

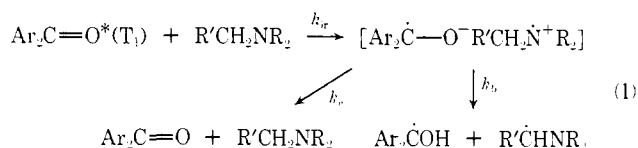
Quenching of Photoexcited Fluorenone by Meta- and Para-Substituted Anilines and Mono-N-substituted Anilines. Some Linear Free-Energy Relationships

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Abstract: Fluorenone is photoreduced by 0.01 *M* *N,N*-dimethylaniline in benzene, $\varphi = 0.59$, $k_{ir} = 4.7 \times 10^8 M^{-1} \text{sec}^{-1}$, and by 0.0086 *M* triethylamine in benzene, $\varphi = 0.83$, $k_{ir} = 1.7 \times 10^8 M^{-1} \text{sec}^{-1}$. Eleven meta- and para-substituted anilines were studied as quenchers for these photoreductions; values of k_q varied from $8 \times 10^7 M^{-1} \text{sec}^{-1}$ for *p*-CN to $1.4 \times 10^{10} M^{-1} \text{sec}^{-1}$ for *p*-OC₂H₅. A plot of $\log k_{ir}$ vs. σ^+ is linear from *p*-OEt to *p*-COCH₃, $\rho = -0.96$; *m*-CF₃, *p*-CO₂Et, and *p*-CN lead to larger decreases in rate. In quenching by aniline NH₂ and aniline ND₂ $k_H/k_D = 1.3$. Mono-*N*-substituted anilines are also quenchers for fluorenone; values of k_q are $1\text{--}7 \times 10^9 M^{-1} \text{sec}^{-1}$ for five mono-*N*-alkylanilines and $8.9 \times 10^9 M^{-1} \text{sec}^{-1}$ for diphenylamine. From the linear relation between σ^+ and known ionization potentials, IP, of a series of meta- and para-substituted anilines, ionization potentials of others are estimated. Values of $\log k_{ir}$ and IP for *N*-methylaniline and diphenylamine fit the linear relationship between $\log k_{ir}$ and IP of meta- and para-substituted anilines. Values of k_{ir} are higher and less sensitive to σ or IP than are those of corresponding compounds lacking aromatic NH. The results are discussed in terms of development of partial positive charge of N and partial hydrogen transfer from aromatic N in the quenching of the triplet. Light-induced reactions of fluorenone and biacetyl with amines are compared, and the relevance of the pK_a of the ketyl radical to reduction and quenching is indicated.

Photoexcited fluorenone, in the singlet or triplet states, interacts with amines, and this may lead to transfer of hydrogen to the ketone or to deactivation. Tertiary aliphatic amines quench fluorescence of the singlet,¹ leading to some photoreduction, possibly *via* the triplet. At low concentrations of amine, <0.01 *M*, reaction is largely of the triplet and leads to efficient photoreduction with overall quantum yields approaching one, accompanied by some quenching.^{1,2} The high quantum yields include reduction of a second, ground-state, fluorenone by amine-derived radical.³ Quantum yields are low at high amine concentration because of singlet quenching.⁴ It has been proposed that such reactions of amines with triplets proceed by rapid interaction, k_{ir} , leading to a charge-transfer complex, followed either by spin inversion, charge destruction and quenching, k_e , or by transfer of hydrogen from α carbon, k_h , eq 1.^{5,6}



Secondary aliphatic amines show similar behavior toward fluorenone,^{1,2} with lower rates of interaction with both excited singlet and triplet and lower quantum yields for photoreduction, 0.05–0.1. Primary aliphatic amines react with the triplet and lead to photoreduction, generally with still lower quantum yields, reflecting high k_e/k_h ratios. Primary amines show in-

creasing quantum yields at high concentration since they do not quench the singlet in hydrocarbon solvent.¹

Tertiary aromatic amines, di-*N*-alkylanilines, are quenching and photoreducing agents for fluorenone. A study of polar effects in these reactions, in which rates of interaction, k_{ir} , rise with electron donation by meta and para substituents, and quantum yields are decreased by both strong electron donation and strong electron withdrawal, has been described.³ Primary aromatic amines, anilines, lacking α -C-H and having low ionization potentials, quench both excited singlet and triplet. They may quench the singlet with rates approaching diffusion control; rates of quenching the triplet show a pronounced polar effect, rising with electron-donating, falling with electron-withdrawing substituents in the benzene ring.⁷ We wish to report an extended and refined study of these systems. Secondary aromatic amines, mono-*N*-alkylanilines, quench excited fluorenone, but, unlike their purely aliphatic analogs, they lead to essentially no photoreduction, despite the presence of α -CH. We wish to report a study of this quenching by mono-*N*-alkylanilines.

Experimental Section

Irradiation. Preparation of solutions, irradiation equipment and procedure, method of spectrophotometric analysis for residual fluorenone at 405 nm, in the 1-cm² photolysis tubes, and the method of calculation of quantum yields have been described.⁵ The quantum yield for photoreduction of 0.0030 *M* fluorenone by 0.010 *M* *N,N*-dimethylaniline in benzene under argon was 0.59 at 405 nm, determined by ferrioxalate actinometry. This solution, used as a secondary actinometer, was irradiated on a rotating wheel simultaneously with similar solutions to which had been added varying concentrations of monoalkylanilines and para- and meta-substituted anilines, and the rates of photoreduction of fluorenone by dimethylaniline were followed. Some of the meta- and para-substituted anilines had been evaluated as quenchers in the photoreduction of fluorenone by triethylamine in benzene, instead of by dimethylaniline.⁷ A solution of 0.0036 *M* fluorenone and 0.0086 *M* triethylamine in benzene, quantum yield 0.83, was used as a secondary actinometer for these experiments.⁷ Generally, effects

(7) G. A. Davis and S. G. Cohen, *Chem. Commun.*, 622 (1970).

(1) G. A. Davis, P. A. Carapellucci, K. Szoc, and J. D. Gresser, *J. Amer. Chem. Soc.*, **91**, 2264 (1969).

(2) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968).

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(4) R. A. Caldwell, *Tetrahedron Lett.*, 2121 (1969).

(5) S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89**, 164 (1967); *J. Phys. Chem.*, **72**, 3783 (1968).

(6) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968).

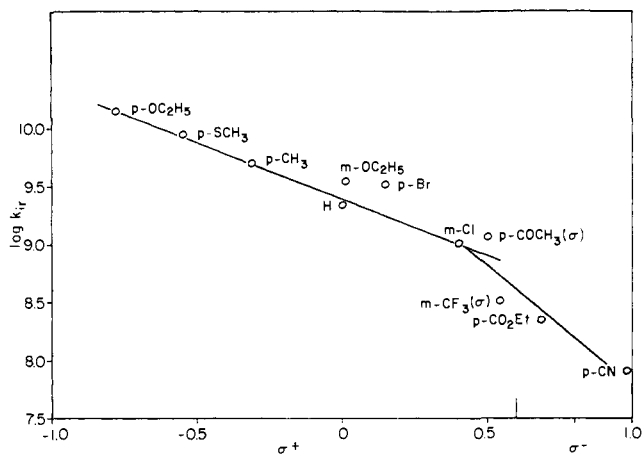


Figure 1. Rates of interaction of fluorenone triplet with meta- and para-substituted anilines, *m*- or *p*-XC₆H₄NH₂; log *k*_{ir} vs. σ^\pm , $\rho = -0.96$.

of three or more different concentrations of each quencher were observed. Runs in which effects of singlet quenching appear, *i.e.*, abnormally high values of φ_0/φ at high concentrations of quencher, were discarded. Maximum concentrations of anilines were generally $<0.02 M$.

Materials. The following materials were used: aniline, Eastman Reagent grade, bp 54° (8 mm); benzene, Eastman Spectro-quality, dried by distillation and stored over P₂O₅; *m*-chloroaniline, Aldrich, bp 82° (3 mm); *N*-cyclohexylaniline, Eastman, bp 74–76° (0.05 mm); D₂O, Stohler Isotope, 99.8% D; *N,N*-dimethylaniline, Eastman, mp 71° (0.8 mm); *p*-ethoxyaniline, Aldrich, bp 85° (0.9 mm); *m*-ethoxyaniline, Eastman, vacuum distilled before use; *N*-ethylaniline, Eastman, bp 88° (15 mm); fluorenone, Eastman, mp 83° from petroleum ether; *N*-isopropylaniline, Eastman, bp 67° (1.2 mm); *N*-methylaniline, Eastman, bp 54° (1.0 mm); *p*-methylaniline, prepared by neutralization of Eastman, *p*-toluidine hydrochloride, bp 78° (9 mm); *p*-thiomethylaniline, Aldrich, bp 100° (2 mm); *m*-trifluoromethylaniline, Aldrich, bp 78° (8 mm). Aniline-*N*-d₂ was prepared by treatment of 3 ml of freshly distilled aniline with two 30-ml portions of D₂O. Analysis by nmr, after vacuum distillation, indicated 99.2% D at the amino N. Analysis by ir of the benzene stock solution indicated $>95\%$ *N*-d after handling.

Results and Discussion

Quenching by Meta- and Para-Substituted Anilines. Quantum yield for reduction of an excited triplet by an amine may be indicated⁸ by eq 2; *a* includes the inter-

$$1/\varphi = 1/af + k_d/afk_{ir}(Am) + k_q(Q)/afk_{ir}(Am) \quad (2)$$

system crossing yield and the extent of reduction of a second ground-state ketone by amine-derived radical; *k*_d is the self- and solvent-induced deactivation rate constant; *f* = *k*_h/(*k*_e + *k*_h), eq 1; *k*_{ir} is as before, eq 1; (Am) and (Q) are respectively concentrations of the reducing agent and quencher; and *k*_q is the rate constant for quenching of the triplet by the quencher. Ratios of rates of photoreduction in the absence and presence of quencher may be treated as ratios of quantum yields, and eq 3 may be derived from eq 2. For a

$$\varphi_0/\varphi = 1 + k_q(Q)/(k_{ir}(Am) + k_d) \quad (3)$$

plot of φ_0/φ vs. (Q), the slope is given in eq 4. For

$$\text{slope} = k_q/[k_{ir}(Am) + k_d/k_{ir}] \quad (4)$$

photoreduction of fluorenone by dimethylaniline in benzene, values of *k*_{ir} and *k*_d/*k*_{ir} were determined pre-

(8) S. G. Cohen and N. M. Stein, *J. Amer. Chem. Soc.*, **93**, 6542 (1971).

viously, $4.7 \times 10^8 M^{-1} \text{sec}^{-1}$ and $0.0013 M$, respectively. These values, combined with measured slopes, lead to values of *k*_q. Some of the anilines had been studied previously⁷ as quenchers for photoreduction of fluorenone by triethylamine in benzene, and slopes for plots of φ_0/φ vs. (Q) were available, but the value of *k*_{ir} was not known for this amine in this solvent. Photoreduction of fluorenone by triethylamine in benzene was studied in the absence of quencher; quantum yields were determined at six concentrations of amine, in the range 0.05–0.005 *M*, and from the ratio of slope to intercept, eq 2, *k*_d/*k*_{ir} was evaluated, $0.0023 M$. The value of *k*_q for quenching of fluorenone triplet by aniline in benzene was determined (see below) by use of it as a quencher for photoreduction by dimethylaniline, $k_q = 2.2 \times 10^9 M \text{sec}^{-1}$. The slope of the plot of φ_0/φ vs. (Q) for quenching by aniline of photoreduction of fluorenone by 0.0086 *M* triethylamine in benzene was $1185 M^{-1}$. From eq 4 and these data, *k*_{ir} for interaction of fluorenone triplet with triethylamine in benzene is calculated, $1.7 \times 10^8 M^{-1} \text{sec}^{-1}$. This value is five times greater than that for this interaction in cyclohexane, possibly because of the greater stabilization of the CT complex in benzene, the more polarizable solvent.

Values of *k*_q (or *k*_{ir}) for quenching of fluorenone triplet in benzene by 11 anilines were determined for assessment of the effects of meta and para polar substituents on the rates of those interactions. Results are summarized in Table I and Figure 1. Values of *k*_{ir}

Table I. Quenching of Fluorenone Triplet in Benzene by Meta- and Para-Substituted Anilines

X	Slope, ^a M ⁻¹	10 ⁻⁹ <i>k</i> _q , M ⁻¹ sec ⁻¹	σ^b	σ^{+b}	σ^{-b}	IP, eV
<i>p</i> -CN	44 ^c	0.08	0.66	0.66	1.00	8.15 ^d
<i>p</i> -CO ₂ C ₂ H ₅	125 ^c	0.23	0.45	0.48	0.68	8.03 ^d
<i>m</i> -CF ₃	64 ^c	0.34	0.54	0.52		8.06 ^d
<i>m</i> -Cl	190 ^c	1.0	0.37	0.40		7.98 ^d
<i>p</i> -COCH ₃	625 ^c	1.2	0.50		0.87	8.04 ^d
H(NH ₂)	420 ^c	2.2	0	0	0	7.70 ^f
H(ND ₂)	320 ^c	1.7	0			
<i>p</i> -Br	1740 ^c	3.2	0.23	0.15		7.81 ^d
<i>m</i> -OC ₂ H ₅	630 ^c	3.4	0.1	0.05		7.74 ^d
<i>p</i> -CH ₃	940 ^c	5.0	-0.17	-0.31		7.52 ^f
<i>p</i> -SCH ₃	1340 ^c	7.0	0	-0.60		7.31 ^d
<i>p</i> -OC ₂ H ₅	2730 ^c	14.0	-0.24	-0.78 ^g		7.20 ^{f,g}

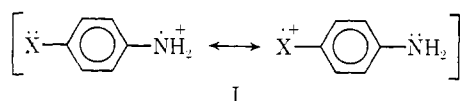
^a Slope of the plot of φ_0/φ vs. concentration of aniline quencher.

^b Values taken from J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 204, 211. ^c Slope reported in ref 7. ^d Estimated from σ^+ and Figure 2. ^e Quenching of photoreduction by 0.01 *M* *N,N*-dimethylaniline, *k*_{ir} = $4.7 \times 10^8 M^{-1} \text{sec}^{-1}$, ref 3. ^f From G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962), normalized to aniline IP = 7.70 eV; K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

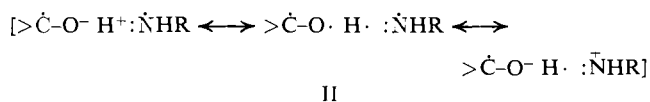
^g Value for *p*-OCH₃ used.

range over two orders of magnitude from slightly under $10^8 M^{-1} \text{sec}^{-1}$ for the *p*-CN compound to $\sim 10^{10} M^{-1} \text{sec}^{-1}$ for the *p*-OEt compound. Rates are increased by electron donation, decreased by electron withdrawal, consistent with a mechanism involving charge transfer. The rate constants for reaction with

the anilines are generally higher and extend over a smaller range than in the reactions of excited fluorenone with the corresponding substituted dimethylanilines,³ which involve both quenching and transfer of H from α -C. In both cases, the rates approach the same diffusion-controlled limit with strong electron-donating substituents. Consideration of Table I and Figure 1 indicates that the values of $\log k_{ir}$ for p -OEt and p -SCH₃ correlate well with σ^- and are in no way correlated by their ordinary σ values which are much more positive. Values of $\log k_{ir}$ for p -CH₃, m -OEt, and p -Br also correlate better with σ^+ than with σ , but here the differences are not great. For m -Cl, values of σ and σ^+ are similar. The correlation with σ^+ is consistent with the development of positive charge at the reacting center in the transition states of the quenching reactions of these compounds, and resonance interaction between the substituent and the reaction center, formula I. However, the rate constants are all rather high,



and the sensitivity to electron donation is low, $\rho = -0.96$, as compared with -1.95 in reactions of fluorenone triplet with substituted N,N -dimethylanilines.³ High reactivity and low sensitivity to the polar effect are consistent with the development of only partial positive charge and the important contribution of partial hydrogen transfer in the transition state.⁹ Such partial abstraction of H from N, facilitated by the stability of the arylamino radical and anion, and by a polar contribution, may be more important in the transition state for this quenching than the contribution of hydrogen transfer from α -C proposed as contributing to high values of k_{ir} in photoreduction by amines.⁹ Involvement of partial hydrogen transfer in the transition is seen in the comparison of the quenching by aniline NH₂ and aniline ND₂, Table I, $k_H/k_D = 1.3$. A purely inductive effect of deuterium on the development of positive charge would lead to an inverse isotope effect.¹⁰ Quenching by reversible, purely homolytic abstraction of H from N would be characterized by a larger kinetic isotope effect. A complex process of charge and hydrogen transfer appears to be involved in this quenching, formula II.



The effects of strong electron-attracting substituents are complex. The m -CF₃ group leads to a large decrease in rate for its σ value. The p -CO₂C₂H₅ and p -CN groups lead to a large decrease in values of k_{ir} , and even their σ^- values are not sufficiently high to lead to an empirical linear correlation. With greater electronegativity in the substituent and higher ionization potential, diminished charge transfer, diminished positive charge and acidity of the $-\text{NH}^+$ ensue, decreasing contribution of proton transfer to the stability of the CT complex and contribution of partial hydrogen trans-

fer to the quenching rate. The p -COCH₃ group, on the other hand, leads to a value of k_{ir} which may correlate with its normal σ value. The p -COCH₃ group also led to a high quenching constant, correlated by σ and accompanied by little photoreduction, in reaction of fluorenone triplet with p -dimethylaminoacetophenone. In that reaction, the rate constant for p -CO₂C₂H₅ was also correlated by its σ value, that for p -CN by its σ^- value.³ The p -benzoyl group had also led to a high quenching constant in quenching by ground-state ketone of the photoreduction of p -aminobenzophenone by triethylamine.⁵

Quenching by Mono-N-substituted Anilines. The mono-N-substituted anilines also led essentially only to quenching of fluorenone, and values of k_q , determined from their effects on photoreduction by N,N -dimethylaniline and triethylamine, are given in Table II. Rate

Table II. Quenching of Fluorene Triplet by Mono-N-substituted Anilines in Benzene

R	Slope, ^a M^{-1}	$10^3 k_{ir}$, $M^{-1} \text{sec}^{-1}$	ϕ	IP, eV
H	420 ^b	2.2	~ 0.00	7.70 ^c
CH ₃	1350 ^b	7.1	~ 0.006	7.39 ^f
C ₂ H ₅	760 ^b	4.2	~ 0.01	
<i>i</i> -C ₃ H ₇	720 ^b	4.2	~ 0.001	
<i>o</i> -C ₆ H ₁₁	750 ^b	3.9		
CH ₂ C ₆ H ₅	680 ^c	1.3	< 0.01	
C ₆ H ₅	4800 ^d	8.9	< 0.01	7.40 ^e

^a Slope of plot of ϕ_0/ϕ vs. concentration of aniline quencher. ^b Quenching of photoreduction by N,N -dimethylaniline, 0.0097–0.011 M . ^c Quenching of photoreduction by 0.0086 M triethylamine, unreported experiment of G. D. Davis. ^d Quenching of photoreduction by 0.0086 M triethylamine, ref 7. ^e See footnote *f*, Table I. ^f A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968), normalized to aniline IP = 7.70 eV; K. Watanabe, *J. Chem. Phys.*, 26, 542 (1957). ^g Taken from L. L. Miller, G. D. Nordbloom, and E. A. Mayeda, *J. Org. Chem.*, 37, 916 (1972).

constants for quenching of fluorenone triplet by the mono-N-alkylanilines are two to three times greater than for the unsubstituted aniline and an order of magnitude greater than the N,N -dialkylanilines.¹¹ Only N -benzylaniline had a lower quenching rate constant than aniline. This lower reactivity of the benzyl compound and the very low quantum yields for photoreduction indicate that α -C–H is not important to the quenching by mono-N-alkylanilines; the inductive effect of the alkyl groups facilitates electrophilic attack by the triplet on the n electrons and H of the NH. A steric effect may account for the larger alkyl groups leading to lower rates than methyl, and electron attraction by the phenyl may lower the reactivity of N -benzylaniline, despite the stability of the potential benzyl radical. The quenching constants for aniline, N -methylaniline, and diphenylamines rise with decreasing ionization potential.

Relationships may be examined between ionization potential, IP, and rates of interaction of an excited triplet with a broader range of compounds and with

(9) J. B. Guttenplan and S. G. Cohen, *J. Amer. Chem. Soc.*, 94, 4040 (1972).

(10) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 181 (1963).

(11) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, 73, 141 (1973).

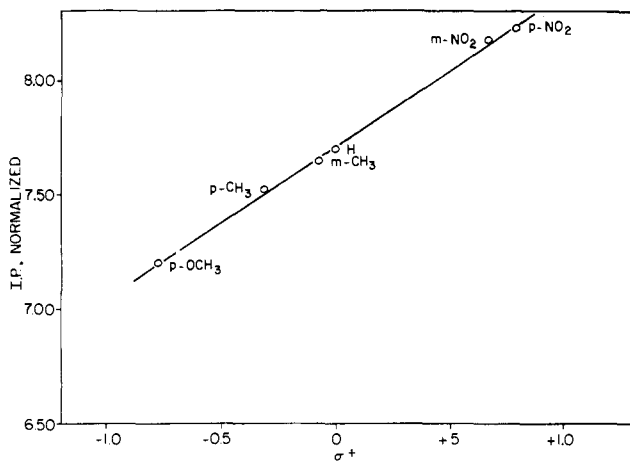


Figure 2. Normalized IP for meta- and para-substituted anilines vs. σ^+ ; values taken from ref 13. Slope = $+0.67 \text{ eV}^{-1}$.

varying donor groups, for which $\rho\sigma$ considerations may not be applied.^{9,12} Examination of the ionization potentials of some meta- and para-substituted anilines¹³ indicates that a linear plot may be drawn of σ^+ vs. these values of IP, slope = 0.67 eV^{-1} , Figure 2. From this plot, ionization potentials of other anilines may be estimated, and they are listed in Table I. The values of $\log k_{ir}$, Table I, may be plotted against IP, Figure 3, slope -1.1 eV^{-1} from p -OEt to p -COCH₃ and -6.3 eV^{-1} from m -Cl to p -CN. The σ^+ treatment may not be applied to the mono- N -substituted anilines, but the values of $\log k_{ir}$ and IP for N -methylaniline and for diphenylamine correlate fairly well with the plot of $\log k_{ir}$ vs. IP for the meta- and para-substituted anilines, Figure 3. Reactions with compounds containing aromatic NH show higher rate constants and a smaller range, lower sensitivity to IP, than do the reactions of fluorenone triplet with compounds which lack aromatic NH: tertiary aromatic amines, primary, secondary, and tertiary aliphatic amines, and an aliphatic thioether.¹² In their reactions with fluorenone triplet, the latter compounds showed rate constants ranging over four orders of magnitude, with slope -2.9 eV^{-1} . Contribution of partial H transfer from aromatic N to the quenching transition appears to lead to the high quenching rates and lower sensitivity to the polar effect. The strong electron-attracting substituents m -CF₃, p -CO₂Et, and p -CN lead to a high dependence on IP, slope = -6.3 eV , as they reduce the positive charge of the $-\text{NH}^+$ and the contribution of proton transfer to quenching.

The tendency of aromatic N-H to be involved in the initial interaction may account for the failure of mono- N -alkylanilines to photoreduce fluorenone, despite the presence of α -C-H which is essential for irreversible photoreduction. It is not clear whether the quenching interaction involves only partial H transfer or leads to more complete abstraction of H from aromatic N and formation of radicals which then regenerate the starting materials, essentially by disproportionation. Such a process might also occur with aliphatic primary and secondary amines and might be involved in the quenching part of the reaction indicated by k_e , eq 1. However, values of k_{ir} for primary and secondary aliphatics

(12) J. B. Guttenplan and S. G. Cohen, *Tetrahedron Lett.*, 2163 (1972).
 (13) G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

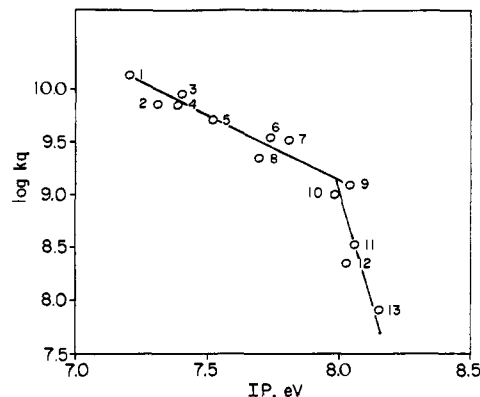
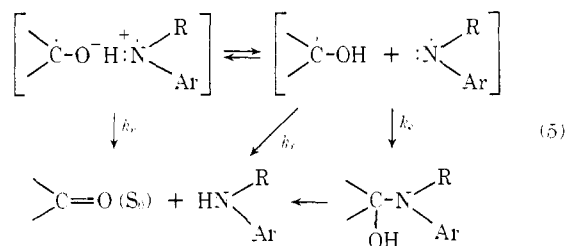
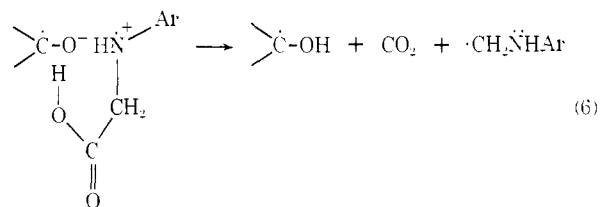


Figure 3. Rates of interaction of fluorenone triplet with meta- and para-substituted anilines and mono- N -substituted anilines vs. IP. Slope = -1.1 eV^{-1} for electron donors and p -Br. Slope = -6.3 eV^{-1} for strong electron-withdrawing substituents. (1) p -OC₂H₅; (2) p -SCH₃; (3) (C₆H₅)₂NH; (4) C₆H₅NHCH₃; (5) p -CH₃; (6) m -OCH₃; (7) p -Br; (8) H; (9) p -COCH₃; (10) m -Cl; (11) m -CF₃; (12) p -CO₂C₂H₅; (13) p -CN.

show the same dependence on ionization potential as do tertiary amines, in reactions with both benzophenone⁹ and fluorenone;¹² the NH of the aliphatic amines does not appear to be involved significantly, consistent with lower stability of alkylamino radicals and lower acidity of alkylamines. The high stability of the arylamino radical favors abstraction of H from N in aromatic primary and secondary amines. This transfer of H from N may involve transfer of a proton in a charge-transfer complex, and ground-state starting materials may result from spin inversion and charge destruction in the CT complex, k_e , or from back transfer of H directly from the radicals, k_r , or after cross combination of the radicals, k_c , eq 5. Evidence for transfer



of a proton in the CT complex may be indicated by an exception to the quenching by secondary anilines seen in the reaction of fluorenone with N -phenylglycine, whereby the glycine is decarboxylated and the fluorenone is reduced, eq 6.¹⁴ While transfer of H from N



of anilines may be favored over transfer from α -C, leading to quenching, transfer from an appropriately located acidic carboxyl was favored still more, and in this case reduction occurred. Unfortunately, the quantum yield for photoreduction was not indicated.

(14) R. S. Davidson, K. Harrison, and P. R. Steiner, *J. Chem. Soc. C*, 3482 (1971).

The pattern of behavior of fluorenone triplet may be compared with that of biacetyl.^{15,16} The two compounds have similar triplet energies, similar reduction potentials, and similar rates of interaction with triethylamine, 1.7×10^8 and $5.7 \times 10^7 M^{-1} \text{ sec}^{-1}$, respectively.¹¹ Biacetyl has a low-lying n, π^* triplet and is photoreduced efficiently by alcohols by direct hydrogen transfer, while fluorenone is not photoreduced by alcohols, presumably because of its π, π^* triplet and inefficient intersystem crossing in this solvent. Quenching of biacetyl singlet and triplet by amines follows a pattern similar to that for fluorenone, and biacetyl is photoreduced by primary and secondary aliphatic amines, possibly more efficiently than is fluorenone, but quantum yields were not reported.¹⁵ Biacetyl triplet is quenched by ring-substituted anilines at rates an order of magnitude lower than those of fluorenone but with similar low sensitivity to polar substituents,¹⁶ $\rho = -0.85$. Comparison of aniline NH_2 and ND_2 , however, indicated an inverse kinetic isotope effect,¹⁵ $k_{\text{H}}/k_{\text{D}} = 0.52$, apparently arising from the inductive effect of deuterium¹² and indicating no important contribution of H transfer to the quenching interaction. The fairly high rate, apparently without assistance from partial transfer of H, and low sensitivity to substituents in the amine indicate that it is a property of biacetyl to form a stable radical anion. Further, despite the n, π^* character which leads to abstraction of H from alcohols, biacetyl is not photoreduced by *N,N*-dialkylanilines but is quenched at high rate,¹⁵ $k_{\text{q}} \sim 10^8\text{--}10^9 M^{-1} \text{ sec}^{-1}$, while fluorenone is reduced by these compounds. The

(15) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **91**, 7113 (1969).

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stability of the radical anion of biacetyl is reflected in its low basicity; the $\text{p}K_{\text{a}}$ of its ketyl radical is 4.4,¹⁷ compared with 9.2^{18,19} for benzophenone and 6.3¹⁹ for fluorenone ketyl. The low basicity, arising from the adjacent, electropositive carbonyl group, leads to low tendency for transfer of a proton from $\alpha\text{-C}$ in the CT complex, and charge destruction and quenching dominate. Both the proton-donating power of the $\alpha\text{-C}$ of the cationic part and the proton-accepting power of the anionic part of the CT complex affect the quantum yields of photoreduction.

The electron-donating property of the donor, indicated by ionization potential, the electron- and hydrogen-accepting properties of the acceptor, indicated by reduction potential and triplet energy, and the availability of hydrogen for partial transfer from N or $\alpha\text{-C}$ in the transition state determine the rates of the initial interaction, k_{ir} .^{9,12} In cases where there is much contribution of hydrogen transfer from N or very little from $\alpha\text{-C}$,²⁰ quenching results, with little photoreduction. Where there is substantial contribution of hydrogen transfer from $\alpha\text{-C}$, photoreduction occurs with good quantum efficiency.

Acknowledgment. This work was supported by the U.S. Atomic Energy Commission, Grants AT(30-1)2499 and AT(11-1)3318.

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Chromic Acid Oxidation of Cyclobutanol¹

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Abstract: The chromic acid oxidation of cyclobutanol has been examined in 97% acetic acid. The preoxidation equilibrium steps leading to ester intermediates were characterized by faster rates of esterification and larger ester equilibrium constants than found for isopropyl alcohol. This presumably arises from smaller steric effects with the small cyclic alcohol. The rates of chromium(VI) and chromium(V) oxidations could be determined spectrometrically, and the spectrum of the intermediate chromium(V) species was derived. The oxidation by chromium(IV) was studied by an analysis of the rate of production of cyclobutanone. Both chromium(VI) and -(V) lead to cyclobutanone whereas chromium(IV) leads to cleavage of the four-membered ring.

We have studied the oxidation of isopropyl alcohol by chromium(VI), -(V), and -(IV)² and have obtained results which are in good agreement with similar studies by Rahman and Roček³ using different experimental methods. The oxidation of isopropyl alcohol is relatively simple in that only acetone is formed.

(1) This investigation was supported by a grant from the National Science Foundation.

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Cleavage products are commonly found in chromic acid oxidation of alcohols, and thus we have applied our experimental approach to one of these compounds, cyclobutanol. This is a particularly useful substrate since Roček and Radkowsky⁴ have demonstrated that cyclobutanol gives extensive cleavage to γ -hydroxybutyraldehyde during chromic acid oxidation. The reaction of cyclobutanol with chromium(IV) formed by the chro-

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