Short Communications

Pakistan J. Sci. Ind. Res., Vol. 16, No. 6, December 1973

HUCKEL MOLECULAR ORBITAL CALCULATION AND SPIN POLARIZATION PARAMETER IN A TRIVALENT NITROGEN: TRIS-*p*-NITROPHENYLAMINE CATION

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(Received July 23, 1973)

Nitrogen hyperfine splitting constant A^N for tris-*p*-nitrophenylamine cation has been reported[1] to be 10.75. But no attempt has been made to do molecular orbital calculations and hence to calculate the spin polarization parameters in this case. A simple Huckel molecular orbital calculation has been carried out and Q^N_{CC} in more-than-one-term equation[2]

$$A^N = Q^N_{NN} P^{\pi}_N + Q^N_{CC} \sum P^{\pi}_C$$

has been calculated.

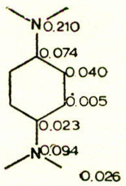

Fig. 1. Huckel spin density distribution in nitrophenylamine cation. The parameters used are taken from literature.[5]

The Huckel spin density distribution[5] is given in Fig. 1 at the atomic positions of the tris-*p*-nitrophenylamine cation. From the spin densities on the central nitrogen atom and adjacent carbon atoms and $Q^N_{NN} = 37$, which has been obtained using HMO method in dihydropyrazine cation,[3] the value of Q^N_{CC} is calculated to be 13.6 gauss. Earlier the value of Q^N_{CC} have been reported to be —2, —4, +2.6, and 9.8, but no value of Q^N_{CC} for a trivalent nitrogen had been reported.[4]

References

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CYCLIC VOLTAMETRIC STUDIES

Part I. 1-Ethyl-4-Carbomethoxypyridinium Iodide in Acetonitrile

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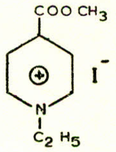
(Received July 5, 1973)

During the cyclic voltametric studies of 1-ethyl-4-carbomethoxypyridinium iodide(I) in acetonitrile, we believe what we observed is the reduction of either the charge transfer complex or of pyridinium iodide–mercury complex.



The following facts and observations led us to believe so:

1. 1-Ethyl-4-carbomethoxypyridinium perchlorate in acetonitrile (with 0.1M tetra-*n*-butylamonium perchlorate (TBAP) as supporting electrolyte) gives only one reversible wave.[1]

2. 1-Ethyl-4-carbomethoxypyridinyl radical reacts with tetrachloromethane with the rate constant 3.3 M^{-1} sec^{-1} in acetonitrile (there is no solvent effect, it is an atom abstraction reaction).[2]

3. 1-Ethyl-4-carbomethoxypyridinium cation (with perchlorate anion) in 1,2-dimethoxy ethane (DME) (with 0.1M tetra-*n*-butylammonium perchlorate as supporting electrolyte), with *Z* value 66, does not give a reversible wave in presence of 4-nitrobenzyl chloride[4] (5×10^{-4} molar) where it is known that pyridinyl radical reacts with 4-nitrobenzyl chloride with the rate constant linearly depending upon *Z* value of the solvent.[5]

Against these facts we observed:

1. 1-Ethyl-4-carbomethoxypyridinium iodide (1×10^{-3} molar) in acetonitrile (with 0.1M TBAP) gave two perfectly reversible waves, the second wave 0.45 volt cathodic to first wave.

2. The reduced species of 1-ethyl-4-carbomethoxypyridinium iodide in MeCN (with 0.1M TBAP), reduced at first reduction potential, does not react with tetrachloromethane (about 1M) appreciably, since at 33 mV/sec scan rate, the first reduction wave remains

completely reversible in presence of 1M tetrachloromethane (showing $t_{\frac{1}{2}} > 10$ sec).

3. The I_p is linearly related to the concn of 1-ethyl-4-carbomethoxypyridinium iodide which means that the equilibrium (a) is appreciably shifted towards the right

$$Py^+ + I^- \rightleftarrows (Py^+, I^-) \quad (1)$$

While there is possibility that tetrachloromethane might be excluded from the charge region around the electrode, we believe that the pyridinium iodide charge transfer complex[6] is reduced, at the first reduction potential, and before it can form pyridinyl radical and iodide ion could diffuse into the bulk, it gets further reduced (at second reduction potential). Or under the influence of electric field mercury forms a complex (PyHgI) with pyridinium iodide, which gets reduced reversibly, at first reduction potential, and gets further reduced (reversibly) at second reduction potential

Experimental

The cyclic voltamogram was recorded using Heath polarographic assembly with servorecorder attached to it. The hanging mercury drop electrode was constructed using gold wire which has been found to work without giving any trouble.[4] A 1½-in and about 20 gauge gold wire was used as reference electrode. 1-Ethyl-4-carbomethoxypyridinium iodide (m.p. 111–12°C) was supplied by Dr. Hajdu. Fisher reagent grade acetonitrile, without further purification, has been found to be satisfactory. Tetrabutyl ammonium perchlorate (Eastman, white label) was used directly and has been found to be satisfactory.

Acknowledgement. We are grateful to Dr. J. Hajdu, State University of New York, Stony Brook, for the sample of 1-ethyl-4-carbomethoxypyridinium iodide.

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