Tetrahedron Letters,Vol.30,No.14,pp 1849-1852,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

A CATION RADICAL FROM 2,6-DIMETHOXYPYRIDINE : INVESTIGATIONS BY IN-SITU RADIOLYSIS ESR

Sıddık İÇLİ

Department of Chemistry, Ege Üniversitesi İZMİR, Turkey

INTRODUCTION

Aromatic compounds are known to form radical cations in non aqueous systems(1), oxidation in strong acids(1,2), electrolytic methods(3) and reactions with metal ions(4) are the routes to form radical cations. The radiolytic procedures in the presence of metal ions were used for the detection of radical cations in aqueous solutions. It has been reported by Schulte-Frohlinde et.al.(5,6) that radical cations may be important in aromatic hydroxylation. Thus the direct proof for the intermedicate existence or radical cations in OH reactions with aromatic systems and the evidences to the mechanism of their formations carries value.

Methoxylated benzenes were studied, to form cation radicals in reaction with OH radicals, Tl^{+2} , Ag^{+2} and SO_4^{-2} in aqueous solution (5,6). Tl^{+2} and Ag^{+2} were produced by reaction of OH with Tl^{+} and Ag^{+} respectively. Some conformational isomers of p-dimethoxybenzene cation radicals have been found at in-situ-radiolysis e.s.r. studies(6). In relation, we have investigated the 2,6-dimethoxypyridine at in-situ-radiolysis e.s.r. for the detection of cation radical.

EXPERIMENTAL

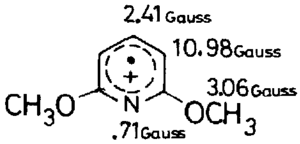
2,6-Dimethoxypyridine was obtained from EGA and was used as received. The in-situ-radiolysis e.s.r. experiments were carried out as described(7). The concentration of the substrate was 2 mM in N_2O saturated solutions. The substrate concentration was kept at 0.2 mM when 2 mM $AgNO_3$ or 1 mM

Tl_2SO_4 was present.

The product analysis for methanol formation was conducted as described(7).

RESULTS AND DISCUSSION

The 2 mM 2,6-dimethoxypyridine in N_2O saturated acidic (pH= 2-4) aqueous solution yielded the cation radical without even the presence of metal salts (Ag^{+2} or Tl^{+2}) at in situ radiolysis e.s.r. studies(Figure 1). Same spectrum was obtained with 0.2 mM substrate 1 mM $TlSO_4$ aqueous solutions at pH range of 2-4. The e.s.r. parameters of the fitted e.s.r. spectrum is shown below :



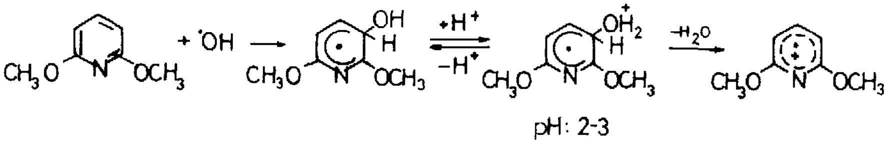
pH: 2.0 - 4.0

g: 2.00325

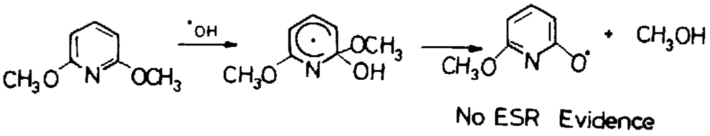
Coupling parameter for all the methyl protons were same.

No conformational isomeric behaviour of methoxy groups were detected in e.s.r. . Cation radical formed on protonation and dehydration of OH-adduct radical, according to the scheme below, is the product of a primary process, as flow rate experiments pointed :

Cation Radical Formation



A product analysis study was done in order to search for methanol abstraction upon an ipso attack, as shown on the scheme below :



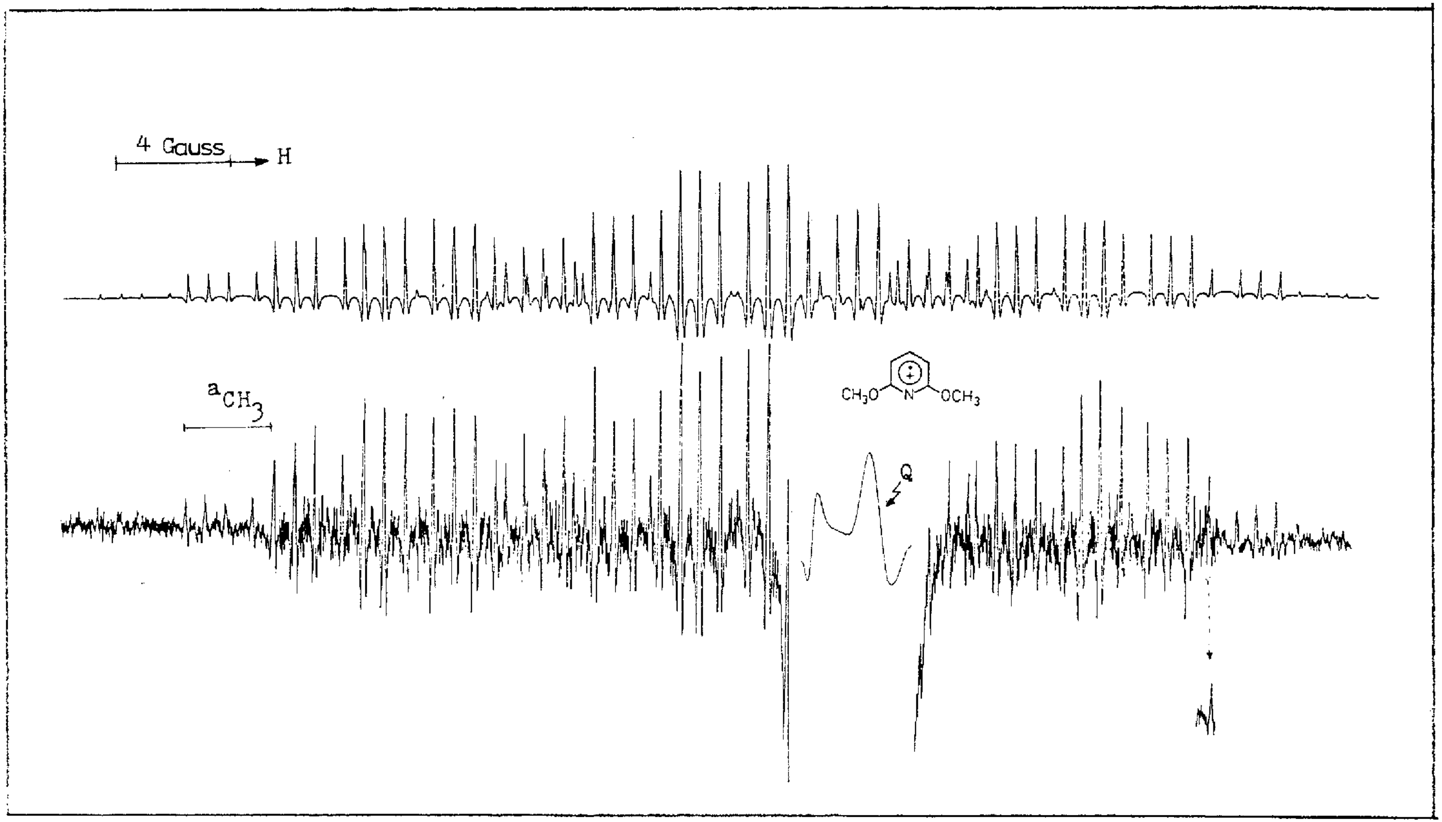


Figure 1 : The e.s.r. spectrum of 2,6-Dimethoxypyridine in aqueous solution.

The yield of methanol was very low ($G^{MeOH} = 0.37$) and no e.s.r. evidence was found for a phenoxyl type radical probably due to the very low yield, i.e. $G = 0.37$, of methanol abstraction. Thus it can be suggested that at low pH values (2-4) the formation of cation radical as in above mechanism is dominant on the reaction of hydroxyl radical with 2,6-dimethoxypyridine.

ACKNOWLEDGEMENTS

This work is mainly carried out at Max-Planck Institute for Radiation Chemistry, Mülheim-Ruhr, W.Germany. The author thanks to the Institute for providing research facilities.

REFERENCES

1. G.Vincow, "Radical Ions", E.T.Kaiser, and L.Kevan, Ed.Interscience, New York, N.Y. 1968.
2. P.D.Sullivan and N.A.Brette, J.Phys.Chem. **79**, 474 (1975)
3. A.Ronlan, J.Coleman, O.Hammerich and V.D.Parker, J.Am.Chem.Soc. **96**, 845 (1974).
4. I.H.Nelson, J.K.Kochi, J.Am.Chem.Soc., **95**, 5060 (1973).
5. P.O'Neill, S.Steenken and D.Schulte-Frohlinde, Angew.Chem.Int.Ed.Engl. **14**, 430 (1975).
6. P.O'Neill, S.Steenken and D.Schulte-Frohlinde, J.Phys.Chem., **79**, 2773 (1975).
7. P.O'Neill, D.Schulte-Frohlinde and S.Steenken, Farad.Dicuss.Chem.Soc., **63**, 141 (1978).

(Received in UK 3 February 1989)