Capto-dative Stabilisation in Amino-substituted Radicals

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The rotational barriers about the C–N bonds in aminoalkyl radicals, $H_2N\dot{C}HR$, were found to be significantly greater when R is an acceptor group than when R is an alkyl group; this is good evidence for capto-dative stabilisation of the ground state radicals.

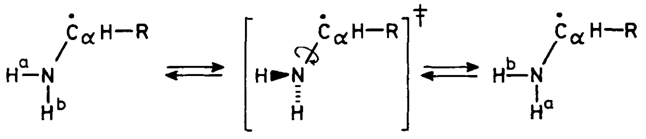
The proposal[1] that radicals would be stabilised by the combined interaction of donor and acceptor substituents at the same centre has been vigorously promoted by Viehe and co-workers in recent years.[2—4] This effect, termed 'capto-dative' (C-D) stabilisation by Viehe had previously been suggested, though under different names, by several other groups of workers.[5—7] Despite the wealth of applications, quantitative evidence in support of the C-D effect has been noticeably sparse. Some theoretical treatments provided supporting evidence,[8] while others indicated negligible C-D stabilisation.[9,10] Kinetic studies of the addition of alkyl radicals to C-D substituted alkenes yielded ambiguous results.[11] Thermochemical studies on the decomposition of 2,3-dimethoxy-2,3-diphenylsuccinonitrile by Rüchardt and coworkers failed to find any C-D effect.[12] The rates of dimerisation of C-D substituted methyl radicals were shown to be diffusion controlled; thus indicating the absence of kinetic stabilisation.[13] This does not, of course, preclude the possibility of thermodynamic stabilisation.[14]

Recently, Sustmann and co-workers determined the barrier to internal rotation in the 1-cyano-1-methoxyallyl radical (**1**).[15] In the transition state (**2**), *i.e.* on 90° rotation about the C(1)–C(2) bond, the unpaired electron is confined to the C-D substituted moiety. Thus, any stabilising C-D effect should cause a lowering in the transition state energy and hence give rise to *lower* rotational barriers in comparison with unstabilised allyl radicals. Sustmann *et al.* found the rotation barrier of (**1**) to be *ca.* 3 kcal mol^{-1}† lower than that of analogous radicals without C-D substitution.[15]

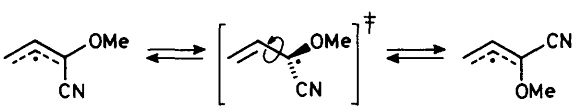
Aminoalkyl radicals (**3**) containing an acceptor substituent (R) should also be subject to C-D stabilisation. In the transition state for rotation about the C–N bond (**4**) the unpaired electron cannot be delocalised onto nitrogen and any C-D stabilisation is lost. It follows that if C-D stabilisation is significant the barriers to rotation about the C–N bonds in C-D substituted aminoalkyl radicals should be *greater* than those of analogous radicals without C-D substitution. We have developed an e.s.r. exchange broadening technique for determining rotational barriers in radicals with amino substituents[16,17] and we have now applied this to several substituted aminoalkyl radicals, some of which could exhibit C-D stabilisation.

The aminoalkyl radicals (**3**, R = Me, Pr^{i}, Bu^{t}, and CO_2Bu^{t}) were generated by photolysis of solutions of the appropriate amine in di-t-butyl peroxide, equations (1) and (2), in the cavity of the e.s.r. spectrometer. In each case hydrogen abstraction occurred mainly at C_α and (**3**) was the only observable radical. For (**3**, R = alkyl) well defined e.s.r. spectra were obtained which showed non-equivalent hyperfine splittings (h.f.s.) from the two amino hydrogens (Table 1). These amino hydrogen h.f.s. [$a(H_N)$] increased strongly with increasing temperature; a(N) showed a small increase with increasing temperature but $a(H_\alpha)$ was virtually temperature independent. The spectra from the alkyl substituted radicals (**3**, R = Me, Pr^{i}, Bu^{t}) all exhibited exchange broadening owing to rotation about the C–N bond in the temperature range 230—310 K with coalescence at *ca.* 260 K. Spectra were simulated assuming a two jump model using a modified version of Heinzer's program.[18] The rotational barriers, found by comparison of the experimental and simulated spectra are given in Table 2; in each case the measured pre-exponential factors were close to the 'normal' value of 10^{13} s^{-1}.

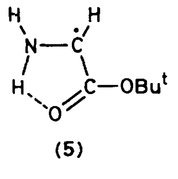
The C-D radical (**3**, R = CO_2Bu^{t}) also gave a well resolved spectrum (h.f.s. in Table 1) but in this case the amino hydrogen h.f.s. decreased with increasing temperature; this probably indicates they have negative signs.[17] Exchange line broadening was observed at much higher temperatures (400—470 K) with coalescence at *ca.* 470 K. Spectra could not be studied above 470 K because of boiling and decomposition and hence comparison with simulations was restricted to the region below coalescence; this is the main reason for the larger error limits in this case (Table 2). The C–N bond rotational barriers, V_0, Table 2, in the three alkyl substituted radicals are all identical to within the experimental error. The magnitude of the barrier (*ca.* 7.5 kcal mol^{-1}) is large in comparison with analogous C–C bond rotational barriers and this is the expected consequence of spin delocalisation onto nitrogen.[17] The barrier is evidently unaffected by the bulk of the alkyl substituent. The rotation barriers in the C-D radicals are all significantly greater than those of the aminoalkyl radicals. The increase, which is a measure of the C-D stabilisation, varies from 3 kcal mol^{-1} for (**3**, R = C≡CH) (the weakest acceptor) to *ca.* 7 kcal mol^{-1} for (**3**, R = CO_2Bu^{t}). In the latter case



(**3**) (**4**)



(**1**) (**2**)



(**5**)

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† 1 kcal = 4.18 kJ.

Table 1. E.s.r. parameters for aminoalkyl radicals $H_2N\dot{C}HR$ (**3**).[a]

R	Temp./K	$a(H_N)$	$a(H_N)$	$a(N)$	$a(H_\alpha)$	a(H, other)
Me	240	2.5	5.5	4.4	14.7	20.7 (3H)
Me_2CH	240	2.1	5.6	4.5	14.7	20.2 (1H)
Me_3C	240	2.0	6.2	4.3	14.6	
Bu^tOCO	240	4.6	5.1	6.0	13.3	

[a] H.f.s. in G, 1G = 10^{-4} T.

Table 2. C–N Bond rotation barriers in aminoalkyl radicals, $H_2N\dot{C}HR$ (**3**).

R	V_0/kcal mol^{-1}	log A/s^{-1}
Me	7.6 ± 0.4	13.2 ± 0.4
Me_2CH	7.3 ± 0.4	13.1 ± 0.4
Me_3C	7.5 ± 0.2	13.4 ± 0.4
Bu^tOCO	14.9 ± 1.2	13.2 ± 0.5
HC≡C	10.5 ± 1.2[a]	13.8 ± 0.7[a]
N≡C	$11 \quad \pm 2$ [a]	

[a] From reference 17.

intramolecular hydrogen bonding (**5**) may contribute to the large barrier. Stabilisation of this magnitude is in good agreement with that found for the rotation barrier in the C-D substituted allyl radical (**1**)[15] and with the results of *ab initio* calculations.[8]

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

$$Bu^tO\cdot + H_2NCH_2R \longrightarrow \underset{(\mathbf{3})}{H_2N\dot{C}HR} + Bu^tOH \qquad (2)$$

In conclusion, C-D substitution in aminoalkyl radicals lowers the ground state energy and hence the C–N bond rotational barrier is increased. The main effect of C-D substitution in allyl radicals is to decrease the transition state energy for C(1)–C(2) bond rotation and hence the rotational barrier is decreased. These two results are therefore complementary and reinforce the conclusion that C-D substitution leads to significant thermodynamic stabilisation in radicals.

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