Deactivation of the Triplet States of Phenyl Ketones by Electron-Donating Ring Substituents[1]

Sir:

Yang and McClure have recently reported that methyl and methoxy substituents lower the quantum yield for photoreduction of acetophenone.[2] We wish to report quenching studies which permit disentanglement of such substituent effects on the various competing processes of the excited triplet states of phenyl ketones.

The ketones listed in Table I were irradiated at 3130 Å as 0.10 M benzene solutions containing varying amounts of 2,5-dimethyl-2,4-hexadiene as quencher. Product yields at 5% or lower conversion were determined by glpc analysis. Absolute quantum yields for appearance of acetophenones (Φ_{II}) were determined by parallel irradiation of acetophenone–piperylene actinometer solutions.[3] Stern–Volmer plots were linear with the slopes listed in Table I as $k_q\tau$ values. In general, *meta* substitution produces the larger decreases in quantum yield while *para* substitution produces the larger increases in triplet-state lifetime. The variations in quantum yield parallel those reported by Yang[2] and those found independently for substituted butyrophenones by Pitts.[4,5]

Table I. Kinetic Data for Photoelimination of Substituted Valerophenones

Ketone[a]	Φ_{II}	ϕ_{BR}	$k_q\tau$, M^{-1}	$1/\tau$,[b] 10^6 sec^{-1}	k_r, 10^6 sec^{-1}	k_i, 10^6 sec^{-1}
$PhCOCH_2CH_2CH_2CH_3$ (VP)	0.33	1.0	36	140	140	
p-MeVP	0.33	1.0	255	20	20	
m-MeVP	0.29	0.87	110	45	39	6.0
p-MeOVP	0.10	0.30	2300	2.2	0.66	1.3
m-MeOVP	0.014	0.042	330	15	0.63	14.4
o-MeOVP	0.15	0.45	1100	4.5	2.0	2.5
$PhCOCH_2CH_2CH(CH_3)_2$ (GMV)	0.25	1.0	11	450	450	
p-MeOGMV	0.16	0.64	850	5.9	3.8	2.1
m-MeOGMV	0.03	0.12	200	25	3.0	22.0

[a] 0.1 M in benzene. [b] k_q assumed to equal $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.

Values of k_r and k_i, the rate constants for intramolecular hydrogen abstraction and radiationless decay, respectively, of the ketone triplets, were dissected from the combined quantum yield and lifetime values as follows. Good evidence has been accumulated that $\phi_{BR} = k_r\tau = \Phi_{II}/\phi_P$ where ϕ_P represents the probability that the biradical primary photoproduct will proceed on to product.[6] In unsubstituted valerophenone and γ-methylvalerophenone, $\phi_{BR} = 1$ and $\phi_P = 0.33$ and 0.25, respectively, in benzene. As a first approximation, we assume that ring substituents affect only the triplet state (ϕ_{BR}) and not ϕ_P. The values of ϕ_{BR} are estimated by dividing measured Φ_{II} values by the assumed ϕ_P values. Combination of these with the $\tau = (k_r + k_i)^{-1}$ values estimated from the quenching data produce the rate constants listed in Table I.

Two effects are apparent. Both *m*- and *p*-methyl groups lower the rate of intramolecular hydrogen abstraction not quite one order of magnitude, while methoxy groups lower reactivity by at least two orders of magnitude. However, the apparent rates of radiationless decay are at least ten times faster for *meta*-substituted ketones than for the analogous *para*-substituted ketones.

The implications of these results as regards the electronic structure of the triplet states of phenyl ketones cannot as yet be fully assessed. There seems little doubt that the lowest triplet states in the substituted phenyl ketones are predominantly π,π^* in character.[2,7] The above kinetic analysis was made on the assumption that only the lowest triplet reacts.

There are, however, three *a priori* possibilities as regards the nature of the reacting triplet: (1) only the n,π^* triplet reacts; (2) only the lower energy (here π,π^*) triplet reacts; (3) both react. The kinetic complexities of this problem can be delineated only in a full paper, but the following points can be made now.

Stern–Volmer plots were linear out to very large values of Φ_0/Φ. Consequently, it is unlikely that two triplet species were reacting unless they have almost identical lifetimes.

The n,π^* and π,π^* triplets of the *para*-substituted ketones lie very close together,[2,7] so that either could react. Whichever actually reacts, it is obvious that it must be of mixed n,π^* and π,π^* character,[8,9] since the values of k_r are too low for a pure n,π^* state and too high for a pure π,π^* state.[10]

The separation between n,π^* and π,π^* triplets in the *meta*-substituted ketones is at least 3 kcal greater than in the *para*-substituted ketones.[5] Consequently, it is possible that the anomalously high apparent values of k_i measure decay of the reactive upper triplet (mostly n,π^*) to the lower, almost unreactive triplet (mostly π,π^*).[11]

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[3] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

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[5] J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5900 (1968).

[6] P. J. Wagner, *ibid.*, **89**, 5898 (1967); P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968).

[7] D. R. Kearns and W. A. Case, *ibid.*, **88**, 5087 (1966).

[8] N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3675 (1964).

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

[10] For a fuller discussion, see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 99 (1968).

[11] There is evidence that rapid reactions of a second triplet can compete with decay to the lowest triplet: (a) P. de Mayo, J. P. Pete, and M. Tchir, *ibid.*, **89**, 5712 (1967); (b) N. C. Yang, R. Loeschen, and D. Mitchell, *ibid.*, **89**, 5465 (1967); (c) R. S. H. Liu and J. R. Edman, *ibid.*, **90**, 213 (1968).

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 spectra[14] probably is safe only in cases of very strong change-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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Correlation between the Photochemical Reactivity and the Nature of Excited States of Acetophenone and Substituted Acetophenones

Sir:

In an earlier communication from our laboratory[1] 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}.

$$\mathrm{ArCOCH_3} \xrightarrow{h\nu} [\mathrm{n},\pi^*]^1 \xrightarrow[\text{crossing}]{\text{intersystem}} [\text{triplet}] \qquad (1)$$

$$[\text{triplet}] + \mathrm{RH} \xrightarrow{k_r} \text{products} \qquad (2)$$

$$[\text{triplet}] \xrightarrow[\text{all nonradiative decay}]{k_{-t}} \mathrm{ArCOCH_3} \qquad (3)$$

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

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 corresponding n,π^* states, most probably through vibronic coupling with the $[\mathrm{n},\pi^*]^3$ state in addition to spin–orbital coupling with the $[\mathrm{n},\pi^*]^1$ 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

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

and

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

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 $[\mathrm{n},\pi^*]^3$ 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 $[\mathrm{n},\pi^*]^3$ state and the π,π^* states and thus will enhance the photochemical reactivity of a $[\mathrm{n},\pi^*]^3$ 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 $[\mathrm{n},\pi^*]^1$ state[4] and vibronically coupled with the $[\mathrm{n},\pi^*]^3$ state.[5] Since we observed that the energy level of the $[\mathrm{n},\pi^*]^1$ state does not vary appreciably among methylated acetophenones (Table II), spin–orbital coupling between the $[\pi,\pi^*]^3$ state and the $[\mathrm{n},\pi^*]^1$ state of these compounds is insufficient to account for the variation of

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

(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 cm^2); we found that the effect of intensity on the quantum yield is minimal or within experimental error.

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