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AUTOXIDATION OF NITROGEN HETEROCYCLES. 1. ULTRAVIOLET SPECTRA OF ALKYLPYRROLES. EVIDENCE FOR A MOLECULAR ASSOCIATION COMPLEX BETWEEN OXYGEN AND 2,5-DIMETHYLPYRROLE IN NON-POLAR MEDIA

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Abstract - Ultraviolet spectroscopy indicates that molecular oxygen associates extensively and reversibly with 2,5-dimethylpyrrole in hydrocarbon solution. The formation of such a molecular association complex is believed to be the first step in the principal autoxidation sequence for this pyrrole.

In the course of our investigations into the storage stability behavior of synthetic fuels, we have examined the autoxidation processes which occur when model nitrogen heterocycles are added as dopants to otherwise stable shale diesel fuels.[1,2] Nitrogen heterocycles of low basicity (e.g., alkylpyrroles) promote the formation of large amounts of insoluble material in stressed fuel samples.[3,4] We have examined the autoxidation of a model compound, 2,5-dimethylpyrrole, in a variety of fuels and model solvents, and under a number of stress conditions. On the basis of the results of this work, which will be described in detail in an ensuing publication, it became evident that an intimate association complex of molecular oxygen with 2,5-dimethylpyrrole could help explain the observed nature of the autoxidation.[3,5]

We have recorded UV spectra of highly pure 2,5-dimethylpyrrole in dodecane and hexane,[6,7] and have confirmed that the principal absorption peak occurs at 209 nm with log ε of approximately 3.9. Upon re-recording spectra of identical samples after a period of time (several minutes to hours later), changes were frequently observed in the spectra. In particular, ε for the peak at 209 nm was seen to increase, with the development of a shoulder peak at 225 nm. The phenomenon was examined in greater detail with the assistance of capillary GC (both FID and nitrogen specific detection) and nmr. These methods failed to show the development of any oxidation products of 2,5-dimethylpyrrole which would explain the changes in UV spectra.

Rapid oxygenation of the pyrrole solution was next effected by bubbling oxygen rapidly through the solution for periods ranging from 5 to 30 min. The UV spectra of all these samples showed a marked increase in the absorption at 209 nm, generally an order of magnitude higher value for ε.[8] Most notable, however, was the appearance of new absorption peaks - typically at 224 nm (log ε approx. 4.4), 275 nm (log ε approx. 3.6), and 282 nm (log ε approx. 3.5). When the oxygenated pyrrolic solutions were subjected to subsequent deoxygenation by bubbling nitrogen gas through the solution for 5 min. or longer, attenuation of all absorption peaks was observed. Prolonged (longer than 15 min) treatment with nitrogen reduced the peak intensities to approximately their original values.[9] Again, GC and nmr failed to indicate the development of any significant intermediate products in the oxygenated solutions. Oxygenated solvent blank runs failed to indicate any absorbance.

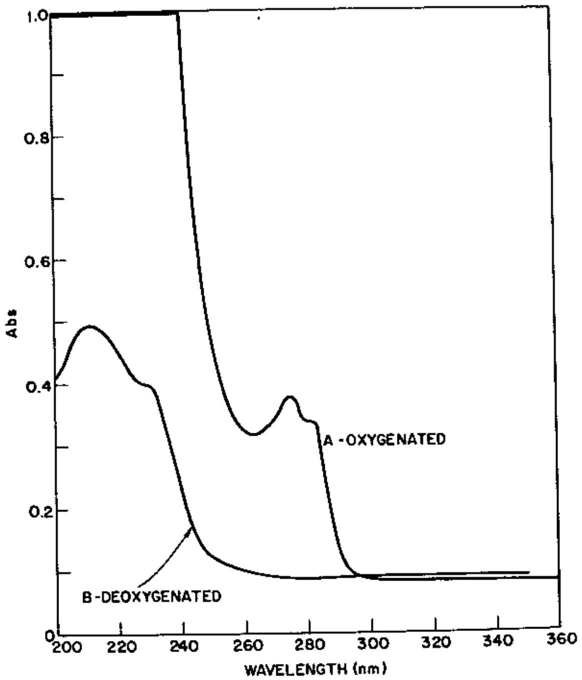

Figure 1. Ultraviolet Spectra of 2,5-Dimethylpyrrole in Dodecane

Figure 1 shows two UV spectra which were recorded with a single sample in dodecane solvent. The oxygenated 2,5-dimethylpyrrole solution appears as the upper trace. The lower trace shows the absorbance of the sample after deoxygenation was accomplished. The lower trace is identical to the spectrum which was obtained with fresh 2,5-dimethylpyrrole before oxygenation was effected. This demonstrates the reversible nature of the complexation.

Hence, it appears that a significant association phenomenon exists between molecular oxygen and 2,5-dimethylpyrrole in solution. It is possible that this association complex is equilibrated with a charge-transfer or electron donor acceptor (EDA) complex. Evans[10] reported that UV spectra indicated the existence of similar complexes of oxygen with other electron-rich aromatics including unsubstituted pyrrole itself, which was found to develop an absorption peak in the 296-300 nm region when saturated with oxygen at atmospheric pressure.[11,12] Lang[13] discovered that iodine formed charge transfer complexes with pyrrole and N-methylpyrrole. Our observation of significant phosphorescence quenching in shale fuel doped with 2,5-dimethylpyrrole may also be consistent with this interpretation.[3,5]

A scheme for the initial stages of the autoxidation of 2,5-dimethylpyrrole in solution is suggested in Figure 2. We postulate the increase in UV absorption is a result of a photo-initiated charge or electron transfer (i.e., absorption of light by the molecular association complex within the solvent cage). In this scheme, the pyrrole would be defined as the likely reducing agent, consistent with the high energy of its HOMO. Similarly, the suggestion of a superoxide anion intermediate appears reasonable as these species are widely known[14] and have been implicated in related redox processes.[15-19]

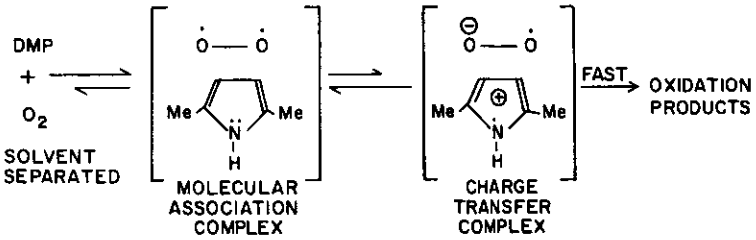

Figure 2. 2,5-Dimethylpyrrole : Oxygen Complex Formation

Such an equilibrium scheme (Figure 2) may qualitatively explain why alkylpyrroles autoxidize so much faster than pyrrole itself, or pyrroles substituted with electron withdrawing groups. If the formation of such a charge transfer complex was rate determining in the autoxidation scheme, the observed kinetics would be followed.[20] This step is kinetically indistinguishable from a rate-limiting formation of the molecular association complex. However, the rapidity of the UV spectral changes upon oxygenation favor the former explanation, as do the results of similar studies.[16] The substituent effects in pyrroles could then affect both the position of the initial equilibrium as well as the crucial HOMO energy level. The thermal redox process which occurs during autoxidation could thus lead to the formation of the same primary oxidation products which result from photoxidation, albeit at a much slower rate.[17]

It has been noted that autoxidation and photoxidation of electron-rich molecules often result in similar product distributions.[15,17] Furthermore, it appears possible that at least in some instances, singlet oxygen may be formed entirely thermally by reaction of an electron-rich molecule with ground-state oxygen.[18,21] Such a process can be thought of as the reverse of charge transfer quenching of singlet oxygen, as outlined in Figure 3.[17] Present experimental techniques are unable to differentiate between the involvement of superoxide anion and thermally generated singlet oxygen in organic redox reactions.[15] Thus, current knowledge dictates that one must consider the involvement of both superoxide and singlet oxygen as possible intermediates in the autoxidation. We are attempting to correlate HOMO energies of sustituted pyrroles with their rates of autoxidation, and will present the results of these studies in due course.

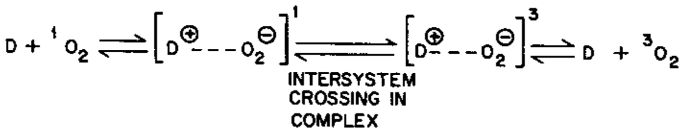

Figure 3. Thermal Singlet-Triplet Oxygen Interconversion in the Presence of an Electron Donor

We conclude that oxygen which is dissolved as a molecular association complex with alkylpyrroles and related electron-rich aromatics may markedly influence the absorption of ultraviolet light.[22] Therefore, it is recommended that recorded spectra of these compounds be taken in both oxygenated and deoxygenated modes so as to avoid problems related to incorrect peak assignment.

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4. Typically, stress is in the dark at 43-80°C with 45-450 ppm N (w/v) of added nitrogen compound in a 300 ml fuel sample.
5. J. V. Cooney, E. J. Beal, M. A. Wechter, G. W. Mushrush and R. N. Hazlett, unpublished work to be submitted to Fuel.
6. Free of detectable impurities by fused silica capillary GC (indicated purity greater than 99.8%), nmr and ir. Fresh samples of 2,5-dimethylpyrrole were stored frozen under an inert atmosphere.
7. A Beckman Model 25 UV-VIS Spectrophotometer was used with 1 cm path quartz cells.
8. Values of log ε for this peak were seen to vary between 4.4 and 5.1. In practice, it did not prove possible to exactly duplicate the absorption spectra even in successive runs with the identical sample.
9. The purity of the nitrogen gas employed appeared to limit the efficiency of the deoxygenations.
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20. We have determined that the autoxidation is first-order with respect to 2,5-dimethylpyrrole with an activation energy of approximately 11-12 kcal/mol in diesel fuel. Curiously, a hindered phenol antioxidant exerted absolutely no inhibitory effect upon the autoxidation. Product analysis data combined with available kinetic results suggest the presence of one predominant autoxidation pathway occurring from 25-80°C. Small solvent effects have been noted; viz., higher dielectric constant solvents appear to slightly speed up the autoxidation. This would be consistent with the generation of a charge transfer intermediate in the rate determining step. We are currently evaluating catalytic effects in the autoxidation. See references 1-3 and 5.

21. G. D. Mendenhall, Photochem. Photobiol., 1978, 28, 475.

22. For an example of the confusion in the literature regarding UV data for alkylpyrroles, see: R. L. Hinman and S. Theodoropulos, J. Org. Chem., 1963, 28, 3052.

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