shape of the uv absorption bands of ketones **1–5** are all very similar, ϵ_{max} does increase with increasing methyl substitution. An increase in ϵ_{max} would result in a larger value of k_f (eq 3) and thus a higher quantum yield of fluorescence (eq 2). In order to normalize for this effect, we have used eq 4 to obtain the relative singlet lifetimes (τ_s^{rel})

$$\tau_s^{rel} = \phi_f^{rel}/\epsilon_{max} \qquad (4)$$

reported in the table. The absolute singlet lifetimes (τ_s) were calculated from the τ_s^{rel} values and the singlet lifetime of 2-pentanone, which we have measured by single-photon counting[5] to be 1.8×10^{-9} sec. Since for alkyl ketones $k_{st} \gg k_f$, and Yang[3] has shown that k_{st} for this series is insensitive to substitution at the γ carbon, we can attribute the decrease in τ_s as we go from **1** to **4** to some special interaction of the n,π* excited singlet state with the γ-C–H bond. Thus, the k_r^s(this work) values given in the table are the increase in the S_1 decay rate ($1/\tau_s$) relative to 2-butanone (**1**). Since these k_r^s values do not distinguish a chemically productive interaction of the n,π* S_1 state with the γ hydrogen from a physical, nonchemically productive interaction, they should be compared to the sum (k_r^s(Yang)) of Yang's rate constants[3] for type II and nonradiative decay from the first excited singlet state. If all the nonradiative decay results from reversion of an initially formed 1,4 biradical to the starting ketone, then k_r^s represents the reactivity toward the initial γ-hydrogen abstraction from S_1.

The agreement between the k_r^s values determined in this work and those determined by Yang and coworkers[3] by chemical-quenching techniques is excellent and clearly demonstrates the applicability and value of using the fluorescence characteristics of compounds to extract information on the reactivity of excited singlet states toward primary photochemical processes. The data also indicate that eq 3 is valid to a reasonable degree of precision for calculating relative k_f values. Attempts to use such a formula to calculate absolute k_f values appears to be accurate only for order of magnitude estimates.[6]

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(4) N. C. Yang, "Reactivity of the Photoexcited Organic Molecule," Wiley, New York, N. Y., 1967, p 149.

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Mass Spectrometric Study of the Reactions of the Hydroxyl Radical with Ethylene, Propylene, and Acetaldehyde in a Discharge-Flow System

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Abstract: The reaction of hydroxyl (OH) radicals with ethylene (C_2H_4), propylene (CH_3CHCH_2), and acetaldehyde (CH_3CHO) has been studied mass spectrometrically in a discharge-flow system at 300°K. Bimolecular rate constants for these reactions are: $k_{OH+C_2H_4} = 1.8 \times 10^{-12}$, $k_{OH+CH_3CHCH_2} = 1.7 \times 10^{-11}$, and $k_{OH+CH_3CHO} = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}. These OH radical reactions are much faster than the corresponding O atom reactions and should play an important role in photochemical smog and in combustion. In OH + C_2H_4 and OH + CH_3CHCH_2, the OH adducts have been observed directly. The overall reaction mechanisms are discussed briefly on the basis of qualitative product analysis.

Reactions of OH radicals with olefins and with aldehydes are of current interest because of their role in combustion[1] and in photochemical smog. In particular, reactions of OH with unsaturated compounds have been proposed as an important chain-propagating step in photochemical oxidations.[2,3] However, the

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(2) D. H. Stedman, E. D. Morris, Jr., E. E. Daby, H. Niki, and B. Weinstock, 160th National Meeting of the American Chemical Society, Chicago, Ill., 1970, Abstract No. WATR 26.