Type II Photoprocesses of Phenyl Ketones. Procedures for Determining Meaningful Quantum Yields and Triplet Lifetimes

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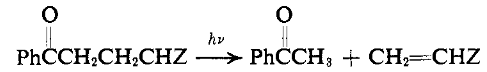
Abstract: Type II quantum yields and triplet lifetimes of phenyl alkyl ketones decrease with conversion whenever the product olefin is an effective triplet quencher. The only meaningful values for such systems are those extrapolated to zero conversion. The type II quantum yield for valerophenone is constant out to 75% conversion in benzene but begins decreasing significantly above 20% conversion in *n*-propyl alcohol or in the presence of 0.020 *M* diene. Product acetophenone apparently does not function as an effective internal filter unless its triplet lifetime is shortened by photoreduction or by quenching. Energy transfer from triplet acetophenone to valerophenone must normally be very efficient. For most phenyl alkyl ketones, type II quantum yields—but not triplet lifetimes—increase with increasing ketone concentration in hydrocarbon solvents. Ground state ketone presumably solvates a biradical intermediate so as to suppress reverse hydrogen transfer. The efficiencies with which various additives enhance type II quantum yields are in the order: pyridine > tetrahydrofuran ~ *tert*-butyl alcohol > butyl ether ~ ethyl acetate ~ ground state ketone > butyronitrile. This order reflects the basicity of the additives and not their polarity. Added *tert*-butyl alcohol enhances quantum yields of different ketones with varying efficiency. For some ketones, quantum yields reach unity at low alcohol concentrations; for others, quantum yields are still rising at high alcohol concentrations; for still others, quantum yields reach maximum values lower than unity at low alcohol concentrations.

Under conditions of steady state illumination, the only kinetic parameter that can be measured directly for photochemical reactions is the overall quantum yield. Any given quantum yield can be expressed as the product of one or more $k_i\tau$ factors, where τ is the lifetime of a metastable intermediate (such as an excited state) and k_i is the rate at which that intermediate reacts to yield either the product or another intermediate which can proceed on to the product whose quantum yield is being measured. Excited state lifetimes can be determined either by nonsteady state flash experiments or by steady state Stern–Volmer quenching studies. With two unknowns—k_i and τ—and two independent, measurable quantities—Φ^0 (quantum yield in absence of bimolecular quenching) and τ—it is possible to determine rate constants for excited state reactions. If accurate values are to be obtained, it is essential that all the experimental factors which might influence Φ values be understood. As part of our investigation of the type II reactions of phenyl ketones, we have determined how Φ varies as a function of conversion, initial ketone concentration, and concentration of various additives. We describe these studies in this paper as a preliminary to our papers describing the structural dependence of k_i and because some of the effects are much larger than might have been estimated from fragmentary accounts in the literature.

Results and Discussion

Quantum Yields as a Function of Conversion. There are at least two phenomena which might lower quantum yields at high conversions: (1) internal filtering by a product and (2) quenching of excited reactant by a product. In the case of the type II reaction of phenyl ketones, the product acetophenone obviously can act as an internal filter. The olefin product can be a triplet quencher if conjugating substituents are located on the β or γ carbons of reactant ketone.



$$\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2CH_2CHZ} \xrightarrow{h\nu} \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} + \mathrm{CH_2{=}CHZ}$$

We first looked at a case where the olefin product would not be expected to be an efficient quencher of triplet ketone, namely the photoelimination of valerophenone. Figure 1 plots the per cent conversion (sum of acetophenone and cyclobutanol formation) as a function of time in benzene; Figure 2 plots acetophenone formation in *n*-propyl alcohol. Irradiations were performed at 25° with 3130-Å light on degassed solutions 0.05, 0.10, or 0.20 *M* in valerophenone. The dashed lines in the plots indicate the expected rates of product formation if quantum yields remain constant. In pure benzene, the quantum yield for photoelimination does not begin to decrease until after 75% conversion, whereas in *n*-propyl alcohol the quantum yield begins to decrease after only 20% conversion and plummets at high conversion.

The behavior in benzene is noteworthy because the acetophenone product obviously is not acting as an effective internal filter. Equation 1 describes the dependence of product concentration [A] on time, where

$$(1 - xy)[\mathrm{A}] - x^2y[\mathrm{K}]_0 \ln\left(1 - \frac{[\mathrm{A}]}{x[\mathrm{K}]_0}\right) = \Phi^0 It \quad (1)$$

x is the chemical yield of internal filter A, y is the ratio ϵ_A/ϵ_K of extinction coefficients of product A and reactant K, and I is the absorbed light intensity. Valerophenone yields both acetophenone and nonabsorbing cyclobutanols, the measured value of x being 0.82 in benzene; in *n*-propyl alcohol, 20% photoreduction competes, so that x is only 0.70. The value of y is 1.0. The solid lines in Figures 1 and 2 indicate the expected dependence of product formation on conversion if acetophenone were a 100% effective internal filter.

The lack of effective internal filtering in benzene must mean that most of the light energy absorbed by the acetophenone is transferred to valerophenone. The 0–0 phosphorescence band of propiophenone and

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[1] Alfred P. Sloan Fellow, 1968–1972.

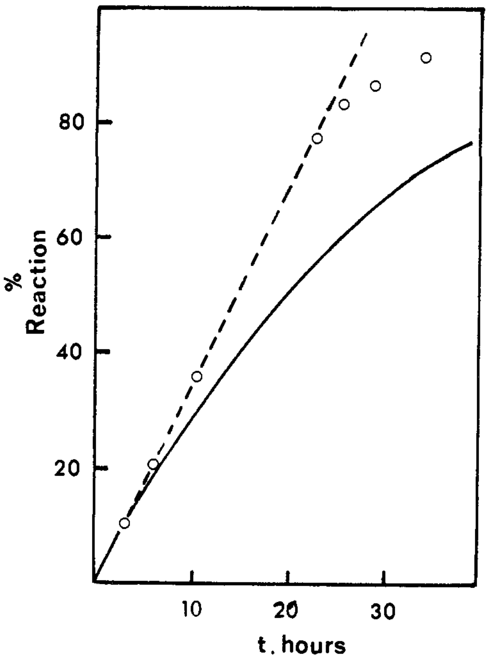

Figure 1. Rate of reaction of 0.10 *M* valerophenone in benzene as a function of time at constant light intensity. Dotted line is extrapolation of low conversion results; solid line is behavior predicted for complete internal filtering by acetophenone product.

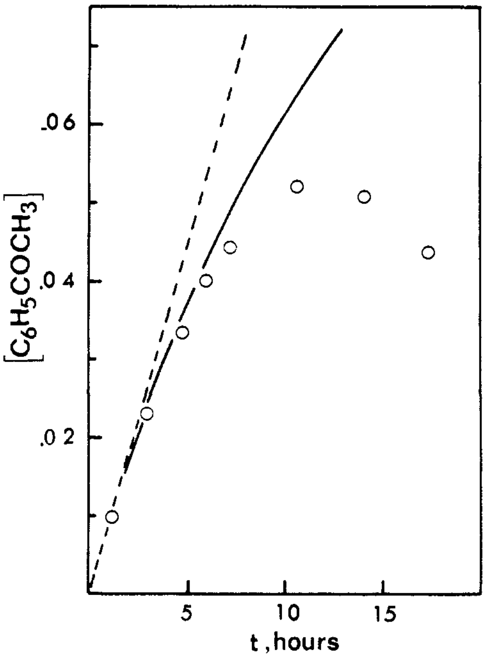

Figure 2. Rate of formation of acetophenone as function of irradiation time; 0.10 *M* valerophenone in 1-propanol.

higher homologs in hydrocarbon solvents is 1 kcal higher than that of acetophenone at 77°K[2] but 0.5 kcal lower at room temperature.[3] Therefore, the proposed energy transfer would be roughly thermoneutral and should proceed with an actual rate constant k_t of at least 10^9 M^{-1} sec^{-1}. The apparent rate constant would be lower because of reversibility, as described by eq 3.[4]

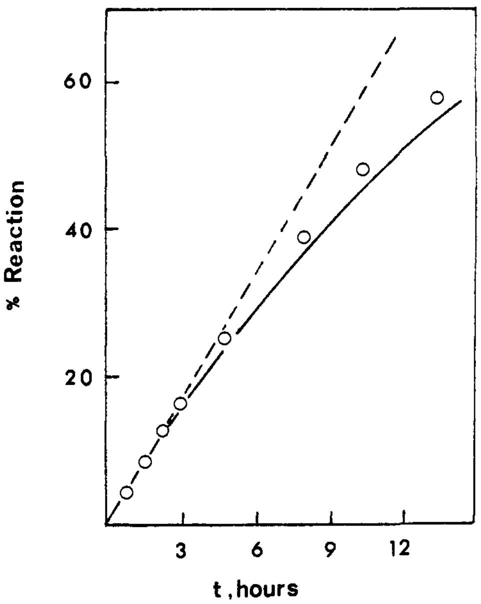

Figure 3. Total rate of reaction of 0.05 *M* valerophenone as a function of time in benzene containing 0.02 *M* 2,5-dimethyl-2,4-hexadiene.

$$ {}^3A^* + K \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} A_0 + K^* \qquad (2) $$

$$ k_t^{\text{obsd}} = \frac{k_t}{1 + k_t\tau_{K^*}[A]} \qquad (3) $$

With the triplet lifetimes of valerophenone and acetophenone known to equal 10^{-8} and 3×10^{-6} sec, respectively,[5,6] $k_t^{\text{obsd}}\tau_{A^*}[K]$ would equal at least 20 at 75% reaction of K; *i.e.*, 95% of the excitation absorbed by acetophenone would still be transferred to valerophenone.

The zero-order kinetics for type II reaction of valerophenone also indicate that the concentration of initially formed enol—which would be a very effective quencher of triplet ketones—never exceeds 10^{-3} *M* (which concentration of styrene would quench 4% of triplet valerophenone). Under our reaction conditions, acetophenone enol was being formed at the rate of 10^{-2} *M*/hr. A pseudo-first-order rate constant of 10 *M*/hr or 3×10^{-3} *M*/sec for enol → ketone tautomerization would be sufficient to keep the enol concentration too low to affect quantum yield. The actual rate must be considerably faster. Even with ketones whose triplets are ten times longer lived than triplet valerophenone, we see no deviation in quantum yields out to 30% conversion.

In *n*-propyl alcohol, the product *vs.* time plot falls off almost as predicted by eq 1. At long times, the yield of acetophenone actually begins to drop, reflecting the competing photoreduction of product by solvent. We have measured the lifetime of triplet propiophenone in primary alcohol solvents as 5×10^{-8} sec. The effective internal filtering in propanol solvent partially reflects the much shorter lifetime of triplet acetophenone relative to its value in benzene, but the competing destruction of product prevents a quantitative evaluation.

This effect of reduced triplet acetophenone lifetime is shown more clearly by the results in Figure 3. With

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[2] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 86, 4537 (1964).

[3] R. G. Zepp, unpublished results.

[4] P. J. Wagner, *Mol. Photochem.*, 1, 71 (1969).

[5] P. J. Wagner, *J. Amer. Chem. Soc.*, 89, 5898 (1967).

[6] W. A. K. Clark, A. D. Litt, and C. Steel, *ibid.*, 91, 5413 (1969).

enough diene present to produce maximum triplet lifetimes of 10^{-8} sec and to quench just under half the type II reaction of valerophenone, and without the complication of competing destruction of product, internal filtering clearly becomes important above 20% conversion. The actual amount of internal filtering is not quite as great as predicted by eq 1. During irradiation, the average valerophenone concentration was twice that of the diene, so that the value of $k_t^{\text{obsd}}\tau_{A*}[K]$ would be expected to be near unity. Some of the energy absorbed by acetophenone still gets to valerophenone. The concentration of diene did not change even after 60% reaction of ketone (by which time every diene molecule had been sensitized to its triplet state five–six times).

These results are important because they indicate that we can safely do quenching studies on the type II reaction at conversions as high as 20%. In fact, the type II reaction is quite well behaved as photoreactions go, behavior such as that depicted in Figure 3 being quite common for many other reactions. With very low ketone concentrations and rather large quencher concentrations, internal filtering during type II photoreactions could approach total efficiency, but no measurable deviations from zero-order kinetics occur at conversions lower than 5% for any type II reaction which does not produce an effective quencher as product.

Next we studied the behavior of four γ-substituted butyrophenones which undergo type II photoelimination to yield olefin products which are effective triplet quenchers. γ-Phenyl-, -vinyl-, -cyano-, and -carbomethoxybutyrophenones yield styrene (E_t ~ 60 kcal),[7] butadiene (E_t = 60 kcal),[8] acrylonitrile, and methyl acrylate, respectively. Because of their low triplet excitation energies, the first two are expected to quench ketone triplets at the maximum rates in solution. The triplet energies of the latter two olefins are not known; they quench triplet phenyl alkyl ketones with rate constants, respectively, 1/5th and 1/11th that displayed by conjugated dienes.

Degassed benzene solutions 0.10 *M* in ketone were irradiated at 3130 Å for various periods. Table I lists the concentrations and quantum yields of acetophenone as a function of irradiation time. In all cases quantum yields decrease significantly with increasing conversion—in contrast to the behavior of valerophenone in benzene.

Straightforward integration of the rate equations for quenching by product yields eq 6, which describes the dependence of observed quantum yield on conversion in terms of (quenching) product concentration.[9]

$$K^* \xrightarrow{1/\tau} P + K_0 \tag{4}$$

$$K^* + P \xrightarrow{k_{qp}} K_0 + P^* \tag{5}$$

$$\Phi_{\text{obsd}}{}^{-1} = \frac{1}{\Phi^0}\,(1 + k_{qp}\tau_{K*}[P]/2) \tag{6}$$

Figure 4 plots the data of Table I according to eq 6. The intercepts yield true Φ^0 values (for 0.1 *M* ketone; see below), the values of which are listed under t = 0 in

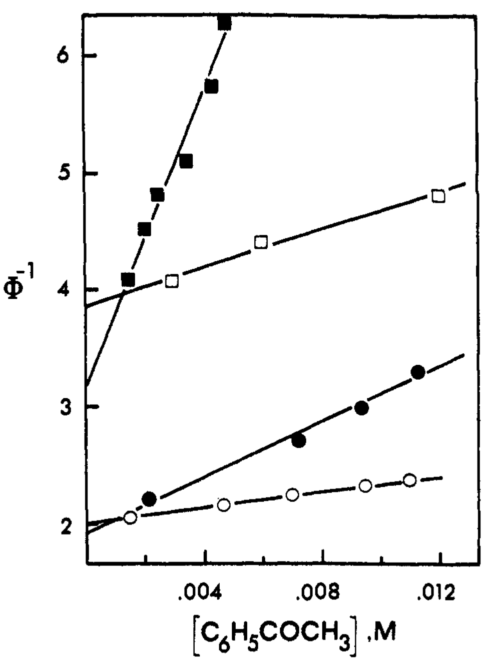

Figure 4. Dependence of quantum yields for acetophenone formation in benzene on conversion: ○, γ-phenylbutyrophenone; ●, γ-carbomethoxybutyrophenone; □, γ-vinylbutyrophenone; ■, γ-cyanobutyrophenone.

Table I. Dependence of Quantum Yields on Conversion in Irradiation of $C_6H_5COCH_2CH_2CH_2R$[a]

R	Time, hr	$[C_6H_5COCH_3]$, *M*	Φ[b]
C_6H_5	0.25	0.0017	0.49
	0.50	0.0032	0.475
	0.75	0.0047	0.465
	1.0	0.0058	0.46
	1.25	0.0070	0.45
	1.50	0.0085	0.445
	1.75	0.0094	0.43
	2.0	0.110	0.42
	0		0.50
$CH{=}CH_2$	0.5	0.0029	0.245
	1.1	0.0058	0.23
	2.5	0.121	0.21
	0		0.26
CO_2CH_3[c]	0.25	0.0023	0.45
	1.1	0.0071	0.37
	1.5	0.0094	0.33
	2.0	0.0114	0.30
	0		0.52
CN	0.50	0.0015	0.245
	0.5[d]	0.0024	0.22
	1.0	0.0030	0.21
	1.5	0.0035	0.195
	2.0	0.0043	0.175
	2.0[d]	0.0048	0.16
	0		0.32

[a] 0.10 *M* ketone solutions in benzene were irradiated at 3130 A. [b] All quantum yields for acetophenone formation corrected for varying light intensities. [c] 0.05 *M* ketone. [d] Separate experiments.

Table I. The slope/intercept values yield regular Stern–Volmer quenching constants which are listed in Table II. Also listed in Table II are the $k_{qp}\tau$ values calculated from independently measured τ values and from k_q values of the four olefins toward triplet butyrophenone. The τ values were determined by normal low conversion Stern–Volmer quenching studies with added dienes. In all cases the data in Table I suggest considerably higher $k_{qp}\tau$ values than expected.

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(7) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).
(8) R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).
(9) K. R. Huffman, C. E. Kuhn, and A. Zweig (*ibid.*, **92**, 599 (1970)) have independently reported an example of quenching by product.

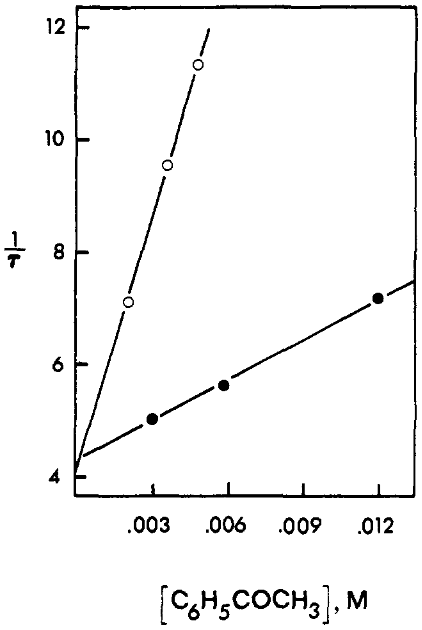


Figure 5. Variation in measured triplet state lifetimes as a function of conversion: ○, γ-cyanobutyrophenone, $1/\tau$ in units of 10^6 sec^{-1}; ●, γ-vinylbutyrophenone, $1/\tau$ in units of 10^8 sec^{-1}.

Table II. Product Quenching Parameters for $C_6H_5COCH_2CH_2CH_2R$

R	$\Phi^{0\,a}$	$k_{qp}\tau^{obsd}$, $M^{-1\,b}$	$k_{qp}\tau^{calcd}$, $M^{-1\,c}$
C_6H_5	0.50	33	13
$CH{=}CH_2$	0.26	42	12
CO_2CH_3	0.52	125	45
CN	0.32	475	250

[a] Reciprocal of intercepts in Figure 5. [b] Slope/intercept from Figure 5. [c] Independently measured k_q values for olefin products multiplied by τ values indicated by intercepts in Figure 6.

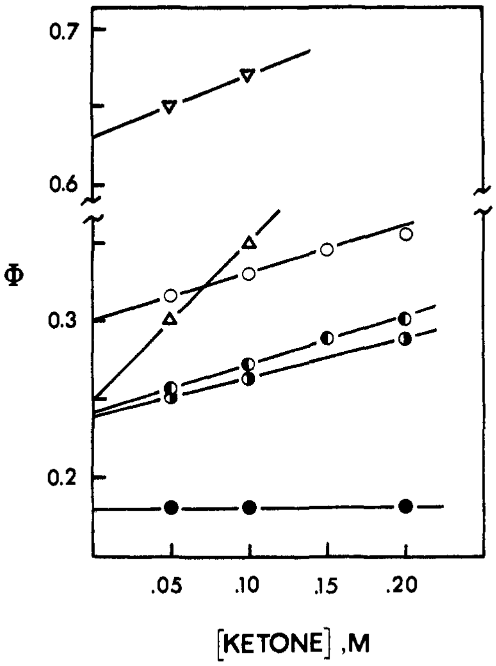


Figure 6. Variation in type II quantum yields as a function of ketone concentration in benzene: ●, β,β-dimethylbutyrophenone; ◑, pentadecanophenone; ◐, δ-methylhexanophenone; ○, valerophenone; △, γ-hydroxybutyrophenone; ▽, methyl δ-benzoylvalerate.

Table III. Dependence of Stern–Volmer Quenching Slopes on Conversion for $C_6H_5COCH_2CH_2CH_2R$[a]

R	$[C_6H_5COCH_3]$,[b] M	$k_q\tau$, M^{-1}
CN	0.0048	440
	0.0036	500
	0.0020	700
	0	1250
CO_2CH_3	0.0093	350
	0.0021	440
	0	475
$CH{=}CH_2$	0.0121	7.0
	0.0058	9.0
	0.0029	10.0
	0	11.5

[a] 0.10 M benzene solutions quenched with 2,5-dimethyl-2,4-hexadiene. [b] Product concentration in samples with no quencher.

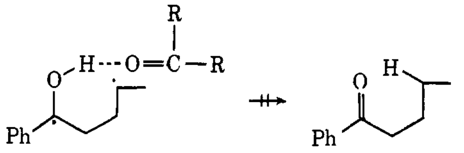
We feel that $k_{qp}\tau$ values derived from the plots in Figure 4 are unreliable for two reasons. As discussed above, in the presence of quencher molecules the probability of triplet acetophenone transferring energy to the butyrophenones is lowered. Therefore, both quenching and internal filtering by acetophenone product could produce larger than expected decreases in quantum yields as a function of conversion.

Effect of Conversion on Quenching Studies. Quenching by products lowers quantum yields because it lowers actual excited state lifetimes. Therefore, triplet lifetimes measured at finite conversions will be too short if products act as quenchers. In fact there should be an exact linear relation between the decrease in Φ with conversion and the decrease in τ with conversion. We have done Stern–Volmer quenching studies on valerophenone under conditions ranging from 2 to 40% maximum conversion and find no significant variation in the measured $k_q\tau$ value. However, Stern–Volmer slopes for the γ-substituted ketones do decrease with conversion, as tabulated in Table III. Figure 5 demonstrates the linear increase in $1/\tau$ with conversion for the γ-cyano- and γ-vinylbutyrophenones. *Both Φ values and $k_q\tau$ values (as their reciprocals) must be extrapolated to zero conversion in cases where a product is a quencher.* Because of the expected and observed parallel dependences of Φ and τ on conversion, zero conversion $k_q\tau$ values can be estimated from the following expression, where the subscript v stands for a

$$\frac{k_q\tau^0}{k_q\tau_v} = \frac{\Phi^0}{\Phi_v} \tag{7}$$

given conversion. In a Stern–Volmer quenching study, the conversion in samples with no added quencher is the amount to be used in eq 7.

Effect of Ketone Concentration on Quantum Yields. We find that the quantum yields for type II reactions of phenyl ketones in hydrocarbon solvents generally increase with increasing ketone concentration. For example, quantum yields of acetophenone formation are 0.33, 0.45, and 0.53 at 0.1, 0.6 and 1.0 M valerophenone in benzene. Further examples are portrayed in Figure 6. This behavior is a special case of the more dramatic increases afforded by small amounts of added alcohols and stronger Lewis bases (see below). In acetone as solvent, the total type II quantum yield for valerophenone approaches unity, just as it does in *tert*-butyl alcohol. Presumably one ketone molecule acts as a weak Lewis base toward the hydroxyl proton of the biradical intermediate from another ketone molecule, thus suppressing reverse transfer of that hydrogen to the γ radical site.[5]



In the case of valerophenone, measured $k_q\tau$ values do not vary with ketone concentration. This result is consistent with our earlier report of small solvent effects on τ^5 and is further evidence that the concentration-dependent quantum yields reflect biradical behavior and not excited state behavior.

The efficiency with which different phenyl ketones enhance their own type II quantum yields varies. Those with electron-rich substituents, such as γ-hydroxybutyrophenone, are noticeably more sensitive to concentration than are simple phenyl alkyl ketones. We have already noted this phenomenon for the pyridyl ketones.[10] In fact, γ-hydroxybutyrophenone is just as effective at raising its own quantum yield as is added *tert*-butyl alcohol at raising valerophenone's quantum yield. The parallel behavior of valerophenone, δ-methylhexanophenone, and pentadecanophenone indicates that the length of the alkyl chain does not influence the solvating power of the ketones.

Some ketones, such as butyrophenone, β,β-dimethylbutyrophenone, and ϵ-cyanohexanophenone, do not display the concentration dependence common to most ketones. There are two possible explanations for this exceptional behavior. First, the biradicals formed from these ketones may be unusually short lived or less readily solvated. Second, quenching by small amounts of impurities in the ketones might coincidentally offset the solvation effect. In fact, synthesis of many of the ketones which we have studied did introduce quenching impurities which were not always easy to remove. Their presence was indicated by *decreasing* quantum yields with increasing ketone concentrations. In most cases we have been able to purify the ketones such that the normal concentration effects were observed. Interestingly, in each case where the concentration dependence of quantum yields improved upon extra purification of ketone, the quantum yield value extrapolated to zero ketone concentration remained unchanged. As regards the three ketones mentioned above, the possibility of impurity quenching is eliminated by our observation that total quantum yields approach unity in the presence of sufficient *tert*-butyl alcohol.

Effects of Additives on Quantum Yields. Figure 7 portrays the response of the type II quantum yield for valerophenone to addition of small concentrations of different weak Lewis bases. The efficiency of quantum yield enhancement is pretty much proportional to each additive's base strength and not to the polarity of the additive in terms of its dielectric constant or dipole moment. Thus, THF and *tert*-butyl alcohol are of comparable efficiency (after correction for ~5% photoreduction by THF). Interestingly, the ability of butyronitrile to enhance quantum yields extrapolates to Barltrop's observation[11] that type II quantum yields do not quite equal unity in dry acetonitrile. We consistently obtain quantum yields near unity in wet acetonitrile and often use acetonitrile containing 2% water to measure maximum quantum yields. Finally, the inability of chlorobutane to influence quantum yields is important as regards the behavior of chloro ketones.

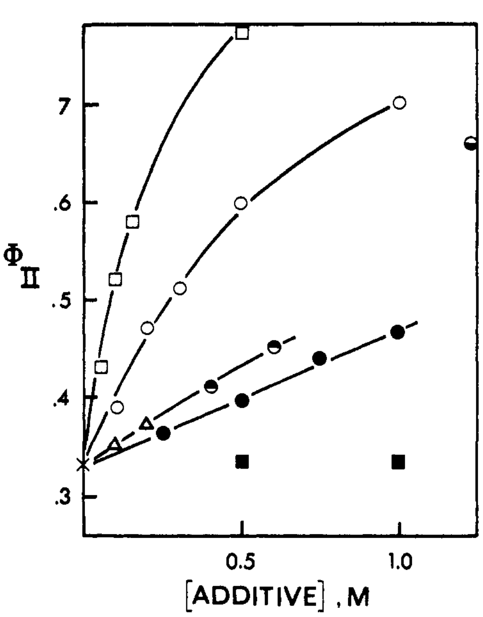


Figure 7. Variations in quantum yield for acetophenone formation from 0.10 *M* valerophenone as a function of additive concentration in benzene: □, pyridine; ○, *tert*-butyl alcohol; ◒, tetrahydrofuran; △, ethyl acetate; ◓, *n*-butyl ether; ●, butyronitrile; ■, 1-chlorobutane.

Concentrating on *tert*-butyl alcohol as additive, we find that different ketones respond quite a bit differently, as indicated in Figure 8. For almost all phenyl ketones, type II quantum yields are enhanced by small concentrations of alcohol. The majority of ketones which we have studied behave like valerophenone, in that the total quantum yield rises to near unity at 2 *M* alcohol. There are two distinct variations. For a few ketones, such as β,β-dimethylbutyrophenone, type II quantum yields rise so gradually with added alcohol that they have not leveled off or reached unity even in alcohol as solvent. For other ketones, total quantum yields level off to a value lower than unity, as exemplified by *p*-methoxy- and δ-chlorovalerophenone.

Since the quantum yield enhancements apparently arise from solvation of the biradical intermediate,[5,12] the effect can be considered quantitatively as quenching of the reverse hydrogen transfer reaction of the biradical. The efficiency of this process, like that of any quenching process, must depend both on the lifetime of the intermediate and on the rate constant of the quenching process. Consequently, the varying $\Delta\Phi/\Delta[\mathrm{alc}]$ values apparent in Figure 8 can reflect substituent effects both on biradical lifetimes and on the ability of the biradicals to form hydrogen bonds. We discuss these points more fully elsewhere.[13] Finally, we assume that all such biradical reversal is suppressed when the type II quantum yield levels off to its maximum value. If this maximum quantum yield is lower than unity, we must then conclude that the triplet ketone also decays by some path other than γ-hydrogen abstraction.

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(10) P. J. Wagner and G. Capen, *Mol. Photochem.*, 1, 173 (1969).

(11) J. A. Barltrop and J. D. Coyle, *J. Amer. Chem. Soc.*, **90**, 6584 (1968).

(12) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *ibid.*, **94**, 7480 (1972).

(13) P. J. Wagner, *et al.*, *ibid.*, **94**, 7506 (1972).

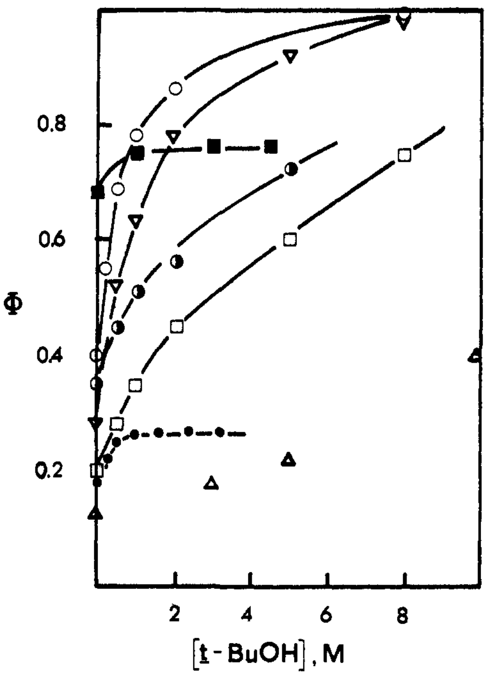

Figure 8. Response of type II quantum yields of various ketones (0.10 *M* in benzene) to addition of *tert*-butyl alcohol: ○, valerophenone; □, β,β-dimethylbutyrophenone; ●, *p*-methoxyvalerophenone; ■, δ-chlorovalerophenone; ▽, γ-methylvalerophenone; ◑, γ-hydroxybutyrophenone; △, α,α-dimethylvalerophenone.

Summary

Type II quantum yields and triplet lifetimes of phenyl ketones decrease with conversion whenever the olefin product is an effective triplet quencher. Internal filtering by product acetophenone is serious only under conditions such that triplet acetophenone is too short lived to transfer energy efficiently to reactant; *e.g.*, in reactive solvents or in the presence of triplet quencher.

In hydrocarbon solvents, type II quantum yields of phenyl ketones normally increase with increasing ketone concentration. Ground state ketone can presumably solvate the biradical intermediates.

In order to be absolutely sure of a Φ^0 value, one must extrapolate measured quantum yields at each of several ketone concentrations to zero conversion and then extrapolate to zero ketone concentration.

Finally, the rate of increase in Φ as a function of concentration of additives varies considerably due to differing basicities of the additives and probably also to different biradical lifetimes.

Experimental Section

Chemicals. Benzene was washed with sulfuric acid, dried, and distilled from phosphorus pentoxide. *n*-Propyl alcohol and *tert*-butyl alcohol were distilled from sodium. Pyridine, butyl ether, and ethyl acetate were distilled before use. THF, butyronitrile, and chlorobutane were reagent grade materials used as received. Ketones were prepared and purified as described in the accompanying paper.[14]

Procedures. These were, in general, as previously described.[5] For each run measuring the effect of differing concentrations of additives or of ketone, all samples were irradiated in parallel for the same length of time. For each run measuring quantum yields of valerophenone reaction as a function of conversion, all samples were placed in the merry-go-round 5 min after the lamp had warmed up and individual samples were removed for analysis at measured time intervals. Slight decreases in the lamp intensity with time were corrected for by irradiating a few samples for a fixed time half-way through the total run and for the last hour of the run. For each run measuring quantum yields of ketones which produce quencher products, equal numbers of identical sample tubes and valerophenone actinometer tubes were introduced simultaneously into the merry-go-round. At various time intervals one tube each of sample and actinometer were removed and analyzed.

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(14) P. J. Wagner and A. E. Kemppainen, *ibid.*, **94**, 7495 (1972).