

Finally, it should be noted that the observed substituent effects do not correlate with uv spectra. It is well known that in the L_a second excited singlet of benzene, to which the lowest triplet corresponds, interaction between an electron-donating substituent and an electron-withdrawing substituent is strongest when the substituents are *para*.¹² Murrell has pointed out that such charge-transfer interaction should be much less important in 3L_a states than in the much higher lying 1L_a states.¹³ Consequently, Porter's correlation of substituent effects on photoreactivity with those on absorption spectra¹⁴ probably is safe only in cases of very strong charge-transfer interaction.

(12) J. Petruska, *J. Chem. Phys.*, **34**, 1120 (1961).

(13) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co., Ltd., London, 1963, p 302.

(14) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

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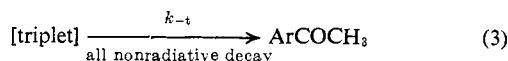
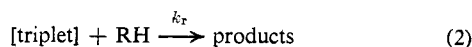
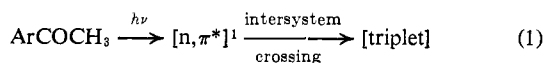
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Correlation between the Photochemical Reactivity and the Nature of Excited States of Acetophenone and Substituted Acetophenones

Sir:

In an earlier communication from our laboratory¹ we found that methylated acetophenones exhibit a low-lying $[\pi, \pi^*]^3$ state (3L_a), yet they undergo photoreduction in 2-propanol with substantial quantum efficiency. Their photochemical reactivities in terms of quantum yields of photoreduction may be qualitatively correlated to their radiative lifetimes, *i.e.*, the shorter the radiative lifetime, the higher the photochemical reactivity. Since the quantum yield (Φ_0) of this photochemical process may be expressed as the ratio of the rate of the photochemical process ($k_r[RH]$) to the sum of the rate of the photochemical process and the rates of all nonradiative decay processes (k_{-t}) (eq 4), the substantial quantum yield of photoreduction of methylated acetophenones may be the result of the variations of both rates, $k_r[RH]$ and k_{-t} .



$$\Phi_0 = \frac{k_r[RH]}{k_r[RH] + k_{-t}} \quad (4)$$

In the current communication we wish to demonstrate that the methylated acetophenones with a low-lying $[\pi, \pi^*]^3$ state are less reactive than acetophenone, yet they also exhibit slower nonradiative decay processes. In addition, we wish to suggest that the reactivity of $[\pi, \pi^*]^3$ states of methylated acetophenones depends on the extent of their mixing with the cor-

responding n, π^* states, most probably through vibronic coupling with the $[n, \pi^*]^3$ state in addition to spin-orbital coupling with the $[n, \pi^*]^1$ state.

In this investigation, the rate constants for photoreduction and those for radiationless decays of four compounds, *p*-trifluoromethylacetophenone, acetophenone, *p*-methylacetophenone, and 3,4-dimethylacetophenone, were determined. The determinations were carried out in degassed solutions of these compounds (0.2 *M*) in benzene containing 2.0 *M* 2-propanol and a variable amount of *cis*-1,3-pentadiene (99%) as the quencher. The wavelength of excitation light is at 3130 Å; the apparatus used has been described previously.^{2,3} Linear Stern-Volmer plots were obtained in all cases within experimental errors. From the familiar expressions

$$\frac{\Phi_0}{\Phi} = 1 + k_q[Q]\tau$$

and

$$\frac{1}{\Phi} = \frac{k_r[RH] + k_{-t}}{k_r[RH]} + \frac{k_q[Q]}{k_r[RH]}$$

where Φ is the quantum yield of the photoreduction in the presence of a quencher, $[Q]$ is the quencher concentration, $[RH]$ is the concentration of 2-propanol, τ is the mean lifetime of the excited state, and k_q is the quenching constant taken as 5×10^9 l. mol⁻¹ sec⁻¹, we obtained the data summarized in Table I.

The data clearly indicate that acetophenones with a low-lying $[n, \pi^*]^3$ state are substantially more chemically reactive but have faster nonradiative decay processes, while acetophenones with a low-lying $[\pi, \pi^*]^3$ state are less chemically reactive but have slower nonradiative processes. The data also suggest that an electron-withdrawing group (CF_3) will reduce the coupling between the $[n, \pi^*]^3$ state and the π, π^* states and thus will enhance the photochemical reactivity of a $[n, \pi^*]^3$ state; electron-donating groups will reduce the coupling between the $[\pi, \pi^*]^3$ state and the n, π^* states and thus will decrease the photochemical reactivity of a $[\pi, \pi^*]^3$ state.¹

Most aromatic carbonyl compounds with a low-lying $[\pi, \pi^*]^3$ state are quite unreactive in photochemical reactions, and they also have relatively long radiative lifetimes. The enhanced photochemical reactivity of $[\pi, \pi^*]^3$ states of methylated acetophenones is generally accompanied by a shortened radiative lifetime of this state.¹ Both observations may be attributed to the mixing of the $[\pi, \pi^*]^3$ state with n, π^* states. The $[\pi, \pi^*]^3$ state is spin-orbitally coupled with the $[n, \pi^*]^1$ state⁴ and vibronically coupled with the $[n, \pi^*]^3$ state.⁵ Since we observed that the energy level of the $[n, \pi^*]^1$ state does not vary appreciably among methylated acetophenones (Table II), spin-orbital coupling between the $[\pi, \pi^*]^3$ state and the $[n, \pi^*]^1$ state of these compounds is insufficient to account for the variation of

(2) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(3) Under the current experimental conditions, the light intensity used varied from 2.1×10^{16} to 2.0×10^{17} quanta/(min cm²); we found that the effect of intensity on the quantum yield is minimal or within experimental error.

(4) M. A. El-Sayed, *J. Chem. Phys.*, **36**, 573 (1962); **38**, 2834, 3032 (1963).

(5) A. A. Lamola, *ibid.*, **47**, 4810 (1967).

(1) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Am. Chem. Soc.*, **89**, 5466 (1967).

Table I

Compound	Φ_0^a	$\tau \times 10^7$ sec	$k_r \times 2 M \times 10^{-4}$ sec $^{-1}$	$k_{-t} \times 10^{-6}$ sec $^{-1}$
<i>p</i> -Trifluoromethylacetophenone	0.72	1.31	552.0 \pm 1.0 ^b	21.0 \pm 2.2 ^b
Acetophenone	0.35	4.07	86.6 \pm 2.2 ^c	15.9 \pm 0.6 ^c
<i>p</i> -Methylacetophenone	0.33	42.3	7.88	1.58
3,4-Dimethylacetophenone	0.069	41.0	1.68 \pm 0.18 ^b	2.27 \pm 0.58 ^b

^a The quantum yield of acetone formation in benzene containing 2 M 2-propanol. ^b The value represents the average of two runs. ^c The value represents the average of three runs.

Table II

Compound	Max, m μ	[<i>n</i> , π^*] ³			[π , π^*] ³		τ_{phos} , sec ^a	
		[<i>n</i> , π^*] ¹ 0-0 band, ^{b,c} m μ	Emis- sion, ^{d,e} m μ	Absorp- tion, ^{b,e} m μ	Emission, ^{d,e} m μ	Absorp- tion, ^{b,f} m μ	In EPA	In methyl- cyclohexane
<i>p</i> -Trifluoromethylacetophenone	333	360	397	384	(383) ^g	0.0007	0.0007	
Acetophenone	326	356	386	372	(373) ^g	0.004 ^h	0.003	
						0.03		
<i>p</i> -Methylacetophenone	325	352		368	392	0.084	0.027	
3,4-Dimethylacetophenone	325	352		367	399	0.17	0.060	

^a Measured at 77°K. ^b By the phosphorescence excitation method; D. R. Kearns and W. A. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966); the accuracy is estimated to be ± 2 m μ . ^c In methylcyclohexane. ^d 0-0 band position; the accuracy is estimated to be ± 1 m μ . ^e In EPA. ^f In EPA-EtI. ^g Calculated. ^h The decay is nonexponential; see N. C. Yang and S. L. Murov, *J. Chem. Phys.*, **45**, 4358 (1966).

their radiative lifetimes and chemical reactivities.¹ However, methylated acetophenones exhibit a [*n*, π^*]³ state slightly above the low-lying [π , π^*]³ state (Table II),¹ and the variation of *n*, π^* character in the [π , π^*]³ state of these compounds may thus be attributed to the vibronic coupling of the [π , π^*]³ with the corresponding [*n*, π^*]³ state in addition to the spin-orbital coupling with the [*n*, π^*]¹ state.

Since the extent of coupling between two states will depend on the energy gap between them, the coupling will increase as the energy gap decreases. The energy level of an *n*, π^* state will shift to the red slightly when the medium is changed from EPA, a polar one, to methylcyclohexane, a nonpolar one, while the energy level of a [π , π^*]³ state exhibits little solvent dependence. The energy gaps between the low-lying [π , π^*]³ state and both the [*n*, π^*]³ and [*n*, π^*]¹ states of methylated acetophenones will therefore decrease when the medium is changed from EPA to methylcyclohexane. This medium change should cause an increased mixing of the [π , π^*]³ state with both the [*n*, π^*]³ and the [*n*, π^*]¹ states, and consequently an increased *n*, π^* character of the low-lying [π , π^*]³ state. This supposition is verified by our experimental observation that the phosphorescence lifetimes of methylated acetophenones are invariably shorter in methylcyclohexane than in EPA.⁶ *We conclude, therefore, that the enhanced photochemical reactivity of the low-lying [π , π^*]³ state of methylated acetophenones may be at least in part attributed to the vibronic coupling of the [π , π^*]³ state with the closely spaced [*n*, π^*]³.*

(6) This was found to be the case also for *m*-methylacetophenone, 3,5-dimethylacetophenone, and 3,4,5-trimethylacetophenone: S. L. Murov, Ph.D. Thesis, University of Chicago, 1966.

(7) The authors wish to thank the National Science Foundation for the support of this work, Professor D. S. McClure and Professor E. C. Lim for some valuable suggestions, and Dr. S. L. Murov for his preliminary investigation, criticism, and stimulation.

(8) NDEA fellow, University of Chicago, 1966-1968.

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Molecular Structure and Photochemical Reactivity. VIII. Type II Photoelimination of Alkenes from Alkyl Phenyl Ketones. Effects of Varying the Alkyl Group

Sir:

In a system in which two competing photochemical primary processes arise from the same excited state and one process leads to the formation of an unstable species that very rapidly reverts back to the parent molecule, the observed over-all quantum yield of the "stable" product is clearly not a valid measure of the "reactivity" of the precursor excited state. While this point has been made for the type II photoelimination process in two different pairs of ketones with γ -H atoms^{1,2} and for a general case in which the unstable chemical intermediate competes with several possible processes,³ the effects of introducing alkyl substituents on the γ -carbon atom of *n*-butyrophenone illustrate this particularly well. The relative insensitivity of Φ_{II} to γ -alkyl substitution (a small decrease is noted) contrasts dramatically with the large increase in the rate of the γ -hydrogen atom transfer.⁴⁻⁶

The ketones listed in Table I were purified, generally by vapor-phase chromatography, and degassed 0.10 M solutions in benzene were irradiated at 3130 Å and 27°, using a merry-go-round apparatus. Yields of acetophenone (1% conversion) were measured by vapor-phase chromatographic analysis. A 0.10 M solution of *n*-butyrophenone in benzene was used as actinometer.

(1) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966).

(2) D. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(3) J. N. Pitts, Proceedings of the 13th Conference on Chemistry at the University of Brussels, Oct 1965; published as "Reactivity of the Photoexcited Organic Molecule," Interscience Division of John Wiley & Sons, Inc., New York, N. Y., 1967, p 115. Professor G. S. Hammond made a similar point at this conference.

(4) For review see P. J. Wagner and F. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(5) J. N. Pitts, Jr., 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, No. P142.

(6) Similar conclusions, reached independently, were reported at the 155th National Meeting, of the American Chemical Society San Francisco, Calif., April 1968, by P. J. Wagner and A. E. Kemppainen (Abstracts, No. P113) and are being published.¹