

1159. The Electron Spin Resonance Spectra of Some Arylammonium Radical-cations.

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By using high flow rates it has been possible to obtain electron spin resonance (e.s.r.) spectra of radical-cations $p\text{-R}'\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2$ provided that R' is an electrophilic group. The spectra which could be analysed are listed.

THE electron spin resonance spectra of the short-lived radical-cations, $(p\text{-R}'\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2)^+$ (I), of $p\text{-NN}$ -dimethylaminobenzaldehyde and of p -aminobenzoic acid were reported from this laboratory in 1962.¹ We have now extended the study of the oxidation of aromatic amines, in our flow apparatus,² by ceric sulphate and report splitting constants for the radicals (I) listed in Table 1. In general, even with the fastest safe flow rates, distinct spectra could be obtained only from amines having electrophilic substituents R' even when the concentrations of the reactants were increased until solubility became a limiting factor. Table 1 gives the minimum concentration of amine that had to be used, with an equivalent amount of oxidant, to give a distinct e.s.r. signal. Of other primary amines, for R = H, spectra could not be detected for R' = H, Me, HO₂C·CH₂, AcNH, F, or Br in 0·05M-solutions and were too indistinct for resolution for R' = Cl and for both α - and β -naphthylamine; for R = Et, spectra could not be detected for R' = H, OMe, or Br. From dimethylaniline, diphenylamine, and phenylhydrazine we also failed to obtain spectra. Since the decay rate of arylamino-radicals is known to be very high,³ a limiting factor may be the rate of one-electron oxidation of the arylamino-cations; unfortunately no suitable alternative oxidants have been found.

The oxidation of NN -dimethyl- p -nitrosoaniline gave a more stable radical-cation, but analysis showed that it was of quinonoid type, $(\cdot\text{ON}:\text{C}_6\text{H}_4:\text{NR}_2)^+$.

TABLE 1.
Hyperfine splitting constants of radical-cations, $p\text{-R}'\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2$.

| Parent amine | | Minimum concn. (M) | MeOH (% v/v) | L.W. (Oe) | S/N | Splitting constants (Oe) | | | |
|--------------|--------------------|--------------------|--------------|-----------|-----|--------------------------|----------------|------------------|--------------|
| R | R' | | | | | $a_{\text{N-R}}$ | a_{N} | $a_{\text{C-H}}$ | |
| | | | | | | <i>ortho</i> | <i>meta</i> | | |
| Me | CHO | 0·001 | 0 | 0·5 | 7 | 12·7 | 10·8 | 5·4 | 1·8 |
| Me | CO ₂ H | 0·001 | 0 | 0·6 | 7 | 12·7 | 10·8 | 5·4 | 1·8 |
| Me | NO ₂ | 0·002 | 30 | 0·7 | 2 | 13·8 | 11·9 | 5·7 | 1·9 α |
| (H | NO ₂ | 0·01 | 30 | 0·8 | 0·2 | 9·5 | 7·8 | 5·7 | 1·8) |
| Et | CHO | 0·001 | 0 | 0·7 | 2 | 6·4 | 10·7 | 5·4 | 1·8 |
| H | CO ₂ H | 0·01 | 10 | 0·7 | 4·5 | 9·6 | 7·8 | 5·8 | 1·9 |
| H | SO ₃ H | 0·1 | 10 | 0·7 | 3 | 9·6 | 7·8 | 5·8 | 1·9 |
| (H | COMe | 0·01 | 10 | 0·6 | 1 | 9·6 | 7·8 | 5·8 | 1·9) |
| (H | CO ₂ Et | 0·05 | 10 | 1·0 | 1 | 9·6 | 7·8 | 5·8 | 1·9) |
| H | OH | 0·01 | 10 | 1·1 | 4·3 | 8·3 | 7·3 | 4·0 | < 0·6 |
| (Me,H | OH | 0·01 | 10 | 0·9 | 1·0 | { 8·6 (H) 14·3 (Me) } | 8·6 | 4·3 | < 0·7) |
| (H | OMe | 0·2 | 0 | 0·7 | 3·3 | ? | ? | 4·3 | < 0·4) |
| H | OEt | 0·2 | 0 | 0·8 | 4·2 | 8·3 | 6·9 | 4·2 | < 0·4 |

L.W. = Average line width of clearly resolved lines.

S/N = Signal:noise ratio for the weakest definable line (C-H split).

$a_{\text{N-R}}$ = Splitting constant for N-H or for C-H of N-Me, etc.

a = Splitting constant for N of NO₂ group = 1·9.

Data given in brackets are tentative assignments from poorly resolved spectra, which however resemble those of analogous, more definable radicals.

¹ T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 1962, 253.

² W. T. Dixon and R. O. C. Norman, *J.*, 1963, 3119.

³ E. J. Land and G. Porter, *Trans. Faraday Soc.*, 1963, 59, 2035.

DISCUSSION

(a) *The Hyperfine Splitting Constants.*—Table 1 shows that the hyperfine splitting, a_N , due to the nitrogen nucleus is smaller when $R = H$ than when $R = \text{alkyl}$, but the aromatic splitting constant $a_{C-H, \text{ortho}}$ increases very little in compensation. Both with p -substituted aryloxy-radicals⁴ and with the radical-anions of aromatic nitro-compounds⁵ it has been found that $a_{C-H, \text{ortho}} - a_{C-H, \text{meta}} = \text{constant}$, indicating that these aromatic radicals have a negative electron spin density at the *meta*-position. This holds for the arylamino-cations (I) also, but Table 2 shows that the constant depends on the type of radical concerned, and on the amount of overall electron spin density associated with the aromatic ring ($a_{C-H, \text{ortho}}$ can be taken as a measure of this).

TABLE 2.

Splitting constants for radicals $p\text{-HO}_2\text{C}\cdot\text{C}_6\text{H}_4\text{X}$.

| X = | (NO ₂) ⁻ | (·NMe ₂) ⁺ | (·NH ₂) ⁺ | O· |
|------------------------------|---------------------------------|-----------------------------------|----------------------------------|-----|
| a_N | 12.6 | 10.8 | 7.8 | — |
| $a_{C-H(\text{ortho-meta})}$ | 2.25 | 3.6 | 3.9 | 4.6 |
| $a_{C-H, \text{ortho}}$ | 3.4 | 5.4 | 5.8 | 6.8 |

(b) *The Radical-cation of p-Aminophenol.*—One-electron oxidation of p -aminophenol could give the tautomeric radicals ($p\text{-HO}\cdot\text{C}_6\text{H}_4\cdot\dot{\text{N}}\text{H}_2$) (II) or ($p\text{-}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_3^+$) (III). Table 1 shows that the radicals formed in acid solution from p -aminophenol and from p -phenetidine have very similar splitting constants, indicating that the radical is a resonance hybrid of type (II) and certainly not an ammonium salt (III). In both these radicals the low values of a_N and of $a_{C-H, \text{ortho}}$ show however that a significant fraction of the total electron spin density must be associated with the oxygen atom.

EXPERIMENTAL

Purified amines were used in water or aqueous methanol. Table 1 shows the percentage of methanol required to obtain the necessary concentration of amine in the flow chamber and to keep the products of oxidation in solution until they had passed through the cell. When required, dialkylation was effected by heating the primary amines with trimethyl or triethyl-phosphate.⁶ The ceric sulphate was dissolved in an excess of sulphuric acid so that the reacting mixture was always acidic (about 0.5M in sulphuric acid). To achieve high flow rates the reactants were admitted to the aqueous solution cell at about 4 ft. of positive water pressure and were sucked through it by a water-pump. The degree of resolution of the spectra is indicated in Table 1 by the signal/noise ratios for the weak side lines of the spectra; in the centre of the spectra there was usually much line overlap.

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⁴ T. J. Stone and W. A. Waters, *J.*, 1964, 213.⁵ P. L. Kolker and W. A. Waters, *J.*, 1964, 1136.⁶ J. H. Billman, A. Radike, and B. W. Mundy, *J. Amer. Chem. Soc.*, 1942, **64**, 2977; D. G. Thomas, J. H. Billman, and C. E. Davis, *ibid.*, 1946, **68**, 895.