

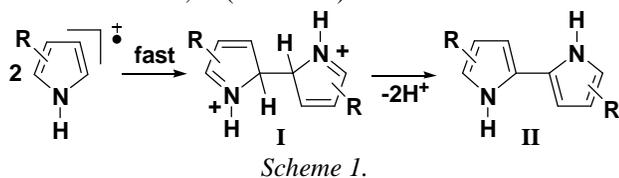
Studies of the Electrochemical Oxidation of Alkyl Pyrroles and Related Compounds

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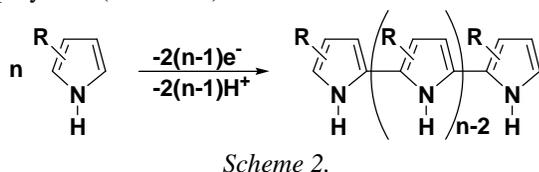
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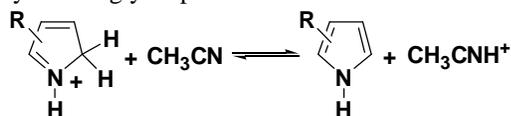
The electrochemical oxidation of pyrrole and substituted pyrroles has attracted considerable interest owing to the many important applications of the products, oligo- and polypyrroles. It is commonly agreed that the initial process in aprotic solvents, such as acetonitrile, is the coupling of two radical cations resulting in a dimer dication, **I**, which by loss of two protons is converted to the neutral dimer, **II** (Scheme 1).



Further oxidation and coupling steps lead to oligomers or polymers (Scheme 2).



Usually, the base accepting the protons is not specified; in other words, it is tacitly assumed that the base is the solvent - supporting electrolyte similarly to what is being observed, e.g., for the dimerization of methoxyarenes. However, for pyrroles both substrates and products are more basic than the commonly used aprotic solvents. For example, the pK_a values for protonated pyrroles are typically in the range 4 to -4, whereas the pK_a value for protonated acetonitrile is close to -10. This means that equilibria of the type shown in Scheme 3 usually is strongly displaced to the left.



In order to gain more insight into the importance of such inherent acid-base reactions, we have studied the electrochemical oxidation of a series of alkyl pyrroles and related compounds. In order to reduce the complexity of the problem, we have initially focused on compounds that owing to proper substitution were believed to be able to undergo dimerization reactions only.

Results obtained by constant current coulometry are shown in Table 1 and it is seen that the number of Faradays required for the complete consumption of substrate in all cases but one is less than 1 F illustrating that an appreciable amount of substrate has indeed been consumed by acting as a base. When coulometry is carried out in the presence of a sterically hindered base such as 2,6-di-*tert*-butylpyridine the consumption of charge is much higher, in most cases close to 2F.

Table 1. Results from constant current coulometry for the

electrochemical oxidation of substituted pyrroles.

| Pyrrole | F ^a | F ^b |
|----------------------------------|----------------|----------------|
| 2,4-Dimethyl | 0.68 | ~2 |
| 2,5-Dimethyl | 0.98 | ~2 |
| 1,2,5-Trimethyl | 1.2 | ~2 |
| 2,4-Dimethyl-3-ethyl | 0.67 | ~1.5 |
| 2,5-Dimethyl-3-ethoxycarbonyl | 0.97 | ~2 |
| 2,3,4-Trimethyl-5-ethoxycarbonyl | 0.75 | 2-3 |

^aIn MeCN; ^bIn MeCN in the presence of 2,6-di-*tert*-butylpyridine.

Related to this is the observation that the rate of the proton transfer reactions leading to **II** are rather slow and often proceed at a time scale comparable to that for slow sweep voltammetry. This gives rise to trace crossing phenomena at low sweep rates as illustrated in Figure 1 for the oxidation of 2,4-dimethyl-3-ethylpyrrole.

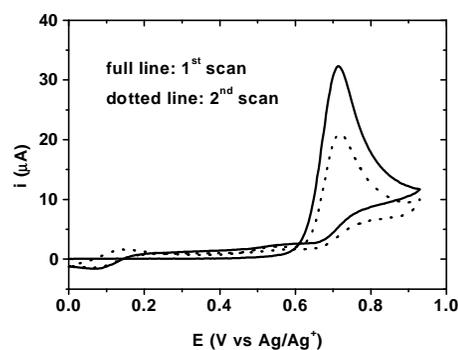
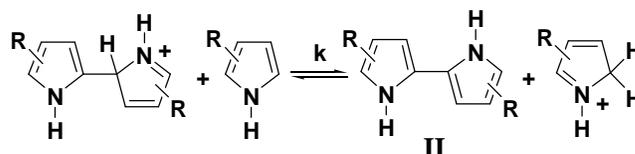
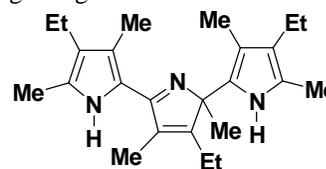


Fig 1. Cyclic voltammogram for the oxidation of 2,4-dimethyl-3-ethylpyrrole in MeCN at $v = 0.2 \text{ V s}^{-1}$.

Slow proton transfer reactions are rather rare in organic electrochemistry, but not exceptional. In the present case it is no surprise that the reactions are slow when it is considered that they involve the exchange of a proton between two pyrrole units, that is between two carbon atoms in a reaction with a low driving force (e.g., Scheme 4). Results obtained by digital simulation has shown that the rate constant k is of the order $10^3 \text{ M}^{-1} \text{ s}^{-1}$.



The results from preparative electrolysis of 2,4-dimethyl-3-ethylpyrrole show that the major product, somewhat unexpectedly, is a trimer with the most likely structure being that given in Scheme 5.



The implications of these and other results for the kinetics and mechanisms of the electrochemical polymerization of pyrroles and similar heteroaromatic compounds will be discussed.