9-Butylazabicyclo[3.3.1]nonane Radical Cation, the First Long-lived Saturated Amine Radical Cation

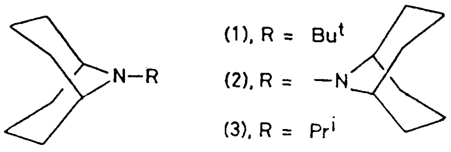
By Stephen F. Nelsen* and Carl R. Kessel

(*Department of Chemistry, University of Wisconsin, Madison, Wisconsin* 53706)

Summary The title amine gives a reversible cyclic voltammetry oxidation wave, and is the first saturated amine not to show electrochemically irreversible oxidation.

Although electron transfer has been shown to be the rate controlling step in many saturated amine oxidations, and interesting correlations of the peak potential for irreversible electrochemical oxidation with rate constants for oxidation[1] have appeared, in no case has it proven possible to measure the thermodynamically significant E° value for a saturated amine, amine radical cation couple,[2] presumably because of exceedingly short radical cation lifetimes under conditions where the amine is present. We report here that the title amine gives a cation radical with a long lifetime in neutral solutions, allowing measurement of E° for the oxidation.

Because rapid loss of a C_α–H proton from tertiary amine radical cations (leading to an easily oxidized aminoalkyl radical and hence very rapid destruction) seemed to be the cause for short lifetimes, we postulated that (**1**)† would have a far greater lifetime than previous systems studied. We recently demonstrated a huge effect on the deprotonation rate for C_α–H hydrogens by their incorporation at the bridgeheads of a 9-azabicyclo[3.3.1]nonanyl ring system by showing that (**2**) gives a dication which persists for at least several seconds in acetonitrile,[3] in contrast to other tetra-alkylhydrazines, which give totally irreversible second oxidation waves in cyclic voltammetry (C.V.) experiments. Compound (**1**)† was obtained by Wolff–Kishner reduction of the 3-keto-compound, prepared by the method of Wiseman.[4] It shows a reversible C.V. wave in acetone



---

† Spectral data are in accord with the reported structure; empirical formula was established by high resolution mass spectroscopy.

($E^\circ = +0{\cdot}74$ V *vs.* S.C.E., $\Delta E_p = 65$ mV) even at a 20 mV s^{-1} scan rate. The electrochemical reversibility of the oxidation of (**1**) demonstrates that even formal localization of charge on a single nitrogen does not result in the very low heterogeneous electron-transfer rate constants which have been suggested on theoretical grounds for radical anions with small π systems.[5] The remarkable persistence of $(\mathbf{1})^{+\cdot}$ is demonstrated by its e.s.r. spectrum, which shows an apparent lifetime of several hours for methylene chloride solutions prepared by tris-(*p*-bromophenyl)amine cation–hexachloroantimonate oxidation. The e.s.r. spectrum consists of a 1:1:1 triplet [a(N) = 19·5 G] of multiplets (many *ca.* 0·2 G splittings could be resolved), $g = 2{\cdot}0041$. The nitrogen splitting and *g*-factor are comparable to those reported for other trialkylamine radical cations,[6] and are clearly different from those of the nitroxide of the compound after loss of the t-butyl group,[7] which might conceivably have been formed (although no oxygen was supposed to have been present, the mis-identification of nitroxides as other radicals has frequently occurred).

The introduction of an α-hydrogen not constrained to lie in the nodal plane of the formal charge-bearing *p*-orbital at nitrogen results in a dramatic decrease in the radical cation lifetime. Thus (**3**),† prepared by sodium cyanoborohydride reductive alkylation of the NH-compound with acetone, gives only a totally irreversible C.V. oxidation wave ($E_p = +0{\cdot}82$ V at 0·5 V s^{-1}, at 25 °C) even at −60 °C and 20 V s^{-1} scan rate; the radical cation from (**1**) has a lifetime at least 10^6 times longer than that from (**3**).

(*Received*, *27th April* 1977; *Com.* 401.)

---

[1] L. A. Hull, B. T. Davs, D. H. Rosenblatt, and C. K. Mann, *J. Phys. Chem.*, 1969, **73**, 2142; J. R. Lindsay Smith and D. Masheder, *J.C.S. Perkin II*, 1976, **47**, and references therein.

[2] Reversible waves have been observed for 1,4-diazabicyclo-octane and two other compounds in which the positive charge appears to be equally shared by two nitrogen atoms; for a review, see J. K. Kochi, 'Free Radicals,' Wiley, New York, 1973, Vol. 2, p. 565.

[3] S. F. Nelsen and C. R. Kessel, *J. Amer. Chem. Soc.*, 1977, **99**, 2392.

[4] J. R. Wiseman, H. O. Krabbenhoft, and R. E. Lee, *J. Org. Chem.*, 1977, **42**, 629.

[5] J. M. Hale, in 'Reactions of Molecules at Electrodes,' ed. N. S. Hush, Wiley–Interscience, New York, 1971, p. 229.

[6] Trimethylamine cation, 20·6 G: R. W. Fessenden and R. Neta, *J. Chem. Phys.*, 1972, **76**, 2857; 1-Aza-adamantane and quinuclidine cations, 21·6 and 25·1 G, respectively: W. C. Danen and R. C. Rickard, *J. Amer. Chem. Soc.*, 1975, **97**, 2303.

[7] G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, 1973, **95**, 6395.