Charge-Transfer Quenching of Triplet α-Trifluoroacetophenones

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Abstract: The effects of ring substituents and of aromatic quenchers on the photoreduction by toluene of α,α,α-trifluoroacetophenone (AF_3) have been measured. A plot of log k_{CT} vs. ionization potential of the donor indicates that $\Delta G^{\ddagger}{}_{CT}$ equals 22% ΔG for full electron transfer. A corresponding plot of log k_{CT} vs. the triplet state reduction potential of ring-substituted AF_3's, if analyzed as linear, would indicate that there is no intrinsic difference in reactivity between n,π* and π,π* triplets but would also indicate that $\Delta G^{\ddagger}{}_{CT}$ equals 42% ΔG. The discrepancy between the 22 and 42% is suggested to involve differing reactivities of n,π* and π,π* triplets. If n,π* triplets are substantially more reactive, the plot vs. triplet reduction potential is expected to curve upward as the equilibrium population of n,π* triplet increases with substitution.

Charge-transfer (CT) quenching of electronically excited molecules is a topic of wide interest.[1] In the case of triplet ketones, quenching by electron donors is now recognized to be very general.[2,3] Several years ago we reported that the low reduction potential of α,α,α-trifluoroacetophenone (AF_3) makes it particularly susceptible to triplet state CT quenching.[4] In this paper we report further results on the photochemistry of AF_3 which address two separate problems.

The quenching of triplet ketones by benzene and by substituted benzenes has attracted interest because it is responsible for short triplet lifetimes in otherwise unreactive aromatic solvents[5] and because electron-deficient benzenes and electron-rich benzenes apparently quench triplet ketone by different mechanisms.[6] We find that triplet AF_3 is quenched by all substituted benzenes by only one CT mechanism, with the ketone acting as acceptor.

Differences between n,π* and π,π* ketone triplets in hydrogen-abstraction reactions are well established and understood.[3,7] However, it is not at all clear how differences in electronic configuration affect rate constants for CT quenching.[3,8] Therefore, we have studied the photoreduction by toluene of eight ring-substituted AF_3 compounds in which the energetic spacing between n,π* and π,π* triplets varies. Scheme I depicts the accepted mechanisms for the photoreduction of AF_3 by toluene and the products of the reaction.

Results

Spectroscopic Properties. Table I lists various spectroscopic properties of the substituted AF_3 compounds which we have studied. UV spectra and reduction potentials were determined in acetonitrile. Phosphorescence was monitored in a 4:1 methylcyclohexane–isopentane glass at 77 K. Three representative spectra are shown in Figure 1. AF_3 itself shows a prominent 1720-cm^{-1} vibrational progression[4] which is even sharper in the CF_3-substituted ketones and which gets more diffuse with electron-donating substituents.

Photoreduction by Toluene. Degassed acetonitrile solutions 0.05 M in ketone and containing various concentrations of toluene were irradiated in parallel at 313 nm. Quantum yields of bibenzyl formation were determined by GC analysis. Valerophenone actinometers[9] were used to measure light intensity. In the case of $m\text{-}CH_3OAF_3$, no reaction was detectable even after 24 h of irradiation. Figures 2 and 3 display standard[10] double reciprocal plots of the data. The slopes and intercepts are recorded in Table II as the parameters in eq 1. In this and earlier[4,11] studies, product ratios were independent of conversion and quencher. Therefore variations in the yield of just one product provide accurate measures of excited-state kinetics.[10]

$$\Phi_{BB}{}^{-1} = \Phi_{max}{}^{-1}\left(1 + \frac{k_d}{k_{CT}[\text{toluene}]}\right) \tag{1}$$

$$1/\tau = k_{CT}[\text{toluene}] + k_d \tag{2}$$

Triplet lifetimes at a given toluene concentration were determined by quenching studies. Degassed acetonitrile solutions 0.05 M in ketone and containing a given concentration of toluene and various concentrations of naphthalene were irradiated in parallel at 365 nm. Stern–Volmer plots (eq 3) of relative bibenzyl yields (Figure 4) provided the slopes listed as $k_q\tau$ values in Table II.

$$\Phi^0/\Phi = 1 + k_q\tau[Q] \tag{3}$$

Scheme I

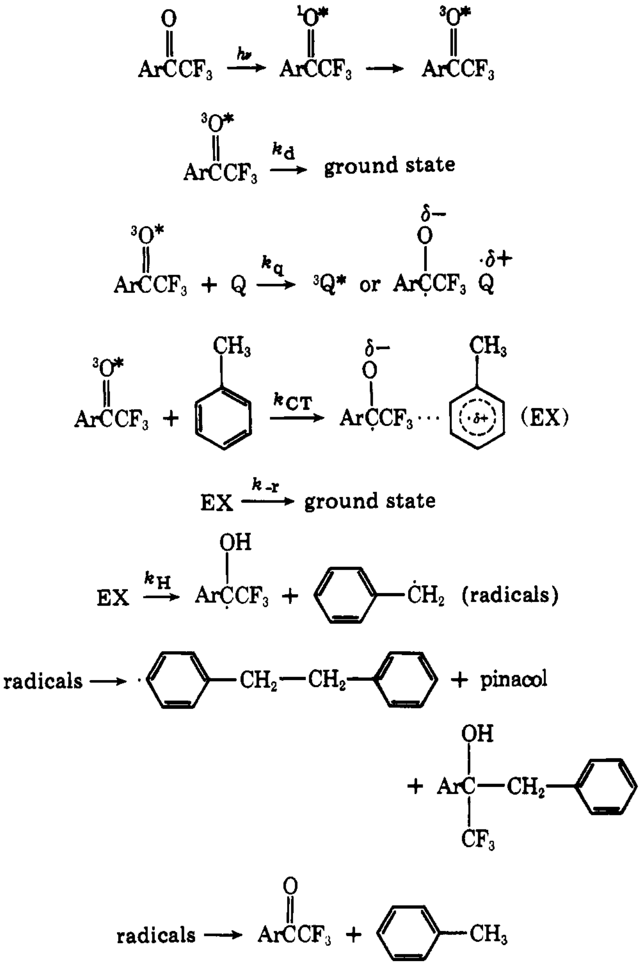

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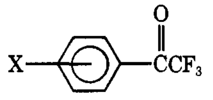
Table I. Spectroscopic and Thermodynamic Properties of Ring-Substituted α-Trifluoroacetophenones



X	^1L_a λ_{max}, nm	E_{0-0}, kcal/mol[a,b]	τ_T, ms[a,c]	$E(A^-/A)$, V[d]	$-E^*_{red}$,[e] kcal
p-CF_3	244	70.4	18	−1.13	44.4
m-CF_3	251	70.6	24	−1.19	43.2
m-Cl	258	69.9	86	−1.25	41.1
H	252	71.0	57	−1.43	38.1
p-Cl	265	68.4	56	−1.30	38.5
m-CH_3	255	69.4	64	−1.45	36.0
p-CH_3	264	69.0	210	−1.51	34.4
p-OCH_3	287	66.5	600	−1.57	30.1
m-OCH_3	258	~63.5	>500	−1.40	31.3

[a] In MCIP at 77 K. [b] 0-0 band of phosphorescence. [c] Lifetime at emission maximum. [d] Half-wave potential, relative to SCE, by cyclic voltammetry in acetonitrile. [e] $E^*_{red} = -E(A^-/A) - E_T$.

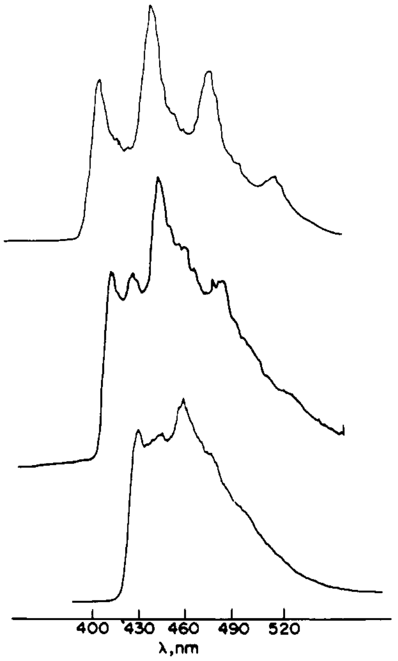


Figure 1. Phosphorescence spectra at 77 K in MCIP glasses of three substituted α-trifluoroacetophenones: top, *p*-CF_3; middle, *p*-CH_3; bottom, *p*-OCH_3.

With k_q assumed to equal 1.0×10^{10} M^{-1} s^{-1},[12] the k_{CT} and k_d values listed in Table II were calculated from the τ and k_d/k_{CT} values. Agreement with previously published values for AF_3 itself[4] was satisfactory.

Degassed acetonitrile solutions containing 0.05 M AF_3, 0.1 or 1.0 M toluene, and various concentrations of the aromatic quenchers listed in Table III were irradiated at 313 nm. Stern-Volmer plots of relative benzyl yields provided the $k_q\tau$ and k_q values listed in Table III. Also listed in Table III are ionization potentials for the quenchers.

Intersystem Crossing Yields. Degassed acetonitrile solutions containing 0.2 M *cis*-1,3-pentadiene and 0.1 M *m*-trifluoromethyl-AF_3, *p*-methoxy-AF_3, or acetophenone were irradiated in parallel at 313 nm. GC analysis indicated that all three ketones sensitized the same amounts, within experimental error, of *trans*-diene formation.[13] Consequently we conclude that ϕ_{isc} for the substituted trifluoroacetophenones is unity, as it is for the unsubstituted AF_3.[4]

Discussion

Nature of Quenching by Substituted Benzenes. Figure 5

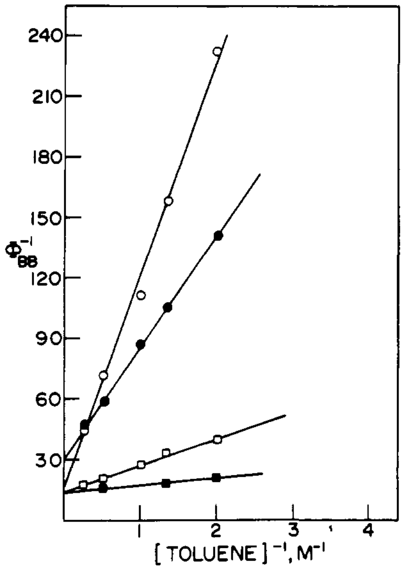


Figure 2. Double reciprocal dependence of quantum yields for bibenzyl formation on toluene concentration: ○, *p*-$MeOAF_3$; ●, *m*-$MeAF_3$; □, *p*-$MeAF_3$; ■, *p*-$ClAF_3$.

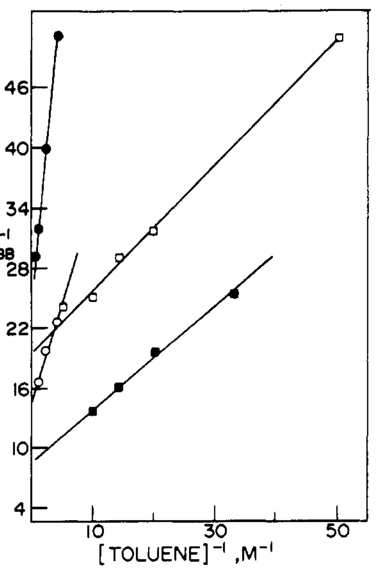


Figure 3. Double reciprocal dependence of quantum yields for bibenzyl formation on toluene concentration: ○, AF_3 itself; ●, *m*-$ClAF_3$; □, *m*-CF_3AF_3; ■, *p*-CF_3AF_3.

Table II. Photokinetics for Reduction of $XPhCOCF_3$ by Toluene[a]

X	ϕ_{BB}^{max} [b]	k_d/k_{CT}	$k_q\tau$, M^{-1} [c]	k_{CT}, $10^7\ s^{-1}$	k_d, $10^7\ s^{-1}$
p-CF_3	0.10	0.05	93[d]	72	3.6
m-CF_3	0.05	0.03	76[d]	100	3.0
m-Cl	0.067	0.13	180	4.9	0.6
H	0.04	0.23	760 (1560)[e]	1.1	0.2
p-Cl	0.075	0.28	1580	0.49	0.14
m-CH_3	0.032	1.8	1150[f]	0.23	0.41
p-CH_3	0.07	1.0	5400	0.09	0.09
p-OCH_3	0.06	6.7	25 600 (24 000)[f]	0.0048	0.035
m-OCH_3	0				

[a] 0.05 M ketone irradiated at 313 or 365 nm in acetonitrile. [b] Reciprocal intercept of double reciprocal plots, eq 1. [c] Stern–Volmer quenching slope, naphthalene quencher, 1 M toluene. [d] 0.1 M toluene. [e] 0.4 M toluene. [f] 2 M toluene.

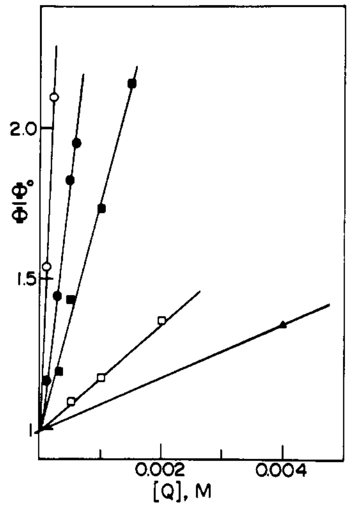


Figure 4. Representative Stern–Volmer quenching plots, naphthalene quencher, bibenzyl monitored at 1.0 M toluene, 0.05 M ketone: ○, *p*-$MeAF_3$; ●, *p*-$ClAF_3$; ■, AF_3 itself; □, *m*-$ClAF_3$; △, *p*-CF_3AF_3 (0.1 M toluene, other points off graph).

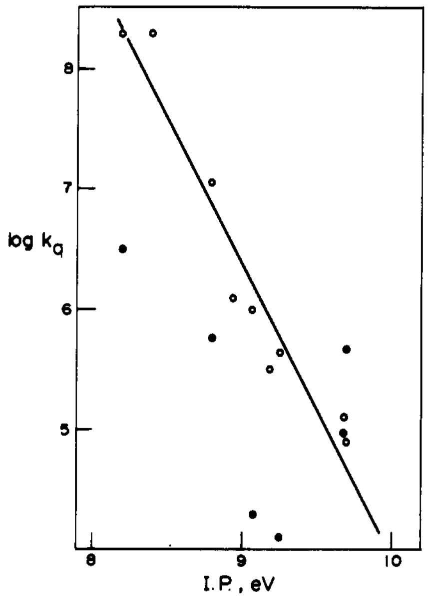


Figure 5. Dependence of quenching rate constants for substituted benzenes on their ionization potentials: ○, triplet AF_3 in CH_3CN; ●, triplet benzophenone in $CFCl_2CF_2Cl$, ref 6c.

displays the dependence of k_q on quencher ionization potential. Such plots have commonly been interpreted as demonstrating the CT nature of the quenching process.[2,4,6,14] With benzophenone, full electron transfer to yield radical ions does not occur even in acetonitrile except with quenchers of very low oxidation (ionization) potential such as *N,N*-dialkylanilines.[15] Since the excited-state reduction potential of AF_3 is 0.5 eV lower than that of benzophenone,[4] electron donors with oxidation potentials as high as 1.3 eV could give radical ions. None of the substituted benzenes in Figure 5 meets that criterion, so quenching must involve only exciplex formation. There is no evidence relating to the possible reversibility of this triplet exciplex formation except the negative evidence of no isotopic effect with toluene-α-d_3.[4]

Table III. Quenching of Triplet 0.05 M $PhCOCF_3$ by Substituted Benzenes in Acetonitrile

substituents	IP, V[a]	$E(D/D^+)$, V[b]	$k_q\tau$, M^{-1} [c,d]	k_q, $10^7\ M^{-1}\ s^{-1}$
1,4-$(OCH_3)_2$		1.34	3800	1200
1,4-$(CH_3)_2$	8.40	1.77		20
OCH_3	8.20	1.76	60	19
CH_3	8.80	1.98		1.1
1,4-$(Cl)_2$	8.94		0.42	0.13
Cl	9.07		0.32	0.10
H	9.25	2.30	0.14	0.045
F	9.19		0.10	0.032
CF_3	9.68		0.04	0.013
CN	9.7		0.02	0.008

[a] J. L. Franklin et al., "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions", U.S. Department of Commerce, National Bureau of Standards, 1969. [b] Reference 17; A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4124 (1964). [c] Bibenzyl formation at 0.1 M toluene monitored. [d] $\tau = 3.0 \times 10^{-5}$ s.

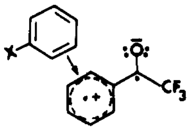
The slope of −2.4/eV in Figure 5 represents only 15% of the −16.4/eV slope expected[16] for full electron transfer and indicates the partial electron transfer in this species of excited CT complex. A comparable slope of −2.4/eV was observed for quenching in benzene.[4] Since oxidation potentials of substituted benzenes in acetonitrile are proportional to 0.68 times their ionization potentials,[17] the slope of Figure 5 would be −3.6/eV if plotted against $E(D/D^+)$. Thus we conclude that the slope is actually 22% as large as would be predicted by the thermodynamics of one-electron transfer.

Included in Figure 5 is an analogous plot of the quenching of triplet benzophenone in benzene.[6c] With triplet AF_3, there is no enhanced quenching by benzonitrile. Two explanations have been put forth for the change in slope observed for benzophenone: (1) with electron-deficient quenchers, the excited ketone may act as an electron donor;[6] (2) with electron-deficient quenchers, radical-like addition of the n,π* triplet ketone to the aromatic may replace CT exciplex formation.[18]

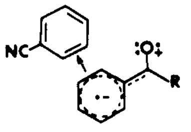
It is possible that AF_3, with its π,π* lowest triplet,[4] does not undergo radical-like additions as readily as does the n,π* triplet of benzophenone. What we regard as a more likely reason for the difference between the two compounds is the 0.5 eV higher oxidation potential of AF_3 relative to that of acetophenone.[19]

Singer has shown that substituents which depress the electron-donating propensity of benzophenone also depress the quenching ability of electron-deficient benzenes.[6c] AF_3 apparently is so difficult to oxidize that its triplet acts only as an acceptor even with benzonitrile.

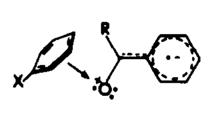
Singer has suggested that that portion of the benzophenone plot in Figure 5 which has the negative slope involves CT from quencher to the vacant n orbital of the n,π^* triplet,[6c] in agreement with Turro's earlier notions.[20] We point out here that, inasmuch as CT quenching involves overlap of the donor orbital with a half-vacant acceptor orbital, the geometry for CT quenching of the π,π^* AF_3 triplet must resemble that for CT quenching of n,π^* triplets by electron-deficient benzenes, even though net electron flow is in opposite directions for the two cases. The following extreme VB representations exemplify the geometric similarities of the different exciplexes.



π,π^*



n,π^*



n,π^*

Ring Substitution. The absolute magnitude of the rate decreases effected by MeO, Me, and Cl substitution are the same as previously reported for hydrogen-atom abstraction by phenyl alkyl ketones,[7] whereas the rate enhancement effect by CF_3 substituents are 25–50 times larger than those on hydrogen abstraction. The substituent effects on hydrogen abstraction are thought to reflect primarily differences in equilibrium populations of n,π^* and π,π^* triplets. Therefore one must ask how such equilibration might affect observed rate constants for CT quenching.

The 77 K phosphorescence lifetimes of all the substituted AF_3's are longer than the 5–10 ms commonly associated with the n,π^* triplets of phenyl ketones.[21] We consider unlikely the possibility that α-fluorination may slow down n,π^* phosphorescence and conclude instead that all of these ketones have π,π^* lowest triplets. As noted previously,[4] α-fluorination significantly lowers the energy of the ^1L_a band in phenyl ketones and would be expected to also lower ^3L_a π,π^* energies.

Only CF_3 substituents lower the phosphorescence lifetime of AF_3. Whereas such substitution raises ^1L_a energies,[7,22] it slightly lowers ^3L_a energies,[23] so that the expected[22] lowering of the $^3n\pi^*$ energy is insufficient to invert the level ordering found in AF_3 itself. An assumption that the 77 K phosphorescence is dominated by 200 s^{-1} emission from 20–30% equilibrium populations of n,π^* triplets[21c] (hence the prominence of a carbonyl stretch vibration in the spectra) yields estimates of 105 and 170 cal/mol for ΔE, the energetic separation of the two triplet levels in p-CF_3 and m-CF_3 substituted AF_3, respectively. The opposite effects of solvent polarity and geometric relaxation on ΔE values[24] are both larger than the 77 K ΔE value, so it is impossible to predict which state is lower in acetonitrile at 25 °C. However, it is likely that, for both CF_3-substituted ketones, n,π^* and π,π^* triplets are populated about equally.

The other substituents all stabilize ^3L_a π,π triplets substantially;[23] on AF_3 they lower E_T, lengthen τ_p, and broaden the phosphorescence spectra, as observed with other phenyl alkyl ketones.[7,21] Consequently we assume 10–20% room temperature $^3n,\pi^*$ populations (χ_N) for the substituted AF_3's with intermediate 77 K lifetimes and χ_N values lower than 1% for the p-methyl and p-methoxy compounds.

Since none of the TFAs has an χ_N value close to unity, the increasing k_{CT} values do indeed parallel χ_N values; it might therefore be possible to interpret substituent effects on TFA reactivity in terms of only n,π^* reactivity. However, π,π^* states are known to be reactive in CT processes. Fortunately, CT reactivity can be correlated with redox potentials. The various linear free energy correlations of quenching rate constants with thermodynamic redox potentials, introduced by Weller[16] and Evans[14] and first applied to triplet ketone reactions by Cohen,[2] all imply a proportionality between $\Delta G^{\ddagger}$ for CT complexation and ΔG for electron transfer.

$$\Delta G = -E_T - E(A^-/A) + E(D/D^+) - T\Delta S - e^2/\epsilon a \qquad (4)$$

In principle, one should be able to plot log k_{CT} equally well against either E_{oxid}(donor) or $E_T + E_{red}$(acceptor), as described by the well-known eq 4 for excited-state electron transfer.[2,16] Surprisingly, the literature contains almost no systematic correlations of k_{CT} for a constant donor toward ketones of varying structures.[8] Figure 6, the counterpart of Figure 5, so plots the reaction rate constants in Table II vs. the excited-state reduction potentials E^*_{red} determined from the data in Table I.

A linear least-squares fit of the data (dashed line) yields a slope of 0.30/kcal (7.0/eV), with a standard deviation of 0.018 but an average deviation of 0.16. Although there is no statistical reason to reject a linear fit of the data, there are chemical reasons to be suspicious. One such is that the slope corresponds to 42% that expected for full electron transfer, double the 22% observed when the donors are varied. Thermodynamically, it is impossible for the acceptor reduction potential to be twice as important as the donor oxidation potential.

The discrepancy cannot be due to differential steric effects because only meta and para substituents were used. One possibility for the discrepancy is that the irreversibility of one-electron oxidations of simple substituted benzenes causes huge errors in polarographically measured half-wave potentials. We doubt that this problem can explain the entire discrepancy, since ΔE_{oxid} would have to be proportional to three times ΔIP instead of the 1.5 times observed experimentally.[17]

The other possible explanation recognizes that the ketones possess increasing n,π^* character as the excited-state reduction potential gets increasingly negative. *Proper analysis of the actual situation involving varying proportions of two different equilibrating triplets indicates that a plot such as in Figure 6 can be linear only if the two triplets have identical intrinsic reactivities.*

The following equations describe the observed rate constant for CT quenching of two proximate, equilibrating triplets, where χ_N is the equilibrium fractional population of the upper n,π^* state and B describes the relative reactivities of the two states.

$$k_{CT}^{obsd} = (1 - \chi_N)k_\pi + \chi_N k_N \qquad (5)$$

$$k_{CT}^{obsd} = k_\pi[1 + \chi_N(B - 1)] \qquad (6)$$

$$B = k_N/k_\pi \qquad (7)$$

Equation 6 indicates that k_{CT}^{obsd} increases with increasing χ_N, at constant ΔG_{CT}, if B exceeds unity. The situation is not that simple, since B is not constant. A given ketone's n,π^* triplet is more energetic than its π,π^* triplet by ΔE and therefore, according to eq 4, is *thermodynamically* more reactive. Any intrinsic reactivity difference between the two triplets is a separate factor. We symbolize this thermodynamics-independent k_N/k_π ratio as R_N. Remembering that Figure 5 implies eq 8, we can separate B into its thermodynamic and configurational factors as in eq 9. The exponential factor must exceed unity (except where $\Delta E = 0$), whereas R_N could a priori have any positive value. Comparison of eq 9 and 10 indicates that B decreases as ΔE decreases and thus as χ_N increases.

$$\log k_{CT} = \beta\Delta G + C \qquad (8)$$

Table IV. Values of $[1 + X_{\mathrm{N}}(k_{\mathrm{N}} - k_{\pi})/k_{\pi}]$ as a Function of ΔE and R_{N}

ΔE, kcal	R_{N} 100	10	3	1	0.33	0.1	0.01
−5.6	100.	10.0	3.0	1.000	0.33	0.101	0.011
−4.2	100.	10.0	3.0	1.003	0.34	0.104	0.014
−2.8	99.	9.9	3.0	1.075	0.35	0.12	0.035
−1.4	91.0	9.2	2.9	1.05	0.45	0.23	0.15
−0.7	76.3	7.9	2.6	1.06	0.56	0.38	0.31
0	50.5	5.5	2.0	1.000	0.67	0.55	0.51
0.7	31.0	3.8	1.67	1.06	0.86	0.79	0.76
1.4	15.3	2.34	1.34	1.05	0.96	0.92	0.91
2.8	3.5	1.24	1.06	1.075	1.0	0.99	0.99
4.2	1.4	1.04	1.01	1.003	1.0	1.0	1.0
5.6	1.06	1.01	1.00	1.000	1.0	1.0	1.0

$$B = R_{\mathrm{N}} e^{\beta \Delta E/RT} \tag{9}$$

$$\chi_{\mathrm{N}} = \frac{e^{-\Delta E/RT}}{1 + e^{-\Delta E/RT}} \tag{10}$$

Substitution of eq 9 and 10 into eq 6 yields eq 11–14, the first two applying to situations where the π,π^* triplet is of lowest energy. Note that ΔE is negative in eq 13 and 14 with the n,π^* triplet lowest (i.e., $\Delta E = E_{\mathrm{n}\pi} - E_{\pi\pi}$).

$$k_{\mathrm{CT}}{}^{\mathrm{obsd}} = k_{\pi}\left[\frac{1 + R_{\mathrm{N}} e^{(\beta-1)\Delta E/RT}}{1 + e^{-\Delta E/RT}}\right] \tag{11}$$

$$\log k_{\mathrm{CT}}{}^{\mathrm{obsd}} = C + \frac{\beta}{RT}\,[E_{\pi,\pi} + E(\mathrm{A}^-/\mathrm{A})] + \log\left[\frac{1 + R_{\mathrm{N}} e^{(\beta-1)\Delta E/RT}}{1 + e^{-\Delta E/RT}}\right] \tag{12}$$

$$k_{\mathrm{CT}}{}^{\mathrm{obsd}} = k_{\pi}\left[\frac{R_{\mathrm{N}} + e^{(1-\beta)\Delta E/RT}}{1 + e^{\Delta E/RT}}\right] \tag{13}$$

$$\log k_{\mathrm{CT}}{}^{\mathrm{obsd}} = C + \frac{\beta}{RT}\,[E_{\mathrm{n},\pi} + E(\mathrm{A}^-/\mathrm{A})] + \log\left[\frac{R_{\mathrm{N}} + e^{(1-\beta)\Delta E/RT}}{1 + e^{\Delta E/RT}}\right] \tag{14}$$

Table IV lists values of the factors in brackets in eq 11 and 13 for various values of ΔE and R_{N}, with β assumed equal to 0.20, as discussed earlier. When ΔE is large and positive, the bracketed factors in eq 11 and 13 approach unity; when ΔE is large and negative, they approach R_{N}. Consequently, as eq 12 and 14 indicate, a plot of log k_{CT} vs. $[E_{\mathrm{T}} + E(\mathrm{A}^-/\mathrm{A}]$ should contain three separate sections. Ketones with $|\Delta E| >$ 3-4 kcal should determine two parallel lines of slope β/RT separated on the ordinate by log R_{N}. Ketones with both triplets populated would determine a roughly S-shaped curve connecting the two lines. Unfortunately, π,π^* triplet energies are not proportional to reduction potentials, as n,π^* energies seem to be,[25] so that no smooth curve could fit the data in a plot such as Figure 6 unless R_{N} was very close to unity.

The two parallel dashed lines in Figure 6 each have slopes of 0.14/kcal ($\Delta\Delta G^{\ddagger} = 0.20\Delta\Delta G$) and are separated by log 100. If these lines describe k_{CT} for pure n,π^* and π,π^* triplets, then $R_{\mathrm{N}} = 100$, and all of the ketones we have studied except the *p*-methoxy derivative are reacting primarily from their n,π^* triplets, whose low equilibrium concentrations are offset both by a large R_{N} and by a larger E_{T} than that of the observed phosphorescence 0,0 band.

Recognizing that our tentative conclusion regarding R_{N} is based entirely on an expectation of equal slopes in plots of log k_{CT} vs. either donor oxidation potential or acceptor triplet reduction potential, we are hesitant to speculate much on possible causes for greater intrinsic n,π^* reactivity in charge-transfer quenching. It may be that the maximum-overlap approach of a π donor to a half-empty benzene π orbital presents more steric and entropic difficulties than its lower-total-overlap approach to the more localized half-empty n orbital on oxygen.

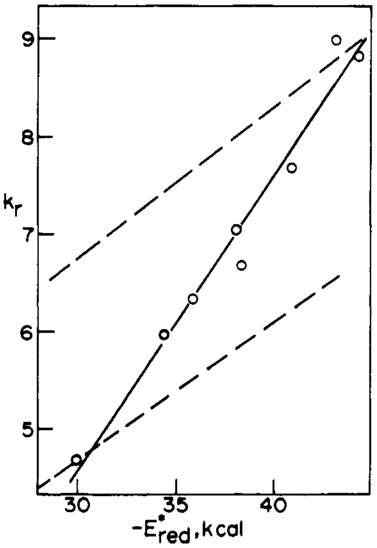


Figure 6. Dependence of reaction rate constants for toluene toward substituted triplet AF$_3$ ($k_r = k_{\mathrm{CT}}$) as a function of the ketones' triplet reduction potentials.

There is solid evidence that CT quenching differs for n,π^* and π,π^* ketone triplets. Rate constants for the latter[8,26] but not the former[8,27] are subject to significant enhancement by polar solvents. Moreover, Cohen and Gutenplan correlated k_{CT} values for various triplet ketones and triethylamine in a plot analogous to our Figure 6. They also found that the slope is unusually high. Most significantly, k_{CT} values for acylnaphthalenes in benzene[26] are a good order of magnitude lower than predicted by the extrapolated correlation of log k_{CT} values for several n,π^* ketones in hydrocarbon solvents.[8]

Apparent k_{d} Values. The triplet decay rates listed in Table II merit mention. The 0.5-ns triplet lifetime of unsubstituted AF$_3$ is important as regards our already reported concentration-dependent CIDNP.[28] The value of k_{d} in benzene is four times larger than in acetonitrile but represents CT quenching by solvent. These k_{d} values in acetonitrile may be determined by self-quenching rates.[6c] However, they decrease two orders of magnitude more or less in parallel with the four order of magnitude decrease in k_{CT} as the ring substituents get more electron donating. This is the opposite order to that observed by Singer[6c] for substituted benzophenones.

The behavior of *m*-methyl-AF$_3$ may provide a clue to the nonreactivity of *m*-methoxy-AF$_3$, whose triplet reduction potential of −31.6 kcal/mol indicates that k_{CT} should be on the order of 10^5 M^{-1} s^{-1}. It has been observed before[29] that ketones with meta electron donors have anomalously high k_{d}

values (self-quenching rates[30]). We suspect that k_d may be so high that quantum yields are too low to be measured at the 2 M toluene used.

Maximum Quantum Yields. The intercepts of the plots in Figures 2 and 3, as recorded in Table II, represent the fraction of triplet ketone–toluene interactions which yield bibenzyl. Total product ratios were not measured for every substituted AF_3. In those cases where it was studied, variations were small and material balances were high. In most cases, $2\phi_{BB}^{max}$ represents the probability that *any* products are formed from triplet AF_3–toluene reactions. These probabilities show some variation (6–20%), with no definite trends. Radiationless decay of the exciplex and disproportionation of the radicals both contribute to the ≥80% inefficiencies and we cannot yet separate the two.

Experimental Section

Solvents. Benzene was purified by treatment with sulfuric acid and distillation from P_2O_5.[7] Acetonitrile was purified by distillation from $KMnO_4$ and K_2CO_3.[31]

Quenchers. Toluene, chlorobenzene, and fluorobenzene were purified as was benzene. Anisole, benzonitrile, and benzotrifluoride were washed with 1 N NaOH, then dried and fractionally distilled. *p*-Dichlorobenzene was sublimed at reduced pressure. *p*-Dimethoxybenzene was recrystallized twice from ethanol. *cis*-1,3-Pentadiene (Chemical Samples Co.) was used as received. Naphthalene was recrystallized three times from ethanol. Valerophenone was available from earlier work.[7]

Ketones. Columbia Organic Chemicals α,α,α-trifluoroacetophenone was distilled on a spinning-band column: bp 50 °C (20 Torr); IR 1720 cm^{-1}; ^{19}F NMR δ 71.5 ($CFCl_3$).

All of the substituted ketones were prepared by the method of Dishan and Levine,[32] namely, refluxing the appropriate arylmagnesium bromide in ether with one-third the molar amount of trifluoroacetic acid. After workup, the ketones were obtained in 35–50% yield by vacuum distillation on a spinning-band column.

p-Methoxy-AF_3: bp 72–73 °C (2 Torr); IR 1712 cm^{-1}; ^{19}F NMR δ 71.1; MS *m/e* 204, 135.

m-Methoxy-AF_3: bp 55–59 °C (3 Torr); IR 1718 cm^{-1}; ^{19}F NMR δ 71.1; MS *m/e* 204, 135.

p-Methyl-AF_3: bp 79–80 °C (22 Torr); IR 1717 cm^{-1}; ^{19}F NMR δ 71.5; MS *m/e* 188, 119.

m-Methyl-AF_3: bp 60–63 °C (~13 Torr); IR 1718 cm^{-1}; ^{19}F NMR δ 71.4; MS *m/e* 188, 119.

p-Chloro-AF_3: bp 83–84 °C (24 Torr); IR 1720 cm^{-1}; ^{19}F NMR δ 71.1; MS *m/e* 208, 139.

m-Chloro-AF_3: bp 75–78 °C (20 Torr); IR 1722 cm^{-1}; ^{19}F NMR δ 71.6; MS *m/e* 208, 139.

m-Trifluoromethyl-AF_3: bp 68–71 °C (22 Torr); IR 1722 cm^{-1}; ^{19}F NMR δ 72.1; MS *m/e* 242, 173.

p-Trifluoromethyl-AF_3: bp 65–70 °C (22 Torr).

All IR and ^{19}F NMR spectra were measured in CCl_4, the latter with $CFCl_3$ as external standard.

Procedures. All solutions were prepared in volumetric flasks; 2.8-mL portions were transferred to constricted 13 × 100 mm Pyrex culture tubes which were degassed in four freeze–thaw cycles and then sealed in vacuo. The sealed tubes were irradiated in parallel on a rotating "merry-go-round"[33] with a 450-W Hanovia mercury arc at the center. The 313-nm band was isolated with an alkaline chromate filter solution,[7] the 365-nm band with a set of Corning No. 7-83 filters.

Product concentrations were determined by GC analysis with FID detectors, usually on an 8 ft × 1/8 in. column containing 4% QF-1, 1% Carbowax 20M on 60/80 Chromosorb G. Pentadiene isomerization was monitored on a 25-ft column containing 25% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P. An Infotronics digital integrator was used to measure areas of product peaks vs. calibrated internal standards.

Instrumentation. UV spectra were recorded on a Cary 17 spectrophotometer; phosphorescence was recorded on an Aminco-Bowman spectrofluorimeter. Phosphorescence lifetimes were measured as previously described.[21c] Reduction potentials were measured at a hanging mercury drop electrode by cyclic voltammetry with a PAR 174A analyzer, generally with a 200 mV/s sweep rate, at 10^{-4} M ketone. Although reductions were only partially reversible for ketones with electron-donating substituents, conditions were close enough to full reversibility that no corrections to measured values were necessary.[34]

Acknowledgment. This work was supported by NSF Grants MPS-70-01753 and CHE-76-11892. We thank Elizabeth Siebert for measuring the reduction potentials and Cynthia Chiu for measuring spectroscopic properties of the ketones.

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