Hydrogen-atom abstraction from dimethylamine in solution: EPR spectroscopic studies and *ab initio* molecular orbital calculations

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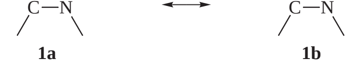
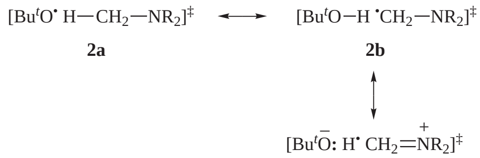
The reactions of photochemically-generated *tert*-butoxyl and of bis(trimethylsilyl)aminyl radicals with dimethylamine in cyclopropane solution have been studied using EPR spectroscopy. Both radicals abstract hydrogen competitively from the NH and CH groups to produce the radicals $Me_2N^{\bullet}$ and $MeNH\dot{C}H_2$, respectively, but the silylaminyl radical shows a greater propensity to attack the less sterically hindered methyl groups. Analogous trends are shown in hydrogen-atom abstraction from propane, the isoelectronic hydrocarbon analogue of dimethylamine. The regioselectivity of hydrogen abstraction from dimethylamine depends upon the concentration of the amine, because association by hydrogen-bonding reduces the number of reactive NH groups relative to the CH groups. The activation energy for hydrogen-atom transfer to $Bu^tO^{\bullet}$ from the NH group of monomeric dimethylamine is 4.6 kJ mol^{-1} less than that for transfer from a CH group, while the Arrhenius *A*-factor for abstraction from the methyl groups is 3.4 times greater than that for abstraction from the NH group, presumably mainly for statistical reasons. Absolute rate constants for hydrogen abstraction have been determined in competition experiments with tetrahydrofuran. Hydrogen-bonding to $Me_2N^{\bullet}$ produces changes in its EPR spectrum in the same direction as, but of smaller magnitude than, does full protonation. *Ab initio* molecular orbital calculations have been carried out for the reactants, products and transition states involved in hydrogen-atom abstraction from dimethylamine by the methoxyl radical, as well as for the hydrogen-bonded complexes formed between $Me_2N^{\bullet}$ and methanol and between $MeO^{\bullet}$ and dimethylamine. The dissociation enthalpies of the NH and CH bonds in dimethylamine are computed to be larger than the currently accepted experimental values and the activation energies for hydrogen-atom transfer from the amine to the methoxyl radical are in good agreement with the experimental values for transfer to the *tert*-butoxyl radical. The experimental and theoretical results are compared with the predictions of a previously-published empirical algorithm for the estimation of activation energies for hydrogen-atom transfer processes.

The regioselectivities with which alkoxyl radicals abstract hydrogen from alkanes are now reasonably well understood. Less is known about the corresponding hydrogen-atom transfer reactions of aliphatic amines and, in particular, the competition between abstraction of hydrogen from carbon and from nitrogen has proved problematic.

Hydrogen abstraction by the *tert*-butoxyl radical from tertiary aliphatic amines takes place preferentially from C–H groups attached to nitrogen and these reactions are extremely rapid,[1] in part because such C–H bonds are relatively weak[2,3] as a result of the large stabilisation of the α-aminoalkyl radical afforded by delocalisation of the unpaired electron onto nitrogen (see structures **1a** and **1b**). Furthermore, the *tert*-butoxyl radical is electrophilic and the α-aminoalkyl radical is nucleophilic with a very low ionisation energy,[2b,4] which leads to effective charge-transfer stabilisation of the transition state **2** (a 'polar effect'), as represented by inclusion of the canonical structure **2c** in a valence-bond description.[5]



1a **1b**



2a **2b** **2c**

As judged by EPR spectroscopy,[6] *tert*-butoxyl radicals abstract hydrogen exclusively from an α-C–H group in a primary aliphatic amine $R^1R^2CHNH_2$. However, primary aminyl radicals of the general type $R\dot{N}H$ have never been detected in solution by EPR spectroscopy[7] and may have very broad lines, which would make their spectra difficult to observe. It is also possible that, should these species be formed by hydrogen transfer from nitrogen, they could rapidly abstract hydrogen from an α-C–H group in the parent amine or rearrange by a formal 1,2-hydrogen atom shift to give the thermodynamically more stable isomeric α-aminoalkyl radical. In this context, we note that *tert*-butylamine ($k_{abstr.} = 3.3 \times 10^6$ dm^3 mol^{-1} s^{-1}), which has no α-C–H groups, is only about five times less reactive than propylamine ($k_{abstr.} = 1.7 \times 10^7$ dm^3 mol^{-1} s^{-1}) towards the *tert*-butoxyl radical at 295 K.[1]

The situation regarding hydrogen-atom abstraction from secondary amines is even less clear. In early work, Roberts and Ingold[8] reported that the EPR spectrum of $Pr^i_2N^{\bullet}$ could be observed when di-*tert*-butyl peroxide (DTBP) was photolysed in the presence of diisopropylamine, but that spectra of $Me_2N^{\bullet}$ and of $Et_2N^{\bullet}$ could not be detected in similar experiments with Me_2NH and Et_2NH. Later, Maeda and Ingold[9] reported that photolysis of DTBP in the presence of a number of other dialkylamines R^1R^2NH (not including dimethylamine) afforded EPR spectra of the corresponding dialkylaminyl radicals $R^1R^2N^{\bullet}$. More recent EPR spectroscopic studies of the reaction of *tert*-butoxyl radicals with *N*-(trimethylsilylmethyl)methylamine, $Me_3SiCH_2N(H)Me$, have shown that hydrogen-atom abstraction takes place at comparable rates from both the NH and CH_2 groups.[10] However, in very recent work by Wayner *et al.*,[3a] where photoacoustic calorimetry was used to determine the strength of the α-C–H bonds in pyrrolidine, piperidine, piperazine and morpholine, it was assumed without comment that *tert*-butoxyl radicals will abstract hydrogen exclusively from carbon in these cyclic secondary amines.†

In view of the apparent inconsistencies in the reports of the reactions of alkoxyl radicals with secondary amines, we have carried out a detailed investigation of the reactivity of the *tert*-butoxyl radicals towards dimethylamine in solution, using EPR spectroscopy to monitor the radicals produced.

Results

EPR spectra were recorded during continuous UV irradiation of samples positioned in the microwave cavity of the spectrometer, using the techniques described previously.[14] *tert*-Butoxyl radicals were generated by photolysis of DTBP [eqn. (1)] and,

$$\mathrm{Bu^tOOBu^t} \xrightarrow{h\nu} 2\mathrm{Bu^tO^\bullet} \qquad (1)$$

in some experiments, this was replaced by tetrakis(trimethylsilyl)hydrazine[15] (TTMH) as a photochemical source of the highly reactive bis(trimethylsilyl)aminyl radical [eqn. (2)].

$$(\mathrm{Me_3Si})_2\mathrm{NN(SiMe_3)_2} \xrightarrow{h\nu} 2(\mathrm{Me_3Si})_2\mathrm{N^\bullet} \qquad (2)$$

Preliminary work highlighted two important characteristics of samples which contained dimethylamine and DTBP or TTMH. Firstly, in order to obtain clean EPR spectra and reproducible results it was crucial to ensure that oxygen and other readily reducible impurities were absent. If traces of oxygen or hydroperoxide (as an impurity present in commercial DTBP) were present, the samples rapidly developed a brown coloration during UV irradiation, weak spectra were obtained and broad EPR signals from persistent radicals rapidly became obtrusive. These problems are probably a consequence of the powerful reducing properties of α-aminoalkyl radicals,[4] although DTBP itself does not appear to be reduced[5,16] at a significant rate under our conditions. Secondly, the EPR spectra obtained depended markedly on the concentration of the amine.

When a cyclopropane solution containing dimethylamine (1.15 mol dm^{-3}) and DTBP (0.60 mol dm^{-3}) was irradiated with UV light at 188 K, the EPR spectrum shown in Fig. 1 was obtained. This can be analysed as a superimposition of the spectra of the dimethylaminyl radical[17,18] $\mathrm{Me_2N^\bullet}$ (**3**) and the *N*-methylaminomethyl radical $\mathrm{MeNH\dot{C}H_2}$ (**4**); computer simulation showed that the value of [**3**]/[**4**] is 4.6 under these conditions. With higher concentrations of amine, the relative concentration of the dimethylaminyl radical decreased and at lower amine concentrations it increased, such that the value of [**3**]/[**4**] extrapolated to zero amine concentration was 6.2 ± 0.6 (see Fig. 2). This limiting value probably reflects the reactivity of isolated dimethylamine molecules while, at higher amine concentrations, hydrogen-bonded dimers and larger oligomers are present.[19] A compromise concentration of 0.52 mol dm^{-3}, the lowest practicable, was chosen for experiments designed to study the unassociated amine.

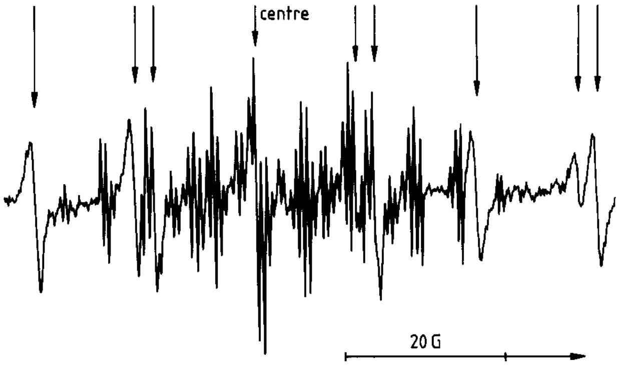


Fig. 1 EPR spectrum obtained during UV irradiation of a cyclopropane solution containing dimethylamine (1.15 mol dm^{-3}) and DTBP (0.60 mol dm^{-3}) at 188 K. The positions of lines in the central region of the spectrum of $\mathrm{Me_2N^\bullet}$ are marked with arrows; the remaining sharp lines constitute the spectrum of $\mathrm{MeNH\dot{C}H_2}$. Two samples were used to compensate for the effects of sample decay with time.

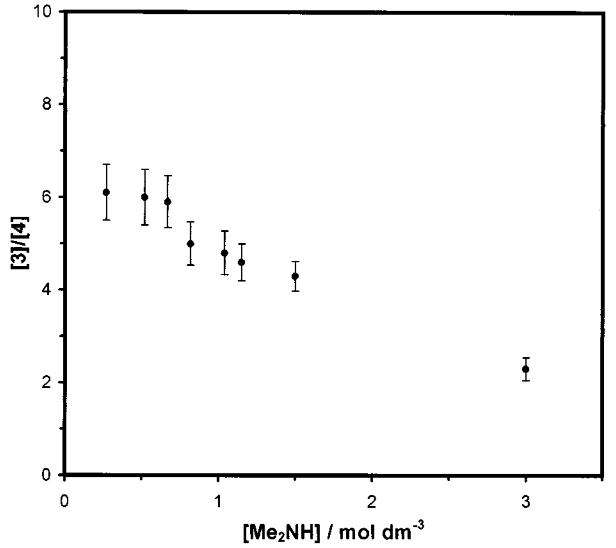


Fig. 2 Variation in the value of [**3**]/[**4**] as a function of amine concentration at 188 K

When the concentration of DTBP was varied at a fixed amine concentration (1.15 mol dm^{-3}), the value of [**3**]/[**4**] remained essentially constant (4.6 ± 0.5) for peroxide concentrations in the range 0.15–1.20 mol dm^{-3}; all subsequent experiments were carried out with a peroxide concentration of 0.60 mol dm^{-3}. It should be noted that, because the linewidth for $\mathrm{Me_2N^\bullet}$ is much greater than that for $\mathrm{MeNH\dot{C}H_2}$ [*e.g.* 1.2 and 0.27 G, respectively, in Fig. 1 (although the latter linewidth is in part determined by the modulation amplitude)] visual inspection of composite spectra often gives the impression that the value of [**3**]/[**4**] is smaller than is actually the case.

The temperature dependence of the reaction of $\mathrm{Bu^tO^\bullet}$ with $\mathrm{Me_2NH}$ was investigated for an amine concentration of 0.52 mol dm^{-3}. The radicals **3** and **4** are expected to undergo diffusion-controlled self- and cross-reactions and the rate constants for these processes will be very similar.[8,20] The ratio of the steady-state concentrations of **3** and **4** will therefore be proportional to the ratio of the rate constants (k_{3a} and k_{3b}) for their formation by abstraction of hydrogen from dimethylamine [eqns. (3*a* and *b*)].[20] A plot of $\log_{10}$ ([**3**]/[**4**]) *vs.* $1/T$ for

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† Danen and Kensler[11] have reported that UV photolysis of DTBP in the presence of azetidine at 173 K affords the EPR spectrum of the azetidinyl radical. Although we have not studied in detail the amines investigated by Wayner *et al.*, the spectrum of the pyrrolidinyl radical[12] [a(N) = 14.68, a(4 H$_\beta$) = 40.30 and a(4 H$_\gamma$) = 0.50 G at 214 K] was detected during UV photolysis of DTBP in the presence of pyrrolidine (*ca.* 2 mol dm^{-3}) in cyclopropane between 187 and 275 K, although other weak lines (which could well be associated with the α-aminoalkyl radical produced by abstraction of hydrogen from carbon) were also present. Thermolysis of DTBP at *ca.* 413 K in the presence of pyrrolidine is reported[13] to give a 73% yield of the 2,2′-dehydrodimer, presumably produced by coupling of two α-aminoalkyl radicals. The bond strength measured by Wayner *et al.* for pyrrolidine is thus likely to represent a mean for the α-CH and NH bonds, weighted according to the selectivity with which *tert*-butoxyl radicals abstract hydrogen from this secondary amine.

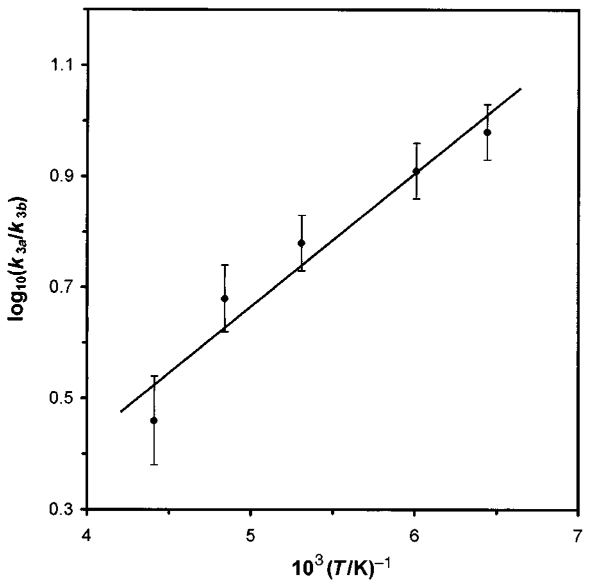
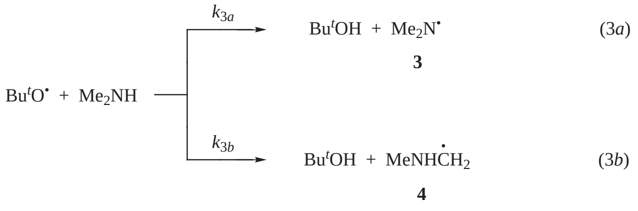


Fig. 3 Arrhenius plot for competitive hydrogen-atom abstraction from dimethylamine (0.52 mol dm^{-3}) by *tert*-butoxyl radicals in cyclopropane



$$\mathrm{Bu^tO^\bullet + Me_2NH} \xrightarrow{k_{3a}} \mathrm{Bu^tOH + \underset{3}{Me_2N^\bullet}} \quad (3a)$$

$$\mathrm{Bu^tO^\bullet + Me_2NH} \xrightarrow{k_{3b}} \mathrm{Bu^tOH + \underset{4}{MeNH\dot{C}H_2}} \quad (3b)$$

experiments between 153 and 226 K (see Fig. 3) conformed to the Arrhenius rate expression (4), in which $\theta = 2.303RT$ kJ

$$\log_{10}(k_{3a}/k_{3b}) = -0.53 + 4.6/\theta \qquad (4)$$

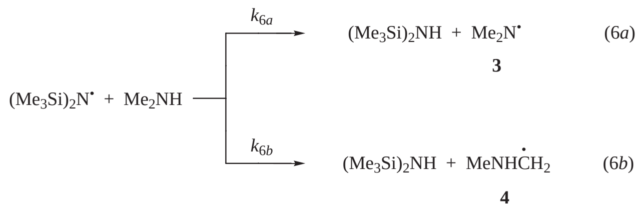
mol^{-1}. Thus, while the *A*-factor for reaction (3*b*) is 3.4 times larger than that for reaction (3*a*), the activation energy for abstraction of hydrogen from nitrogen is 4.6 kJ mol^{-1} smaller than that for abstraction from carbon.

tert-Butoxyl radicals react very rapidly with tris(dimethylamino)phosphine (TDMAP) according to eqn. (5), *via* an

$$\mathrm{Bu^tO^\bullet + (Me_2N)_3P \longrightarrow Me_2N^\bullet + Bu^tOP(NMe_2)_2} \quad (5)$$

unstable intermediate phosphoranyl radical adduct.[21] UV irradiation of a cyclopropane solution containing DTBP, TDMAP (0.90 mol dm^{-3}) and Me_2NH (1.15 mol dm^{-3}) afforded only the EPR spectrum of the dimethylaminyl radical up to 225 K, confirming that the aminyl radical does not abstract hydrogen from the amine to give **4** under these conditions.

When TTMH (0.32 mol dm^{-3}) was photolysed in the presence of Me_2NH (1.15 mol dm^{-3}) in cyclopropane at 186 K, the EPR spectrum shown in Fig. 4(*a*) was recorded. The selectivity with which $(Me_3Si)_2N^\bullet$ abstracts hydrogen from the amine is clearly very different from that of $Bu^tO^\bullet$ and the relative concentration of the carbon-centred radical **4** is now much greater [eqns. (6*a* and *b*)]. As before, the value of [**3**]/[**4**] increased as the value of [Me_2NH] decreased and extrapolation to zero amine concentration gave the value of (k_{6a}/k_{6b}) to be *ca.* 0.8 at 188 K, as compared with *ca.* 6 for (k_{3a}/k_{3b}) at the same temperature. The EPR parameters for the radicals **3** and **4**, which are dependent on the hydrogen-bond donor properties of the medium, are given in Table 1.



$$\mathrm{(Me_3Si)_2N^\bullet + Me_2NH} \xrightarrow{k_{6a}} \mathrm{(Me_3Si)_2NH + \underset{3}{Me_2N^\bullet}} \quad (6a)$$

$$\mathrm{(Me_3Si)_2N^\bullet + Me_2NH} \xrightarrow{k_{6b}} \mathrm{(Me_3Si)_2NH + \underset{4}{MeNH\dot{C}H_2}} \quad (6b)$$

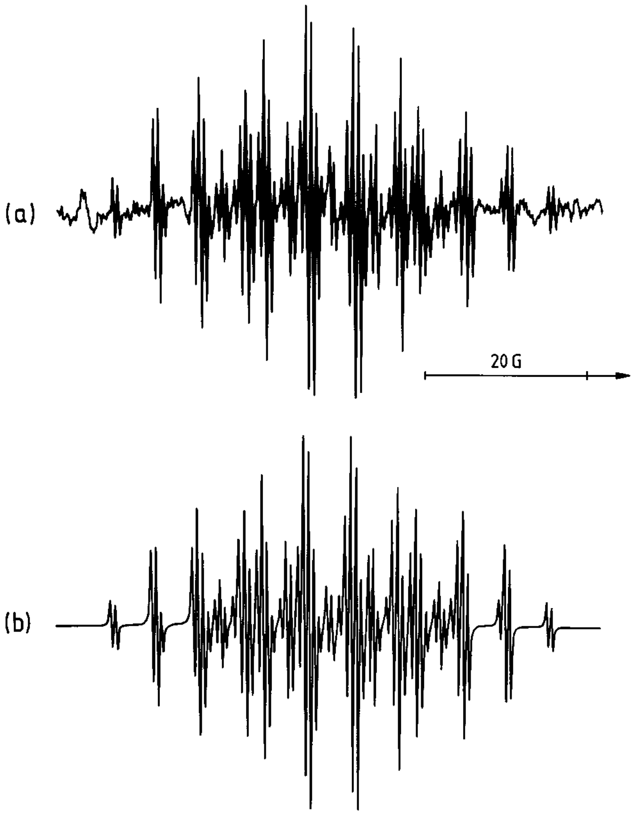
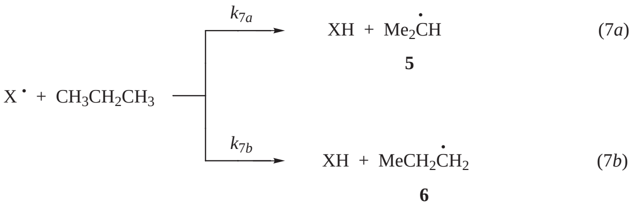


Fig. 4 (*a*) EPR spectrum obtained during UV irradiation of a cyclopropane solution containing dimethylamine (1.15 mol dm^{-3}) and TTMH (0.32 mol dm^{-3}) at 186 K. A weak spectrum of $Me_2N^\bullet$ is present alongside that of $MeNH\dot{C}H_2$. (*b*) Computer simulation of the spectrum of $MeNH\dot{C}H_2$ using the parameters given in Table 1.

The relatively small value of [**3**]/[**4**] obtained with TTMH provides strong experimental evidence that **4** does not abstract hydrogen from dimethylamine to give **3** under the reaction conditions. This result would be expected, since there is no evidence that the reverse process takes place (see above) and there is little doubt that the C–H bond in dimethylamine is weaker than the N–H bond (see later).

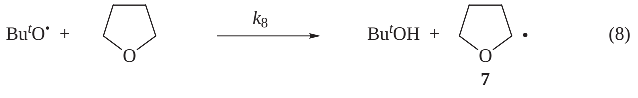
Propane and dimethylamine are isoelectronic and hydrogen-atom abstraction from this alkane to give the isopropyl radical **5** and the propyl radical **6**, analogues of **3** and **4**, respectively, was examined for comparison [eqn. (7)]. At 188 K, the value of (k_{7a}/k_{7b}) was 12.1 when $X = Bu^tO^\bullet$ and 3.4 when $X = (Me_3Si)_2N^\bullet$, a trend analogous to that shown for hydrogen-atom abstraction from dimethylamine.



$$\mathrm{X^\bullet + CH_3CH_2CH_3} \xrightarrow{k_{7a}} \mathrm{XH + \underset{5}{Me_2\dot{C}H}} \quad (7a)$$

$$\mathrm{X^\bullet + CH_3CH_2CH_3} \xrightarrow{k_{7b}} \mathrm{XH + \underset{6}{MeCH_2\dot{C}H_2}} \quad (7b)$$

The absolute reactivity of dimethylamine towards hydrogen-atom abstraction by *tert*-butoxyl radicals was determined in the usual way[14,20,22] by competitive reaction with tetrahydrofuran (THF) [eqn. (8)], on the basis that the relative rates of abstrac-



(8)

Table 1 EPR parameters for the dimethylaminyl radical **3** and the *N*-methylaminomethyl radical **4** at 187 ± 1 K in cyclopropane

Radical	Source[a]	*g*-Factor	*a*/G
3	A	2.0047_4	14.80 (N), 27.10 (6 H)
3	B	2.0047_0	15.00 (N), 27.51 (6 H)
4	C	2.0028_3	13.80 (1 H_α), 13.20 (1 H_α), 5.92 (N), 5.11 (3 H_γ), 0.55 (N*H*)

[a] A = photolysis of DTBP (0.60 mol dm^{-3}) in the presence of TDMAP (0.60 mol dm^{-3}); B = photolysis of DTBP (0.60 mol dm^{-3}) in the presence of TDMAP (0.60 mol dm^{-3}) and dimethylamine (1.15 mol dm^{-3}); C = photolysis of TTMH (0.32 mol dm^{-3}) in the presence of dimethylamine (1.15 mol dm^{-3}).

tion from the amine ($k_{abstr.}$) and their temperature dependences are given by eqns. (9) and (10), where X˙ is either **3** or **4**. The

$$(k_{abstr.}/k_8) = [X^{\bullet}][THF]/[7][Me_2NH] \qquad (9)$$

$$\log_{10}(k_{abstr.}/k_8) = \log_{10}(A_{abstr.}/A_8) + (E_8 - E_{abstr.})/\theta \qquad (10)$$

Arrhenius rate expression for k_8 has been determined previously by laser-flash photolysis[23] and is given by eqn. (11).

$$\log_{10}(k_8/dm^3\ mol^{-1}\ s^{-1}) = (8.7 \pm 0.8) - (10.5 \pm 4.2)/\theta \qquad (11)$$

Experiments were carried out between 147 and 228 K, with a fixed amine concentration of 0.52 mol dm^{-3} and with a THF concentration of 3.08 mol dm^{-3}, to yield the relative rate expressions given in eqns. (12) and (13); at 188 K the results

$$\log_{10}(k_{3a}/k_8) = 0.15 + 4.3/\theta \qquad (12)$$

$$\log_{10}(k_{3b}/k_8) = 0.79 + 0.1/\theta \qquad (13)$$

were essentially independent of the THF concentration in the range 2.36–4.52 mol dm^{-3}. Combining eqns. (12) and (13) with the rate of hydrogen-atom abstraction from THF [eqn. (11)] gives the absolute rate expressions shown in eqns. (14) and (15)

$$\log_{10}(k_{3a}/dm^3\ mol^{-1}\ s^{-1}) = 8.9 - 6.2/\theta \qquad (14)$$

$$\log_{10}(k_{3b}/dm^3\ mol^{-1}\ s^{-1}) = 9.5 - 10.4/\theta \qquad (15)$$

for abstraction from nitrogen and from carbon, respectively, in dimethylamine. At 188 K the values (in $dm^3\ mol^{-1}\ s^{-1}$) of k_{3a} and k_{3b} are 1.5×10^7 and 4.1×10^6, respectively; at 300 K these values increase to 6.6×10^7 and 4.9×10^7, respectively.

The relative and absolute kinetic data obtained should not be regarded as highly accurate, because of the various experimental difficulties inherent in this type of work. The linewidths in the EPR spectra of **3** and **4** are very different, making the estimation of relative radical concentrations difficult. The dependence of [**3**]/[**4**] on [Me_2NH], because of association of the amine, causes problems and the extent of association will be somewhat temperature dependent, even at the low concentration employed. It is thus not easy to estimate errors for the Arrhenius parameters presented in eqns. (14) and (15). The corresponding errors given in the literature[23] for reaction (8) [see eqn. (11)] appear to be rather larger than might be expected and we suggest that the activation energies obtained for reactions (3*a*) and (3*b*) are probably accurate to within ±2–3 kJ mol^{-1}, although the value of ($E_{3b} - E_{3a}$) (4.6 kJ mol^{-1}) will be more accurate.

Table 2 EPR parameters for the dimethylaminyl radical at 187 ± 1 K in the presence of alcohols[a]

Alcohol	[ROH]/ mol dm^{-3}	*g*-Factor[b]	*a*(N)[b]/G	*a*(6 H)[b]/G
MeOH	0.60	2.0046_2	15.34	27.77
MeOH	1.20	2.0044_0	15.47	28.06
MeOH	2.40	2.0043_0	15.58	28.15
MeOH	3.60	2.0041_9	15.67	28.23
$EtMe_2COH$	0.60	2.0046_6	15.08	27.55
$EtMe_2COH$	1.20	2.0044_0	15.26	27.87
$EtMe_2COH$	2.40	2.0043_7	15.30	27.89
$EtMe_2COH$	3.60	2.0042_2	15.40	27.99
CF_3CH_2OH	0.60	2.0044_1	15.80	28.29
CF_3CH_2OH	1.20	2.0043_3	15.88	28.32
CF_3CH_2OH	2.40	2.0041_1	15.99	28.55
CF_3CH_2OH	3.60	2.0040_1	16.05	28.64
$(CF_3)_2MeCOH$[c]	0.30	2.0043_3	15.38	27.84
$(CF_3)_2MeCOH$[c]	0.60	2.0042_8	15.50	27.98
$(CF_3)_2MeCOH$[c]	1.20	2.0042_1	15.60	28.08

[a] The aminyl radical was generated by photolysis of DTBP (0.60 mol dm^{-3}) in the presence of TDMAP (0.23–0.90 mol dm^{-3}) and the spectroscopic parameters were extrapolated to zero aminophosphine concentration. [b] Corrected for second-order effects. [c] Cyclopropane–dimethyl ether (8 : 1 v/v) solvent; this alcohol is relatively immiscible in cyclopropane alone.

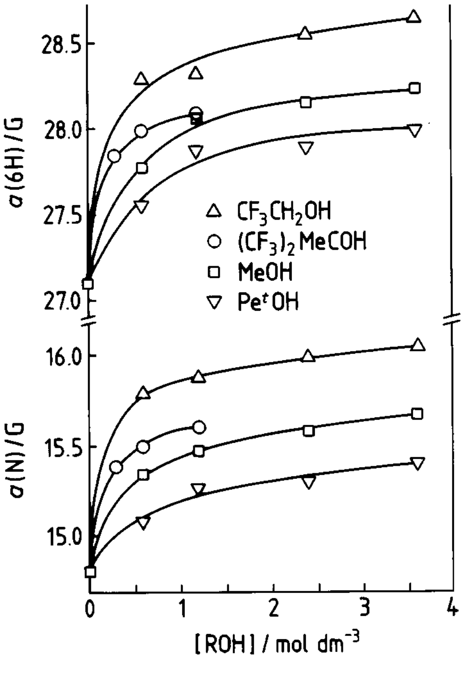


Fig. 5 Dependence of *a*(N) and *a*(6 H) for the dimethylaminyl radical, extrapolated to zero TDMAP concentration, on the presence of alcohols at 187 ± 1 K in cyclopropane or cyclopropane–dimethyl ether

Effects of alcohols on the EPR spectrum of the dimethylaminyl radical

Abstraction of hydrogen from nitrogen in dimethylamine by an alkoxyl radical yields the dimethylaminyl radical adjacent to the newly-formed alcohol molecule. Hydrogen-bonding between an aminyl radical and an alcohol would be expected to affect the EPR spectrum of the former and this effect was studied by generating $Me_2N^{\bullet}$ **3** by displacement from TDMAP in the presence of different concentrations of alcohols at 188 K. The alcohol would be expected to undergo competitive hydrogen-bonding to the aminophosphine and, to circumvent this problem, the EPR parameters were extrapolated to zero TDMAP concentration to obtain the data given in Table 2. It is evident that both *a*(N) and *a*(6 H) are larger in the presence of alcohols and that the increases in coupling constants depend on both the nature and concentration of the alcohol; the results are shown graphically in Fig. 5. The *g*-factor of **3** is reduced in the presence of alcohols (see Table 2). Dimethyl ether was required as a co-solvent in experiments with $(CF_3)_2MeCOH$ and it was shown that, in the absence or presence of methanol, the EPR parameters of **3** were the same in cyclopropane and in cyclopropane–dimethyl ether.

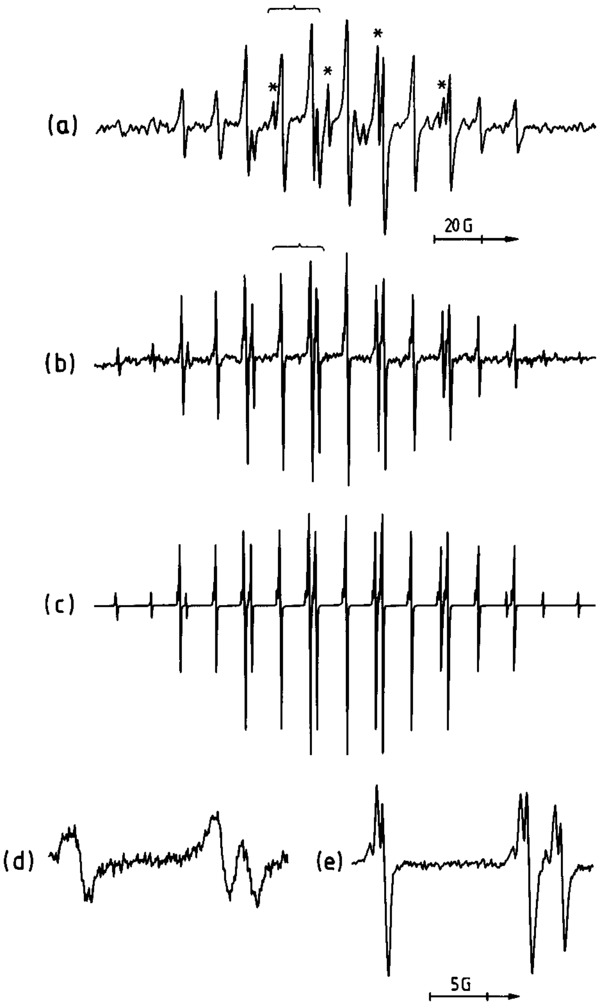
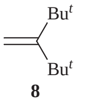


Fig. 6 (*a*) EPR spectrum of the dimethylaminyl radical generated by UV irradiation of DTBP in the presence of $(Me_2N)_3P$ (0.60 mol dm^{-3}) at 188 K. The lines marked with asterisks arise from the *tert*-butyl radical which is formed as a secondary product by the reaction of $Bu^tO^\bullet$ with $(Me_2N)_2POBu^t$ (see ref. 21). (*b*) As for (*a*), but in the additional presence of methanol (3.6 mol dm^{-3}). (*c*) Computer simulation of (*b*) including second-order effects. (*d*) and (*e*) Expansions of the region shown bracketed in (*a*) in the absence and presence, respectively, of methanol (3.6 mol dm^{-3}). The instrumental conditions (apart from the gain) are the same for both spectra.

The natural linewidth for the EPR spectrum of **3** is significantly smaller in the presence of alcohols and this is strikingly evident in Fig. 6, which shows the spectrum in the absence and presence of methanol. When the alcohol is present, the lines are sufficiently narrow for second-order effects[24] to be resolved and the spectrum appears much more intense, although the radical concentration is essentially unchanged.

Aminium radical cations $R_2\dot{\overset{+}{N}}H$ undergo addition to alkenes appreciably more rapidly than do the corresponding neutral aminyl radicals $R_2N^\bullet$.[25] Dimethylaminyl radicals hydrogen-bonded to alcohols would be expected to have properties reminiscent of the fully-protonated form and so evidence for their addition to alkenes was sought by EPR spectroscopy. However, even in the presence of high concentrations of 2,2,2-trifluoroethanol (3.6 mol dm^{-3}), no evidence could be found for addition to 1,1-di-*tert*-butylethylene **8** (1.2 mol dm^{-3}), to *tert*-butyl vinyl ether **9** (1.2 mol dm^{-3}) or to ethylene itself (4.2 mol dm^{-3}) and only the EPR spectrum of hydrogen-bonded **3** was detected up to 260 K; no addition was detected in the absence of alcohol. The alkene **8** should give a relatively persistent adduct radical, which would facilitate its detection, and the electron-rich alkene **9** should be a good acceptor for a hydrogen-bonded aminyl radical, which would be expected to exhibit relatively electrophilic behaviour.[25c]



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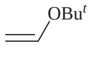

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Molecular orbital calculations

Hydrogen-atom abstraction from dimethylamine by the methoxyl radical was investigated by *ab initio* molecular orbital methods, using the GAUSSIAN 94 package of programs.[26] The hydrogen-bonded complexes formed between the methoxyl radical and dimethylamine and between methanol and the dimethylaminyl radical were also studied. The geometries of reagents, products and transition states were optimised using the gradient method, in conjunction with the 6-31G(d,p) basis set, together with Møller–Plesset perturbation theory taken to second-order and excluding the core electrons. Spin-restricted calculations were performed for closed-shell molecules and spin-unrestricted calculations for radicals [(U)MP2(fc)/6-31G(d,p) level]. For the open-shell species, the values of $\langle S^2 \rangle$ were in the range 0.75–0.78. The set of normal harmonic frequencies was computed for each structure, first in order to characterise it as a local minimum or as a transition state and then, after scaling by a factor of 0.93,[27] to obtain the zero-point vibrational energy (ZPVE) and thermal contribution $(H_{298} - H_0)$ to the enthalpy at 298.15 K. Single-point calculations were then carried out for each structure at the QCISD(T)/6-311G(d,p) level [which also gives the energy at the (U)MP2(fc)/6-311G(d,p) level] and at the (U)MP2(fc)/6-311+G(3df,2p) level. Combination of these results, according to eqns. (16) and (17), gives the energy effectively at the

$$E[\text{QCISD(T)/6-311+G(3df,2p)}] \approx E[\text{QCISD(T)/6-311G(d,p)}] + \Delta\text{MP2} \quad (16)$$

$$\Delta\text{MP2} = E[\text{(U)MP2/6-311+G(3df,2p)}] - E[\text{(U)MP2/6-311G(d,p)}] \quad (17)$$

QCISD(T)/6-311+(3df,2p) level.[28] The total energy at 0 K (E_0) and the enthalpy at 298 K (H_{298}) were calculated as indicated in eqns. (18) and (19) and all the results are given in Table 3;

$$E_0 = E[\text{QCISD(T)/6-311+G(3df,2p)}] + \text{ZPVE} \quad (18)$$

$$H_{298} = E_0 + (H_{298} - H_0) \quad (19)$$

selected geometrical parameters are given in Table 4 and key structures are illustrated in Fig. 7.

At this level, the radical $MeNH\dot{C}H_2$ **4** is computed to be more stable than the isomeric $Me_2N^\bullet$ **3** by 5.1 kJ mol^{-1} and the enthalpy changes at 298 K associated with the isodesmic reactions (20) and (21) are calculated to be −48.2 and −52.9

$$H_3C^\bullet + Me_2NH \longrightarrow H_4C + MeNH\dot{C}H_2 \quad (20)$$

$$H_2N^\bullet + Me_2NH \longrightarrow H_3N + Me_2N^\bullet \quad (21)$$

kJ mol^{-1}, respectively. If the values of $D_{298}(H_3C\text{–}H)$ and $D_{298}(H_2N\text{–}H)$ are taken to be 438.5 and 449.4 kJ mol^{-1}, respectively,[29] the dissociation enthalpies for the C–H and N–H bonds in dimethylamine are calculated to be 390 and 397 kJ mol^{-1}, respectively.

The values of D_{298}(C–H) and D_{298}(N–H) for dimethylamine were also calculated directly, as the enthalpy changes for reaction (22) ($Y^\bullet = MeNH\dot{C}H_2$ or $Me_2N^\bullet$) using the standard

$$Y\text{–}H \longrightarrow Y^\bullet + H^\bullet \quad (22)$$

Table 3 Energies and enthalpies obtained from *ab initio* calculations

		Electronic energy/Hartree[a]								
Molecule	Point group	(U)MP2/ 6-31G(d,p)[b]	(U)MP2/ 6-311G(d,p)	QCISD(T)/ 6-311G(d,p)	(U)MP2/ 6-311+G(3df,2p)	QCISD(T)/ 6-311+G(3df,2p)	ZPVE[c]/ kJ mol^{-1}	E_0/Hartree	$H_{298} - H_0$[c,d]/ kJ mol^{-1}	H_{298}/Hartree
MeOH	C_s	−115.382 009	−115.436 315	−115.468 799	−115.513 795	−115.546 279	129.4	−115.497 007	11.3	−115.492 719
$MeO^{\bullet}$	C_s	−114.709 905	−114.760 557	−114.798 706	−114.831 075	−114.869 224	94.0	−114.833 413	10.4	−114.829 451
Me_2NH **10**	C_s	−134.723 622	−134.772 481	−134.829 693	−134.861 121	−134.918 333	233.4	−134.829 424	14.2	−134.824 008
$Me_2N^{\bullet}$ **3**	C_{2v}	−134.067 271	−134.113 719	−134.174 396	−134.198 528	−134.259 205	195.6	−134.184 713	15.3	−134.178 897
$MeNH\dot{C}H_2$ **4**	C_1	−134.069 203	−134.118 674	−134.174 775	−134.206 056	−134.262 157	199.2	−134.186 283	14.3	−134.180 829
11	C_1	−249.422 997	−249.524 327	−249.625 361	−249.683 509	−249.784 543	321.2[e]	−249.662 196	23.0[e]	−249.653 455
12	C_1	−249.419 974	−249.521 605	−249.621 408	−249.681 718	−249.781 521	322.5[e]	−249.658 678	23.1[e]	−249.649 876
13	C_1	−249.463 081	−249.564 294	−249.657 096	−249.723 566	−249.816 368	330.9	−249.690 337	27.4	−249.679 886
14	C_1	−249.441 277	−249.541 066	−249.636 523	−249.697 687	−249.793 144	331.9	−249.666 724	26.5	−249.656 626
H_4C	T_d	−40.364 626	−40.379 176	−40.405 749	−40.405 705	−40.432 278	113.6	−40.388 933	10.0	−40.385 176
$H_3C^{\bullet}$	D_{3h}	−39.692 705	−39.707 191	−39.732 113	−39.731 401	−39.756 323	75.0	−39.727 773	10.9	−39.723 637
H_3N	C_{3v}	−56.383 217	−56.408 786	−56.428 407	−56.450 578	−56.470 199	86.6	−56.433 409	10.0	−56.433 409
$H_2N^{\bullet}$	C_{2v}	−55.709 963	−55.732 640	−55.754 436	−55.768 484	−55.790 280	48.2	−55.768 149	9.9	−55.768 149

[a] 1 Hartree = 2625.5 kJ mol^{-1}. [b] Geometrically-optimised structures. [c] To obtain these values, frequencies were scaled by a factor of 0.93 to account for their overestimation at this level of theory (see ref. 27). [d] Low frequencies (<500 cm^{-1}) were treated as molecular vibrations, rather than internal rotations. [e] One negative vibrational frequency, ignored in the calculation.

Table 4 Selected geometrical parameters for structures optimised at the (U)MP2(fc)/6-31G(d,p) level

Molecule	Point group	Bond lengths (Å), bond angles (°) and dihedral angles (°)
MeOH[a]	C_s	1.421 (CO), 1.086 (CH*), 1.093 (CH), 0.963 (OH), 106.5 (H*CO), 112.5 (HCO), 107.3 (COH), 108.6 (HCH)
$\mathrm{MeO^\bullet}$[b]	C_s	1.387 (CO), 1.097 (CH*), 1.092 (CH), 104.9 (H*CO), 112.5 (HCO), 110.9 (HCH)
$\mathrm{Me_2NH}$ **10**	C_s	1.456 (CN), 1.089 ($\mathrm{CH^1}$), 1.089 ($\mathrm{CH^2}$), 1.099 ($\mathrm{CH^3}$), 1.014 (NH), 111.7 (CNC), 108.7 (CNH), 109.6 ($\mathrm{H^1CN}$), 108.9 ($\mathrm{H^2CN}$), 114.1 ($\mathrm{H^3CN}$), −176.3 ($\mathrm{H^1CNC}$), 65.8 ($\mathrm{H^2CNC}$), −54.5 ($\mathrm{H^3CNC}$), −56.5 ($\mathrm{H^1CNH}$)
$\mathrm{Me_2N^\bullet}$ **3**	C_{2v}	1.445 (CN), 1.087 ($\mathrm{CH^1}$), 1.096 ($\mathrm{CH^2}$), 110.6 (CNC), 110.2 ($\mathrm{H^1CN}$), 110.9 ($\mathrm{H^2CN}$), 59.4 ($\mathrm{H^2CNC}$)
$\mathrm{MeNH\dot{C}H_2}$ **4**		1.393 ($\mathrm{C^1N}$), 1.453 ($\mathrm{C^2N}$), 1.080 ($\mathrm{CH^1}$), 1.080 ($\mathrm{CH^2}$), 1.089 ($\mathrm{CH^3}$), 1.088 ($\mathrm{CH^4}$), 1.094 ($\mathrm{CH^5}$), 1.010 (NH), 117.1 (CNC), 117.5 ($\mathrm{H^1CH^2}$), 115.2 ($\mathrm{NCH^1}$), 115.6 ($\mathrm{NCH^2}$), 113.0 ($\mathrm{HNC^1}$), 108.6 ($\mathrm{H^3CN}$), 109.4 ($\mathrm{H^4CN}$), 113.5 ($\mathrm{H^5CN}$), 176.9 ($\mathrm{H^1CNH}$), 43.6 ($\mathrm{H^1CNC}$), −56.8 ($\mathrm{C^1NC^2H^3}$), −174.6 ($\mathrm{C^1NC^2H^4}$), 63.5 ($\mathrm{C^1NC^2H^5}$)
$[\mathrm{MeO\cdots H\cdots NMe_2}]^\bullet$ **11**	C_1	1.392 (CO), 1.452 ($\mathrm{C^1N}$), 1.453 ($\mathrm{C^2N}$), 1.325 (O···H), 1.103 (N···H), 113.6 (COH), 110.2 ($\mathrm{C^1NH}$), 108.5 ($\mathrm{C^2NH}$), 112.2 ($\mathrm{C^1NC^2}$), 153.0 (NHO), 34.3 (COHN)
$[\mathrm{MeO\cdots H\cdots CH2NHMe}]^\bullet$ **12**[c]	C_1	1.399 (CO), 1.426 ($\mathrm{C^1N}$), 1.459 ($\mathrm{C^2N}$), 1.378 (O···H*), 1.189 (C···H*), 103.5 (COH*), 112.7 (NCH*), 113.1 ($\mathrm{C^1NC^2}$), 167.4 ($\mathrm{C^1H^*O}$), −40.9 ($\mathrm{COH^*C^1}$), −56.2 ($\mathrm{H^*C^1NC^2}$)
$\mathrm{MeOH\cdots {}^\bullet NMe_2}$ **13**	C_1	1.416 (CO), 1.445 ($\mathrm{C^1N}$), 1.443 ($\mathrm{C^2N}$), 0.973 (OH), 1.959 (N···H), 106.3 (COH), 153.1 (OHN), 112.1 ($\mathrm{C^1NC^2}$), −83.5 (COHN)
$\mathrm{MeO^\bullet\cdots HNMe_2}$ **14**	C_1	1.391 (CO), 1.456 ($\mathrm{C^1N}$), 1.456 ($\mathrm{C^2N}$), 2.289 (O···H), 1.015 (NH), 93.1 (COH), 143.8 (OHN), 111.7 ($\mathrm{C^1NC^2}$), 17.5 (COHN)
$\mathrm{H_4C}$	T_d	1.086 (CH)
$\mathrm{H_3C^\bullet}$	D_{3h}	1.074 (CH)
$\mathrm{H_3N}$	C_{3v}	1.013 (NH), 106.1 (HNH)
$\mathrm{H_2N^\bullet}$	C_{2v}	1.024 (NH), 102.7 (HNH)

[a] Staggered conformation: H* is the unique hydrogen atom attached to C. [b] H* is the unique hydrogen atom. [c] H* is the hydrogen atom being transferred.

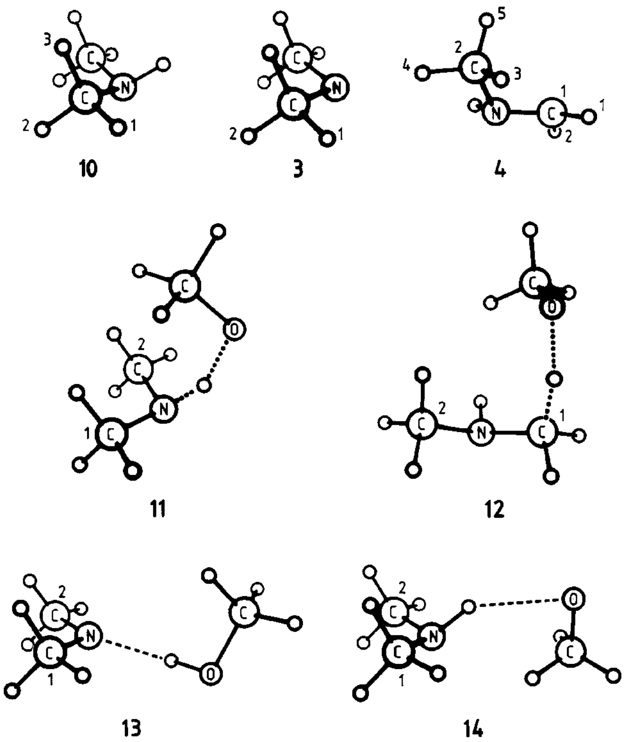


Fig. 7 Optimised structures determined by *ab initio* calculations at the (U)MP2/6-31G(d,p) level

G2(MP2) method as implemented in GAUSSIAN 94.[26] The values obtained by this procedure were 394 kJ $\mathrm{mol^{-1}}$ for the C–H bond and 400 kJ $\mathrm{mol^{-1}}$ for the N–H bond, in good agreement with the results derived by consideration of the isodesmic reactions (20) and (21).

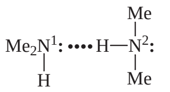
The calculated value of D_{298}(N–H) is appreciably greater than the experimental value[29a] of 383 kJ $\mathrm{mol^{-1}}$. However, a recent *ab initio* calculation by Jursic[30] has yielded 390 kJ $\mathrm{mol^{-1}}$ and the same author obtained still higher values using density functional methods [*e.g.* a calculation at the BLYP/6-31+G(d) level gave 394 kJ $\mathrm{mol^{-1}}$].‡

Burkey *et al.*[2b] originally reported that, like the N–H bond strength in the series $\mathrm{NH_3}$, $\mathrm{MeNH_2}$ and $\mathrm{Me_2NH}$, the C–H bond strength for the series of methylamines $\mathrm{MeNH_2}$, $\mathrm{Me_2NH}$ and $\mathrm{Me_3N}$ also showed a marked decrease with the degree of alkylation at nitrogen. However, Gela and Colussi[2a] found that the C–H bond in $\mathrm{Me_3N}$ was only slightly weaker than that in $\mathrm{MeNH_2}$. The experimental value of D_{298}(C–H) in dimethylamine reported by Burkey *et al.* was 364 kJ $\mathrm{mol^{-1}}$, much smaller than the value (390 kJ $\mathrm{mol^{-1}}$) calculated in the present work. Most recently, Wayner *et al.*[3a] have concluded that there is little or no dependence of D_{298}(C–H) on the degree of alkylation at nitrogen and have recommended a value of 386 kJ $\mathrm{mol^{-1}}$ for D_{298}(C–H) in dimethylamine, on the basis of *ab initio* calculations and photoacoustic calorimetric experiments (however, see the comments made above regarding this work).

The calculated activation enthalpies for abstraction of hydrogen from nitrogen (transition state **11**) and from carbon (transition state **12**) in dimethylamine by the methoxyl radical are 0.0 and 9.4 kJ $\mathrm{mol^{-1}}$, respectively and these values may be converted to Arrhenius activation energies by addition of *RT* at 298 K, to give 2.5 and 11.9 kJ $\mathrm{mol^{-1}}$, respectively.[31] The binding enthalpies of the hydrogen-bonded complexes **13** and **14**, relative to the separate radicals and hydrogen-bond donor molecules, were computed to be 21.7 and 8.3 kJ $\mathrm{mol^{-1}}$, respectively.

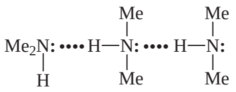
Discussion

Abstraction of hydrogen from dimethylamine by either $\mathrm{Bu^tO^\bullet}$ or $\mathrm{(Me_3Si)_2N^\bullet}$ takes place competitively from NH and CH groups. As the amine concentration is decreased, the relative extent of abstraction from nitrogen increases and this can be understood in terms of amine association by hydrogen-bonding to form first a dimer and then larger oligomers.[19] For example, in the hydrogen-bonded dimer **15** the bridging hydrogen atom would be expected to be unreactive towards abstraction.[32] If hydrogen-bonding is viewed as partial proton transfer, the terminal NH group and the methyl groups attached to $\mathrm{N^1}$ would



$$\mathrm{Me_2}\underset{\mathrm{H}}{\mathrm{N}}{}^{1}\!:\cdots\cdots\mathrm{H}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{N}}}{}^{2}\!:$$

15



$$\mathrm{Me_2}\underset{\mathrm{H}}{\mathrm{N}}:\cdots\cdots\mathrm{H}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{N}}}:\cdots\cdots\mathrm{H}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{N}}}:$$

16

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‡ Zero-point energies and thermal corrections were not taken into account in this work.

be expected to show slightly reduced reactivity compared with the corresponding groups in a free amine molecule. However, the methyl groups attached to N^2 might be a little more reactive than those in a free molecule and thus the relative rate of hydrogen abstraction from carbon should be about twice as large as for monomeric dimethylamine. Only the terminal NH groups should be reactive in higher oligomers, such as the trimer **16**, and hydrogen abstraction from carbon will become increasingly favoured as the extent of association increases.

The temperature dependence of the relative rates of hydrogen abstraction from NH and CH bonds in monomeric dimethylamine by *tert*-butoxyl radicals shows that the Arrhenius *A*-factor for abstraction from carbon is *ca.* 3.4 times larger than that for abstraction from nitrogen. This is reasonable because there are six times as many CH bonds as NH bonds per molecule. The activation energy for abstraction from nitrogen is *ca.* 4.6 kJ mol^{-1} less than that for abstraction from carbon and a similar value (4.2 kJ mol^{-1}), less accurate on account of the weaker EPR spectra involved, was obtained from similar experiments in the presence of THF, which also enabled the absolute rates of abstraction to be estimated. The absolute activation energies obtained for abstraction from NH and CH bonds by $Bu^tO^\bullet$ were *ca.* 6.2 kJ mol^{-1} and *ca.* 10.4 kJ mol^{-1}, respectively, and these values are in good agreement with the corresponding activation energies (2.5 and 11.9 kJ mol^{-1}, respectively) calculated by *ab initio* methods for abstraction of hydrogen from dimethylamine by the methoxyl radical.

The experimental activation energy for abstraction from the NH group is very small, close to (and probably limited by) that for diffusion in the reaction medium; the activation energy for abstraction from a CH group is larger, even though this is the weaker bond. Transfer of a hydrogen atom between electronegative elements, such as between two oxygen atoms in the reaction of an alkoxyl radical with a monomeric alcohol [eqn. (23)], typically involves a relatively small activation energy.[32a,33,34] Focussing attention on the three-centre–three-electron interaction in the transition state **17**, Zavitsas and co-workers have associated such low activation energies with the relatively small anti-bonding interaction between the atoms A and B when the A–B bond is weak, as is the case in a peroxide.[33,35] It has also been proposed that low activation energies for the transfer of a hydrogen atom between oxygen and nitrogen atoms can be rationalised in a similar way, because the O–N bond is also relatively weak.[9,35]

$$R^1O^\bullet + R^2OH \longrightarrow R^1OH + R^2O^\bullet \qquad (23)$$

$$\underset{\textbf{17a}}{[A{\uparrow}\cdots H{\downarrow}\cdots{\uparrow}B]^\ddagger} \longleftrightarrow \underset{\textbf{17b}}{[A{\downarrow}\cdots H{\uparrow}\cdots{\downarrow}B]^\ddagger}$$

As an extension of the well-known Evans–Polanyi equation, we recently proposed a simple algorithm [eqn. (25)], derived by correlation analysis, which relates the activation energies for 65 selected exothermic or thermoneutral H-atom transfer reactions of the type (24) to ground-state properties of the four

$$A^\bullet + H{-}B \longrightarrow A{-}H + B^\bullet \qquad (24)$$

species involved.[36] In eqn. (25), $f = (D_{AH}D_{BH}/D_{H_2}{}^2)$, where the

$$E_a = E_0 f + \alpha\Delta H^\circ(1 - d) + \beta\Delta\chi_{AB}{}^2 + \gamma(s_A + s_B) \quad (25)$$

quantities D_{AH}, D_{BH} and D_{H_2} are the bond dissociation enthalpies for AH, BH and H_2, respectively, and $\Delta H^\circ = (D_{BH} - D_{AH})$. The term $\Delta\chi_{AB}$ is the difference in Mulliken electronegativities of $A^\bullet$ and $B^\bullet$, the terms s_A and s_B are structural parameters characteristic of the radicals $A^\bullet$ and $B^\bullet$, and d is the 'delocalisation term', the value of which measures the extent of unpaired electron delocalisation in the radical $B^\bullet$. The parameters E_0, α, β and γ are constants, which were obtained from multiple regression analysis of the experimental data.

The $\beta\Delta\chi_{AB}{}^2$ term in eqn. (25) represents the part played by 'polar effects' in reducing the activation energy for H-atom transfer. In the same way that the strength of the bond between A and B in the molecule A–B is increased by ionic resonance when these two atoms or groups differ in electronegativity, so the transition state $[A\cdots H\cdots B]^\bullet$ for H-atom abstraction from H–B by $A^\bullet$ should be subject to increasing stabilisation by charge transfer as $\Delta\chi_{AB}{}^2$ increases. Of course, eqn. (25) would be expected to fail whenever factors that were not included in its derivation are important in the transition state.

Using eqn. (25) in conjunction with the bond dissociation enthalpies computed in this work, the activation energies for abstraction of hydrogen from the NH and CH groups in dimethylamine are calculated to be 21.4 and 2.1 kJ mol^{-1}, respectively.§ Although the calculated activation energy for abstraction from carbon is 8.3 kJ mol^{-1} less than the experimental value for E_{3b}, the discrepancy is not unduly large considering the uncertainty in the value of $\Delta\chi_{AB}$ and the exceptionally large contribution to the stability of the transition state for the formation of **4** that is predicted to arise from polar effects ($\beta\Delta\chi_{AB}{}^2 = -36.3$ kJ mol^{-1}).

The activation energy for abstraction of hydrogen from nitrogen by *tert*-butoxyl radicals calculated on the basis of eqn. (25) is 15.2 kJ mol^{-1} larger than the experimental value of E_{3a}. The algorithm (25) also overestimates the activation energy for abstraction of hydrogen from monomeric alcohols by alkoxyl radicals.[36] We have attributed the latter discrepency to the fact that eqn. (25) does not take account of any possible stabilising hydrogen-bonding-type interaction in the transition state for transfer of a hydrogen atom between electronegative atoms. A similar explanation may be applicable here for the abstraction of hydrogen from the NH group of dimethylamine by *tert*-butoxyl radicals, *i.e.* the transition state could be stabilised by an electrostatic interaction between the electropositive bridging hydrogen atom and the adjacent electronegative oxygen and nitrogen atoms. However, the transition state **11** and the hydrogen-bonded complexes **13** and **14** differ appreciably in geometry and in orbital overlaps so that it is not clear to what extent the transition state will retain the hydrogen-bond stabilisation present in **13** and **14**. In the transition state **11,** the in-flight hydrogen atom is part of a 3-centre–3-electron bond, while in the complexes **13** and **14** it forms part of a formal 3-centre–4-electron system. It is also possible that the relatively small anti-bonding interaction[33,35] between oxygen and nitrogen in the transition state could in part, or even in the main, be responsible for the discrepancy and further theoretical work will be necessary in order to clarify the situation. In principle, the algorithm (25) could be extended to take account of both an A–B anti-bonding interaction and hydrogen-bond stabilisation although, as we have noted previously,[36b] these two effects will often correlate for hydrogen-atom transfer between electronegative atoms.

The bis(trimethylsilyl)aminyl radical is more electrophilic than a dialkylaminyl radical and the NH bond in $(Me_3Si)_2NH$ is stronger than that in a simple dialkylamine;[15] in many ways $(Me_3Si)_2N^\bullet$ behaves like an alkoxyl radical, but it is more sterically-demanding than $Bu^tO^\bullet$.[15,38] Steric effects are probably

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§ The constants were taken from ref. 36*b*; the *s*-factor for $Me_2N^\bullet$ **3** was assumed to be the same as that for $H_2N^\bullet$. The ionisation energy of **3** was estimated to be *ca.* 9.21 eV, as the value for $H_2N^\bullet$ less the difference in the ionisation energies for Me_2NH and H_3N.[37] The electron affinity of **3** (1.0 eV)[37] and the ionisation energy of $MeNH\dot{C}H_2$ **4** (5.9 eV)[2b] were taken from the literature. The electron affinity of **4** should be more negative than that (−0.38 eV)[36a] of $MeO\dot{C}H_2$ and was, somewhat arbitrarily, taken to be −0.5 eV. The electronegativities of **3** and **4** are thus 5.11 and 2.70 eV, respectively. The parameter *d* was set to zero for formation of **3** and to 0.44 for formation of **4**.[36]

responsible for the different regioselectivities of $(Me_3Si)_2N^•$ and $Bu^tO^•$ in their reactions with dimethylamine and with propane, the former radical showing a greater tendency to abstract from the less-hindered terminal methyl groups. Similar differences in selectivity are shown in hydrogen-atom abstraction reactions of these two radicals with 2-methylpropane (Me_3CH).[15b]

The natural linewidth shown by the EPR spectrum of the dimethylaminyl radical **3** is rather large in the absence of hydrogen-bond donors. In the presence of alcohols considerable line-narrowing occurs, which may be related to the stiffening of the CNC bending vibration as a consequence of hydrogen-bonding between the alcoholic hydroxy group and the nitrogen σ lone pair, although the precise nature of the dominant line-broadening mechanism is not clear. Certainly, the cyclic pyrrolidinyl radical, in which the CNC angle will be much less easily deformed, shows narrower lines (see above), as apparently[11] does the cyclic aziridinyl radical, which is of similar size to $Me_2N^•$.

Rao and Symons[39] have reported that hydrogen-bonding to matrix-isolated $H_2N^•$ causes an increase in the isotropic nitrogen hyperfine coupling constant and it seems likely that this effect is a result of increased spin-polarisation of the σ lone-pair electrons when these are associated with a hydrogen-bond donor. A similar increase in a(N) is found when the π-radical **3** is fully protonated to give the aminium radical cation $Me_2\dot{N}\overset{+}{H}$ which is planar at nitrogen. The value of $a(6\ H_\beta)$ also increases upon protonation, as a consequence of more effective hyperconjugation because of the closer energetic match between the CH_3 π-group orbital and the N-2p$_\pi$ formal SOMO.¶[25a,40] The g-factor of **3** decreases from 2.0047 to 2.0036 as a result of protonation.[40]

Clearly the effects of alcohols on the EPR spectrum of **3** can be understood on the basis that hydrogen-bonding between the OH group and the σ lone pair of electrons on the nitrogen atom (see structure **13**) causes changes in the same direction as, but of smaller magnitude than, does full protonation. The mobile equilibrium shown in eqn. (26) presumably exists in solution

$$\underset{\mathbf{3}}{Me_2\dot{N}\colon} + (ROH)_n \rightleftharpoons \underset{\mathbf{17}}{Me_2\dot{N}\colon\cdots HOR(ROH)_{n-1}} \qquad (26)$$

and both association to form **17** and dissociation of this hydrogen-bonded complex are rapid on the EPR timescale, accounting for the absence of any detectable splitting from the proton attached to nitrogen. The observed values of a(N), a(6 H) and g will be weighted averages of the properties of **3** and **17** and will depend on the position of the equilibrium (26) and the spectroscopic parameters for **17**, which will in turn depend on the strength of the hydrogen-bond. The observed hyperfine splittings and their dependences on [ROH] can thus be understood in terms of the acidities and steric demands of the alcohols involved. However, even hydrogen-bonding to the relatively acidic trifluoroethanol is insufficient to promote the addition of **3** to alkenes to a point when this reaction becomes detectable by EPR spectroscopy below room temperature.

Experimental

EPR spectra were recorded during continuous UV irradiation of samples positioned in a standard variable temperature insert in the microwave cavity of a Varian E-109 or a Bruker ESP-300 spectrometer operating at 9.1–9.4 GHz.[14] The light source was a 500 W mercury discharge lamp (Osram HBO 500 W/2) and the optical system has been described previously.[14a] Samples were prepared using a vacuum line and were sealed in evacuated Suprasil quartz tubes (3 mm id, 0.5 mm wall). The temperature of the sample during photolysis was determined, using the method described previously,[14] by careful measurement of the value of $a(H_\beta)$ for the isobutyl radical in cyclopropane. The heating effect at full light intensity varied between 5 and 7 K depending on conditions.

Relative radical concentrations were determined by double integration of appropriate lines in each spectrum and/or by computer simulation of the composite spectrum; concentration ratios were extrapolated to zero UV irradiation time when necessary to overcome the effects of sample depletion. Care was taken to avoid selective saturation[10a] of the spectra. Computer simulations of spectra were obtained using a modified version of ESRSPEC2,[41] extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > \frac{1}{2}$, and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian. The experimental methods for determination of relative rate constants using the EPR method have been described in detail previously.[14,20,22]

Materials

Di-*tert*-butyl peroxide (98%, Aldrich) was washed repeatedly with 5% w/v aqueous sodium iodide containing 2% w/v sulfuric acid, until no more iodine was liberated. It was then washed successively with water, saturated aqueous sodium hydrogen carbonate, and saturated brine, before being dried ($MgSO_4$), passed down a column of basic alumina (activity 1) and finally distilled (bp 46–47 °C/76 Torr); it was stored under argon at 4 °C. Tetrakis(trimethylsilyl)hydrazine was prepared as described previously.[15b]

Dimethylamine (Aldrich) was freeze–thaw degassed, trap-to-trap distilled onto calcium hydride, left to stand at 0 °C and then trap-to-trap distilled into a storage vessel. Cyclopropane (Union Carbide) and dimethyl ether (Fluka) were used as received, apart from rigorous freeze–thaw degassing on the vacuum line. Tetrahydrofuran was distilled under argon from sodium diphenylketyl. *tert*-Pentyl alcohol was distilled from sodium metal under argon, CF_3CH_2OH and $(CF_3)_2MeCOH$ were kept over activated molecular sieves and distilled under argon; methanol (Aldrich 99.8% anhydrous grade) was used as received. 1,1-Di-*tert*-butylethylene was prepared as described in the literature[42] and *tert*-butyl vinyl ether (Aldrich) was used as received.

Tris(dimethylamino)phosphine (TDMAP, Aldrich) was distilled under reduced pressure and stored in sealed ampoules under argon. To reduce the possibility of any reaction between TDMAP and alcohols prior to photolysis, samples were kept in liquid nitrogen and thawed and mixed by repeated inversion in a solid CO_2–ethanol bath immediately before insertion into the EPR spectrometer.

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¶ The coupling constants for $Me_2\dot{N}\overset{+}{H}$ in 90% aqueous sulfuric acid at 304 K are a(N) = 19.28, a(6 H) = 34.27 and a(N*H*) = 22.73 G.[40]

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