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A FACILE GENERATION OF RADICAL CATIONS VIA THE ACTION OF NITROXIDES

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Abstract: Radical cations of aromatic amines and heteroaromatics were generated via the action of nitroxides in methylene chloride in the presence of trifluoroacetic acid.

Interest in radical cations has dramatically expanded since last decade. Chemical methods which have been used to generate radical cations involve oxidation in concentrated sulfuric acid, oxidation by Lewis acids, by halogens and by metal ions etc.[1] We wish to report in this communication a simple method for producing radical cations by stable nitroxides: 2,2,6,6-tetramethyl-4-chloropiperidinyl-1-oxy (1a), 2,2,6,6-tetramethylpiperidinyl-1-oxy (1b) and 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxy (1c).

1a and the substrates (2 - 8) were mixed in degassed methylene chloride containing 1 - 7 % trifluoroacetic acid (TFA), then the sample tube was placed into the cavity of Bruker 200D ESR Spectrometer. It was observed that the ESR signal of 1a diminished gradually while another signal appeared and increased in intensity. Substrates which have been studied include p-phenylenediamine (2), N,N,N',N'-tetramethyl-p-phenylenediamine (3), thianthrene (4), Phenothiazine (5), N-methylphenothiazine (6), carbazole (7) and triphenylamine (8). Computer simulation of the spectra obtained shows that the corresponding radical cations were formed from 2 to 7; in the case of 8, the radical cation of N,N,N',N'-tetraphenylbenzidine was obtained, apparently via dimerization of the intermediate triphenylamine radical cation followed by oxidation. The rate of these reactions was dependent upon both the character of the substrate and the concentration of TFA. For example, the reaction between 1a and 2 proceeded quite slowly, and after 120 minutes residual 1a was still observed, while the reaction between 1a and 3 went very fast, only a few minutes after mixing the signal of 1a disappeared, leaving alone that of $3^{+\cdot}$. Representative spectra are illustrated in Figures 1 and 2. Similar results were obtained when radical 1b or 1c was used in lieu of 1a. No ESR signal was observed under the same experimental conditions in the absence of 1, however.

It is known that nitroxide is a weak oxidant, e.g., vitamin C and cys-

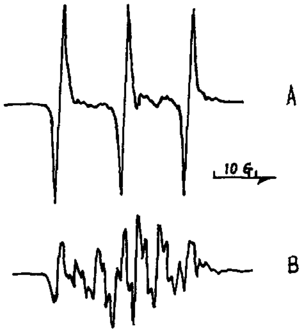


Fig.1. ESR spectra of 1a and $2^{\dagger}$, A. 10 min., B. 120 min. after mixing (10^{-2}M 1a and 2 in CH_2Cl_2 containing 6.7 % TFA)

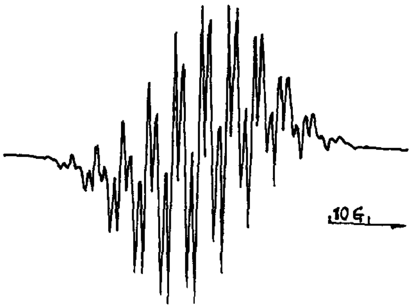
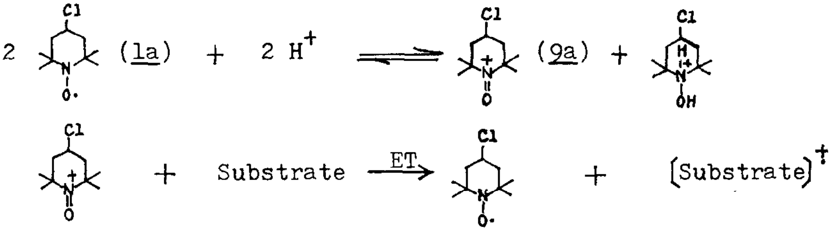


Fig.2. ESR spectra of $3^{\dagger}$, 5 min. after mixing (10^{-2}M 1a and 3 in CH_2Cl_2 containing 3 % TFA)

teine can be oxidized by a nitroxide via ET process [2,3]. In the present case, however, no reaction was observed in the absence of TFA, indicating that electron transfer did not take place directly between 1a and the substrates. Recently Semmelhack et al.[4] reported that active oxidizing agent oxoammonium ion (in our case, 9) was formed during an electrooxidation reaction of alcohols mediated with nitroxides. It was also proposed [5] that oxoammonium ion was formed from the disproportionation of nitroxide in the presence of hydrogen chloride. The nitroxide 1a is extremely stable in pure methylene chloride but its ESR signal decayed rapidly after the addition of TFA and then reached a relative stable level. Thus it seems likely that the nitroxide 1a disproportionates firstly to the more active oxidant 9a in the presence of TFA and the latter oxidizes the substrate to its radical cation by ET pathway. TFA can also serve as a stabilizing agent for the radical cations [6,7]. Detailed kinetic investigation is in progress.



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