1,3-Dioxane (**3**),[29] 2-methyl-1,3-dioxane (**4**),[30] 2-methoxy-1,3-dioxane (**5**),[9] 4-methyl-*cis*-6-methyl-1,3-dioxane (**6**),[31] 2-methoxy-*cis*,*cis*-4,6-dimethyl-1,3-dioxane (**7**),[12b] 2-methoxy-*trans*,*trans*-4,6-dimethyl-1,3-dioxane (**8**),[12b] 2-methyl-*cis*,*cis*-4,6-dimethyl-1,3-dioxane (**9**),[12a] and 2-methyl-*trans*,*trans*-4,6-dimethyl-1,3-dioxane (**10**)[12b] were all prepared and purified by literature procedures. They were characterized by $^{1}$H NMR, $^{13}$C NMR, and IR spectroscopy and had physical constants in agreement with those previously recorded. All were obtained pure with the exception of dioxane **10** which contained approximately 8% of the epimer **9** (as determined by GLC analysis). The dioxanes were stored over $K_2CO_3$ and distilled before use.

Diphenylmethan-*1-d*-ol-*d* was prepared by treatment of benzophenone (2.0 g, 11 mmol) with lithium aluminum deuteride (0.25 g, 6 mmol) in dry ether (25 mL). After 2 h at reflux the solution was cooled, and a 2.5% solution of NaOD in $D_2O$ (1.0 mL) was added. The usual workup gave the required deuterated alcohol (1.45 g, 72%): mp 69–70 °C; mass spectrum, *m/e* (relative intensity) 186 ($M^+$, 94%), 185 (4%), 184 (2%).

**Methods. (a) EPR Spectrometry.** Mixtures of di-*tert*-butyl peroxide and one or two substrates in a peroxide to total substrate ratio of approximately 2:1 (w/w) were degassed by bubbling with nitrogen for 10–15 min and then irradiated in the cavity of the spectrometer. Relative radical concentrations were determined by integration of EPR signals.

**(b) Gas Chromatography.** Solutions containing mixtures of approximately equal amounts of dioxanes (total dioxane concentration $\approx$ 0.01 M), di-*tert*-butyl peroxide (0.1–0.5 M), and pyridine (10% v/v) in carbon tetrachloride were degassed and irradiated in the Rayonet reactor. Aliquots were removed at intervals (4–24 h) and, after addition of an internal standard, were analyzed by gas chromatography. Various mixtures of dioxanes were studied including inter alia: **7** and **8**; **9** and **10**; **5**, **7**, and **8**; **4**, **9**, and **10**; **3** and **6**; **3**, **4**, and **5**; **6**, **8**, and **9**. Results of different experiments were consistent as were results obtained from aliquots taken from the same mixture at different times.

Solutions containing dioxanes **7** and/or **8** (total dioxane concentration = 0.01 M) and benzophenone (0.01 M) in benzene were degassed, irradiated in the Rayonet reactor, and analyzed by gas chromatography. When perdeuteriobenzene was used as solvent, the mixture was also examined by $^{2}$H NMR; no signal other than that for the solvent was detected, although gas chromatography revealed that epimerization of the substrate had occurred. A solution of dioxane **8** (0.06 M), diphenylmethan-*1-d*-ol-*d* (0.15 M), and benzophenone (0.10 M) in benzene was subjected to irradiation. Gas chromatography after 1 h revealed that an equilibrium mixture of **7** and **8** had been formed. After 12-h irradiation the reaction mixture was concentrated, deuteriochloroform was added, and the solution was filtered. The $^{2}$H NMR spectrum showed resonances at $\delta$ 4.7 and 5.0 (integral ratio 1:2) assigned to the dioxanes **19** and **20**, respectively, on the basis of comparison with $^{1}$H NMR spectra determined under similar conditions.

**Acknowledgment.** We gratefully acknowledge the helpful comments of Dr. K. U. Ingold, who we also thank for making results available to us prior to publication. This work was supported by the Australian Research Grants Committee.

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# Absolute Rate Constants for the Reactions of *tert*-Butoxyl, *tert*-Butylperoxyl, and Benzophenone Triplet with Amines: The Importance of a Stereoelectronic Effect[1]

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**Abstract:** Absolute rate constants have been determined for the reactions of *tert*-butoxyl, *tert*-butylperoxyl, and benzophenone triplet with a variety of amines. All three reagents abstract hydrogen from the carbon $\alpha$ to nitrogen with rate constants which are much greater than those for the corresponding reactions with hydrocarbons and isostructural ethers. This rate enhancement is attributed to polar effects on the transition state and to the stabilization of $\alpha$-aminoalkyls. These product radicals are stabilized by conjugation between the unpaired electron and the nitrogen lone pair, and, as a result, the hydrogen abstractions show a pronounced stereoelectronic effect with abstraction being most facile when the C–H bond being broken is eclipsed with the axis of the nitrogen lone-pair orbital.

The reactions of amines with oxy radicals[2,3] and the triplet states of ketones[4-6] have intrigued chemists for many years. Product studies in nonpolar solvents have shown that hydrogen abstraction takes place at the carbon atom adjacent to nitrogen.[2-6] Much of the fascination of these reactions lies in the fact that they appear to be far more rapid than hydrogen abstractions from hydrocarbons. This observation prompted Cohen[7] and Davidson[8] to propose that an *electron*-transfer complex, I, plays an important role in ketone photoreduction. I later became called a "*charge*-transfer complex"[9-15] although Yip and his colleagues described the distinction as being "more semantic than real".[9] Complete electron transfer[16] to form ions (reaction 3) can compete with

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[1] Issued as NRCC No. 18895.
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hydrogen abstraction (reaction 2) under specific conditions, i.e., in polar solvents and with amines having low oxidation potentials such as *N*,*N*-dialkylanilines[17] and 1,4-diazabicyclo[2.2.2]octane (DABCO).[18,19]

$$R_2C{=}O^* + R_2NCHR_2 \rightarrow \underset{\text{I}}{[R_2\dot{C}\text{-}O^- \; R_2\dot{N}^+CHR_2]} \qquad (1)$$

$$\text{I} \rightarrow R_2\dot{C}\text{-}OH + R_2N\dot{C}R_2 \qquad (2)$$

$$\text{I} \rightarrow R_2\dot{C}\text{-}O^- + R_2\dot{N}^+CHR_2 \qquad (3)$$

While there have been numerous measurements of rate constants for ketone photoreduction, there have been few for the reactions of alkoxyl[3f] and alkylperoxyl radicals with amines. This is a surprising omission since it is well-known that *tert*-butoxyl and benzophenone triplet generally abstract hydrogen with similar rate constants[5,22] and that *tert*-butylperoxyl, while less reactive, follows the same pattern of reactivity with hydrocarbon substrates.[23] We therefore reasoned that a kinetic investigation of the reactions of all three might provide some interesting insights into the reaction mechanisms.

The absolute rate constants measured in this work demonstrate quantitatively that the reactions of benzophenone triplet, *tert*-butoxyl, and *tert*-butylperoxyl with amines in nonpolar solvents are far more rapid than those at similar sites in hydrocarbons. In addition, rate constants for the reactions of benzophenone triplet are much greater than those for *tert*-butoxyl, whereas with hydrocarbon substrates these reagents show similar reactivity.[5,22] However, perhaps the most interesting finding is that the reactions show a substantial stereoelectronic effect.[12c,24-26] That is, hydrogen is transferred most rapidly when the C–H bond involved is eclipsed with the nitrogen lone-pair orbital.

## Experimental Section

**Materials.** All materials were commercially available; trimethylamine and perdeuteriotrimethylamine (ex Merck, Sharp and Dohme, Canada) were used as received. Solvents were spectroscopic grade and were used without further purification. Solids were purified by sublimation. Di-*tert*-butyl peroxide was purified by chromatography through alumina which removes traces of the hydroperoxide impurity. All amines were purified by standard procedures[27] and were distilled and stored under nitrogen. In some instances they were further purified by preparative VPC. In all cases their purity was >99% (VPC analysis). The pure amines, when stored in the absence of air, were colorless, not "yellow oils" as is often reported.

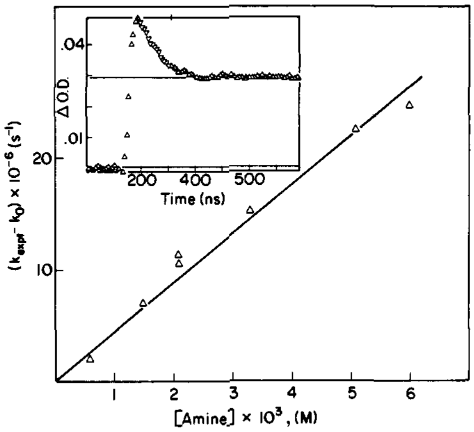
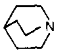
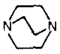
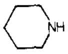
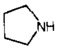


Figure 1. Plot of the rate of triplet decay (corrected for decay in neat solvent) for benzophenone reacting with pyrrolidine. Insert: representative trace for pyrrolidine = 0.0021 M in benzene.

Table I. Rate Constants for the Reaction of *tert*-Butoxyl, Benzophenone Triplet, and *tert*-Butylperoxyl with Amines

| | | *t*-BuO· $k_6$,[a] $M^{-1}\,s^{-1}$ | $Ph_2CO^*$ $k_{1,2}$,[a] $M^{-1}\,s^{-1}$ | *t*-$BuO_2$· $nk_{19}$,[b] $M^{-1}\,s^{-1}$ |
|---|---|---|---|---|
| $Me_3N$ | I | $1.1 \times 10^8$ | | |
| $Et_3N$ | II | $1.8 \times 10^8$ | $4.1 \times 10^9$<br>$3.0 \times 10^9$ [c] | 23 |
|  | III | $6.0 \times 10^6$ | | |
|  | IV | $2.8 \times 10^7$ | $3.1 \times 10^9$ | 4.8 |
| $PhN(Et)_2$ | V | $1.3 \times 10^8$ | | 48 |
|  | VI | $7.9 \times 10^7$ | | 21 |
|  | VII | $9.5 \times 10^7$ | $4.4 \times 10^9$ | 380 |
| *n*-$PrNH_2$ | VIII | $1.7 \times 10^7$ | | |
| *sec*-$BuNH_2$ | IX | | $2.3 \times 10^8$ [c] | |
| *t*-$BuNH_2$ | X | $3.3 \times 10^6$ | $6.4 \times 10^7$ [c] | |

[a] At 22 °C. [b] At 30 °C. [c] Reference 15.

**Apparatus.** EPR experiments were generally carried out by using a Varian E 104 spectrometer equipped with a 500-W mercury arc lamp. The output of the lamp was filtered through a cobalt–nickel filter solution[28] so as to remove much of the visible and most of the infrared radiation. In some experiments, a Molectron UV-24, nitrogen laser emitting at 337 nm with a repetition rate of 50 Hz was used as the light source in which case the modulated signal from the spectrometer was processed through a boxcar integrator before being output onto a recorder. This proved to be a satisfactory method for generation of transient radicals in standard systems, e.g., generation of $Me_2\dot{C}OH$ by photolysis of a di-*tert*-butyl peroxide/2-propanol mixture. Spectral parameters were determined as previously described.[28]

The laser flash photolysis equipment has been described in detail elsewhere.[29] Briefly, pulses (337.1 nm, 8 ns, 1–10 mJ) from the Molectron nitrogen laser were used for sample excitation. The transient absorbances in the reaction were monitored by using a detection system with nanosecond response at a preselected wavelength. Signals from the detector system were processed through an R7912 Tektronix transient digitizer and were analyzed by using a dedicated PDP11 computer. All experiments were carried out at 22 °C under oxygen-free conditions.

## Results

**Reactions of Benzophenone Triplet with Amines.** Rate constants for the quenching of benzophenone triplet by amines were measured by using the laser flash photolysis equipment. All experiments were carried out by using benzene as solvent, and the decay of the triplet was monitored at 540 nm where its extinction

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(19) The reactions of amines with triplet states in magnetic fields are efficient enough to compete with triplet, spin-lattice, relaxation and have therefore been used in many chemically induced magnetic polarization experiments.[18,20] Moreover, the amine-derived radical products are sufficiently reactive as to be capable of transferring polarization to other molecules.[20,21]

(20) See, for example: Roth, H. D. *Mol. Photochem.* **1973**, *5*, 91; Roth, H. D.; Manion, M. L. *J. Am. Chem. Soc.* **1975**, *97*, 6886; Closs, G. L.; Czeropski, M. S. *Ibid.* **1978**, *53*, 321; Hore, P. J.; Joslin, C. G.; McLaughlan, K. A. *Chem. Soc. Rev.* **1979**, *8*, 29.

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coefficient is much higher than that of the ketyl radical.[30] Rate constants for quenching were obtained from plots of pseudo-first-order rate constants for triplet decay as a function of quencher concentration. A representative plot is shown in Figure 1; the insert in Figure 1 shows a typical decay trace. The difference between the prepulse and final levels is due to absorbance from $Ph_2\dot{C}OH$ radicals produced in the quenching process. We were very selective in our choice of amines since the literature already contains abundant kinetic information on this subject.[4,7,8,15] Those amines were examined which showed a significant stereoelectronic effect in their reactions with *tert*-butoxyl and *tert*-butylperoxyl. The rate constants obtained are given in Table I. It should be stressed that these are molecular rate constants and may contain contributions from physical quenching and from reactions at sites other than at the $\alpha$-carbon (vide infra).

**Reactions of *tert*-Butoxyl with Amines.** *tert*-Butoxyl radicals were generated by the photodecomposition of di-*tert*-butyl peroxide by using the laser flash photolysis equipment. Apart from a small dilution effect, the UV absorption of the sample mixtures at 337 nm was unaffected by addition of amine. Rate constants for the reaction of *tert*-butoxyl with a variety of amines were determined by using diphenylmethanol as a probe. This technique has been described elsewhere[31,32] and circumvents the problem that the transients derived from the substrate of interest often do not absorb strongly in the UV–visible spectrum.[33] Equations 4–7 show the essential part of the reaction mechanism.

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2t\text{-BuO}\cdot \qquad (4)$$

$$t\text{-BuO}\cdot + Ph_2CHOH \rightarrow t\text{-BuOH} + Ph_2\dot{C}OH \qquad (5)$$

$$t\text{-BuO}\cdot + {>}N\text{–}HC{<} \rightarrow t\text{-BuOH} + {>}N\text{–}\dot{C}{<} \qquad (6)$$

$$t\text{-BuO}\cdot \rightarrow \text{pseudo-first-order decay} \qquad (7)$$

Reaction 5 leads to the generation of diphenylhydroxymethyl which has a strong and therefore easily monitored absorption at 540 nm.[30] Reaction 7 includes two components: attack of *tert*-butoxyl on the parent peroxide and its $\beta$-scission to acetone and methyl. The latter reaction is too slow in nonpolar solvents to be significant on the time scale of these experiments. In addition to reactions 4–7, radical–radical processes can become of importance at high excitation doses. As in earlier work,[31,32] tests were carried out in order to ensure that the excitation doses used for the measurements were low enough so that second-order processes could be safely ignored.

In a typical experiment, a series of samples containing a constant concentration of diphenylmethanol and variable concentrations of amine were prepared. The solvent used was a 1:2 mixture of benzene–di-*tert*-butyl peroxide. Laser excitation of the sample generated *tert*-butoxyls in a process that for all practical purposes can be regarded as instantaneous. In part, the *tert*-butoxyls generated diphenylhydroxymethyl on a time scale which is fast compared to subsequent radical–radical reactions. The formation of this transient was monitored and followed pseudo-first-order kinetics according to eq 8. The experimental traces were similar

$$\ln\left((A_\infty - A_t)/A_\infty\right) = -k_{\text{exptl}}t \qquad (8)$$

in quality to that shown in the Figure 1. $A_t$ and $A_\infty$ are the transient absorbances at the absorption maximum at time $t$ and at the plateau region, respectively.[31,32] $k_{\text{exptl}}$ is the pseudo-first-order rate constant which is related to the rate constants of interest as

$$k_{\text{exptl}} = k_7 + k_5[Ph_2CHOH] + k_6[{>}N\text{–}HC{<}] \qquad (9)$$

or, taking $k_0 = k_7 + k_5[Ph_2CHOH]$

$$k_{\text{exptl}} = k_0 + k_6[{>}N\text{–}HC{<}] \qquad (10)$$

Values of $k_6$ were obtained from plots of $k_{\text{exptl}}$ vs. the substrate concentration and standard deviations for $k_6$ were typically ±10%. The data are summarized in Table I. The concentrations of diphenylmethanol used were generally in the range 0.06–0.14 M, and values of $k_0$ were in accord with results obtained previously.[29-31] Values of $k_6$ were independent of the concentration of diphenylmethanol when the latter was varied by a factor of 2.

In the case of *N,N*-diethylaniline, it was possible to detect the amine-derived radical, $PhN(C_2H_5)\dot{C}HCH_3$, directly, and diphenylmethanol was not therefore required as a probe. Equation 9 was used to analyze the data; of course the second term is zero since $[Ph_2CHOH] \equiv 0$. The value for $k_6$ of $9 \times 10^7$ $M^{-1}$ $s^{-1}$ obtained by direct detection is considered to be less accurate than that obtained by using diphenylmethanol because of the weaker absorbances obtained.

The rate constants $k_6$ represent molecular reactivities as was the case with benzophenone triplet. However, numerous product studies[5] indicate that hydrogen abstraction at the $\alpha$-hydrogen is the dominant reaction. EPR experiments were carried out with all of the amines reported on Table I, in order to characterize the $\alpha$-aminoalkyls formed by hydrogen abstraction.

Solutions of di-*tert*-butyl peroxide (10% v/v), amine (10% v/v), and solvent (isooctane, cyclopropane, propane, or *tert*-butylbenzene) were photolyzed directly in the cavity of the EPR spectrometer, using a high-pressure mercury lamp. This is normally a perfectly satisfactory technique for radical generation.[35] However, only for $(CH_3)_3N$ and $(CD_3)_3N$ were strong signals obtained. The other amines gave very weak signals which only in the case of triethylamine could be interpreted. To avoid the possibility that the amines were screening the peroxide photolysis, we used a nitrogen laser as a light source so that the peroxide could be preferentially photolyzed at 337 nm. This was equally unsuccessful, as were our attempts to flow dilute solutions of amines through the spectrometer so as to avoid the possibility that the $\alpha$-aminoalkyls were exchanging hydrogen rapidly with the parent amines. Since there is no particular problem in detecting such radicals in matrices,[36] we conclude that the large number of hyperfine interactions[36] coupled with the general absence of sharp spectral lines preclude easy detection of these radicals.[37] In support of this view, we note that the spectrum of $\dot{C}H_2N(CH_3)_2$ is unique in having very sharp lines ($\Delta H_{\text{pp}} = 0.25$ G)[39] and that aminyls are the only radicals detected by EPR during hydrogen abstraction at some secondary amines,[40] even though C–H abstraction is favored over N–H abstraction (vide infra), and therefore $\alpha$-aminoalkyls must also be produced.

The H/D isotope effect for hydrogen abstraction was measured by using the standard EPR competition technique.[41] The reaction scheme is given in eq 11–16. Since reactions 14–16 are diffu-

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2t\text{-BuO}\cdot \qquad (11)$$

$$t\text{-BuO}\cdot + (CH_3)_3N \xrightarrow{k_H} t\text{-BuOH} + \cdot CH_2N(CH_3)_2 \qquad (12)$$

$$t\text{-BuO}\cdot + (CD_3)_3N \xrightarrow{k_D} t\text{-BuOD} + \cdot CD_2N(CD_3)_2 \qquad (13)$$

$$\cdot CH_2N(CH_3)_2 + \cdot CH_2N(CH_3)_2 \rightarrow \text{nonradical products} \qquad (14)$$

$$\cdot CH_2N(CH_3)_2 + \cdot CD_2N(CD_3)_2 \rightarrow \text{nonradical products} \qquad (15)$$

$$\cdot CD_2N(CD_3)_2 + \cdot CD_2N(CD_3)_2 \rightarrow \text{nonradical products} \qquad (16)$$

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(31) Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 296. Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *Ibid.* **1978**, *100*, 4520.

(32) Small, R. D., Jr.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49.

(33) Absolute rate constants for hydrogen abstraction have also been determined in a flash photolysis experiment by using EPR detection.[34] The results obtained by the two techniques are in reasonable agreement.

(34) Wong, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 1235.

(35) Griller, D. *Magn. Reson. Rev.* **1979**, *5*, 1.

(36) Wood, D. E.; Lloyd, R. V. *J. Chem. Phys.* **1970**, *52*, 3840; **1970**, *53*, 3932.

(37) Some simple, protonated $\alpha$-aminoalkyls have been detected, albeit with difficulty, by using the relatively high rates of radical generation accessible by flow techniques.[38]

(38) Anderson, N. H.; Norman, R. O. C. *J. Chem. Soc. B* **1971**, 993.

(39) The other spectral parameters are $a^{N} = 6.96$, $a^{N}(6\text{ H}) = 3.95$ G, $a^{H}(2\text{ H}) = 13.23$ G, and $g = 2.00287$, in cyclopropane solvent at 20 °C; cf. ref 36.

(40) Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 328.

(41) Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc. B* **1971**, 1823.

sion-controlled processes and the radicals are of almost identical size, we can make the normal assumption that $2k_{14} = k_{15} = 2k_{16}$ whence[41,42]

$$k_H/k_D = \frac{[\cdot CH_2N(CH_3)_2][(CD_3)_3N]}{[\cdot CD_2N(CD_3)_2][(CH_3)_3N]} \quad (17)$$

Although the spectra of the two radicals overlap considerably, it was possible to find a window where a line from each spectrum could be integrated. Eight values of $k_H/k_D$ were measured over the temperature range +15 to −93 °C and can be represented by eq 18, where $\theta = 2.3RT$ kcal mol$^{-1}$. At 20 °C $k_H/k_D = 1.4 \pm$

$$\log (k_H/k_D) = (-0.14 \pm 0.07) + (0.36 \pm 0.7)/\theta \quad (18)$$

0.7 with the error arising principally from error in integration of the EPR signals. Although the error on the absolute value of the isotope effect is large, its temperature dependence is much more accurate, since it is fairly insensitive to integration errors. We can therefore conclude that the isotope effect is small not only from its absolute value but particularly because it has an extremely small temperature dependence.[45]

**Reactions of *tert*-Butylperoxyl with Amines.** There is some evidence that peroxyl radicals are substantially more reactive toward amines than to isostructural ethers or indeed hydrocarbons.[2,46–48] We have therefore determined absolute rate constants for the reactions of *tert*-butylperoxyl with a series of amines by using the standard kinetic EPR technique.[49]

Amines such as triethylamine, pyrrolidine, and *N,N*-dimethylaniline are sufficiently reactive toward *tert*-butylperoxyl that the self-reactions of these radicals (reaction 20) can be completely suppressed by moderate concentrations of the amine at 303 K and below.

$$t\text{-BuO}_2\cdot + \text{>N-HC<} \rightarrow t\text{-BuOOH} + \text{>N-}\dot{\text{C}}\text{<} \quad (19)$$

$$t\text{-BuO}_2\cdot + t\text{-BuO}_2\cdot \rightarrow \text{products} \quad (20)$$

Rate constants for reaction (19) can therefore be determined by monitoring the decay of $t$-BuO$_2\cdot$ as a function of amine concentration. *tert*-Butylperoxyls were generated by photolysis of di-*tert*-butyl ketone in oxygen-saturated 3-methylpentane solutions containing 0.02–0.2 M amine. Equation 21 was used to fit the pseudo-first-order decay traces, and the values of $nk_{19}$ obtained for a variety of amines are given in Table I. Standard deviations for $nk_{19}$ were typically ±20% and again these rate constants represent molecular reactivity.

$$-d[t\text{-BuO}_2\cdot]/dt = nk_{19}[t\text{-BuO}_2\cdot][\text{>N-HC<}] \quad (21)$$

In eq 21, $n$ is the number of *tert*-butylperoxyls destroyed by each molecule of amine. This factor has not been determined experimentally but is almost certainly 2 because the peroxyl derived in the reaction of the α-aminoalkyl radical with oxygen almost certainly reacts very rapidly with a second $t$-BuO$_2\cdot$.

## Discussion

The photoreduction of benzophenone by amines is a complicated and experimentally difficult subject. Recent results, obtained by flash photolysis,[15] have shown that the quantum yield for the reaction is close to 1.0 for a variety of amines.[50] Much lower quantum yields obtained in studies of the reduction products are now thought to be misleading[15] since they occur because starting materials are, in part, regenerated during the reaction[51a] (eq 23). For a further complication of the issue, CIDEP studies[51b] have shown that α-aminoalkyl radicals react with ground-state benzophenone to reduce it to the ketyl (eq 24). Indeed, α-aminoalkyls generated via reaction 22 have often been used[21a,52–54] to reduce carbonyl compounds such as biacetyl[21a,52] and camphorquinone[53] in polarization-transfer experiments.

$$\text{Ph}_2\text{CO}^* + \text{>N—CH}_2\text{—CH}_2\text{—R} \rightarrow \text{Ph}_2\dot{\text{C}}\text{OH} + \text{>N—}\dot{\text{C}}\text{H—CH}_2\text{—R} \quad (22)$$

$$\text{Ph}_2\dot{\text{C}}\text{OH} + \text{>N—}\dot{\text{C}}\text{H—CH}_2\text{—R} \rightarrow \text{Ph}_2\text{CO} + \text{>N—CH}_2\text{—CH}_2\text{—R} \quad (23)$$

$$\text{Ph}_2\text{CO} + \text{>N—}\dot{\text{C}}\text{H—CH}_2\text{—R} \rightarrow \text{Ph}_2\dot{\text{C}}\text{OH} + \text{>N—CH=CH—R} \quad (24)$$

Despite these problems it can be concluded that benzophenone reacts with amines with high quantum yields. It is further possible to assign approximate rate constants for the reaction of different classes of amines[15] (see Table I): tertiary ≃ secondary (ca. 3 × 10$^9$ M$^{-1}$ s$^{-1}$) > primary (ca. 2 × 10$^8$ M$^{-1}$ s$^{-1}$) > (CH$_3$)$_3$CNH$_2$ (6 × 10$^7$ M$^{-1}$ s$^{-1}$).[15] Since amines with α-C–H bonds react more rapidly than (CH$_3$)$_3$CNH$_2$, we conclude that these rate constants for the former are associated with overall α-hydrogen abstraction. Moreover, since *tert*-butylamine is much more reactive than *tert*-butyl alcohol[15] the rate constant for the reaction of this amine must represent the rate of N–H abstraction. It follows from these data that α-C–H abstraction is the dominant process in amines containing both α-C–H and N–H bonds.

Our principal observation in this work is that the photoreduction of benzophenone by amines is much faster than the analogous reactions of *tert*-butoxyl and indeed photoexcited acetone.[9] This contrasts with the normal behavior of these reagents in C–H abstraction since they generally react with similar rate constants[5,22] and suggests that a charge-transfer contribution to the transition state is quite significant. This conclusion is supported by the reactivity order tertiary ~ secondary > primary which parallels the ease with which the nitrogen atom can release an electron.[9]

$$[\text{>N—HC<} \;\; \dot{\text{X}} \leftrightarrow \text{>N}^+\text{=C<} \;\; \dot{\text{H}}\,\text{X}^- \leftrightarrow \text{>N—}\dot{\text{C}}\text{<} \;\; \text{HX}]$$

It is tempting to draw other inferences from the data in Table I: specifically, that the rate of reaction with DABCO is retarded by a stereoelectronic effect. However, this would assume that the quantum yields for these reactions are similar which is an assertion we are reluctant to make.

*tert*-Butoxyls react with amines following the reactivity pattern of benzophenone triplets. Thus, for different classes of amines with α-C–H bonds typical rate constants are tertiary (ca. 2 × 10$^8$ M$^{-1}$ s$^{-1}$) > secondary (ca. 8 × 10$^7$ M$^{-1}$ s$^{-1}$) > primary (ca. 2 × 10$^7$ M$^{-1}$ s$^{-1}$). Again *tert*-butylamine reacts less readily than other amines but more readily than typical hydrocarbon substrates for which primary C–H abstractions proceed with rate constants of ca. 10$^4$–10$^5$ M$^{-1}$ s$^{-1}$.[31] This suggests that N–H abstraction takes

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(42) Combination:disproportionation ratios for simple radical–radical reactions are now thought to be controlled by the relative orientations of the radicals in the solvent cage.[43] It, therefore, follows that the effect of deuteration on these ratios[44] is a manifestation of a cage effect and has no effect on the rate of radical destruction when this is diffusion controlled.

(43) Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1976**, *8*, 341; *Helv. Chim. Acta* **1978**, *61*, 2130, 2463. Lehni, M.; Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1979**, *11*, 705.

(44) See, for example: Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 1813; Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441.

(45) Isotope effects of this magnitude have been reported for photoreduction of nitrobenzenes by amines and have been cited as evidence for an electron-transfer mechanism. Döpp, D.; Müller, D.; Weiler, H. "EUCHEM Conference on Organic Free Radicals", Cirencester, England, Sept 10–14, 1979; Döpp, D.; Müller, D. *Recl. Trav. Chim. Pay-Bas* **1979**, *98*, 297.

(46) Latypova, F. N.; Aleksandrov, A. L.; Zlot-skii, S. S.; Rakhmankulov, D. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 951.

(47) Pliss, E. M.; Aleksandrov, A. L.; Mikhlin, V. S.; Mogilevich, M. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 2259 and previous papers in this series.

(48) Bakhturidze, G. Sh.; Aleksandrov, A. L.; Edilashvili, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 515.

(49) Furimsky, E.; Howard, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 369.

(50) These results rely upon the assumption that the quantum yield for photoreduction of benzophenone by benzhydrol is 2.0.[15]

(51) (a) Cohen, S. G.; Stein, N. *J. Am. Chem. Soc.* **1969**, *91*, 3690. (b) McLaughlan, K. A.; Sealy, R. C. *Chem. Phys. Lett.* **1976**, *39*, 310.

(52) McLaughlan, K. A.; Sealy, R. C.; Wittmann, J. M. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 926.

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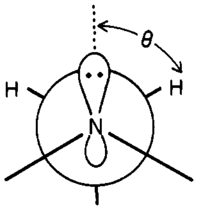
(54) A report of exciplex formation in the reaction of benzil with triethylamine[55] has been reinterpreted in these terms.[56]

(55) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 7740.

(56) Scaiano, J. C., unpublished results.

place with a rate constant of $3.3 \times 10^6$ M$^{-1}$ s$^{-1}$. These rate constants represent some of the most rapid C–H abstractions known for *tert*-butoxyl and are only equaled by abstractions at cyclohexadienes[57] or other highly conjugated molecules,[32] which proceed with rate constants in the range $10^7$–$10^8$ M$^{-1}$ s$^{-1}$.

Perhaps the most interesting result to emerge from the *tert*-butoxyl reactions is that quinuclidine (III) and DABCO (IV) are about 1 order of magnitude less reactive than other tertiary amines. We suggest that this is due to a stereoelectronic effect so that H abstraction is most rapid when the $\alpha$-C–H bond being broken can be eclipsed with the nitrogen lone pair.[58] In both III and IV the $\alpha$-C–H bonds are held with a dihedral angle, $\theta$, ca. 60°, and are therefore less labile than amines where C–N bond rotation allows more favorable conformations.



The very existence of a stereoelectronic effect suggests that stabilization in the product radical is substantially reflected in the transition state. Conjugation between the unpaired electron and the nitrogen lone pair is responsible for the stabilization and clearly manifests itself in the EPR parameters of $\alpha$-aminoalkyls. In these radicals the $\alpha$-hydrogen hyperfine splittings, $a^{H_\alpha}$, of ca. 14 G are much less than those for alkyl radicals (ca. 21 G) and are quite similar to those of allyl[59] and benzyl.[59] Furthermore these radicals show substantial hyperfine splittings from nitrogen, $a^N$ (ca. 5 G) and $\gamma$-hydrogens (ca. 4 G) which indicates substantial delocalization of the unpaired electron from $C_\alpha$ to nitrogen. Interestingly, $a^{H_\alpha}$ increases and $a^N$ decreases in the order tertiary, secondary, primary amine,[36] indicating that delocalization is more effective with tertiary amines than with primary which is exactly reflected in their reactivities. It is therefore hardly surprising that amines show reactivities similar to those of conjugated hydrocarbons.

The small isotope effect which was found in the reactions of $(CH_3)_3N$ and $(CD_3)_3N$ does not deter us from this view of the reaction mechanism. The high reactivity of the $\alpha$-C–H bonds in amines and the concurrent conjugation in $\alpha$-aminoalkyls suggests that the $\alpha$-carbon–hydrogen bond is weak and, hence, that the reaction with *tert*-butoxyls is quite exothermic. Small H/D isotope effects are therefore not unreasonable. They are predicted both by the London–Eyring–Polanyi–Satio calculations and by bond energy–bond order theory[60] and are found in the reactions of *tert*-butoxyl with tri-*n*-butyltin hydride and deuteride for which $k_H = 2.0 \times 10^8$ M$^{-1}$ s$^{-1}$ and $k_H/k_D = 1.23 \pm 0.15$ at 22 °C.[61]

*tert*-Butylperoxyl radicals react more rapidly with amines than with hydrocarbons or ethers. Thus, the rate constant for reaction with pyrrolidine is 380 M$^{-1}$ s$^{-1}$ at 30 °C while that for the isostructural ether, tetrahydrofuran, is 3.4 M$^{-1}$ s$^{-1}$[62] and that for cyclopentane is $9 \times 10^{-3}$ M$^{-1}$ s$^{-1}$.[63] However, the most interesting aspect of the *tert*-butylperoxyl data is their unequivocal demonstration of the stereoelectronic effect. Pyrrolidine (VII) in which $\theta \simeq 30°$ is by far the most reactive compound studied in this work even though it is a secondary amine. In addition, piperdine (VI) in which the most favorably placed hydrogens have $\theta \simeq 180°$ is as reactive as triethylamine. However, the tertiary amine DABCO (IV) which has $\theta \simeq 60°$ is the least reactive of all the amines investigated.

## Summary

Absolute rate constants have been determined for hydrogen abstraction by benzophenone triplet, *tert*-butoxyl, and *tert*-butylperoxyl at several amines. The reactions are far more rapid than those at hydrocarbons and are subject to substantial stereoelectronic control, reflecting the importance of conjugation between the incipient radical center and the nitrogen lone pair. Polar contributions to the transition state are probably responsible for the difference in reactivity between *tert*-butoxyl and benzophenone triplet.

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