

EPR AND ELECTROCHEMICAL INVESTIGATION OF TERTIARY AROMATIC AMINES

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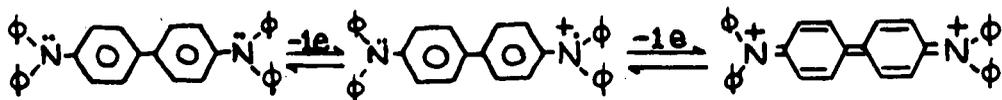
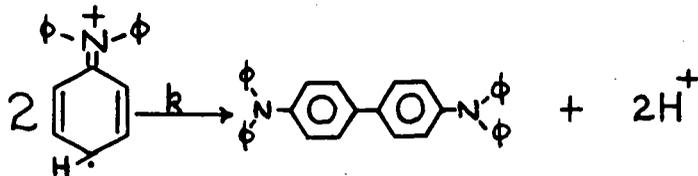
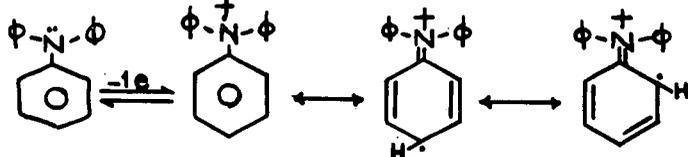
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Interest in the anodic oxidation reactions of organic compounds led to a study of the electrode processes associated with the electrochemical oxidation of some tertiary aromatic amines in nonaqueous media, primarily acetonitrile. These electrode processes were found to have homogeneous chemical reactions associated with them in many cases, some of which were quite surprising in nature. Substituted triphenylamines were investigated, but generalizations to the electrochemical behavior of other aromatic amines should be possible. Substituent and steric effects were found to have surprisingly great influences over the rates of follow-up reactions associated with the primary electrode processes, but these were found to be entirely predictable from the electron distribution in the amine cation radicals as shown by Hückel molecular orbital (HMO) calculations.

Triphenylamine (TPA), the parent molecule for most of these compounds, was studied in detail, and it was determined by a number of independent methods that the electrode processes and associated chemical reactions are as shown below:



The initial electrode reaction is a one-electron oxidation of TPA to the cation radical, $\text{TPA}^{\cdot+}$, which is quite unstable.¹

1. E. T. Seo, et al., J. Am. Chem. Soc., 88, 3498 (1966).

The presence of the cation radical was confirmed by rapid-sweep cyclic voltammetry (which showed the initial redox couple to be fairly reversible at 1500 V./min., i.e., cathodic current was observed corresponding to reduction of the cation radical back to the parent species) and visible absorption spectroscopy.¹ Two of the cation radicals (or a cation and a parent molecule - it is difficult to distinguish between the two mechanisms electrochemically) couple rather rapidly ($k=10^3 \text{ l.mole}^{-1}\text{sec.}^{-1}$) at the para ring positions to form N,N,N',N'-tetraphenylbenzidine (TPB), with concomitant liberation of two protons due to coupling. TPB is more easily oxidized than TPA, so reactions (3) also occur at the potential of TPA oxidation, completing the ECE process.

The presence of TPB as the end-product was detected by matching up peak potentials of the cyclic voltammograms of TPA and TPB, by comparing the epr spectra generated by oxidation of the amine and the benzidine (they are identical) and by detection of the visible absorption peak of $\text{TPB}^{\cdot+}$ upon electrolysis of TPA in situ in a Cary spectrometer¹.

Substitution at the para positions of the phenyl rings in TPA had a great effect upon this electrode process. If all three para positions were blocked with substituents, a stable cation radical was generated and this species did not undergo the characteristic coupling reaction. These cation radicals were stable enough that the epr spectra could be generated electrolytically and these spectra were then interpreted in terms of the parent molecules, thus confirming the initial one-electron electrochemical behavior. The substituents used were: OMe, Me, F, Cl, Br and COOMe. The cyclic voltammetry of all these molecules was initially a one-electron, completely reversible process, with $i_{pc}/i_{pa} = 1.0$ at all scan rates. The second oxidation step of all of these is irreversible, and the follow-up reactions are very complex and diverse.

When only one or two of the para positions are blocked, coupling at an open para site takes place readily, the rate of coupling being markedly dependent upon the number and type of substituents. It was not unexpected that if two sites were blocked instead of one (di- as compared to monosubstituted TPA's), the coupling rate was diminished (with the same substituent in both cases), but the effect of various substituents was quite surprising. The methoxy group has a tremendous stabilizing effect upon these cation radicals; 4-methoxy-TPA coupled at a very slow rate (as compared to $k=10^3$ for TPA). On the other hand, nitro groups in the para positions of TPA appeared to accelerate the coupling reaction to an extraordinary degree. Although the coupling rate of 4-nitro-TPA could not be accurately measured, it was estimated at $k=10^4$ from chronopotentiometric data. Other substituents appeared to behave normally. Again, when benzidines were formed, they were identified by matching of peak

potentials of cyclic voltammograms, by obtaining identical epr spectra from the benzidine and the amine, and by generating similar visible absorption spectra. In all cases that could be verified, para-benzidines were the only detectable product.

A few ortho-substituted TPA's were also investigated and it was found that substituent effects were somewhat diminished and that twisting of the ring or rings with a substituent considerably altered the electron distribution in these molecules. In the mono-ortho-substituted TPA's (substituents = OMe, Me, Cl), the effect of the substituents was to twist the substituted ring so that interaction with the rest of the molecule was considerably diminished. This increased the unpaired electron density in the unsubstituted rings, thus accelerating the coupling reaction relative to TPA. The substituents do have an effect, though diminished, upon the unsubstituted rings, as evidenced by the fact that each of the substituted TPA's has a different coupling rate, determined qualitatively by chronopotentiometry ($i\tau^{1/2}/C$ vs. i plots).

When all three rings are substituted at one ortho position, the molecules are more symmetrical and substituent effects become more of a differentiating factor. Each of these couples at a rate slower than that of TPA, and they are in the order: OMe < Me < Cl. In the case of the methoxy derivative, tri-o-anisylamine, the corresponding benzidine was also available (tri-ortho-substituted TPA's and corresponding benzidines courtesy of Dr. Cecil Frye, Dow Corp., Midland, Michigan) and it was verified as before that the amine couples to form the corresponding para-benzidine. The cyclic voltammograms, epr spectra and visible absorption peaks matched up nicely. It was assumed that the methyl- and chloro-substituted analogs behaved similarly, since the data from these compounds correlated with those from the methoxy derivative.