Generation and Reactivity of Aminyl and Aminylium Radicals

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Summary Photolysis of *N*-nitropiperidine under neutral conditions generates the piperidinyl radical and under acidic conditions the piperidinylium radical, indicated by their addition reaction with cyclohexene.

It has been claimed[1,2] that the aminyl radicals generated from tetra-alkyltetrazenes do not undergo addition to a simple double bond. In contrast, the aminyl radicals (or the metal-complexed aminyl radicals) generated from chloramine[2,3] and nitrosamine[4] decompositions add to olefins very efficiently. We now demonstrate that nitramine photolysis can generate aminyl or aminylium radicals depending on the solution acidity, and that these radicals differ substantially in reactivity.

One might reasonably expect nitramine photolysis to cause homolysis of the N–N bond, although there are literature reports indicating otherwise.[5] This is considered to be the best model reaction since a nitramine remains unaffected under weakly acidic conditions in which an aminyl radical (pK_a *ca.* 7) is rapidly protonated. Irradiation through a Vycor filter of *N*-nitropiperidine (1 g) in MeOH, 0·05 N in HCl, in the presence of cyclohexene (0·65 g) under nitrogen gave a mixture of the addition products (2-nitro- and 2-methoxy-1-piperidinocyclohexanes, 2-piperidinocyclohexanone oxime and a piperidinocyclohexene). The same reaction under oxygen gave a mixture of unstable *cis*- and *trans*-1-nitrato-2-piperidinocyclohexanes which were immediately reduced by lithium aluminium hydride to the corresponding *cis*-alcohol (m.p. 83—85 °C) and *trans*-alcohol (m.p. 30—32 °C) in 71% yield and a 1 : 1 ratio. This reaction resembles nitrosopiperidine photoaddition in weakly acidic conditions under nitrogen and oxygen in which the piperidinylium radical acts as the reactive intermediate.[4,6] A similar photolysis in neutral MeOH under nitrogen gave piperidine and *N*-formylpiperidine which were derived by hydrogen abstraction of the piperidinyl radical from MeOH; no addition product to cyclohexene could be detected. The photoreactions are illustrated in equations (1) and (2).

$$C_5H_{10}NNO_2 \xrightarrow[\text{MeOH}]{h\nu} \cdot NO_2 + C_5H_{10}N\cdot \rightarrow \text{H-abstraction} \qquad (1)$$

$$C_5H_{10}N\cdot + H^+ \rightleftharpoons C_5H_{10}NH\cdot^+ \xrightarrow[C_6H_{10}]{\qquad} \text{Addition} \qquad (2)$$

The quantum yield of nitropiperidine disappearance in neutral MeOH is 4·8 while in 0·1N—2N H_2SO_4 either in the presence or absence of oxygen and cyclohexene it is 7·4—7·8. These data suggest that the reactive species is the piperidinyl radical in neutral photolysis and the piperidinylium radical in acidic photolysis.

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[1] S. Shih, R. J. Buenker, S. D. Peyerimhoff, and C. J. Michejda, *J. Amer. Chem. Soc.*, 1972, **94**, 7620; *cf.* B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1961, 1228.

[2] R. S. Neal, N. L. Marcus, and R. G. Scheppers, *J. Amer. Chem. Soc.*, 1966, **88**, 3051.

[3] F. Minisci, R. Galli, and G. Pollina, *Chim. Ind.* (*Milan*), 1965, **47**, 736; F. Minisci, R. Galli, and M. Cecere, *ibid.*, 1966, **48**, 132.

[4] Y. L. Chow, *Accounts Chem. Res.*, 1973, **6**, 354.

[5] D. V. Banthorpe and J. A. Thomas, *J. Chem. Soc.*, 1965, 7158; J. M. Flournoy, *J. Chem. Phys.*, 1962, **36**, 1106; K. Suryanarayanan and S. Bulusu, *J. Phys. Chem.*, 1972, **76**, 496; J. W. Bodnar and C. Rowell, *J. Chem. Phys.*, 1972, **56**, 707.

[6] Y. L. Chow, J. N. S. Tam, C. J. Colón, and K. S. Pillay, *Canad. J. Chem.*, 1973, **51**, 2469.