

EVOLUTION MECHANISMS OF L.C.O. GAS-OILS DURING STORAGE AND CHEMICAL MODELING OF ASPHALT AGING.

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ABSTRACT

In order to control or arrest the instability of L.C.O gas-oils during storage using efficient stabilizing additives it is necessary to determine structures and reaction mechanisms involved in these degradation processes. The oxidation of phenalene into phenalene, alkylindoles and thiophenols play a crucial role in color change and sediment formation. The condensation reaction between phenalene and 2-methylindole in presence of stoichiometric amount of para-toluenesulfonic acid leads to a complex mixture of compounds. Seven sets of compounds have been isolated by chromatography and spectroscopically identified. A reaction mechanism is proposed and experimentally supported. It is suggested that the phenalene and its derivatives can be partly representative models of the structures involved in asphalt aging.

INTRODUCTION

The evolution of refining processes has lead to an increase in the production of catalytically-cracked distillates. Before, these products particularly the L.C.O. (Light Cycle Oil), were used as diluents of heavy fuels. The decrease of the consumption in heavy fuels and the increase in auto and diesel fuels have lead refiners to introduce limited amounts of L.C.O. in domestic fuels and gas-oils. However these products are often unstable. It is well-known that storage of unstable diesel fuels can result in the color change and formation of organic sediments that have deleterious effects on fuel systems and engine components. An extensive review of this problem of instability in liquid fuels is given by Batts (1). Stabilization of these products can be carried out by hydrotreatment, but this method is too expensive. On the other hand, classical antioxidants are ineffective. In spite of studies made, degradation reaction

mechanisms are still not well-known. In order to control or arrest the instability of L.C.O. gas-oils during storage using efficient stabilizing additives, it is necessary to determine structure and reaction mechanisms involved in these degradation processes. The presence of sulfur compounds, nitrogen heterocycles and condensed ring polycyclic oxidizable hydrocarbon compounds will bring about gas-oils instability which is also influenced by traces metal impurities such as copper. The decisive role of oxidizable sulfur compounds has been determined (2,3). Among the sulfur compounds, the thiophenols, because of their ability to oxidize into sulfonic acids, are the more deleterious (4,5). This observation can be easily rationalized by the fact that condensation reactions between nucleophilic derivatives such as nitrogen heterocycles (6), especially alkylindoles which are electron-rich (7) and electrophilic substrates essentially aromatic in nature, are acid catalyzed. The above mentioned electrophilic aromatic substrates are most likely to result from the presence of oxidizable hydrocarbons in gas-oils (8). Among the condensed ring polycyclic oxidizable hydrocarbons present in the L.C.O. gas-oils, the particular role of phenalene has first been emphasized by Pedley et al. (5). Furthermore phenalenyl radical has been identified in L.C.O. by E.S.R. (9), also phenalene seems to be an obvious choice for model studies of the behavior of oxidizable hydrocarbons in L.C.O. gas-oils.

EXPERIMENTAL

The condensation reaction between phenalenone 1 and 2-methylindole 2 in presence of para-toluenesulfonic acid 3 and spectroscopic NMR and IR data of the isolated compounds have previously been well describe (10,11), as have the two dimensional NMR experiments and hydrogenation reaction to determine the structures of the five tautomers of 2-methylindolylphenalene.

The two isomers 6 and 7 of bis(2-methylindolyl)phenalene have been synthesized as follows:

2-methylindolylphenalanone 10 (0.4mM, 120mg); 2-methylindole 2 (0.4mM, 58mg) (Aldrich Chemical Company) and para-toluenesulfonic acid 3 (0.4mM, 69mg) (Aldrich Chemical Company) were introduced in a round bottom flask and dissolved in 20ml of methanol. This solution was left under magnetic stirring in the dark under argon for 24 hours. The resulting colored green solution was washed with 20ml of an aqueous solution of sodium bicarbonate (saturated) and extracted with 3 * 20ml of ether. A dark precipitate obtained after evaporation on a steam bath was chromatographed on flash silica (Merck silica having particle size 0,040-0,063mm; 230-400 mesh ASTM), using a mixture of dichloromethane/pentane : 1/1 as eluent. We obtained 100mg of 6.

The second isomer 7 (40mg) was obtained using the same procedure in mixing 9 (0.1mM, 30mg); 2 (0.1mM, 13mg) and 3 (0.1mM, 17mg) in 15ml of methanol. The NMR and IR spectroscopy data of these two isomers have been described previously (10).

RESULTS AND DISCUSSION

Our work provide further informations on the origin of coloration and sediment formation in L.C.O. gas-oils. The pioneering work in this area is the one of Pedley et al. (5,12), who reacted 2-methylindole in methanol with either phenalanone or phenalene in

presence of paratoluenesulfonic acid. In the first case 2-methylindolylphenalene was isolated, whereas in the second case bis(2-methylindolyl)phenalene was obtained.

In order to understand these degradation reactions which occur in L.C.O. gas-oils during storage, we have studied the condensation reaction between the phenalenone 1 and 2-methylindole 2 in presence of stoichiometric amount of para-toluenesulfonic acid 3 in methanol. We have shown that this reaction leads to a complex mixture of compounds. Seven sets of compounds have been isolated by chromatography and spectroscopically identified (Fig.1). The mechanism of this reaction has been studied and experimentally supported (10).

Phenalene 4, phenalanone 8 result from a disproportionation reaction of a key intermediate, similar to the one isolated by Murata (13) during the reduction of phenalenone with NaBH_4 .

The 2-methylindolylphenalene 5 and bis(2-methylindolyl)phenalene 6 and 7 exist under the form of a complex mixture of tautomers.

The tautomerism between the five structures A,B,C,D,E of 2-methylindolylphenalene 5 has been studied in great details by Tort et al. (13) using two dimensional high field (500 MHz) NMR spectroscopy. The relative proportions of each tautomer could be determined using the integration of the ^1H signals of the methylene groups and of the indole methyl group (Fig.2). The bis(2-methylindolyl)phenalene is in fact a mixture of two isomers 6 and 7, each one existing under the form of tautomers. The ^1H NMR spectrum of this mixture is too complex to be analyzed. The isomer 6 and 7 could be obtained separately by reacting 1 equivalent of 2-methylindolylphenalanone 10 with 1 equivalent of 2-methylindole 2 and 1 equivalent of 2-methylindolylphenalanone 9 with 1 equivalent of 2-methylindole 2 in presence of paratoluenesulfonic acid in methanol. The tautomerism between the four structures F,G,H,I of 6 and the two structures J,K of 7 have been determined by NMR spectroscopy (Fig.3). These structures have also been confirmed by catalytic hydrogenation reactions on PtO_2 of each mixture of tautomers (Fig.2 and Fig.3).

As phenalene 4 oxidizes easily into phenalenone 1 (12,14), it can be assumed that the monoindolylphenalenones 11 to 13 and bis(indolyl)phenalenones 14,15 have respectively their origin in monoindolylphenalene 5 and bis(indolyl)phenalenes 6 and 7. However as the reaction has been carried out under argon, the latter oxidation process might have been occurred by disproportionation reaction. We have shown that phenalenone 1, in presence of 2-methylindole 2 and para-toluenesulfonic acid 3 lead to an unstable intermediate which disproportionates to form 5, 11, 12 and 13. Compounds 6, 7, 14 and 15 can be formed in the same way by reaction of 11, 12 or 13 with 2 in acid medium. Furthermore, 5, 6 and 7 are unstable and oxidize easily into the corresponding ketones in presence of air and light. These oxidation reactions seem to take place via the corresponding phenalenyl radicals which have been observed by U.V. spectroscopy of 5, 6 and 7 in chloroform solutions.

It is now clear that as soon as phenalenone is present in L.C.O. gas-oils, it will condense in presence of acid with nitrogen heterocycles such as 2-methylindole to form products which are colored, and insoluble in L.C.O. gas-oils, especially when they are in the

form of ammonium salts of the acid which has played the role of catalyst for the condensation reaction.

Questions which arise from this work are :

- what is the origin of phenalene or phenalane correlated structures?
- does phenalene proceed from phenalane by dehydrogenation?
- is it possible to arrest the phenalene oxidation, using classical anti-oxidants ?

The oxidation of phenalene into phenalenone, which occurs via the phenalenyl radical as we have seen, is likely to proceed by a classical chain reaction mechanism, where the first initiation step yielding the phenalenyl radical would result from the abstraction of one of the allylic-benzylic hydrogen by triplet oxygen which is not thermodynamically favored, but could be possible in this case with the highly delocalised phenalenyl radical formed. This oxidation reaction could also involve an ene reaction (15) of singlet oxygen on phenalene, especially as the phenalenone is known to be an efficient sensitizer (16) and could lead to the formation of an alkoxy peroxy radical, which as the phenalenyl, can play the role of propagating species. The role of a classical antioxidant such as 2,6-ditertiobutyl 4-methylphenol would be to quench these propagating species by being itself oxidized or dimerized. We have shown that 2,6-ditertiobutyl 4-methylphenol as well as α -tocopherol are inefficient in inhibiting the oxidation of phenalene into phenalenone. This means that phenalene oxidizes faster than these antioxidants.

The origin of phenalene or phenalane is a more difficult question. L.C.O. gas-oils have their origin in fluid catalytic cracking of vacuum distillates of petroleum crudes. During this process, aromatization might occur to generate structures similar to those also present in asphaltenes. It was therefore of interest to know whether it would be possible to interconvert phenalene, phenalenone, phenalane and phenalanone by oxido-reductive processes. We have demonstrated that phenalane might be oxidized under mild conditions using 20% VO(acac)₂, oxygen in refluxing methanol. The phenalane can also be dehydrogenated into phenalene with sulfur or DDQ. In addition, we have oxidized phenalenone by ozone into ketal lactone and 1,8-naphthalic anhydride. The latter compound is formed during the aging of asphalt (17).

Accordingly, it does not seem unreasonable to postulate that the phenalenic derivatives could be partly at the origin of the sensitivity of asphaltenes to oxygen leading to asphalt aging. Phenalene type structures can indeed be found in asphaltenes models which result from spectroscopic analysis (18), although the determination of asphaltene structural composition is presently a matter of controversy (19).

CONCLUSION

The condensation reaction between phenalenone and 2-methylindole in presence of para-toluenesulfonic acid leads to a complex mixture of products which is more complex than it was initially described by Pedley et al. (12). The compounds reported are representative of the structures responsible for the color and sediments observed in unstable L.C.O. gas-oils. The oxidation of phenalene into phenalenone via the phenalenyl radical plays a crucial role in the condensation reaction and in the color and sediment formation. This oxidation reaction is

not inhibited by classical antioxidants. Phenalane and phenalenic structures could be reasonably considered partly representative models of the structures at the origin of asphalt aging.

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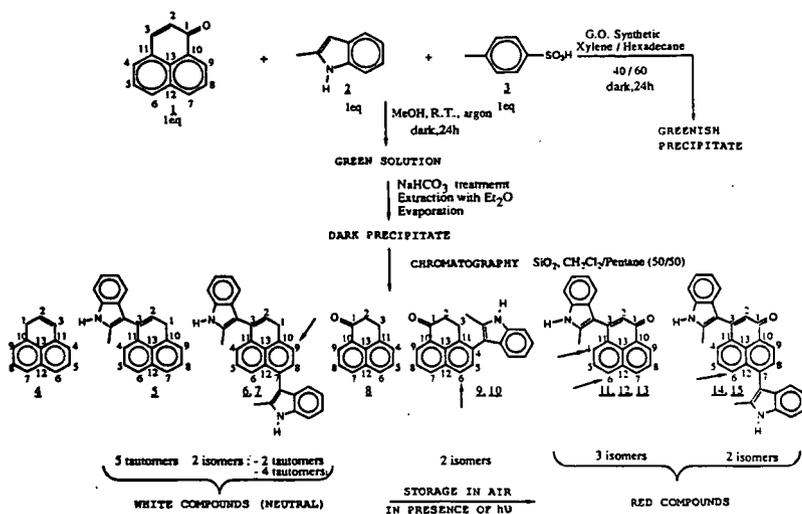


Figure 1: Compounds isolated after reaction of phenalene 1 with 2-methylindol 2 in presence of stoichiometric amount of para-toluenesulfonic acid 3.

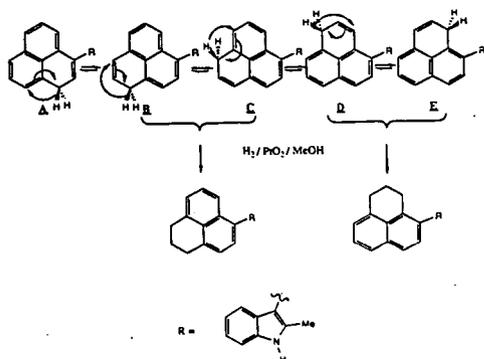


Figure 2: Tautomers of 2-methylindolylphenalene 5.

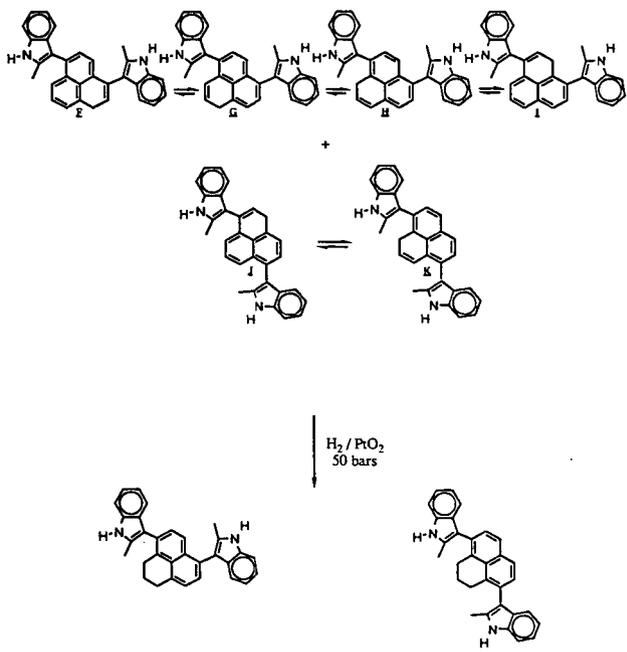


Figure 3: Tautomers of bis(2-methylindolyl)phenalene 6 and 7.