EFFECT OF SOLVENT IN THE PHOTOREDUCTION AND QUENCHING OF BENZOPHENONE BY TRIETHYLAMINE, 1-AZABICYCLO[2.2.2]-OCTANE AND 1,4-DIAZABICYCLO[2.2.2]OCTANE

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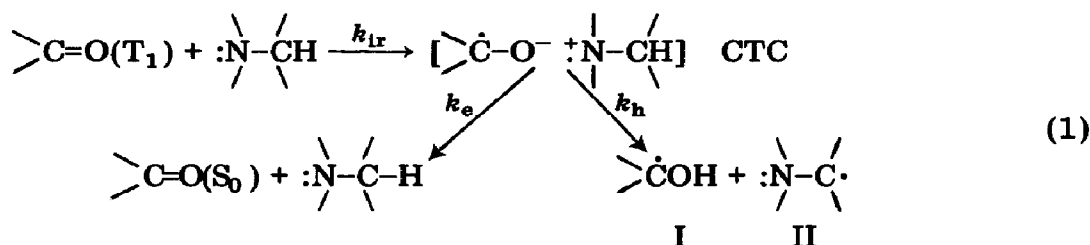*Department of Chemistry, Brandeis University, Waltham, Mass. 02154 (U.S.A.)*

Summary

Photoreduction of benzophenone by triethylamine (TEA) is efficient in tert-butyl alcohol, acetone and acetonitrile (φ = 0.8 - 1.1) and somewhat less efficient in benzene in which evidence of a light-absorbing quenching transient (LAT) is found. Photoreduction by the bridgehead bicyclic amine quinuclidine (1-azabicyclo[2.2.2]octane (ABCO)) is less efficient (φ = 0.08 - 0.22) with lower quantum yield in the polar solvents and higher quantum yield in the less polar solvents despite formation of a LAT. Photoreduction by the corresponding bridgehead bicyclic diamine 1,4-diazabicyclo[2.2.2]octane (DABCO) is still less efficient (φ = < 0.001 - 0.09) again with lower quantum yield in the polar solvent and the higher in the hydrocarbon. In 1:1 water–pyridine photoreduction of 4-carboxybenzophenone by TEA is efficient (φ_{ketyl} = 1) by ABCO is very inefficient (φ_{ketyl} = 0.0004) and by DABCO leads only to quenching. Low quantum yields for the reduction by ABCO and DABCO in polar solvents are accompanied by high values of the interaction rate constant k_{ir}. The results are interpreted in terms of charge transfer interaction between excited triplet carbonyl and non-bonding electrons of the amines. The effects of hyperconjugation and charge delocalization in the charge transfer complex (CTC) and the role of charge transfer complexation and of disproportionation and dissociation to free ions as light-wasting processes are discussed.

1. Introduction

Photoreduction by amines may show very high rate constants and resulting low sensitivity to physical quenchers but, despite this and the generality of their reducing action, quantum yields do not approach the maximum theoretical limiting values which may be achieved in the less general and more readily quenched photoreduction by alcohols [1 - 3]. Light-

wasting processes, which regenerate starting materials and do not take place in the reactions with alcohols, occur in the reactions of excited ketones with amines [4]. One way to account for these properties is to postulate that photoreduction by amines proceeds by rapid interaction at the non-bonding (n) electrons of the amino nitrogen (with a rate constant k_{ir}) leading to a charge transfer complex (CTC); this would be followed either by formation of ketyl and α-aminoalkyl radicals (I and II), by hydrogen transfer from an alpha carbon to the carbonyl oxygen (rate constant k_h) or by regeneration of starting materials by spin inversion and charge destruction (rate constant k_e) [3, 5, 6]:

$$\text{>C=O(T}_1) + :\text{N-CH} \xrightarrow{k_{ir}} [\text{>C-O}^- \ ^+\text{N-CH}] \quad \text{CTC}$$

$$k_e \swarrow \qquad \searrow k_h$$

$$\text{>C=O(S}_0) + :\text{N-C-H} \qquad \text{>COH} + :\text{N-C·} \tag{1}$$

$$\text{I} \qquad \text{II}$$

In contrast, the photoreduction by amines might involve, not a common intermediate CTC, but two separate concurrent processes: interaction at the n electrons of the nitrogen leading to quenching (k_e) and direct abstraction of hydrogen from α-C (k_h).

Moreover, an alternative light-wasting process is the direct formation of free radical anion and cation [7] from interaction at the lone-pair electrons of nitrogen, in addition to the formation of the CTC. Such free radical ions may largely disproportionate to starting materials since they are essentially spin paired.

In this study we examined the influence of structural properties in tertiary amines and of solvents on the quantum yields and interaction rate constants in the photoreduction of benzophenone and 4-carboxybenzophenone. Triethylamine (TEA), the bridged bicyclic monoamine (1-azabicyclo[2.2.2]octane (ABCO)) and the analogous diamine 1,4-diazabicyclo-[2.2.2]octane (DABCO) were chosen for this study.

2. Experimental

2.1. Materials

The solvents and amines were distilled: acetonitrile (MC and B spectroquality) b.p., 81 °C; benzene (Eastman Spectrograde) b.p., 80 °C; tert-butyl alcohol (MC and B) b.p., 82 °C; sec-butylamine (Eastman) b.p., 63 - 64 °C; pyridine (Fisher ACS) b.p., 115 °C; TEA (Eastman) b.p., 88 - 89 °C. Distilled amines were used immediately or stored under nitrogen. Solids were crystallized: benzophenone (Fisher) m.p., 47.5 - 48.5 °C; 4-benzoylbenzoic acid (Aldrich) m.p., 202 - 202.5 °C; DABCO (Aldrich) was crystallized from benzene–hexane and sublimed. Naphthalene was obtained from Fisher and

potassium ferrioxalate from K and K. ABCO was prepared as follows: quinu-clidine hydrochloride (Aldrich, 5 g) was dissolved in 6.6 ml of water at 0 °C, treated with 3.5 ml of cold 10 N NaOH, saturated with salt and extracted with three portions of cold ether. The extract was dried at 0 °C with sodium sulfate, transferred to a sublimator which was cooled by tap water and evacuated using an aspirator shielded by a drying tube. Ether was taken off at room temperature, the residue was sublimed at 90 - 100 °C and stored in a freezer under nitrogen.

2.2. Irradiations

2.2.1. Benzophenone
Procedures for carrying out irradiations of benzophenone solutions have been described previously [6]. In the analysis for residual benzophenone at $1\,666\ cm^{-1}$, 3 ml aliquots were concentrated in vacuum, the residue was taken up in 10 ml of benzene and the per cent transmittance was measured against benzene in 0.5 mm NaCl cells and converted to optical density. The presence of transients was assessed from absorbances at 300 - 400 nm.

In the study of retardation by DABCO of the photoreduction of 0.008 M benzophenone by 0.1 M sec-butylamine in acetonitrile, analysis of benzo-phenone was made at 344 nm. In each of the following pairs are given respec-tively the values of the concentration of DABCO and the ratio of the un-retarded to the retarded rate of reduction: 0.00297 M, 2.54; 0.0104 M, 3.35; 0.0158 M, 4.15; 0.0241 M, 5.70; 0.0285 M, 6.08; 0.0404 M, 8.60.

2.2.2. 4-Benzoylbenzoic acid
The quantum yield was determined on the Bausch and Lomb 38-86-01 monochromator as previously described [5]. The light intensity was moni-tored with a potassium ferrioxalate actinometer (φ = 1.25 [8]). Photolysis was carried out at 366 nm, which is close to the maximum lamp output on the wheel. Residual ketone was followed on a Beckman D.U. or on a Cary 14 spectrophotometer at 360 nm. The rate of photolysis was corrected for non-opacity [9, 10]. For the photoreduction of 0.008 M 4-benzoylbenzoic acid by 0.02 M TEA in 1:1 (by volume) water–pyridine at pH 12, φ_{366} = 0.48. This value is identical with that calculated by correcting for concentration effects [6] the reported value φ = 0.68 [5] obtained for 1 M TEA in an opaque system. The procedure for the irradiation of 4-benzoylbenzoic acid on the wheel has been described previously [5, 6]. Residual ketone was followed at 360 nm; light-absorbing transients (LATs) were not observed when spectra were obtained on the Cary 14 spectrophotometer. Relative rates were obtained from the initial slopes of plots of per cent reaction versus time or from linear least square slopes of plots of optical density (OD) versus time.

2.2.3. Benzophenone phosphorescence

Quenching of the phosphorescence of benzophenone was studied on a Farrand MK-1 spectrofluorimeter. Tubes were degassed to less than 0.04 mmHg. Excitation was at 380 nm and the emission spectrum was observed at 350 - 600 nm. There were peaks at 430, 450 and 470 nm; the intensity at 450 nm was monitored for I_0/I values at varying concentrations of TEA, ABCO and DABCO. The slopes of plots of I_0/I *versus* concentration of amine were: (a) in benzene, TEA, 1.6×10^4 M^{-1}; ABCO, 1.2×10^3 M^{-1}; DABCO, 1.55×10^4 M^{-1}; (b) in tert-butyl alcohol, TEA 2.06×10^4 M^{-1}; ABCO, 8.3×10^2 M^{-1}; DABCO, 5.26×10^3 M^{-1}; (c) in acetonitrile, ABCO, 6.3×10^2 M^{-1}; DABCO, 3.1×10^4 M^{-1}.

3. Results

In preliminary experiments irradiations of 0.008 M benzophenone and 0.01 M TEA were carried out in several solvents and evidence for a LAT was sought by examination in the spectrophotometer at short time intervals. Solution in pyridine and ethyl acetate showed a large increase in optical density and these solvents were not used further. A solution in acetonitrile showed no evidence of a LAT, tert-butyl alcohol showed a small induction period before a decrease in OD was observed, while solutions in acetone and benzene showed small initial increase followed by steady linear decrease in OD. Photoreductions were studied in the last four solvents at higher initial concentration of benzophenone (0.08 M) to minimize effects due to light absorption by any LAT, and at a higher initial concentration of the amino compound, (0.2 - 0.3 M) which, because of high values of k_{ir}, would minimize effects of even a diffusion-controlled quenching LAT present in low concentration. Relative rates of reduction were determined on a rotating wheel, with a solution of 0.08 M benzophenone and 0.3 M TEA in acetonitrile irradiated simultaneously as a secondary actinometer ($\varphi = 1.04$). Rates were converted to quantum yields which, with values of k_{ir}, are given in Table 1.

Quantum yields for photoreduction by TEA were relatively independent of solvent. They appeared highest in acetonitrile, somewhat lower in tert-butyl alcohol and acetone and lowest in benzene (in which an interfering LAT was observed). However, in the photoreduction of benzophenone by ABCO the highest quantum yields were observed in benzene and tert-butyl alcohol despite the presence of a LAT, and the lowest quantum yields were observed in acetone and acetonitrile, in which no LAT was observed. Photoreduction by DABCO was least efficient and was similar to ABCO in effects of the solvent on the quantum yield.

Quantum yields for photoreduction of 0.008 M 4-benzoylbenzoate in a more polar medium (1:1 water–pyridine at pH 12) showed a similar dependence on the structure of the amine. Photoreduction with 0.02 M TEA occurred with a quantum yield for the formation of ketyl of 0.96, which is similar to that at higher concentration of this amine in acetonitrile. Reduction

TABLE 1

Effects of solvent on quantum yields and rate constants in the photoreduction of benzophenone (B) and 4-benzoylbenzoate (CB) by TEA, ABCO and DABCO

Ketone	Solvent	TEA (0.3 M)		ABCO (0.2 M)		DABCO (0.2 M)	
		φ [a]	k_{ir} [b] $\times 10^{-9}$ $(M^{-1} s^{-1})$	φ [a]	k_{ir} [b] $\times 10^{-9}$ $(M^{-1} s^{-1})$	φ [a]	k_{ir} [b] $\times 10^{-9}$ $(M^{-1} s^{-1})$
B	C_6H_6	0.56 [c]	2.5	0.21 [c]	0.18	0.09 [c]	2.4
(0.08 M)	$(CH_3)_3COH$	0.95	2.2	0.19 [c]	0.09	0.02	0.57
	CH_3COCH_3	0.78	—	0.10	—	<0.001	—
	CH_3CN	1.04	3.8 [d]	0.08	0.22 [e]	<0.001	11 [f]
CB	$H_2O–C_5H_5N$ [g]	0.96	0.83 [h]	0.0004	0.047 [i]	0.000	0.7 [i]
(0.008 M)							

[a] Quantum yield for the formation of the ketyl radical.
[b] Values obtained by phosphorescence quenching except when otherwise indicated.
[c] Evidence for a LAT observed.
[d] From ref. 11; [B] $\approx$ 0.01 M, [TEA] $\approx 10^{-3}$ M.
[e] From the value for DABCO and the ratio of their slopes in phosphorescence quenching.
[f] From use of DABCO as a quencher for the photoreduction by sec-butylamine.
[g] 1:1 (by volume), pH 12, 0.02 M amine.
[h] Obtained from competition experiments with naphthalene as physical quencher, [6].
[i] From use as quencher of photoreduction by TEA.

by ABCO in this medium was very inefficient and DABCO showed no reduction and acted only as a quencher. Complications due to LATs and the accelerating effect of a high concentration of amine are not observed in this medium [5, 6].

Values of k_{ir} (Table 1) were obtained from the quenching of phosphorescence of benzophenone by the three amines in benzene and tert-butyl alcohol, the triplet lifetime in benzene ($\tau_0 = 6.5 \times 10^{-6}$ s [12]) and in tert-butyl alcohol (9.2×10^{-6} s [6]) and application of the equation
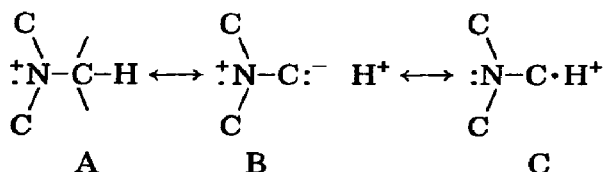
$$I_0/I = 1 + \tau_0 k_{ir}[Q] \tag{2}$$

Scattered light, possibly Raman, from solutions of TEA in acetonitrile prevented useful study of phosphorescence quenching in this system. Plots of I_0/I versus concentration of ABCO and DABCO were obtained and had slopes of 6.3×10^2 M^{-1} and 3.1×10^4 M^{-1} respectively. The emission lifetime of benzophenone in acetonitrile is relatively long ($0.2 - 1 \times 10^{-4}$ s) and variations were noted from day to day and ascribed to trace contamination [13, 14]. Because of these difficulties we have obtained k_{ir} values by competition quenching experiments. The high value of k_{ir} for DABCO in acetonitrile that may be inferred from the value of the slope for phosphorescence quenching and the very low efficiency of reduction allow it to be studied as a quencher. The slope of a plot of R_0/R (i.e. rate of photoreduction in the absence over that in the presence of varying concentrations of DABCO) versus concentration of DABCO in the photoreduction of 0.008 M benzophenone by 0.1 M sec-butylamine in acetonitrile was 192 M^{-1}. This is equal

to $k_q/(k_d + k_{ir}[RH])$, $k_d = 2 \times 10^7$ s^{-1} [5] and $k_{ir} = 3.8 \times 10^8$ M^{-1} s^{-1} [5]. The k_{ir} value for ABCO in acetonitrile is obtained from the ratio of the slopes (0.020) for quenching of phosphorescence by ABCO and DABCO. Values of k_{ir} for ABCO and DABCO in this system were obtained by using them as quenchers for the photoreduction by 0.02 M TEA. Values of R_0/R at 0.10 M ABCO and at 0.02 M DABCO were 1.24 and 1.72 respectively.

4. Discussion

By studying tertiary amines, we eliminate the interference of hydrogen transfer and disproportionation due to N—H [15]. The transfer of hydrogen from α-C in the CTC (eqn. (1)) corresponds to hyperconjugative stabilization of the amine radical cation which may be described as follows:

$$
\begin{array}{ccccc}
\text{C} & & \text{C} & & \text{C} \\
\diagdown \quad \diagup & & \diagdown & & \diagdown \\
\overset{+}{\text{·N}}-\overset{|}{\text{C}}-\text{H} & \longleftrightarrow & \overset{+}{\text{·N}}-\text{C:}^- \;\; \text{H}^+ & \longleftrightarrow & \text{:N}-\text{C·H}^+ \\
\diagup \quad \diagdown & & \diagup & & \diagup \\
\text{C} & & \text{C} & & \text{C} \\
\text{A} & & \text{B} & & \text{C}
\end{array}
$$

This indicates how transfer of the α-H is facilitated and how α-H may facilitate formation of a CTC.

The ionization potentials of TEA, ABCO and DABCO are 7.5 [16], 7.7 [17] and 7.2 [17] eV respectively. Non-planarity of the radical cation may raise the ionization potential of ABCO; through-bond interaction [18, 19] of the non-bonding orbitals of the two nitrogens of DABCO may outweigh this and lead to the lower ionization potential. Benzophenone was chosen in this study since with its less favorable reduction potential and higher triplet energy, relative to fluorenone, it may be more dependent on the availability of an easily transferrable α-hydrogen.

Values of k_{ir} for TEA are high, exceeding 10^9 M^{-1} s^{-1} in benzene, tert-butyl alcohol and acetonitrile. tert-Butyl alcohol does not appear to decrease k_{ir} as it might by hydrogen bonding, possibly because of steric effects in the two tertiary compounds. The lower value in the 4-benzoyl-benzoate—water—pyridine systems may be due to hydrogen bonding by water [20, 21]. The value in acetonitrile is higher than in benzene as might be expected in an electron transfer or charge separation process [7].

The values of k_{ir} for ABCO are lower than those for TEA by more than an order of magnitude and are comparable with those for a primary aliphatic amine [5]. The value in benzene is lower than would be expected from its ionization potential. The rigid bicyclic structure of ABCO, which prevents planarity and inhibits overlap of the n electrons of the bridgehead nitrogen with those of the α-C—H bond, may decrease contributions of structures like B and C to the radical cation and decrease k_{ir}. Formation of carbocations and carbon-centered radicals is also retarded in such bridgehead positions. t-Butyl alcohol and aqueous pyridine lead to small decreases in k_{ir}, possibly

owing to hydrogen bonding [20, 21]; acetonitrile appears to lead to little or no increase.

The value of k_{ir} for DABCO in benzene is high and similar to that for TEA. The lower ionization potential of DABCO does not lead to higher k_{ir} but the values are quite high and approach diffusion control, and thus may no longer be sensitive to decreasing ionization potential. The decrease in hyperconjugative stabilization of the bridgehead radical cation may in this case be compensated for by the interaction of the non-bonding orbitals of the two nitrogens [22]. The lower values in the hydroxylic media may arise from hydrogen bonding to these exposed n electrons. The higher value in acetonitrile may indicate solvation of the more diffuse charge in the radical cation.

Quantum yields for photoreduction by TEA are far higher in all solvents than for reduction by ABCO and DABCO. The n orbital on nitrogen and the α-C—H orbital may become parallel and overlap. The hyperconjugative forms contribute to the radical cation and the acidic α-hydrogen is transferred efficiently to the radical anionic species, leading to the resonance-stabilized α-aminoalkyl radical. The quantum yields are relatively little affected by polarity of the solvent, as was also observed in photoreduction by primary aliphatic amines [5]. The lower quantum yield in benzene than in the more polar solvent may be due in part to a LAT. If a CTC mechanism is assumed, the acyclic amine allows ready formation of a CTC in all the solvents, and the two subsequent processes, hydrogen transfer (k_h) and decay to the ground state (k_e), each convert the dipolar CTC to a neutral species, and in this case do so at similar rates and appear to be similarly affected by change in polarity of the solvent. A polar solvent may increase both the extent of charge separation in the CTC and the contribution of the hyperconjugative forms to the radical cationic part, leading to little change or slight increase in the yield of radicals.

The bridgehead radical cations from ABCO and DABCO do not have important hyperconjugative contributions to their structure. There is little interaction between the positive charge on nitrogen(s) and the α-carbon and little assistance to transfer of α-H beyond an acidifying inductive effect. The inefficient overlap may lead to a less stabilized α-aminoalkyl radical than in the acyclic compounds, to less or no contribution of this kind of stabilization to the transition state for the transfer of the α-H to the radical anion, and to a lower rate of hydrogen transfer. The values of k_{ir} indicate sufficient charge transfer for effective perturbation of the excited triplet and mixing with the singlet amine, and decay to the ground state could occur in the CTC and lead to low quantum yields for formation of radicals. The positive charge on the radical cation from DABCO may be diffuse because of N—N interaction, and this may further decrease the hyperconjugative contribution and the yield of radicals. High solvent polarity may stabilize the CTC and increase charge separation without a concomitant effect on the radical cationic part in the absence of a significant hyperconjugative contribution to its structure. This may further increase the energy gap between the

CTC and the transition state for the formation of radicals. The opposite trends in lifetimes [6, 12 - 14] of excited benzophenone and in quantum yields of ABCO and DABCO in benzene, t-butyl alcohol and acetonitrile (Table 1) may indicate that self-quenching and solvent-induced quenching cannot account for the observed dependence of quantum yield on solvent.

The situation in benzene may be summarized in the reaction coordinate diagram (Fig. 1). Excitation and intersystem crossing bring benzophenone to the triplet, the energy of which is 69 kcal above that of the ground state. The reaction with TEA is somewhat slower than diffusion controlled and may have an activation energy. In singlet quenching when ΔG for CTC formations is less than -10 kcal mol^{-1} the reaction is diffusion controlled [23]; in the present case ΔG may be about -5 kcal mol^{-1}. The barrier for return to ground state is shown to be greater than that for the formation of radicals. Bond energy considerations [24] may place the energy of radicals at about 59 kcal above that of the ground state. Reaction with DABCO (dotted line) is also very rapid owing to the N-N stabilized radical cation, and the CTC is at a level similar to or slightly below that from TEA. Since there is little hyperconjugative stabilization of the radical cation and little N-α-C stabilization of the radical, the barrier to hydrogen transfer is placed higher than that for TEA. Reaction with ABCO passes over a higher barrier to form a less stable CTC but the barrier to hydrogen transfer may be a little less than with DABCO. Return to the ground state is facile.

In a more polar solvent the levels of the CTCs are lowered. The level of the transition state for formation of radicals from TEA is also lowered, leading
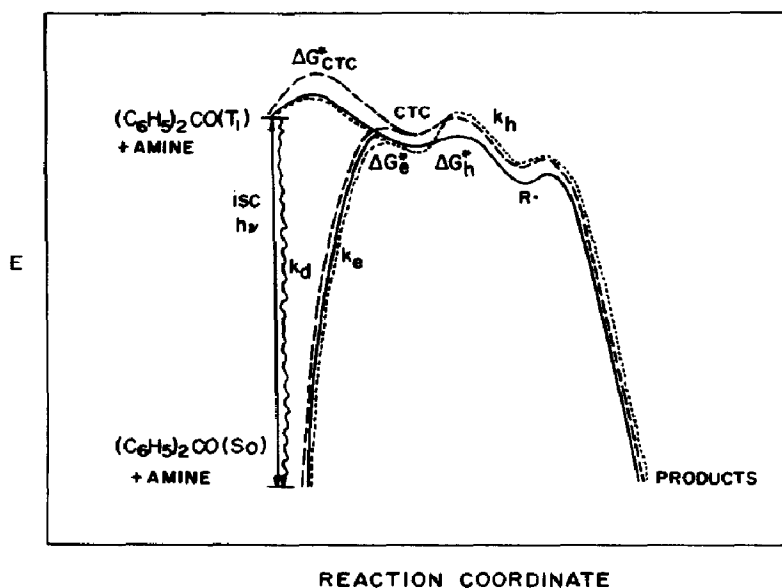

REACTION COORDINATE

Fig. 1. Benzophenone triplet and tertiary amines in benzene: ———, TEA; $\cdots$, DABCO; ---, ABCO.

to little change in the yield of radicals; the levels for ABCO and DABCO are not lowered, leading to lower quantum yields. In the case of DABCO high charge transfer in polar solvents may lead largely to free radical ions which disproportionate to ground state starting materials. This is indicated in studies of chemically induced dynamic nuclear polarization [25], photoconductivity [26] and spectroscopic identification of radical ions [27].

Finally, it may be noted that these reactions need not proceed via formation of a CTC as a common intermediate but may involve two independent processes. Interaction of the triplet at the n electrons may lead only to quenching (k_{ir}) followed by k_e, or formation and disproportionation of radical ions. Direct interaction at α-C—H may lead to radicals, facilitated by a polar contribution to the transition state, as with alcohols [2]. Steady state kinetics do not distinguish between the two alternatives, and structural features, ionization potential and solvent polarity may have similar effects in the dual reaction process as in one proceeding via a CTC mechanism. A remarkable similarity of rates of the two independent processes is required to account for the efficient reduction by acyclic amines. But this may be no more remarkable than the similar values of k_e and k_h required by the CTC mechanism. The CTC mechanism may explain high k_{ir} values with amines, yet wastage of light energy may result from disproportionation of ketyl- and tertiary-amine-derived radicals.

Acknowledgment

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