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Hydrogen Abstraction from Amines: Formation of Aminyl vs. α-Aminoalkyl Radicals[1]

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Abstract: A series of electron paramagnetic experiments were carried out which showed that dialkylaminyl radicals do not readily attack dialkylamines to form α-aminoalkyl radicals. These results disprove earlier conclusions that such processes were the major pathways for formation of α-aminoalkyl radicals in free radical reactions involving dialkylamines. By contrast, *tert*-butoxyl radicals were found to efficiently abstract hydrogen from amines. Rate constants for C–H and N–H abstraction by *tert*-butoxyl were respectively 6.5×10^7 and 1.1×10^7 for Me_2NH, 6.6×10^7 and 1.0×10^7 for Et_2NH, 1.3×10^7 and 3×10^6 for n-$PrNH_2$, 7×10^6 and 3×10^6 for n-$BuNH_2$, and 3.3×10^6 for t-$BuNH_2$ (units $M^{-1}\ s^{-1}$).

Hydrogen abstraction from amines can lead to the formation of aminyl or α-aminoalkyl radicals. However, the extent to which these processes occur is a controversial subject.[2–6]

In a recent study[3] of the reactions of *tert*-butoxy radicals with dialkylamines, it was concluded that at 25 °C both radicals were formed but the reaction to give α-aminoalkyl radicals was dominant, i.e., $k_1 > k_2$ (eq 1 and 2). This view was contested on the

$$t\text{-BuO}\cdot + (\text{RCH}_2)_2\text{NH} \rightarrow t\text{-BuOH} + \text{RCH}_2\text{NH}\dot{\text{C}}\text{HR} \quad (1)$$

$$t\text{-BuO}\cdot + (\text{RCH}_2)_2\text{NH} \rightarrow t\text{-BuOH} + (\text{RCH}_2)_2\text{N}\cdot \quad (2)$$

basis of results obtained in a study of the photooxidation of dialkylamines by 9-phenanthrenecarbonitrile,[4] in which it was proposed that the major pathway to α-aminoalkyl radicals involved hydrogen abstraction from dialkylamines by aminyl radicals (eq 3) and that reaction 1 was relatively insignificant.

$$(\text{RCH}_2)_2\text{N}\cdot + (\text{RCH}_2)_2\text{NH} \rightarrow (\text{RCH}_2)_2\text{NH} + \text{RCH}_2\text{NHCHR} \quad (3)$$

In view of the general importance of free radical processes involving amines,[2] we have carried out a series of electron paramagnetic resonance (EPR) experiments to test the proposal that reaction 3 can be a major source of α-aminoalkyl radicals.

Experimental Section

Materials. All materials were commerically available. Solvents were spectroscopic grade and were purified by standard proceedures.[7] Diphenylmethanol was sublimed shortly before use so as to remove impurities of benzophenone. Di-*tert*-butyl peroxide was washed with aqueous silver nitrate solution, dried, and passed through a column of alumina so as to remove impurities of olefins and *tert*-butyl hydroperoxide. Amines were purified by literature methods.[7] After purification they were colorless and remained so while stored under nitrogen.

Apparatus. EPR spectra were recorded on a Varian E104 spectrometer. Samples were photolyzed directly in the cavity of the instrument by using a 1000-W mercury–xenon lamp as the light source. The output of the lamp was filtered through a cobalt–nickel filter solution so as to remove much of the visible and most of the infrared radiation.[8] The laser flash photolysis equipment has been described in detail elsewhere.[9] All samples were carefully deoxygenated before use.

Results and Discussion

In this work we set out to test the proposal[4] that reaction 3 can be a major source of α-aminoalkyl radicals. To do this, we generated dialkylaminyl radicals in solution and monitored their reactions in the presence of amines.

The reactions of *tert*-butoxyl radicals with tris(dialkylamino)phosphines serve as excellent sources of dialkylaminyl radicals, (eq 4 and 5).[10] Laser flash photolysis was used to verify

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}\cdot \quad (4)$$

$$t\text{-BuO}\cdot + (\text{R}_2\text{N})_3\text{P} \rightarrow t\text{-BuOP(NR}_2)_2 + \text{R}_2\text{N}\cdot \quad (5)$$

$$t\text{-BuO}\cdot + \text{Ph}_2\text{CHOH} \rightarrow t\text{-BuOH} + \text{Ph}_2\dot{\text{C}}\text{OH} \quad (6)$$

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

that *tert*-butoxyl radicals react more readily with aminophosphines than with amines, i.e, $k_5 > k_1$ and k_2, which is an obvious requirement in the present context.

The laser flash photolysis technique has been described in detail elsewhere.[9] Briefly, *tert*-butoxyl radicals were generated by photodecomposition of di-*tert*-butyl peroxide in benzene (2:1, v/v) by using pulses (337.1 nm, 8 ns, 1–10 mJ) from a Molectron nitrogen laser (reaction 4). Diphenylmethanol (0.06–0.14 M) was used to probe the lifetime of *tert*-butoxyl. It reacts to form the diphenylhydroxymethyl radical that has a strong and easily monitored absorption at 540 nm[11] (reaction 6).

When an aminophosphine was added to the reaction mixture, there was an increase in the pseudo-first order rate constant, k_{exptl}, for the growth of the 540-nm absorption. Reactions 4–7 show the essential parts of the reaction mechanism, and 8 and 9 relate the rate constants of interest as

$$k_{\text{exptl}} = k_7 + k_6[\text{Ph}_2\text{CHOH}] + k_5[(\text{R}_2\text{N})_3\text{P}] \quad (8)$$

or if $k_0 = k_7 + k_6[\text{Ph}_2\text{CHOH}]$

$$k_{\text{exptl}} = k_0 + k_5[(\text{R}_2\text{N})_3\text{P}] \quad (9)$$

Measurements of k_{exptl} as a function of phosphine concentration gave $k_5 = 1.0 \times 10^9$ and $1.7 \times 10^9\ M^{-1}\ s^{-1}$ for $(Et_2N)_3P$ and $(Me_2N)_3P$, respectively. These rate constants are close to the diffusion-controlled limit[12] and are much greater than those for reactions of *tert*-butoxyls with amines. For example, the overall reactivity of Et_2NH toward *tert*-butoxyl radicals, i.e., $k_1 + k_2$,

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is 7.5 × 10^7 M^{-1} s^{-1}.[13] Hence, for the purpose of this work reactions 5 and 6 represent an excellent method for the generation of dialkylaminyl radicals.

Continuous photolysis of mixtures of di-*tert*-butyl peroxide (30% v/v) and $(Et_2N)_3P$ (15% v/v) at 25 °C in isooctane solvent in the cavity of the EPR spectrometer gave an excellent spectrum of $Et_2N\cdot$ (reactions 4 and 5).[14] The solution was flowed (0.5 mL/min) through the sample cell so as to avoid the accumulation of light absorbing products that screen the photolysis. When Et_2NH (1 M) was added to this mixture, the spectrum was unchanged, there being no sign of the spectrum due to EtNHĊHMe.[15] Moreover, when the intensity of the photolyzing light, I_0, was reduced by using neutral density filters, a plot of log (I_0) vs. log $[Et_2N\cdot]$ had a slope of 0.55 ± 0.5, indicating that $Et_2N\cdot$ was destroyed by bimolecular self-reaction (eq 10). There

$$R_2N\cdot + R_2N\cdot \rightarrow \text{non-radical products} \qquad (10)$$

was no significant "first-order" contribution to the kinetics that would have been expected if reaction 3 had been of significance. Similar results were obtained with the combination $(Me_2N)_3P$ and Me_2NH. Thus under the conditions of relatively high radical concentrations used in these EPR experiments ($[R_2N\cdot] \simeq 10^{-6}$ -10^{-7} M), reaction 3 was unimportant. The rate constant for reaction 10 is high, $k_{10} \simeq 10^9$ M^{-1} s^{-1} (vide infra), when taken together with the other experimental observations, this implies that $k_3 <$ ca. 10^3 s^{-1} at 25 °C.

Additional EPR experiments were carried out to measure the ratio of rate constants k_1/k_2. This ratio is equal to the ratio of the steady-state concentrations of α-aminoalkyl and aminyl radicals observed during continuous sample photolysis on the assumption that the rate constants for self-reactions of these radicals are equal.[16] There is substantial support for this assumption since studies of the self-reactions of small unhindered aminyls[17] and α-aminoalkyls[18] indicate that these are diffusion-controlled processes and hence are likely to proceed with similar rate constants for radicals of about the same size.

The EPR spectra of α-aminoalkyl radicals are notoriously difficult to detect in solution because of the large number of hyperfine interactions and their sensitivity to microwave power saturation.[3] However, we were able to obtain spectra of high quality by flowing the samples and by using a powerful light source with an efficient lamp housing. The optimum conditions for recording these spectra were 1.0 mW (power) and 0.25 G (modulation amplitude), whereas for aminyl radicals appropriate conditions were 5 mW and 1.6 G. Corrections for the difference in conditions were made by using the signal from a ruby disk located in the spectrometer cavity as a standard. The spectroscopic parameters for $Me_2N\cdot$,[14] $Et_2N\cdot$,[14] $MeNH\dot{C}H_2$,[19] $Et\dot{C}HNH_2$,[15] and $Pr\dot{C}HNH_2$[15] are similar to those previously reported. The low-temperature spectrum of EtNHĊHMe corresponded to that described in the literature[15] although at higher temperatures it became more complicated, suggesting the presence of two conformers of the radical.

When primary amines, including methylamine, were used as substrates, we were only able to detect the EPR spectra of α-aminoalkyl radicals. A number of experiments were carried out in an attempt to detect *t*-BuṄH from *tert*-butylamine. However, in this case only the spectra of unidentified persistent radicals were detected which were not eliminated when the amine was purified by preparative gas chromatography. Thus, we cannot unequivocally rule out the possibility that monoalkylaminyl radicals abstract hydrogen from primary amines to give α-aminoalkyl radicals.

Table I. Rate Constants for the Reactions of *tert*-Butoxyl Radicals with Amines

amine	$k_1 + k_2$,[a] M^{-1} s^{-1}	k_1/k_2[b]	k_1, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}
Me_2NH	7.6 × 10^7	5.9	6.5 × 10^7	1.1 × 10^7
Et_2NH	7.6 × 10^7[c]	6.3	6.6 × 10^7	1.0 × 10^7
n-$PrNH_2$	1.6 × 10^7	*d*	1.3 × 10^7[d]	3.3 × 10^6[d]
n-$BuNH_2$	1.0 × 10^7	*d*	7.0 × 10^6[d]	3.3 × 10^6[d]
t-$BuNH_2$	3.3 × 10^6[e]			3.3 × 10^6[e]

[a] Determined by using laser flash photolysis; experimental error ±10%. [b] Determined by using EPR; experimental error ±20%. [c] Reference 13. [d] No aminyl radical detected, k_2 assumed to be equal to that for *t*-$BuNH_2$. [e] Reference 3.

Ratios of radical concentrations and hence k_1/k_2 are reported in Table I. The overall reactivities of the amines toward *tert*-butoxyl radicals, i.e., $k_1 + k_2$, were determined by using the laser flash photolysis technique described above. A combination of the data leads to separate values of k_1 and k_2. From these data and the qualitative EPR observations it seems clear that reaction 1 is the dominant pathway by which *tert*-butoxy radicals react with amines. Similar conclusions have been drawn in studies of hydrogen abstraction from amines by triplet ketones.[6] However, it has been shown that the overall process can be catalyzed in a fascinating way by the introduction of thiols (reactions 11 and 12).[6]

$$t\text{-Bu}\dot{N}H + RSH \rightarrow t\text{-BuNH}_2 + RS\cdot \qquad (11)$$

$$RS\cdot + EtCH(NH_2)Me \rightarrow RSH + Et\dot{C}(NH_2)Me \qquad (12)$$

One interesting feature of the data given in the Table is that the absolute rate constants for both C–H and N–H abstraction are greater for the secondary amines. This trend follows the variation in amine C–H and N–H bond strengths. Thus, the C–H bond dissociation energies for Me_3N, Me_2NH, and $MeNH_2$ are 84, 87, and 94 kcal mol^{-1}, respectively,[20] while the N–H bond dissociation energies for Me_2NH, $MeNH_2$, and NH_3 are 92, 100, and 107 kcal mol^{-1}, respectively.[21]

Earlier reports[4] that stressed the importance of reaction 3 may require reinvestigation or may have been based on experiments carried out at extremely low radical concentrations where the rates of radical–radical reactions compete far less effectively with this process.[22] In addition, the present results suggest that α-aminoalkyl radicals are likely to have been formed in a kinetic EPR study of dialkylaminyl radical rearrangements[5] but that they went undetected because of the complexity of their spectra. If this assessment is correct, then rate constants reported for these rearrangements are likely to be too low by a factor of ca. 5.[5]

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Registry No. Atomic hydrogen, 12385-13-6; *tert*-butoxyl radical, 3141-58-0; dimethylamine, 124-40-3; diethylamine, 109-89-7; propylamine, 107-10-8; butylamine, 109-73-9; *tert*-butylamine, 75-64-9; di-*tert*-butyl peroxide, 110-05-4; tris(diethylamino)phosphine, 2283-11-6; diethylaminyl radical, 29685-06-1; tris(dimethylamino)phosphine, 1608-26-0; methylamine, 74-89-5.

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