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Nanosecond Flash Studies of Reduction of Benzophenone by Aliphatic Amines. Quantum Yields and Kinetic Isotope Effects

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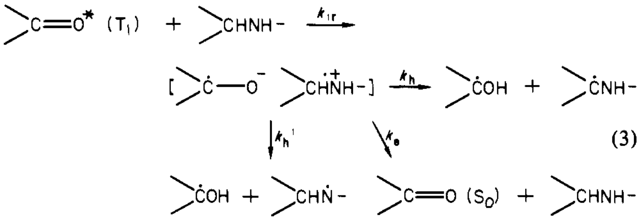
Abstract: Nanosecond flash photolysis, steady irradiation, and deuterium substitution studies have been carried out on solutions of benzophenone with added reductants. Quantum yields (φ_{ketyl}) for reduction in benzene of benzophenone triplet to ketyl radical, based on $\varphi = 2$ for benzhydrol (I), were ~1 for cyclohexane (II), *tert*-butylamine (III), 2-aminobutane (IV), cyclohexylamine (V), di-*n*-propylamine (VI), and triethylamine (VII), ~0.7 for 1,4-diazabicyclo[2.2.2]octane (VIII), and ~0 for *tert*-butyl alcohol (IX). Thus, quenching, without radical formation by H abstraction from N and/or α-C, does not occur with common aliphatic amines but does with Dabco (VIII). The latter quenching is markedly increased by small additions of acetonitrile; the flash spectrum from this compound indicates formation of a triplet amine CT complex or radical ion pair. Triplet-reductant interaction rate constants, k_{ir}, are high for the amines ($\sim10^8$–10^9 M^{-1} s^{-1}) but also show significant deuterium kinetic isotope effects: 1.9 with III-*N*-d_2; 1.4 with IV-*N*-d_2; 1.2–1.3 with IV-α-*C*-d. It is proposed that k_{ir} measures H atom abstraction, favored in the transition state by an initial charge-transfer interaction. Overall steady irradiation quantum yields of reduction by amines, φ_{Red}, are much lower than φ_{ketyl}. This is attributed to disproportionation reactions of ketyl and alkylaminyl radicals for primary and secondary amines, and, possibly, aminoalkyl radicals for tertiary amines. In the case of *tert*-butylamine, the rate constant for disproportionation is obtained from the decay kinetics of ketyl radical and leads to φ_{Red} in agreement with that directly measured.

Photoreduction of benzophenone by primary and secondary aliphatic amines leads to benzpinacol and imines.[1] Quantum yields for reduction by primary amines may be greater than unity at high ketone concentrations,[2] as found also for reduction by 2-propanol.[3] The amine reaction was therefore interpreted, analogously, as formation of ketyl and α-aminoalkyl radicals (eq 1) followed by reduction of a second ground-state ketone by α-aminoalkyl radical (eq 2). However, the reactions differ in that reduction by amines shows much higher rate constants[2,4] and may be effective with π,π^* and charge-transfer triplets[5-9] which are generally not reduced by alcohols. Moreover, limiting quantum yields observed in reduction by amines are less than the maximum value of 2 which may be approached in reduction by 2-propanol.[3] Thus, it was proposed that the reactions involve initial, very rapid electron or charge transfer, k_{ir}, which would facilitate subsequent hydrogen transfer, k_{h}, but might also allow competitive spin inversion and return to ground state, k_{e} (eq 3). This mechanism gained support from correlation of values of k_{ir} with reduction potentials of excited carbonyls and ionization potentials of donors[10] and from observation of transient products of electron transfer in some cases.[11,12] The proposed quenching appeared analogous to that of excited aromatic hydrocarbon singlets by amines.[13]

$$\mathrm{{>}C{=}O^{*}\ (T_1) + {>}CHNH{-} \rightarrow {>}\dot{C}OH + {>}\dot{C}NH{-}} \tag{1}$$

$$\mathrm{{>}C{=}O\ (S_0) + {>}\dot{C}NH{-} \rightarrow {>}\dot{C}OH + {>}C{=}N{-}} \tag{2}$$



(3)

Alternatively, overall quantum yields might be decreased by back-reactions of radicals. Photoreduction of benzophenone by hydrazine[14] must proceed via N-centered radicals and is inefficient. It had been suggested[2] that loss of quantum efficiency in photoreduction by primary and secondary amines might follow abstraction of H from N (eq 3, k_{h}'). The resulting alkylaminyl radicals, like α-aminoalkyl radicals, might reduce ground-state ketone (eq 4), but regeneration of starting materials by back-reaction with ketyl radical (eq 5) might be greatly favored. Direct transfer of hydrogen between oxygen and nitrogen appears to be rapid.[15] Also, in this case radical combination is equivalent to disproportionation (eq 5), as is the case in the efficient regeneration of starting materials from ketyl and thiyl radicals in inhibition by thiols of photoreduction by alcohols.[16]

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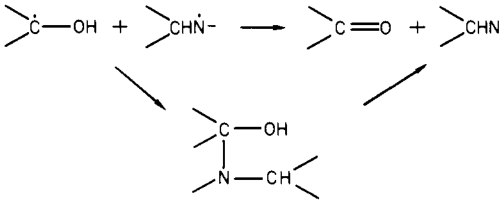

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We now wish to describe laser-flash studies of benzophenone with aliphatic amines that address these questions. A preliminary partial report has been made.[17] The results show that ketyl radical

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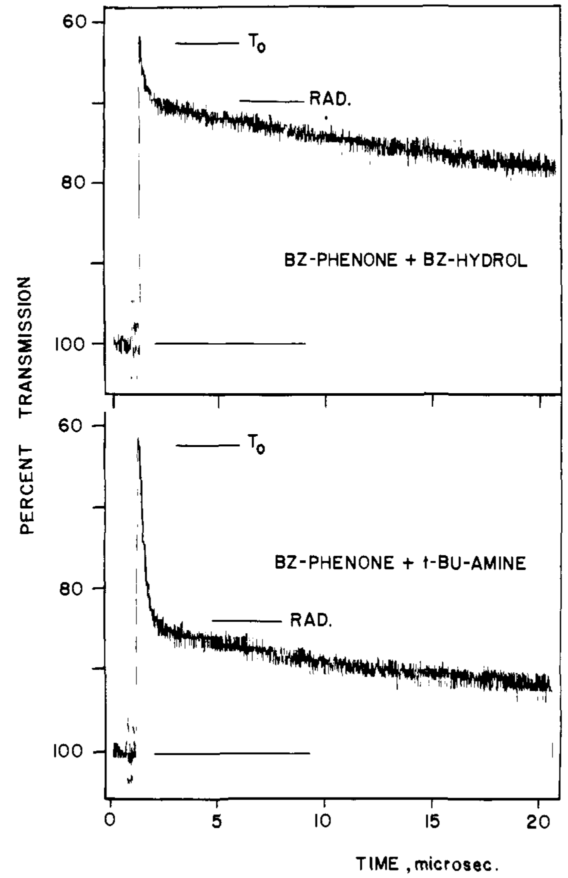

Figure 1. Flash oscillograms showing changes in sample transmission at $\lambda = 530$ nm, following laser flash at 347 nm. Indicated values T_0 and Rad correspond respectively to formation of initial benzophenone triplet and total ketyl radical. Conditions: cell path 1 cm; total sweep time 20 μs. Solutions of 4×10^{-3} M benzophenone in benzene containing (upper curve) 0.6 M benzhydrol ($\Delta D_R^{\infty}/\Delta D_T^0 = 0.768$) and (lower curve) 0.05 M *tert*-butylamine ($\Delta D_R^{\infty}/\Delta D_T^0 = 0.377$) at room temperature.

is generally formed with $\varphi \approx 1.0$. Thus significant primary return to ground state (eq 3), k_e, does not occur. Loss of quantum efficiency in photoreduction by primary and secondary amines is caused by the processes of eq 3, k_h', and eq 5.

Experimental Section

Materials. Benzene (Eastman spectral grade) was dried by removal of the water azeotrope. Cyclohexane and toluene (Fisher certified) were used directly. *tert*-Butyl alcohol (Eastman) was distilled; bp 82 °C. Benzophenone (Fisher certified) was recrystallized from ethanol; mp 48–49 °C. Benzhydrol was zone refined; mp 68–69 °C. *tert*-Butylamine (Aldrich), bp 48–46 °C, 2-aminobutane (Aldrich), bp 64 °C, di-*n*-propylamine (Eastman), bp 108–110 °C, and triethylamine (Aldrich), bp 89 °C, were distilled and stored under nitrogen. 1,4-Diazabicyclo[2.2.2]octane was recrystallized twice from benzene–petroleum ether and sublimed. Deuterium oxide, 99.8%, was from Stohler Isotopic Chemicals.

tert-Butylamine-*N*-d_2 and 2-aminobutane-*N*-d_2 were prepared by stirring the ordinary amines overnight with a 10-fold excess of D_2O, separating, distilling, and repeating the process. The products were finally redistilled over CaO and showed no N–H bands at 3200 and 3330 cm^{-1}.

2-Aminobutane-α-*C*-*d* was prepared by reduction of 2-butanone oxime with lithium aluminum deuteride;[18] the α-C–H peaks centering at 2.8 ppm were absent and the mass spectrum of the sulfonamide showed a peak at 213, indicating incorporation of one deuterium.

Methods. Flash photolysis studies were carried out by using 347-nm excitation from a Q-switched, frequency-doubled ruby laser. The apparatus and procedures have been described previously.[19] Test solutions were 0.004 M benzophenone in benzene with varying concentrations of donor in 1 × 1 cm Pyrex cells fitted with Teflon closures degassed by several freeze–pump–thaw cycles and placed under argon at 1 atm. Transient absorptions were followed over the range 360–700 nm. Conversion to triplet per flash was slight (~0.5%); total exposure of each sample was kept small, and solute concentrations remained essentially constant during a flash run. In the absence of donor, no long-lived transients were seen and the spectrum corresponded to the benzophenone triplet.[20,21] Addition of reductant shortened the triplet lifetime and led to long-lived ketyl radical.[20,22]

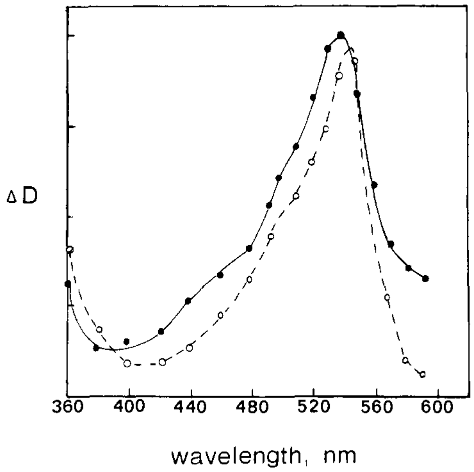

Figure 2. Flash transients in 4×10^{-3} M benzophenone–0.50 M benzhydrol solution: solid trace, immediately after flash (triplet); dashed trace, after completion of triplet decay (ketyl). The relative intensities of two spectra are arbitrary.

Rate constants, k_{ir}, for primary interaction between benzophenone triplet and reductants were determined from the dependence of the effective pseudo-first-order triplet decay constant on reductant concentration $[R]$.

$$k_{\mathrm{eff}} = k_0 + k_{ir}[R] \qquad (6)$$

Yields of benzophenone ketyl radical were determined from the absorbances of triplet and ketyl at 530 nm, in the presence of sufficient donor to trap at least 90% of the triplet. Typical flash oscillograms obtained under these conditions are shown in Figure 1. The yield of ketyl radical from the triplet is proportional to the ratio $r = \Delta D_R^{\infty}/\Delta D_T^0$, where ΔD_T^0 and ΔD_R^{∞} are respectively the transient absorbances corresponding to initial formation of triplet immediately after the flash and to total formation of radical. These values were obtained by treating the flash data by a computational procedure given previously for the kinetic situation of overlapping first- and second-order transient decay.[23] In the frequent case where the radical lifetime is much greater than that of the triplet, ΔD_R^{∞} is given conveniently by a short extrapolation of the radical decay curve back to zero time[23] (Figure 1, "rad"). The measured r ratios were converted to quantum yields by comparison with the value for complete trapping of triplet by benzhydrol, for which we take $\varphi_{\mathrm{ketyl}} = 2$.[24] This method does not require knowledge of the absolute extinction coefficients of the triplet radical nor corrections for variations in laser output between flashes. The unquenched triplet lifetimes were checked in each run (3000–4000 ns) and all r measurements were made at donor concentrations adjusted to keep the lifetime close to 300 ns. Corrections to the yields were applied for the fraction of unreacted triplet, calculated from the lifetimes in absence and presence of donor. Within the precision of our yield measurements (±3%), ΔD_T^0 may be taken as the apparent initial maximum of the transient absorbance. The time resolution of our measurements is limited by the flash duration (~30 ns) not by photometer response. Hence the "true" peak of the triplet concentration appears shortly after flash initiation. For a triplet lifetime of about 300 ns, the value of ΔD_T^0 would be raised about 10% above the apparent peak by extrapolation to zero time. Theoretically, neither the apparent nor the extrapolated values is correct, although they each differ only slightly from the true unquenched maximum. However, since the triplet lifetimes were nearly the same for all donors, similar fractional errors appear in all the $\Delta D_R^{\infty}/\Delta D_T^0$ values, including the calibration with benzhydrol. When

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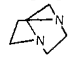
Table I. Pulsed-Laser and Steady-State Photolysis of 0.004 M Benzophenone–Donor Systems. Quantum Yields of Ketyl Radical, φ_{ketyl}, and Overall Reduction, φ_{Red}

donor			solvent	% triplet trapped	$\Delta D_R^{\infty}/\Delta D_T^0$ [a]	quantum yield	
no.	compd	M				φ_{ketyl}	φ_{Red}
I	$(C_6H_5)_2CHOH$	0.6	C_6H_6	94	0.771	2.00	0.96[b]
I	$(C_6H_5)_2CHOH$	0.6	CH_3CN	94	0.835	2.00	
II	c-C_6H_{12}	neat		93	0.39	1.01	
III	*t*-$C_4H_9NH_2$	0.050	C_6H_6	94	0.368	0.96	0.06
III	*t*-$C_4H_9NH_2$	0.020	CH_3CN	92	0.436	0.95	
IV	*sec*-$C_4H_9NH_2$	0.010	C_6H_6	93	0.378	1.00	0.54
IV	*sec*-$C_4H_9NH_2$	0.005	CH_3CN	91	0.430	0.96	
V	c-$C_6H_{11}NH_2$	0.008	C_6H_6	93	0.359	0.95	0.49
VI	*n*-$(C_3H_7)_2NH$	0.001	C_6H_6	93	0.336	0.90	0.34
VI	*n*-$(C_3H_7)_2NH$	0.001	CH_3CN	94	0.458	0.98	
VII	$(C_2H_5)_3N$	0.001	C_6H_6	93	0.378	1.00	0.3[c]
VII	$(C_2H_5)_3N$	0.001	CH_3CN	95	0.484	1.02	
VIII		0.0005	C_6H_6	95	0.280	0.73	0.09[d]
			1% CH_3CN	95	0.196	0.51	
			2% CH_3CN	95	0.186	0.48	
			5% CH_3CN	95	0.155	0.40	
			10% CH_3CN	95	0.074	0.19	
IX	*t*-C_4H_9OH	1.0	C_6H_6	~0	~0	~0	

[a] Average of four measurements, agreeing within ±3%. [b] Secondary actinometer; ref 24. [c] Probably decreased by light-absorbing transients. [d] Reference 39.

relative values of the *r*'s are taken, the error essentially cancels.

The rate constant for benzophenone ketyl dimerization was obtained from radical decay measurements at both 540 and 525 nm, on 0.002 M benzophenone in benzene containing 0.25 M benzyhydrol. The radical absorption coefficient was taken as $\epsilon_{540} = 4340$;[25] from this value and the measured radical spectrum, $\epsilon_{525} = 3200$.

Steady-irradiation quantum yields for photoreduction of benzophenone were obtained from the decrease of the 340-nm absorption of samples irradiated to ~10% reduction on a rotating wheel, carrying solutions of benzophenone–0.6 M benzhydrol as actinometer; $\varphi = 0.96$.[24]

Results

1. Transient Spectra. Figure 2 shows the transient spectra observed (a) immediately after the flash and (b) after completion of initial rapid decay (Figure 1) in a benzophenone–benzhydrol solution in benzene. The peaks at 530 and 540 nm agree with locations given earlier for triplet[20,26] and ketyl radical,[20,22] respectively. Similar spectra were obtained for the amine donors. The relatively low reactivity of *tert*-butylamine required measurements on this compound to be carried out at higher concentrations than those for the other amines. Under these conditions, the ketyl radical spectrum was somewhat broadened and progressively red shifted with increasing amine concentration, up to 20 nm at 1 M amine. However, at the amine concentrations used in determination of radical yields, this effect introduced negligible error. The spectral shift may be due to complexation of ketyl and amine. No indication of benzophenone–amine ground-state interaction was seen in any of the spectra of our test solutions.

In the particular case of Dabco, and not the other amines, the spectrum in benzene taken immediately after the flash showed, in addition to the triplet maximum near 530 nm, a second lower intensity band, $\lambda_{\max} \approx 650$ nm (Figure 3) (ketyl radical formed in this solution showed the normal spectrum). The initial long-wave absorption shifted to 710 nm and increased in intensity in 40% acetonitrile in benzene, without noticeable change in the triplet band at 530 nm, and it was still present after 800 ns, when the triplet had completely decayed (Figure 3). No ketyl radical is formed at this high concentration of acetonitrile. The decay of the long-wave band was first order, and lifetime increased with increasing acetonitrile in benzene: 0.3, 1.5, and 2.0 μs in 10%, 40%, and neat acetonitrile, respectively.

2. Quantum Yields. Table I gives the quantum yields of ketyl radical from various donors, relative to that from benzhydrol taken as 2; the yields are corrected for the small fraction of triplet not trapped. Quantum yields are also given for overall photoreductions at the same donor concentrations.

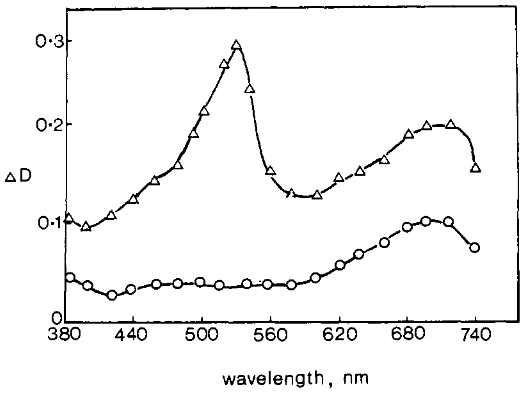


Figure 3. Transient spectra in 4 × 10^{-3} M benzophenone–10^{-3} M Dabco in 40% v/v acetonitrile–benzene solvent: Δ, directly after flash; O, 0.8 μs after flash.

Ketyl radical was formed with essentially the same quantum efficiency from neat cyclohexane and from 0.05–0.001 M solutions in benzene and in acetonitrile of all the amines except Dabco; *this uniform yield was within experimental error, half that from benzhydrol.* It would be most unlikely that this result arose from any circumstance other than quantum yield $\varphi = 2$ from benzhydrol and $\varphi \simeq 1$ from the other donors (eq 7 and 8). A similar argument has been used previously to derive $\varphi = 1$ in the case of reduction of fluorenone triplet by amines, in which closely concordant $\Delta D_R^{\infty}/\Delta D_T^0$ ratios were observed for several different cases.[27] Dabco in benzene gave a lower yield of ketyl radical, $\varphi \approx 0.7$. The yield was further decreased by small amounts of acetonitrile, falling to $\varphi \approx 0.2$ in 10% acetonitrile and 0 in 40% acetonitrile. *tert*-Butyl alcohol, even at 1 M, did not lead to a detectable yield of ketyl radical, $\varphi < 0.03$.

$$(C_6H_5)_2C{=}O^*\ (T_1) + (C_6H_5)_2CHOH \rightarrow 2(C_6H_5)_2\dot{C}OH \qquad \varphi = 2 \tag{7}$$

$$(C_6H_5)_2C{=}O^*\ (T_1) + RH \rightarrow (C_6H_5)_2\dot{C}OH + R\cdot \qquad \varphi \approx 1 \tag{8}$$

While quantum yields for formation of ketyl radical by amines III–VII were all essentially unity, steady-irradiation quantum

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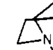
Table II. Pulsed-Laser Photolysis of 0.004 M Benzophenone-Donor Systems

donor				
no.	compd	M	solvent	k_{ir}, M^{-1} s^{-1}
I	$(C_6H_5)_2CHOH$		C_6H_6	9.0×10^6,[a] 7.5×10^6 [b]
III	t-$C_4H_9NH_2$	0.002-0.02	C_6H_6	6.4×10^7, 7.0×10^7 [b]
III	t-$C_4H_9NH_2$	0.002-0.02	CH_3CN	1.1×10^8
IV	*sec*-$C_4H_9NH_2$	0.001-0.01	C_6H_6	2.3×10^8, 2.5×10^8 [b]
IV	*sec*-$C_4H_9NH_2$	0.001-0.01	CH_3CN	3.0×10^8
V	c-$C_6H_{11}NH_2$	0.001-0.01	C_6H_6	3.3×10^8
VI	n-$(C_3H_7)_2NH$	0.0001-0.005	C_6H_6	3.4×10^9
VII	$(C_2H_5)_3N$	0.0001-0.005	C_6H_6	3.0×10^9, 2.3×10^9 [b]
VIII		0.00006-0.003	C_6H_6	4.5×10^9
		0.00005-0.0006	C_6H_6:CH_3CN (3:2)	8.9×10^9

[a] Reference 29. [b] Reference 28.

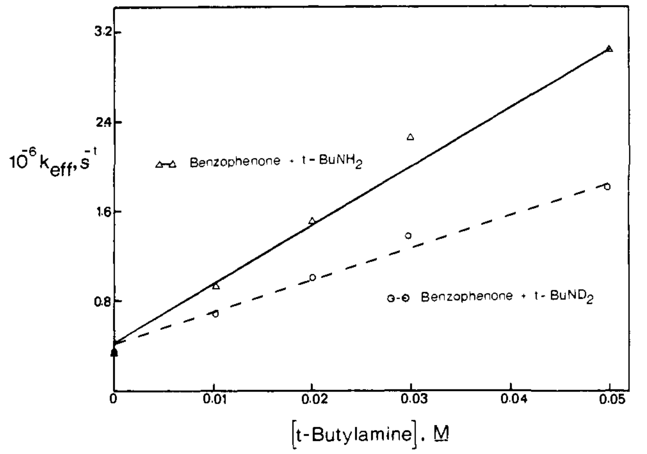


Figure 4. Determination of k_{ir} and isotope effect for reaction of benzophenone triplet and *tert*-butylamine. Effective triplet first-order decay constant vs. amine concentration: △, *tert*-butylamine-NH_2; ○, *tert*-butylamine-N-d_2.

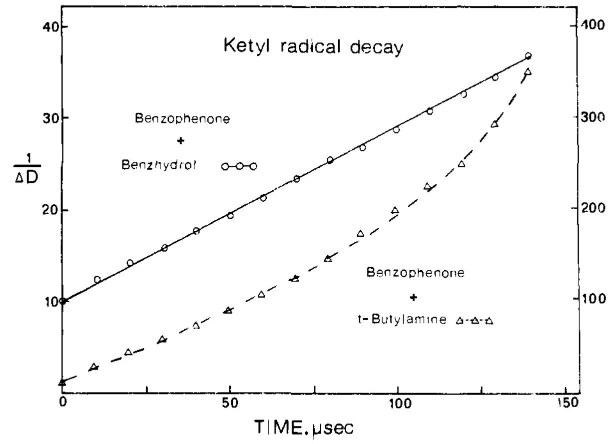


Figure 5. Second-order kinetic plots (ΔD^{-1} vs. time) in 4×10^{-3} M benzophenone ($\lambda = 525$ nm): ○, in 0.25 M benzhydrol; △, in 0.05 M *tert*-butylamine.

yields for overall reduction varied widely ($\varphi_{Red} = 0.06$–0.54) and were much lower than those in the reduction by benzhydrol ($\varphi_{Red} \approx 1$). Notably, it was lowest for *tert*-butylamine; a low quantum yield was observed initially ($\varphi \approx 0.06$), and after a short period of irradiation, further loss of absorption at 340 nm ceased.

3. Transient Kinetics. (a) Triplet Interactions. The observed first-order triplet decay constants were linear in donor concentration, Figure 4, giving (eq 6) the interaction rate constants, k_{ir}, listed in Table II. Values of k_{ir} for several of these compounds, determined previously by phosphorescence intensity measurements,[28] are also given in Table II and agree well with the present work.

Values of k_{ir} in benzene rose from 6.4×10^7 M^{-1} s^{-1} for *tert*-butylamine to $\sim 3 \times 10^8$ M^{-1} s^{-1} for the other primary amines 2-aminobutane and cyclohexylamine, to quite high values[10,28] ($>10^9$ M^{-1} s^{-1}) for the secondary and tertiary amines di-n-propylamine, triethylamine, and Dabco. For *tert*-butylamine and 2-aminobutane, k_{ir} was 70% and 30% higher, respectively, in acetonitrile than in benzene, while that for Dabco was doubled in 40% acetonitrile in benzene. The value for benzhydrol (9.0×10^6 M^{-1} s^{-1} [29]) is lower than those for the amines but somewhat higher than that for 2-propanol (1.8×10^6 M^{-1} s^{-1} [28]). It is noteworthy that 1 M *tert*-butyl alcohol in benzene had no observable effect on decay of the triplet, consistent with no detectable radical formation. The triplet lifetimes were 2.5 and 2.6 μs in the absence and presence of the alcohol, respectively.

(b) Radical Decay. Ketyl radical decay with benzhydrol as donor (eq 9) followed excellent second-order kinetics, in agreement

$$2(C_6H_5)_2\dot{C}OH \rightarrow (C_6H_5)_2C(OH)C(OH)(COH_5)_2 \quad (9)$$

with previous observations[20] (Figure 5). Data taken on benzene solutions, 0.002 M in benzophenone and 0.25 M in benzhydrol and with extinction coefficients given above, led to $2k_9 = 6.0 \times 10^8$ and 6.3×10^8 M^{-1} s^{-1}, measured at 525 and 540 nm, respectively. These values are in reasonable agreement with earlier data,[20] which give $2k_9 = 7.2 \times 10^8$ M^{-1} s^{-1}, again taking $\epsilon = 4340$ M at the radical peak. A value of 2.5×10^8 M^{-1} s^{-1} has been reported.[25]

When formed in reduction by 0.05 M *tert*-butylamine, the ketyl radical disappeared more rapidly, with complex kinetics (Figure 5). In this case, there is only one type of donor radical derived from the amine: that obtained by H atom abstraction from N. Moreover, the overall photoreduction yield is very low while $\varphi_{ketyl} \approx 1$. This sytem thus lends itself to analysis of the radical decay in terms of mixed-radical back-reactions. Two reactions in addition to ketyl dimerization may be considered (eq 10–13). A

$$(C_6H_5)_2\dot{C}OH + (CH_3)_3CNH\cdot \rightarrow (C_6H_5)_2C{=}O + (CH_3)_3CNH_2 \quad (10)$$

$$2(CH_3)_3CNH\cdot \rightarrow \text{products} \quad (11)$$

$$-d((C_6H_5)_2\dot{C}OH)/dt = 2k_9((C_6H_5)_2\dot{C}OH)^2 + k_{10}((C_6H_5)_2\dot{C}OH)((CH_3)_3CNH\cdot) \quad (12)$$

$$-d((CH_3)_3CNH\cdot)/dt = 2k_{11}((CH_3)_3CNH\cdot)^2 + k_{10}((C_6H_5)_2\dot{C}OH)((CH_3)_3CNH\cdot) \quad (13)$$

search program based on the Runge–Kutta method[30] led to a numerical solution of these differential equations. With $2k_9 = 6.2 \times 10^8$ M^{-1} s^{-1} and initially equal concentrations of ketyl and aminyl radicals, a best fit to the ketyl decay curve was obtained with $k_{10} = 3 \times 10^9$ M^{-1} s^{-1} and $2k_{11} = 2 \times 10^7$ M^{-1} s^{-1}, as shown in Figure 6.

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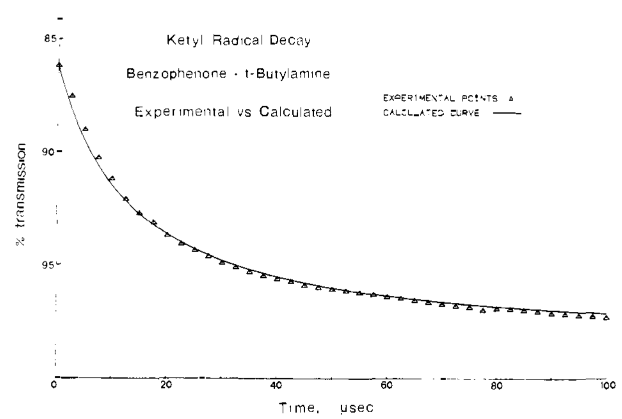

Figure 6. Radical decay in benzophenone–*tert*-butylamine solutions ($\lambda = 525$ nm). Fit of decay data to rate constants for termination reactions k_9, k_{10}, and k_{11} (see text): —, calculated percent transmission starting at observed value ($t = 0$) at end of triplet decay; Δ, directly observed values.

Table III. Pulsed-Laser Photolysis of 0.004 M Benzophenone–Primary Amine Systems. Effects of N–D and α-C–D

amine	M	k_{ir}, M^{-1} s^{-1}	k_H/k_D
t-$C_4H_9ND_2$	0.01–0.08	3.6×10^7	
t-$C_4H_9NH_2$[a]	0.01–0.08	6.4×10^7	1.8
t-$C_4H_9ND_2$[b]	0.01–0.05	3.0×10^7	
t-$C_4H_9NH_2$[c]	0.01–0.05	5.6×10^7	1.9
sec-$C_4H_9ND_2$[b]	0.01–0.06	1.7×10^8	
sec-$C_4H_9NH_2$[c]	0.01–0.06	2.4×10^8	1.4
sec-$C_4H_9NH_2$-α-*C-d*	0.01–0.06	1.86×10^8	
		1.80×10^8	
sec-$C_4H_9NH_2$-α-C-H	0.01–0.06	2.25×10^8	1.2
		2.31×10^8	1.3

[a] Table I. [b] In benzene saturated with D_2O. [c] In benzene saturated with H_2O.

The steady-state quantum yield for photoreduction by an amine is given by eq 14, with the assumptions that the quantum yield

$$\varphi = 2k_9/[2k_9 + k_{10}(k_9/k_{11})^{1/2}] \qquad (14)$$

of triplet is unity, all triplets react by abstraction of H from N, and termination occurs by reactions 9–11. The above values of k_9, k_{10}, and k_{11} led to $\varphi = 0.04$ for the benzophenone–*tert*-butylamine system, to be compared with the observed initial value of $\varphi \approx 0.06$.

4. Isotope Studies. Information about the nature of the hydrogen-abstraction processes was sought in the study of deuterium isotope effects with *tert*-butylamine-*N*-d_2, 2-aminobutane-*N*-d_2, and 2-aminobutane-α-*C*-*d*. The yield of ketyl radical and its spectrum were the same in the *tert*-butylamine-*N*-d_2 and the protio systems. Values of k_{eff}, determined with no amine and at four concentrations of amine, were linear in concentration of amine (Figure 4) and led to values of k_{ir} (eq 6; Table III). To ensure that the isotope effect was not decreased by exchange of ND_2 with traces of H_2O, we studied protio- and deuterio-*tert*-butylamine systems in benzene and in benzene saturated with H_2O and D_2O, respectively. The water, in both cases, lowered the values of k_{ir} by ~15%, possibly due to hydrogen bonding with amine,[4] but increased the isotope effect little, from 1.8 to 1.9. Benzene solutions saturated with H_2O and D_2O were then used in the study of 2-aminobutane-NH_2 and -*N*-d_2, respectively (Table III). A low isotope effect was observed, in the *N*-d_2 system (1.4), and a still lower isotope effect was found in the α-*C*-*d* system (1.2–1.3).

Discussion

1. Formation and Disproportionation of Radicals. Our results show that photoreduction of benzophenone by *tert*-butylamine forms ketyl radical with a high rate constant and $\varphi_{ketyl} \approx 1$, while *tert*-butyl alcohol does not react significantly. We conclude that aliphatic NH transfers H efficiently to benzophenone triplet. The very low overall reduction yield with *tert*-butylamine indicates that ketyl and aliphatic aminyl radicals largely react to regenerate starting materials, as had been proposed for reactions of benzophenone[12] and fluorenone[31] ketyls with anilino[12,31] and mono-*N* alkylanilino[31] radicals. This is supported by the decay kinetics of benzophenone ketyl, when formed from *tert*-butylamine (Figures 5 and 6), which are consistent with the very rapid reaction of ketyl and aminyl radicals, less rapid ketyl coupling, and slower aminyl coupling, and led to a steady-state-reduction quantum yield in agreement with the observed low value.

The reaction with triethylamine occurs with very high rate constant and $\varphi_{ketyl} \approx 1$. Thus, the triplet also abstracts H efficiently from the α-C of aliphatic amines. In reactions with compounds IV, V, and VI, which contain both N–H and α-C–H, H may be abstracted from either position and, probably, in part from both. Further, formation of kethyl radical with $\varphi = 0.9$–1.0 from the amines of varied structure (compounds III–VII; Table II) indicates that quenching without formation of ketyl radical (eq 2; k_e) does not occur to a significant extent in photoreduction of benzophenone by the common aliphatic amines. Loss of quantum efficiency in reductions by primary and secondary amines may now be attributed to formation and disproportionation of ketyl and alkylaminyl radicals (eq 5). Disproportionation appears to be dominant with N-centered and unimportant with C-centered radicals. This may account for the lower quantum yields which are commonly observed in photoreduction by secondary rather than by primary amines.[2,4] The N–H bond energies in methyl- and dimethylamine are reported to be 103 and 96 kcal/mol, respectively. The weaker N–H bond may lead to a greater proportion of abstraction from N of secondary amines and to a larger fraction of radical back-reaction by disproportionation for secondary compared to primary amines. Similarly, ***higher*** quantum yields in photoreduction by 2-aminobutane-*N*-d_2 and cyclohexylamine-*N*-d_2 rather than by the protio compounds[2] would arise from a lower proportion of abstraction from N in deuterio rather than protio systems; and higher quantum yields in photoreduction by cyclohexylamine rather than by the α-C–D compound[2] would arise from a higher proportion of abstraction from N in the latter. In the case of primary amines, evidence has not been found for disproportionation reactions of the C-centered α-aminoalkyl radicals. Residual amine, after photoreduction of benzophenone by excess optically active 2-aminobutane in benzene, showed no racemization.[2]

In reduction by triethylamine, the low quantum yield may be due in part to light-absorbing transients which are formed during irradiation in nonpolar solvents[2,9] and are very efficient quenchers.[33] The occurrence of secondary reactions between amine-derived radicals and ground-state ketone (eq 2) further complicates the situation. Thus, a lower rate of oxidation by ground-state ketone of tertiary-amine-derived rather than primary- or secondary-amine-derived radicals[34] provides more time for them to enter into combination[5,35] or disproportionation reactions, thereby reducing yield. When light-absorbing transients are not present and transfer of a second reducing group to ground-state ketone is rapid, as appears to be the case in aqueous systems, tertiary amines lead to higher reduction quantum yields than primary and secondary amines,[4] consistent with absence of N–H.

Quenching by Dabco. This amine shows a very high interaction rate constant, k_{ir}, which increases with solvent polarity, and a lower yield of ketyl radical than from the nonbridgehead amines; this yield is decreased by small increments of acetonitrile (Tables I and II). These facts strongly suggest an initial charge or electron transfer, followed in part by charge recombination and quenching and in part by proton transfer and radical formation. Support for these processes in this system is found in CIDNP[36] and in

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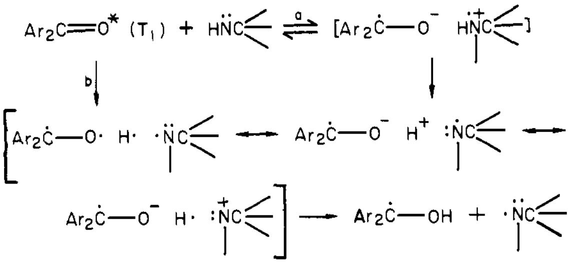
picosecond flash[37] studies. The absorption of the flash transient band (650–700 nm; Figure 3) is close to that of the ketyl radical anion.[38] However, its short lifetime (about 1 μs) and first-order decay kinetics indicate that free ion radicals are not formed under our conditions. It seems likely that this species is either the charge-transfer complex (triplet exciplex) itself or a solvent-shared ion pair, in which radical ions are partially solvated.[13,39] Formation of such a species and quenching, k_e, are favored in the Dabco system by the high stability of the radical cation[40] and the nature of the α-C-centered radical. The bicyclic structure decreases overlap between the n orbital of N and α-C–H orbitals and thus decreases stabilization of the α-aminoalkyl radical. This also decreases the contribution of hyperconjugation to the transition state, as may be indicated by a lower value of k_{ir} for quinuclidine, the bridgehead bicyclic analogue of triethylamine, than is consistent with its low ionization potential.[10] Transfer of H from α-C is thereby made more difficult and quenching, k_e, occurs. Increasing the polarity of the solvent may stabilize the CT complex more than the transition state for formation of neutral radicals and further decrease the yield of radicals. The primary radical yield in reaction with Dabco thus depends on the rate of proton transfer following the initial electron transfer, relative to that of back-transfer and quenching. The quantum yield for the overall reduction in benzene[41] (0.09) is much lower than that for formation of ketyl radical (Table II) and for photoreduction by triethylamine. Oxidation of this amine-derived radical by ground-state ketone would be quite slow, leading, if it occurred, to an enamine unstabilized by conjugation. Thus this radical would persist to disproportionate and combine with ketyl.[35]

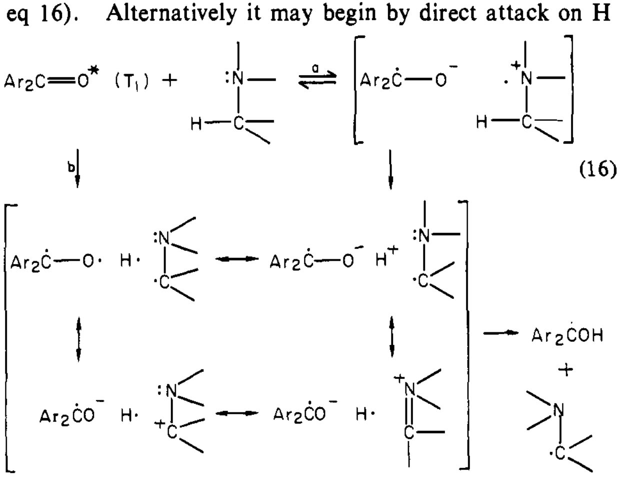
Isotope Effects and the Nature of the Transition State. The deuterium kinetic isotope effects (Table III) occurring in both N–D and α-C–D systems show that values of k_{ir} in reactions with the common aliphatic amines pertain to processes in which N-H and/or α-C-H, as may be present, are stretched in the transition states.[10] The representation of eq 3, in which k_{ir} refers simply to a charge-transfer process, must therefore be further modified for amine systems in nonhydroxylic solvents, except perhaps for Dabco.

(a) Abstraction from N. The isotope effect for abstraction by benzophenone triplet of H from N of *tert*-butylamine (1.9) is substantial, particularly for so high a rate constant ($k_{ir} > 10^7$ M^{-1} s^{-1}). This effect is lower than that for abstraction of H from α-C of 2-propanol[42] (2.8) which has a lower rate constant[28] ($\sim 10^6$ M^{-1} s^{-1}). In contrast, there is no isotope effect in the rate of reduction by 2-propanol-*O-h* compared with 2-propanol-*O-d*.[42] Effective oxidants such as persulfate,[43] *tert*-butoxy radical,[44] and photoexcited quinones[45] may abstract H from the O of alcohols. Triplet acetophenone is reported to abstract H from the O of 1-phenylethanol.[46] In the special case of cyclopropanol, benzophenone triplet abstracts H from O, facilitated presumably by the energy of concomitant rupture of the strained cyclopropyl ring.[47] However the similarity in photoreduction of benzophenone by 2-propanol and 2-propanol-*O-d*,[42] ESR studies,[45] the absence of ketyl radical in irradiation of benzophenone in the presence of *tert*-butyl alcohol (Table I) and quantum yield $\sim$1.0 in photoreduction of benzophenone by benzhydrol[24] demonstrate that triplet benzophenone does not generally abstract H from the O of alcohols, in competition with its decay and abstraction from α-C, although it does abstract H efficiently from the N of amines. The rapid abstraction from N may begin via charge-transfer interaction (step a of eq 15), which may reverse to triplet and amine but not readily to ground state because of spin restrictions,[48] and proceed to a transition state for hydrogen (proton) transfer, facilitated by delocalization (eq 15). Alternatively, the process might begin by direct attack on H (step b of eq 15) with similar polar stabilization and little, if any, difference at the transition state from the process which begins by charge transfer (eq 15a). The N–H bond energies, $\sim$103 and 96 kcal/mol in primary and secondary amines, are considerably higher[32] than had been reported previously, 92 and 86 kcal/mol, respectively.[49] The proposed higher value for N–H_2 is comparable to that for O–H in alcohols. The marked difference in reactivity of benzophenone triplet toward these two groups would arise from the lower ionization potential and ease of charge transfer from N, followed essentially by proton transfer. In an abstraction by the triplet of H from O there would be essentially no polar contribution to the transition state. The homolytic gas-phase bond energies would thus become less relevant.


(15)

The kinetic isotope effects in the 2-aminobutane systems are lower than for *tert*-butylamine-*N*-d_2, 1.4 for N–D and 1.2–1.3 for α-C–D. They correspond to processes of still higher rate constant ($>10^8$ M^{-1} s^{-1}) and might therefore be expected to be lower. However the true isotope effects for the individual abstractions are higher than those obtained from the k_{ir} values. These observed values are averages for processes in which the triplet reacts by abstraction from *both* positions; with each deuterio compound, an undiminished contribution to k_{ir} is made by the protio moiety, NH_2 to α-C–D compound, α-C–H to the ND_2 compound. Thus the true deuterium isotope effects in reactions of the reducing amines are also substantial.

(b) Abstraction from α-C in Amines. Abstraction of H from α-C, as of a tertiary amine, may begin by reversible charge transfer and go on to a transition state which is stabilized by polar contributions and in which the α-C–H bond is stretched (process a of eq 16). Alternatively it may begin by direct attack on H (process b of eq 16) with a similarly stabilized transition state. The latter process is formally similar to that in abstraction of α-H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from an alcohol or ether.[50] The α-C–H bond energy in methyl amine[51] now appears to be similar to that in methanol[52] (94 kcal/mol), and the values would be decreased somewhat in both cases for secondary and tertiary α-C–H to values substantially less than those for N–H and O–H bonds. The direct abstraction might be more rapid from α-C–H of amines than from alcohols due to greater polar contribution to the transition state. However the much higher rate constants indicate initial charge transfer (process a of eq 16).

Reaction of a triplet with a primary or secondary amine that contains both N–H and α-C–H may also begin by reversible charge transfer which channels to two transition states, one in which the N–H bond is stretched, as in step a of eq 15, and one in which the α-C–H is stretched, as in step a of eq 16, leading to abstraction from N and α-C, respectively. Alternatively two independent reactions may occur, one starting by abstraction from N, as in eq 15b, the other from α-C as in process b of eq 16. However, abstraction from N in these systems, which contain α-CH, need not lead essentially entirely back to starting materials as it does with *tert*-butyl amine. These aminyl radicals may be oxidized to imines by ground-state ketone (eq 4), and the efficiency of the reduction would be determined by the relative rates of this to that of disproportionation (eq 5).

The very high rate constants, the general effectiveness of reduction by amines, the observation of radical ions in the benzophenone–*tert*-butylamine system in hydroxylic solvents,[6] and the occurrence of the k_e process in aminoketones[53,54] and in reactions with Dabco[36,37] and quinuclidine[41] support the initial charge-transfer mechanisms, a processes of eq 15 and 16, over initial attack on N–H and α-C–H, b processes of eq 15 and 16. Support for the initial charge-transfer mechanism is also found in photoreduction by methionine.[55] In this system a high value of k_{ir} indicates that the reaction starts by charge transfer with S, a process which normally leads to low radical yield and to little reduction.[56] High quantum yield is then best explained by subsequent charge transfer from N to $S^{+\cdot}$ and reaction of the $N^{+\cdot}$ species.

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Solvent Dependence of the Kinetics of Formation and Dissociation of Cryptate Complexes

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Abstract: The rates of dissociation of a variety of alkali metal cations and Ca^{2+} cryptates have been measured in several solvents. These have been combined with measured stability constants to give the corresponding formation rates. The dissociation rates are very sensitive to solvent variation, covering a range of more than 9 orders of magnitude. Except for (2,1,1) cryptates, formation rates are all within the range 10^6–10^9 M^{-1} s^{-1}. Changes in stability constants, whether from a change in the cation, ligand, or solvent, are largely reflected in changes in dissociation rates. The properties of the transition state, particularly with respect to solvent variation, most closely resemble those of the reactants, suggesting that the transition state lies close to the reactants. The dissociation rates increase sharply with increasing donor number of the solvent, whereas the formation rates decrease but are much less sensitive to solvent variation. On the basis of these correlations, formation rates in water are much lower than expected and dissociation rates much higher than expected. It is suggested that this is due to the H-bonded interactions between water and the electronegative atoms (O and N) of the ligands.

Introduction

Most of the applications of the synthetic macrocyclic ligands are based on their ability to form stable complexes with metal ions and their selectivity toward metal cations. These equilibrium properties, however, only give information about the initial and final states of the system. From both a practical and mechanistic point of view, the dynamic characteristics of the process of complexation and decomplexation are important. Of particular interest are the kinetic origin of the ligand selectivities and also the mechanism by which the solvent molecules associated with the uncomplexed cations are replaced during complexation.

Caldin and Bennetto[1,2] have considered the influence of solvent on ligand substitution reactions at some divalent transition-metal cations in terms of the Eigen–Wilkins[3] mechanism for ligand substitution and found evidence of a strong influence of solvent structure on the relative rates of ligand substitution and solvent exchange. The effects are particularly marked when bidentate or tridentate ligands are involved. To date, however, there have been no systematic studies of the effect of solvent on the formation and dissociation rates of complexes formed between alkali and alkaline earth cations and macrocyclic ligands. These systems are of interest both in relation to the general problem of ligand exchange and substitution at metal centers and to ligand-facilitated transport of ions through membranes.[4-6] In addition, there now

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