Study the oxidation stability of local base oil using Azophenol derivatives

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Abstract:

2-(tert-butyl)-4-(((4-methoxyphenyl)-phenol (Ia) and 2-(tert-butyl)-4-(4-nitrophenyl)diazegenyl(Ib) were produced as the local oil supply antioxidant and examined. The structures were clarified using standard analytical techniques (elemental analysis FT-IR, 1H-NMR and mass spectroscopy). Oxidation stability was investigated before and after adding various Ia and Ib concentrations through change in total acid number (TAN) and viscosity. The findings were discussed and the effectiveness classified as follows: Ia > Ib, Ia > Ib. A good agreement with the experimental findings was shown by the quantum chemical calculations (E-HOMO, E-LUMO and E-LUMO-HOMO).

Keywords: Local base oil, Oxidation stability, Total Acid Number (TAN), Viscosity, Quantum chemical calculations.

1.Introduction

Complex mixes of hydrocarbons and additives comprise of lubricating oil. It plays an important function in internal combustion engines and is utilised to reduce the friction of the moving components and to clean the various parts. The oil lubrication process is a highly complicated process in which the basic oil is degraded and additives are reduced simultaneously [1, 2].

Motor oils degradation may influence motor characteristics, such as development of combustion chamber deposits (CCDs)[3-9] and particle emissions[10]. Oxidation and heat damage engine oil[11, 12]. Motor oil oxidation may be investigated using several techniques [13, 14].

Without lubricant additives, the development of a modern engine would be impossible. Since then, in collaboration with the oil and automotive industries, the lubricants business has focused on promoting the longevity and performance of engine and drive systems using lubricants. Advances in vehicle design are the beginning of new performance demands which, in turn, drive the development of new lubricant and additive technologies[15, 16].

The inclusion of antioxidants was thus extremely necessary to preserve the oil by reducing oxidation degradation during industrial application[17]. Most of the compact Azo compounds exhibit antioxidant, anti-corrosive and anti-wear characteristics [15, 18, 19]. Two novel azo phenols have been produced and investigated for local basic oil as antioxidants.

1. Experimental

1.1 Raw material and Chemicals

The base oil sample was delivered from Co-operative Petroleum Co. with boiling range of 260-290°C. Chemical products were bought from Sigma, Aldrich, and Merek Companies.

1.2 Physicochemical characterisation of the base oil supplied:

The physical-chemical characteristics of base oil evaluated by ASTM.

1.3 Synthesis

Azophenols have been produced in two stages [15]

Aniline derivatives (a-b) diazotization (0.05 mol) was dissolved in distilled water and (0.5) was hydrochloric acid. The liquid was cooled to 0°C in an ice bath, and a stirring drop wise sodium nitride solution (NaNO2) (0.05 mol) was then added. The resultant mixture was swirled at 0°C for 30 min, maintaining the temperature between 0 to 5°C.

Coupling

2-tert is added to the sodium hydroxide solution (0.05 mol). Butyl phenol (0.05 mol) forms the phenoxide complex (I). The solution was then chilled to 0–5 °C and applied to the diazonium compounds (a – b). The reaction mixture was acidified into compounds after addition (Ia – b). The product was removed and recrystallized from ethanol production, respectively, 82 percent, 90 percent.

Prepared compounds (Ia and Ib) characterization:

In this phase, the following techniques were used to characterise all prepared azodys;

Primary analysis

Elemental microanalysis for isolated solid dyes C, H, N and S were conducted using CHNS-932 (LECO) Vario Elemental Analyzers in the Microanalytical Center of Cairo University.

Fourier Infrared Spectroscopy Transform (FT-IR)

The sample’s absorption spectrum (FT-IR) was obtained using a 1650 spectrophotometer type APerkin-Elmer FT-IR; model "Vector 22."

Spectroscopy of HNMR

The chemicals produced were characterised by 1HNMR. Spectroscopy. Using 1HNMR. Type a 300 MHz variable with TMS as internal standard (Germany 1999), (University of Cairo).

Spectroscopy of mass

The mass spectroscopy was performed using the SHIMADZU GC/MS-QP5050A direct intake unit (D1-50).
Study of Oxidation Stability

In accordance with the ASTM standard D-943 test procedure, the thermal oxidation stability test was performed. The oil sample is reacted to the Fe and Cu catalysts at 120 °C at various times with oxygen (99.95% pure) (24, 48, 72, 96 h).

Total number of acids

In accordance with the ASTM D-664 potentiometric titration technique, a total acid number (TAN) was calculated for fresh and all oxidised oleic samples with or without addition of azo compounds at various concentrations (50, 100 and 200 ppm). The samples were warmed to 400°C and shaken for 10 minutes before to the test.

Viscosity

Viscosity at 400°C for fresh and all oxidised oil samples was performed in the glass capillary viscometer procedure with or without the addition of azo compounds at various concentrations (50 100 and 200 ppm) according to ASTM D- 445-IP 71.

Quantum chemical calculation

Hyperchem software version 8.03 for quantum chemical calculations from hypercubeInc[20].

3. Results and discussion

Evaluation of base stock

The physico-chemical properties of local base stock used in this study represent in table (1).

Table (1) discussed the physico chemical characteristics of the base stock sample under study. The viscosity at 40°C is 52.34 cSt. And the total acid nounder is 0.067 mg KOH / gram.

Characterization of the prepared azo phenols compounds (Ia-Ib):

The prepared compounds were characterized by elemental analysis, IR, 1H-NMR spectrophotometer and electron ionization mass spectroscopy (EI-MS).

3.2.1. Elemental Analysis:

Elemental analysis was performed for the synthesized azophenols (Ia-Ib), and the obtained results are shown in Table (2).

The data obtained from Table show that the calculated values of the elements were in good compatibility with the found.

IR Spectroscopy:

IR spectroscopy for the synthesized azophenols (Ia-Ib) tabulated in table (3).

The data obtained in table (3), illustrate the functional groups of compound Ia - Ib.

![Scheme (1) Preparation of Ia and Ib.](image-url)
Table (1) the physicochemical properties of the Base Stock.

<table>
<thead>
<tr>
<th>Test</th>
<th>RESULT</th>
<th>TEST METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 15.5 °C, g / L</td>
<td>0.8817</td>
<td>ASTM D - 1298</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>-6</td>
<td>ASTM D - 97</td>
</tr>
<tr>
<td>Viscosity @ 40 °C</td>
<td>52.34</td>
<td>ASTM D - 445</td>
</tr>
<tr>
<td>Viscosity @ 100 °C</td>
<td>7.41</td>
<td>ASTM D - 445</td>
</tr>
<tr>
<td>Viscosity Index (VI)</td>
<td>92</td>
<td>ASTM D - 2270</td>
</tr>
<tr>
<td>Total Acid Number (TAN)</td>
<td>0.067</td>
<td>ASTM D - 664</td>
</tr>
<tr>
<td>Color</td>
<td>2.5</td>
<td>ASTM D - 1500</td>
</tr>
<tr>
<td>Ash Content, wt %</td>
<td>0.003</td>
<td>ASTM D - 482</td>
</tr>
<tr>
<td>Copper Corrosion</td>
<td>Ia</td>
<td>ASTM D - 130</td>
</tr>
<tr>
<td>Flash point, oc</td>
<td>220</td>
<td>ASTM D - 92</td>
</tr>
<tr>
<td>Aniline point</td>
<td>100.5</td>
<td>ASTM D - 611</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>468.9</td>
<td>-</td>
</tr>
</tbody>
</table>

Table (2) Elemental analysis of synthesized azophenols Ia-lb.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>110</td>
<td>71.81</td>
<td>7.09</td>
<td>9.85</td>
<td>8.67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ia</td>
<td>160</td>
<td>64.20</td>
<td>6.49</td>
<td>14.04</td>
<td>13.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ib</td>
<td>3440</td>
<td>2958</td>
<td>1585</td>
<td>1265</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ib</td>
<td>3467</td>
<td>2958</td>
<td>1590</td>
<td>1269</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (3) Infra-Red spectra of Ia –Ib.

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>OH cm⁻¹</th>
<th>CH aliphatic</th>
<th>C=C</th>
<th>N=N</th>
<th>C-O-C</th>
<th>C-Br</th>
<th>NO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>3440</td>
<td>2958</td>
<td>1585</td>
<td>1265</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ia</td>
<td>3467</td>
<td>2958</td>
<td>1590</td>
<td>1269</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (4) ¹H NMR for prepared compounds (Ia-Ib).

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>H¹Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>9.61</td>
</tr>
<tr>
<td>Ib</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Table (5) Mass spectroscopy for Ia and Ib.

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>Molecular formal</th>
<th>m/z obs.</th>
<th>m/z cal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>C₁₇H₂₀N₂O₂</td>
<td>284</td>
<td>284</td>
</tr>
<tr>
<td>Ib</td>
<td>C₁₈H₂₁N₃O₃</td>
<td>299</td>
<td>299</td>
</tr>
</tbody>
</table>

Fig. (1) Mass spectroscopy of the prepared compound (Ia).
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Fig. (2) Mass spectroscopy of the prepared compound (lb).

Scheme (2) Routes of fragmentation (la).

Scheme (3) Routes of fragmentation (lb).
3.2.3 $^1$HNMR

The following are shown in Table 4: Due to the attachment of the -OH to the aromatic ring, which makes the hydroxyl proton more blind, the large chemical shift ($\delta$) of the hydroxyl proton (a) (9.61-10.6 ppm) (because of the high electronegativity of the aromatic ring through conjugation). The aromatic protons (b, c, d, e and f) have distinct values of chemical shift ($\tau$), since they are unsymmetrical. The aliphatic protons (g and h) vary in their location to the aromatic ring. 3.

3.3. Assessment of produced chemicals as base oil antioxidant add-ons:

The investigation of the oxidation stability of a base oil shows that it is capable of oxidation of the oil under heat stress with stand and in the presence of a copper catalyst. The production of carbonyl group Figure 4 is prevented by the additives, i.e. by adding azophenols to the oil as part of heat oxidation, the overall acid level is always reduced. Total acid values are listed in Tables (6) and shown visually in Figure 5.

Table 6 and Figure 5 show that Ia and Ib additives are present. Total acid values are provided for 24, 48, 72 and 96 hours following thermal oxidation of the base oil. First of all, by raising the additive dosage from 50 parts per million to 200 parts per million, the overall acid numbers drop. Second, the total acid figures have always shown a bad result; with base oil either all times intervals.

It is possible to observe that the findings are varied by 24 hours studying the impact of additive concentrations employed on the total number of acids after thermal oxidation. The excellent efficient results were obtained at all doses for component Ia. When we utilised 200 parts per million (TAN 0.022 mg of COH/g sample) concentration after 24 hours.

<table>
<thead>
<tr>
<th>Time</th>
<th>Base oil Total Acid Numbers, mg KOH / g Sample x $10^2$</th>
<th>Base oil+ Ia</th>
<th>Base oil+ Ib</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50ppm</td>
<td>100ppm</td>
<td>200ppm</td>
</tr>
<tr>
<td>24</td>
<td>0.58</td>
<td>.0545</td>
<td>0.0540</td>
</tr>
<tr>
<td>48</td>
<td>1.19</td>
<td>0.093</td>
<td>0.0652</td>
</tr>
<tr>
<td>72</td>
<td>1.96</td>
<td>0.135</td>
<td>0.111</td>
</tr>
<tr>
<td>96</td>
<td>2.77</td>
<td>0.150</td>
<td>0.141</td>
</tr>
</tbody>
</table>

Table (8) Variation of viscosity with Oxidation Time and Concentration Ia-Ib.

<table>
<thead>
<tr>
<th>Time</th>
<th>Base oil Kinematic Viscosity @ 40°C, Cst.</th>
<th>Ia</th>
<th>Ib</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50ppm</td>
<td>100ppm</td>
<td>200ppm</td>
</tr>
<tr>
<td>24</td>
<td>69.4</td>
<td>54.81</td>
<td>53.12</td>
</tr>
<tr>
<td>48</td>
<td>75.2</td>
<td>55.81</td>
<td>52.31</td>
</tr>
<tr>
<td>72</td>
<td>81.4</td>
<td>56.23</td>
<td>54.82</td>
</tr>
<tr>
<td>96</td>
<td>96.2</td>
<td>57.97</td>
<td>55.10</td>
</tr>
</tbody>
</table>
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3.3.2. Change in viscosity:

Date of the cinematic viscosity of the basic oil with and without additions is shown in Table (7) and Figure (6).

The findings in table 7 showed that viscosity rates varied from 54.81 to 57.97 Cst (100 ppm) and 52.82 to 54.01 Cst following thermal oxidation of the base oil up to 96 hours in the presence of antioxidants Ia. The effectiveness of these antioxidants is rated as follows from prior findings at a concentration of 200 ppm: Ia > Ib. Ia > Ib. The presence of additive antioxidants retards base oxidation either with oxygen reactions or with primary oxidation products, such as organic radicals. This stops the radical reaction of the chain. Therefore, antioxidants preserve the lubricant sacrificially and are depleted gradually throughout this process. Once antioxidants are exhausted, the oxidation of the base oil is permitted to interact at high temperatures with the liquid. The oxidation of basic stocks leads to bigger oligomeric molecules, and smaller oxidation products for other fractions. [22]

3.4. Quantum chemical calculation

For possible relations with the inhibitor efficiency of the azo molecule, the calculation of certain quantum chemical parameters such as the energy in the molecular orbital, EHOMO (high occupied molecular orbital energy) and ELUMO (lowest occupied molecular orbital energy) were determined in Figure 7 and Table 4. HOMO energy is frequently linked with the capacity to donate electron to a molecule. Less negative HOMO energies as well as better adsorption connections and possibly higher inhibitory effectiveness are typically read as [23], as shown in Table 4, where the energy gap in the compound Ia is the lowest. The theoretical calculations are also consistent with the experimental findings.
4. Conclusion

We may infer from the findings gained in this study by indicating:

- All Azo phenol compounds shown to be antioxidant successful
- Increasing the concentration, both TAN and viscosity always decrease.
- We observed the most effective chemical Ib because of the donor group’s presence.
- The results show that for all chemicals the highest effective concentration is 200 ppm.

Reference


