

AUTOXIDATION OF NITROGEN HETEROCYCLES. 2. KINETIC MEASUREMENTS
OF THE AUTOXIDATION OF 2,5-DIMETHYLPYRROLE

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Abstract - The autoxidation of 2,5-dimethylpyrrole in dodecane is believed to proceed by a charge transfer mechanism. Kinetics measurements are presented which are consistent with this hypothesis.

We have previously reported spectroscopic evidence for a molecular association complex between oxygen and 2,5-dimethylpyrrole (DMP) in non-polar solvents⁴. We have postulated that the rate-determining step for the reaction between alkyl pyrroles and oxygen involves an initial electron transfer, within a molecular association complex formed in the solvent cage, from the pyrrole nucleus to the LUMO of the oxygen atom, Figure 1.

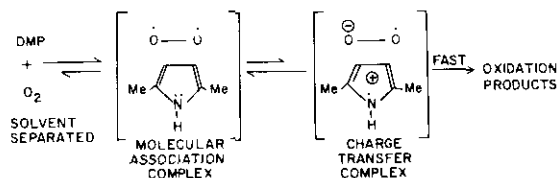


Figure 1. 2,5-Dimethylpyrrole: Oxygen Complex Formation

In order to test the hypothesis shown in Figure 1, we have examined the relationship between the observed pseudo-first order rate constants for the autoxidation of various substituted pyrroles and their anodic oxidation potentials (Table 1).

Salmon has presented experimental evidence that supports the hypothesis that the ease of oxidation of pyrrole derivatives is primarily dependent upon the magnitude of the π dipole moment of the pyrrole nucleus⁵.

The results in Table 1 suggest that there is a crude correlation between the observed E_p and the rate constant for the autoxidation (runs 2 and 4, 5 and 9). Presumably, replacement of a pyrrole hydrogen with a group able to donate electron density towards the π -system results in a decrease in the oxidation potential of the pyrrole. This would correspond to a raising of the HOMO energy of the pyrrole ring and would be expected to lead to an increase in the rate constant for the autoxidation scheme of Figure 1.

The rate constants reported in Table 1 indicate that the autoxidation of 2,5-dimethylpyrrole in dodecane has an activation energy of approximately 15 kcal/mole. The corresponding entropy of activation for this reaction is approximately -43 e.u. Further support for the postulated mechanism (Figure 1) is provided by the observed variation in k with change in solvent polarity for the autoxidation of 2,5-DMP (runs 3, 6-8). The transition state for the initial charge transfer complex is probably more polar than the starting reagents (DMP + O_2). Thus, an increase in solvent polarity would be expected to lower the E_a for the formation of the charge transfer complex which would result in an increase in the observed pseudo-first order rate constant for the autoxidation.

Additionally, it should be noted that unlike typical hydrocarbon autoxidations, the mechanism depicted in Figure 1 would be insensitive to the presence of radical chain scavengers (hindered phenols) in the reaction medium. We have found this to be the case^{6,7}.

In summary, the kinetics data presented here support a mechanism involving the formation of a charge transfer complex in the autoxidation of alkyl pyrroles.

Table 1

<u>Pyrrole</u>	<u>Solvent</u>	<u>Temp (°C)</u>	<u>k(x10⁶sec⁻¹)</u>	<u>Ep(mV)</u>
1) 2,5-dimethyl	dodecane	60°	0.85	-
2) 2,5-dimethyl	dodecane	65°	1.01	570
3) 2,5-dimethyl	dodecane	70°	1.56	-
4) 1,2,5-trimethyl	dodecane	65°	1.96	630
5) 2-carboxaldehyde	dodecane	65°	<0.10	1380
6) 2,5-dimethyl	1,2,4-trichloro- benzene	70°	6.04	-
7) 2,5-dimethyl	(1/1)1,2,4-trichloro- benzene/nitrobenzene	70°	14.86	-
8) 2,5-dimethyl	nitrobenzene	70°	24.10	-
9) unsubstituted	dodecane	65°	<0.20	1250

1. Rate constants are reproducible to within ±10%.
2. Measured in CH₃CN containing .1M lithium perchlorate using Pt vs. Ag/AgNO₃ electrodes and using 2 mM pyrrole concentrations.

EXPERIMENTAL

A typical kinetic experiment is described below. A 500 ml three neck round bottom flask was equipped with a reflux condenser, a rubber septum, magnetic stir bar, and an oxygen inlet valve. The three neck flask was then emersed into a Sargent-Welch kinetic water bath Model S-84810 such that the water level extends up to the midpoint of the neck of the flask. An air driven magnetic stirrer was situated under the round bottom flask.

The solvent (400 ml) and internal standard (tridecane) were introduced into the round bottom flask and the flask was subsequently purged with oxygen.

Control experiments showed that purging at a modest flow rate for approximately 5 minutes provided essentially a pure oxygen atmosphere.

The water bath was warmed to the reaction temperature and the temperature maintained at $\pm 0.1^\circ\text{C}$ with insulation and a Sargent-Welch Model ST Thermonitor. The appropriate pyrrole was introduced into the round bottom flask such that a concentration of 400 ppm (weight of nitrogen/volume of solvent) was achieved. The oxygen atmosphere was again established prior to the start of the kinetic run. Constant stirring was applied during the course of the experiment. The extent of the pyrrole autoxidation was monitored by capillary column GC quantification of 1 ml aliquots of the reaction mixture.

A Varian gas chromatograph model 3700 with a flame ionization detector (FID) and equipped with a 50-m 0.21-mm i.d. wall-coated open tubular (OV-101) fused silica capillary column was used. A carrier gas flow of 1 ml/minute was combined with an inlet split ratio of 60:1 and a temperature program with an initial hold at 110°C for 5 minutes, a ramp of $4^\circ/\text{minute}$, and a final temperature of 260°C .

The chromatogram was recorded and integrated on a Hewlett-Packard Model 3390A reporting integrator.

The pseudo first order rate constant was calculated from the slope of a linear regression plot (correl. ≥ 0.90) of the change in pyrrole concentration (natural log) versus the time (sec).

When dodecane was used as solvent the pyrrole was consumed to the extent of 30-50%. In all other solvent systems the pyrroles were consumed to the extent of 50-100%. All of the pyrroles examined were commercially available. They were used without further purification. Capillary GC revealed that all of the pyrroles had $>98\%$ purity.

The solvents used were Aldrich Gold Label or Fisher Certified and were used without further purification.

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