

basic site.<sup>43-45</sup> Studies for oxygen 1s core binding energies were initially thought to show slightly different correlations for singly and doubly bonded oxygen.<sup>43</sup> However, later studies, based on improved core binding energy measurements, showed that all hydroxyl, ether, aldehyde, and ketone organic bases fit a single correlation.<sup>44</sup>

This good correlation was confined to molecules more basic than H<sub>2</sub>O due to the unavailability of reliable data for more weakly basic species. The data reported in the present work provide the basis for testing such a correlation over a much larger basicity range for a greater variety of functional groups. A plot of gas-phase proton affinity as a function of oxygen 1s binding energy is shown in Figure 2 for all of the oxygen bases examined in the present study and several others more basic than H<sub>2</sub>O. It may be readily seen that an excellent correlation between the two quantities exists over a range of basicities of a least 100 kcal mol<sup>-1</sup>. In addition, a variety of inorganic oxygen bases such as O<sub>2</sub>, CO<sub>2</sub>, SO<sub>3</sub>, SO<sub>2</sub>F<sub>2</sub>, OCS, and SO<sub>2</sub> is included. These results thus show that the gas-phase proton affinity of a molecule is intimately related to the core binding energy of the most basic atomic site in the molecule. The relationship between proton affinity in kcal mol<sup>-1</sup> and oxygen 1s core binding energy in eV given by eq 30 may thus be used to predict proton affinities for molecules for which the core binding energy is known. For example, ozone,

$$PA(B) = (438.90 - 0.8(O_{1s}B.E.))23.06 \quad (30)$$

O<sub>3</sub>, has measured oxygen 1s binding energies of 541.5 eV for the terminal oxygens and 546.2 eV for the central oxygen.<sup>46</sup> From these data it is possible to predict that O<sub>3</sub> will protonate on a terminal oxygen with a proton affinity of 131 kcal mol<sup>-1</sup>. Such interpolations should prove extremely valuable in situations such as this where the difficulty in handling of the species makes an equilibrium proton affinity determination impractical.

## Conclusion

Multiple overlap proton transfer equilibria measurements have been used to define a new absolute proton affinity scale for the basicity region less basic than H<sub>2</sub>O. The data predict a proton affinity of CO of 145.6 kcal mol<sup>-1</sup>, roughly 3 kcal mol<sup>-1</sup> greater than previously accepted based on appearance potential data. More recent ab initio calculations and considerations of translational energy release upon fragmentation support the new higher value. Good agreement for proton affinities of the hydrogen halides with those determined by molecular beam photoionization studies of the van der Waals dimer is obtained. For molecules less basic than CH<sub>4</sub>, the present scale plus previous flowing afterglow data allow prediction of new proton affinities for CO<sub>2</sub>, N<sub>2</sub>, Xe, and HF. Some discrepancy appears to exist between equilibrium and appearance energy determinations of the proton affinity of the oxygen atom.

Correlations between oxygen 1s binding energy and proton affinity reveal a strong interdependence of these two quantities. The core binding energies may be used to predict proton affinities for molecules where experimental determination would be difficult.

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**Registry No.** H<sub>2</sub>S, 7783-06-4; CF<sub>3</sub>CH<sub>2</sub>OH, 75-89-8; CS<sub>2</sub>, 75-15-0; H<sub>2</sub>O, 7732-18-5; CF<sub>3</sub>CN, 353-85-5; C<sub>2</sub>H<sub>4</sub>, 74-85-1; CF<sub>3</sub>COCl, 354-32-5; SO<sub>2</sub>, 7446-09-5; OCS, 463-58-1; (CF<sub>3</sub>)<sub>2</sub>CO, 1479-49-8; HI, 10034-85-2; CF<sub>3</sub>I, 2314-97-8; SO<sub>2</sub>F<sub>2</sub>, 2699-79-8; C<sub>2</sub>H<sub>6</sub>, 74-85-1; CO, 630-08-0; HBr, 10035-10-6; N<sub>2</sub>O, 10024-97-2; CF<sub>3</sub>Br, 75-63-8; CF<sub>3</sub>Cl, 75-72-9; NF<sub>3</sub>, 7783-54-2; HCl, 7647-01-0; CH<sub>4</sub>, 74-82-8; CO<sub>2</sub>, 124-38-9; SO<sub>3</sub>, 7446-11-9; CF<sub>3</sub>CO<sub>2</sub>H, 76-05-1; CH<sub>2</sub>O, 50-00-0; HCO<sub>2</sub>H, 64-18-6; CH<sub>3</sub>OH, 67-56-1; CH<sub>3</sub>CHO, 75-07-0; (CH<sub>3</sub>)<sub>2</sub>O, 115-10-6; (CH<sub>3</sub>)<sub>2</sub>CO, 67-64-1; F<sub>3</sub>PO, 13478-20-1.

## Laser Flash Photolysis Study of the Photochemistry of Ring-Substituted $\beta$ -Phenylpropiophenones<sup>1</sup>

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**Abstract:** The triplet states of an extensive series of ring-substituted  $\beta$ -phenylpropiophenones have been characterized by phosphorescence emission spectroscopy and in laser flash photolysis studies. Substitution in the  $\beta$ -phenyl ring has only a small effect on the triplet lifetime, determined at -70 °C for the series, and on the Stern-Volmer slopes for triplet quenching by 1-methylnaphthalene determined in benzene and *tert*-butyl alcohol solutions at room temperature. Substitution in the 1-phenyl ring, on the other hand, has a more pronounced effect on the triplet lifetime. This is attributed to a dependence of the efficiency of  $\beta$ -phenyl deactivation on the degree of  $n, \pi^*$  character of the lowest triplet state. Arrhenius parameters for triplet decay were determined in toluene and methanol solutions for  $\beta$ -phenyl-*p*-methoxypropiophenone. The rather low pre-exponential factor obtained in these experiments is provided as evidence for a rather specific geometry for deactivation in the excited state. Stern-Volmer quenching of  $\beta$ -phenylpropiophenone triplets by 1-methylnaphthalene was investigated in a series of nine solvents of widely differing polarity and viscosity. The effects are quite small, indicating a compensation of changes in  $k_q$  by the triplet lifetime. The triplet-state behavior of  $\beta$ -phenylpropiophenone moieties in polymeric systems was investigated with a series of copolymers of methyl methacrylate and the methacrylate esters of hydroxy-substituted phenylalkyl ketones. Stern-Volmer quenching of the polymeric ketones with 1-methylnaphthalene indicates that there is essentially no difference between the behavior of polymer-incorporated  $\beta$ -phenylpropiophenone moieties and that of the analogous monomeric derivatives.

The ability of aromatic rings to deactivate  $n, \pi^*$  carbonyl triplets has been recognized for a number of years.<sup>4-6</sup> For example, this

is the reason why the triplet lifetimes for ketones such as benzophenone never exceed a few microseconds in benzene at ambient

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**Table I.** Structure of the Ketones Examined and the O–O Phosphorescence Band of Representative Examples

substrate	X =	Y =	$\lambda_{ph},^a$ nm
I	H	H	400
II	2-CH <sub>3</sub>	H	398
III	3-CH <sub>3</sub>	H	403
IV	4-CH <sub>3</sub>	H	399
V	2,4,6-(CH <sub>3</sub> ) <sub>3</sub>	H	392
VI	2-CH <sub>3</sub> O	H	398
VII	3-CH <sub>3</sub> O	H	399
VIII	4-CH <sub>3</sub> O	H	399
IX	3-Cl	H	402
X	4-Cl	H	399
XI	4-HO	H	
XII	3-CN	H	400
XIII	4-CN	H	400
XIV	3-CF <sub>3</sub>	H	398
XV	4-CH <sub>3</sub> CO <sub>2</sub>	H	
XVI	H	4-Cl	
XVII	H	4-CH <sub>3</sub> O	
XVIII	H	4-CH <sub>3</sub> CO <sub>2</sub>	401

<sup>a</sup> In a 1:1 methylcyclopentane:isooctane glass at 77 K. Excitation at 310 nm; the value of  $\lambda_{ph}$  corresponds to that of the O–O band maximum ( $\pm 2$  nm). The spectrum of XVII was clearly that of a  $\pi, \pi^*$  triplet state.

temperatures. The process can become remarkably efficient when it takes place intramolecularly; such is the case for  $\beta$ -phenylpropiophenone which has a lifetime of ca. 1 ns in solution at room temperature and is, for all practical purposes, photostable. In 1970, three papers from three independent laboratories clearly illustrated the effect,<sup>7–9</sup> which in fact has been known for over 40 years.<sup>10</sup> Recent work from our laboratory<sup>11</sup> has demonstrated the importance of conformational effects upon the kinetics of the deactivation process.

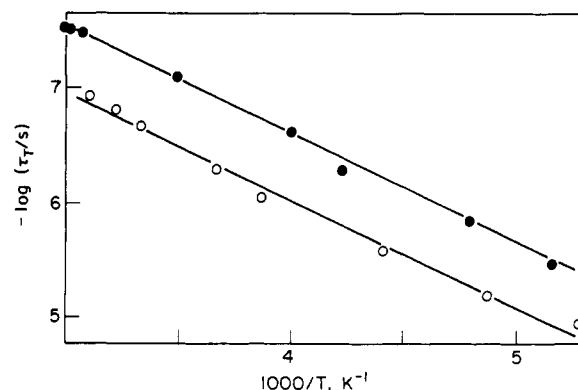
While the efficient intramolecular deactivation by aromatic rings has been recognized for many years, the only detailed time-resolved study was published while this paper was being reviewed.<sup>12</sup> We have undertaken a detailed study of the transient photoprocesses occurring in the photochemistry of various ring-substituted  $\beta$ -phenylpropiophenones, as well as solvent and temperature effects. Further, since these molecules could be useful as polymer photostabilizers, we have also examined the photo-behavior of polymer-bound  $\beta$ -phenylpropiophenone moieties. While detailed polymer degradation studies will be reported elsewhere,<sup>13</sup> a preliminary report of the transient photochemistry is included here. These studies suggest that polymer binding does not modify substantially the efficiency of deactivation by  $\beta$ -phenyl rings.

A separate study<sup>14</sup> has shown that all the ketones under study are essentially photostable, with quantum yields of ketone consumption below  $10^{-2}$  in all cases, and in fact below  $10^{-3}$  in most examples examined here. It should therefore be noted that product

**Table II.** Representative Triplet Lifetimes in Toluene at 190 K

substrate	$\tau_T$ , ns	$\sigma^{+a}$	IP, <sup>b</sup> eV
I	13 $\pm$ 6	0	8.78
II	16 $\pm$ 8		8.45
III	25 $\pm$ 5	–0.065	8.75
IV	27 $\pm$ 5	–0.256	8.37
V	63 $\pm$ 7		
VI	62 $\pm$ 7		
VII	43 $\pm$ 5	0.047	
VIII	23 $\pm$ 8	–0.648	(8.6)
IX	43 $\pm$ 5	0.399	
X	30 $\pm$ 10	0.035	8.90
XII	60 $\pm$ 10	0.562	
XIII	41 $\pm$ 8	0.674	9.76
XIV	60 $\pm$ 8	0.520	
XVII	3600 $\pm$ 100		

<sup>a</sup> Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley, New York, 1922; p 152. <sup>b</sup> From Baker, A. D.; May, D. P.; Turner, D. W. *J. Chem. Soc. B* **1968**, 22 (corresponds to the substituted toluenes).



**Figure 1.** Arrhenius plots for the decay of triplet XVII in toluene (●) and in methanol (○), monitored at 400 nm.

formation cannot be expected to be a relevant process in the interpretation of transient phenomena.

## Results

All the monoketones studied can be regarded as substituted  $\beta$ -phenylpropiophenones, I – XVIII.

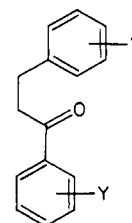


Table I lists the various substrates, along with the position of the O–O phosphorescence band for most of them. The phosphorescence in 1:1 methylcyclohexane:isooctane is similar to that in isopentane; in methylcyclohexane alone the O,O band moves to ca. 12 nm shorter wavelength, an effect that is well documented in the literature.<sup>15</sup> Both the phosphorescence and the absorption spectra clearly show that the presence of a  $\beta$ -phenyl ring, substituted or not, does not introduce any significant perturbations on the spectroscopic properties of the benzoyl chromophore. While hardly surprising, it is important to emphasize that the differences in behavior between pairs of ketones, such as propiophenone and  $\beta$ -phenylpropiophenone (I), should be attributed to efficient triplet deactivation and not to differences in the properties of the chromophores themselves.

All the experiments in the following sections have been carried out on deaerated samples, using the pulses (337.1 nm) from a nitrogen laser for excitation.

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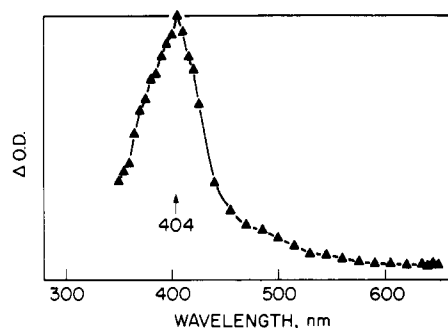


Figure 2. T-T absorption spectra for XVII, monitored in toluene at  $-36^{\circ}\text{C}$ .

**Direct Measurement of Triplet Lifetimes.** With the exception of XVII, the triplet lifetimes were generally too short to be suitable for direct determination at ambient temperatures with nanosecond laser photolysis techniques. However, they all showed sufficient temperature dependence that they could be determined directly at 190 K. Table II gives the values obtained in toluene, each one being a weighted average of 2–6 measurements, where the T-T absorptions were monitored at various wavelengths in the 350–420 nm region.

In the case of  $\beta$ -phenyl-*p*-methoxypropiophenone (XVII), we found that the triplet lifetime was sufficiently long that it could be easily measured directly over a wide temperature range. Measurements were carried out between 190 and 335 K in toluene and methanol. Data for both solvents are shown in Figure 1. Analysis of the data lead to

$$-\log(\tau_T) = (10.43 \pm 0.15) - (4.35 \pm 0.18)/\theta \text{ in toluene}$$

and

$$-\log(\tau_T) = (9.83 \pm 0.28) - (4.34 \pm 0.32)/\theta \text{ in methanol}$$

where  $\theta = 2.3RT$  in kcal mol $^{-1}$  and errors are quoted as  $\pm 2\sigma$ . Figure 2 illustrates the T-T absorption spectrum of XVII, which is essentially identical with the one recorded in our laboratory for *p*-methoxyacetophenone. The triplet lifetime of XVII was also recorded in several solvents at 300 K, leading to values of 71, 230, 260, 283, and 350 ns in isopentane, methanol, hexyl alcohol, glycol, and *tert*-butyl alcohol, respectively.<sup>16</sup>

**Determination of Stern–Volmer Constants for the Quenching by 1-Methylnaphthalene.** For those substrates where the direct detection of the triplet was not possible at 300 K, we used a Stern–Volmer type of approach. In this method one adds to the samples a triplet quencher such that (a) it is transparent at the laser excitation wavelength (b) it yields an easily detectable signal, usually its own triplet, as a result of triplet quenching, and (c) the rate constant for triplet quenching by this substrate is known or can be easily estimated. Work from our and other laboratories has shown that naphthalenes are frequently convenient choices,<sup>17</sup> particularly when a nitrogen laser (337.1 nm) is used for excitation; in our case we have used 1-methylnaphthalene. In this method the transient absorption ( $A_{420}$ ) due to the 1-methylnaphthalene triplet is monitored at 420 nm for different quencher concentrations. The values of  $A_{420}$  are expected to follow the dependence of eq 1, provided that only one kinetically distinct donor triplet

$$\frac{1}{A_{420}} = a + \frac{a}{k_q \tau_T [\text{MN}]} \quad (1)$$

is present and that triplet 1-methylnaphthalene is the only species leading to significant transient absorption at 420 nm. The pa-

Table III. Stern–Volmer Data for the Quenching of Substituted  $\beta$ -Phenylpropiophenones by 1-Methylnaphthalene at 300 K

substrate	$k_q \tau_T, \text{M}^{-1}$	
	<i>tert</i> -butyl alcohol	benzene
I	7.4	4.2
II	8.0	6.8
III	8.2	6.5
IV	7.0	7.3
V	7.7	4.3
VI	8.8	4.0
VII	7.7	4.6
VIII	8.1	4.0
IX	13.3	7.8
X	10.2	4.3
XI	7.0	7.8
XI (+ base)	2.6	
XII	25.0	18.3
XIII	14.8	12.7
XIV	19.5	12.6
XV	5.6	
XVI	14.0	6.2
XVIII	13.8	

Table IV. Solvent Effects on the Stern–Volmer Slopes for  $\beta$ -Phenylpropiophenone (I) at 300 K

solvent	$k_q \tau_T$	$\eta^a$	$\epsilon$	$k_q'^b$
benzene	4.2	0.60	2.28	$5.9 \times 10^9$
<i>tert</i> -butyl alcohol	7.4	3.30	10.9	
ethylene glycol	6.2	14	49	
acetonitrile	4.8	0.36	26.5	$8.1 \times 10^9$
hexadecane	7.8	3.34	1.9	$4.0 \times 10^9$
<i>n</i> -heptane	10.1	0.39	1.92	$(1.1 \times 10^{10})^c$
2-propanol	7.7	2.0	20.1	$4.7 \times 10^9$
methanol	4.4	0.61	38.6	$8.3 \times 10^9$
carbon tetrachloride	3.7	0.97	2.23	$4.2 \times 10^9$

<sup>a</sup>cP. <sup>b</sup> $k_q'$  is the rate constant for quenching of *p*-methoxyacetophenone by 2,5-dimethyl-2,4-hexadiene in the same solvent at 300 K; Leigh, W. J.; Scaiano, J. C., unpublished results. <sup>c</sup>Value for quenching by 1,3-pentadiene in isooctane.

parameter  $a$  is a constant incorporating several experimental parameters, and MN stands for 1-methylnaphthalene.

The concentrations of 1-methylnaphthalene required in experiments of this type are naturally dependent upon the lifetime of the donor triplet. In the systems examined herein, the highest concentrations required were  $\leq 0.3$  M. Under these conditions 1-methylnaphthalene (which has an extinction coefficient of  $0.34 \text{ M}^{-1} \text{ cm}^{-1}$  at 337 nm) absorbs  $\leq 5\%$  of the excitation light. While a correction can be included in eq 1 to account for this,<sup>18</sup> we have found that doing so results in changes in the  $k_q \tau_T$  values which are insignificant within our error limits. Thus, our data, collected in Table III, do not include this minor correction.

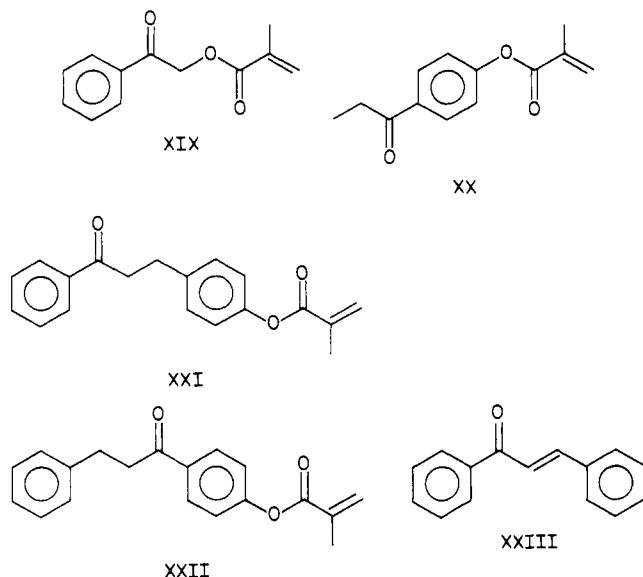
In the case of  $\beta$ -phenylpropiophenone, we also carried out a study of solvent effects. Table IV summarizes the values of  $k_q \tau_T$  obtained, along with the solvent viscosities and dielectric constants. We have also included in the same table rate constants for triplet quenching ( $k_q'$ ) which have been measured in an independent study. Quite clearly, the values of  $k_q \tau_T$  do not follow the solvent dependency of  $k_q'$ ; in fact in many cases an inversion is observed, suggesting that viscosity may have more of an effect on  $\tau_T$  than on  $k_q'$ . We note that  $k_q$  will be expected to be somewhat larger than  $k_q'$  (i.e., 1-methylnaphthalene is a better quencher than dienes).

**Triplet Deactivation in Polymer Systems.**  $\beta$ -Phenylpropiophenone moieties were incorporated in polymer matrices by copolymerizing the methacrylate esters of hydroxy-substituted  $\beta$ -phenylpropiophenones (XXI and XXII) with methylmethacrylate or styrene. The latter was also copolymerized with chalcone (XXII). Suitable model monomers without  $\beta$ -aryl rings (XIX and XX) were also prepared and copolymerized. The two acetates

(16) No indication of charge-transfer intermediates (such as those proposed by Wilson and Halpern) could be detected under our experimental conditions: Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7279; **1981**, *103*, 2412; Wilson, T.; Frye, S. L.; Halpern, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 3600.

(17) E.g.: Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* **1980**, *13*, 815. Beck, G.; Dobrowolski, G.; Kiwi, J.; Schnabel, W. *Macromolecules* **1975**, *8*, 9.

(18) Where this condition is not met a small correction becomes necessary: Nicodem, D. E.; Scaiano, J. C., to be published.



in Table I (XV and XVIII) serve as monomeric models for polymer-incorporated XXI and XXII. Table V summarizes the data obtained by combination of direct and Stern-Volmer studies such as those discussed above. The values of  $k_q$  obtained for polymers where  $\beta$ -phenyl deactivation is unimportant were used in order to estimate  $\tau_T$  values from the Stern-Volmer slopes for copolymers containing XXI, XXII, and XXIII, where direct detection at room temperature is not possible.

### Discussion

Absorption and phosphorescence spectra, as well as energy-transfer studies, all indicate that the carbonyl chromophore in ketones having  $\beta$ -aryl groups does not differ significantly from the chromophore in the case of the unsubstituted ketone. This is consistent with earlier studies where this particular characteristic had been examined.<sup>12</sup> Which then are the effects that control or determine the efficient deactivation of the excited triplet? Our results with  $\beta$ -phenyl-*p*-methoxypropio-phenone (XVII) clearly show that  $\pi, \pi^*$  triplets are substantially less prone to  $\beta$ -phenyl deactivation than their  $n, \pi^*$  counterparts. Similar effects have been observed in the case of the Norrish type I and type II reactions,<sup>19-22</sup> where we concluded that the reaction in the methoxy derivative takes place from a thermally populated  $n, \pi^*$  triplet, in agreement with an earlier proposal by Wagner.<sup>20</sup> Thus, *p*-methoxy substitution decreases the reactivity by ca. a factor of 100, which independent reports by Lewis<sup>23</sup> and Wagner<sup>20</sup> have attributed to ca. 1%  $n, \pi^*$  populations in the Norrish types I and II reactions. We propose that the same ideas apply to deactivation by  $\beta$ -phenyl rings. We find that the difference of about two orders of magnitude caused by *p*-methoxy substitution is in all cases the result of a 2-3 kcal/mol increase in activation energy. Table VI summarizes the Arrhenius parameters obtained here and in earlier reports for  $\beta$ -phenyl deactivation and the Norrish types I and II reactions. The activation energy differences are always consistent with the expected energy gaps in the case of *p*-methoxybenzoyl chromophores.<sup>19-21</sup> It would seem fortuitous for three unrelated reactions to follow this pattern of reactivity, unless the factor that determines these differences is exactly the same in all cases. We therefore propose that deactivation by  $\beta$ -aryl rings takes place from, and indeed requires, an  $n, \pi^*$  triplet state. This explanation seems more consistent with experiment than the suggestion by Kilp<sup>12</sup> that the decrease in reactivity upon *p*-methoxy substitution

**Table V.** Triplet Lifetimes, Stern-Volmer Slopes, and Quenching Constants for Various Copolymers at 300 K

copolymer	$k_q \tau_T$ , M <sup>-1</sup>	$k_q^a$	$\tau_T$ , ns	
			direct	Stern-Volmer <sup>b</sup>
XIX/MMA <sup>c</sup>		$(5.0 \pm 0.5) \times 10^9$	1100	
XX/MMA		$(4.7 \pm 0.5) \times 10^9$	3700	
XXI/MMA	$8 \pm 3$			$2 \pm 1$
XXII/MMA	$15 \pm 5$			$3 \pm 1$
XXIII/styrene	$14 \pm 1$		$(46)^d$	$3 \pm 1$

<sup>a</sup> In units of M<sup>-1</sup> s<sup>-1</sup> (for 1-methylnaphthalene), from laser photolysis experiments. <sup>b</sup> Using the  $k_q$  values obtained for the copolymers in the first two entries of this table. <sup>c</sup> MMA = methyl methacrylate. <sup>d</sup> At 213 K.

**Table VI.** Comparison of Arrhenius Parameters for Reactions of  $n, \pi^*$  and  $\pi, \pi^*$  Triplets in Hydrocarbon Solvents

substrate	process	$k(300 \text{ K})$	$E_a^a$	ref
valerophenone	Norrish type II	$1.8 \times 10^8$	4.0	19, 24
<i>p</i> -methoxyvalerophenone	Norrish type II	$1.3 \times 10^6$	6.9	19
$\gamma$ -methylvalerophenone	Norrish type II	$4.9 \times 10^8$	2.7	19, 24
<i>p</i> -methoxy- $\gamma$ -methylvalerophenone	Norrish type II	$9.5 \times 10^6$	5.5	19
pivalophenone	Norrish type I	$8.5 \times 10^6$	7.3	19
<i>p</i> -methoxypivalophenone	Norrish type I	$2.9 \times 10^5$	10.0	19
isobutyrophenone	Norrish type I	$7.4 \times 10^3$	12.0	19
<i>p</i> -methoxyisobutyrophenone	Norrish type I	68.1	14.9	19
I	$\beta$ -phenyl quenching	$1 \times 10^9$	$\sim 2.3$	this work
XVII	$\beta$ -phenyl quenching	$1.8 \times 10^7$	4.4	this work

<sup>a</sup> In kcal/mol.

reflects an intrinsic lower reactivity of the  $\pi, \pi^*$  state.

A comparison of pre-exponential factors is also rather informative. In nonpolar solvents the values of  $\log(A/s^{-1})$  are typically  $\sim 13$  for the Norrish type I process,  $\sim 11$  for the type II, and  $\sim 10.5$  for  $\beta$ -phenyl quenching. Quite clearly, the transition-state configuration for the last process is even tighter than that for the Norrish type II reaction which requires a cyclic, six-center transition state. This is in line with the conformational dependence observed earlier for the kinetics of  $\beta$ -phenyl quenching<sup>11</sup> and provides an explanation for why the efficiency of the intramolecular deactivation so vastly exceeds that of intermolecular quenching of phenyl alkyl ketone triplets by aromatic solvents. From the rate of quenching of acetophenone triplets by benzene ( $k = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ), we calculate an effective molarity of ca.  $5 \times 10^4 \text{ M}$  for the intramolecular deactivation process; effective molarities of this magnitude are normally indicative of a "tight" transition state.<sup>25</sup>

In all three reactions the  $A$  factors are rather insensitive to *p*-methoxy substitution; indeed, the mechanism proposed involves the same transition state (and therefore similar entropic requirements), regardless of the  $n, \pi^*$  or  $\pi, \pi^*$  character of the low-lying triplet state.

The  $A$  factor for XVII (see Figure 1) shows some solvent dependence,  $\log(A/s^{-1})$  being 10.43 in toluene and 9.83 in methanol. The difference is outside our error limits, and a simple examination of Figure 1 suggests that the effect is indeed real. We propose that hydrogen bonding at the carbonyl center in the case of methanol restricts the access required for deactivation to occur and that this is reflected as a modest entropic contribution to the pre-exponential factor.

The Stern-Volmer slopes for I in various solvents (Table IV) show a remarkably small dependence on solvent viscosity, under conditions where  $k_q$  is expected, and indeed known, to be solvent

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dependent.<sup>26</sup> We can only conclude that changes in  $k_q$  are almost quantitatively compensated by changes in  $\tau_T$ . Such an effect is consistent with the idea that the rate of intramolecular quenching for  $n, \pi^*$  triplets is mainly controlled by the ability of the substrate to achieve a critical conformation; an increased viscosity slows down this process in much the same manner as it slows down intermolecular (diffusion controlled) energy transfer. In other studies we have observed that when molecular motion is severely restricted (for example, by inclusion in zeolite channels) the triplet lifetime of I can be enhanced by over five orders of magnitude.<sup>27</sup>

The insensitivity of  $k_q\tau_T$  to solvent viscosity is in agreement with earlier experiments that showed that  $k_q\tau_T$  for I is almost temperature independent,<sup>11</sup> as well as with the  $k_q\tau_T$  and  $\tau_T$  values in Tables II and III.

Triplet lifetimes and  $k_q\tau_T$  values are also rather insensitive to substituent effects on the  $\beta$ -aryl ring (see Tables II and III). A modest correlation with  $\sigma^+$  can be detected, but even this is rather poorly defined. Furthermore, we find a similarly poor correlation of  $\tau_T$  with the ionization potentials of the corresponding substituted toluenes (Table II), even though one might expect this correlation to be somewhat more meaningful than that with  $\sigma^+$ , if triplet deactivation proceeds via an exciplex<sup>28</sup> or charge-transfer mechanism. We also note that a  $\sigma^+$  correlation may not be applicable to a through-space interaction, where o, m, and p become simply a point of attachment, but not the site where electronic effects are probed. Should the absence of substituent effects be taken to mean that charge transfer does not play a role in the quenching process? In fact, we do believe that charge transfer does make an important contribution in the transition state for quenching. Quite simply, this is not the rate-determining step. Just as substituent effects would be masked in a diffusion-controlled intermolecular process, the same ideas apply to intramolecular deactivation. While the process probably does involve charge transfer, just as it does in the intermolecular process, the kinetics are controlled by the conformational adjustments mentioned before. Along this line, it is interesting to note the somewhat longer lifetimes observed for the *o*-methoxy and 2,4,6-trimethyl derivatives (VI and V). In these derivatives, the presence of bulky ortho substituents may effect some restriction to attaining the proper orientation for deactivation.

The small variations in  $k_q\tau_T$  in Table IV support this viewpoint. In the case of XVII, where direct lifetime measurements are possible, we observe the expected trend with solvent viscosity, but the variations are not as large as expected from the change in viscosity. This probably reflects the fact that here the process is not entirely controlled by molecular motion, which is presumably competitive with population and depopulation of the  $n, \pi^*$  state which is also expected to occur in the  $10^8$ – $10^{10}$  s<sup>-1</sup> time domain.<sup>29</sup> The process resembles many other carbonyl processes where conformational control can play an important role; these have been recently reviewed by Wagner.<sup>30</sup>

Rates of isoenergetic energy transfer from phenyl alkyl ketones (e.g., propiophenone, acetophenone, isobutyrophenone) to  $\gamma$ -methylvalerophenone are of the order of  $1 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> in hydrocarbon solution at room temperature.<sup>31</sup> Here, reversible energy transfer is precluded by the short triplet lifetime of the acceptor. We would thus expect I to irreversibly quench aromatic ketone triplets with a similar rate constant, and indeed this is the case.<sup>13</sup> This would suggest that these molecules, or similar moieties incorporated into vinyl monomers, could behave as polymer photostabilizers. Table V shows the results of a series of experiments in which we explored this question. Quite clearly the triplet still undergoes intramolecular quenching with almost the same rate constant as in monomeric systems, regardless of whether the deactivating structure is part of or simply connected to the main polymer backbone. Further work on polymer photostabilization

is currently in progress and will be reported elsewhere.

## Conclusion

Carbonyl triplets are efficiently deactivated intramolecularly by  $\beta$ -aryl groups. The process requires an  $n, \pi^*$  triplet state; molecules having low-lying  $\pi, \pi^*$  states react via a mechanism involving thermal population of the upper  $n, \pi^*$  state, requiring the same type of equilibration which takes place in the Norrish types I and II reactions. The quenching process typically leads to triplet lifetimes in the neighborhood of 1 ns at room temperature and 10–60 ns at 190 K and is rather insensitive to substituent effects. It is suggested that while the quenching probably involves charge-transfer interactions, its kinetics are controlled by molecular motions. Measured preexponential factors, solvent and substituent effects all support this conclusion. Preliminary results in polymer systems suggest that the use of  $\beta$ -aryl ketones as polymer photostabilizers deserves further examination.

## Experimental Section

Ultraviolet absorption spectra were recorded on a Cary-Varian 219 spectrometer. Phosphorescence emission spectra were recorded on a Perkin-Elmer LS-5 spectrofluorometer equipped with a PE Model 3600 data station and a rectangular quartz Dewar, using 7-mm cylindrical quartz sample tubes.

Laser flash photolysis experiments employed the pulses (337.1 nm, 3–10 mJ, ca. 8 ns) from a Moletron UV-24 nitrogen laser for excitation. Samples were contained in  $3 \times 7$  or  $7 \times 7$  mm<sup>2</sup> rectangular cells built with Suprasil quartz (Vitro Dynamics). All samples were deoxygenated by bubbling with dry nitrogen. Quenchers were added as aliquots of the neat material or standard solutions. Further experimental details and a full description of the instrument have been reported elsewhere.<sup>32</sup> The solutions had optical densities of  $\sim 0.7$  (monoketones) or  $\sim 0.4$  (polymers) in a 3-mm cell.

Methylcyclopentane, isooctane, toluene, acetonitrile, *n*-heptane, methanol, carbon tetrachloride, and 2-propanol were Aldrich Gold Label and used as received. Benzene was washed with concentrated sulfuric acid, water, and saturated bicarbonate, dried over calcium chloride, and distilled from calcium hydride. *tert*-Butyl alcohol (Fisher Reagent) was distilled from calcium hydride. Ethylene glycol (Aldrich) was used as received.

Ketones I–X, XII–XIV, XVI, and XVII were prepared from the corresponding substituted acetophenones and benzyl alcohols by the method of Pratt and Evans.<sup>33</sup> Melting points and/or spectral data (IR, <sup>1</sup>H NMR) coincided closely with previously reported data in each case.

Ketones XI and  $\beta$ -phenyl-4-hydroxypropiophenone (XXIV) were prepared by condensation of the corresponding substituted benzaldehyde and acetophenone, followed by catalytic hydrogenation with Raney nickel.<sup>34</sup> The melting points of these compounds matched the literature values.<sup>34</sup> XV and XVIII were prepared by condensation of XI and XXIV, respectively, with acetyl chloride in 10% aqueous sodium hydroxide and pyridine, respectively.

Ketones XIX and XXI were prepared by condensation of  $\alpha$ -hydroxyacetophenone (Aldrich) and XV, respectively, with methacryloyl chloride (Aldrich) in 10% aqueous sodium hydroxide. Ketones XX and XXI were prepared from 4-hydroxypropiophenone (Aldrich) and XXIV, respectively, and methacryloyl chloride in pyridine. The methacrylate esters were purified prior to copolymerization by rapid column chromatography with silica gel and methylene chloride as eluant. The <sup>1</sup>H NMR spectra of these compounds were consistent with their proposed structures, although no further characterization was carried out. Chalcone (Aldrich) was recrystallized once from ethanol.

Copolymers of XIX–XXII and methyl methacrylate were prepared as follows: Methyl methacrylate (Aldrich) was washed twice with 10% sodium hydroxide to remove the stabilizer and then washed once with water and dried over anhydrous sodium sulfate. The purified methyl methacrylate (5 g) was combined with ca. 0.5 g of the ketone and azobisisobutyronitrile (0.1 g), dissolved in benzene (7 mL), and placed in a 30-mm Pyrex tube. The mixture was degassed by the freeze-pump-thaw method (3 cycles), sealed, and placed in a hot-water bath at 50 °C for 2–5 h. The tube was opened and methanol (20 mL) was added to the viscous mixture to quench the polymerization. The polymer was purified by 5–8 dissolution/precipitation cycles with purified benzene and methanol and finally dissolved in benzene and freeze-dried under vacuum.

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The yield of purified polymer was generally 0.3–0.5 g.

The chalcone/styrene copolymer was prepared and purified in a similar fashion, starting from chalcone (0.5 g), freshly distilled styrene (5.0 g), azobis(isobutyronitrile) (0.1 g), and benzene (7 mL). The yield of purified polymer was 0.35 g.

The compositions of the above polymers were determined by UV spectroscopy, from the absorbances at 345 nm of standard samples in benzene solution. The extinction coefficient of the  $n, \pi^*$  absorption in these copolymers was assumed to be the same as that of propiophenone in benzene. The compositions of the polymers determined in this way corresponded to incorporation of 8–12% ketone.

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**Registry No.** I, 1083-30-3; II, 84839-91-8; III, 95465-70-6; IV, 1669-50-7; V, 95465-71-7; VI, 95465-72-8; VII, 15101-68-5; VIII, 1669-49-4; IX, 58122-03-5; X, 5739-39-9; XI, 17791-25-2; XII, 62584-66-1; XIII, 59824-24-7; XIV, 95465-73-9; XV, 95465-74-0; XVI, 5739-37-7; XVII, 5739-38-8; XVIII, 95465-75-1; XIX/MMA, 95465-63-7; XX/MMA, 95465-65-9; XXI/MMA, 95465-67-1; XXII/MMA, 95465-69-3; XXIII/styrene, 49555-98-8; 1-methylnaphthalene, 90-12-0.

## Aqualigand Dissociation of $[\text{Ce}(\text{OH}_2)_9]^{3+}$ in the $5d \leftarrow 4f$ Excited State

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**Abstract:** Hydrated  $\text{Ce}^{3+}$  ions in aqueous solution are predominantly in a tricapped trigonal structure of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$ . However, an equilibrium between  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  and  $[\text{Ce}(\text{OH}_2)_8]^{3+}$  exists in aqueous solution. Upon the  $5d \leftarrow 4f$  excitation, one of the aqualigands of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  dissociates in the excited state and an emission band exclusively comes out from  $^*[\text{Ce}(\text{OH}_2)_8]^{3+}$ . In ethylene glycol, however, the emissions not only of the long-lived excited species  $^*[\text{Ce}(\text{OH}_2)_9]^{3+}$  (48 ns) but also of the short-lived excited species  $^*[\text{Ce}(\text{OH}_2)_8]^{3+}$  (430 ps) were detected upon intense laser pulse excitation. The rise transient which indicates an increase of  $[\text{Ce}(\text{OH}_2)_8]^{3+}$  immediately after the excitation was also observed in ethylene glycol. The lifetime of  $^*[\text{Ce}(\text{OH}_2)_9]^{3+}$  in solution is controlled by the rate of aqualigand dissociation.

Five absorption bands are observed in a region between 37 and  $51 \times 10^3 \text{ cm}^{-1}$  with single crystals of  $\text{Ce}^{3+}$  doped lanthanum(III) ethylsulfate enneahydrate (Ce:La-ES).

In the crystal,  $\text{Ce}^{3+}$  is in a ligand field of nine water molecules such as in  $[\text{Ce}(\text{OH}_2)_9]^{3+}$ . The ultraviolet bands are assigned to five Kramers doublets which are the excited  $^2D(5d^1)$  multiplet split by the ligand-field interaction and the spin-orbit coupling of a cerium  $5d$  electron.<sup>1,2</sup>

Two resolved luminescence bands are also detected at 30 and  $32 \times 10^3 \text{ cm}^{-1}$  at liquid-nitrogen temperature. The excitation spectrum of the luminescence conforms to the absorption spectrum. The twin emission bands, which cannot be resolved at ambient temperatures, are ascribed to the transitions to the  $^2F_{5/2}$  and  $^2F_{7/2}$  substates, two components of the ground  $^2F(4f^1)$  multiplet, which are split almost exclusively by the spin-orbit coupling of a cerium  $4f$  electron.<sup>1,2</sup>

Hydrated  $\text{Ce}^{3+}$  ions in aqueous solution show the absorption bands which correspond to those observed with Ce:La-ES. The hydrated ions must be in a similar structure as found in the single crystal. However, the aqueous solution displays an extra weak absorption band at  $34 \times 10^3 \text{ cm}^{-1}$ . The band cannot be detected with Ce:La-ES even if a high concentration of  $\text{Ce}^{3+}$  and/or a thick crystal are used.<sup>1</sup> The ligand-field splitting of the  $^2D(5d^1)$  manifold gives not more than five Kramers doublets. A partial dissociation of the coordinated waters in aqueous media has been proposed.<sup>3</sup> Recent X-ray studies on the aqueous solutions concluded that the hydrated ions  $\text{La}^{3+}$  through  $\text{Nd}^{3+}$  are nine coordinated and those between  $\text{Nd}^{3+}$  and  $\text{Tb}^{3+}$  are transitional between nine and eight.<sup>4,5</sup> However, the weak band at  $34 \times 10^3 \text{ cm}^{-1}$  provides sound evidence of the partial dissociation. For the aqueous solution of  $\text{Ce}^{3+}$  ion, an emission band is observed at  $28 \times 10^3 \text{ cm}^{-1}$  instead of the band

observed at  $30\text{--}32 \times 10^3 \text{ cm}^{-1}$  with the Ce:La-ES regardless of the excitation wavelengths in the band of the dissociated species or in the five-component absorption bands of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$ .<sup>1</sup> The luminescence comes out exclusively from a dissociated species such as  $[\text{Ce}(\text{OH}_2)_8]^{3+}$ . The luminescence of the hydrated  $\text{Ce}^{3+}$  ion in aqueous media decays in a single exponential of 45 ns regardless of the excitation wavelengths, while that of Ce:La-ES decays in a shorter lifetime of 27 ns.<sup>2</sup>

Upon the  $5d \leftarrow 4f$  excitation of  $\text{Ce}^{3+}$  ion, one of the aqualigands in  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  dissociates in solution. However, a greater Stokes shift observed on Ce:La-ES indicates that a deformation of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  occurs in the excited state but does not result in bond dissociation in the crystal.

In the present work, a very fast aqualigand dissociation of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  in the excited state was studied.

### Experimental Section

**Materials.** Cerium(III) ethylsulfate enneahydrate (Ce-ES) was obtained by the method of Ketelaar.<sup>6</sup>  $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ ,  $(\text{C}_2\text{H}_5)_2\text{SO}_4$ , and  $\text{BaCO}_3$  were commercially available and of reagent grade.

Ethylene glycol was purified by distillation under reduced pressure.

**Solutions for Measurements.** For measurements, the crystals of Ce-ES were dissolved in  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and ethylene glycol. Absorption, emission, and excitation spectra of Ce-ES in solution were exactly coincident with the spectra of  $\text{Ce}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$  in solution. The perchlorate is a weaker ion pair forming salt; however, it is too deliquescent to be used for quantitative preparation of solutions.

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