

## THE SIGNIFICANCE OF THE OXIDATION OF 2,5-DIMETHYLPYRROLE IN OXIDATIVE FUEL STABILITY

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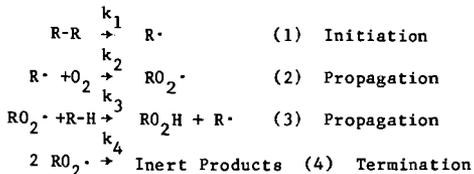
### INTRODUCTION

Alkylpyrroles have been known to promote sediment formation and discoloration of petroleum distillates for over thirty years.<sup>1-4</sup> There has been much effort directed towards understanding the detailed mechanism of alkylpyrrole promoted sediment formation in petroleum distillates.<sup>(5-9)</sup> In addition, the Fuels Section of the Naval Research Laboratory has been involved in investigating the mechanism of alkylpyrrole sediment formation in shale derived synfuels.<sup>(10-14)</sup> It is the intent of this article to critically review some of the postulated mechanisms for alkylpyrrole promoted sediment formation in fuels and then to comment on the significance of these mechanisms to our overall understanding of the field of oxidative fuel stability in general.

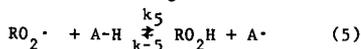
### I. The Reaction of Oxygen with Organic Molecules

The fundamental chemical reactions involved in sediment formation in fuels are generally believed to start by the reaction of ground state triplet oxygen with various reactive organic molecules which are components of the fuel. There are at least two fundamentally different types of reactions that can occur between triplet oxygen and organic molecules.

By far the most common type of reaction between organic molecules and triplet oxygen is free radical initiated oxidation of organic compounds by molecular oxygen. The accepted chain mechanism which satisfactorily rationalizes this type of reaction is summarized as the following:



Where R-R is the initiator and R· and RO<sub>2</sub>· represent the carbon radical and the chain-carrying peroxy radical respectively.(15,16) Many of the current fuel antioxidants have been developed to address this type of Scheme. For instance, the effectiveness of both phenolic and amine antioxidants can be simplistically attributed to their breaking of the radical chain as shown in (5):



A → non chain products

Where A-H represents the antioxidant.(17) If k<sub>5</sub> is larger than k<sub>3</sub> then the oxidation is inhibited until the antioxidant is consumed.

A second class of antioxidants are the so called "preventive antioxidants".(18) These include metal deactivators, UV light deactivators, and peroxide decomposers. The first two deactivators are designed to inhibit the initiation step and also inhibit the decomposition of peroxides. Peroxide decomposers, as the name suggests, destroy peroxides without generating free radicals in the process.

The second type of fundamental reaction that can occur between triplet oxygen and organic molecules has only recently been thoroughly investigated.

Thomas Bruice and coworkers have reported detailed studies on the mechanism of biological oxidation with flavoenzyme mixed function oxidases.(19) Bruice has shown that the initial mechanism for the formation of the biologically active form of the flavoenzyme mixed function oxidase [4] involves the oxidation of compounds [1] by triplet oxygen to yield the radical ion pair [2] (Scheme I). Forward reaction occurs with the collapse of [2] to form the more stable covalent intermediate [3] which can capture a proton to yield [4]. The Bruice group has very eloquently shown i) that formation of [2] is the rate determining step and ii) that the transition state of the rate limiting step is very similar in structure to [2].

In the Bruice mechanism it is important to note that structural features in the organic molecule (i.e. oxidation potential) must be such that, when coupled to the reduction of triplet oxygen, the reaction is not overly endergonic.

Sinhababu and Borchardt have recently reported polarographic and spectroscopic data which suggests the oxidation of 5,7-dihydroxytryptamine [5] involves an electron transfer from compound [5] to oxygen, resulting in radical ion pair [6] (Scheme II).(20) Recombination of superoxide with the incipient free radical would produce hydroperoxide anion [7] which upon protonation yields hydroperoxide [8]. Hydroperoxide [8] is unstable and undergoes further reaction yielding the reactive quinones [9] and [10].

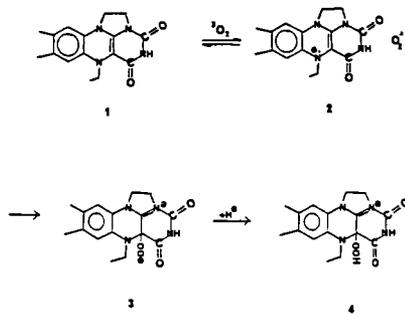
Aside from the above mentioned studies there have been few detailed mechanistic studies of the reaction of organic molecules with low oxidation potentials with ground state triplet oxygen.

## II. Characteristics of DMP Sediment

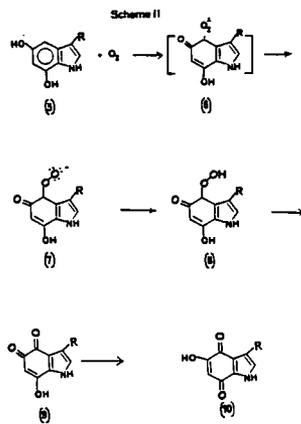
Cooney and Wechter have reported the depletion of added 2,5-DMP in a shale-derived diesel fuel correlated with oxygen uptake by the doped fuels (11). Sediment analysis data indicate that the sediment is derived from oxidation of the DMP with no incorporation of fuel constituents. In addition, analysis of the sediment derived from oxidation in a pure organic solvent also indicates the sediment is derived from DMP oxidation.

No changes were observed in the g.c. traces of stressed fuel sample with increasing length of stress. Also, stress runs in dodecane indicate the absence of any soluble oxidation products from DMP. Thus, the soluble primary oxidation

Scheme I



Scheme II



products derived from DMP are highly reactive and are rapidly converted to insoluble sediment, thereby thwarting direct attempts at their characterization.

Analysis of the sediment derived from stressing DMP doped fuels suggests the sediment arises from oxidative self condensation of the DMP (formation of dimers, trimers and tetramers). Spectroscopic analysis suggests that in the sediment the pyrrole nucleus is intact and that the CO, CO<sub>2</sub>H, N-H, CH<sub>2</sub>, CH<sub>3</sub>, moieties are present. Elemental analysis of the sediment yields a molecular formula of approximately C<sub>6</sub>H<sub>7</sub>NO<sub>2</sub>, regardless of the stress conditions. In addition, mass spectral studies, of the DMP derived sediment have lead Frankendorf et.al(7-9) to suggest some possible partial structures for the DMP sediment.

### III. The Mechanism of Pyrrole Autoxidation

Smith and Jenson(21) have reported a detailed study of the oxidation of neat 1-alkylpyrroles. The detection of peroxide intermediates and the isolation and characterization of the oxidation products from 1-methylpyrrole, lead to the proposal that 1-alkylpyrrole reacts with oxygen by a free radical peroxy addition process (Scheme III).

Free radical reactions have also been invoked to rationalize the autoxidative oligomerization of DMP.(7-9) Li et.al. have reported esr evidence of pyrrole radicals during the oxidation of DMP and NMP (N-methylpyrrole) using fuel as the diluent. This observation lead Li et.al. to propose the partial reaction sequence shown for sediment formation (Scheme IV).(6)

This mechanism has merit in that a rationalization is provided for the observation that the rate of DMP oxidation is much more rapid than the rate of NMP oxidation (based on oxygen uptake studies). The fact that radical A can be stabilized through resonance and radical B can not, could account for the increased rate of formation of A relative to B.

One major weakness with proposing free radical mechanisms for alkylpyrrole autoxidation schemes is that in both fuels and pure organic solvents, the presence of radical chain scavenger antioxidants has little effect on the rate of alkylpyrrole oxidation.(12)

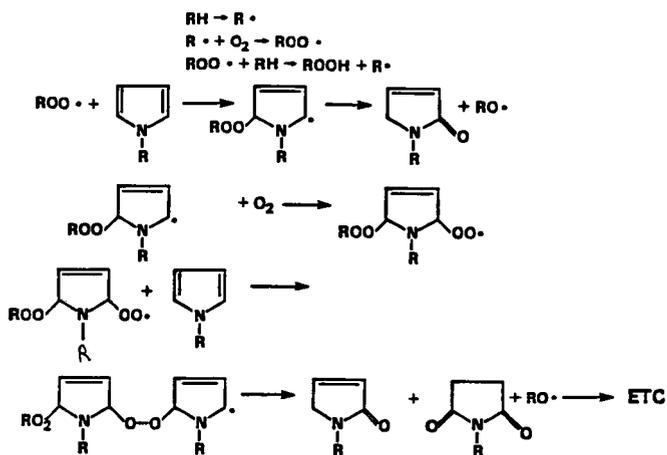
In fact, the autoxidation of DMP in 1,2,4-trichlorobenzene, in the presence of vitamin E, had only a slight depressive effect on the rate of DMP oxidation.(22) This is surprising in view of the fact the vitamin E is one of the most efficient radical scavengers known.(23)

Clearly, Li et.al.(6) have detected the presence of pyrrole radicals during the oxidation of DMP and NMP. Smith and Jenson's(21) data can be nicely rationalized in terms of the pyrrole oxidation involving radical reactions. However, our vitamin E experiment suggests that the DMP free radical intermediate observed by Li et.al. is not on the reaction coordinate leading to product formation (sediment).

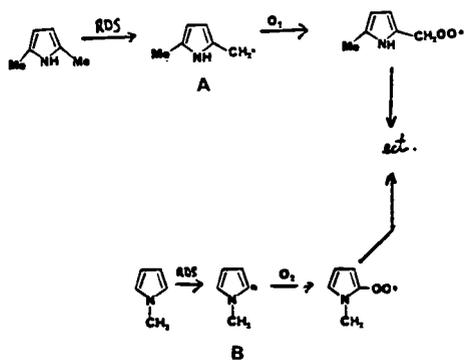
In our studies(12-14) on the mechanisms of the reaction of triplet oxygen with alkylpyrroles, several different organic solvents were utilized rather than fuels as diluent. In this manner the fundamental oxidation reaction could be studied without the potential complicating interactive effects that can occur in fuels.(10) In both fuels and pure organic solvents the oxidation of alkylpyrroles results in the formation of an intractable red-brown product. Presumably, this sediment is composed of oligomeric oxidized pyrrole nuclei (Vida Supra). In addition we have thus far found no evidence for any intermediates in the alkylpyrrole oxidation in the hydrocarbon solvents utilized in our study.

Thus our understanding of the mechanism of alkylpyrrole oxidation is based on an interpretation of our crude kinetic studies of these reactions. We have suggested, (12-14) as shown in Scheme 5, the first step of the oxidation involves

Scheme III



Scheme IV



the reversible formation of a molecular association complex between the alkylpyrrole and dissolved oxygen. This hypothesis is supported by previously published UV spectroscopic data; in addition, such association complexes between triplet oxygen and electron-rich molecules are well known(24).

The rate determining step depicted in Scheme 5 utilizes the alkylpyrrole as an electron donor and oxygen as an electron acceptor. Such a mechanistic sequence qualitatively explains why electron rich pyrroles autoxidize so much faster than pyrrole itself or than pyrroles substituted with electron withdrawing groups (25-27). Additionally, this scheme accounts for the observation that there exists a correlation between the pyrrole anodic oxidation potential and the pseudo-first-order rate constant for the oxidation(13). As already mentioned, similar redox processes have been implicated in the oxidation of dihydroflavins and tyrtamine derivatives with triplet oxygen.(19,20) The observed ESR signal reported by Li et.al. (6) during DMP oxidation can also be rationalized as arising from a strong, single-electron donor-acceptor affinity between the pyrrole and triplet oxygen (28).

As shown in Scheme 5, the charge transfer complex is postulated to be in equilibrium with an endoperoxide intermediate. Such endoperoxides are believed to be intermediates in the photochemical dye-sensitized oxidation of pyrroles(25). Such a common intermediate for both sensitized photooxidation and oxidation could thus account for the observation that many photochemical oxidations and oxidations produce the same type of oxidation products(26,27).

We have recently suggested that when the kinetic and thermodynamic parameters, for the alkylpyrrole oxidation in various hydrocarbon solvents, are compared the observed trends can be rationalized as being consistent with the mechanism proposed in Scheme 5.(14)

There is one unifying theme in the previously discussed work of Bruce(19), Borchardt(20) and our pyrrole oxidation studies.(12-14) In all of these investigations the initial step in the oxidation sequence has been suggested to involve the transfer of an electron from an organic substrate to ground state triplet oxygen. We shall classify this type of oxidation reaction as "electron transfer initiated oxidation."

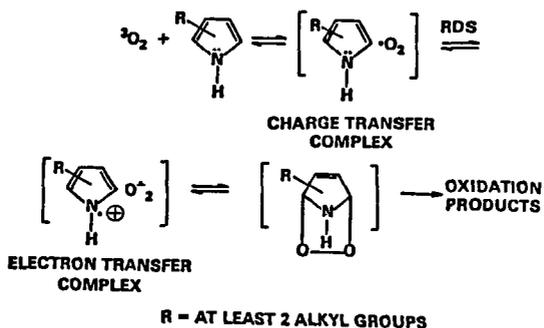
Electron transfer initiated oxidation in fuels is very complex mechanistically due to the plethora of potential interactive effects that can occur with fuel components. For instance, Frankenfeld et.al.(7-9) have shown that when certain fuels are doped with DMP and certain codopants (pyrrole or trimethylamine or certain sulfur compounds) less sediment is produced than expected during simulated storage stability tests. We have found that the oxidation of DMP in the presence of FeCl<sub>3</sub> results in a (5-10) fold increase in the rate of sediment formation.(22) Undoubtedly, much more research is necessary before we are in the position to fully understand electron transfer initiated oxidation reactions and their impact on the oxidative storage stability of fuels.

#### IV. Recent Developments in the Understanding of Autoxidation Reactions in Fuels

Based on stress/sediment formation studies, Frankenfeld et.al.(8), have correlated the sediment formation propensity of various aromatic nitrogen heterocycles with their structure (Scheme 6). Our oxidation studies in model fuel systems have allowed us to further probe the heterocycle structure-sediment formation relationship.

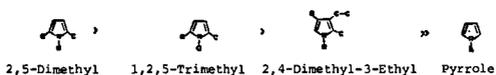
First, each heterocycle has at least two distinct oxidation pathways available. Both, free radical initiated and electron transfer initiated oxidation occurs to some extent for each heterocycle. However, the rate of each reaction pathway may be very different. The rate constant for oxidation is dependent both on the structure of the heterocycle and on the experimental conditions of the oxidation reaction. For example, we have suggested the oxidation of DMP, TMP, and kryptopyrrole (and presumably all poly alkylpyrroles) procede via an electron

Scheme V

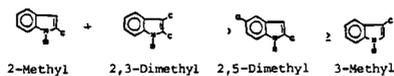


Scheme VI

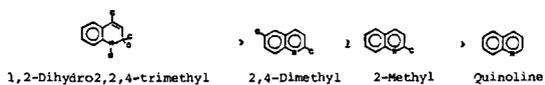
A. Pyrroles



B. Indoles



C. Quinolines



Influence of structure on reactivity of various nitrogen heterocycles toward sediment formation. Reactivity decreases from top of list to the bottom (A>B>C) and left to right. (From reference 7)

transfer initiated oxidation process. Li and Li(6) have shown that during the oxidation of DMP there is ESR evidence for the existence of DMP free radicals, presumably arising from free radical initiated oxidation. Under the experimental conditions employed in our pyrrole studies, the rate of the electron transfer initiated oxidation pathway is many times more rapid than the rate of free radical initiated oxidation. However, nitrogen heterocycles that do not have the appropriate oxidation potential to undergo electron transfer oxidation might have, in the presence of an initiator, a sufficient rate constant for free radical oxidation. Therefore, free radical initiated oxidation can also result in sediment formation if the final oxidation products are insoluble in the diluent. We have found this to be the case in the oxidation in 3-methylindole in D-11.

Second, the amount of sediment produced during oxidation is not necessarily related to the rate of oxidation. The intrinsic solubility of the products formed during the oxidation is another major factor in the amount of sediment produced during oxidation.

For instance, we have confirmed that DMP oxidation produces more sediment than the analogous oxidation of TMP with both fuel and dodecane as diluent. However, we have previously shown that the rate of TMP oxidation is more rapid than the analogous oxidation of DMP in organic solvents. Therefore, the final oxidation products of TMP must be more soluble than the corresponding DMP oxidation products.

#### V. The Significance of DMP Oxidation to our overall understanding of Oxidative Storage Stability of Fuels.

We believe that due to the diligent work of many research groups over the course of many years we are just starting to gain new insight into the complex chemistry involved in prolonged fuel storage. The oxidation of DMP is a very important reaction in that it is the first example of what we believe to be a significant reaction in the prolonged storage of fuel, namely, electron transfer initiated oxidation. Just how significant this mode of oxidation is in fuel chemistry is not yet fully comprehended. In principal, any electron rich organic molecule can undergo electron transfer initiated oxidation and thus promote sediment formation. Also preliminary data indicates that certain metals can catalyze electron transfer initiated oxidation.

Indeed, we are only beginning to understand the significance of this reaction in the field of oxidation storage stability of fuels. We are continuing our efforts to provide a greater degree of understanding of electron transfer initiated oxidation.

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