Photoreduction of α-Trifluoroacetophenone. Competitive Charge Transfer and Hydrogen Abstraction[1a]

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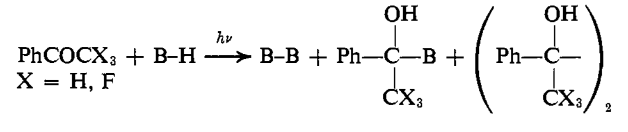
Abstract: A kinetic comparison of the photoreduction of acetophenone (AH_3) and α,α,α-trifluoroacetophenone (AF_3) indicates the following. Since the ability of benzene ($k_q = 7 \times 10^5\ M^{-1}\ sec^{-1}$) and alkylbenzenes to quench triplet AF_3 does not depend on their C–H bond strengths but does depend on their ionization potential, it is concluded that they quench triplet AF_3 by a rapid charge-transfer process. A small polar solvent effect and the low slope of a log k_q *vs.* IP plot suggest only ~20% electron transfer in the triplet CT complex. If the aromatic has benzylic hydrogens, the CT complex can transfer a proton to the carbonyl oxygen to yield the radical intermediates normally found in photoreductions. Proton transfer and reverse charge transfer to regenerate ground-state reactants compete about equally in the CT complex formed from triplet AF_3–toluene. The reactivity of cyclohexane indicates that triplet AF_3 does abstract hydrogen atoms directly, and more rapidly than does triplet AH_3. Deuterium isotope effects indicate that triplet AF_3 reacts with cumene both by charge transfer and by direct hydrogen atom abstraction, with toluene almost exclusively by the former process. Thus, the overall effect of α-fluorine substitution on triplet acetophenone is to increase the rates of both hydrogen abstraction and charge transfer complexing. The latter process is enhanced more, so that it becomes the predominant photoreduction mechanism for AF_3 and alkylbenzenes. These rate enhancements are particularly interesting because the phosphorescence of AF_3 indicates a π,π* lowest triplet, with a n,π* triplet so close that it must be significantly populated and thus reactive at room temperature.

Despite the many studies on the photoreduction of ketones, especially benzophenone,[2,3] there have been very few investigations of the effects of substituents *not conjugated* to the carbonyl or benzoyl system on excited state reactivity. Consequently, we have carefully compared the photoreduction of α,α,α-trifluoroacetophenone (AF_3) with that of acetophenone (AH_3) itself and report here how the strongly electron-withdrawing fluorines change the reactivity and the nature of the triplet state.

Results

Products of Photoreduction. We find that AF_3, like acetophenone itself,[4] undergoes photoreduction in benzene solution in the presence of 2-propanol, cyclohexane, and many substituted toluenes. Because of the rapid buildup of colored by-products, we did not study the propanol reduction carefully. With all the hydrocarbons, the products obtained upon irradiation are the diastereomeric pinacols, the bibenzyl (or bicyclohexyl), and the cross-coupling product. With cyclohexane, cyclohexylbenzene was also observed in four times the yield of bicyclohexyl. With the other reductants, however, no products other than the three mentioned above could be detected by vpc analysis. Relative yields of the two products containing the B group were estimated by vpc analysis and are listed in Table I. In the case of *p*-xylene, these two products accounted for 94% of AH_3 reacted and 90% of AF_3 reacted. We assume comparably high material balances for all reductants.



$$\mathrm{PhCOCX_3 + B\text{-}H \xrightarrow{h\nu} B\text{-}B + Ph\text{—}\overset{OH}{\underset{CX_3}{C}}\text{—}B + \left(Ph\text{—}\overset{OH}{\underset{CX_3}{C}}\text{—}\right)_2}$$

X = H, F

Quantum yields of product formation at 313 nm were determined as a function of reductant concentration in benzene for all the compounds listed in Table I.[5] Maximum conversions (ketone reacted) were 6%.

Table I. Yields of Products from Irradiation of Acetophenone and α-Trifluoroacetophenone[a]

Substrate	BB/CC[b]	Y_{BB}[c]
	Acetophenone	
p-Xylene	0.76	0.30
Cumene	0.63	0.28
Toluene	0.61 (0.50)[d]	0.27
Toluene-α-d_3	0.60	0.27
	α-Trifluoroacetophenone	
p-Xylene	0.53	0.26
m-Xylene	0.46	0.24
o-Xylene	0.48	0.24
Mesitylene	0.76	0.30
p-Methoxytoluene	0.20	0.14
p-Fluorotoluene	0.48	0.24
p-Chlorotoluene	0.42	0.23
p-Cyanotoluene	~0.031[e]	~0.03
Toluene	0.46	0.24
Toluene-α-d_3	0.45	0.24
Cumene	0.51	0.25
Cumene-α-d_1	0.48	0.24
Cyclohexane	0.085	0.08

[a] Irradiated at 313 nm in benzene solution. [b] Ratio of bibenzyl or bicyclohexyl to cross-coupling product. [c] Yield of bibenzyl: BB/(2BB + CC). [d] Reference 4b. [e] Bibenzyl product thermally unstable.

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[1] (a) Preliminary communication; *J. Amer. Chem. Soc.*, **92**, 5806 (1970); (b) Alfred P. Sloan Fellow, 1968–1972; (c) from Ph.D. Thesis of R. A. L.

[2] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961); G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961).

[3] C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

[4] (a) S. G. Cohen and B. Green, *ibid.*, **91**, 6824 (1969); (b) D. Bellus and K. Schaffner, *Helv. Chim. Acta*, **52**, 1010 (1969).

[5] Complete tables of quantum yields will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-3669. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

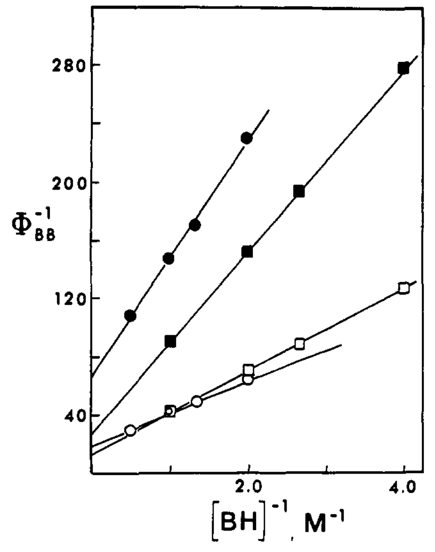

Figure 1. Dependence of quantum yield of bibenzyl formation on substrate concentration, α-trifluoroacetophenone: (○) toluene; (●) toluene-α-d_3; (□) cumene; (■) cumene-α-d.

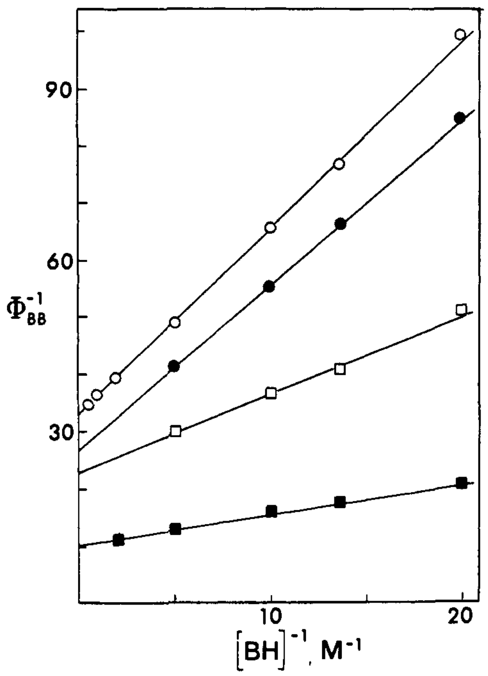

Figure 2. Dependence of quantum yield of bibenzyl formation on substrate concentration, α-trifluoroacetophenone: (○) m-xylene; (●) o-xylene; (□) mesitylene; (■) p-methoxytoluene.

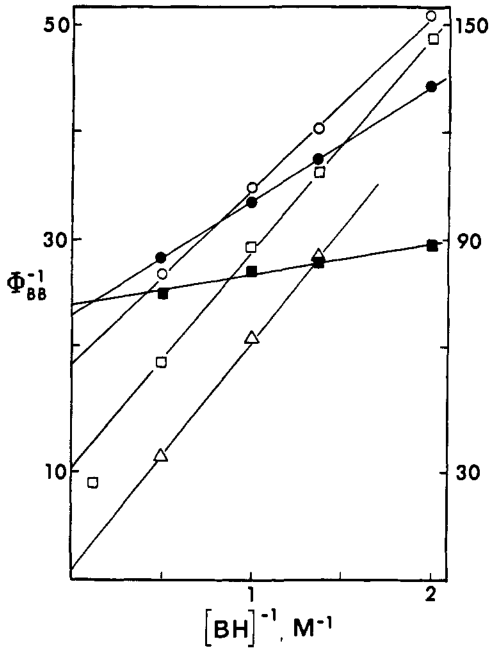

Figure 3. Dependence of quantum yield of bibenzyl formation on substrate concentration, α-trifluoroacetophenone: (○) p-chlorotoluene; (●) p-fluorotoluene; (■) p-xylene; (△) cross-coupling product from p-cyanotoluene (right ordinate); (□) bicyclohexyl (left ordinate × 50).

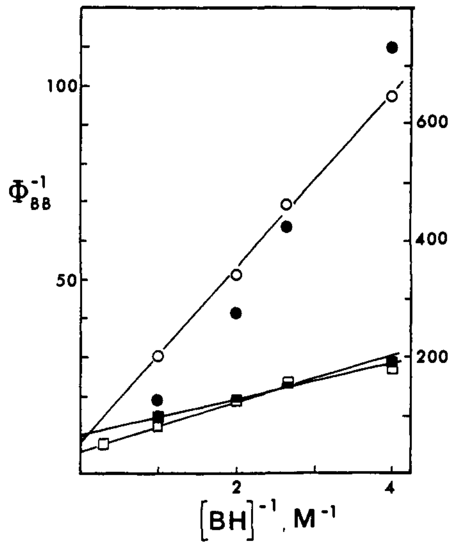

Figure 4. Dependence of quantum yield of bibenzyl formation on substrate concentration, acetophenone: (○) toluene; (□) cumene; (■) p-xylene; (●) toluene-α-d_3 (right ordinate).

Actinometry was provided by parallel irradiation of 0.1 M valerophenone solutions.[6] Figures 1–4 display plots of reciprocal quantum yield *vs.* reciprocal reductant concentration, which in all cases are satisfyingly linear. Table IV list the values of the reciprocal intercepts and of the slope/intercept ratios under the columns headed Φ_{BB}^{max} and k_d/k_r, respectively.

Quenching studies were performed on the p-xylene and toluene photoreduction of both ketones in benzene and of AF_3 in acetonitrile. Degassed solutions containing 0.10 M ketone, 0.001 M of a high-boiling n-alkane as internal standard, 0.25–0.3 M xylene or toluene, and various concentrations of naphthalene or p-di-*tert*-butylbenzene were irradiated at 365 or 313 nm, respectively, to conversions $\leqslant 5\%$. Stern–Volmer plots of relative bixylyl or bibenzyl yields were linear, as shown by Figures 5–7; the slopes are indicated as $k_q\tau$ values in Table II. Since k_q for quenching of several ketone triplets by naphthalene equals $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ in benzene,[7] $1/\tau$ values for AH_3 and AF_3 were calculated on the basis of that k_q value and are plotted as a function of p-xylene concentration in Figure 9.

Intersystem crossing yields of AF_3 and AH_3 were compared by parallel irradiation at 313 nm of degassed

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[6] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **94**, 7495 (1972).

[7] G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, **315**, 163 (1970).

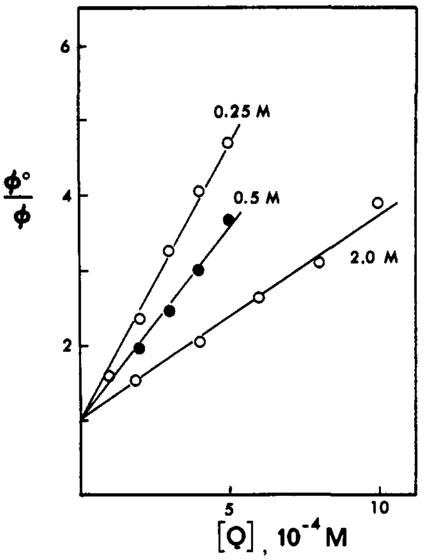

Figure 5. Stern–Volmer plots for naphthalene quenching of photoreduction of α-trifluoroacetophenone by *p*-xylene at various *p*-xylene concentrations.

Table II. Quenching of Photoreductions in Benzene[a]

Ketone	Substrate	Concn, *M*	Quencher	$k_q\tau$, M^{-1}
AH_3	*p*-Xylene	0.25	Naphthalene	7560
		0.50		5050
		1.0		4600
		1.5		3570
		2.0		2610
		2.5		2160
AF_3	*p*-Xylene	0.10	Naphthalene	300
		0.50		94
		1.0		48
		1.5		34
		1.0[b]		55
		0.5	DTBB	0.25
	Toluene	0.5	DTBB	1.05

[a] [Ketone] = 0.1 *M*, 366 nm. [b] Acetonitrile solvent, $k_q = 1 \times 10^{10}\ M^{-1}\ sec^{-1}$: I. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, **94**, 3859 (1972).

benzene solutions 0.1 *M* in either ketone and 0.20 *M* in *cis*-1,3-pentadiene. The trifluoro ketone is 96% as effective as acetophenone itself in photosensitizing the isomerization, from which Φ_{isc} for AF_3 is concluded to be nearly unity.[8]

Spectroscopy of $PhCOCF_3$. The uv spectrum of AF_3 in heptane is very similar to that of AH_3 except that λ_{max} for the intense $^1A \rightarrow {}^1L_a$ transition occurs at 250 nm instead of 238 nm, a 5.8-kcal stabilization. The phosphorescence of AF_3 was studied at 77°K in isopentane, methylcyclohexane, and ethanol. In the former two solvents, the spectra are identical (Figure 8), with 0–0 bands at 4035 Å (70.9 kcal/mol), a prominent progression compounding to the ground-state carbonyl stretch at 1720 cm^{-1}, and weaker vibronic bands at $\sim$800 and $\sim$1000 cm^{-1}. In both solvents phosphorescence decay is completely exponential through 3 half-lives, with τ_p = 57 msec. In ethanol, the 0–0 band occurs at 4080 Å (70.0 kcal/mol), the spectrum is broader but still displays a pronounced carbonyl progression, and τ_p equals 200 msec through 5 half-lives.

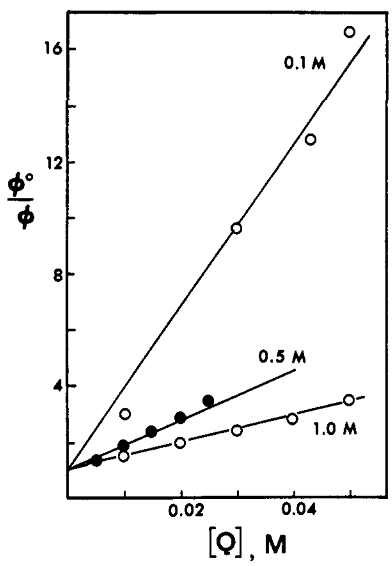

Figure 6. Stern–Volmer plots for naphthalene quenching of photoreduction of acetophenone by *p*-xylene at various *p*-xylene concentrations.

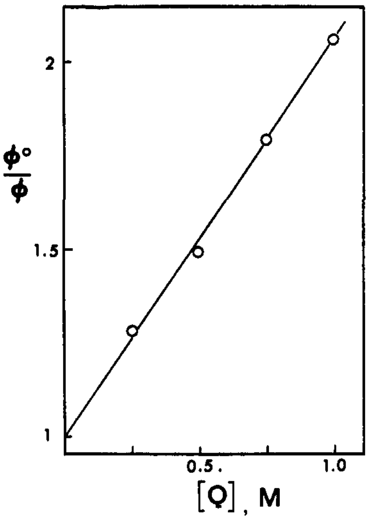

Figure 7. Stern–Volmer plot for di-*tert*-butylbenzene quenching of the photoreduction of α-trifluoroacetophenone by 0.5 *M* toluene.

The many-component phosphorescence previously reported[9] may have resulted from residual impurities in the ketone.

Reduction potentials of AH_3 and AF_3 were determined polarographically on degassed DMF solutions 10^{-3} *M* in ketone and 0.1 *M* in tetrabutylammonium iodide. Measured half-wave potentials, relative to a standard calomel electrode, are −2.06 and −1.42 eV, respectively, for AH_3 and AF_3.

Discussion

Triplet Rate Constants. As Figure 9 reveals, the rate of decay of the triplet ketones is a linear function of *p*-xylene concentration, indicative of a bimolecular reaction between triplet ketone and ground-state reductant. Equations 1–3 are completely general and allow an unbiased *kinetic* analysis of bimolecular photoreactions; k_d is the rate of triplet decay in the absence of reductant and k_r is the second-order rate constant for reaction of

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

(9) R. N. Griffin, *Photochem. Photobiol.*, **7**, 159 (1968).

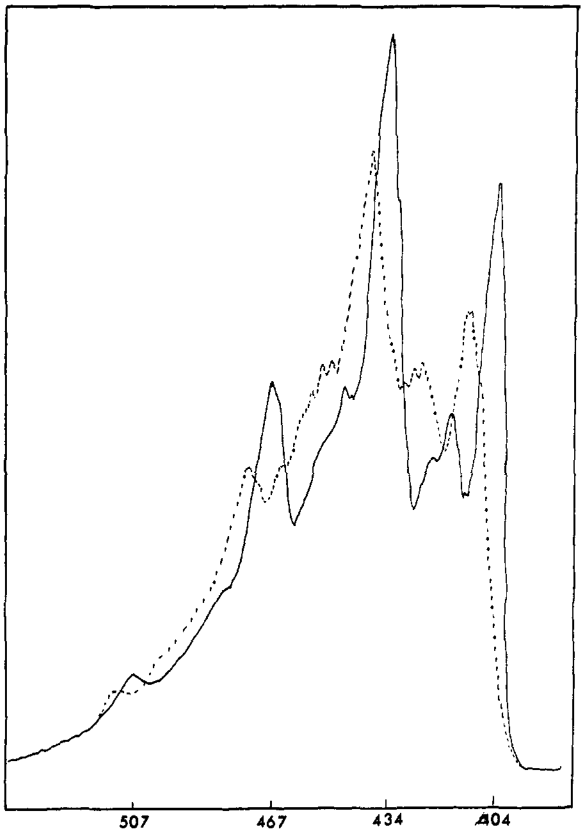


Figure 8. Phosphorescence of α-trifluoroacetophenone at 77°K: (—) in methylcyclohexane or isopentane; (- - -) in ethanol.

the triplet ketone with reductant. A *mechanistic* analysis of the nature of the processes which these rate constants measure is presented in the following section.

$$1/\tau = k_d + k_r[\mathrm{BH}] \qquad (1)$$

$$\Phi_{\mathrm{BB}}^{-1} = (\Phi_{\mathrm{BB}}^{\max})^{-1}\left(1 + \frac{k_d}{k_r[\mathrm{BH}]}\right) \qquad (2)$$

$$\Phi_{\mathrm{BB}}^{\max} = \Phi_{\mathrm{ISC}} P_{\mathrm{p}} Y_{\mathrm{BB}} \qquad (3)$$

Equation 2 expresses the well-known linear relationships plotted in Figures 1-4. Equation 3 divides $\Phi_{\mathrm{BB}}^{\max}$ into three components: (1) intersystem crossing quantum yield; (2) the probability, P_{p}, that metastable intermediates proceed on to products rather than reverting to ground state of reactant; and (3) Y_{BB}, the actual chemical yield of bibenzyl (maximum = 50%). Φ_{ISC} is within experimental error of unity for both ketones, so that $\Phi_{\mathrm{BB}}^{\max}$ represents the probability that reaction of triplet ketone with reductant actually leads to bibenzyl rather than to other products or to quenching. Variations in $\Phi^{\max}$ values are analyzed below. Since Y_{BB} values toward a given hydrocarbon are very similar for both ketones, different $\Phi^{\max}$ values for AH_3 and AF_3 reflect primarily different P_{p} values. These are listed in Table IV.

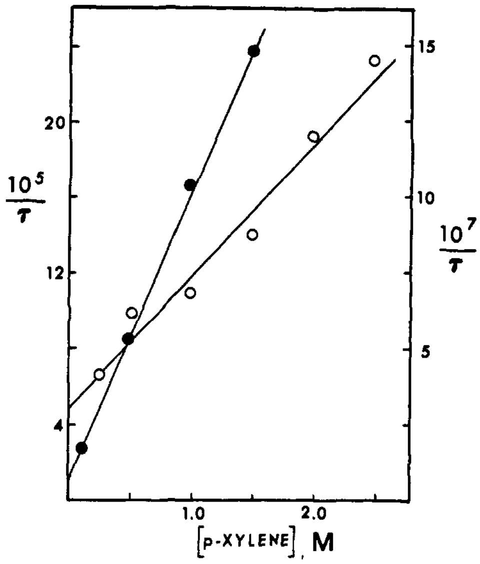


Figure 9. Rate of triplet decay of acetophenone (○) (left ordinate) and α-trifluoroacetophenone (●) (right ordinate) as a function of *p*-xylene concentration.

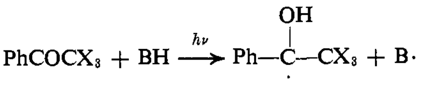
Table III. Kinetic Data for Photoreduction of Acetophenone and α-Trifluoroacetophenone by *p*-Xylene

Quantity	AH_3	AF_3
k_d/k_r, M	1.0	0.091
k_r, $10^6\ M^{-1}\ \mathrm{sec}^{-1}$	0.7	97
k_d, $10^6\ \mathrm{sec}^{-1}$ [a]	0.5	7.0
k_d, $10^6\ \mathrm{sec}^{-1}$ [b]	0.7	8.8

[a] Intercepts of Figure 9. [b] From k_d/k_r values.

The slopes and intercepts in Figure 9 yield values of k_r for *p*-xylene and k_d, respectively. The *p*-xylene plots in Figures 3 and 4 give independent measures of k_d/k_r. For both AH_3 and AF_3, agreement between the two independent measurements is well within experimental error, as shown in Table III. In order to calculate k_r values for all the other reductants, we have used the presumed constant k_d values determined from the *p*-xylene k_d/k_r values and the *p*-xylene k_r values determined from Figure 9. These k_d values are slightly higher than the intercepts of Figure 9 and seem preferable because of the long extrapolations to [BH] = 0, especially for AF_3. Table IV summarizes the kinetic data for both ketones.

Mechanism of Photoreduction. Since both AH_3 and AF_3 yield similar ratios of the three possible radical coupling products, we conclude that photoreduction of each proceeds through similar radicals. However, the two ketones differ in that maximum quantum yields are



$$\mathrm{PhCOCX_3} + \mathrm{BH} \xrightarrow{h\nu} \mathrm{Ph{-}}\overset{\mathrm{OH}}{\underset{\cdot}{\mathrm{C}}}\mathrm{{-}CX_3} + \mathrm{B}\cdot$$

only half as large for AF_3 as for AH_3 and in that the pattern of variation in k_r with the structure of BH is strikingly different for the two triplets.

It is almost universally accepted that the photoreduction by hydrocarbons of acetophenone,[4] like that of benzophenone,[2,3] proceeds by direct hydrogen atom abstraction from substrate by the lowest triplet, which is an n,π* state.[10] The relative reactivities of toluene, *p*-xylene, and cumene toward triplet AH_3 are exactly what would be expected for an alkoxy-radical-like species[11,12] and agree well with those in a previous report.[3] There

(10) A. A. Lamola, *J. Chem. Phys.*, **47**, 4810 (1967).

(11) C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967).

(12) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960).

Table IV. Kinetic Parameters for Photoreduction of Acetophenone and α-Trifluoroacetophenone in Benzene

Substrate	$\Phi_{BB}{}^{max}$	P_p	k_d/k_r, M	k_r 10^6 M^{-1} sec^{-1}
		Acetophenone		
p-Xylene	0.10	0.33	1.0	0.70
Cumene	0.18	0.65	2.5	0.28
Toluene	0.13	0.47	5.8	0.12
Toluene-d_3			$\geq$30	$\sim$0.02
		α-Trifluoroacetophenone		
p-Xylene	0.040	0.16	0.091	97 (200)[a]
m-Xylene	0.030	0.13	0.10	88
o-Xylene	0.038	0.16	0.11	80
Mesitylene	0.044	0.15	0.061	140
p-Methoxytoluene	0.098	0.70	0.053	170
p-Fluorotoluene	0.044	0.18	0.48	18
p-Chlorotoluene	0.053	0.23	0.84	10
p-Cyanotoluene	0.008	0.30	20	0.4
Toluene	0.053	0.22	1.2	7.3
Toluene-α-d_3	0.015	0.062	1.2	7.3
Cumene	0.073	0.29	2.0	4.4
Cumene-α-d_1	0.039	0.16	2.5	3.5
Cyclohexane	0.002	0.03	1.8	4.7
p-Di-*tert*-butylbenzene				13.5[b]
Benzene				0.90[c]

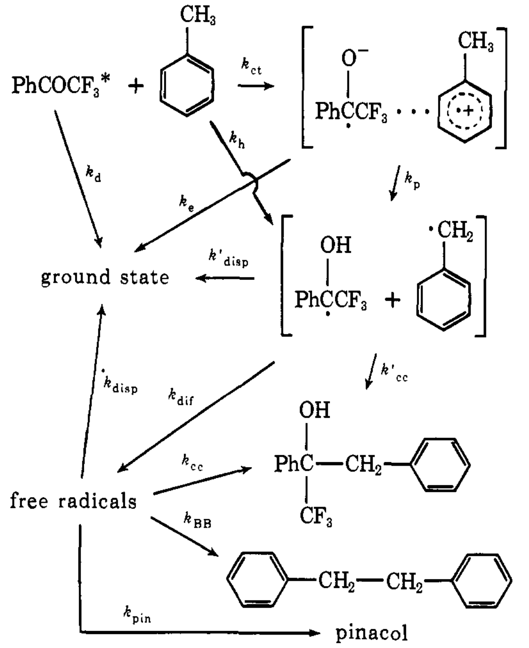
[a] Acetonitrile. [b] From Figure 7 and Table III. [c] k_d/[benzene].

is a significant deuterium isotope effect on k_r. For example, Φ_{BB} at 1 M toluene-α-d_3 is only $^1/_6\Phi_{BB}$ at 1 M toluene-α-h_3. Unfortunately, as Figure 4 shows, a plot of the acetophenone–toluene-α-d_3 data according to eq 2 curves upward, so an exact k_r value could not be determined. The curvature is probably due to unimolecular radical reactions (addition to solvent or scavenging by residual oxygen) beginning to compete with bimolecular radical coupling at the very low steady state radical concentrations produced in this unusually low quantum yield reaction. We have estimated a k_r value from the 2 M Φ_{BB} by assuming that $\Phi_{BB}{}^{max}$ is the same as for toluene itself. A $k_H/k_D \geq 5$ results.

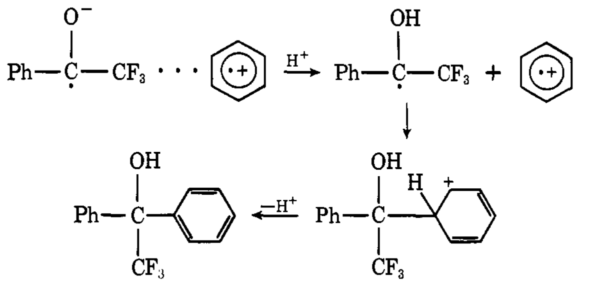
The k_r values for AF$_3$ do not, however, vary with C–H bond strength in the manner expected for a hydrogen atom abstraction. There is *no* deuterium isotope effect with toluene and only a slight one with cumene (see below). Moreover, cumene and cyclohexane are less reactive than toluene. Cyclohexane is more reactive than toluene toward both alkoxy radicals and triplet ketones[3] because of the significant electron-withdrawing inductive effect of the benzene ring. Triplet AF$_3$ surely must be more electrophilic than triplet AH$_3$, so the rate of hydrogen abstraction by triplet AF$_3$ from cyclohexane should be considerably faster than from toluene.

We conclude that the primary interaction of triplet AF$_3$ with aromatic molecules does not involve hydrogen atom abstraction but rather charge-transfer complexation. The resulting complex can then dissociate, with transfer of a benzylic proton to oxygen, to form the normal radicals involved in photoreduction; or it can dissociate by reverse charge transfer to two ground-state reactants, thus lowering the maximum quantum yield for reduction. Only such a competition can explain the deuterium isotope effect on Φ^{max} values. Scheme I exemplifies the mechanism for toluene. This kind of CT process has been implicated in some metal-catalyzed oxidations of alkylbenzenes[13] and is exactly analogous to the CT photoreduction of less electrophilic ketone triplets by amines,[14] except that a π donor rather than an n donor is involved.

Scheme I



The very rapid decay of triplet AF$_3$ in benzene and the efficient quenching of triplet AF$_3$ by *p*-di-*tert*-butylbenzene are both evidence consistent with the charge-transfer hypothesis. Bryce-Smith has independently provided rather spectacular evidence for such CT complexing by observing the acid-catalyzed photoaddition of benzene to AF$_3$.[15] His results are readily accommodated by the above scheme, with an external proton substituting for a benzylic proton.



In the case of toluene (Scheme I) the lack of any isotope effect on k_r indicates that $k_{ct} \gg k_H$. We discuss below the limits of this inequality. Our picture of the CT complex is not meant to imply that complete transfer of one electron has occurred with the formation of a pair of radical ions; we discuss below the extent of electron transfer in the complex. The complex is presumably an exciplex. The scheme does not include reversible complex formation because there is no evidence for any reversibility. There certainly can be no equilibrium established between excited ketone and complex, otherwise the observed k_r values would equal $k_{ct}(k_p + k_e)/k_{-ct}$ and would display sizable isotope effects. If complex formation is partially reversible, it cannot be significantly so, since observed k_r values would then equal $k_{ct}(k_p + k_e)/(k_{-ct} + k_p + k_e)$ and would display

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[13] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **91**, 6830 (1969).

[14] S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968).

[15] D. Bryce-Smith, G. B. Cox, and A. Gilbert, *Chem. Commun.*, 914 (1971).

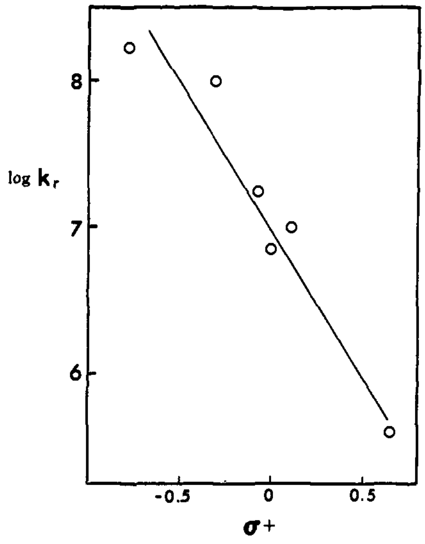

Figure 10. Hammett plot for quenching of triplet α-trifluoroacetophenone by substituted toluenes.

a diminished isotope effect. For example, if $k_{-\mathrm{ct}}$ is even $^1/_3$ as fast as $(k_p + k_e)$, and if $k_e = k_p$ and $k_p^H/k_p^D = 6$, as deduced below, a k_r^H/k_r^D value of 1.2 would result. Such a value represents a conservative estimate of our maximum likely experimental error; so we can conclude that $k_{-\mathrm{ct}} \leqslant (k_p + k_e)/3$. Only a combination of flash kinetics and temperature variations can establish whether complex formation is at all reversible.[16,17] For the sake of simplicity, we assume in the ensuing discussion that $k_r = k_{\mathrm{ct}}$.

Substituent Effects on k_r for AF$_3$. Figures 10 and 11 plot log k_r values for the substituted toluenes *vs.* Hammett σ^+ values[18] and ionization potentials,[19] respectively. Although *p*-cyanotoluene is only 1/400 as reactive as *p*-methoxytoluene, the Hammett plot does not show very good correlation. Least-squares analysis indicates a ρ value of -2.0. This large negative value contrasts sharply with the -0.35 value found for hydrogen abstraction by *tert*-butoxy radicals[20] but is on the same order as that found in the photoreduction of fluorenone by substituted anilines.[21]

Charge-transfer processes should correlate best with ionization potentials[22] (or oxidation potentials[23]) of the donor. Figure 11 depicts the excellent correlation for our AF$_3$ k_r values: Δ log k_r/ΔIP is -2.36 eV^{-1} or -0.10 kcal^{-1}. The rate at which benzene itself quenches triplet AF$_3$ lies on the line described by the toluenes. This excellent correlation provides corroboration of the CT nature of the quenching process and its independence of C–H bond strength. The only two compounds whose reactivities are not well correlated are cumene and di-*tert*-butylbenzene. Presumably the larger alkyl groups cause some steric hindrance to complexation. This discrepancy illustrates what must be the major fault[24] in such correlations of bimolecular processes with the unimolecular ionization process.

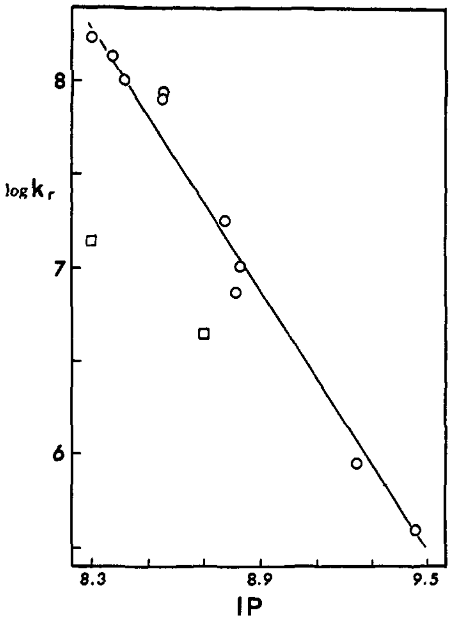

Figure 11. Correlation of rate constant for quenching of triplet α-trifluoroacetophenone by aromatics with their ionization potentials. Data in Table IV. (□) Cumene and di-*tert*-butylbenzene.

Direct Hydrogen Abstraction. The fact that AF$_3$ is photoreduced normally by cyclohexane indicates that triplet AF$_3$ can abstract hydrogen atoms directly, since it is most unlikely that cyclohexane can function as an effective electron donor. Its measured k_r value is some 10^3 times larger than the extrapolation of Figure 11 to an IP > 10.[19] The magnitude of k_r ($=k_H$) toward cyclohexane is interesting in two other respects. First, it is about 20 times larger than what would be expected for triplet AH$_3$.[3,25] Consequently the α-fluorine substitution does enhance the rate of direct triplet state hydrogen atom abstraction. Second, it suggests that a small amount of direct hydrogen abstraction can compete with charge transfer from the alkylbenzenes.

Quantum Yields. As indicated above, the intercepts of the plots in Figures 1–4 yield values of P_p, the probability that the primary photoproduct goes on to stable products. In the case of AH$_3$ with all substrates and AF$_3$ with cyclohexane, P_p is determined only by the partitioning of the benzyl (B·) and ketyl (K·) radicals. With AF$_3$ and the alkylaromatics, P_p is also determined by the partitioning of the CT complex, as described by eq 4. It is important to point out that P_p values are *not* affected by the extent of reversibility of exciplex formation.

$$P_p = \left(\frac{k_p}{k_e + k_p}\right)\left[\frac{k'_{cc}}{k'_{cc} + k_{dif} + k_{disp}} + \left(\frac{k_{dif}}{k'_{cc} + k_{dif} + k'_{disp}}\right)Q^{-1}\right] \quad (4)$$

$$Q = 1 + \frac{k_{disp}[K\cdot][B\cdot]}{k_{cc}[K\cdot][B\cdot] + k_{BB}[B\cdot]^2 + k_{pin}[K\cdot]^2} \quad (5)$$

P_p values for AF$_3$ are only half of those for AH$_3$ to-

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ward toluene, cumene, and *p*-xylene. The deuterium isotope effects on P_p values for AF_3 indicate that most of the difference between AF_3 and AH_3 involves decay of the CT complex, since any isotope effect on P_p caused by the behavior of the radicals would be small and *inverse*.[26] If one assumes that the entire difference in P_p values for AH_3 and AF_3 involves the CT complex, then $k_e = k_p$ and the isotope effect of 3.5 on P_p for AF_3–toluene indicates a k_p^H/k_p^D ratio of 6. The probable small isotope effect on the behavior of the ketyl radicals[26] would increase the actual value of k_p^H/k_p^D to perhaps 8. It is possible that the ketyl radicals formed from AF_3 undergo somewhat more disproportionation back to ground-state reactants than do those from AH_3,[27] in which case k_p^H/k_p^D would be somewhat lower than estimated.

With all the competing rate processes involved, it is impossible to discuss substituent effects on individual radical reactions, but a few general observations can be made. First, 50–75% of the radicals seem to disproportionate back to ground-state reactants for both AH_3 and AF_3. With cyclohexane the percentage is apparently even higher. This fact points out the danger of equating relative quantum yields and relative k_r values.[3] It is worth noting that the quantum yield at 8 *M* cyclohexane is 40% larger than predicted by the lower concentration data (Figure 3). This change must reflect the lower rate of triplet quenching by the diluted benzene cosolvent.

Second, with AH_3 the yield of bibenzyl relative to cross-coupling product is actually somewhat greater than statistical. This fact suggests that very little coupling takes place between the two initially formed radicals while they are held in the solvent cage. The first term in the bracketed factor in eq 5 is close to zero. Apparently disproportionation is considerably flavored over coupling when the two radicals $K\cdot$ and $B\cdot$ react.

With AF_3, bibenzyl yields are almost exactly statistical except for *p*-methoxy- and *p*-cyanotoluene. Only with *p*-methoxytoluene does the total quantum yield of products exceed 50%. One likely cause is a large decrease in the rate of disproportionation between $K\cdot$ and $B\cdot$ radicals.[27]

Competitive Charge Transfer to and Direct Hydrogen Abstraction by AF_3. The small isotope effect that we found for cumene, $k_r^H/k_r^D = 1.25$, probably is outside of experimental error because we took great pains to ensure the purity of the reactants. This isotope effect can be interpreted in two ways. As indicated above, partially (~50%) reversible exciplex formation would produce such an isotope effect. However, so would competitive direct hydrogen atom abstraction, a possibility suggested by the reactivity of cyclohexane toward triplet AF_3. We studied cumene-*α*-*d* precisely because, of all the alkylbenzenes that we studied, cumene should be the most likely to provide some competitive hydrogen abstraction. On the assumption that $k_H/k_D = 5$ for direct hydrogen abstraction,[26] the observed isotope effect on k_r, if completely due to competing hydrogen abstraction, would indicate that 25% of the reaction of triplet AF_3 with cumene involves direct hydrogen abstraction, $k_H = 1.1 \times 10^6\ M^{-1}\,\text{sec}^{-1}$. This kind of rate constant would suggest one on the order of $4 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ for toluene, only 5% the total reactivity of toluene toward triplet AF_3 and too little to provide a measurable isotope effect. The much smaller isotope effect on P_p for cumene relative to that observed for toluene cannot be explained by reversibility of exciplex formation but is necessary evidence for direct hydrogen abstraction from cumene competing with charge-transfer complexing. Our final reason for concluding that cumene reduces triplet AF_3 by two competitive processes is the reasonable relative rate constants derived from that conclusion. The value of the k_H (cyclohexane)/k_H(cumene) rate ratio which we derive is 4, *larger* than the value of ~1 reported for triplet acetophenone.[3] The increase certainly would reflect the enhanced electrophilicity of triplet AF_3. If we had estimated too much hydrogen abstraction by triplet AF_3 from cumene, our cyclohexane/cumene rate ratio would be too *low*.

Extent of Electron Transfer in AF_3–Aromatic Exciplex. Weller[23] and Mataga[28] and their coworkers have described detailed studied of CT quenching of excited aromatics by amines. In high dielectric media such as acetonitrile, such quenching produces free-radical ions and proceeds at diffusion-controlled rates, provided that the aromatic's excitation energy ($E_{0,0}$) exceeds the sum of the amine's oxidation potential, $E(D/D^+)$, and the aromatic's reduction potential, $E(A/A^-)$; *i.e.*, when ΔG_{ct} is negative.[23] When $\Delta G_{ct} = 0$, $k_q = 10^9\ M^{-1}\ \text{sec}^{-1}$. With aromatics of insufficient excitation energy

$$\Delta G_{ct} = -E_{0,0} + E(D/D+) - E(A/A-) - T\Delta S + e_0^2/\epsilon R \quad (6)$$

or amines of too high oxidation potential, so that ΔG_{ct} is positive and electron transfer becomes endothermic, k_q is reduced by a $\exp(-\Delta G_{ct}/RT)$ factor, such that a plot of log k_q *vs.* ΔG_{ct} has a slope of -16.5/eV.[23] In nonpolar solvents, quenching rate constants are considerably lower and strong exciplex emission occurs, apparently because of only partial electron transfer in the complex[28] and reversible complexation.[16]

Our Figure 11 has a slope of only -2.3/eV, so that $\Delta G^{\neq}$ for the reaction is proportional to only 20% ΔG_{ct}.[29] Our one experiment in acetonitrile (Tables II and IV) indicates that k_r for AF_3–xylene is only twice as large as it is in benzene. Similar small polar solvent effects obtained for CT quenching of benzophenone[30] and various phenyl alkyl ketones[31] have prompted us to suggest[31] that such quenching involves only partial electron transfer. The small slope of Figure 11, together with the small solvent effect, indicates that only partial electron transfer occurs in CT quenching of triplet AF_3. In valence bond terms, we would describe the wave function for the exciplex by eq 7, with $b^2 \approx 0.20a^2$ ($A = AF_3$, D = aromatic).

$$\Psi(D\cdot\cdot A)^* = a\psi(D + A^*) + b\psi(D\cdot^+ + A\cdot^-) \quad (7)$$

CT Quenching. AH_3 *vs.* AF_3. The generality of CT

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[29] It has been found that oxidation potentials of aromatics are directly proportional to their ionization potentials: $E_{1/2}(\text{ox}) = 0.83\text{IP} + \text{constant}$: W. C. Neikam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, **111**, 1190 (1964).

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quenching of ketone triplets has been recognized only recently.[24a,30] Both Cohen and we have noted that aromatics are much less effective quenchers than are n donors of similar ionization potentials; nonetheless, we both suggested[1a,30] that quenching of triplet phenyl ketones by benzene does involve CT complexing. Others have suggested that the short lifetimes of triplets in benzene[25] are due to radical addition.[32] In this respect, a comparison of our Figure 11 with Cohen's plot for the quenching of triplet benzophenone by substituted benzenes[30] is revealing. The plots have comparable slopes. There are only slight differences expected and observed[24a] between rates of CT quenching of acetophenone and benzophenone triplets, since benzophenone's lower reduction potential[33] is offset by its lower triplet energy.[34] Therefore differences between AF_3 and AH_3 must be nearly identical with those between AF_3 and benzophenone. We find a difference of 0.54 eV (12.4 kcal) in the $[E_{0,0} + E(A^-/A)]$ values for AF_3 and AH_3. Triplet benzophenone and triplet AF_3 are quenched at the same rate by aromatics of ~0.75 eV different ionization potentials. This observation means that both quenching processes are close to diffusion controlled as long as $-\Delta G_{ct}$ exceeds the same (near-zero) value. The 0.75 eV difference in IP may actually equal the 0.54 eV difference in oxidation potentials.[29] A given aromatic quenches triplet AF_3 more rapidly than triplet benzophenone by a factor of approximately 35. This rate difference corresponds to a $\Delta\Delta G^{\ddagger}$ of 2.2 kcal, 20% of the difference in ΔG_{ct} for the two ketones. Since quenching of both AF_3 and AH_3 respond identically to redox potential differences, we conclude that they both involve CT complexing with only a modest degree of electron transfer.

Charge Transfer *vs.* Hydrogen Atom Abstraction. Since we have just concluded that substituted benzenes can quench triplet AH_3 by a CT process, we must note the possibility that photoreduction of AH_3 and benzophenone by alkylbenzenes may proceed partially by the same CT process responsible for the majority of AF_3 photoreduction. CT quenching becomes the dominant photoreduction mechanism for AF_3 simply because the α-fluorine substitution so enhances the rate of CT quenching relative to that of hydrogen abstraction. Until we can obtain better measures of isotope effects on AH_3 photoreductions, we will not be able to better describe the competition between the two processes.

In this regard, we must also note the distinction between the two processes. Cohen has proposed that they are two extremes of a mechanistic continuum and suggested that photoreduction of benzophenone by alcohols may be a specific example of an intermediate case, with the transition state involving both C–H stretching and charge transfer.[14] We have recently argued in favor of this hypothesis.[6] Partial transfer of charge from either 2-propanol or toluene to a triplet ketone certainly can lower C–H bond strength; such stabilization of transition states for hydrogen transfer is readily understandable. On the other hand, it is difficult to envisage how C–H stretching could stabilize a transition state leading to electron transfer. Gutenplan and Cohen have recently suggested just this possibility.[30] However, any significant C–H stretching in the transition state would produce a detectable primary isotope effect. Since we find *no* isotope effect for AF_3–toluene, we feel safe in assigning the major triplet state interaction with alkylaromatics to a process involving no C–H stretching. Consequently, we prefer to discuss our results in terms of two distinct processes: one involving partial electron transfer and no C–H stretching; one involving primarily C–H stretching with or without charge-transfer stabilization.

Nature of Triplet AF_3. It is well known that α-halogens stabilize the $n \rightarrow \pi^*$ transitions of ketones, presumably by some mixing of the π^* orbital with the C–X σ^* orbital.[35] It is very interesting that AF_3 undergoes no loss of fluoride ion such as observed for α-chloro ketones.[36] The uv and phosphorescence spectra of AF_3 indicate that its L_a π,π^* triplet lies somewhere below 71 kcal in benzene and 70 kcal in ethanol. We interpret[37] the phosphorescence lifetimes to indicate that the π,π^* triplet is slightly lower in energy than the n,π^* triplet. However, they lie so close together that they are probably both populated at room temperature. Since both n,π^* and π,π^* triplets of ketones are reduced by charge transfer from amines,[14,38] it is possible that AF_3 reacts with aromatics from both levels. Hydrogen abstraction probably involves only the n,π^* triplet.[39] Equation 8 indicates the rate constants which comprise k_r, where $X_{n,\pi}$ and $X_{\pi,\pi}$ are the fractions of n,π^* and π,π^* triplets populated at equilibrium.

$$k_r^{obsd} = X_{\pi,\pi}k_{ct}^{\pi} + X_{n,\pi}k_{ct}^{N} + X_{n,\pi}k_{H} \qquad (8)$$

If the 58-msec phosphorescence at 77°K does come from an equilibrium mixture of both triplet levels, they are probably ~170 cal apart, in which case $X_{n,\pi}$ would equal $^1/_3$ at room temperature. Since k_{ct}^{π} values are generally considerably lower than k_{ct}^{N} values,[14,38] it is likely that k_r^{obsd} very nearly equals $X_{n,\pi}k_{ct}^{N}$, except for cyclohexane, of course.

The distinct structure of the phosphorescence of AF_3 is quite interesting. Usually, whenever aryl alkyl ketones display long-lived phosphorescence such that they are judged to have π,π^* lowest triplets, their spectra become quite broad and do not display a distinctive vibrational progression corresponding to the carbonyl stretch. The strong carbonyl progression evident in the phosphorescence of AF_3 may be another indication of emission from the upper n,π^* state and may also involve, in an as yet undetermined manner, the amount of vibronic mixing of the two triplets.[40] *It is equally possible that the carbonyl progression is characteristic of π,π^* emission in systems*

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in which the lowest π^* orbital is predominantly carbonyl-like.

Experimental Section

Chemicals. Benzene was purified as usual.[26] Acetophenone (Matheson Coleman and Bell) was vacuum distilled. AF_3 (Columbia Organic) as received contained ~10% impurities (vpc analysis). It was purified by spinning band distillation at atmospheric pressure. The center cut was >99.9% pure to vpc analysis. The absence of quenching impurities was indicated by the same triplet lifetime at two different ketone concentrations.

Toluene, *p*-chlorotoluene, *p*-fluorotoluene, cumene, the xylenes, mesitylene, and cyclohexane were purified similarly to benzene, by sulfuric acid washing followed by distillation. *p*-Cyanotoluene was merely distilled from phosphorus pentoxide; *p*-methoxytoluene was first washed with 1 *N* sodium hydroxide. Toluene-d_3 was used as obtained in a sealed vial from Merck Sharp and Dohme.

Cumene-α-*d* was prepared by reducing α-chlorocumene with a 1:1 molar ratio of lithium aluminum deuteride and aluminum trichloride. $LiAlD_4$ (4.7 g) was covered with 100 ml of freshly distilled glyme. A slurry of 14.8 g of $AlCl_3$ in 100 ml of glyme was added slowly to the stirred suspension. The mixture was brought to reflux, whereupon 34 g of α-chlorocumene in 75 ml of glyme was added dropwise over a 1-hr period. After another hour reflux, the solution was cooled, quenched with 100 ml of wet ether, and hydrolyzed in 100 ml of 10% aqueous sulfuric acid. After extraction with ether, the combined ether layers were washed with sodium bicarbonate solution and then dried over anhydrous magnesium sulfate. The ethers were removed by distillation on a spinning band column. The crude cumene was washed with cold sulfuric acid, which process removed all α-methylstyrene by-product. Fractional distillation yielded a sample of cumene-α-*d* which was >99.95% pure to vpc analysis and 96.4% deuterated by mass spectral analysis.

cis-1,3-Pentadiene (chemical samples) was distilled prior to use. Naphthalene was recrystallized from ethanol. *p*-Di-*tert*-butylbenzene, obtained from student Friedel–Crafts alkylation of benzene, was recrystallized three times from methanol, mp 77–78°.

Bibenzyl, bicumyl, and bi-*p*-xylyl, for product identification and vpc standardization, were commercial products twice recrystallized from methanol. Bicyclohexyl was prepared by the method of Wilds and McCormack,[41] a coupling reaction of cyclohexyl bromide induced by cobaltous chloride. *p*-Methylbenzyl Grignard was added to AF_3 to obtain the cross-coupling product for standardization and identification. The pinacol from AF_3 was obtained by irradiation in 2-propanol.

Procedures. Samples were prepared, degassed, and irradiated as previously described.[26] For naphthalene quenching experiments, the 365-nm region of the mercury arc was isolated with a set of Corning No. 7083 filters.

Vpc analyses were usually performed on an Aerograph Model 600D, with flame ionization detector and Model 328 temperature programmer and recorded on a L&N Speedomax H recorder fitted with a Disc integrator. Photoproducts were identified by their vpc retention times. The two diastereomeric pinacols were, of course, common products. Most analyses were performed on a 6 ft × $^1/_8$ in. column packed with 5% SE-30 on AW Chromosorb W. With cyclohexane and *p*-fluorotoluene the order of retention times is BB, CC, pinacol; with *p*-chloro-, *p*-methoxy-, and *p*-cyanotoluenes, mesitylene, and cumene the order is just the opposite. The xylene and toluene photosylates were analyzed on a 6-ft column packed with 4% QF-1, 1.2% Carbowax 20M on Chromosorb G.

Actual yields of products were determined by direct standardization relative to *n*-alkanes from C_{12} to C_{20} for bicumyl, bibenzyl, bixylyl, bicyclohexyl, and phenyltrifluoromethyl-*p*-methylbenzylcarbinol. Since FID responses are very nearly linear with the number and oxidation states of carbon atoms in a molecule, the responses of the products from other substrates were estimated. Any errors would affect only $\Phi^{\max}$ values and not any of the rate constants.

Phosphorescence spectra and lifetimes of AF_3 were measured on the apparatus of Professor Alfred Haug[37] in the MSU-AEC Plant Research Laboratory.

Reduction potentials of the ketones were measured at a dropping mercury electrode with a Sargent Model XV polarograph. A saturated potassium chloride bridge connected sample solutions (10^{-3} *M* ketone and 0.1 *M* tetrabutylammonium iodide as supporting electrolyte in DMF) to a freshly calibrated standard calomel electrode. Each ketone produced 2 waves. Half-wave potentials for the first waves were determined. The AH_3 value of −2.06 eV compares with literature values of −1.99[23] and −2.12.[42]

Acknowledgment. This work was supported by a National Science Foundation grant.

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