Stabilising Influence of a Strong Acid Medium on Tertiary Aminium Radicals

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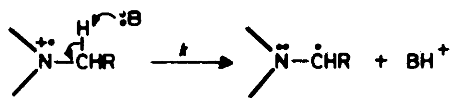
Summary The pseudo first-order rate constants for the disappearance of tertiary aminium radicals in solution reveal the stabilising influence of a strong acid medium.

Most saturated tertiary aliphatic aminium radicals have very short lifetimes in aqueous solution and thus only a limited number of these species have been observed directly by spectroscopic methods.[1] That the major cause of the short lifetimes of tertiary aminium radicals is their rapid loss of an α-proton to give an α-amino radical [equation (1)] has been elegantly demonstrated by Nelsen and Kessel[2] who generated the long-lived 9-t-butylazabicyclo[3.3.1]nonane radical cation. Loss of an α-proton from this species is difficult since the bridgehead α-protons are constrained to lie in the nodal plane of the *p*-orbital of the nitrogen of the radical cation. We report here how increasing the acidity of the medium can be used to increase the stabilities of the radical cations from tertiary aliphatic amines.



(1)

The Table records the pseudo first-order rate constants, as measured by e.s.r. spectroscopy, for the disappearance of the triethylaminium radical and some more limited data on a selection of other aminium radicals in trifluoroacetic-sulphuric acid solutions at 258 K. In a typical experiment a sample (0·3 cm^3) was removed from a solution of triethylchlorammonium chloride in a mixture of conc. sulphuric acid and trifluoroacetic acid (1·9 M H_2SO_4), and was thermostatted at 258 K in the cavity of the e.s.r. spectrometer before it was irradiated with a 100 W high-pressure mercury arc u.v. lamp. The lifetime of the radical cation was obtained by recording the decay with time of one of the more intense absorptions near the centre of the e.s.r. spectrum after the u.v. light was switched off.

Table. Pseudo first-order rate constants (k)[a] and half-lives ($t_{\frac{1}{2}}$)[a] for the disappearance of some tertiary alkyl aminium radicals[b] in acid solution at 258 ± 2 K.

Aminium radical	Conc. H_2SO_4 in CF_3CO_2H/mol l^{-1}	$-H_0$[c]	10^3 k/s^{-1}	$t_{\frac{1}{2}}$/min
$Et_3N^{\cdot+}$	0	3·0	60	0·20
$Et_3N^{\cdot+}$	0·23	6·2	38	0·33
$Et_3N^{\cdot+}$	0·94	7·3	18	0·66
$Et_3N^{\cdot+}$	1·9	8·1	6·6	1·8
$Et_3N^{\cdot+}$	4·4	9·0	5·1	2·3
$Et_3N^{\cdot+}$	5·7	9·9	4·1	3·0
$Et_3N^{\cdot+}$	9·4	10·0	0·98	12
$Et_3N^{\cdot+}$	16·8	10·5	0·25	45
$Me_3N^{\cdot+}$	1·9	8·1	23	0·5
$Pr_3N^{\cdot+}$	1·9	8·1	1·2	9·8
N-Methyl-pyrrolidinium	1·9	8·1	15	0·88

[a] Error in rate constants and half-lives is estimated to be ±30%. [b] All the radical cations gave e.s.r. spectra in accord with their reported structures. [c] H_0 values are based on primary aromatic amine indicators (H. H. Hyman and R. A. Garber. *J. Amer. Chem. Soc.*, 1959, **81**, 1847; C. H. Rochester in, 'Acidity functions,' Academic Press, New York, 1970).

Since the disappearance of the triethylaminium radical was first-order with respect to the concentration of the radical cation, self-destructive disproportionation or dimerisation processes can be ruled out in favour of either a unimolecular decay or a pseudo first-order solvent mediated proton elimination. The dramatic increase in stability of the triethylaminium radical with the acidity of the medium, especially in the more acidic solutions, suggests that the latter mechanism is more likely. Thus with increasing acidity the concentration of species capable of acting as a base (*e.g.*, unprotonated trifluoroacetic acid) for the removal of an α-proton from the radical cation [equation (1)] decreases. Preliminary studies using super acid media show that the lifetime of the triethylaminium radical can be increased still further; *e.g.*, in a conc. sulphuric acid–fluorosulphonic acid mixture (1·42 M H_2SO_4) at 258 K, $t_{\frac{1}{2}} = 63$ min, and in pure fluorosulphonic acid at 295 K, $t_{\frac{1}{2}} = 17$ min. The absence of spectra from the α-amino-radical suggests that this species is rapidly destroyed and is not stabilised by the reaction conditions.

The pseudo first-order rate constants for the disappearance of a selection of tertiary alkyl aminium radicals can be used to reveal the influence of stereoelectronic effects on the stabilities of the radical cations. Some preliminary results (Table) reveal that the lifetimes of the aminium radicals increase in the series $Me_3N^{+\bullet} < Et_3N^{+\bullet} < Pr_3N^{+\bullet}$, probably reflecting the increased electron donation and steric hindrance of the larger alkyl groups. Further, the *N*-methylpyrrolidinium radical, in which the nitrogen can attain a relatively unstrained planar configuration, has a lifetime between that of trimethyl- and triethyl-aminium radical.

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[2] S. F. Nelsen and C. R. Kessel, *J.C.S. Chem. Comm.*, 1977, 490.